STEP Materials Development
Task 2.06.02.02
Supercritical Transformational Electric Power Generation (STEP)

Level 2 Milestone Report

Collective Summary of sCO2 Materials Development
Part I: Influence of cycling temperatures on compatibility of polymers in super-critical carbon dioxide for power generation systems

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ABSTRACT

Polymers such as PTFE (polytetrafluorethylene or Teflon), EPDM (ethylene propylene diene monomer) rubber, FKM fluoroelastomer (Viton), Nylon 11, Nitrile butadiene (NBR) rubber, hydrogenated nitrile rubber (HNBR) and perfluoroelastomers (FF_202) are commonly employed in super critical CO_2 (sCO2) energy conversion systems. O-rings and gaskets made from these polymers face stringent performance conditions such as elevated temperatures, high pressures, pollutants, and corrosive humid environments. In FY 2019, we conducted experiments at high temperatures (100°C and 120°C) under isobaric conditions (20 MPa). Findings showed that elevated temperatures accelerated degradation of polymers in sCO2, and that certain polymer microstructures are more susceptible to degradation over others. In FY 2020, the focus was to understand the effect of sCO2 on polymers at low (10 MPa) and high pressures (40 MPa) under isothermal conditions (100°C). It was clear that the same selectivity was observed in these experiments wherein certain polymeric functionalities showed more propensity to failure over others. Fast diffusion, supported by higher pressures and long exposure times (1000 hours) at the test temperature, caused increased damage in sCO2 environments to even the most robust polymers. We also looked at polymers under compression in sCO2 at 100°C and 20 MPa pressure to imitate actual sealing performance required of these materials in sCO2 systems. Compression worsened the physical damage that resulted from chemical attack of the polymers under these test conditions.

In FY 2021, the effect of cycling temperature (from 50°C to 150°C to 50°C) for polymers under a steady sCO2 pressure of 20 MPa was studied. The aim was to understand the influence of cycling temperatures of sCO2 for typical polymers under isobaric (20 MPa) conditions. Thermoplastic polymers (Nylon, and PTFE) and elastomers (EPDM, Viton, Buna N, Neoprene, FF202, and HNBR) were subjected to 20 MPa sCO2 pressure for 50 cycles and 100 cycles in separate experiments. Samples were extracted for ex-situ characterization at 50 cycles and upon the completion of 100 cycles. Each cycle constituted of 175 minutes of cycling from 50°C to 150°C. The polymer samples were examined for physical and chemical changes by Dynamic Mechanical and Thermal Analysis (DMTA), Fourier Transform Infrared (FTIR) spectroscopy, and compression set. Density and mass changes immediately after removal from test were measured for degree of swell comparisons. Optical microscopy techniques and micro computer tomography (micro CT) images were collected on select specimens. Evaluations conducted showed that exposures to super-critical CO2 environments resulted in combinations of physical and/or chemical changes . For each polymer, the dominance of cycling temperatures under sCO2 pressures, were evaluated. Attempts were made to qualitatively link the permanent sCO2 effects to polymer micro-structure, free volume, backbone substitutions, presence of polar groups, and degree of crystallinity differences. This study has established that soft polymeric materials are conducive to failure in sCO2 through mechanisms of failure that are dependent on polymer microstructure and chemistry. Polar pendant groups, large atom substitutions on the backbone are some of the factors that are influential structural factors.

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1 Introduction: Materials Development for Super-critical CO_2 service

The Brayton Cycle based on super-critical CO_2 as a working fluid is a non-conventional concept for converting thermal energy to electrical energy. These systems boast high cycle efficiency which automatically lead to lower cost, lower water usage, and in the case of fossil fuel heat sources, lower greenhouse gas (GHG) emissions. At high pressures, sCO2 is a high-density working fluid which also permits smaller equipment sizes, plant footprints and lower capital costs. However, in both open and closed Brayton-type cycle systems employing supercritical CO_2 (sCO2) as the working fluid, gas environments are hot and corrosive and present challenging requirements of strength and environmental resistance for materials of construction. In some instances, peak operating temperatures in the turbines in closed-cycle systems approach 500-700°C at 200 bar, while it opened-cycle systems, temperature of 1150°C at 300 bars can be seen [1]. Furthermore, in these systems, the cycles require that hot, lower-pressure turbine exhaust be used to pre-heat high-pressure sCO2 entering the external heater or combustor just upstream of the turbine. Therefore, there is a need to match alloy performance properties with the performance requirements of individual components. This may impact the design of the components themselves [2].

The range of available alloys with the pre-requisite strength and corrosion-resistance under these extreme conditions of operation, in particular for applications having elevated turbine inlet temperatures, are limited. If alloys are employed under conditions beyond current experience, practical acceptance will depend on successful qualification testing involving close collaboration among equipment manufacturers, materials suppliers, and materials research and development groups. Even at nominal operating temperatures, in support of a commercially viable solution, it is important to develop understanding of materials behavior for meaningful product lifetimes. While the testing of existing material choices may lead to the most exotic and expensive materials solutions, keeping in mind the cost impact is important because excessively high cost could prevent industry from integrating sCO2 into their energy conversion portfolios.

For commercially viable material solutions, it is important to develop understanding of materials properties, behavior, and performance under real power cycle operating conditions for meaningful product lifetimes. Both metal alloys and polymeric classes of materials are used in sCO2 power conversion cycles, albeit for very different parts of the operation. While metal alloy seals and component materials can stand high temperatures for reasonable exposure times and high pressures, elastomeric O-rings used in different components for sealing purposes are soft polymeric materials that will behave quite differently in sCO2 environments. Combinations of high pressures and temperatures especially in cyclic conditions with possible presence of moisture and other corrosive by-products can create extremely demanding environments for both families of materials [3]. Therefore, material degradation mechanisms for short term or longer-term exposures to sCO2 environments must be considered. These can include fatal effects such as corrosion and related damage-accumulation for alloys and explosive decompression behavior for polymeric O-rings. Current and future efforts should keep these material performance knowledge gaps in the forefront.

In the following section, we will present a brief review of current know-how on compatibility of polymeric materials in super-critical CO_2 environments. This section will present findings from our STEP FY 2019 and FY 2020 effort, for comparison to FY 2021 work, which is the focus of this report.

1.1 Polymer Materials Development

The development of super-critical CO_2 energy conversion systems requires a multi-materials approach that utilizes the most effective combination of materials to achieve safe, cost-effective construction and operation. Polymers such as Viton, polyetheretherketone (PEEK), ethylene propylene diene monomer (EPDM), ethylene propylene rubber (EPR), and polytetrafluorethylene (PTFE or Teflon) are utilized in various extreme environments of sCO2 energy conversion systems. For e.g. Viton, PEEK, EPR and Neoprene are used in pressure relief valves and pressure transducers. EPDM, EPR and Teflon are often used in turbomachinery (pressure boundary connections) and Nylon and PEEK are used in valve seats. Elastomers such as neoprene and nitrile butadiene rubber (NBR or Buna N) used in seals and pressure relief valves and pressure transducers, are found to exhibit low absorption of sCO2. Numerous other XRD-resistant elastomer grades such as Aflas®, East-O-Lion 985® (HBNR) etc., are available depending on service, temperature etc. Typically, high hardness elastomers, with high filler loadings are used for these applications. Others such as Viton and PTFE are found to be unstable for the same applications (Figure 1). Therefore, in trunnion valves, nylon or PEEK back up rings are required immediately behind Viton O-ring. EPDM is a candidate that shows good promise in turbomachinery and VCO fittings in Coriolis meters. For extremely elevated temperatures (400°C) and pressures (4400 psi/30 MPa), elastomeric seals are replaced by PTFE-alloys which are spring-loaded with extremely fine surface finish for improved sealing.

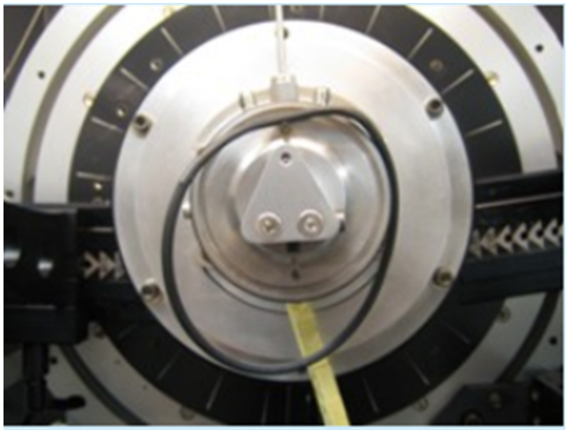


Figure 1. Failure seen with Viton O-ring in sCO2 service environments

Elevated temperatures (200-700°C) and pressures (4400-6000 psi) and combinations thereof, creep and fatigue conditions, corrosive environments due to moisture, pollutants from combustion products and impurities such as volatiles from polymers acting as contaminants and diluents in sCO2 are examples of various stress environments these polymers experience in energy conversion systems. Under benign operating conditions, polymers can be exposed to 1000 psia pressures during loop fill and saturation pressures during shut-down at room temperature. Extreme operating conditions such as in turbomachinery can accelerate explosive decompression with increase in pressures and temperatures. Elastomeric seals can be shredded in the process. Pressure and temperature cycling, transient exposure times, rapid pressurization and depressurization rates, and hydrostatic pressure effects combined with the compatibility of polymers with sCO2 under these conditions are critical factors towards defining material performance limits.

Most knowledge of polymer and monomer interactions with CO_2 was derived from the unique fact that super-critical carbon dioxide (sCO2) can be used as a solvent in many polymerization processes [4-7] due to its non-toxic, non-flammable and relative inertness. These applications have revealed a definite relationship between polymer microstructure and sCO2 effects. Polymer backbones with carbonyl groups, C-F bonds and double bonds show elevated CO_2 absorption. O-rings with these functionalities in their backbones (Viton, Kalrez, Teflon, and Silicone) showed the greatest loss of CO_2 from sealed fixtures [8]. It was found that polymers with greater flexibility of backbone, high free volume, lower glass transition temperature (Tg), and weak interactions between polymer segments such as in elastomers exhibited higher solubility in sCO2 over those that did not have the above microstructure [9]. On the other hand, since CO_2 is a weakly polar solvent, it cannot dissolve highly polar or hydrogen-bonded polymers such as poly (acrylic acid) [10]. High solubility and low diffusivity under prolonged conditions of exposure of these polymers to sCO2, as compared to N2, O2 or H2 gas behavior in the same type of polymers, leads to degradation mechanisms such as plasticization and lowering of polymer glass transition temperature [11]. CO_2 at weight concentrations of 8-10% can plasticize common glassy polymers with glass transition temperatures in the 8-100°C range to below room temperature [12]. These effects can be cumulative and are responsible for failure modes varying from slow leakages to formation of internal blisters, voids and cracks and consequent explosive rapid decompression (XRD) in the material. Long-term aging, swelling, plasticization, blister and crack formation can add up over service lifetimes and result in polymer failure leading to expensive repairs and down-times. Both physical and mechanical properties of polymers can be affected drastically by explosive decompression and plasticization effects when exposed to sCO2 under normal and extreme environments seen in energy conversion systems [13]. Another major source of concern for polymers in sCO2 use is the effect of impurities such as SO_x and NO_x that can produce strong acids in the presence of water which can in turn catalyze hydrolysis [14]. Hydrolysis means depolymerization and release of leached molecules in the gas. If the smaller molecules do not leach out, the hydrolysis causes breakdown of the polymer and destroys its integrity and microstructure.

1.2 Summary of FY2019 and 2020 findings

Significant amount of testing of polymers in sCO2 has been conducted at lower pressures (1000-1800 psig/7-12 MPa), lower autoclave velocities and slightly-above room temperature (55-60°C) conditions. However, these conditions do not mimic the service conditions that these materials will see in actual power cycles. Therefore, our baseline investigation in FY 2019 aimed at examining polymer compatibility effects at higher temperatures (100°C and 150°C) under an isobaric sCO2 system pressure (3625 psig/ 20MPa) at a flow rate of 0.06 kg/hour (24 ml/min) for 1000 hours. Polymers exposed included FF202, EPDM, PEEK, Nylon, Neoprene, PTFE, Viton, EPR and Buna N. Samples were withdrawn at t=200 hours and at the end of the test and characterized for physical and chemical effects because of the exposure. Physical effects were seen in the form of changes in mechanical properties such as storage modulus, formation of cracks and surface texturization changes in the polymers. Chemical changes were seen in the form of changes in glass transition temperatures and molecular changes in FTIR spectra. Permanent deformation was measured as compression set for elastomers. Our studies pointed to thermoplastics being more stable with respect to polymer performance properties over elastomers at these temperatures.

Elastomers showed the most dramatic changes in properties after exposure. Of the elastomers, EPDM and FF202 worked well for 100°C exposures. EPDM and EPR were not susceptible to changes due to sCO2 to a great extent because of their non-polar nature. At elevated temperatures (150°C), FF202 seemed to be superior in performance

While the FY 2019 effort focused on investigating the influence of temperatures on polymeric materials, investigations in FY 20 involved studying a large suite of thermoplastics and elastomers at varying sCO2 pressure conditions under isothermal conditions. Temperature of test was kept at 100°C instead of 150°C, to distinguish observable effects due to pressure while preventing additional temperature-related effects. Although, increasing the test pressures from 10 MPa to 40 MPa did enhance diffusion effects, our work showed that a combination of longer times of exposure and pressures does more damage in polymers than static pressures alone. This finding could be also partially influenced by the isothermal conditions chosen for this year's study. Higher temperatures (150-200°C) in combination with medium-to-high sCO2 pressures (20-30 MPa) for long exposure times, all possible within the sCO2 service realms, is speculated to be the most damaging of all combination environments.

In addition to the above study of sCO2 pressure effect on whole free-standing O-rings, a smaller group of selected elastomers ranging from most stable to least stable in sCO2, in specially designed compression fixtures. This was to be able to evaluate the polymer response under mechanical loading in sCO2 environment, mimicking actual use conditions as seals. From FY 2020, storage modulus, glass transition temperature, FTIR and compression set data for free-standing O-rings, Neoprene showed the most change in physical and chemical properties and damage in sCO2. Buna N, showed some changes in properties in sCO2 exposures and HNBR did not show drastic changes in the properties. For these reasons, these three chemistries were selected for mechanical testing after the compressed state exposures. Results showed that, Neoprene, Buna N and HNBR O-rings tested under compression, failed at much lower strains than in the free-standing uncompressed test condition. Neoprene failed at about 120-130% strain and Buna N at 190-300% strain after sCO2 exposure. HNBR, on the other hand, failed at 220-240% strain and much higher stresses (5000-8000 psi), which is comparable to the mechanical properties of these O-rings under zero compression testing. A level 3 report on FY 2020 work was submitted to DOE/STEP in March 2021 outlining all the conclusions from the study.

This report on FY 2021 effort, present conclusions from the study of the influence of cycling temperatures under isobaric sCO2 pressures. Cyclic testing can shed light on dynamic effects that can be encountered in actual service environments as part of sCO2 power generation cycles and were deemed necessary to provide a comparison to findings from previous studies (FY 2019, FY 2020) on these soft materials under static conditions.

Sandia National Laboratories (SNL), CA partnered with University of Wisconsin to conduct these experiments. All sCO2 exposures with polymers were performed at the University of Wisconsin and material damage characterization and data analyses was done by SNL, CA.

2 Experimental details

2.1.1 Test Conditions

The design and set-up of the sCO2 test rig at the University of Wisconsin and its conversion from being able to run primarily static tests to dynamic thermal cycling in FY 2021 required much discussion and planning. In temperature cycling experiments, the test set-up, with polymer specimens in place, was heated from 50°C to 150°C in 30 minutes followed by a dwell time at 150°C for an hour. At the end of the dwell time, the autoclave was cooled from 150°C to 50°C at a fast rate. This cooling step, that took 55 minutes, was enabled with the use of cooling fans that were directed to the space between the autoclave exterior and the heat-trapping insulation around it (Figure 2). A Lab View program was developed to control the autoclave through the thermal cycling process (Figure 3). Any changes in pressure during the cooling process was to be compensated by adjustment in flow rates to maintain steady sCO2 pressure at 20 MPa (Figure 4).

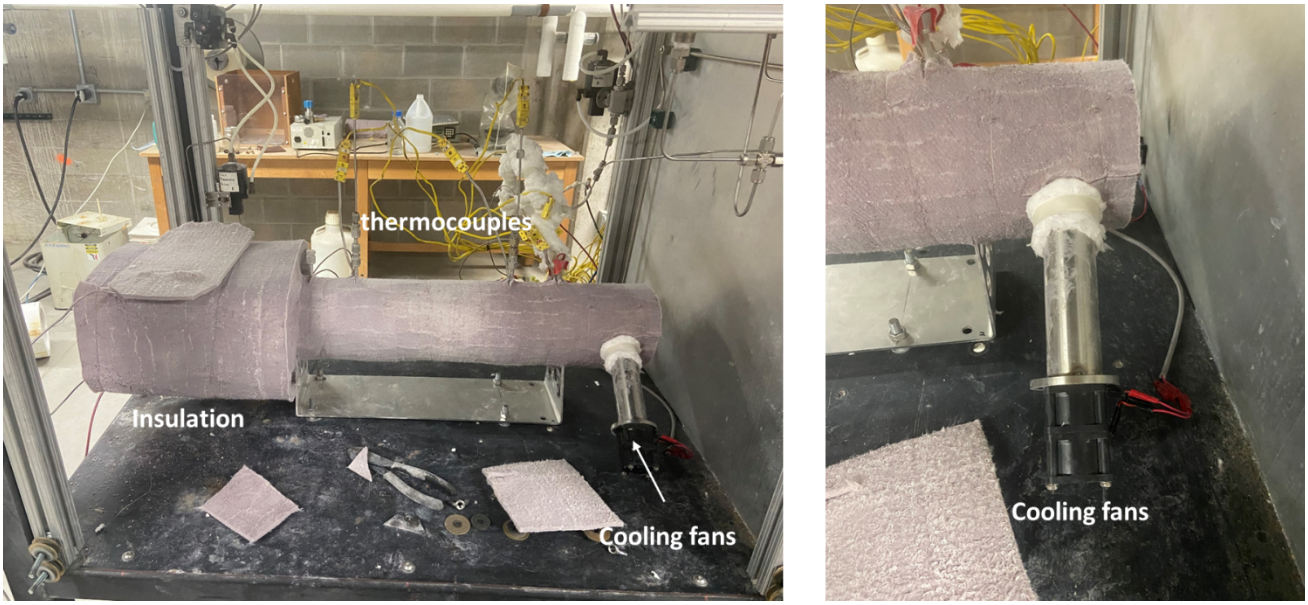
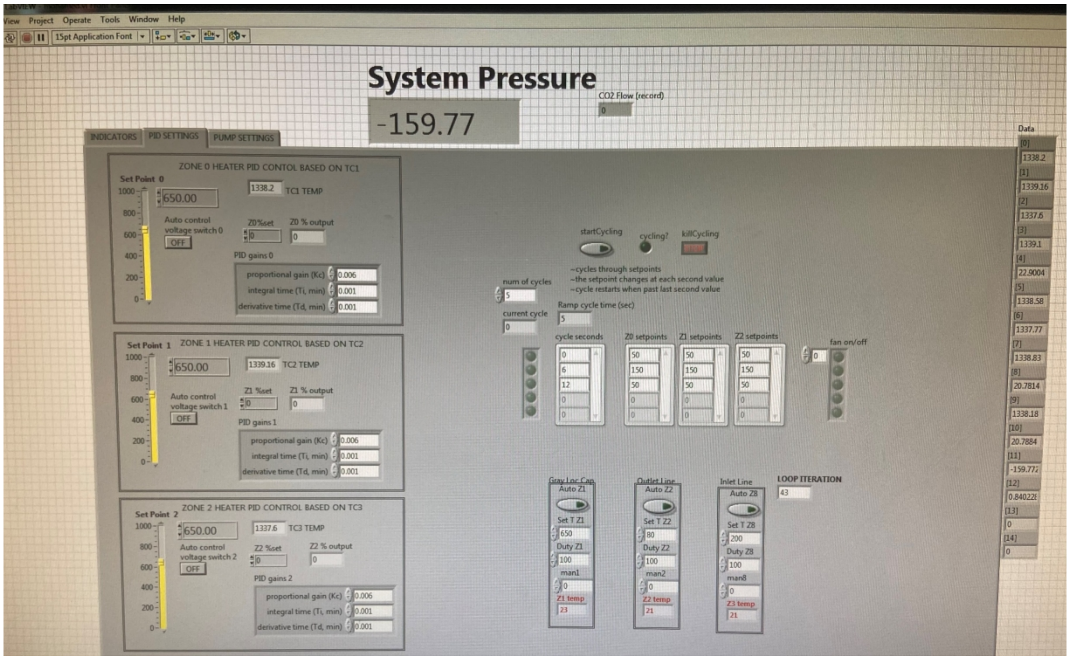


Figure 2. Experimental set-up at the University of Wisconsin, Madison for dynamic thermal cycling of polymers under sCO2 exposure

Thermal cycling was monitored using multiple thermocouples, placed strategically about the autoclave. For the thermal cycling conditions described in the previous paragraph, each cycle, which included a dwell time of 30 minutes between cycles at 50°C, lasted a total of 175 minutes.



System Pressure -159.77
CO2 Flow (record) 0

ZONE 0 HEATER PID CONTOL BASED ON TC1
Set Point 0: 650.00
TC1 TEMP 1338.2
Auto control voltage switch 0
Z0 %set 0
Z0 % output 0
PID gains 0
proportional gain (Kc) 0.006
integral time (Ti, min) 0.001
derivative time (Td, min) 0.001

ZONE 1 HEATER PID CONTROL BASED ON TC2
Set Point 1: 650.00
TC2 TEMP 1339.16
Auto control voltage switch 1
Z1 %set 0
Z1 % output 0
PID gains 1
proportional gain (Kc) 0.006
integral time (Ti, min) 0.001
derivative time (Td, min) 0.001

ZONE 2 HEATER PID CONTROL BASED ON TC3
Set Point 2: 650.00
TC3 TEMP 1337.6
Auto control voltage switch 2
Z2 %set 0
Z2 % output 0
PID gains 2
proportional gain (Kc) 0.006
integral time (Ti, min) 0.001
derivative time (Td, min) 0.001

~cycles through setpoints
~the setpoint changes at each second value
~cycle restarts when past last second value

num of cycles 5
current cycle 0
Ramp cycle time (sec) 5
fan on/off 0

cycle seconds	Z0 setpoints	Z1 setpoints	Z2 setpoints
0	50	50	50
6	150	150	150
12	50	50	50
0	0	0	0
0	0	0	0

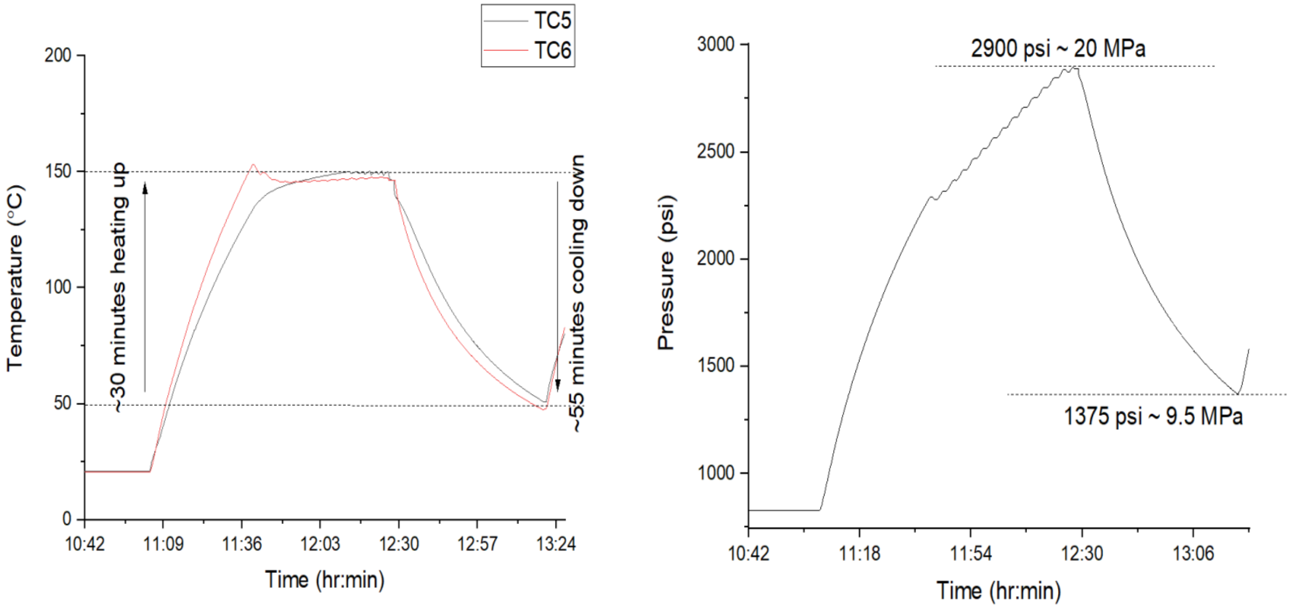
Gray Loc Cap	Outlet Line	Inlet Line
Auto Z1	Auto Z2	Auto Z8
Set T Z1 650	Set T Z2 80	Set T Z8 200
Duty Z1 100	Duty Z2 100	Duty Z8 100
man1 0	man2 0	man8 0
Z1 temp 23	Z2 temp 21	Z3 temp 21

LOOP ITERATION 43

Data

[0]	1338.2
[1]	1339.16
[2]	1337.6
[3]	1339.1
[4]	22.9004
[5]	1338.58
[6]	1337.77
[7]	1338.83
[8]	20.7814
[9]	1338.18
[10]	20.7884
[11]	-159.77
[12]	0.84022
[13]	0
[14]	0

Figure 3. LabView program that controlled dynamic thermal cycling of polymers under sCO2 exposure in the experimental set-up at the University of Wisconsin, Madison



Temperature change

Pressure change

Figure 4. Plots showing changes in temperature and pressure during thermal cycling of polymers under sCO2 exposure

Two experiments, a 50-cycles test lasting a total of 6.5 days and a second at 100 cycles that lasted 13 days, were conducted this year. Based on FY 2019 and FY 2020 studies, a total of eight polymers were chosen for this study. These included Polyamide(Nylon 6,6), polytetramethylene (PTFE), Buna N(NBR), Viton (FKM), FF-202 (perfluoroelastomer), Ethylene propylene diene monomer (EPDM), Polychloroprene (Neoprene), and Hydrogenated Nitrile butadiene rubber (HNBR). Due to material acquisition delays, only five out of the 8 O-rings types were tested in the 50-cycle test whereas all 8 chemistries were exposed to sCO2 for the 100 cycles test. Multiple specimens (one and 3/8" ID O-rings) of each polymer were introduced into high-pressure autoclave at 20 MPa (Figure 5). Super critical CO2 pressure in the test autoclave was maintained during thermal cycling by controlling flow rate of the gas through the system. Samples were withdrawn at the end of the tests and shipped to Sandia where ex-situ characterization was completed on the samples and data compared to t = 0 hours (control) for chemical and physical changes.

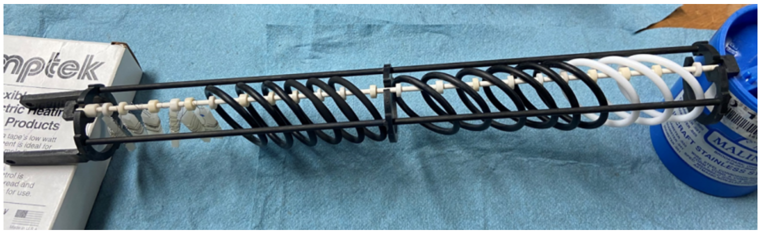


Figure 5. Picture showing the loading of O-rings on fixtures in the autoclave for the experiments

2.1.2 Polymer characterization

All the polymers for the two tests were characterized for physical and chemical properties prior to sCO2 exposure. After removal from the test, O-rings were characterized for properties changes that could indicate polymer erosion, solubility, or degradation in sCO2 environments under thermal cycling test conditions.

The selection of chemical and physical characterization methods was dictated by sCO2 effects expected for these polymers based on their behavior in actual energy conversion systems. Table 1 below shows a comprehensive description of polymer properties and appropriate characterization methods used in this study.

Table 1 Polymer characterization and relation to physical/chemical effects

Polymer property	**Characterization technique**
Density	ASTM D 792 (Archimedes principle)
Mass	Gravimetric measurements with lab scale with ±0.1 mg sensitivity
Glass transition temperature (T_g) and modulus changes	Dynamic Mechanical Thermal Analysis (DMTA)
Molecular and structural changes	ATR-Fourier Transform Infra-Red Spectroscopy (ATR-FTIR)
Texturing and surface damage	Optical Microscopy
Compression set	(ASTM D395 Method B)
Internal voids and damage	Micro Computer Tomography (Micro-CT)

Density of the exposed and non-exposed specimens was measured following ASTM D792. Sample densities and masses were measured immediately after removal from the autoclave as well as more than 48 hours later. Density was measured with the goal of checking for absorption and retention of sCO_2 that can cause swelling in polymers and mass was measured for loss of volatiles from the polymer during depressurization.

Dynamic mechanical thermal analysis (DMTA) is a characterization method commonly used to study the viscoelastic nature of polymer in which a sinusoidal stress is applied and the strain in the material is measured as changes in storage and loss moduli. The temperature of the sample is varied such that the variations in the modulus can be used to pinpoint the glass transition temperatures of the material. In the context of this study, sCO2 can change the glass transition temperature (T_g) as well as the storage modulus of the polymer.

ATR-FTIR (Attenuated Fourier Transform Infra-Red) can measure the effect of sCO2 leading to permanent molecular changes that manifest in the spectra as peak loss, peak shifts or new peaks. It is important to generate the spectra of the polymers prior to exposure for comparison.

Surface damage and texturing was studied using optical microscopy at high magnifications. Internal voids and cracks because of rapid rates of depressurization were better characterized using a standard micro-CT method. X-ray computed tomography (XCT) uses a series of two-dimensional radiographic images taken by rotating a sample in an x-ray beam. The 2D pixels collected this way are reconstructed to generate a three-dimensional data set of radiographic density in a solid cylinder. In a further step, the 3D data set permits the creation of 2D images representing virtual slices thorough the entire internal volume of the object capable of producing close to a thousand 2D slices and 3D rendering movies. By use of appropriate x-ray energy, filters, secondary filters, and beam hardening, it is possible to image features such as voids, cracks, and clusters of fillers in low atomic number materials (e.g. polymers) which contain particles of relatively high atomic number (e.g. fillers and other adventitious materials).

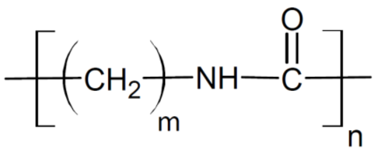
Images collected by micro-CT (micro computed tomography) provide a tremendous amount of information on the state of the polymers after gas exposures and enable discerning the source of voids, cracks and other anomalies in the sample due to gas diffusion. This high-resolution 3D microscopy enables imaging very fine scale internal structure of polymers non-destructively. This technique was invaluable in our study towards understanding high pressure sCO2 effects in elastomeric polymers based on gas diffusion and solubility. Micro CT images provided evidence of damage evolution in the form of voids around particles and cracks across the polymer matrix. As part of sample preparation, each specimen of O-ring material was mounted above the head of a dress-makers straight pin using glue. Although every effort was made to make each specimen as vertical as possible, there was some variation in the precise alignment of the specimens because these were hand-cut from sample sheets. The orientation of the specimen in the test fixture was marked for repeatability of loadability. For this work, a micro CT machine (Zeiss Xradia 520 Versa) which has a potential resolution of better than 1 micron, was used. Each elastomer sample was imaged at ~4.6 mm field of view and a pixel size of ~4.6 micron to see the entire width of the O ring. The center section of each O-ring was imaged at higher resolution. In a few cases, either because of compression set or because of sample curvature, a voxel size of 2.5 micron was needed so that the entire diameter of the central section was in the image.

Compression set was measured using ASTM D395 Method B wherein the specimen is compressed to 75% of its original height over a set time and temperature which is used to calculate permanent deformation of the polymer after exposure. In our study, if the polymer has undergone chemical changes in the form of loss of crosslinking and become “soft”, it would manifest itself as a large compression set.

3 Results and discussion

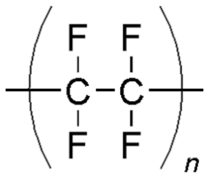
Polymer characterization data before and after exposure to sCO2 was used to understand physical and chemical effects produced in polymers due to the high diffusivity and solubility, and low polarity of sCO2 in these systems. Physical effects in the polymers range from change in modulus/strength to surface or internal voids and cracks due to rapid depressurization. Chemical effects range from change in molecular structure, plasticization of matrix leading to drop in glass transition temperature and increased compression. The molecular structures of the eight polymers tested in FY 2021 under sCO2 exposures are as shown below in Figure 6.

(a)



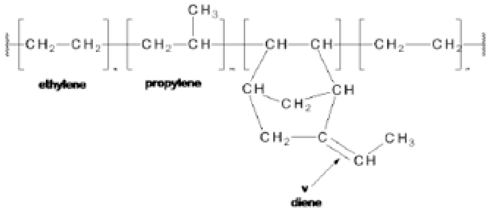
$$-\left[\left(CH_2\right)_m-NH-\overset{\overset{\displaystyle O}{\|}}{C}-\right]_n-$$

(b)

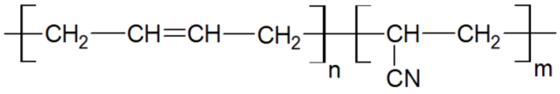


$$-\left(CF_2-CF_2\right)_n-$$

(c)

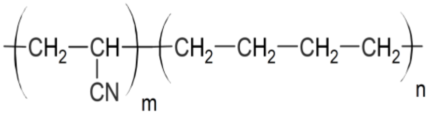


(d)



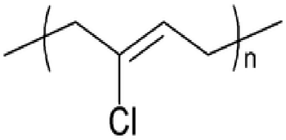
$$-\left[CH_2-CH=CH-CH_2\right]_n-\left[CH(CN)-CH_2\right]_m-$$

(e)

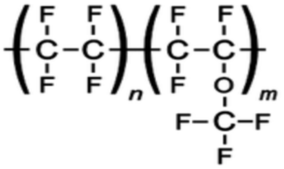


$$-\left(CH_2-CH(CN)\right)_m-\left(CH_2-CH_2-CH_2-CH_2\right)_n-$$

(f)

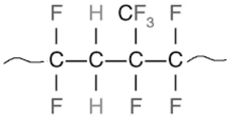


(g)



$$-\left(CF_2-CF_2\right)_n-\left(CF_2-CF(OCF_3)\right)_m-$$

(h)



$$\sim CF_2-CH_2-CF(CF_3)-CF_2\sim$$

Figure 6. Molecular structures of polymers (a) Polyamide (nylon 6,6) (b) Polytetrafluoroethylene PTFE (c) EPDM Rubber (d) NBR/Buna N (e) HNBR (f) Neoprene (g) FF 202 and (h) Viton A

3.1 Mass and density changes

Super-critical CO_2 is a state of CO_2 in which it behaves both as a fluid and a gas. In this state, CO_2's gaseous nature can allow for easy diffusion through the polymers while it is also dense enough to behave like a liquid to allow for solubilization. Density changes can mean retention of sCO2 and are indicative of a polymer's ability to allow sCO2 diffusion and the solubility of the polymer in sCO2. Mass and density are related properties. Mass changes in polymers are measured with the goal of checking to see if they tend to retain sCO2 even after removal from the test due to high solubility of the latter in the polymer. It is also a measure of the possible loss of volatiles from these polymers during the process of depressurization. Loss of plasticizers as a volatile can cause the polymer to lose its elasticity with time and result in a loss of sealing ability.

For all 8 polymers exposed to sCO2 under thermal cycling conditions, mass and density either increased or decreased after thermal cycling in sCO2. Mass change measurements show that thermoplastics nylon, and PTFE polymers experience a mass gain. FF202, HNBR, and Neoprene, show a decrease in mass. Whereas, EPDM, and Viton, shows an increase in mass. Viton shows the largest mass gain at 4% with EPDM at 2.5% (Figure 7). Mass loss for NBR and Neoprene are substantial at 5% whereas that for FF202 and HNBR are much lower. It is speculated that polymers with large fluorine atoms on the backbone (FF-202) and an absence of double bonds in the microstructure (HNBR) hinder sCO2 transport into the polymer and show small mass differences (Figure 8). Whereas polymers with polar side groups encourage sCO2 migration and show a tendency to bind to sCO2. This latter effect is seen with Buna N, and Neoprene in Figure 7. These polymers show large decreasing mass with 50 cycles which could mean that sCO2 diffusion is encouraged by polar groups present on backbone and that loss of volatiles with sCO2 diffusion is a possibility. EPDM has polar double bonds in its molecular structure and Viton has a backbone that is only partially hindered by bulky -F atoms. These structural features could be responsible for mass gains seen in these polymers.

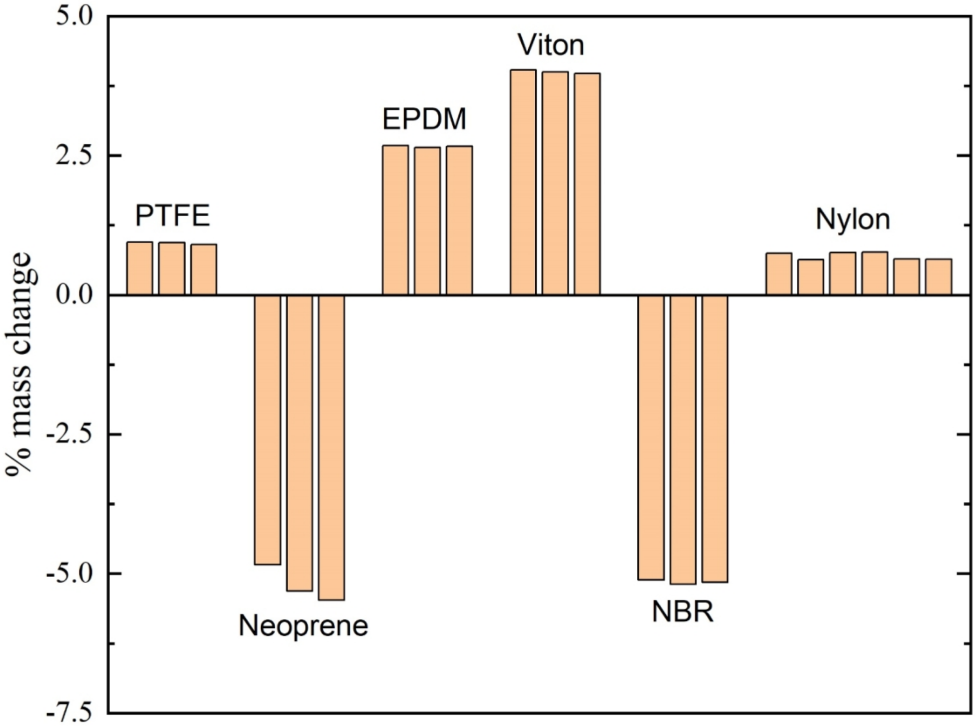


Figure 7. Mass changes in polymers after 50 thermal cycles between 50°C and 150°C in sCO2

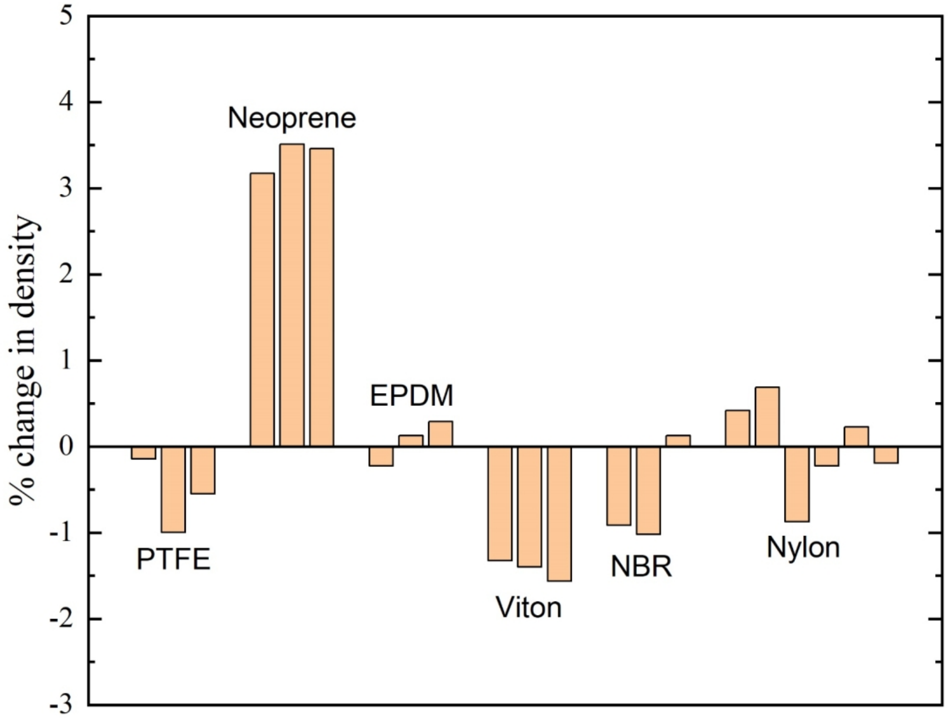


Figure 8. Density changes in polymer after 50 thermal cycles between 50°C and 150°C in sCO2

Density measurements are directly indicative of the degree of swell in polymers. While thermoplastics do not show a massive change (both PTFE and nylon are under 1%), elastomers can swell to different extents, depending on molecular structure and affinity to sCO2. Molecular structures with a pendant polar group such as -Cl in Neoprene show affinity to the polarity of sCO2 and show an initial increase in density (decreased swell). A sCO2 effect such as described can result in the seal losing its ability to seal upon exposure and over time and many numbers of sCO2 cycles, be susceptible to explosive decompression phenomena. Polymers with large fluorine atoms on the backbone (FF-202, Viton) hinder sCO2 transport into the polymer and show small mass differences. Viton and FF-202 with bulky F atoms can show steric hinderance to sCO2 diffusion and hence do not show massive swelling or decreased densities in sCO2. Whereas, polymers with polar side groups encourage sCO2 migration and show a tendency to bind to sCO2. This latter effect is seen with Buna N, HNBR, PUR, and Neoprene. These polymers show large changes in density with time which could mean that sCO2 diffusion is encouraged by polar groups present on backbone and that loss of volatiles with sCO2 diffusion is a possibility. Repeated increase and decrease in volumes of polymers as seals can result in the seal losing its ability to seal upon exposure and over time and after many numbers of sCO2 cycles, be susceptible to explosive decompression phenomena.

3.2 Complex moduli and glass transition temperature changes

Dynamic mechanical thermal analyses (DMTA) of polymers before and after sCO2 exposures can indicate interesting trends for changes in complex moduli (storage and loss) and glass transition temperatures (T_g). The viscoelastic natures of the polymers respond to sCO2 exposure and show interesting trends with thermal cycling exposure. Complex moduli for polymers can be changed with different interactions of polymers with sCO2 such as absorption and retention of the gas, which can lead to plasticization and solubilization of the polymers. Typically, in such circumstances, a lowering of the storage modulus is seen.

If there are interactions that can result in weak crosslinking between polar groups on the polymer and the polar sCO2 molecule, then, a higher storage modulus, compared to unexposed polymer, can be expected. Glass transition temperatures are indicative of the breaking of existing crosslinks or the formation of new ones in the polymers. For thermal cycling between 50°C and 150°C, the test temperatures are above the glass transition temperatures for elastomers tested. For thermoplastics, nylon and PTFE, the test temperatures and associated thermal cycling, can show significant influences because Nylon has a glass transition temperature of 70°C and PTFE, 137°C, which fall in the thermal cycling regime. At the time of the writing of this report, DMTA data is being generated on polymers, after 50 and 100 thermal cycles, and findings will be submitted as part of a Level 3 report by March 2022.

3.3 Compression set for elastomers

Compression set for a polymer is a measure of its capability to permanently deform when a set load is applied for a certain length of time at a certain given temperature. A high compression set number is undesirable because it indicates the polymer’s susceptibility to being deformed such that it is incapable of proper sealing. When rubbers are saturated with sCO2, they tend to be softer due to a plasticization effect of the polymer matrix. This softening effect can cause the compression set of the polymer to be higher after exposure than before. Higher pressures can exacerbate this permanent deformation in elastomers. It is important to note that compression set is a property of elastomers and cannot be measured for thermoplastics which are semi-crystalline in nature. At the time of the writing of this report, compression set data is being generated on polymers after 50 and 100 thermal cycles, and findings will be submitted as a Level 3 report by March 2022.

3.4 ATR-FTIR data for polymers in sCO2

Attenuated total reflectance-Fourier transform infra-red spectroscopy (ATR-FTIR) was used to detect molecular changes in polymers after exposure to sCO2. The attenuated total reflectance method was used to make measurements on polymers before and after 50 and 100 cycles of thermal exposure to 20 MPa of sCO2. FTIR analyses data is being generated at the time of the writing of this report, and findings will be submitted as part of a Level 3 report by March 2022.

3.5 Optical microscopy imaging of polymers in sCO2

Optical microscopy was used to study surface changes and texturization effects on the polymers exposed to sCO2. Surface attack was evident for some polymers at high magnifications. In some polymers, though the surface was not worn out, there was a ring flattening effect that was clearly seen. Surface texturizations varied from smoothening out of the surface to deep striations. Optical microscopy data on polymers, after 50 and 100 thermal cycles, is being generated, at the time of the writing of this report, and findings will be submitted as a Level 3 report by March 2022.

4 Conclusions

Based on FY 2019 effort, it was observed that increasing temperatures support faster diffusion of sCO2 and result in greater attack on the polymers. In FY 2020 work, the effect of pressures was examined. Although, increasing pressures did enhance diffusion effects, our work showed that a combination of longer times of exposure and pressures does more damage in polymers than pressures alone. Higher temperatures in combination with higher pressures and long exposure times, all possible within the sCO2 service realms, is speculated to be the most damaging of all combination environments. A Level 3 report summarizing all the findings from FY 2020 was published in March 2021 [17].

Past work described above has shown trends in polymer exposures to high pressure sCO2 under isothermal conditions that could be corelated to their materials' properties and structures. Physical effects were seen in the form of changes in mechanical properties such as storage modulus, and compression set and in the form of cracks and surface texturization changes in the polymers. Chemical changes were seen in the form of possible structural changes in FTIR spectra. Overall, elastomers were more susceptible to sCO2 attack compared to thermoplastics which showed the least molecular changes, the least swelling and negligible changes in modulus and glass transition with exposure to sCO2.

Based on polymer property changes observed, it is speculated that polymers with -C-F bonds, such as FF-202, Viton and PTFE, are capable of slowing down diffusion of sCO2 due to the presence of the large fluorine atoms on the polymer backbone that provide steric hinderance. Polymers with -C=O and -C-Cl and -C-CN (such as PEEK, Nylon (-C=O), Neoprene (-C-Cl) and Buna N (-C-CN)) groups on the backbone or as pendant groups seem to be capable of the same interactions with sCO2. These Vander Wal's interactions upon exposure to sCO2 seem to result in higher modulus for these polymers with or without change in glass transition temperatures. EPDM and EPR were not susceptible to changes due to sCO2 to a great extent because of their non-polar nature. Polymer polarity and presence of bulky substitution groups on the backbone are all influential on sCO2 resistance and compatibility behavior in the same.

In continued efforts with regards to compatibility of polymers in sCO2 environments, we studied the influence of cycling temperatures under isobaric pressure on these soft materials in FY 2021. Cyclic testing can reproduce effects that can be encountered in actual service environments with respect to sCO2 power generation cycles. Due to COVID-19 delays causing material acquisition and delays in testing, a small portion of the FY 2021 effort is still in progress and all findings will be recorded in a supplemental report to be submitted to DOE by March 2022.

In future work, mitigation of O-ring damage with the help of barrier coatings, new material chemistries and formulating using the right materials and designing for high temperature use (up to 700°C) have been identified as a need for sCO2 power generation systems.

5 References

1. Quadrennial Technology Review 2015 Advancing Clean Electric Power Technologies
Chapter 4: Technology Assessments

2. Review paper, “Review of supercritical carbon dioxide (sCO2) technologies for high-grade waste heat to power conversion”, Marchionni, M., et. al., SN Applied Sciences, March 2020

3. “Selection of materials for high pressure CO2 transport”, Shiladitya Paul et.al., Paper presented at the Third International Forum on the Transportation of CO2 by Pipeline, Newcastle, June 2012

4. Peach, J., and Eastoe, J., Beilstein J. Org. Chem. 2014, **10,**1878-1895

5. Nalawade. S. P., Picchioni, F., Janssen, L.P.B.M., Prog. Polym. Sci. **31** (2006) 19-43

6. C. Boyere et.al, European Polymer Journal **61** (2014) 45-63

7. Tuminello W H, Dee G T and McHugh M A, 1995: 'Dissolving perfluropolymers in supercritical carbon dioxide'. Macromolecules, Vol 28, pp1506-1510

8. Tunison, Harmon, “Materials Evaluation in Supercritical CO2”, Presentation at the Supercritical CO2 Power Cycle Symposium, 2014, Pittsburg, PA

9. “Supercritical Carbon dioxide: In Polymer Reaction Engineering, edited by Maartje F. Kemmere and Thierry Meyer, Wiley-VCH, Weinham, 2005

10. Rindfleisch F, DiNoia T P and McHugh M A, 1996: 'Solubility of polymers and copolymers in supercritical CO_2'. Journal of Physical Chemistry, Vol 100, pp15581-15587

11. Lesisenheimer B., Fritz T., Final proceedings of the 4th IIR-Gustav Lorentzen conference 2001, 207

12. Berens A R, Huvard G S, Korsmeyer R W and Kunig F W, 1992: 'Application of compressed carbon dioxide in the incorporation of additives into polymers'. Journal of Applied Polymer Science, Vol 46, pp231-242

13. Davies O M, Arnold J C and Sulley S, 1999: 'The mechanical properties of elastomers in high-pressure CO_2'. Journal of Materials Science, Vol 34, pp417-422

14. Parker M E, Meyer J P and Meadows S R, 2009: Carbon dioxide enhanced oil recovery-injection operations technologies'. Energy Procedia, Vol1, pp3141-3148

15. Shiladitya Paul, Shepherd Richard and Woollin, Paul, “Selection of materials for high pressure CO2 transport”, Paper presented at Third International Forum on the Transportation of CO2 by pipeline, Newcastle, June 2012

16. “Fundamentals and Applications of Supercritical Carbon Dioxide (sCO2) Based Power Cycles”, edited by Klaus Brun, Peter Friedman, and Richard Dennis, Woodhead Publishing, Elsevier, 2017

17. Level 3 report submitted to DOE March 15th 2021 entitled “*Collective Summary of sCO2 Materials Development Part I: Influence of changing pressures at low temperature on compatibility of polymers in super-critical carbon dioxide for power generation systems” SAND 2021-3142 R*

STEP Materials Development
Task 2.06.02.02
Supercritical Transformational Electric Power Generation (STEP)

Level 2 Milestone Report

Collective Summary of sCO2 Materials Development
Part II: Re-establishment of Sandia National Labs super-critical carbon dioxide testing autoclave capability for exposure of metal alloys and polymers

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STEP Materials Development
Work Package: Materials Development (Metal alloys) FY 2021
Level 2 Milestone Report: M3ST-20SN020212014

ABSTRACT

The super critical carbon dioxide testing capability at Sandia National Laboratories, Livermore, CA testing capability was first stood-up in 2014. The system was not used much afterwards until 2021 when DOE provided STEP funds to re-instate the capability for critical material development research. In FY 2021, the capability was restored from a state of disrepair and non-use to an acceptable working condition. Shake down tests have shown that the capability can be useful towards remaining metal alloys FY 2021 work. We have finished the first experiment consisting of low pressure (450 psi/3 MPa), high temperature (650°C) exposure of fatigue and tensile specimens of HN 230 and 800H alloys to CO2 gas for 168 hours using this capability. Leaks in the seven thermocouple ports that measure temperatures along the length of the 2-meter-long autoclave was the reason for the choice of low-pressure conditions. These will be addressed by taking the autoclave insulation apart and resealing the thermocouples to be able to perform super-critical carbon dioxide runs with the same metal alloys at higher pressures (20 MPa) and high temperatures. The tensile and fatigue specimens will be tested at high temperature and fractography will be conducted on the fractured specimens. A report outlining the experiments and findings will be released to the DOE STEP program in March 2022.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

6 Background

The Brayton Cycle based on super-critical CO_2 as a working fluid is a non-conventional concept for converting thermal energy to electrical energy. These systems boast high cycle efficiency which automatically lead to lower cost, lower water usage, and in the case of fossil fuel heat sources, lower greenhouse gas (GHG) emissions. At high pressures, sCO2 is a high-density working fluid which also permits smaller equipment sizes, plant footprints and lower capital costs. However, in both open and closed Brayton-type cycle systems employing supercritical CO_2 (sCO2) as the working fluid, gas environments are hot and corrosive and present challenging requirements of strength and environmental resistance for materials of construction. In some instances, peak operating temperatures in the turbines in closed-cycle systems approach 500-700°C at 200 bar, while it opened-cycle systems, temperature of 1150°C at 300 bars can be seen [1]. Furthermore, in these systems, the cycles require that hot, lower-pressure turbine exhaust be used to pre-heat high-pressure sCO2 entering the external heater or combustor just upstream of the turbine. Therefore, there is a need to match alloy performance properties with the performance requirements of individual components. This may impact the design of the components themselves [2].

The range of available alloys with the pre-requisite strength and corrosion-resistance under these extreme conditions of operation, in particular for applications having elevated turbine inlet temperatures, are limited. If alloys are employed under conditions beyond current experience, practical acceptance will depend on successful qualification testing involving close collaboration among equipment manufacturers, materials suppliers, and materials research and development groups. Even at nominal operating temperatures, in support of a commercially viable solution, it is important to develop understanding of materials behavior for meaningful product lifetimes. While the testing of existing material choices may lead to the most exotic and expensive materials solutions, keeping in mind the cost impact is important because excessively high cost could prevent industry from integrating sCO2 into their energy conversion portfolios.

For commercially viable material solutions, it is important to develop understanding of materials properties, behavior, and performance under real power cycle operating conditions for meaningful product lifetimes. Both metal alloys and polymeric classes of materials are used in sCO2 power conversion cycles, albeit for very different parts of the operation. While metal alloy seals and component materials can stand high temperatures for reasonable exposure times and high pressures, elastomeric O-rings used in different components for sealing purposes are soft polymeric materials that will behave quite differently in sCO2 environments. Combinations of high pressures and temperatures especially in cyclic conditions with possible presence of moisture and other corrosive by-products can create extremely demanding environments for both families of materials [3]. Therefore, material degradation mechanisms for short term or longer-term exposures to sCO2 environments must be considered. These can include fatal effects such as corrosion and related damage-accumulation for alloys and explosive decompression behavior for polymeric O-rings. Current and future efforts should keep these material performance knowledge gaps in the forefront.

The availability of a properly functioning in-house sCO2 testing capability can be crucial to addressing knowledge gaps through specific and focused experiments for conducting compatibility research for metal alloys and polymers used in sCO2 environments. The focus of the rest of this Level 2 report will be on our efforts towards the development of one such capability at Sandia National Labs, Livermore, CA in FY 2021.

6.1 Recent SNL R&D efforts for Materials Compatibility in sCO2 (FY2018-20)

Topics of investigation for metal alloys investigated in FY 2018-FY2020 primarily revolved around material compatibility with CO_2. This work includes testing of metallic component materials. The investigation employed both traditional elevated temperature and pressure oven testing, as well as application of fundamental science to characterize the chemical processes involved between the metals and CO_2. Material investigations in 2019 focused on alloy corrosion in compact heat exchangers.

Past studies have shown that sCO2 corrosion occurs through the formation of metal carbonates, oxide layers, and carburization [4], and alloys with Cr, Mo and Ni generally exhibit less corrosion [5]. While stainless steels may offer sufficient corrosion resistance at the lower range of temperatures seen by the sCO2 Brayton cycles, more expensive alloys such as Inconel and Haynes are typically needed for the higher temperature regions. The FY 2020 study investigated the effects of corrosion on the Haynes 230 alloy, focusing on changes in the mechanical properties. A tube furnace (Figure 1) was used for CO2 exposures of HN 230 alloy for 500, 1000, and 1500 hours at 650°C at atmospheric pressures of CO2. After CO_2 exposure, the tensile specimen samples were tested in tension at 750°C to failure. Additional tensile specimens that had no CO_2 exposure were also tested for comparison. The mechanical behavior was assessed as a function of CO_2 exposure times and correlated with measurements from the failed samples.

Figure 1. Tube furnace used for high temperature CO_2 corrosion tests.

No discernable difference was seen in the response with increased CO_2 exposure time. This material in its wrought form appears to be insensitive to CO_2 exposure at 650°C. A level 3 report with all the details of these experiments and the findings (SAND 2020-13305 R) was released to the DOE in March 2021. These results will provide a baseline for comparison to diffusion bonded forms of this alloy which we were not able to acquire in FY 2020-21 due to COVID but will seek in FY 2022. Additionally, the planned 750°C fatigue testing of the remaining specimens will determine if the alloy remains insensitive when subjected to repeated loadings. This remaining work will be performed in FY22 Q1 along with other specimens described below.

6.2 FY 2021 experiments with metal alloys using Sandia's sCO2 capability

The super critical carbon dioxide testing capability at Sandia National Laboratories, Livermore, CA testing capability was first stood-up in 2014. It was used to conduct a few experiments focused on corrosion testing of metal alloys in super critical carbon dioxide, under the auspices of the STEP program. The system was not used much afterwards until 2021 when DOE provided STEP funds to re-instate the capability for critical material development research.

In FY 2021, the capability was restored from a state of disrepair and non-use to an acceptable working condition. Over the course of nine months, we were able to methodically identify the working and non-working parts of the system with thorough step-by-step section-by-section analyses in a safe and organized effort. While most effort was spent on restoring heating and pumping functions to achieve full temperature and pressure capabilities, rate of gas usage, leaks and flow rates are all critical to understand and follow, with proper instrumentation and controls in place, during an experiment. Changes included installation of a new super critical pump, new temperature controllers, and a completely updated Pressure Safety Data Package (PSDP). Shake down tests have shown that the capability, as it is today, can be quickly readied for use after a few more changes, towards completing FY 2021 metal alloys exposures of HN 230 and 800H in sC2 environments.

We have finished the first experiment consisting of low pressure (450 psi/3 MPa), high temperature (650°C) exposure of fatigue and tensile specimens of HN 230 and 800H alloys to CO2 gas for 168 hours, using this capability. This will be compared to the data from the experiments performed in 2020 using the tube furnace. It is to be noted that the tube furnace experiments ran 500-1500 hours, unlike the 168 hours of exposure in the recent experiment. Albeit, a superficial comparison of the data can help validate the use of the sCO2 autoclave for both CO2 and sCO2 experiments.

Leaks in the seven thermocouple ports that measure temperatures along the length of the 2-meter-long autoclave was the reason for the choice of low-pressure conditions. In next steps, this issue will be addressed by taking the autoclave insulation apart and resealing the thermocouples to be able to run super-critical carbon dioxide runs with the same metal alloys at higher pressures (10-20 MPa) and high temperatures (650°C). The tensile and fatigue specimens will be tested at high temperature (750°C) and fractography conducted on the fractured specimens. A report outlining the experiments and findings will be released to the DOE STEP program in March 2022.

7 References

[1] Quadrennial Technology Review 2015 Advancing Clean Electric Power Technologies Chapter 4: Technology Assessments

[2] Review paper, “Review of supercritical carbon dioxide (sCO2) technologies for high-grade waste heat to power conversion”, Marchionni, M., et. al., SN Applied Sciences, March 2020

[3] “Selection of materials for high pressure CO2 transport”, Shiladitya Paul et.al. , Paper presented at the Third International Forum on the Transportation of CO2 by Pipeline, Newcastle, June 2012

[4] Moore, R and Conboy, T., METAL CORROSION IN A SUPERCRITICAL CARBON DIOXIDE – LIQUID SODIUM POWER CYCLE. Sandia National Laboratories Report, SAND2012-0184, 2012.

[5] Loriers, H., Leclercq, D. and Darras, R, “Corrosion Des Aciers Faiblement Allies Dans Le Gaz Carbonique Aux temperatures Moyennes” Journal of Nuclear Materials Vol. 24, pp. 144-159, 1968.