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subject: Critical knowledge gaps for compatibility of polymers with super-critical CO_2 for power generation systems

The purpose of this memo is to highlight the findings of an extensive literature survey and interviews with experts on the behavior of polymers in super-critical CO2 energy conversion systems that demonstrate foremost that there are critical knowledge gaps in this area that need to be addressed to improve design, reliability and lifetimes of system components. There are two brief discussions presented here: 1. SCO2 effects in polymers and associated mechanisms of failure 2. Summary of knowledge gaps identified in polymer/SCO2 interactions and science-based R&D to address the same

1. SCO2 effects on polymers in energy conversion systems

The development of super-critical CO2 energy conversion systems requires a multi-materials approach that utilizes the most effective combination of materials to achieve safe, cost-effective construction and operation. The application-based selection of polymers finds common polymers such as Viton, polyetheretherketone (PEEK), ethylene propylene diene monomer (EPDM), ethylene propylene rubber (EPR) and polytetrafluorethylene (PTFE or Teflon) 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. Elevated temperatures (700°C) and pressures (4400 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. In this section, an attempt has been made to describe common SCO2 effects seen with polymers in power generation environments as well as mitigation strategies that are being adopted to counter the same.

Most knowledge of polymer and monomer interactions with CO2 was derived from the unique fact that super-critical carbondioxide (sCO2) can be used as a solvent in many polymerization processes [1-4] 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 CO2 absorption. O-rings with these functionalities in their backbones (Viton, Kalrez, Teflon, and Silicone) showed the greatest loss of CO2 from sealed fixtures [5]. 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 [6]. On the other hand, since CO2 is a weakly polar solvent, it cannot dissolve highly polar or hydrogen-bonded polymers such as poly (acrylic acid) [7]. 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 [8]. CO2 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 [9]. 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.

Of all failure mechanisms normally encountered with polymers in SCO2, explosive decompression is the most destructive. Elastomers inherently contain voids and rigid inclusions that are produced during manufacture. Fluids or gases in contact with the material are absorbed and diffuse throughout the material. XRD is normally caused by fast uncontrolled release of trapped gas in the elastomers when positive high pressures are removed and the part depressurizes. The material that is supersaturated with CO2 releases the dissolved gas and this results in nucleation and growth of internal gas bubbles which forms surface blisters and eventually leads to can cause mechanical damage such as extrusion and blistering and eventual shredding of the elastomer (Figure 1).

Figure 1. Examples of failures in elastomers in SCO2 service due to explosive decompression

Table 1 shows the approximation of permeation coefficients and explosive decompression impact for different gases in common elastomers. The higher the solubility/diffusivity ratio, the greater the effect of explosive decompression. This ratio is highest for CO2 amongst all the gases shown, which means that the polymers will exhibit maximum CO2 effects over any other gas.

Gas type	**Permeation coefficient (Q)**	**Diffusion coefficient (D)**	**Solubility coefficient (S)**	**S/D**
N2	1	1	1	1
CO2	24	1	24	24
CH4	3.4	0.7	4.9	7
He	15	60	0.25	0.004
O2	3.8	1.7	2.2	1.29

Table 1: Approximation of permeation, diffusion and solubility coefficients of various gases through common elastomers

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 [10]. 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.

Several measures can be adopted to prevent failure modes such as XRD and extend polymer lifetimes in SCO2 service. XRD can be prevented at manufacture-specified depressurization rates which are usually slow and gradual. However, these slow depressurization rates are not capable of accommodating transient conditions in SCO2 service such as emergency shut-downs and blow-downs. At low temperatures such as in blow-downs, elastomers become harder, less resilient and lose their memory. These require special XRD resistant o-rings as standard elastomers become hard and can no longer follow stem lateral movement. Polymers such as Teflon, nylon and stiffer polymers (80-90 durometer) are often used where appropriate [11]. Sometimes, design of the O-ring groove geometry and a high groove fill can also be used to help minimize XRD damage to elastomers. However, under extreme operating conditions, even design considerations can prove ineffective [12].

Figure 2. Failure seen with Viton O-ring due to SCO2 exposure

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 elastomer XRD-resistant 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 2). 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 (700°C) and pressures (4400 psi), elastomeric seals are replaced by PTFE-alloys which are spring-loaded with extremely fine surface finish for improved sealing [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 [11].

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 breakdown and destroys its integrity and microstructure.

2. Knowledge gaps identified and proposed R&D plan

The above interactions of SCO2 with polymers define their mutual compatibility and in their function as seals, liners and O-rings in power generation systems, they dictate component safety, reliability and lifetimes. Therefore, based on what is already known in this area, it is critical for us to identify the future areas of research that must be pursued to address some of the material performance limitations in the form of new material exploration and test method development. Based on conversations with subject matter experts and an exhaustive literature search, listed below are some of the knowledge gaps that can benefit:

a. Significant amount of testing of polymers in SCO2 has been conducted in lower pressures (1000-1800 psig) lower autoclave velocities and low temperature (55-60°C) conditions. This does not mimic the conditions that these materials will see in actual power cycles. It would be valuable to study the effect of higher temperatures (60°C-150°C range), pressures (4000-6000 psig) and velocities (TBD) on compatibility in terms of SCO2 effects such as increased polymer solubility, degradation and erosion under these conditions. The testing can be in cycling or static exposure modes.
b. Polymer properties have traditionally been studied ex-situ in static SCO2 environments in autoclaves followed by removal from these chambers. Such experiments do not reflect the in-situ changes that can happen in the autoclave in the presence of SCO2 which may be lost **before** analysis can be performed on the exposed polymers. Therefore, attempts must be made to study dynamic thermo-mechanical polymer properties such as glass transition changes and modulus in-situ. One such apparatus is being readied to study H2 effects on polymers at PNNL, Richland, WA.
c. Cycling experiments (pressure or temperature cycling) that include rapid cycling for 10,000 cycles minimum in SCO2 with polymers where physical property changes can be followed ex-situ by sample characterization such as dimensional, volume, or mass changes, optical void analysis, hardness, modulus, and mechanical strength changes can be useful to understand aging effects due to cycling. One such recipe for rapid cycling (Figure 3) may involve soaking the specimens for a few hours (t_s = 36 hours) in SCO2 environments followed by lowering the pressure to a minimum (time taken t_d = 4 seconds), holding there at minimum pressure for time t_L of 5 seconds, followed by a ramp to high pressures during t_F of 15 seconds followed by hold at high pressures for t_H of 5 seconds giving a total of 29 seconds per cycle without soak. The pressures or temperatures selected for this type of rapid cycling must be as close as feasible to service conditions to be useful in predicting polymer behavior in actual SCO2 use.

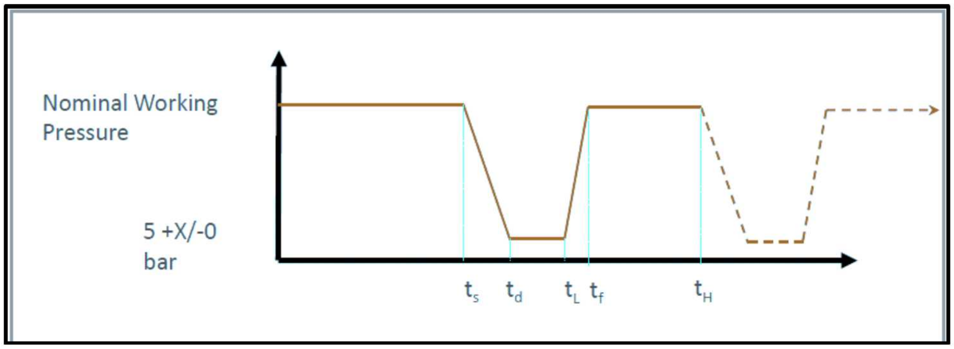

Figure 3. Recipe suggested for rapid cycling of polymers in SCO2 to study aging due to cycling.

d. The development of new materials (co-polymers, polymer blends) tailored to meet the stringent requirements of a power generation system needs to be supported by what we already know about polymer behavior in SCO2 so far and can be aimed at higher performance or lower cost. Polymer interactions with SCO2 is sufficiently well-researched to provide a starting platform for this type of materials development work.
e. There have been some attempts to study the leakage seen with O-rings held compressed in fixtures in SCO2 autoclaves [5]. This study could be further enhanced with longer term cycling with O-rings under known compression loading at high pressures and temperatures for accelerated aging under load. Data generated from such experiments can provide valuable insight into behavior of these soft materials as seals under conditions that mimic service conditions in power generation systems.
f. Pollutants from polymers in the form of volatiles released during depressurization and impurities such as SO_x and NO_x are contaminants in SCO2 and potential sources of degradation of the polymers. These can have long-term as well as short-term effects, especially under extreme conditions of temperature and pressure with moisture present. The chemical changes undergone by polymers as result of these contaminants over an extended period often goes unmonitored until catastrophic failure occurs. Periodic sampling of the head-space of the SCO2 gas for analysis coupled with gas chromatography and mass spectroscopy (GC/MS) will allow for the monitoring of the contaminants. This data added to what we know about polymer degradation mechanisms accelerated by the presence of these contaminates, can help with predicting the lifetimes of the seals and the O-rings.
g. Models to predict permeation, and diffusion of SCO2 through polymers under power generation cycle extremes are not common and if developed, can help establish predictability and a deeper understanding of possible mechanisms with respect to failure modes such as explosive decompression.
h. There are no current established test methodologies for polymers in SCO2. Attempts to adapt standards that exist for testing these materials in air or H2 can be adapted for testing in SCO2.

In summary, based on what we know about interactions of polymers used with SCO2 in power generation systems, there are knowledge gaps that need to be addressed to allow full exploitation of this technology. A few key areas for investment of future R&D efforts within this realm are summarized in this memo. Sandia National Laboratories is fully prepared with trained knowledgeable staff and necessary equipment for testing to investigate and fulfill the responsibility of using science-based R&D to answer some of these difficult but important questions in the arena of polymers in SCO2 power generation cycles.

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