Materials compatibility in supercritical CO_2 environments applicable to power generation systems

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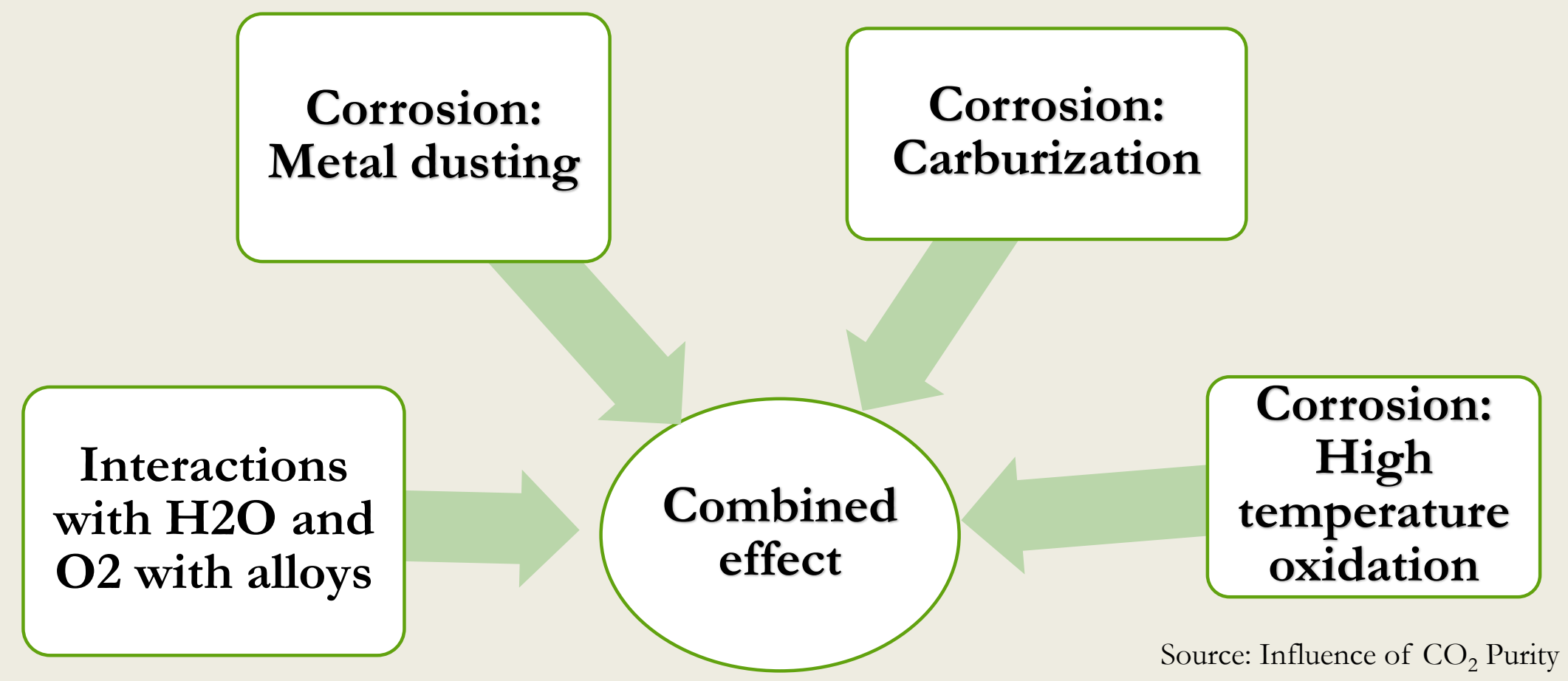
Department of Energy Supercritical Transformational Electric Power (STEP) program

"The mission of the Supercritical Transformational Electric Power (STEP) program is to design, build, and operate a 10 MWe pilot scale facility using an indirect-fired sCO_2 power cycle, **demonstrate component performance and cycle operability over a range of operating conditions**, and show progress towards a lower cost of electricity." NETL.DOE.gov

Materials compatibility for supercritical CO_2 environments:
Addresses the challenges of degradation of materials in sCO_2 environments by elucidating mechanisms of sCO_2-materials interactions with the goal improved material selection in component design

Mechanisms of degradation in metal alloys

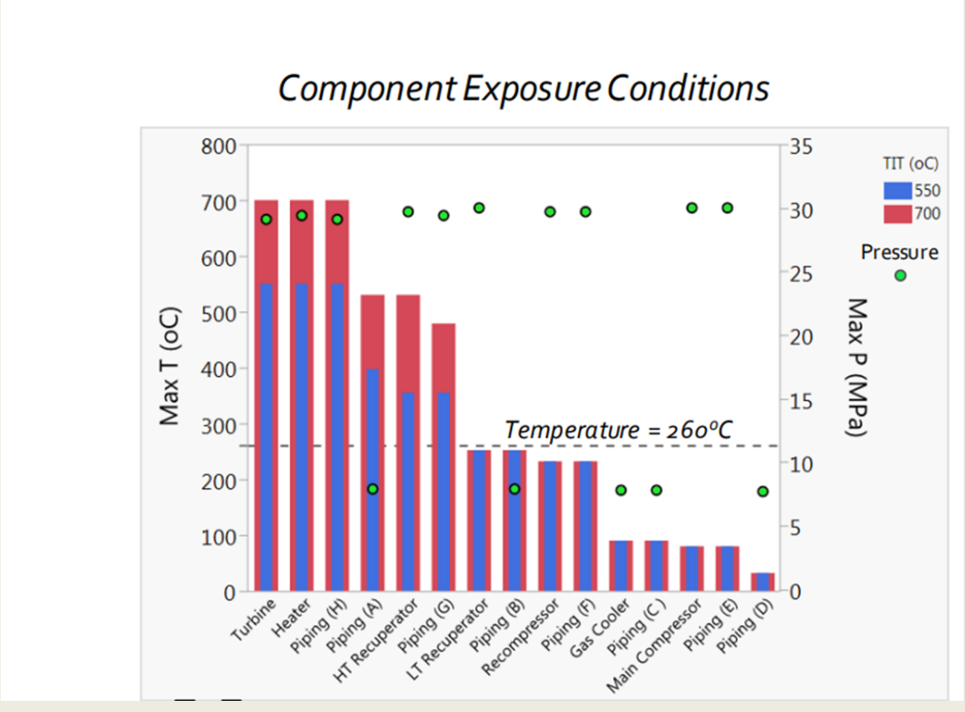

Corrosion: Metal dusting

Corrosion: Carburization

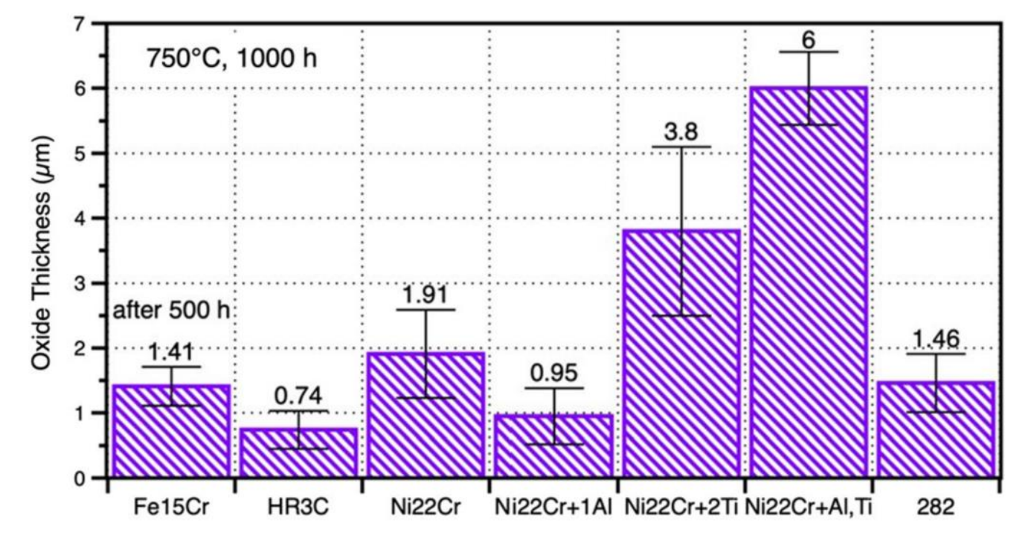
Interactions with H2O and O2 with alloys

Combined effect

Corrosion: High temperature oxidation

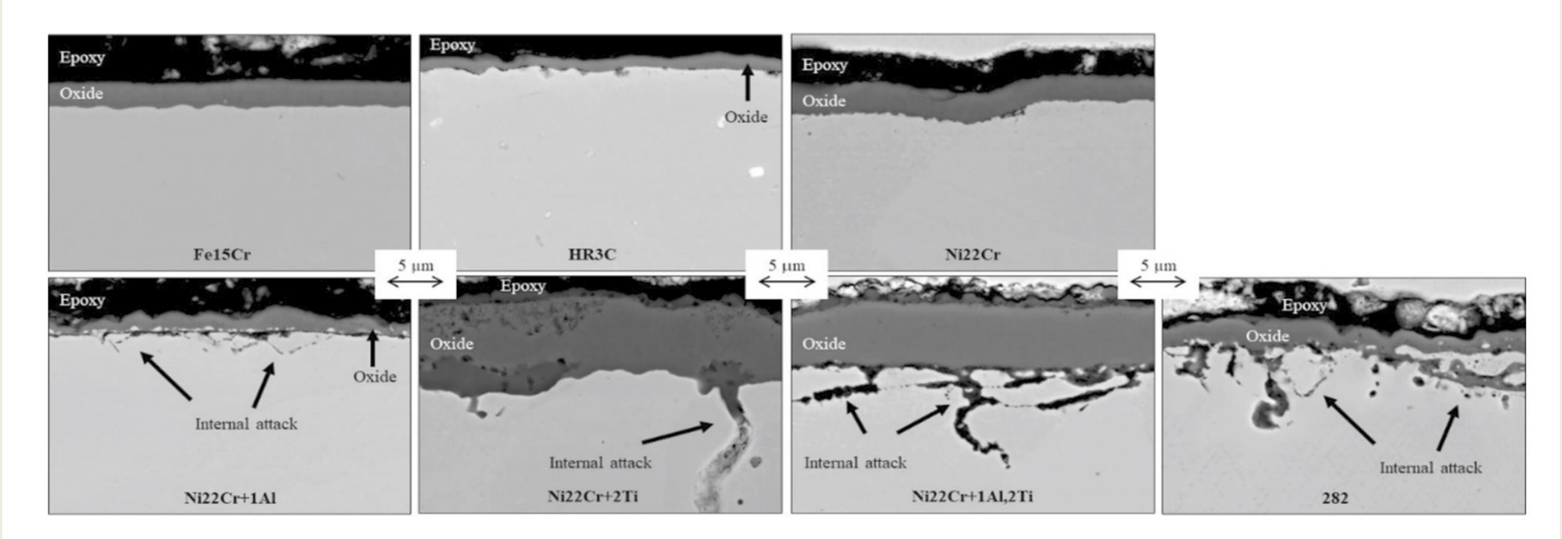


Source: Influence of CO_2 Purity on the Corrosion of Structural Alloys for Supercritical CO_2 Power Cycles; Matt Walker[1], E. Withey[2]; 6th International Supercritical CO_2 Power Cycles Symposium, Pittsburgh, PA, March 28th 2018



Measured oxide thicknesses after 1,000 h at 750°C in 30 MPa sCO_2 with 50 ppm $^{16}O_2$ and $H_2{}^{18}O$

SEM-backscattered electron images; specimens exposed for 500 h (Fe15Cr) and 1,000 h (the rest) at 750°C in 30 MPa sCO_2 with 50 ppm $^{16}O_2$ and $H_2{}^{18}O$



Source: A Tracer Study on sCO_2 Corrosion with Multiple Oxygen-Bearing Impurities Juho Lehmusto · Anton V. Ievlev · Ercan Cakmak · James R. Keiser · Bruce A. Pint; Oxidation of Metals (2021) 96:571–587

Mechanisms with impurities present

- Faster oxidation rates in Fe and Ni-based alloys
- Moisture increases the number of grain boundaries which act as diffusion routes leading to carburization beneath the scale

$$CO_2(g) \rightarrow CO(g) + \tfrac{1}{2}\, O_2(g)$$
$$2CO(g) \rightarrow CO_2(g) + C(s)$$

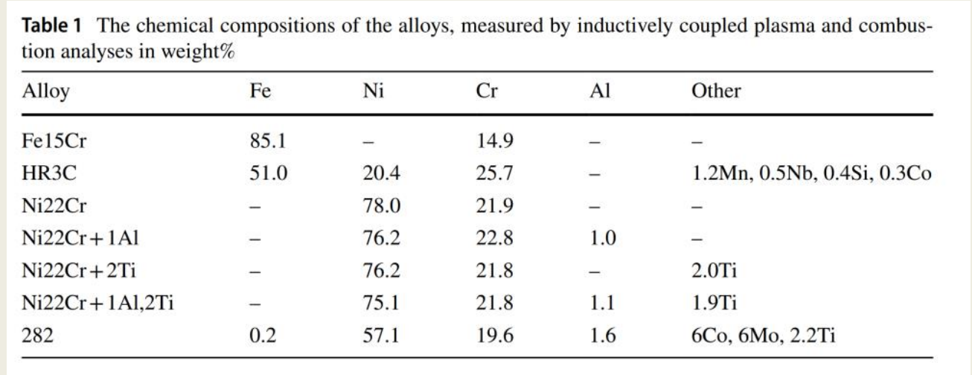


Table 1 The chemical compositions of the alloys, measured by inductively coupled plasma and combustion analyses in weight%

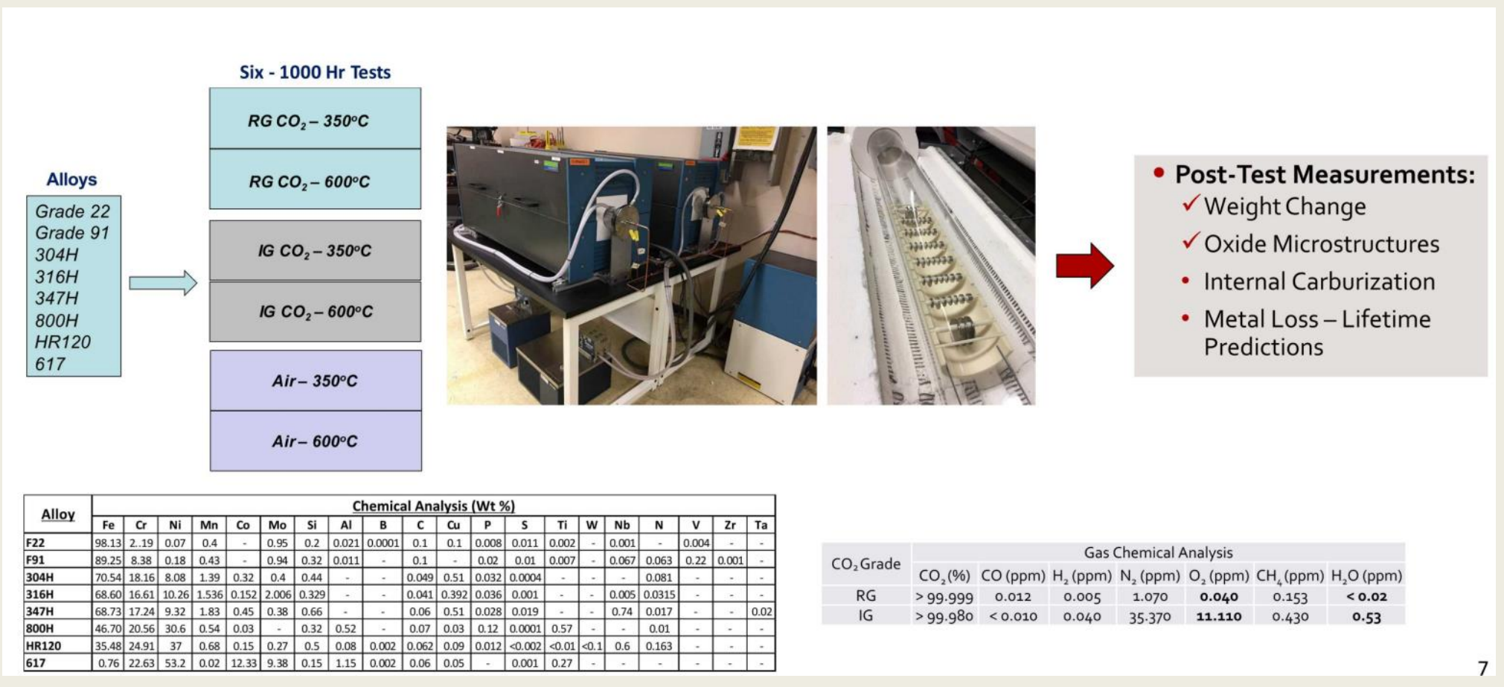
Alloy	Fe	Ni	Cr	Al	Other
Fe15Cr	85.1	–	14.9	–	–
HR3C	51.0	20.4	25.7	–	1.2Mn, 0.5Nb, 0.4Si, 0.3Co
Ni22Cr	–	78.0	21.9	–	–
Ni22Cr + 1Al	–	76.2	22.8	1.0	–
Ni22Cr + 2Ti	–	76.2	21.8	–	2.0Ti
Ni22Cr + 1Al,2Ti	–	75.1	21.8	1.1	1.9Ti
282	0.2	57.1	19.6	1.6	6Co, 6Mo, 2.2Ti

Metal alloy compatibility in sCO_2 – FY 2016-2019

- Alloy recommendations consider surface oxidation and not internal carburization
- All corrosion data collected using reagent grade (RG)CO_2 over industrial grade (IG)CO_2
- Most corrosion studies are conducted at ambient pressures; influence of impurities at ambient and high pressures can change known effects
- Structural alloy corrosion has only been evaluated in terms of sample weight gain, rather than by the more useful metric of metal loss

Materials support for sCO_2 system development

- **Turbine degradation**
- **Bearing foil materials (coatings)**
- **Systems for in-situ measurement of materials corrosion**

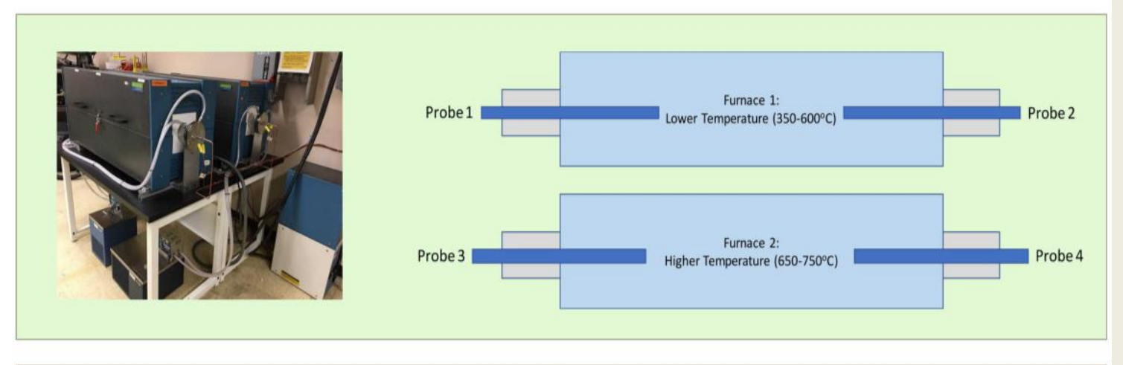


- **Post-Test Measurements:**
  - ✓ Weight Change
  - ✓ Oxide Microstructures
  - Internal Carburization
  - Metal Loss – Lifetime Predictions

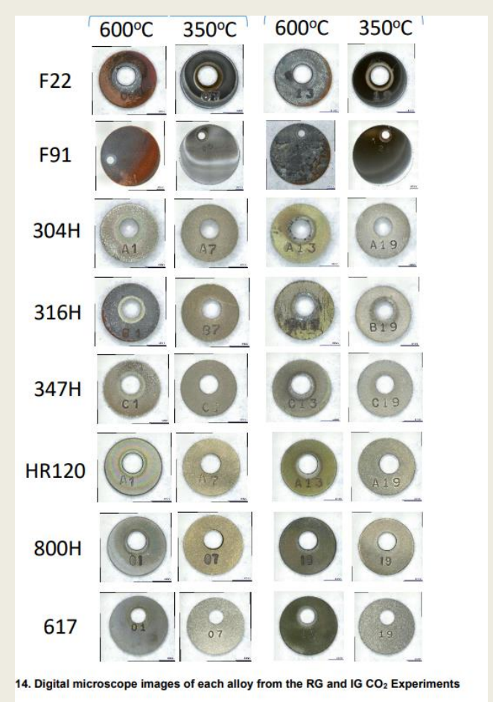
Alloy	Fe	Cr	Ni	Mn	Co	Mo	Si	Al	B	C	Cu	P	S	Ti	W	Nb	N	V	Zr	Ta
	Chemical Analysis (Wt %)																			
F22	98.13	2..19	0.07	0.4	-	0.95	0.2	0.021	0.0001	0.1	0.1	0.008	0.011	0.002	-	0.001	-	0.004	-	-
F91	89.25	8.38	0.18	0.43	-	0.94	0.32	0.011	-	0.1	-	0.02	0.01	0.007	-	0.067	0.063	0.22	0.001	-
304H	70.54	18.16	8.08	1.39	0.32	0.4	0.44	-	-	0.049	0.51	0.032	0.0004	-	-	-	0.081	-	-	-
316H	68.60	16.61	10.26	1.536	0.152	2.006	0.329	-	-	0.041	0.392	0.036	0.001	-	-	0.005	0.0315	-	-	-
347H	68.73	17.24	9.32	1.83	0.45	0.38	0.66	-	-	0.06	0.51	0.028	0.019	-	-	0.74	0.017	-	-	0.02
800H	46.70	20.56	30.6	0.54	0.03	-	0.32	0.52	-	0.07	0.03	0.12	0.0001	0.57	-	-	0.01	-	-	-
HR120	35.48	24.91	37	0.68	0.15	0.27	0.5	0.08	0.002	0.062	0.09	0.012	<0.002	<0.01	<0.1	0.6	0.163	-	-	-
617	0.76	22.63	53.2	0.02	12.33	9.38	0.15	1.15	0.002	0.06	0.05	-	0.001	0.27	-	-	-	-	-	-

CO_2 Grade	CO_2 (%)	CO (ppm)	H_2 (ppm)	N_2 (ppm)	O_2 (ppm)	CH_4 (ppm)	H_2O (ppm)
	Gas Chemical Analysis						
RG	> 99.999	0.012	0.005	1.070	**0.040**	0.153	**< 0.02**
IG	> 99.980	< 0.010	0.040	35.370	**11.110**	0.430	**0.53**

Influence of CO_2 purity on the corrosion of structural alloys for sCO_2 power cycles



- Run probes of 2 different alloys in two separate temperature ranges in CO_2
- Long duration tests up to 1500 hours
- Witness coupons (3) of each alloy included for extraction at 500 hour intervals (500hrs, 1000hrs, and 1500hrs)
- Lower T Candidates: 9Cr-1Mo (grade 91), 316, 304, 310, 347H
- Higher T Candidates: 800H, HR120, 617, 625, 230, 740H



14. Digital microscope images of each alloy from the RG and IG CO_2 Experiments

Statistical Analysis Summary of Alloy Weight Change Differences for RG and IG CO_2

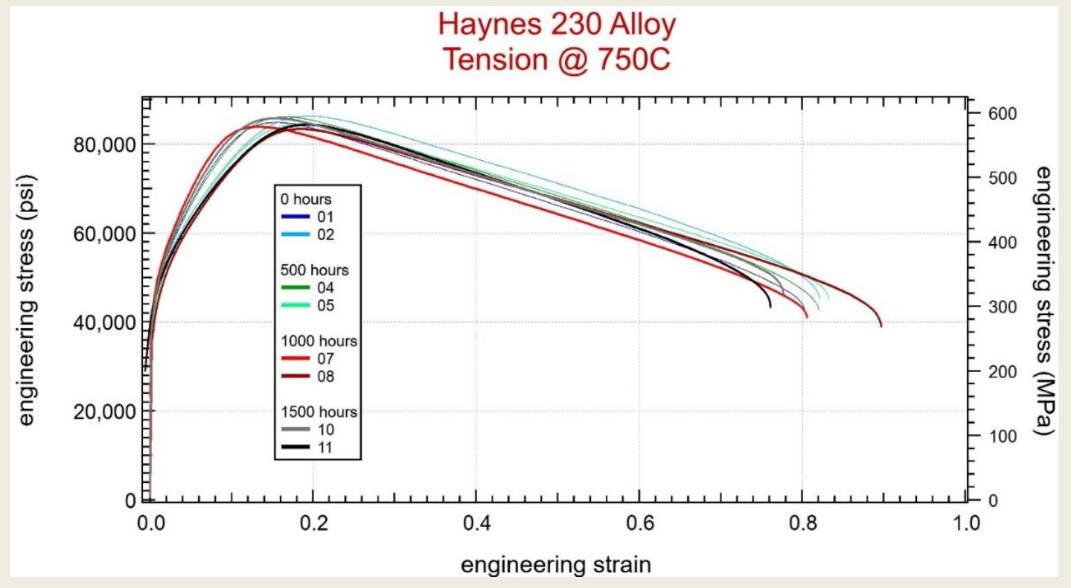
	350°C		600°C	
Alloy	**500 hrs**	**1000 hrs**	**500 hrs**	**1000 hrs**
F22	IG = RG	IG = RG	IG = RG	IG = RG
F91	IG = RG	IG = RG	IG = RG	IG = RG
304H	IG = RG	IG = RG	IG = RG	IG = RG
316H	IG > RG	IG > RG	IG = RG	IG = RG
347H	IG = RG	IG = RG	RG > IG	IG = RG
800H	IG = RG	IG = RG	IG = RG	IG = RG
HR120	IG = RG	IG = RG	IG = RG	IG = RG
617	IG = RG	IG = RG	IG = RG	RG > IG

Gas chemistry (RG vs IG CO_2) has very little influence on alloy corrosion

Metal alloy compatibility in sCO_2 – FY 2019-2021

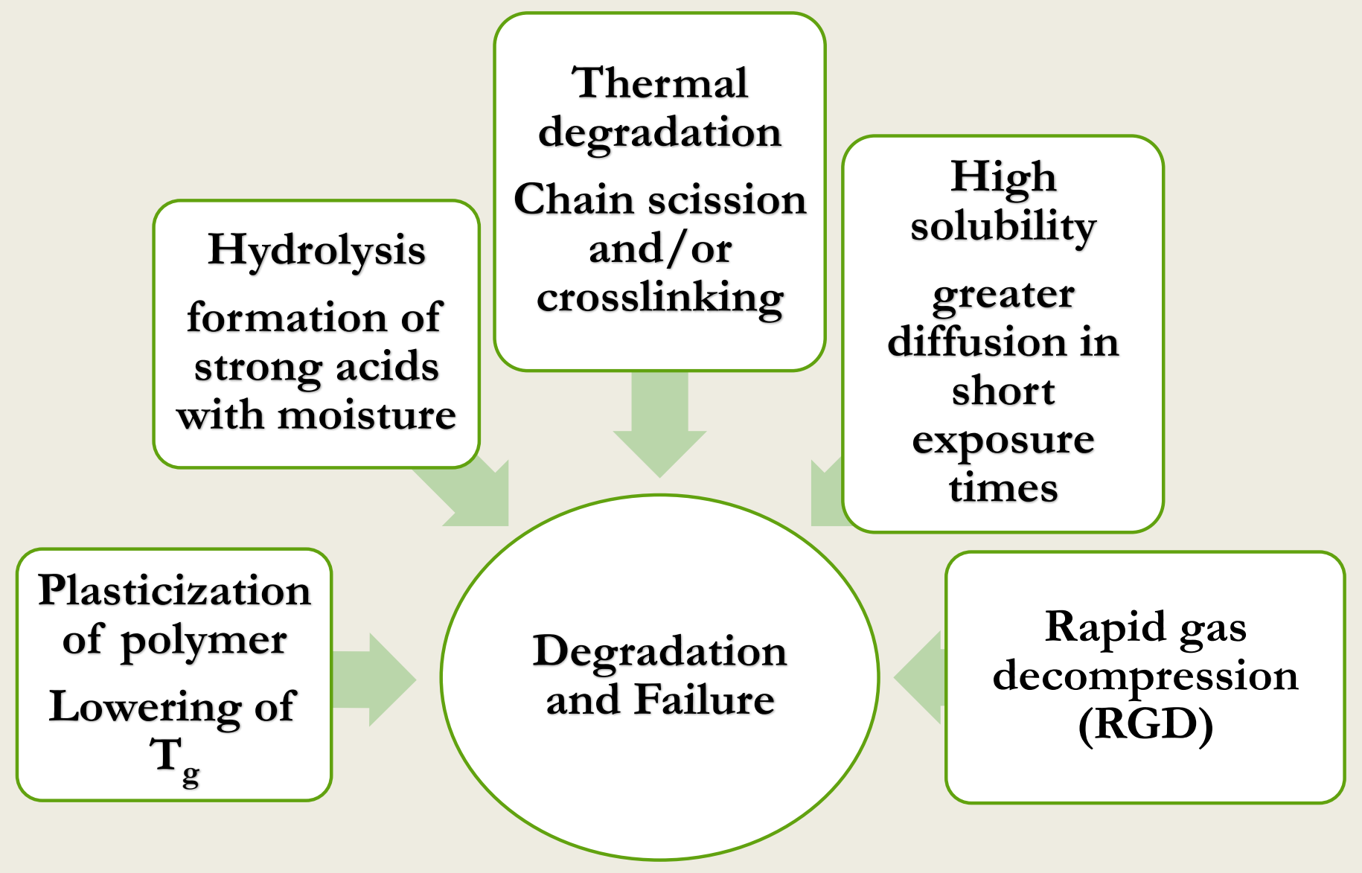
- High temperature CO_2 on Haynes 230 alloy was investigated by subjecting the alloy samples to CO_2 at 650ºC for 500, 1000, and 1500 hours
- Atmosphere was maintained with a constant flow of CO_2 from a gas cylinder at 150-200 mL/min
- After CO_2 exposure, the tensile specimen samples were tested in tension at 750ºC to failure
- For the eight tensile tests, data was collected at 1000 Hz for the following signals: displacement, 50-kip load cell, 10-kip load cell, extensometer, top thermocouple, and bottom thermocouple

Effect of High Temperature CO_2 on Haynes 230 Alloy



Mechanisms of degradation in polymers

Amorphous or semi-crystalline polymer


Thermal degradation
Chain scission and/or crosslinking

Hydrolysis
formation of strong acids with moisture

High solubility
greater diffusion in short exposure times

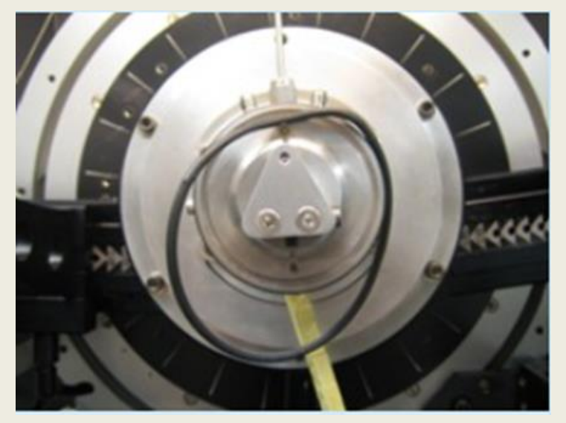
Plasticization of polymer
Lowering of T_g

Degradation and Failure

Rapid gas decompression (RGD)

Degree of crystallinity, substitution on backbone, molecular weight, crosslink density, glass transition temperature T_g, chain alignment/ packing

For turbines	
Inlet total pressure	21 MPa (3045 psi)
Inlet total temperature	753 K (480°C)
Mass flow rate	1270.5 kg/s
Outlet static pressure	7.35 MPa (1065 psi)



Failure seen with Viton O-ring due to sCO_2 exposure

Pressure transducers

Pressure relief valves

Examples of failures in elastomers in sCO_2 service due to explosive decompression

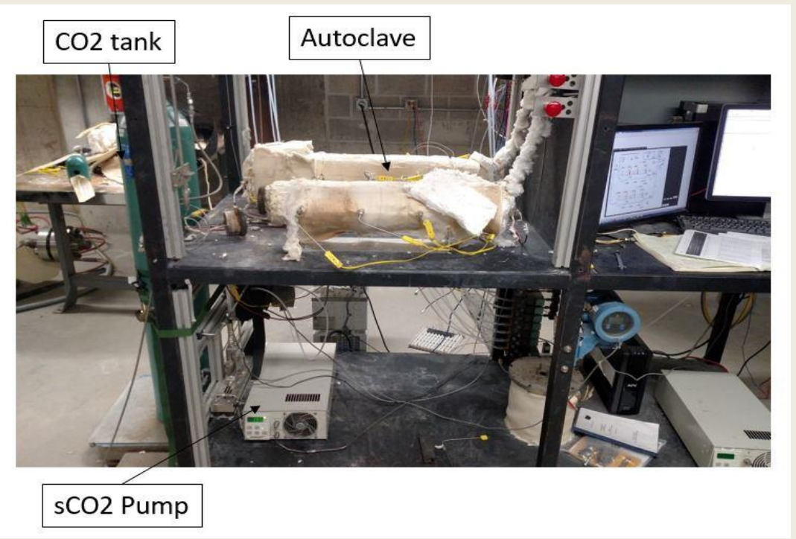
Turbo machinery seals

Valve seats

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

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

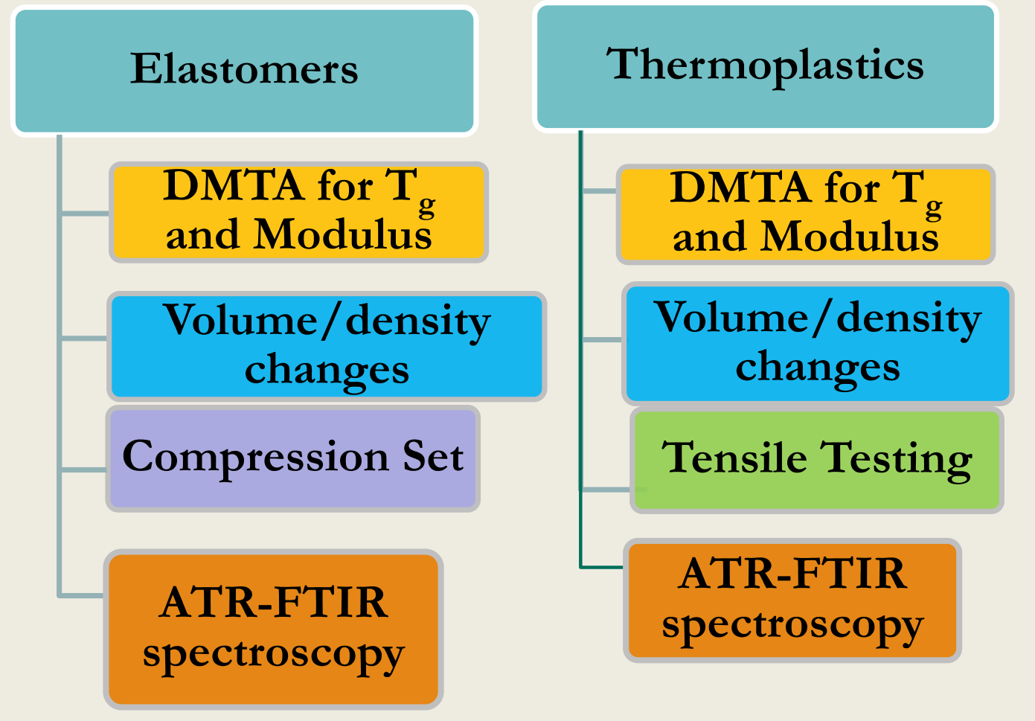
sCO_2 test equipment



O-ring sample holder for autoclave

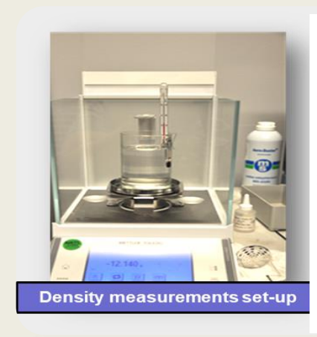
O-ring compression jig used in sCO_2 exposure; 25% deflection shim used

Ex-situ characterization for sCO_2 effects

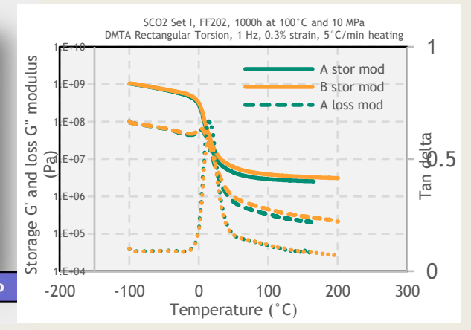

Elastomers
- DMTA for T_g and Modulus
- Volume/density changes
- Compression Set
- ATR-FTIR spectroscopy

Thermoplastics
- DMTA for T_g and Modulus
- Volume/density changes
- Tensile Testing
- ATR-FTIR spectroscopy

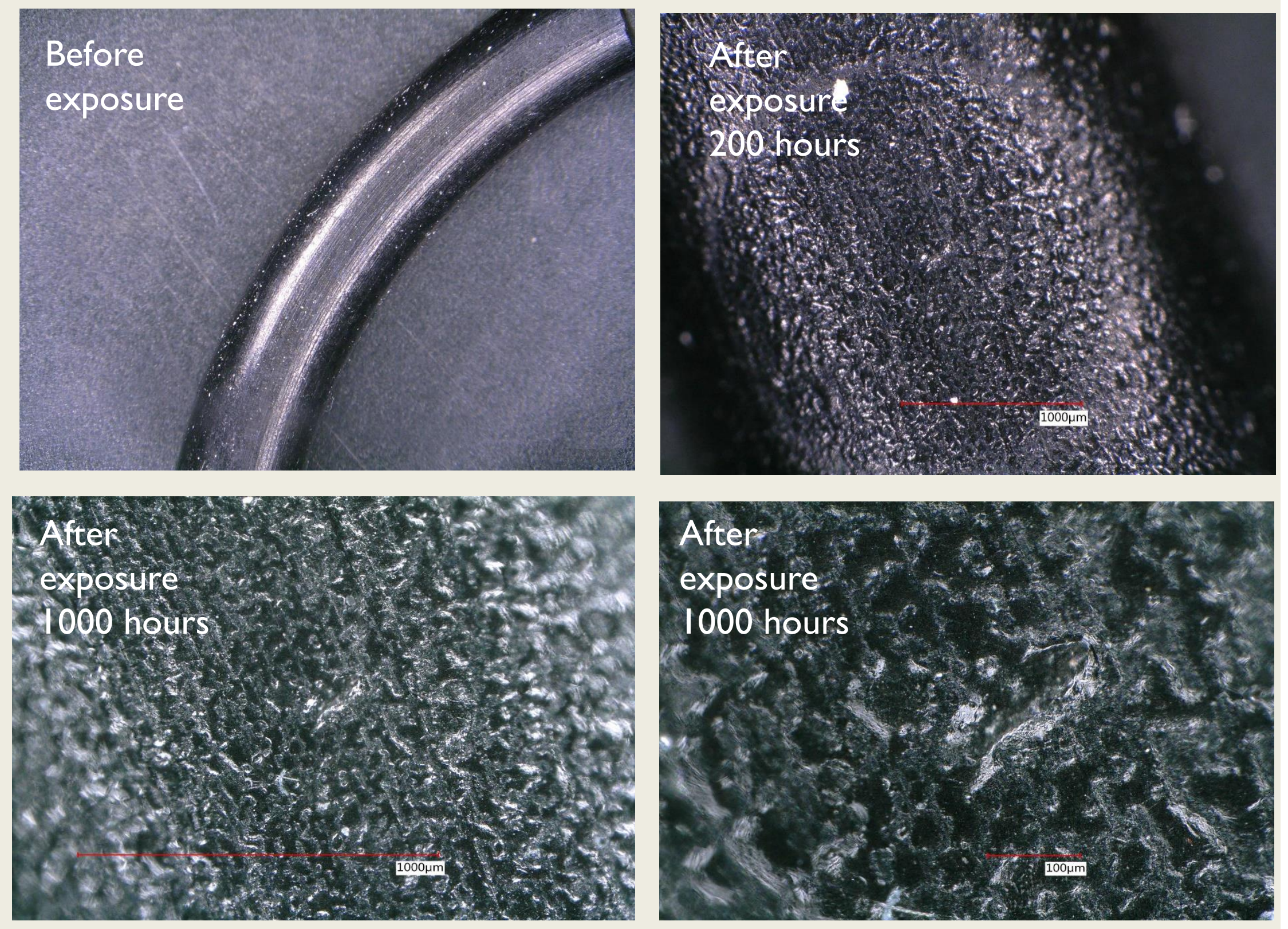
Compression set test



Density

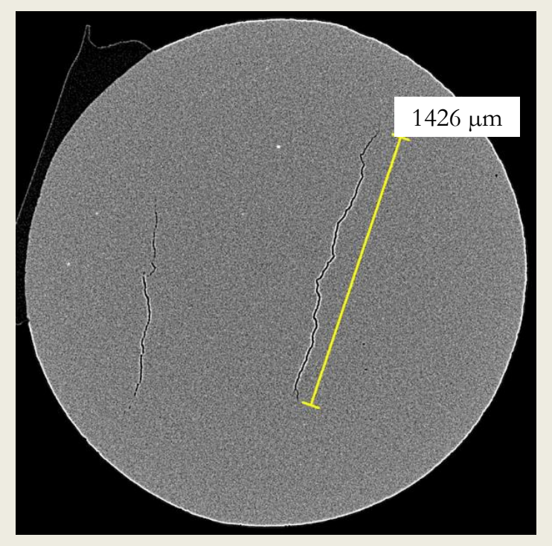


Optical microscopy images on Neoprene 100°C exposure @ 20 MPa sCO_2 pressure

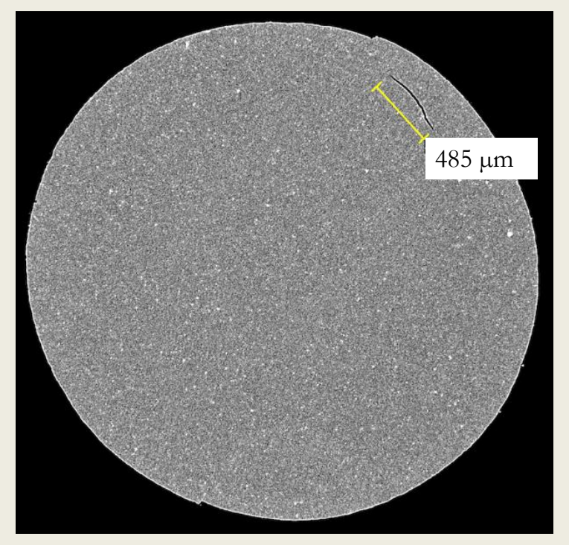


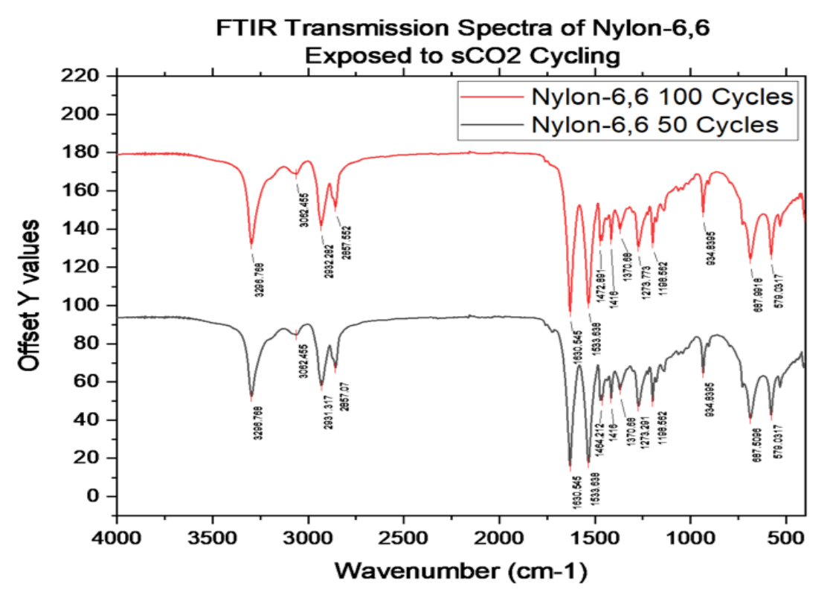
Micro-Computed tomography images for FFKM FF202 and EPDM rubbers: 150°C exposure @ 20 MPa sCO_2 pressure

FFKM FF202: 500-1500 μm length cracks in the interior



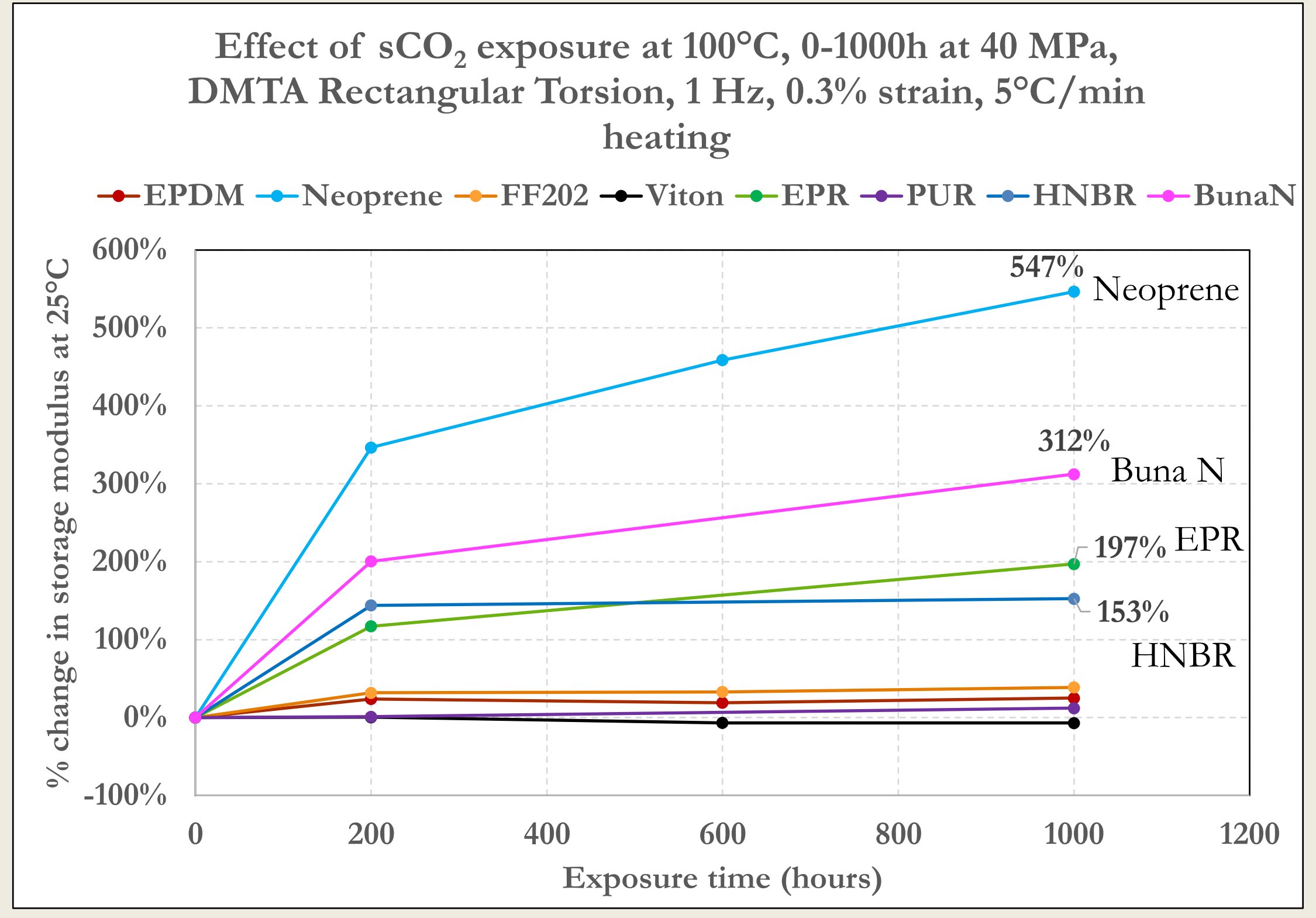
EPDM: 400-475 μm length cracks in the interior





Isobaric Cycling temperatures sCO_2 exposure: 20 MPa pressure for 50-150-50°C thermal cycling

Dynamic Mechanical Thermal Analysis (DMTA) on different elastomers: Exposure to 40 MPa sCO_2 at 100°C



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