US-UK Phase 3 Task 1 Oxidation in Supercritical Fluids, NETL

NATIONAL ENERGY TECHNOLOGY LABORATORY

Gordon R. Holcomb

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Supercritical Steam

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Steam conditions and net plant efficiencies for pulverized coal power plants

Nomenclature	Conditions	Net Plant Efficiency (HHV)
Subcritical	2400 psi/1050°F/1050°F (165 bar/566°C/566°C)	35%
Supercritical (SC)	3600 psi/1050°F/1075°F 248 bar/566°C/579°C)	38%
Ultra-Supercritical (USC)	>3600 psi/1100°F/1150°F (>248 bar/593°C/621°C)	>42%
Advanced Ultra-Supercritical (A-USC)	4000-5000 psi/1300-1400°F (276-345 bar/704-760°C)	>45%

adapted from EPRI Report 1022770, 2011

Categories are materials related, largely due to creep strength

- **USC: advanced ferritic & austenitic steels required**
- **A-USC: nickel-base superalloys required**

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sCO_2 Power Cycles – Indirect

- **Recompression sCO_2 Brayton Cycle**
  - Widely proposed for Concentrated Solar and Nuclear Energy due to their relatively narrow temperature range requirements
  - The split recuperator allows a portion of the high pressure sCO_2 to bypass the LTR to balance its heat duty and improve efficiency
  - For Fossil Energy applications, consideration must be given to use the significant thermal energy remaining in the combustion flue gas after passing through the PHX

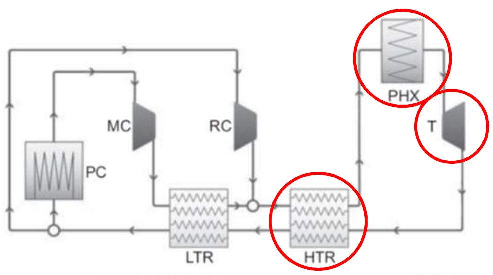


Figure 12.3 Recompression cycle. *HTR*, high-temperature recuperator; *LTR*, low-temperature recuperator; *MC*, main compressor; *PC*, primary cooler; *PHX*, primary heat exchanger; *RC*, recycle compressor; *T*, turbine.

High Temperature Components

T as high as 760°C
P as high as 350 bar
Essentially pure sCO_2
Our tests at
- 720°C/245 bar
- 700°C/200 bar
- 700°C/1bar
- 99.999% pure sCO_2

sCO_2 Power Cycles – Direct

- **Semi-open sCO_2 Brayton Cycle**
  - Oxycombustion using O_2 instead of air to burn fuel
  - More akin to gas turbines (indirect cycles more akin to steam turbines)
  - Higher turbine inlet temperatures and thus higher efficiencies
  - High pressure sCO_2 output allows for CO_2 transport and sequestration
  - Working fluid not pure CO_2, but contains other combustion products including H_2O

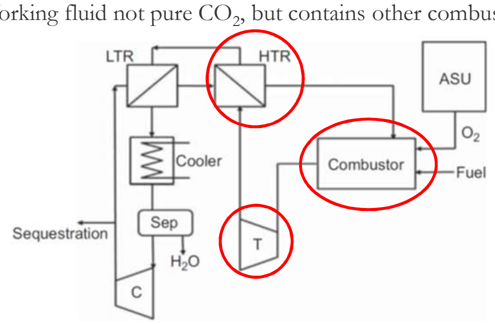


Figure 12.15 Direct-fired simple supercritical CO_2 Brayton cycle (Strakey et al., 2014). *ASU*, air separation unit; *C*, compressor; *HTR*, high-temperature recuperator; *LTR*, low-temperature recuperator; *T*, turbine.

High Temperature Components

T as high as ~1250°C
P as high as 350 bar
Our tests at
- 750°C/1 bar
- $CO_2/H_2O/O_2$ Mixtures
- Future tests to include SO_2

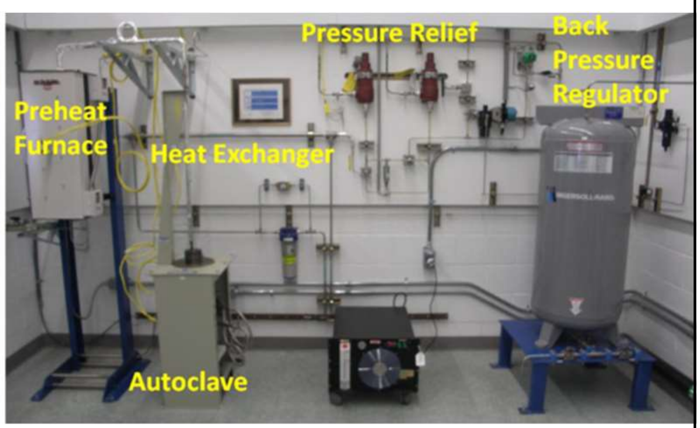
Experimental Exposures

500 h exposure increments

- **sH_2O**
  - 700°C/200 bar
  - Initiated more careful water purity practices
- **sCO_2**
  - 700°C/200 bar
  - 99.999% CO_2
  - Round Robin Activities (Oregon State University is lead organization)
- **aCO_2**
  - 700°C/1 bar
  - 99.999% CO_2, pO_2 monitored
- **$DFCO_2$**
  - 750°C for Ni-base alloys
  - Lower Temperature for Fe-base alloys
  - CO_2 + 4% H_2O + 1% O_2 (+1000 ppm SO_2) at 1 bar
  - CO_2 + H_2O at up to 250 bar (possible upgrade to include O_2)

Experimental Exposures

USC Steam Autoclave



- **Flow controlled with a high pressure pump**
- **Pressure controlled with a back pressure regulator**
- **ASME dual rated to 704°C/346 bar and 760°C/228 bar**
- **Autoclave body made of 230**

Experimental Exposures

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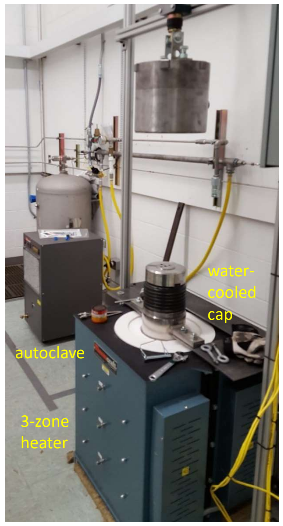
sCO_2 Autoclave

- Flow controlled with a high pressure pump
- Pressure controlled with a back pressure regulator
- ASME rated to 800°C/277 bar
- Autoclave body made of 230
- Capability to operate with up to 25% water
- Three zone furnace with set points adjusted for a flat temperature zone where samples are located



Experimental Exposures

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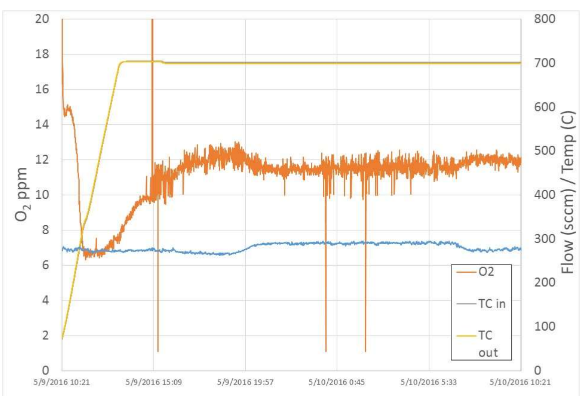
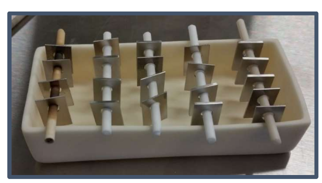
aCO_2 Monitoring of pO_2





Experimental Exposures

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Direct Fired CO_2

- **Mass flow controllers for CO_2 and O_2**
- **Syringe pump for H_2O**
- **Atmospheric pressure**
- **750°C**
- **DF29**
  - High water content case
  - 70% CO_2, 0.7% O_2, 29.4% H_2O
- **Future tests, DF4**
  - Natural gas fuel based
  - 95% CO_2, 1% O_2, 4% H_2O

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Alloys

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- **Ni-base commercial alloys**
  - 625, 600, 740H, 230, 263, 282, 617, 120
- **Fe-base commercial alloys**
  - 304H, 316L, 800, 310S, E-Brite, T91
- **Ni-base model alloys**
  - Low Cr internal oxidation model alloys: Ni5Cr, Ni2.3Al4.6Cr
  - Function of Cr: Ni12Cr, Ni14Cr…..Ni24Cr
  - Function of Si: Ni22Cr with 0, 0.1, 0.3, 0.6, 0.9, 1.2, and 1.5Si
- **Fe-base model alloys**
  - Function of Si: Fe22Cr with 0, 0.1, 0.3, 0.6, 0.9, 1.2, and 1.5Si
  - Function of Si: Fe22Ni22Cr with 0, 0.1, 0.3, 0.6, 0.9, 1.2, and 1.5Si

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Why Si?

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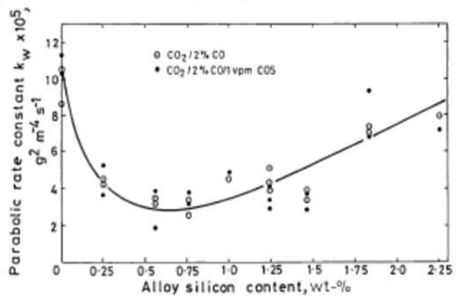
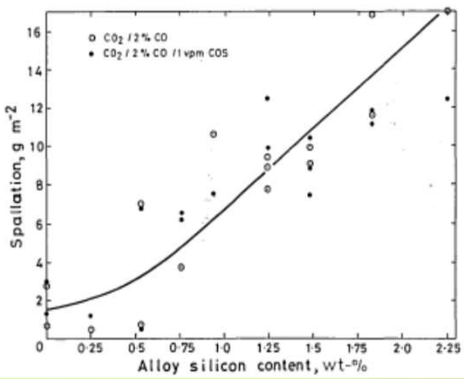
- Small alloy additions of Si can lead to the formation of an amorphous SiO_2 layer at the metal-oxide interface
- Besides enhancing chromia formation, SiO_2 can also act as a barrier to C diffusion (and limit carburization)
- Lobb, Sasse, and Evans 1989 showed benefits in CO_2 containing gases
  - k_p at a min at 0.5 to 1.0 wt% Si
  - Increase in spalling at above 0.6 wt% Si



2 Variation of parabolic rate constant k_w with alloy Si content for 20Cr–25Ni–Nb steel at 900°C



Results—Ni-xCr Alloys (5-24Cr)

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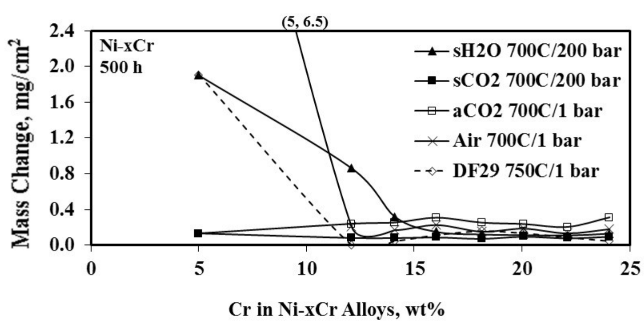
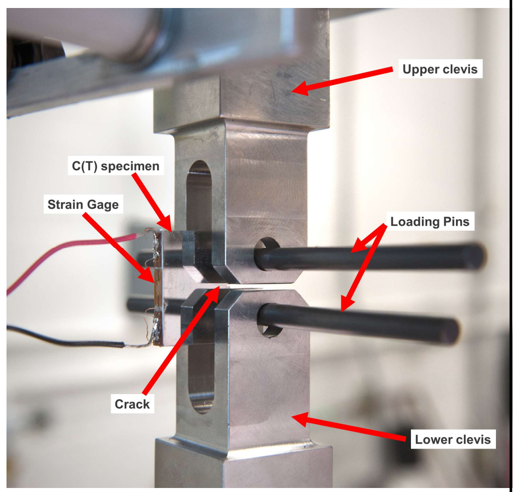


Critical Cr level for chromia formation/stability (after 1000 h):

- Between 5-12 Cr in DF29 and Air
- Chromia scales maintained in pure CO_2
- Between 12-14 Cr in sH_2O

Fatigue Crack Growth—Experiment

- ASTM standard E647
- Typically use compact tension specimen C(T)
- Least amount of material to yield the greatest amount of information
- Utilize servo-hydraulic load frame for controlled cycle of sample
- Load control for precise control of waveform
- Higher frequency testing utilizes sine wave for stability
- Lower frequency testing utilizes triangular waveform for symmetric strain rates



Alloys and Samples

Alloy	Fe	Cr	Ni	Co	Mo	Si	Ti	Al	Mn	Cu	V	Nb	C
347H	Bal	17.6	9.1	0.1	0.2	0.3			1.1	0.1	0.1	0.7	0.05
* 282	0.2	19.4	Bal	10.1	8.7		2.2	1.4					0.06
625	3.4	22.1	Bal		8.9	0.1	0.2	0.1	0.1	0.2		3.3	0.05

Compact Tension Specimens
Nominally 22 × 23 × 3 mm

Ground surfaces to 600 grit

Triplicate Specimens in each test

Fatigue Crack Growth—Results (H282)

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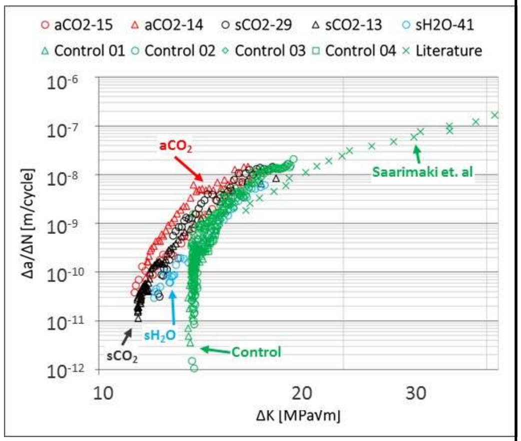
- Tested the effect of prior exposure on threshold ΔK
  - Gas exposure at 730°C for 500 hours
    - Supercritical gas at 200 Bar
    - Ambient gas at 1 Bar
- Loading at R = 0.1, f = 40 Hz, sinusoidal waveform
- Apparent reduction in ΔK_{th} with high temperature gas exposure
- Increase in threshold $\Delta a/\Delta N$ for CO_2 exposed samples
- Repeatable effect
  - Multiple samples
  - Multiple labs
- Speculate effect may be due to residual stress in samples
- An additional test after exposure in a vacuum is underway



Acknowledgement & Disclaimer

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Acknowledgement

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