Materials for Supercritical CO_2 Applications

A Tutorial

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Tutorial on
Materials for Supercritical CO_2 Applications

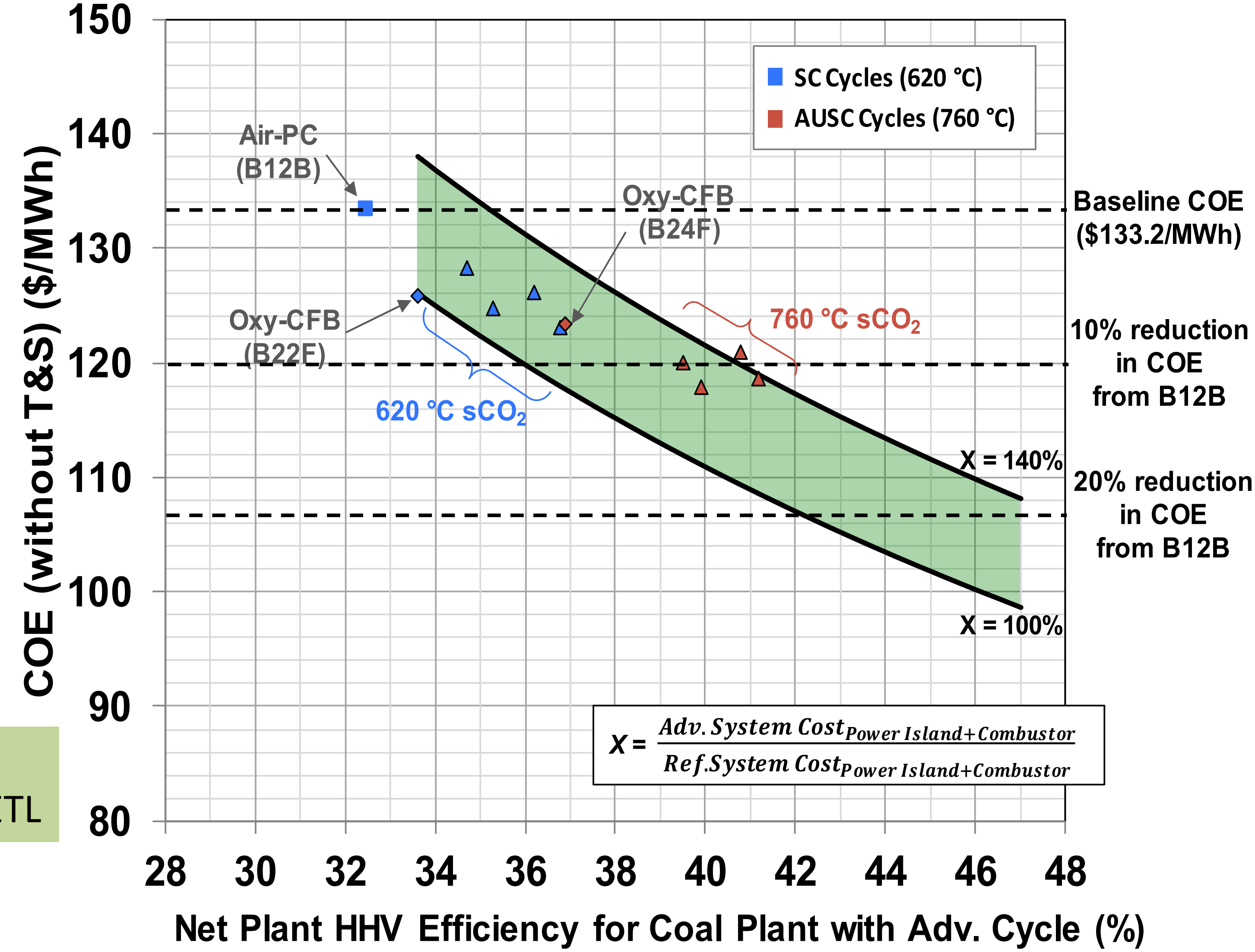
OUTLINE

Part I: What are sCO_2 cycles and why are materials important?

INTRODUCTION AND OBJECTIVES

Motivation - 1

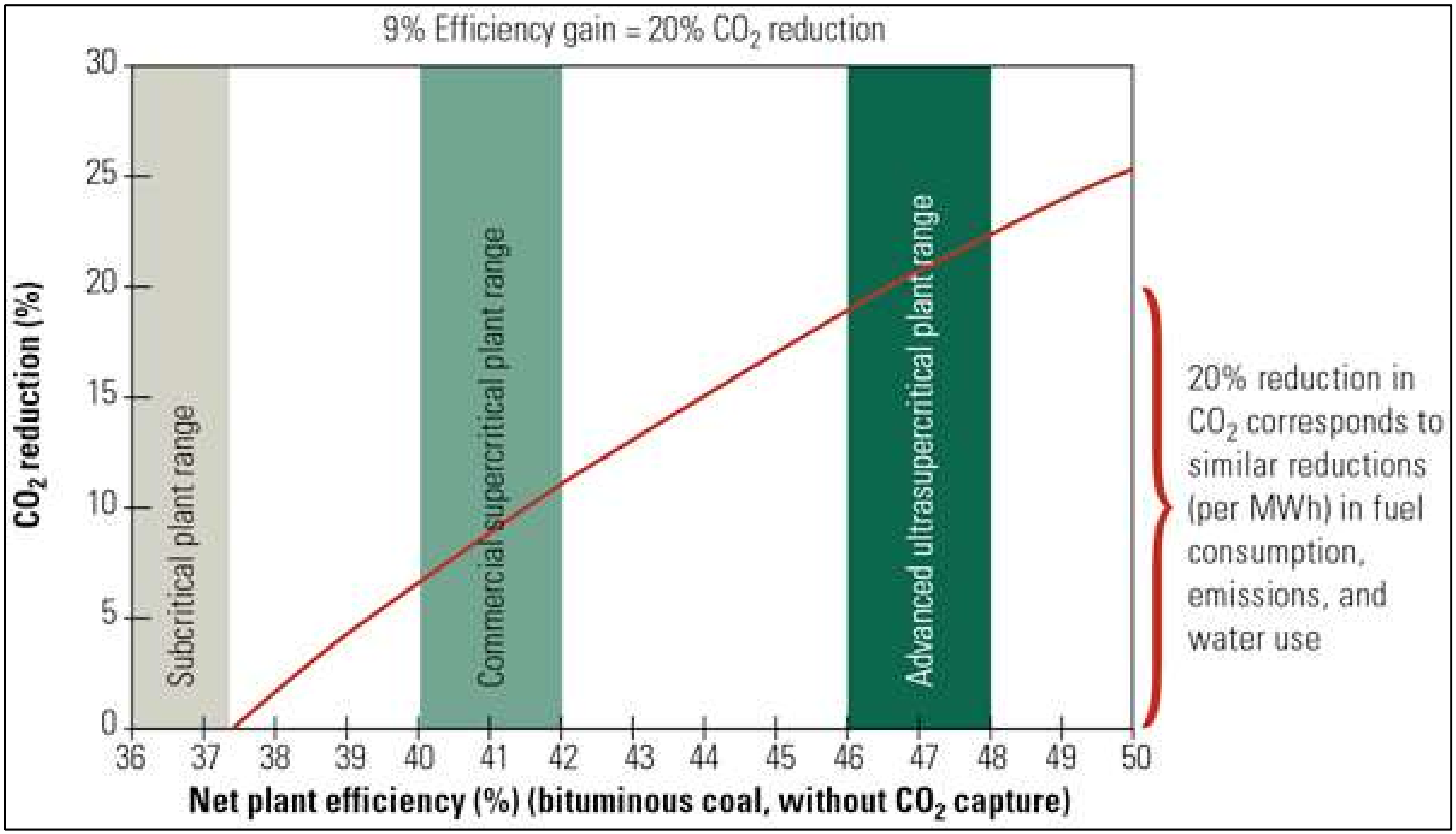
Cost of Electricity (COE)



Source: DOE-NETL

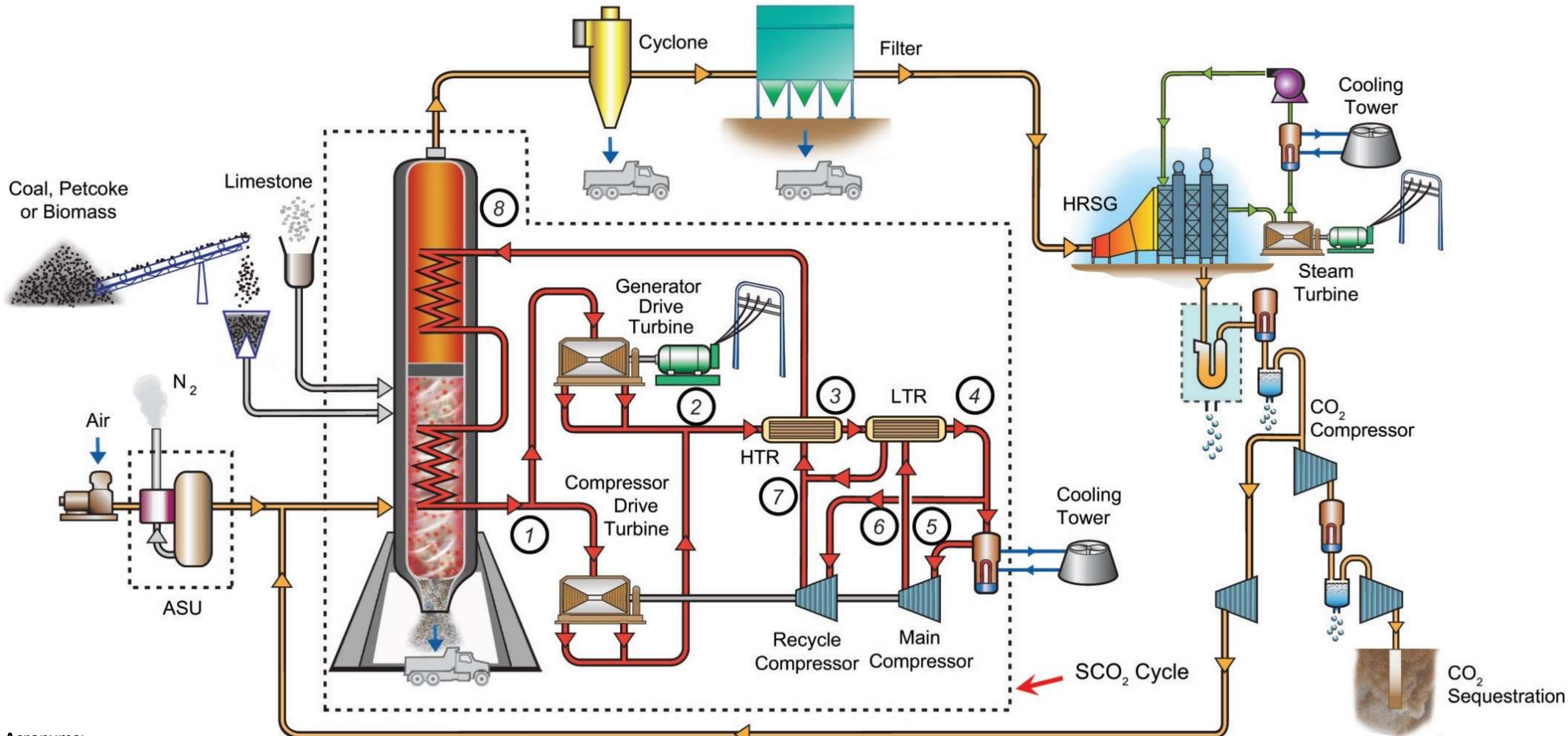
Motivation - 2

(Fuel and Water consumption & CO_2 Emissions)



Power Magazine May 2011

"Reference Case" – Oxycombustion (coal, petcoke, or coal + biomass)



Acronyms:
ASU: Air Separation Unit
HTR: High Temperature Recuperator
LTR: Low Temperature Recuperator
HRSG: Heat Recovery Steam Generator

- **Turbine inlet temp: 1,300 F (700C)**
- **Net power output (MWe): 544**
- **Steam turbine power (MWe): 27**
- **sCO_2 turbine power (MWe): 676**
- **CO_2 captured (%): ~98**
- **Net efficiency (%, HHV)): 38.3**
- **Net heat rate (Btu/kWh): 8,910**

~9% Efficiency Improvement

Key Factors Influencing Performance

- Operating conditions of components (temperature, pressure, flow rates, static and dynamic loads)
- Influence of sCO_2 (oxidation, corrosion)
- Material selection (composition, impurities, form/shape)
- Material properties (tensile, yield, creep, fatigue)
  - Effects of treatments (welding, cold work, annealing)
- Materials availability and cost
  - In desired forms, shapes (e.g., pipes, plates)
- Conformance with safety codes
  - National (e.g., ASME B&PV) and local

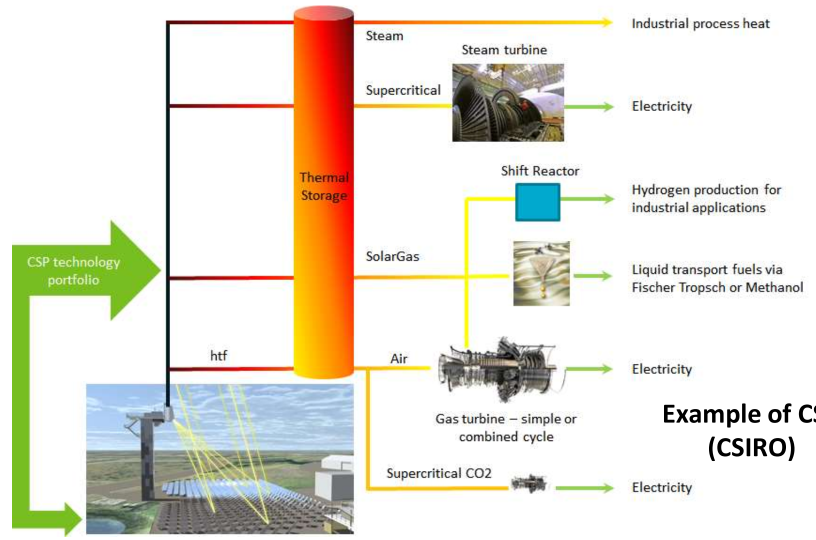
Reference Case Material Summary

	COMPONENT	MATERIAL TYPE	SUPPORTING TECH BASE	RISK / RATIONALE
Heat Exchanger	HEX, <1,000F	Austenitic Stainless Steel	Various	High Technology Readiness Level (TRL) for lower pressures
	HEX, >1,000F	Ni-Cr, solid solution strengthened alloys	USC/A-USC Steam	$SCCO_2$ oxidation, Weldable, moderate strength
Turbo-Machinery	Compressor housing	Steel casting	UK Nuclear Magnox / AGR	High TRL for lower pressures
	Compressor Impeller	(trades incomplete)	Cryo Propellant Turbopump	High TRL, Low temp limits oxidation
	Compressor Rotor	Alloy Steel	Various	High TRL, Low temp limits oxidation
	Seals, Dry Gas	Ceramics / Cermet coating	Process Industries	Accelerated wear in $SCCO_2$
	Turbine Hsg	Ni-based casting alloys	A-USC Steam	Low TRL (in development)
	Turbine Disk	Ni-base superalloy	Gas / Power Turbine	Tech Base is shorter life, $SCCO_2$ Oxidation, Creep
	Turbine Blade	High Cr, Ni-base superalloy Ni-base superalloy + Pt-Al	Gas / Power Turbine	Tech base is shorter life , $SCCO_2$ Oxidation, Creep, HCF
	Ducts, <1,000F	Austenitic Stainless Steel	Various	High TRL for lower pressures
	Ducts, >1,000F	High Cr, Ni-base superalloy	USC Steam	Low TRL. Oxidation, Creep., Demonstrated weldability.
Balance-of-Plant	High Temp. Valves	Austenitic/Nickel-based	A-USC Steam	Intermediate TRL, not tested in service, supply chain questionable
	High Temp. Piping	Austenitic/Nickel-based	USC/A-USC Steam	High TRL, but supply chain is not established for many needed components

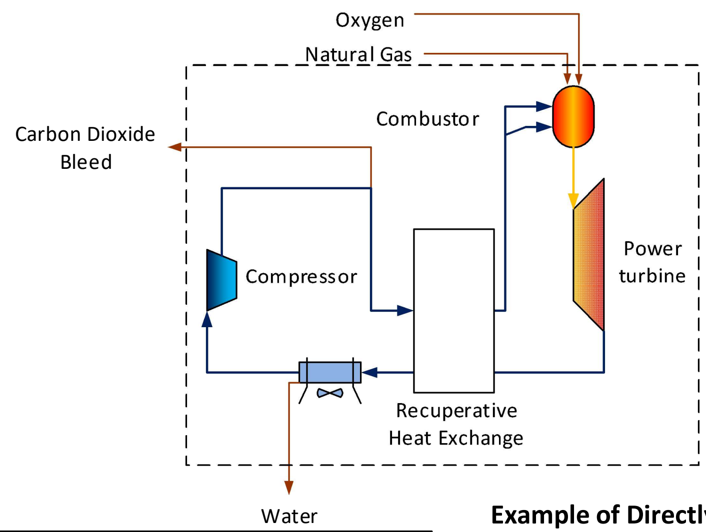
Departures from Reference Case

- **Multiple applications of sCO_2 power cycle are being considered; Examples include:**
  1. **Waste heat utilization (lower temperature)**
  2. **Other indirectly-heated systems with varying temperatures (e.g., nuclear, solar)**
  3. **Directly-heated systems that deliver combustion products at supercritical conditions with 'impurities'**

     -- e.g., H_2O, O_2, N_2, Ar, NOx, SOx, HCl



Example of CSP (CSIRO)



Example of Directly-heated System (Allam Cycle)

Materials selection and qualifying them will depend on operating conditions for each application

Materials Data Required for Reference Case

- A number of candidate materials are being independently evaluated for applications at temperature and pressures similar to the Reference Case (Section II of this Tutorial)
  - Creep strength and long-term stability (boiler alloys)
  - Fireside corrosion
  - Fabrication and design
  - Rotors, discs and blades (steam turbines)
  - Erosion and oxidation of blade materials (steam turbines)
  - Castings
- Materials data associated with sCO_2 environment and compatibility are under various stages of investigation (Section III of this Tutorial)
  - Corrosion and oxidation
- Maturing of plant designs and definitions will likely trigger
  - Determination of availability and costs
  - Applicability of existing code rules and/or need for code review

A Full Compendium of Similar Materials Data Should be the Ultimate Goal

Objectives of Tutorial

1. Provide data and information from the existing/ongoing A-USC program
2. Provide data and information from ongoing corrosion and sCO_2 compatibility tests
3. Exchange information with participants
   - Confirming and/or contradicting current data from tests or test loops
   - Need for new data, experiments and standards for inter-comparison of data
4. Obtain feedback for future tutorials

Part II: U.S. DOE/OCDO A-USC Steam Boiler & Turbine Consortium

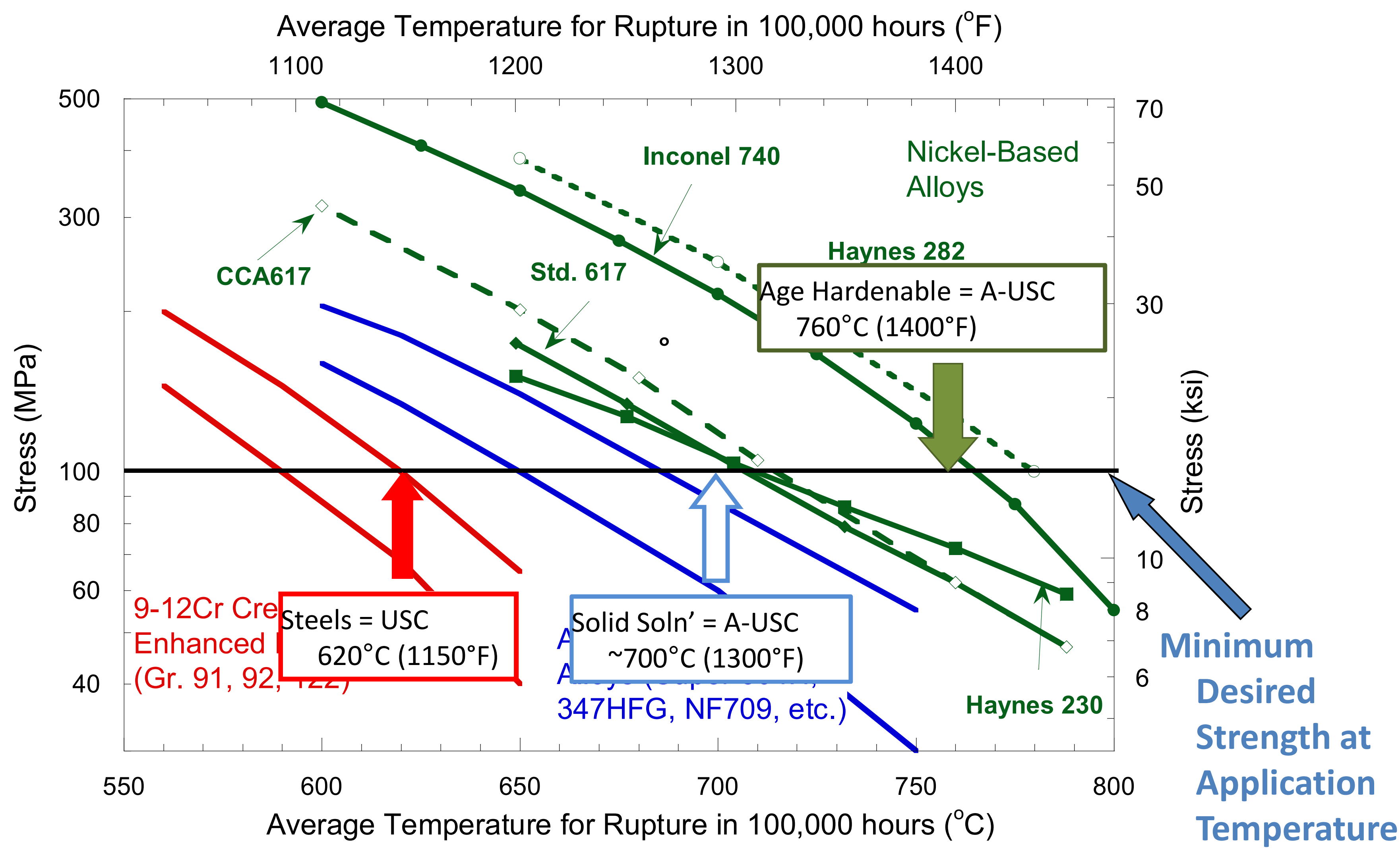
FOUNDATIONAL MATERIALS R&D

Part II: Perspectives from a Related Program

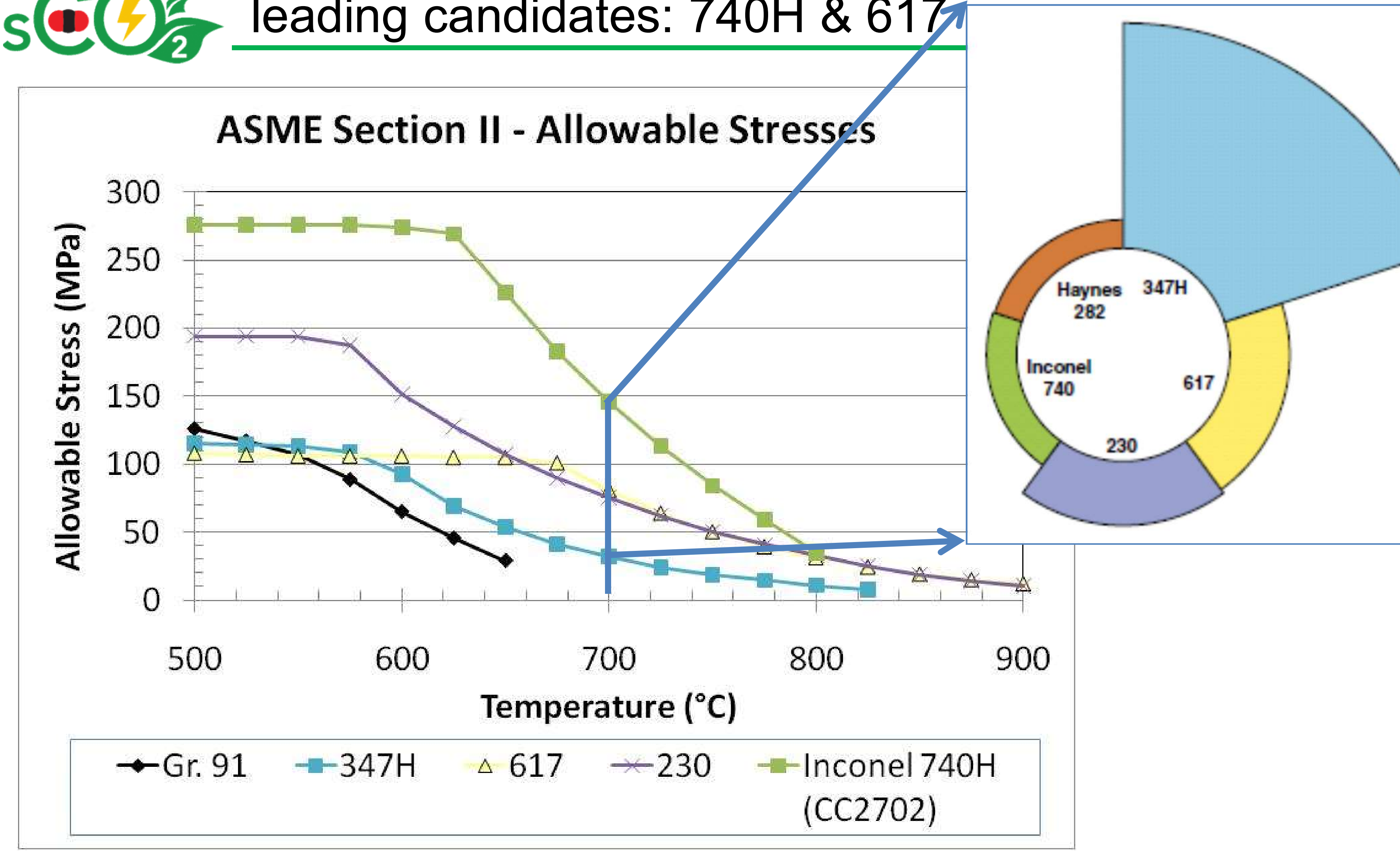
OUTLINE

- **Economics of high-strength nickel-based alloys**
- **Background U.S. DOE/OCDO A-USC Materials Consortium**
- **Major successes from the unique government-industry consortium**
- **A view on how A-USC Materials R&D enables sCO_2 and how we can leverage experience**

Materials Limit the Current Technology: *Today's State-of-the-Art Steam Power Plants are defined by steel technology*



Economics Comparison between two leading candidates: 740H & 617

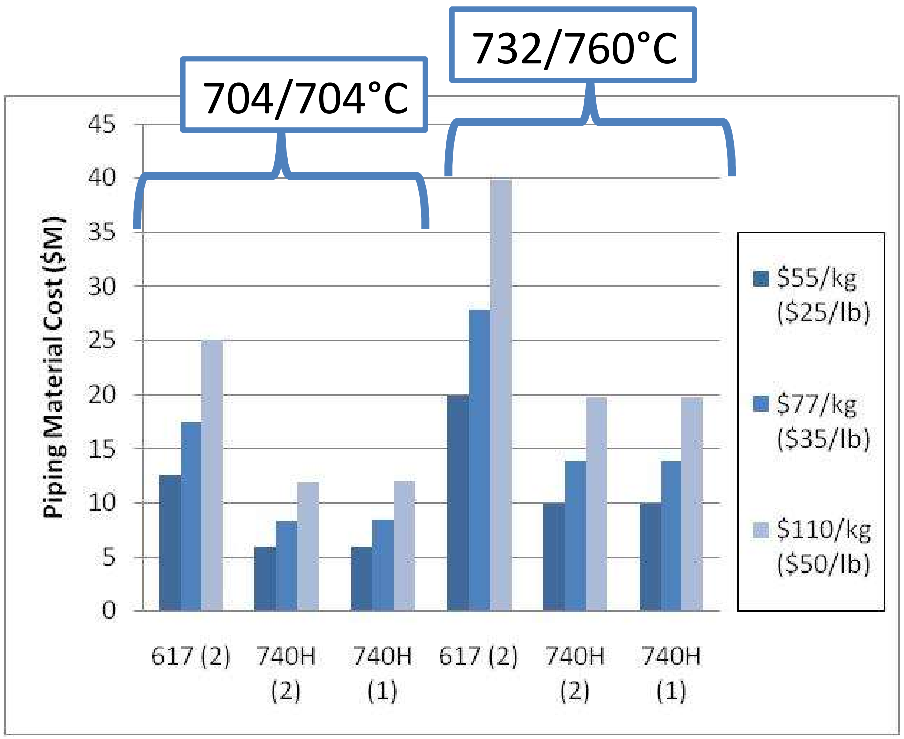


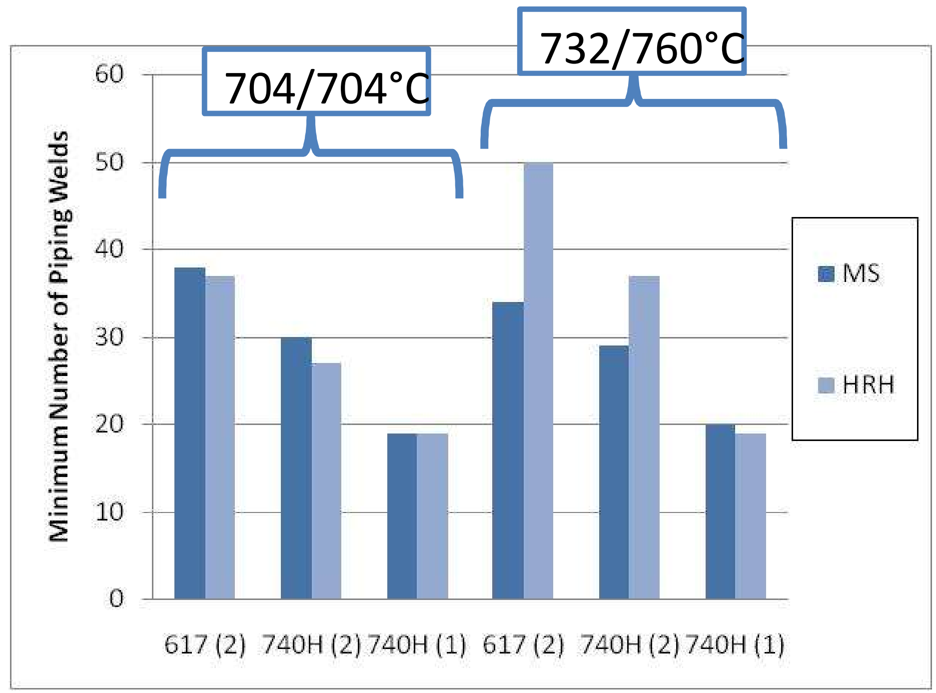
Higher Allowable Stress for Inconel 740H = Thinner Pipe Walls

Higher-strength alloys provide an avenue for cost savings

Shingledecker et. al, 2012: IEA Clean Coal Centre Workshop (Vienna, Austria)

- **A-USC plant design study showed using 740H compared to alloy 617 for a main steam and hot-reheat piping system:**
  - Reduced piping material cost (less material) by a factor of ~2
  - Reduced welding cost (less welds)
  - Provided a buffer for nickel-based alloy price fluctuations



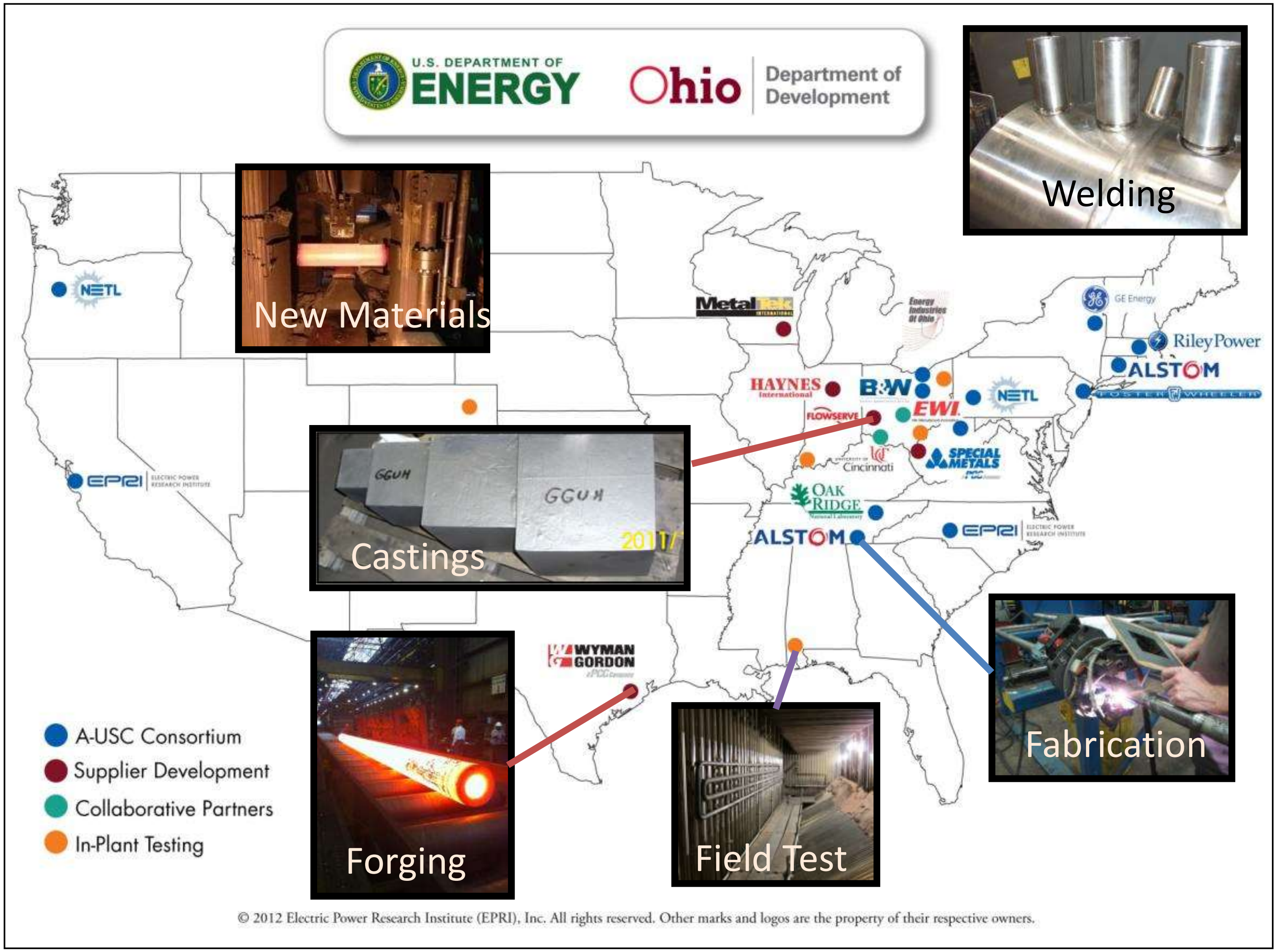


U.S. Department of Energy (US DOE) / Ohio Coal Development Office (OCDO) A-USC Steam Boiler and Turbine Consortia

Federal – State – National Laboratory

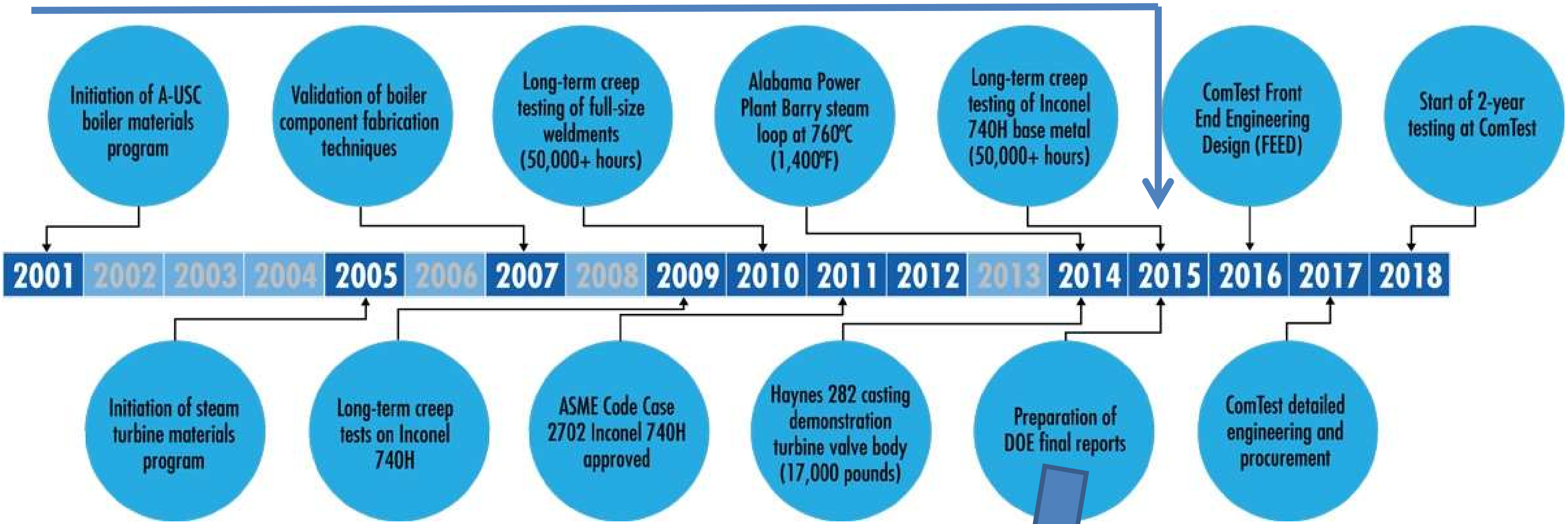
Non Profit – For Profit

Cost Sharing Consortium



US DOE/OCDO A-USC Materials Consortium Provides a Technical Foundation for High-Temperature Materials

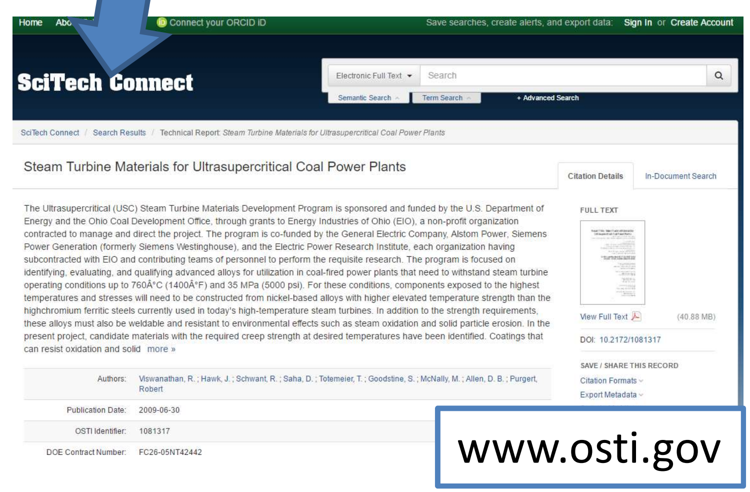
A-USC Materials R&D



15 Year Effort to develop the materials technology to build and operate an A-USC boiler with steam temperatures up to 760C

Reports:

- A-USC Boiler (>1100pages): Purgert, Robert et al. *Boiler Materials for Ultra Supercritical Coal Power Plants*. United States: N. p., 2015. Web. doi:10.2172/1346714.
- A-USC Turbine Phase I: Viswanathan, R. et al. *Steam Turbine Materials for Ultrasupercritical Coal Power Plants*. United States: N. p., 2009. Web. doi:10.2172/1081317.
- A-USC Turbine Phase II: Purgert, Robert et al. *Materials for Advanced Ultrasupercritical Steam Turbines*. United States: N. p., 2015. Web. doi:10.2172/1243058.



Foundational knowledge serves as basis for sCO2

Recent Results: In-Plant Testing at 760°C (1400°F) Operating Steam Corrosion Test Loop

Southern Company – Plant Barry

- **Phase 1**
  - Extensive laboratory testing &air-cooled probes in boiler
  - Steam-cooled loop (high S coal)
- **2nd Steam Loop**
  - **World's first steam loop operating at 760°C (1400°F)**
  - **Removed from service after 33 months with >16,000hrs in operation**
  - **Evaluations = little to no wastage**

Materials include:
740H, CCA617, HR6W,
Super 304H, Coating,
Overlays, and Others

Fabrication in Alstom Chattanooga TN shop

Prior to Welding

Being Welded

After Assembly

Boiler Fabrication Successes

- **No significant changes to fabrication techniques were required**
- **R&D was used to make changes to ASME Section I Table PG-19**
- **Full-size laboratory testing**
- **Initial tests on Inconel 740 led to additional phase 2 work on cold-work effects on creep which was needed for the code case**



Major Step: Code Case 2702 (Inconel®740H) now Approved for Use in Section I and B31.1

- **Maximum Use Temperature: 800°C (1472°F)**
- **Rules for:**
  - Chemistry
  - Heat-treatment
  - Welding
  - Post-weld heat-treatment
  - Cold-forming
  - Weld strength reduction factors

CASES OF ASME BOILER AND PRESSURE V

Approval Date: September 26, 20

Code Cases will remain available for use u
by the applicable Standards Commi

Case 2702
Seamless Ni-25Cr-20Co Material
Section I

Inquiry: May precipitation-hardenable Ni-25Cr-20Co alloy (UNS N07740) wrought sheet, plate, rod, seamless pipe and tube, fittings and forgings material conforming to the chemical requirements shown in Table 1, the mechanical properties listed in Table 2, and otherwise conforming to the applicable requirements in the specifications listed in Table 3 and in this Case be used in welded construction under Section I rules?

Reply: It is the opinion of the Committee that precipitation-hardenable Ni-25Cr-20Co alloy (UNS N07740) wrought sheet, plate, rod, seamless pipe and tube, fittings and forgings as described in the Inquiry may be used in welded construction complying with the rules of Section I, provided the following rules are met:

(a) Material shall be supplied in the solution heat treated and aged condition. Solution heat treatment shall be performed at 2,010°F (1100°C) minimum for 1 hr per 1 in. (25 mm) of thickness but not less than ½ hr. Aging shall

(d) Postw
tory. The po
1,400°F to 1
4 hr for thic
1 hr per addit
nal weld sea
nent, a weld
in accordanc
peratures ab

(e) After cold forming to strains in excess of 5%; after any swages, upsets, or flares; or after any hot forming of this material, the component shall be heat treated in accordance with the requirements specified in (a). No local solution annealing may be performed. The entire affected component or part that includes the cold-strained area and transition to unstrained material must be included in both heat treatments. The calculations of cold strains shall be made as described in Section I, PG-19.

(f) The maximum use temperature is 1,472°F (800°C).

(g) S_u and S_y values are listed in Tables 5 and 5M and Tables 6 and 6M, respectively.

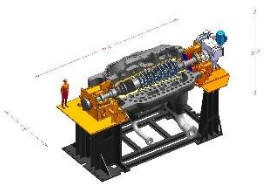
(h) Physical Properties. See also Tables 7 and 7M, Physical Properties.

A parallel effort is now underway with DOE/ORNL to develop a code case data package for Haynes 282 (single step age)

Transformational technologies will need A-USC materials and components demonstrated

A-USC Materials Foundation R&D Consortium (Boiler and Turbine)

sCO_2 R&D



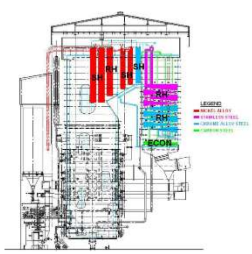
A-USC ComTest

sCO_2 PILOT (STEP, NETPOWER)

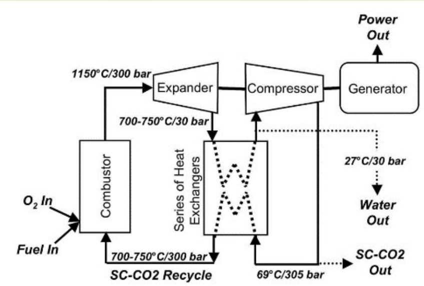
A-USC DEMO Plant

A-USC DEMO Topping/Retrofit/Repowering

sCO_2 DEMO



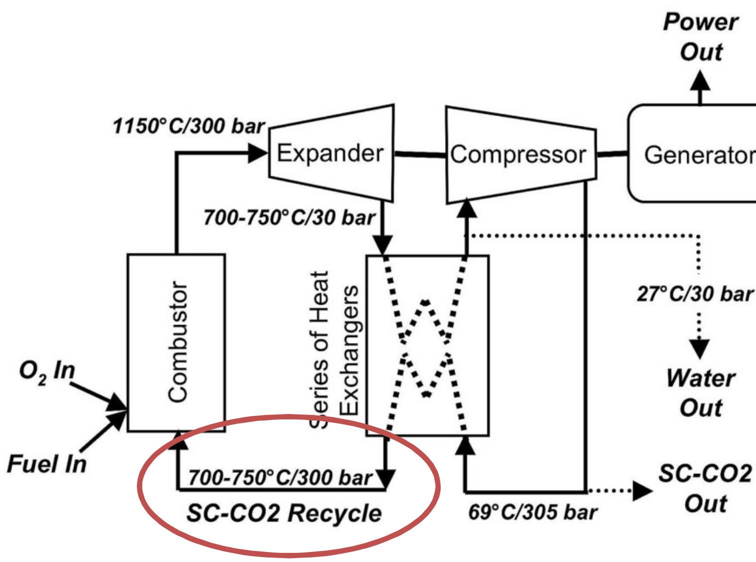
A-USC Foundation Enables Transformational Technologies



Alternative Supercritical CO_2 (sCO_2) Power Cycles Need Advanced (A-USC) Materials Technology

NET Power Cycle 25MW Demo

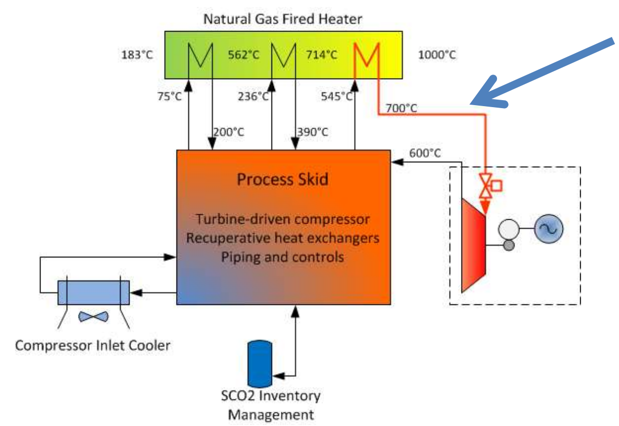
Gas-Fired 100% Carbon Capture Modified CO_2 Brayton Cycle is planning to use Inconel 740H for High-Temperature CO_2 piping



Scale-up to 250MW will require large diameter nickel-based alloy piping

Partners: NET Power, CB&I, Toshiba, Excelon

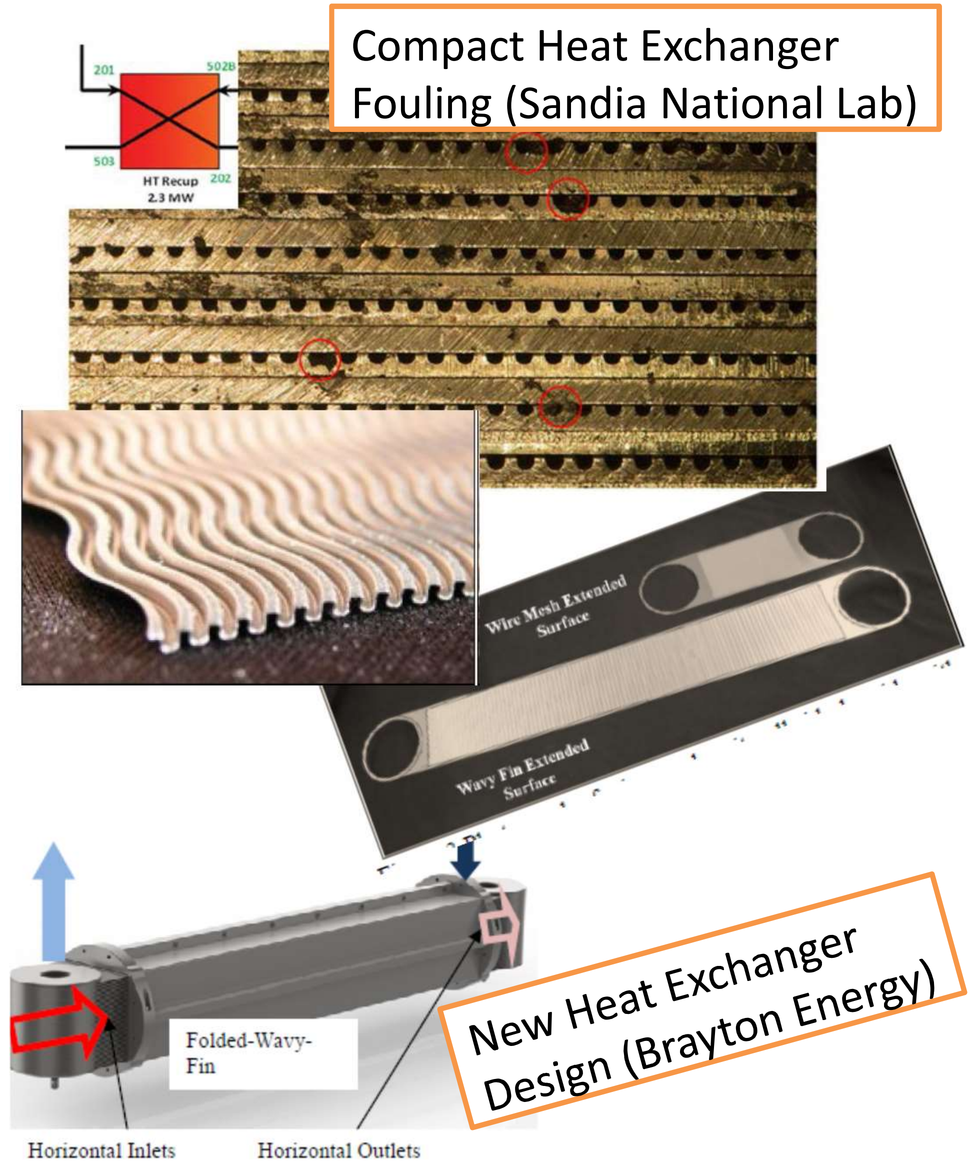
DOE Sun-Shot sCO_2 Brayton Cycle: 1MW Closed Cycle Test Facility



Piping, valves, castings, forgings, welding are applicable

sCO_2 Brayton Cycle Compact Heat Exchangers: Unique Materials Challenges

- **4-10X Heat-Duty compared to Rankine Cycle**
- **Designs:**
  - Expensive: ‘40%’ the cost of the entire plant
  - Small channels
  - Large surface area
- **Thermal fatigue resistance**
- **Creep of thin sections**
- **Brazing/diffusion bonding**
- **Corrosion/oxidation in sCO_2**
  - Closed cycles: build-up of impurities
  - Open cycles: combustion by-products
  - Blockage, pluggage, reduced performance



Summary: US DOE/OCDO A-USC Consortium

- **Unprecedented success in developing the materials technology to enable A-USC Steam cycles up to 760°C (1400F)** ***based on pre-competitive R&D by a consortium of manufacturers, national laboratories, and research organizations***
  - Extensive laboratory and shop R&D
  - Field applications for fireside corrosion

- **sCO_2 can leverage the success of the consortium & foundational high-temperature materials R&D**
  - Materials are a cross-cutting technology
  - Unique Material considerations for sCO_2 include environmental interactions, turbine materials, and compact heat exchangers

Part III: Materials in CO_2 Environments

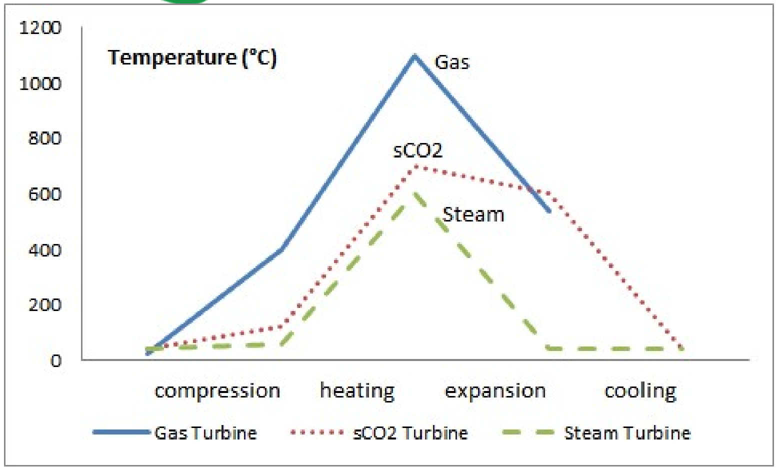
MATERIALS FOR SCO_2 POWER CYCLES

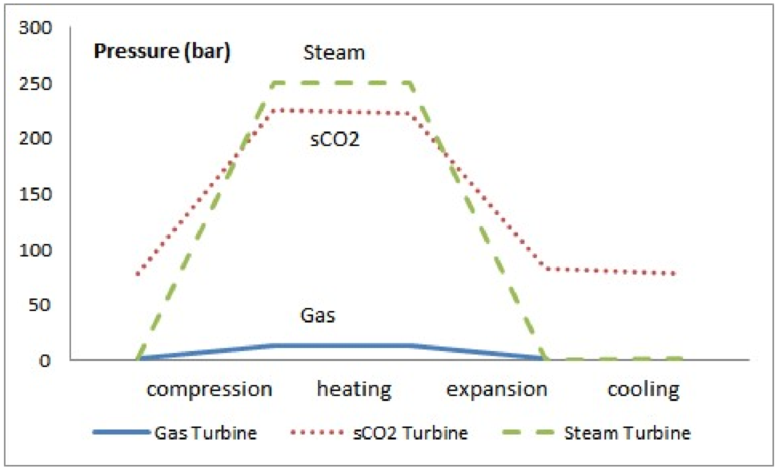
Part III: Materials for sCO_2 Power Cycles

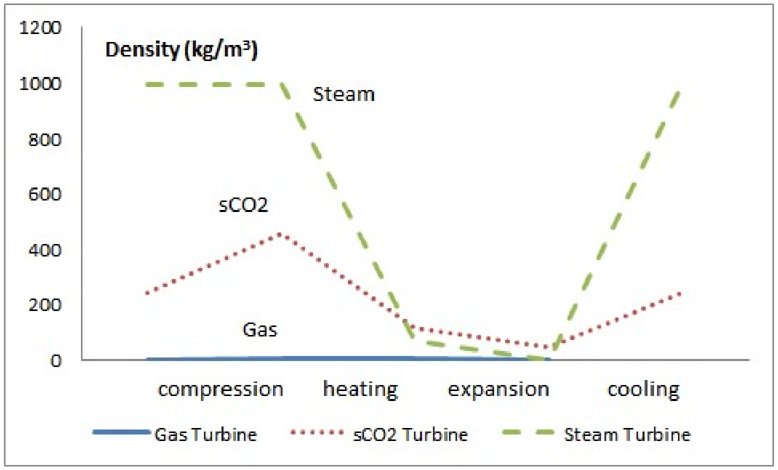
OUTLINE

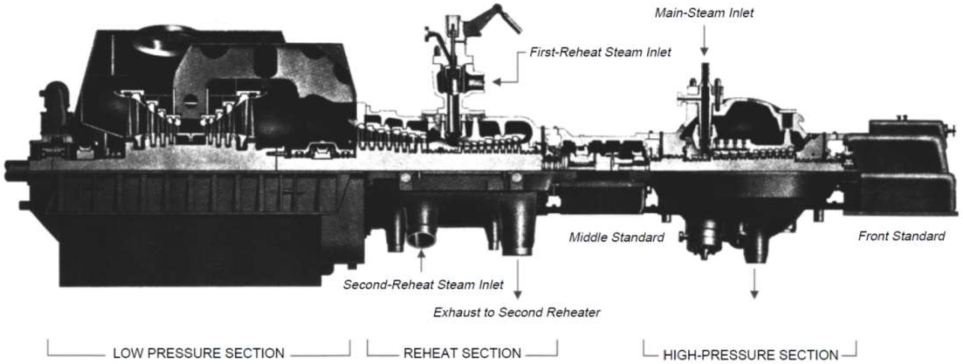
- **Operating conditions and material requirements**
  - Steam and gas turbines vs. sCO_2 power cycles
- **Materials technical challenges**
  - Knowledge gaps
- **Materials in CO_2 environments**
  - Previous experience, sCO_2 testing
  - Current and planned testing to address gaps

Comparison of Operating Conditions

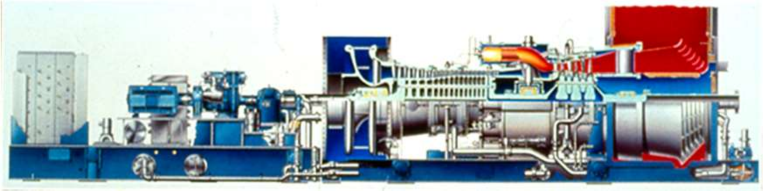








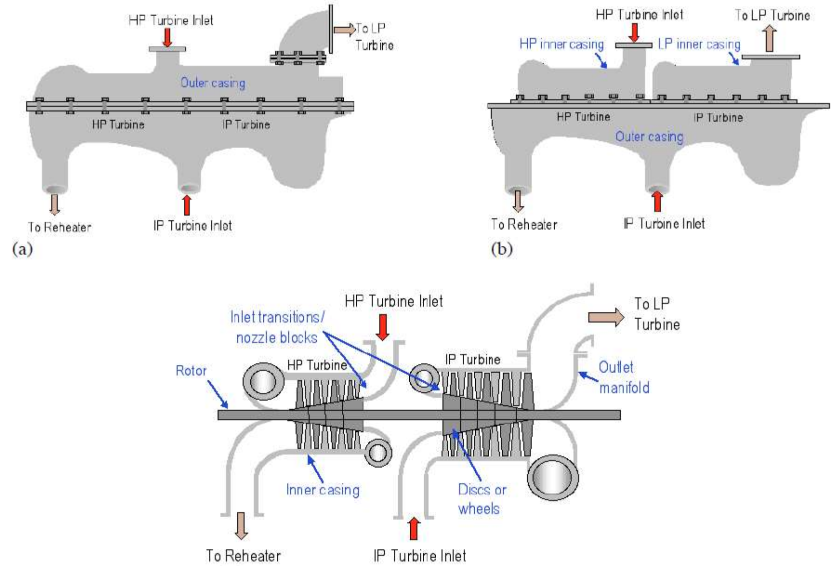
[Philo 6 Steam – Electric Generating Unit, ASME International, 2003]



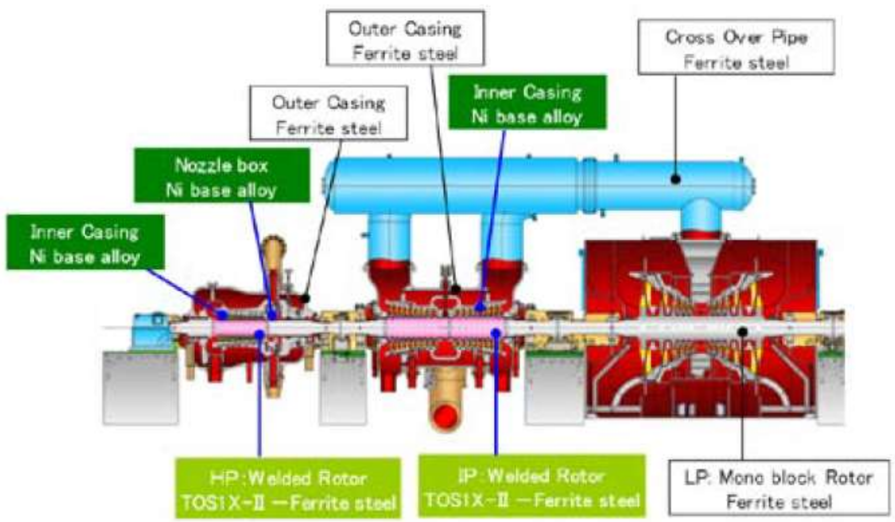
[GE Power Systems]

Steam Turbine Requirements and Materials

- **Relatively small range of materials**
  - Good match of thermal properties
  - High temperature strength at acceptable cost
- **Main components**
  - Turbine casing/shell
  - Bolting
  - Rotors and disks
  - Vanes and blades
- **Turbine casing/shell**
  - Large, complex shapes
  - Pressure containment
  - High creep strength, castability, weldability
  - Oxidation resistance
  - 9Cr, 12Cr steels, Ni-base alloys
- **Bolting**
  - Resistance to stress relaxation
  - Thermal compatibility
  - Low notch sensitivity
  - Ferritic steels, Ni-base alloys
- **Rotors and disks**
  - High creep strength, forgeability, weldability
  - 9Cr, 12Cr steels, Ni-base alloys
- **Vanes and blades**
  - High creep strength, machinability
  - 12Cr steel, Ni-base alloys

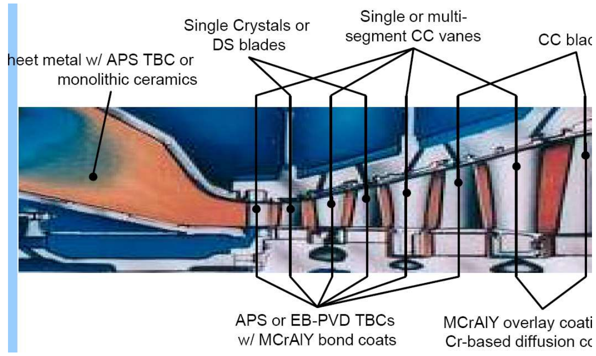


[Wright, et al., Materials Issues for Turbines for Operation in Ultra-Supercritical Steam]

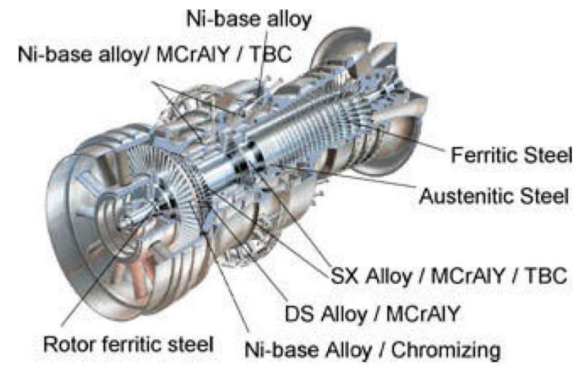


[Babcock & Wilcox, Technical Paper BR-1884, 2011]

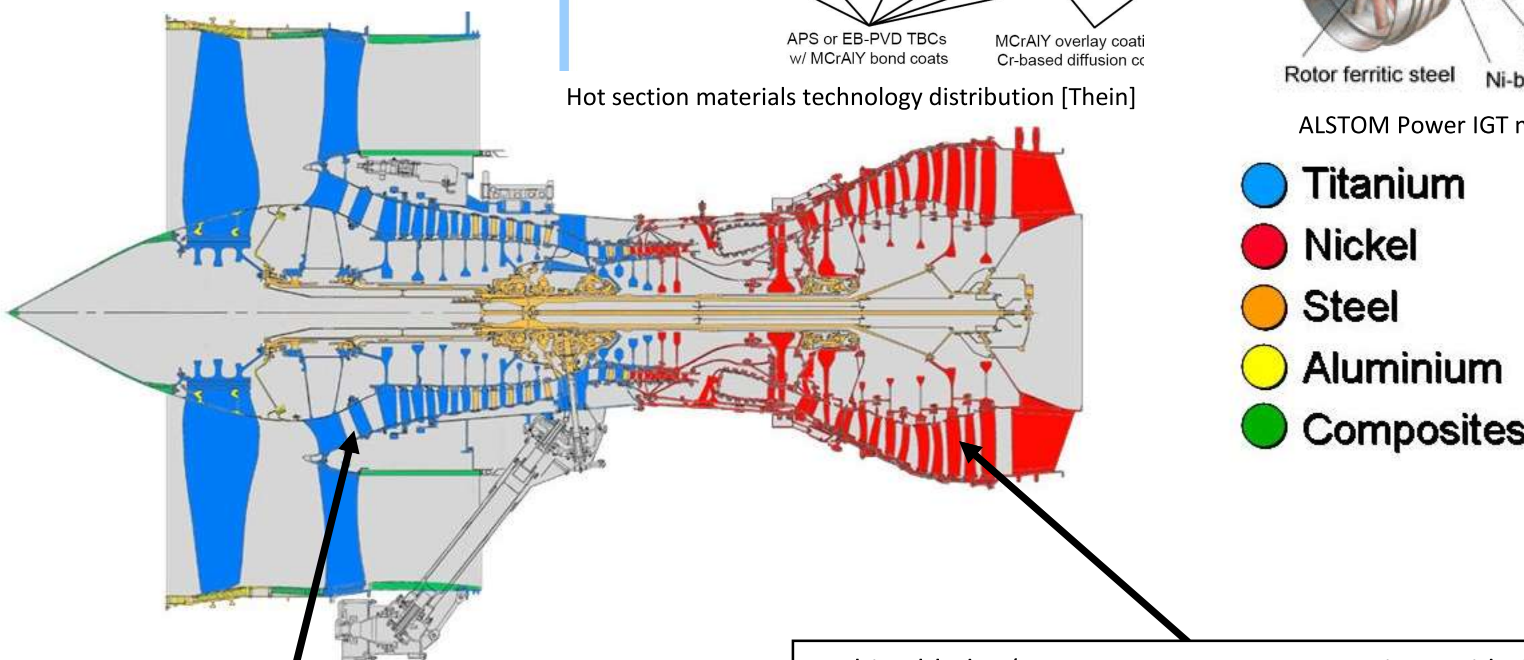
Gas Turbine Requirements and Materials



Hot section materials technology distribution [Thein]



ALSTOM Power IGT materials usage [Oakey]



Fan blades (fatigue, bird strike, erosion, corrosion, fretting fatigue)
Fan disks (burst, LCF, HCF)
Compressor blades (fatigue, erosion, corrosion)
Compressor disks (burst, LCF, HCF, corrosion)

Turbine blades (creep, stress rupture, corrosion, oxidation, HCF, thermal fatigue, fretting fatigue)
Turbine vanes (creep, thermal fatigue, corrosion)
Turbine disks (burst, LCF, HCF, creep, corrosion)
Shafts (bird strike, whirling, LCF)
Casing, bearings (bird strike, LCF, containment)

[adapted from Rolls-Royce figure]

sCO_2 Brayton Cycle Materials

	COMPONENT	MATERIAL TYPE	SUPPORTING TECH BASE	RISK / RATIONALE
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	Compressor Impeller	(trades incomplete)	Cryo Propellant Turbopump	High TRL, Low temp limits oxidation
	Compressor Rotor	Alloy Steel	Various	High TRL, Low temp limits oxidation
	Seals, Dry Gas	Ceramics / Cermet coating	Process Industries	Accelerated wear in $SCCO_2$
	Turbine Hsg	Ni-based casting alloys	A-USC Steam	Low TRL (in development)
	Turbine Disk	Ni-base superalloy	Gas / Power Turbine	Tech Base is shorter life, $SCCO_2$ Oxidation, Creep
	Turbine Blade	High Cr, Ni-base superalloy Ni-base superalloy + Pt-Al	Gas / Power Turbine	Tech base is shorter life , $SCCO_2$ Oxidation, Creep, HCF
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	High Temp. Piping	Austenitic/Nickel-based	USC/A-USC Steam	High TRL, but supply chain is not established for many needed components

Materials Technical Challenges

Current Knowledge

- **Existing materials/mechanical properties**
  - OK for main components (piping, valves, turbomachinery, etc.)
- **Environmental considerations – high temperature sCO_2**
  - Corrosion testing – short-term, coupons, representative temps/pressures, mass gain (vs. depth)

Gaps Remaining/Technical Challenges

- **Availability**
  - Code compliant materials/qualified alloys; design codes
  - Supply chain – in required forms and sizes
- **Environmental considerations – high temperature sCO_2**
  - Longer-term (short-term testing inadequate – breakaway corrosion, intergranular corrosion)
  - Testing under "real" conditions (flow, stress, impurities – H_2O, O_2, others; indirect vs. direct cycles)
  - Reliability of data
  - Mechanical property degradation
- **Performance of actual components/material forms**
  - Thin sections – property differences, effect of geometry
  - Diffusion bonded, brazed, welded joints – corrosion resistance
  - Erosion, fouling of microchannel heat exchangers
  - Thermal fatigue, creep-fatigue interactions, high blade bending loads/temperature + pressure combinations
- **Other challenges and considerations**
  - Coatings
  - Non-metallics – degradation of seals via swelling, rapid gas depressurization
  - Leverage previous work – comparison to steam and SCW corrosion, pressure effects

Materials are available…but gaps remain…efforts are required to complete the picture.

Materials in CO_2 Environments

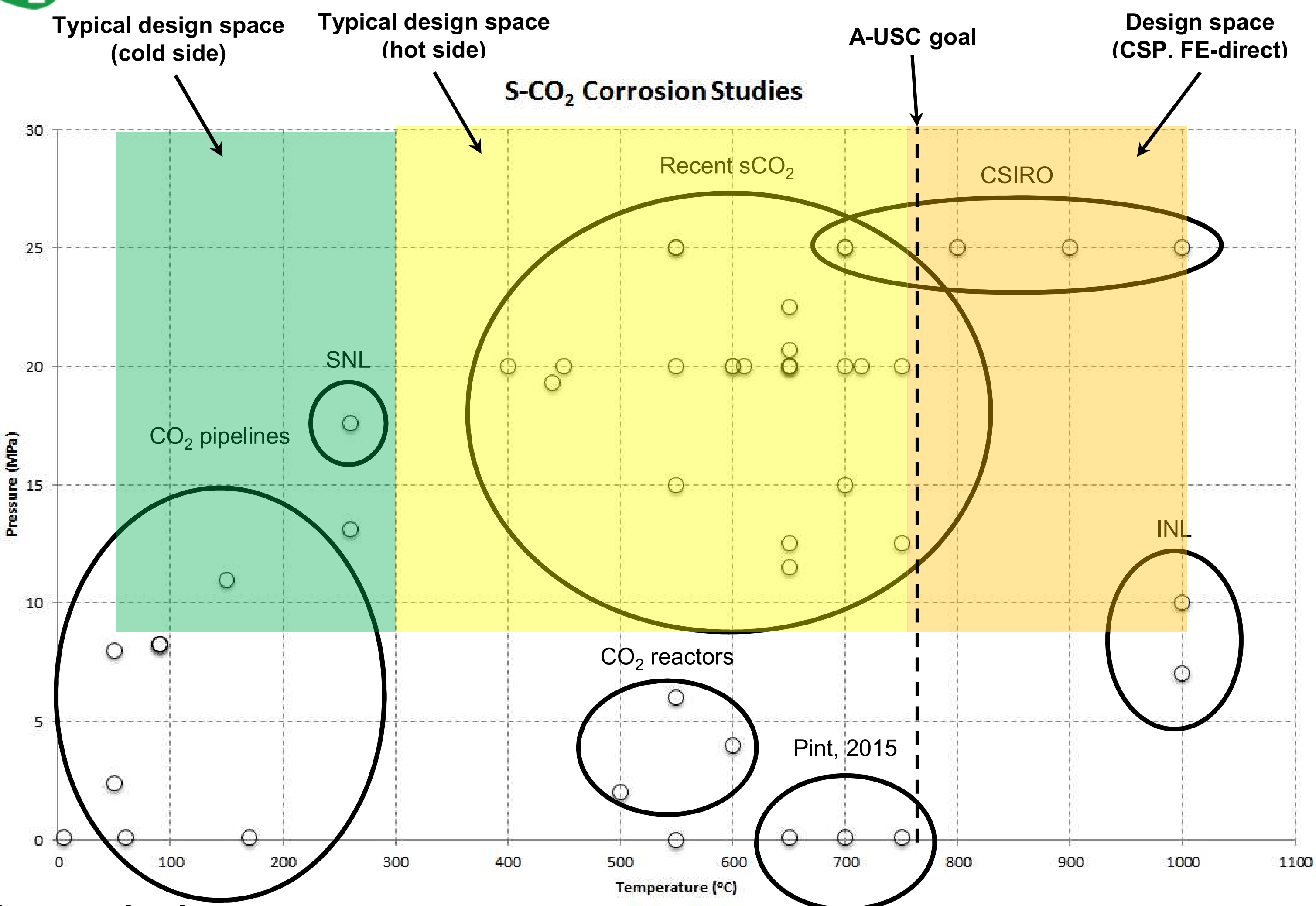
Previous Experience

- **CO_2 gas-cooled Magnox reactors**
  - Many reactor years of operation
  - Structural material behaviour well-characterized
  - High temperature (650 °C) but low pressure (< P_c)
  - Corrosion rates higher under stress
  - Breakaway corrosion caused by exfoliation and nucleation of oxides – mainly influenced by exposure time and/or CO_2 gas pressure
- **Oil and gas industry CO_2 experience**
  - Enhanced oil recovery (EOR), CO_2 transport pipelines
  - Effects of contaminants
  - High pressure (<21 MPa) but low temperature (< 200 °C)
  - Pure, dry – virtually inert < 500 °C
  - Significant corrosion of steels and nickel alloys with ppm H_2O, > 600 °C
  - Austenitic alloys better than ferritic-martensitic steel
  - High levels of Cr and Ni increase corrosion resistance

High Temperature sCO_2 Corrosion Testing

Organization	Temp. (°C)	Pres. (MPa)	PV Material	Materials Tested	CO_2 Purity	Operational Status
INL [Oh et al., 2006]	1000	7	IN617, 304SS	Ni-base: IN617 ODS: MA 754, MA 758	-	2 rigs, both decommissioned
TIT [Furukawa et al., 2010]	600	20	316SS	Martensitic: 12 Cr Austenitic: 316SS	99.995%	Not in-use?
CEA [Rouillard, 2009]	550	25	316SS	FM: T91 Austenitic: 316SS, 253MA, 800H	-	Not in-use?
MIT [Dunlevy, 2009]	750	22-27	IN625	FM: F91, HCM12A Austenitic: 316SS, AL-6XN, 800H Ni-based: IN690, 693, 718, 725, 740, 740+, PE-16, Haynes 230, IN625 ODS: PM2000	99.9999%	In-use
UWisconsin-Madison [Roman, 2013]	650 750	27 21	IN625	FM: HCM12A, NF616 Austenitic: 310SS, 316SS, 347SS, AL-6XN, 800H Ni-based: Haynes 230, IN625, PE-16 AFA: -OC6, -OC7, -OC10 ODS: PM2000	99.95% 99.999%	Several rigs, in-use
CarletonU/NRCan [Saari, 2014]	700 750	25 15	IN625	Austenitic: 316SS Ni-based: IN625, IN718, IN738	99.95%	In-use
KAIST [Lee, 2014]	700	25	IN625	FM: G91 Austenitic: 310SS, 316SS, 347SS, 800H Ni-based: Alloys 600, 625, 690	99.999%	2 rigs, in-use
ORNL/GTI [Pint, 2015]	927	55	Haynes 282	Housing, disk, and blade alloys	-	In-use
OSU [Tucker, 2014]	800	26	Haynes 230	Austenitic steels, Ni-base alloys	-	In-use
DNV-GL [Kung, 2016]	750	20	-	FM: Gr. 91, VM12, Crofer 22H Austenitic: 304SS, 310SS Ni-based: 617, 740H	99.955 Impurities	In-use
SNL [Walker, 2016]	650	31	IN625	Carbon steel: X65Q	99.5%	In-use
CSIRO [Stein, 2016]	1000	25	various	HR120, 160; Haynes 230, 188, 282	-	In-use

(High Temperature) sCO_2 Testing



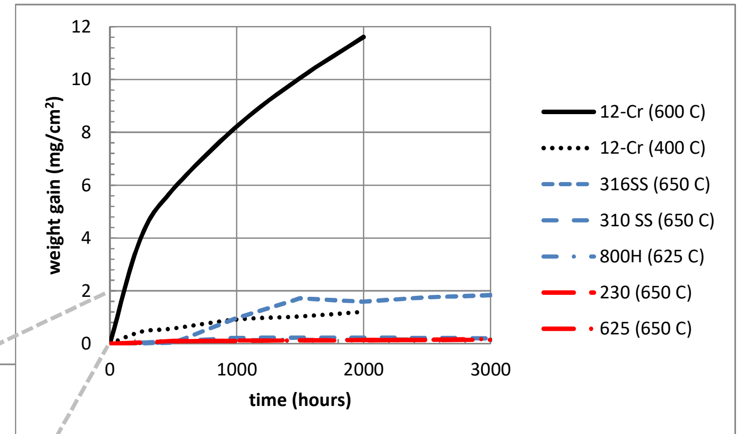
- **Characterization**
  - Weight gain/corrosion layer thickness
  - Scales/mechanisms
- **Various materials tested (steels (FM, austenitic), nickel alloys)**

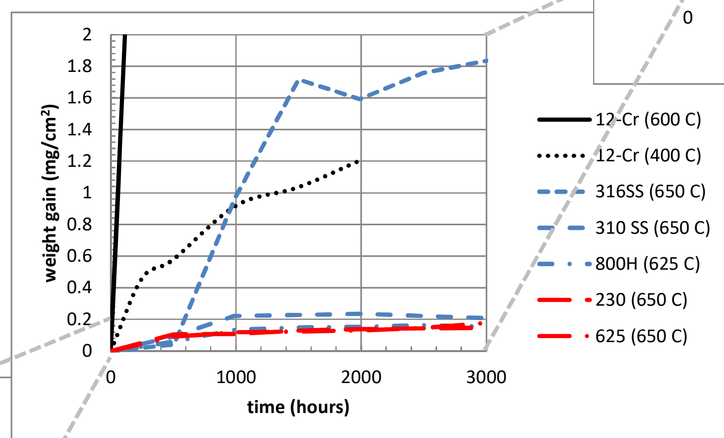
sCO_2 Corrosion Testing – Results

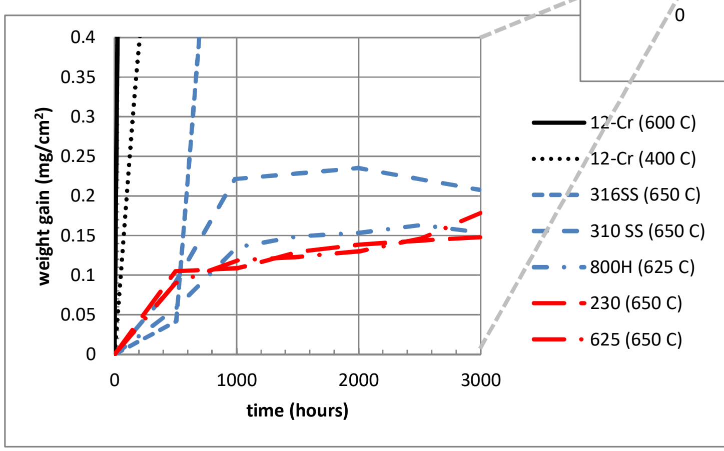
General Weight Gain Trends

FM > austenitic > nickel-base

Fe-Cr (<12% Cr) > Fe-Cr-Ni (>16% Cr) > Ni-Cr-X (>16% Cr)

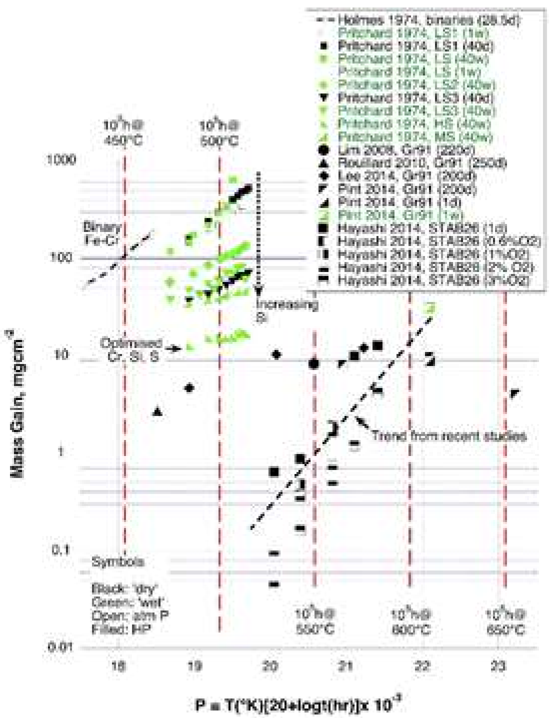


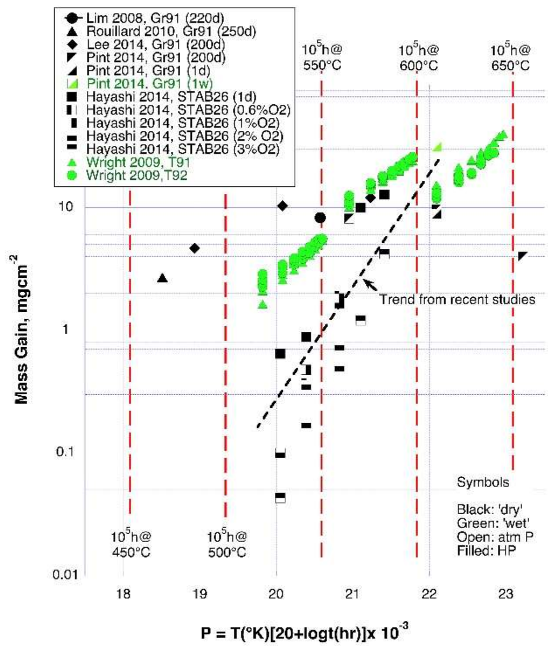




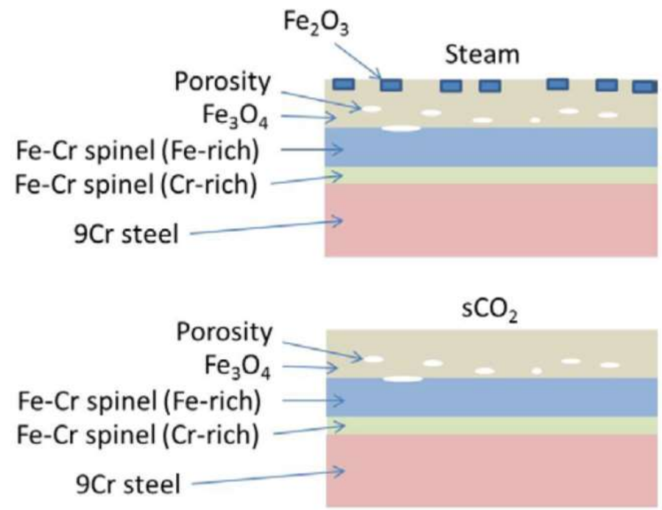
sCO_2 Corrosion Testing – Results

Ferritic Steels





Ferritic steels in CO_2 (left) and recent data vs. steam (right) [Wright, EPRI 2015]



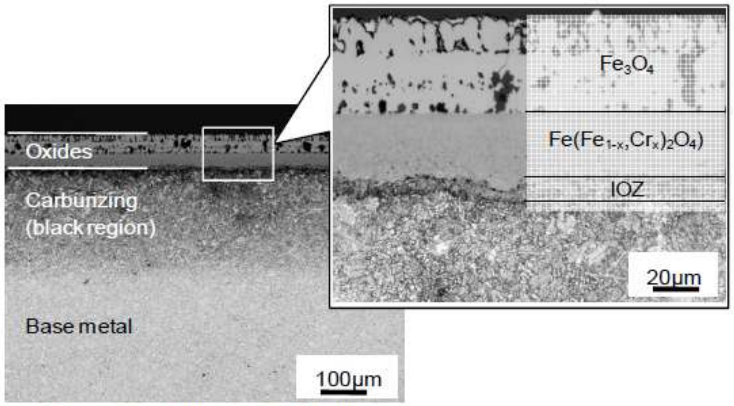
Schematic of oxidation products on 9-Cr steels in steam and sCO_2 [Strakey, 2014]

- Larson-Miller plots for comparison
- Mass gain plotted
- CO_2 and recent sCO_2
- Recent sCO_2 and steam

Mass gains for sCO_2 and steam are approx. similar…the scale morphologies in sCO_2 would be similar to those in steam.

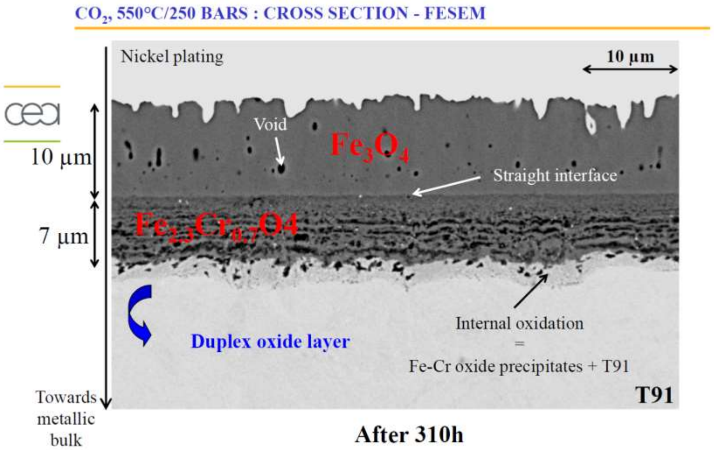
sCO_2 Corrosion Testing – Results

Ferritic Steels



(a) 12Cr-steel, 20MPa 600ºC 1000h

[Furukawa et al., JPES, 2010]



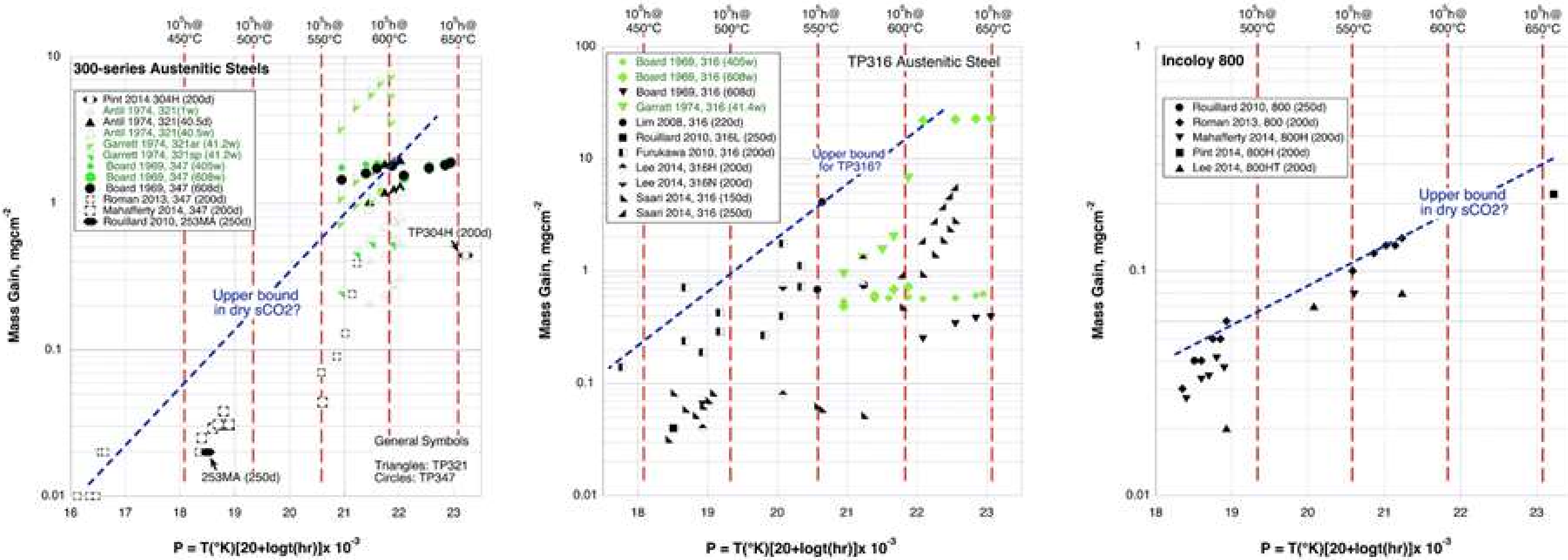
[Rouillard, sCO_2 PCS 2011]

- 12Cr Martensitic steel
- Two successive layers, no breakaway corrosion
  - Outer: Fe oxide, Fe_3O_4
  - Inner: Fe+Cr oxide, $Fe(Fe_{1-x},Cr_x)_2O_4$
- Thin internal oxide zone (IOZ) between base metal and inner layer
- Carburizing observed near surface in base metal
  - Factor in breakaway corrosion, degradation of ductility

- T91 9Cr F-M steel
- Duplex oxide layer
  - Outer: magnetite, Fe_3O_4
  - Inner: spinel, $Fe_{3-x}Cr_xO_4$
- Internal oxidation also
- Extrapolation to 20 years
  - Corrosion layer thickness = 500 μm
- Static tests at 50 °C @ 10 MPa
  - No corrosion observed
- Flowing CO_2
  - Similar oxide scale at 550 °C @ 1 bar (+ outer Fe_2O_3 haematite)

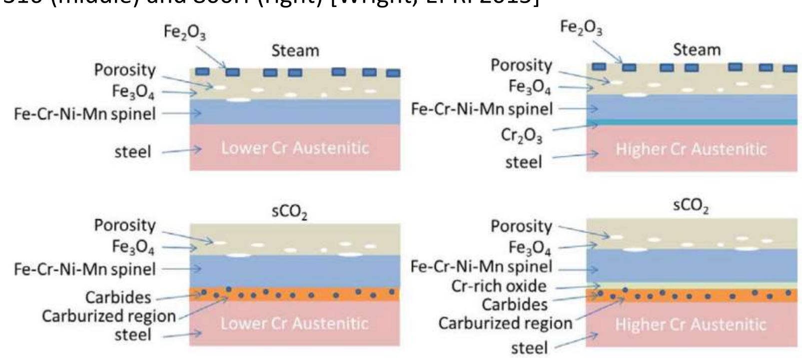
sCO_2 Corrosion Testing – Results

Austenitic Steels



Austenitic steels in CO_2 (left), and higher-strength austenitics TP316 (middle) and 800H (right) [Wright, EPRI 2015]

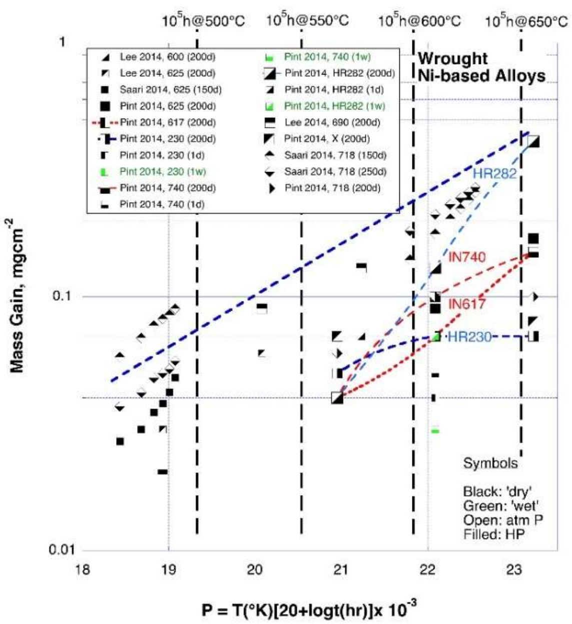
- Larson-Miller plots for comparison
- Mass gain plotted
- CO_2 and recent sCO_2

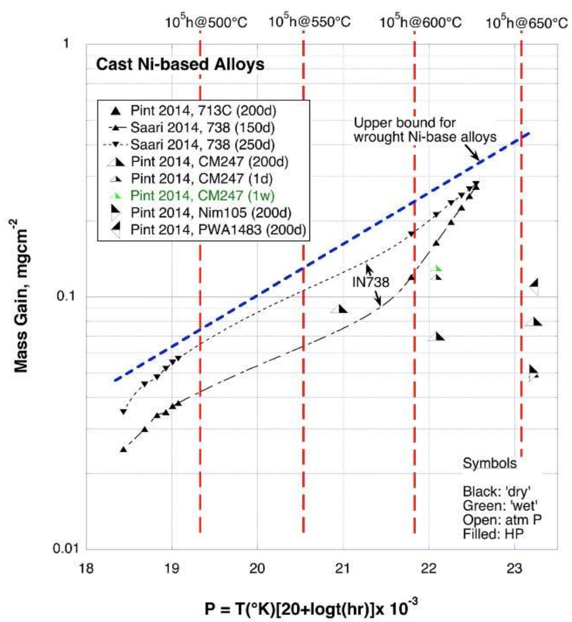


Schematic of oxidation products on austenitic steels in steam and sCO_2 [Strakey, 2014]

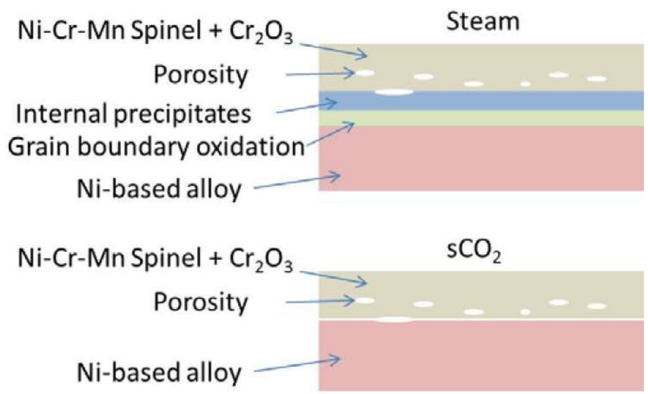
sCO_2 Corrosion Testing – Results

Nickel-base Alloys





Nickel-base alloys in CO_2 (wrought alloys left and cast alloys right) [Wright, EPRI 2015]



Schematic of oxidation products on nickel-base alloys in steam and sCO_2 [Strakey, 2014]

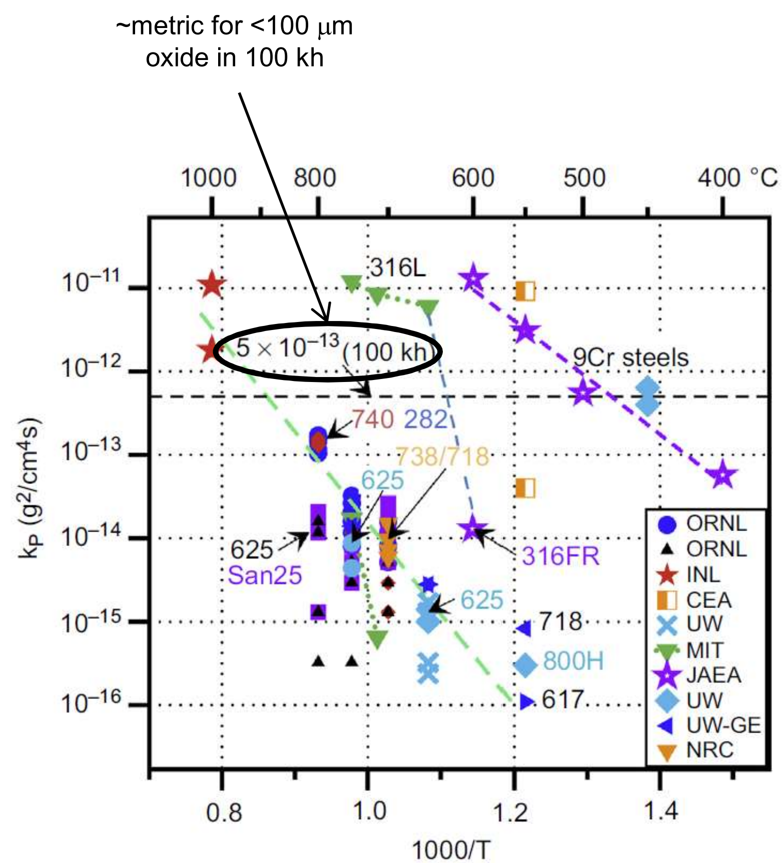
- Larson-Miller plots for comparison
- Mass gain plotted
- Recent sCO_2

Summary of Main Findings

- **Alloys with high Cr and Ni, and Ti and Al more corrosion resistant**
  - Build a stable, tight oxide layer that resists corrosion
- **Alloys with low Cr levels less corrosion resistant**
  - Build a duplex layer with that does not resist corrosion well
- **In general, decreasing corrosion resistance:**

Nickel Ni-Cr-X Cr>16%	**Austenitic Fe-Cr-Ni Cr>16%**	**FM Fe-Cr Cr<12%**
IN625	800H	12Cr
IN617	AL6-XN	HCM12A
Haynes 230	316SS	NF616
IN718	310SS	T91
IN738		

- **Increased corrosion with temperature**
- **Not much (if any) pressure effect**



[Pint and Brese, 2017]

Summary of Main Findings

PRELIMINARY TECHNOLOGICAL RECOMMANDATIONS FOR STEELS

From past studies carried out in the 60-70's for MAGNOX reactors and AGR :

CO_2 + 1%vol CO + 300 vpm H_2O + 300 vpm H_2 + 350 vpm CH_4 at 20-40 bars

Grade	Mild steels	9Cr-1Mo steel	Austenitic steels (316L type)	Austenitic steels (310 type, Nimonic 80, PE16)
T_{max}	<350°C	<450°C	<660°C	>660°C

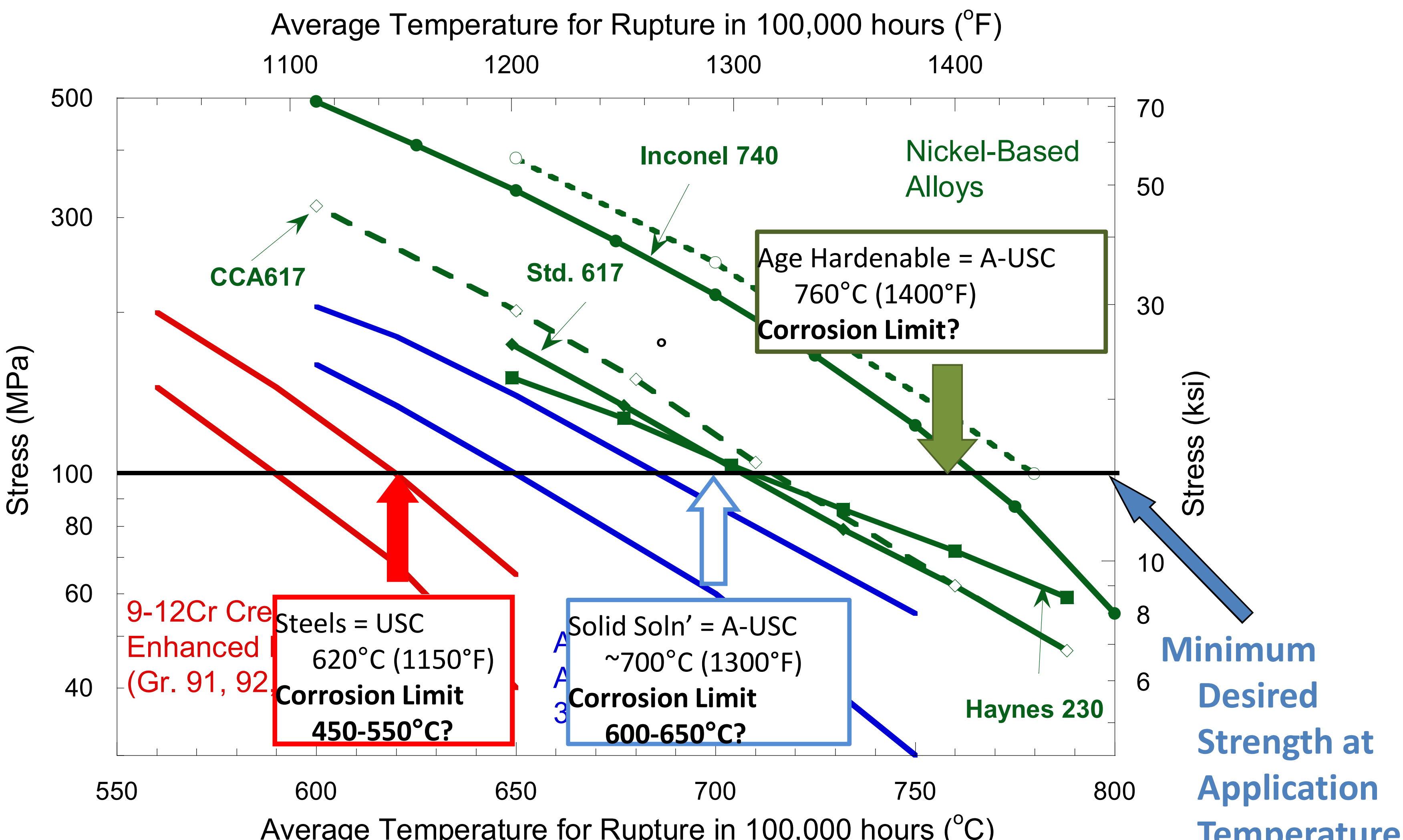
- « Breakaway oxidation » possible = Fast oxidation kinetics which incubation time and kinetics depend on Temperature (bad), CO_2 total pressure (bad), % Si (good), [H_2O] in CO_2(g) (bad)
- At 520°C and 40 bars, 9Cr steel is on « breakaway oxidation » before 30 years if %Si < 0,45 wt%
- For using « mild steel » at T > 350°C, %Si has to be > 0,4% or [H_2O] < 50 vpm (reasons ?)

Corrosion behaviour os« Mild steel » with %Si > or < 0,4% under SC-CO_2 at 250 bars at 400°C ?

40

[Rouillard, sCO_2 PCS 2011]

Summary of Main Findings



Where are the temperature cut-offs for different materials when corrosion is considered?

Materials Technical Challenges (Revisited)

Current Knowledge

- **Existing materials/mechanical properties**
  - OK for main components (piping, valves, turbomachinery, etc.)
- **Environmental considerations – high temperature sCO_2**
  - Corrosion testing – short-term, coupons, representative temps/pressures, mass gain (vs. depth)

Gaps Remaining/Technical Challenges

- **Availability**
  - Code compliant materials/qualified alloys; design codes
  - Supply chain – in required forms and sizes
- **Environmental considerations – high temperature sCO_2**
  - Longer-term (short-term testing inadequate – breakaway corrosion, intergranular corrosion)
  - Testing under "real" conditions (flow, stress, impurities – H_2O, O_2, others; indirect vs. direct cycles)
  - Reliability of data
  - Mechanical property degradation
- **Performance of actual components/material forms**
  - Thin sections – property differences, effect of geometry
  - Diffusion bonded, brazed, welded joints – corrosion resistance
  - Erosion, fouling of microchannel heat exchangers
  - Thermal fatigue, creep-fatigue interactions, high blade bending loads/temperature + pressure combinations
- **Other challenges and considerations**
  - Coatings
  - Non-metallics – degradation of seals via swelling, rapid gas depressurization
  - Leverage previous work – comparison to steam and SCW corrosion, pressure effects

Materials are available…but gaps remain…efforts are required to complete the picture…and they are underway!

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Availability

- **Code compliant materials/qualified alloys; design codes**
  - IN740H code case approved
  - Haynes 282 code case in progress
  - Design codes for valves, heat exchangers?
- **Supply chain – in required forms and sizes**
  - Market pull to enable capability

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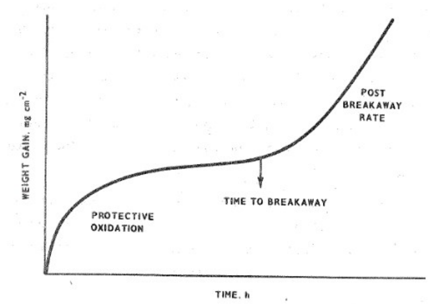
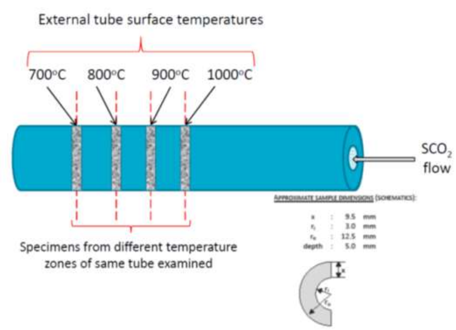
Environmental Considerations

- **Longer-term (short-term testing inadequate – breakaway corrosion, intergranular corrosion)**
  - Currently max test duration in range of 3-6 kh
  - Carburization and internal oxidation leading to breakaway corrosion, exfoliation
- **Testing under "real" conditions (flow, stress, impurities – H_2O, O_2, others; indirect vs. direct cycles)**
  - GTI/Oak Ridge National Laboratory
    - C-ring testing (stressed material) in sCO_2 (750 °C, 20 MPa,1000 hours)
    - Various materials (housing, disk, blade) [Keiser, 2016]
  - Various labs examining effects of impurities, CO_2 composition
    - Testing in impurities expected in "semi-open" fired configurations [Shingledecker, 2016]
  - CSIRO
    - Pressure vessel as test specimen (stressed material)



[Ferguson, BNES 1974]

[Keiser, sCO_2 PCS 2016]



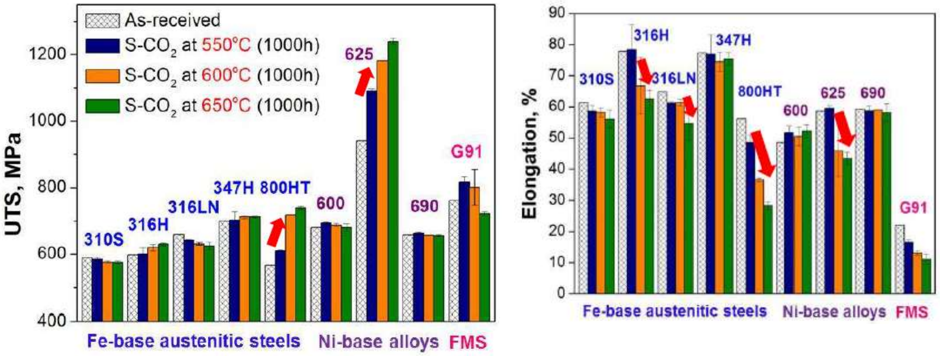
[CSIRO]

Environmental Considerations

- **Reliability of data**
  - Round Robin Testing and Fundamental Modeling (US DOE Nuclear Energy University Programs)
  - Various test facilities, but previously no formal test program to validate data consistency
  - Comparable and reproducible results desired
  - Proposed work:
    - Round robin test plan for sCO_2 corrosion testing
    - Organization of sCO_2 Materials Group to guide future testing
    - Elucidate mechanisms of sCO_2 corrosion
  - Lead: OSU, Collaborators: UofW-Madison, ORNL, NETL, Carleton University, KAIST, EPRI
- **Mechanical property degradation**
  - Compact tension specimens exposed, study subsequent fatigue crack growth [Holcomb, 2016]
  - Evaluate effects of sCO_2 exposure on tensile properties [Pint, 2016] and [Jang, 2014]

Organization	Maximum Temperature	Maximum Pressure	Chamber Volume	Flow rate (mL/min)	Autoclave Material
OSU	800°C	26 MPa	1235 cm^3	0-24	Haynes 230
UW (2 systems)	750°C	25 MPa	900 cm^3	0-24	Inconel 625
	760°C	38 MPa	(combined)	0-24	Haynes 282
ORNL	850°C	30 MPa	1400 cm^3	0-24	Haynes 282
NETL	800°C	28 MPa	1040 cm^3	0-24	Haynes 230
Carleton	750°C	25 MPa	1150 cm^3	0-250	Inconel 625
KAIST	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[Holcomb, sCO_2 PCS 2016]



[Jang, sCO_2 PCS 2014]

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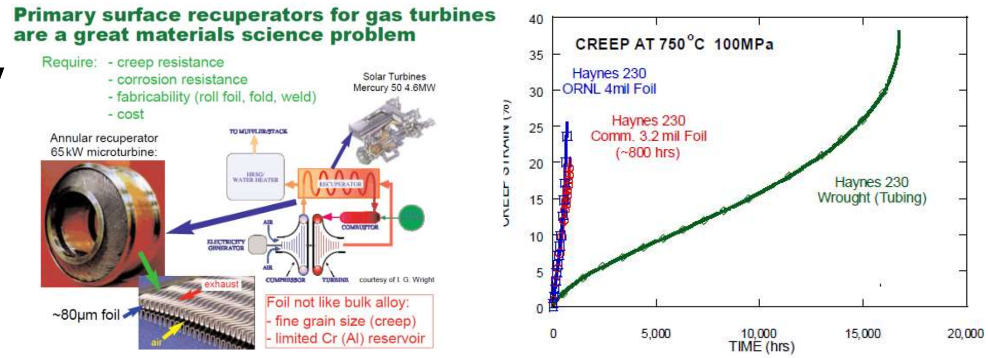
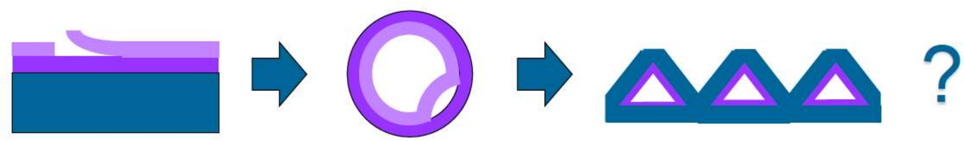
  - Leverage previous work – comparison to steam and SCW corrosion, pressure effects

Performance of Actual Components/Material Forms

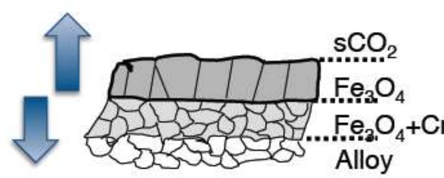
- **Thin sections – property differences, effect of geometry**
  - Creep debit for thin sections [Pint, 2016]
  - Oxide thickness not extent of damage [Pint, 2016]
  - Heat flux, stress from complex geometries [Kung 2016]
- **Diffusion bonded, brazed, welded joints – corrosion resistance**
- **Erosion, fouling of microchannel heat exchangers**
  - Is erosion a real problem – fluid or debris, exfoliation? [Fleming, 2014]
  - Oxide scale itself may cause blockage [Sabau, 2016]
- **Thermal fatigue, creep-fatigue interactions, high blade bending loads/temperature + pressure combinations**

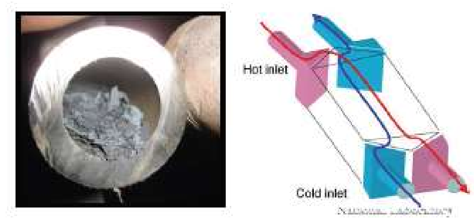


[Pint, 2015]



[Kung, sCO_2 PCS 2016]





[Sabau, sCO_2 PCS 2016]

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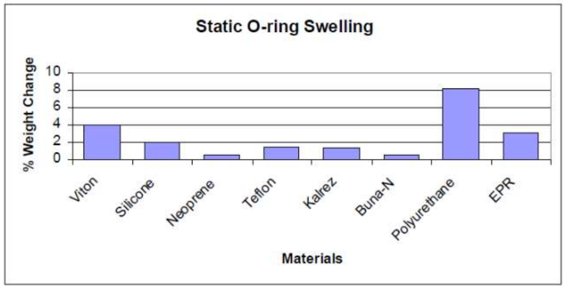
Other Challenges and Considerations

- **Coatings**
  - Allow use of lower-cost alloys or push corrosion limit of material
- **Non-metallics – degradation of seals via swelling, rapid gas depressurization**
  - [Tunnison, 2009] and oil and gas studies
- **Leverage previous work – comparison to steam and SCW corrosion, pressure effects (testing in CO_2)**
  - Extend ORNL/EPRI exfoliation model for steam to sCO_2 [Sabau, 2016]
    - Exfoliation of oxide scales on boiler tubes
    - Predicts scale failure and loss based on evolution of oxide
  - Little pressure effect seen in sCO_2 – low pressure CO_2 testing OK?



[Tunnison, 2015]

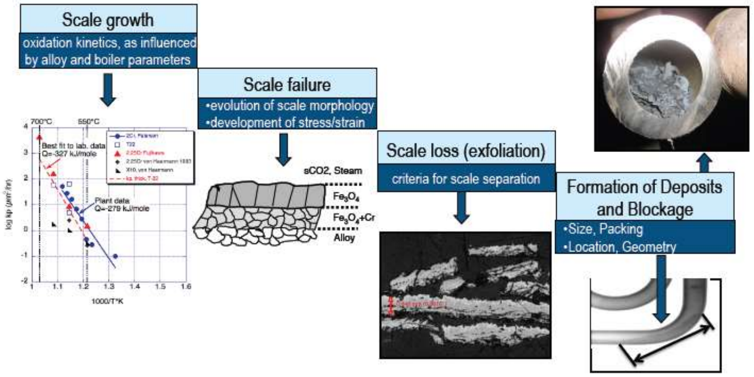
Polymers – Rapid Gas Depressurization (RGD)

Rapid depressurization after a polymer seal is diffused with S-CO_2 can damage the seal as the S-CO_2 quickly expands to escape the seal

RGD is increased by:

- High pressure
- High gas concentration
- High decompression rate
- High temperature
- Poor seal constraint

[sCO2 Fundamentals Tutorial, 2013]



[Sabau, sCO_2 PCS 2016]

Part IV: Summary

SCO_2 CAN BENEFIT FROM A COLLABORATIVE MATERIALS APPROACH

Gaps: Turbomachinery – Work in Progress

- **Compressors**
- **Turbine blades:**
  - Oxidation/corrosion in sCO_2
  - Erosion
  - Optimal coating technologies
- **Rotors**
- **Sealing surfaces at these higher pressures**
- **Lower temperature seals**
  - De-gassing
- **Others?**

Gaps: Heat Exchangers – Work in Progress

- **High temperature corrosion rates, exfoliation, and mechanisms are not well understood**
- **Strong desire to maximize use of less expensive alloys**
- **Long-term performance, at high-temperature, of brazed, welded, or diffusion- bonded joints is unknown**
- **Short-list of code approved materials for highest temperatures**
- **Potential alloys in various states of code certification**
- **Properties needed by designers may be different in very thin sections due to processing:**
    - Creep
    - Fatigue
    - Thermal mechanical fatigue and creep-fatigue
    - Oxidation, spallation of oxide scales

Gaps: Balance-of-Plant – Work in Progress

- **High-mass flow requires large piping for larger applications**
  - Fabrication/welding of nickel-based materials
- **Limitations in current supply chain**
  - Limited materials to choose from
  - Need production of fittings, forgings, casting, etc.
  - Valve vendors ‘not up to speed’ on market developments
- **Codes & Standards**
  - Valve codes are highly restrictive for materials & pressures/temperatures
- **Erosion and wear performance of hardfacing and alternatives**
- **Valves and instrumentation**
- **Others?**

Summary and Recommendation

- **Selection and qualification of materials for sCO_2 applications is a function of operating conditions and environment**
  - Corrosion and oxidation characteristics are unique to sCO_2
- **Severity of temperature, pressure conditions for the reference case are analogous to those experienced in A-USC conditions**
- **This tutorial draws on data available to-date from the A-USC program and other ongoing sCO_2-focused tests**

A coordinated effort similar to A-USC materials program is recommended

Leverage data and process to accelerate maturing selection and qualification of materials for sCO_2 plant components (address the Gaps)

Thank You!

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