



Influence of CO₂ Purity on the Corrosion of Structural Alloys for Supercritical CO₂ Power Cycles

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*Exceptional
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national
interest*

6th International Supercritical CO₂ Power Cycles Symposium
Pittsburgh, PA
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ENERGY

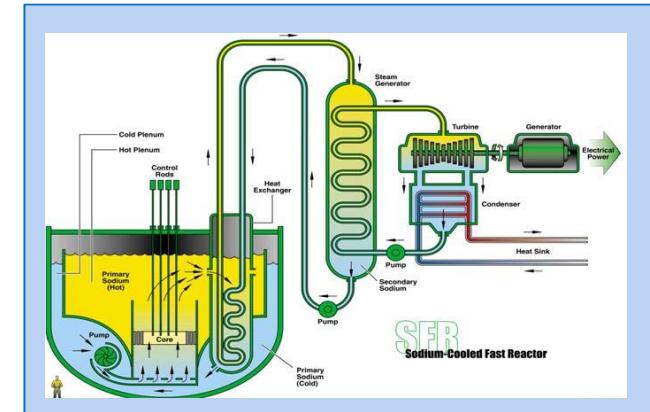
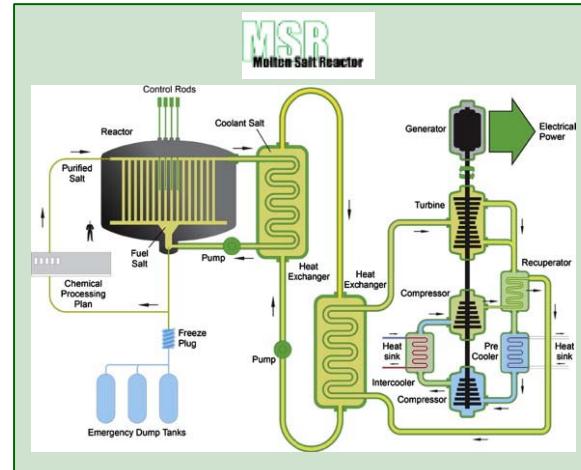
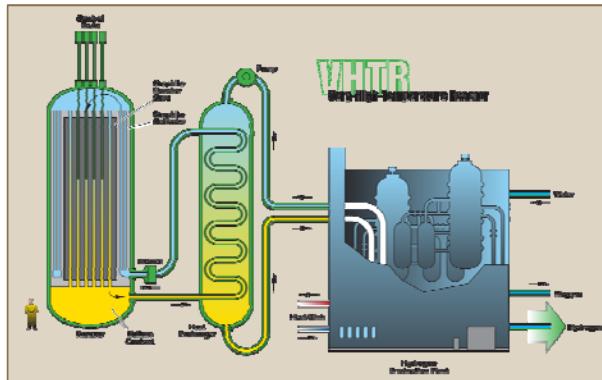


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Advanced nuclear reactor concepts aim for advances over existing LWRs



DOE Advanced Nuclear Reactor Program



Advanced reactors are intended to provide advancements in the following areas:

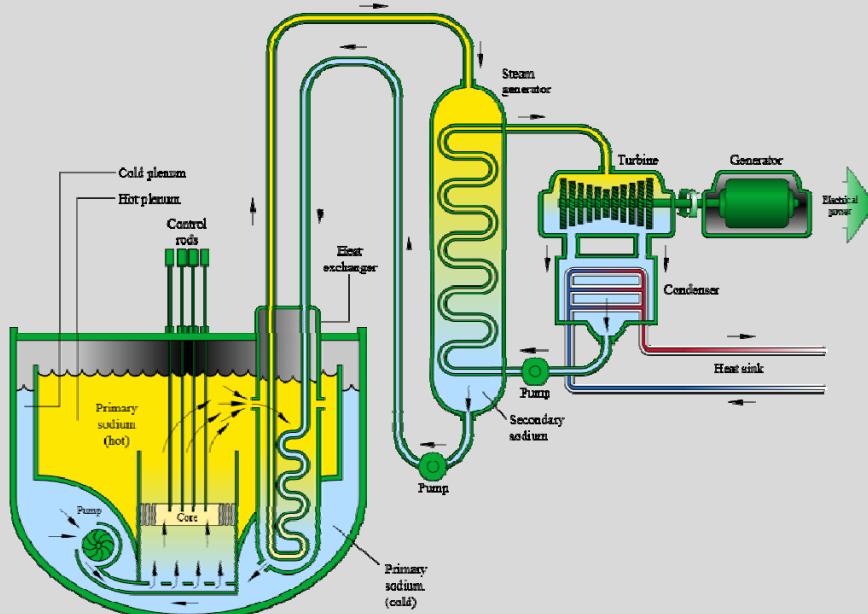
- Sustainability
- Safety
- Reliability
- Economics
- Non-proliferation

Considering energy conversion systems for Sodium Fast Reactors



Sodium Fast Reactor Concept

Sodium Fast Reactor (SFR)



Characteristics:

- Sodium coolant
- 550°C outlet temperature
- High thermal efficiency

Fast reactor concepts are important for meeting sustainability goals

- Efficient resource (fissile material) utilization and generation
- Waste minimization (consumption of LWR actinides)

Research program established to develop and integrate a Supercritical CO₂ Energy Conversion System in place of the Conventional Steam Rankine System

- Sandia is teaming with Argonne to develop this system

Distinct challenges exist with materials for sCO₂ EC Systems



Focus Areas for sCO₂ Materials Development

- Two areas identified where materials contributions are critical to the successful development of this technology :

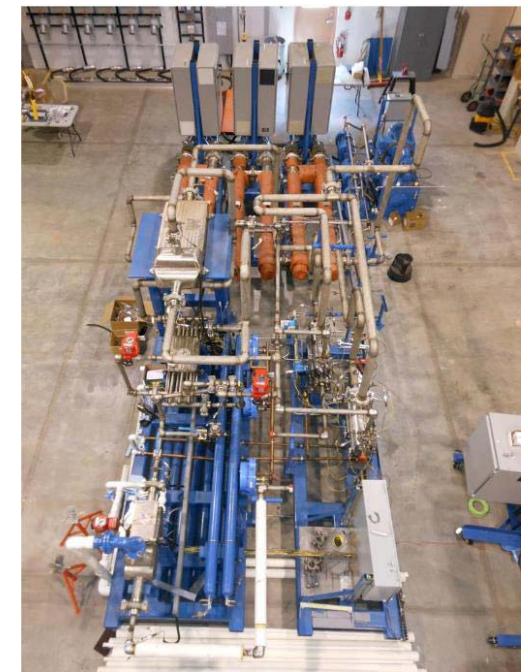
1. Alloy Selection for sCO₂ EC Systems

- T<550°C: SFR
- T>550°C: HTGR and MSR

2. Materials Support for sCO₂ System Development

- Turbine Degradation
- Bearing Foil Materials (coatings)
- Systems for In-situ Measurement of Materials Corrosion
- sCO₂/Polymer Interactions

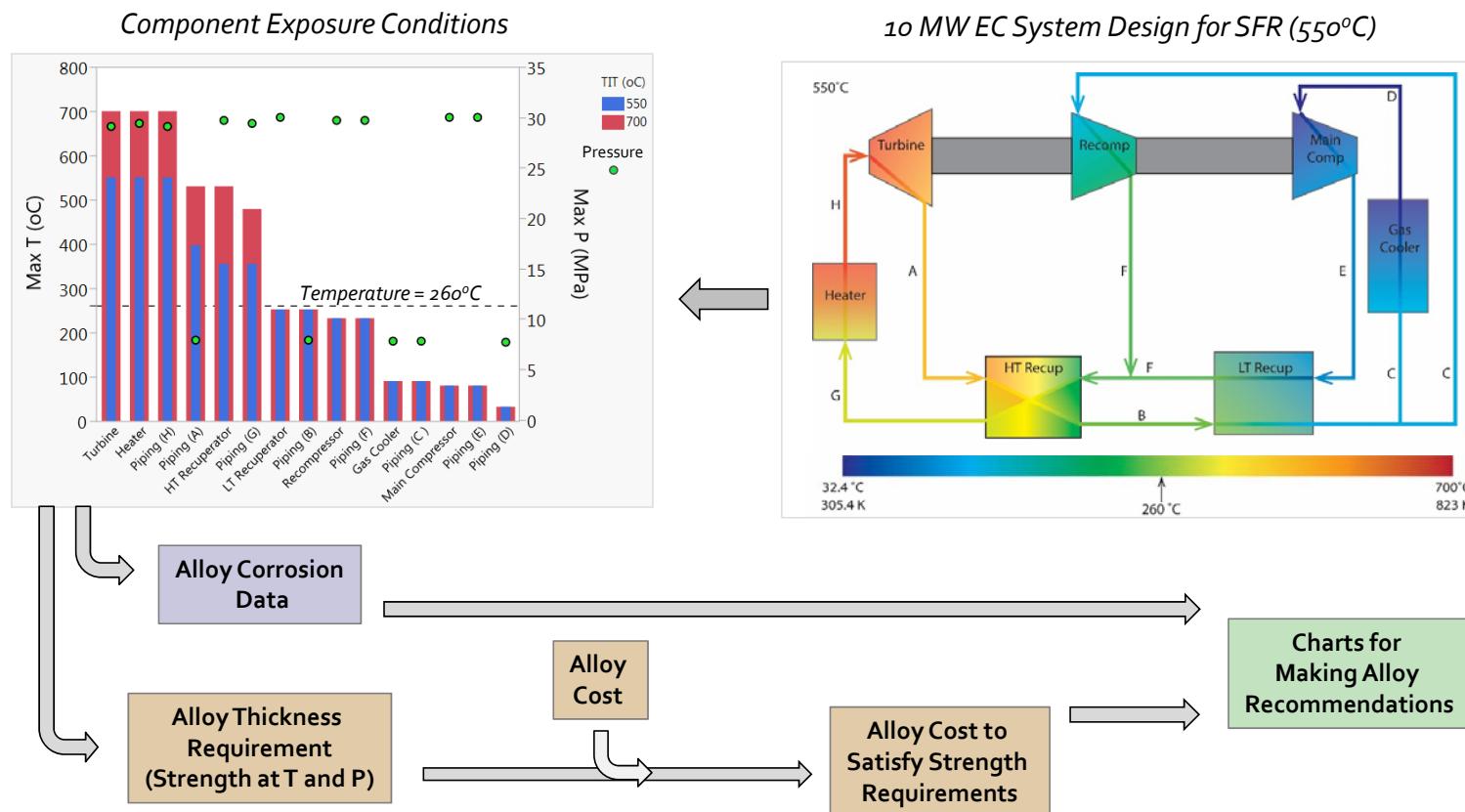
Sandia National Laboratory
250 kW sCO₂ RCBC



Informed decision making process used for selecting component alloys



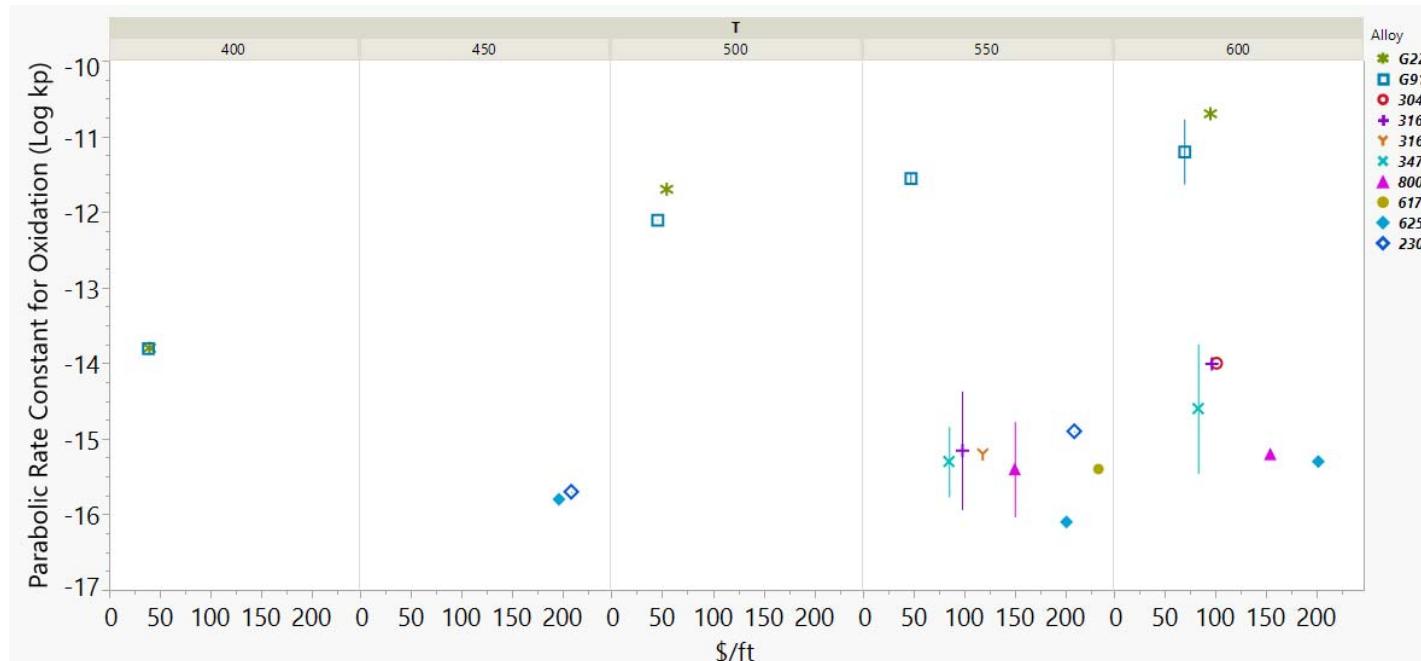
10 MW SFR Energy Conversion System



Alloys recommendations made using available data – caveats exist



10 MW SFR Energy Conversion System Candidate Alloys



▪ Alloy Recommendations for SFR EC

- Temperatures > 400°C: 347H, 316H, 316L
- Temperatures < 400°C: G22, G91

▪ Caveats

- Alloy costs calculated using alloy chemistry and market elemental prices
- Only considers surface oxidation and not internal carburization
- All corrosion data collected using RG CO₂ rather than IG CO₂

Evaluating the impact of CO₂ gas chemistry on alloy corrosion



Corrosion Experimental Overview



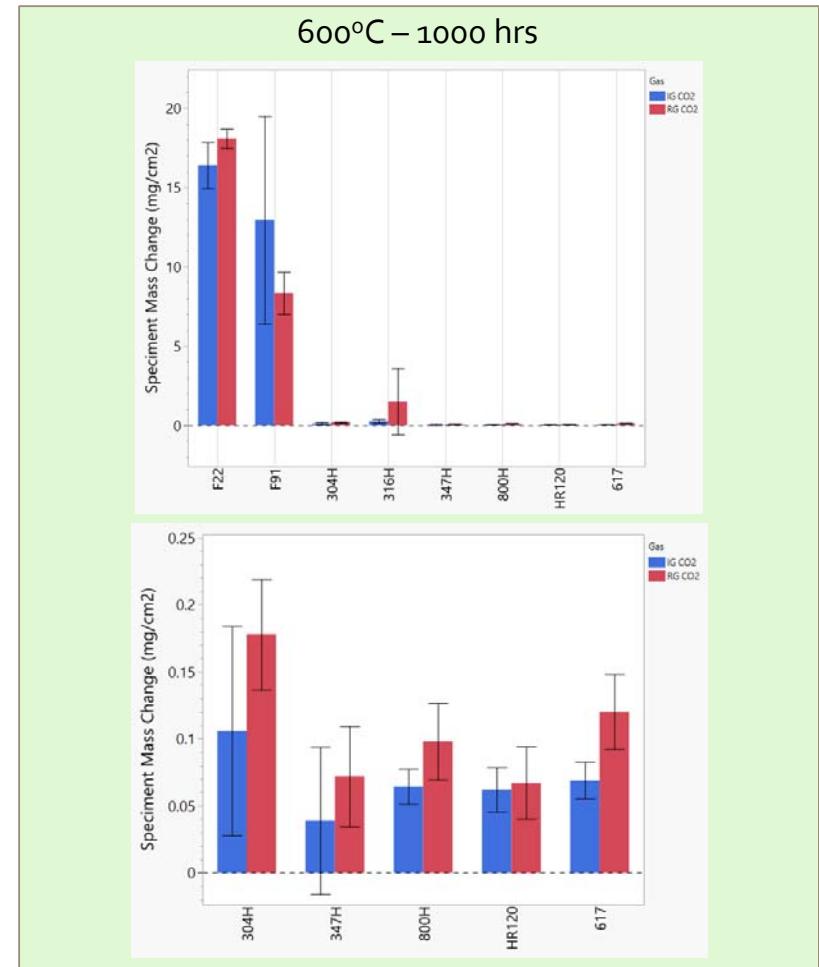
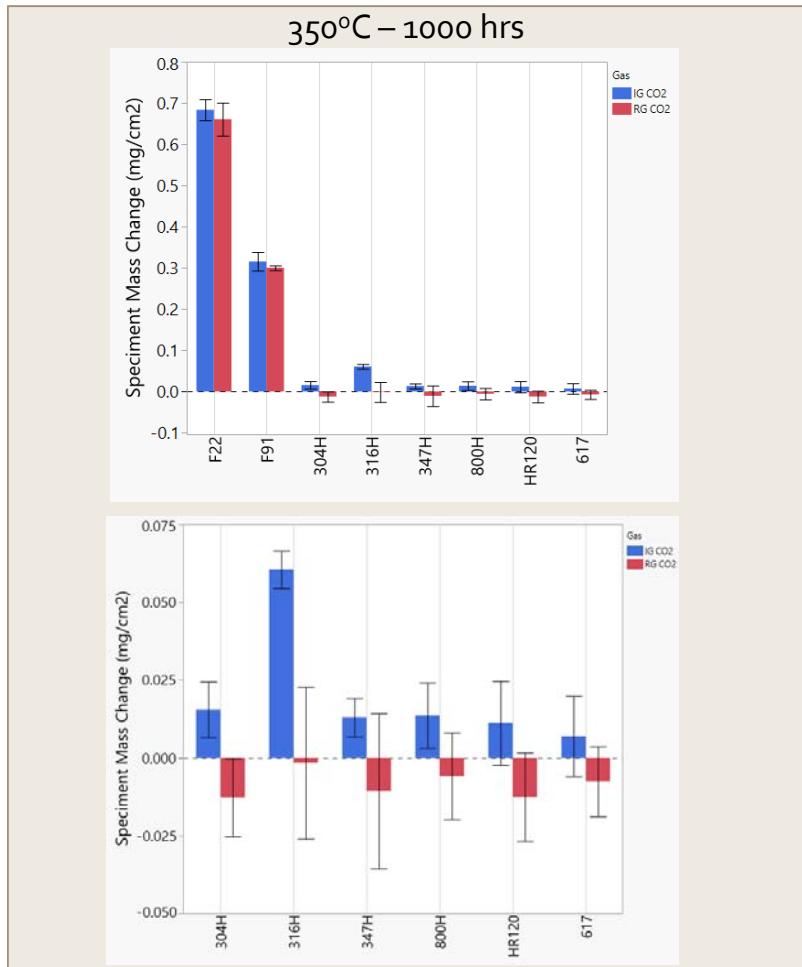
Alloy	Chemical Analysis (Wt %)																			
	Fe	Cr	Ni	Mn	Co	Mo	Si	Al	B	C	Cu	P	S	Ti	W	Nb	N	V	Zr	Ta
F22	98.13	2.19	0.07	0.4	-	0.95	0.2	0.021	0.0001	0.1	0.1	0.008	0.011	0.002	-	0.001	-	0.004	-	-
F91	89.25	8.38	0.18	0.43	-	0.94	0.32	0.011	-	0.1	-	0.02	0.01	0.007	-	0.067	0.063	0.22	0.001	-
304H	70.54	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	Gas Chemical Analysis						
	CO ₂ (%)	CO (ppm)	H ₂ (ppm)	N ₂ (ppm)	O ₂ (ppm)	CH ₄ (ppm)	H ₂ O (ppm)
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

After the ferritic alloys, 316H is the most susceptible to corrosion in CO₂



Alloy Specimen Mass Changes

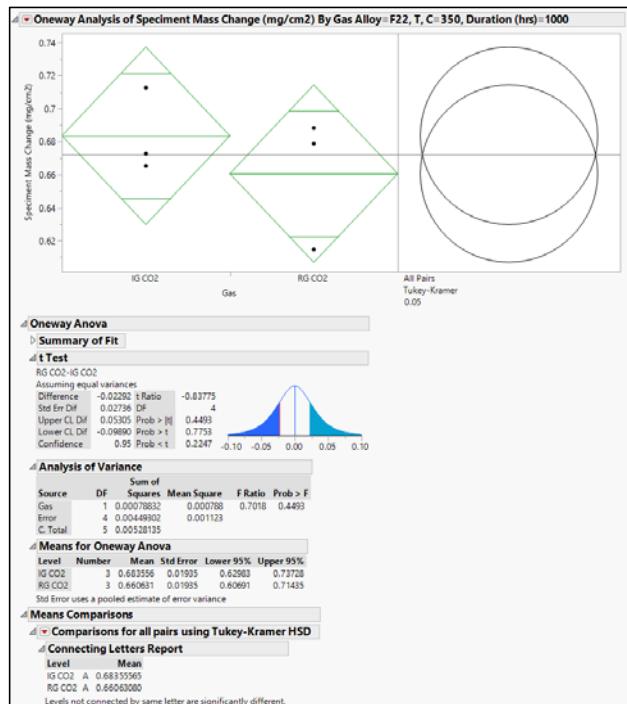




Gas chemistry (RG vs IG CO₂) has very little influence on alloy corrosion

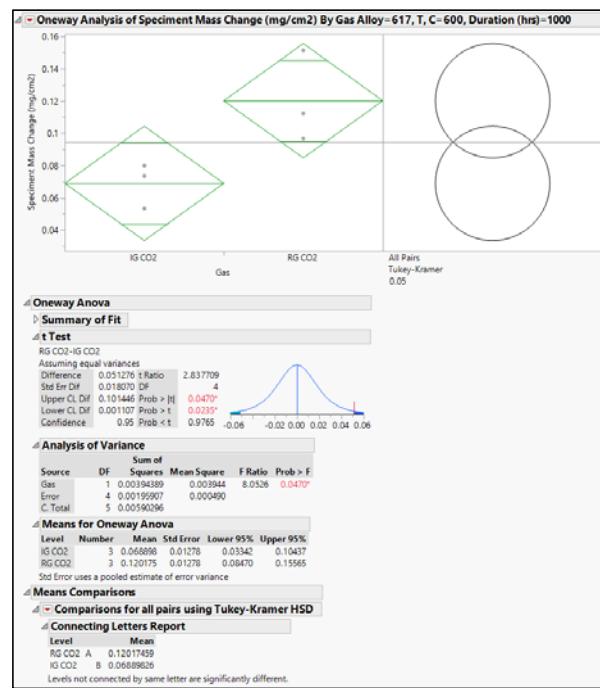
Statistical Analysis for Different Gas Chemistries

Statistically Significant Difference
Does Not Exist



Comparing weight gain data for F22 at 350°C in RG and IG CO₂

Statistically Significant Difference
Does Exist



Comparing weight gain data for 617 at 600°C in RG and IG CO₂

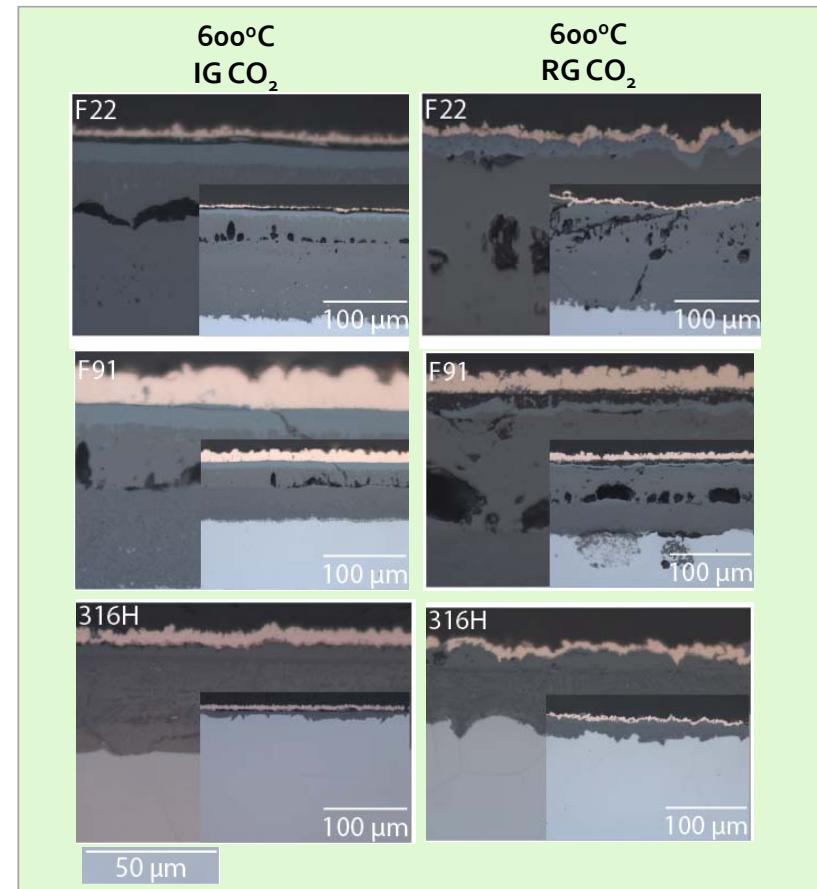
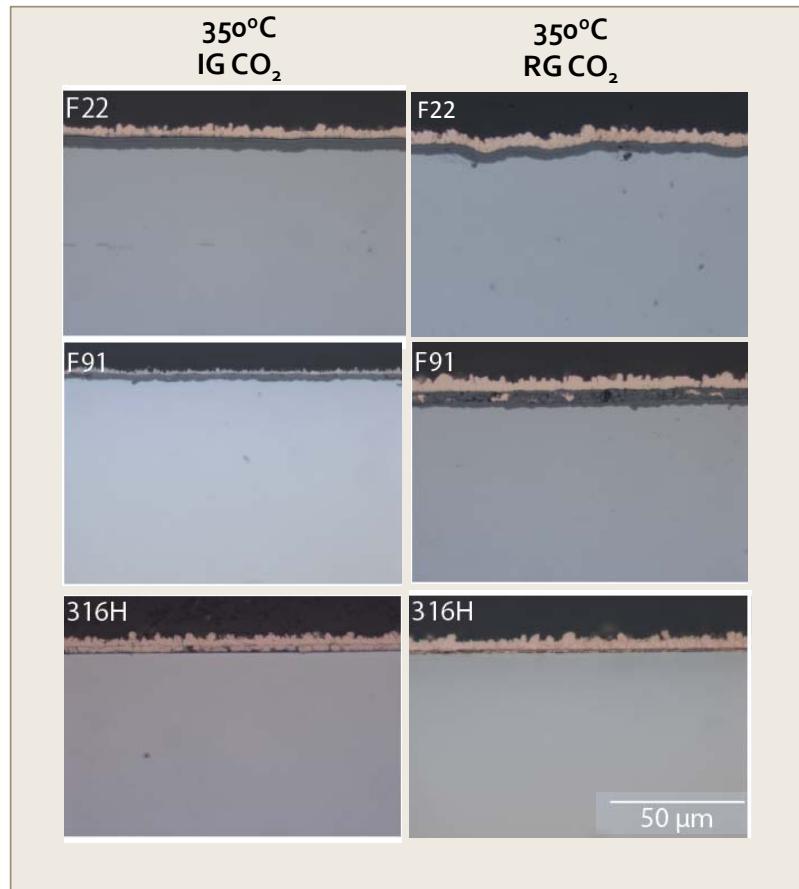
Statistical Analysis Summary of Alloy Weight Change Differences for RG and IG CO₂

Alloy	350°C		600°C	
	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 CO₂) has very little influence on surface oxide



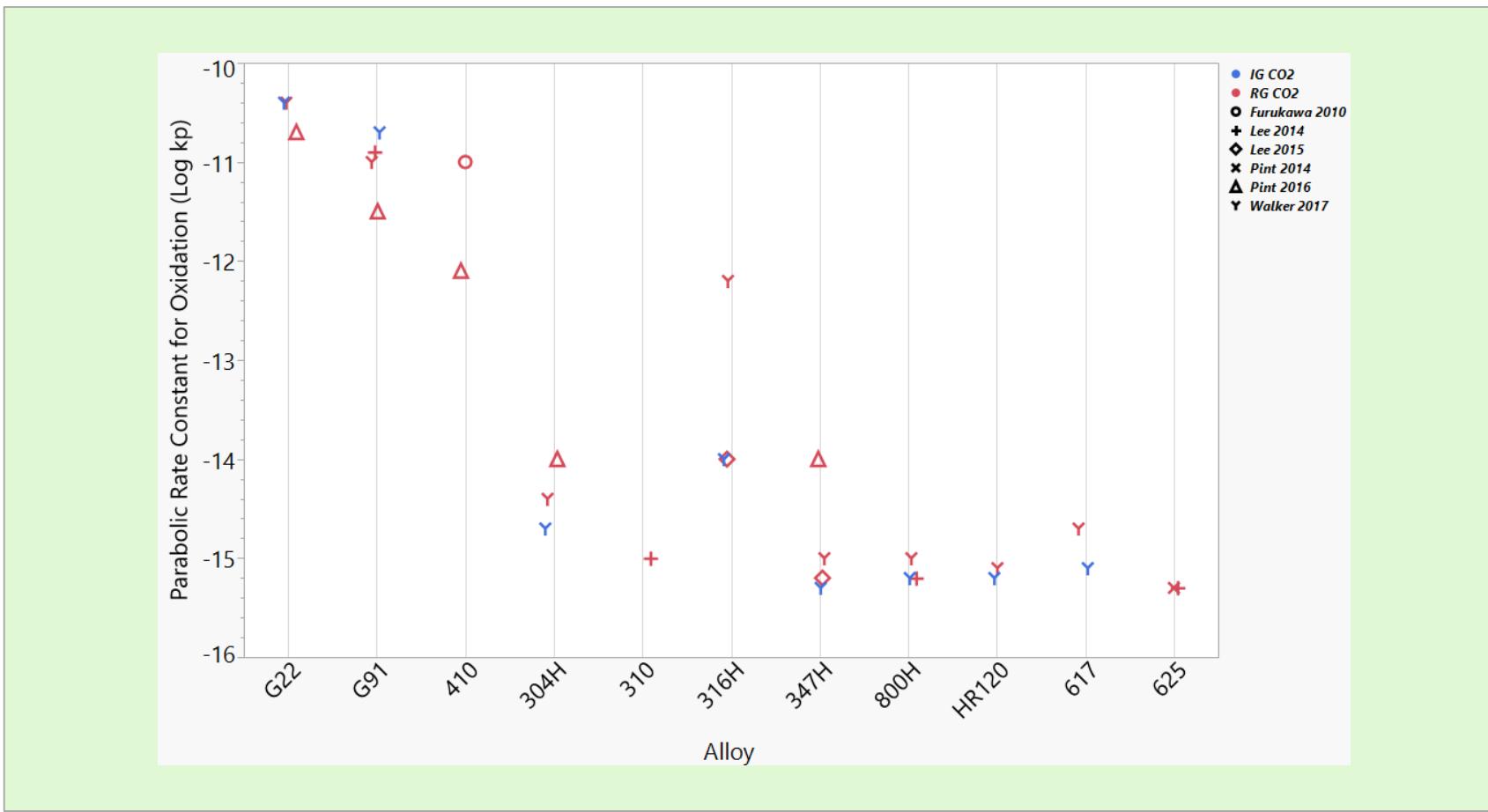
Alloy Specimen Oxide Microstructures



Valuable observations in comparing to results from other researchers



Comparison with Prior Results at 600°C



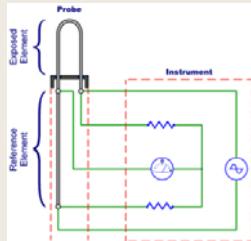
Developing a unique capability for sCO₂ energy conversion systems



In-situ Alloy Corrosion Monitoring

in-situ Carbon Dioxide Corrosion Monitoring

- Systems are currently being built where alloy selections are made with limited data
- Capability for real time monitoring of component alloy corrosion in these systems is extremely valuable:
 - Reduces risk for system developers
 - Provides the opportunity to piggyback learning for material behavior in these systems
- ER is a simple, robust technique that measures Electrical Resistance across a metallic element
- As the element increases in resistance due to corrosion this is correlated to a loss in the element thickness

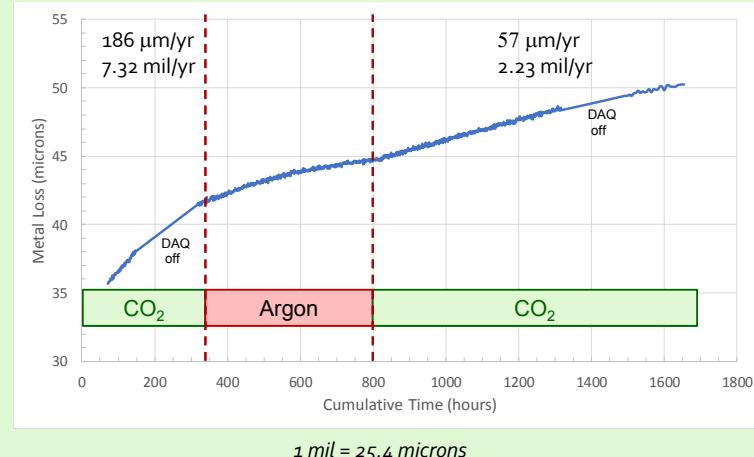


$$R_{probe} = \rho \frac{L}{A}$$



- Photo of 316L ER device with heat shield removed
- Reference element is internal to the device

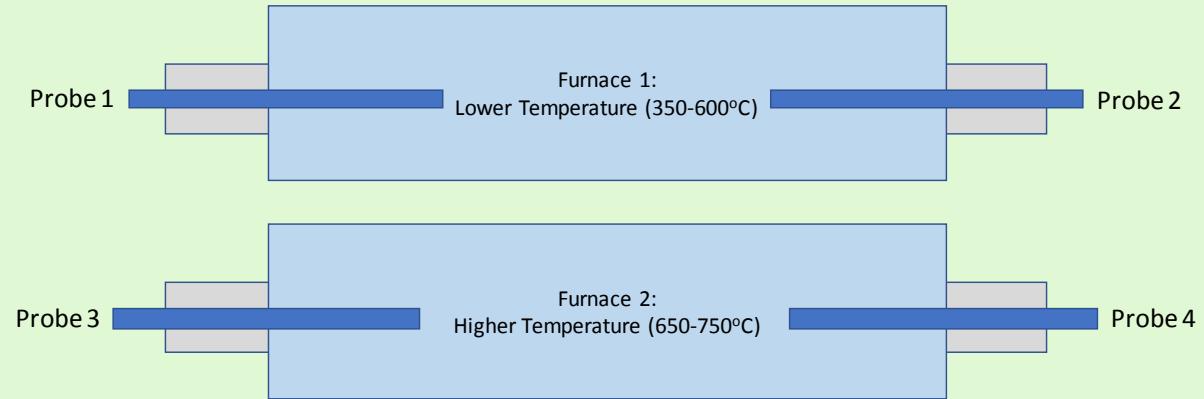
Shake down results over 1600 hours of continuous testing at 650°C in IG CO₂





Validation of in-situ corrosion monitoring with alloy witness coupons

In-situ Alloy Corrosion Monitoring – Next Steps



- Run probes of 2 different alloys in two separate temperature ranges in CO₂
- 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



Significant new understanding has been achieved for alloy corrosion in CO₂ gases

Summary and Overview of Future Work

- **Concerns with Existing Data:**

- Alloy corrosion data has predominantly been obtained using research grade CO₂, while the lower purity industrial grade CO₂ will be used in a real system
- There is very limited alloy corrosion data available at lower temperatures relevant for sodium fast reactor (SFR) energy conversion system applications
- Alloy corrosion investigations have primarily considered surface oxidation and not internal carburization
- Structural alloy corrosion has only been evaluated in terms of sample weight gain, rather than by the more useful metric of metal loss

- **Achievements through recent research:**

- Long duration (1000-hour) corrosion data has been obtained for 8 alloys at two temperatures relevant to an SFR EC system (350°C and 600°C) in both RG and IG CO₂
- Statistical analysis of alloy weight change data indicates very little change in alloy corrosion behavior for these two temperatures between RG and IG gases
- Comparison of recent results to others at higher pressures indicate minimal influence of pressure on corrosion in CO₂
- A recent lab shakedown test has demonstrated significant potential for ER in-situ corrosion probes in CO₂ systems

- **Overview of Future Work:**

- Complete analyses for alloy internal carburization using nanoindentation hardness techniques
- Complete analyses for alloy metal loss through chemical cleaning study (calculate alloy lifetimes)
- Evaluate/develop *in-situ* corrosion monitoring technology for sCO₂ EC systems



Acknowledgements

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Questions?



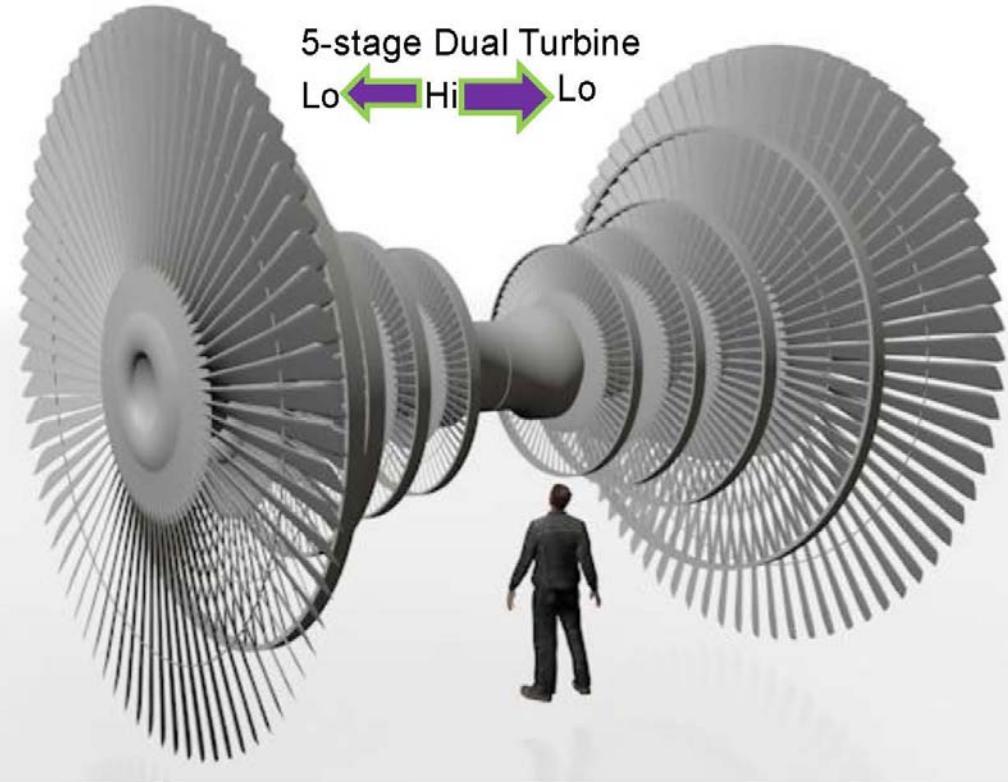
Backup Slides

Developing a transformative energy conversion system



Supercritical CO₂ (sCO₂) Energy Conversion Systems

5-stage Dual Turbine
Lo ← Hi → Lo



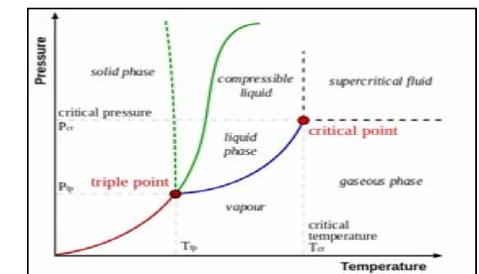
20 meter Steam Turbine (300 MWe)
(Rankine Cycle)

Motivation for sCO₂ Energy Conversion Systems

- *High Efficiency (>40%)*
- *Compact Turbomachinery that is easily scalable*
- *Reduced Cost*



1 meter sCO₂ (300 MWe)
(Brayton Cycle)



Critical Point for CO₂:
31.1°C (87.98°F) and 7.39 MPa (1071 psi)



Table 2. Corrosion Sample Dimensions

Alloy	Diameter (in)	Thickness (in)
F22	0.47	0.063
F91	1.25	0.063
304H	0.47	0.188
316H	0.47	0.125
347H	0.47	0.040
800H	0.50	0.063
HR120	0.47	0.063
617	0.61	0.063

Table 3. Chemical Analysis for CO₂ Gases

T, °C	CO ₂ Grade	Gas Chemical Analysis						
		CO ₂ (%)	CO (ppm)	H ₂ (ppm)	N ₂ (ppm)	O ₂ (ppm)	CH ₄ (ppm)	H ₂ O (ppm)
600	RG	> 99.999	0.054	0.021	3.097	0.110	0.355	< 0.02
350	RG	> 99.999	0.012	0.005	1.070	0.040	0.153	< 0.02
600	IG	> 99.98	< 0.010	0.040	35.370	11.110	0.430	0.53
350	IG	</= 99.98	< 0.010	0.040	> 80	> 60	0.420	0.81

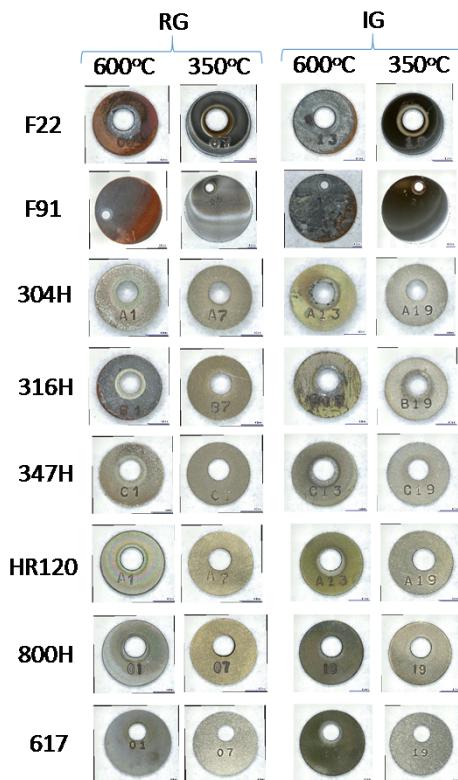


Figure 15. Polished cross-sections of each alloy in IG and RG CO₂ at 350°C for 1000h

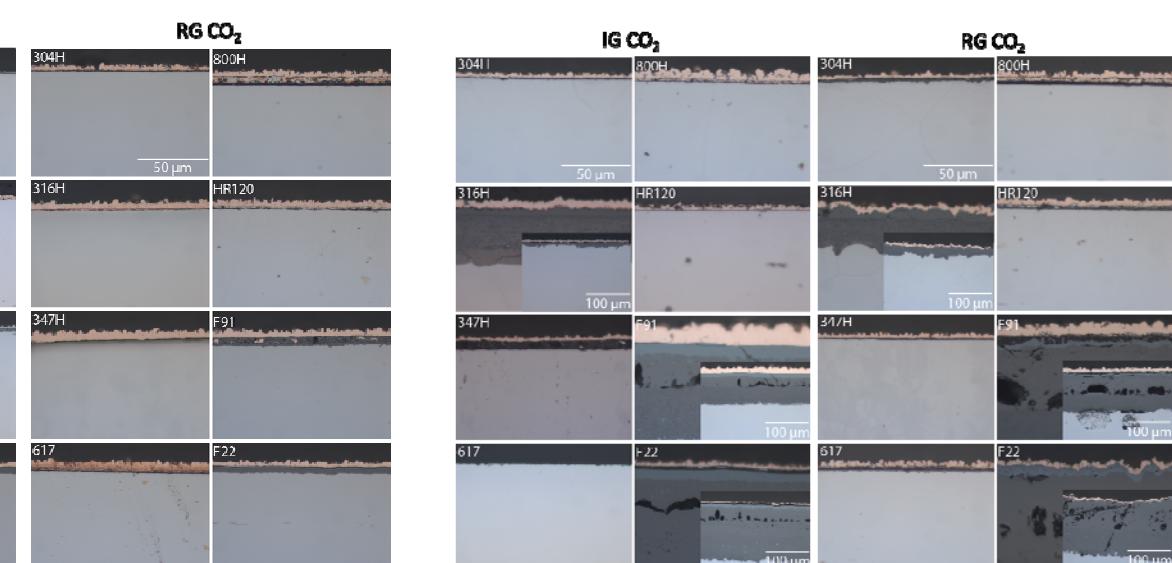


Figure 16. Polished cross-sections of each alloy in IG and RG CO₂ at 600°C for 1000h



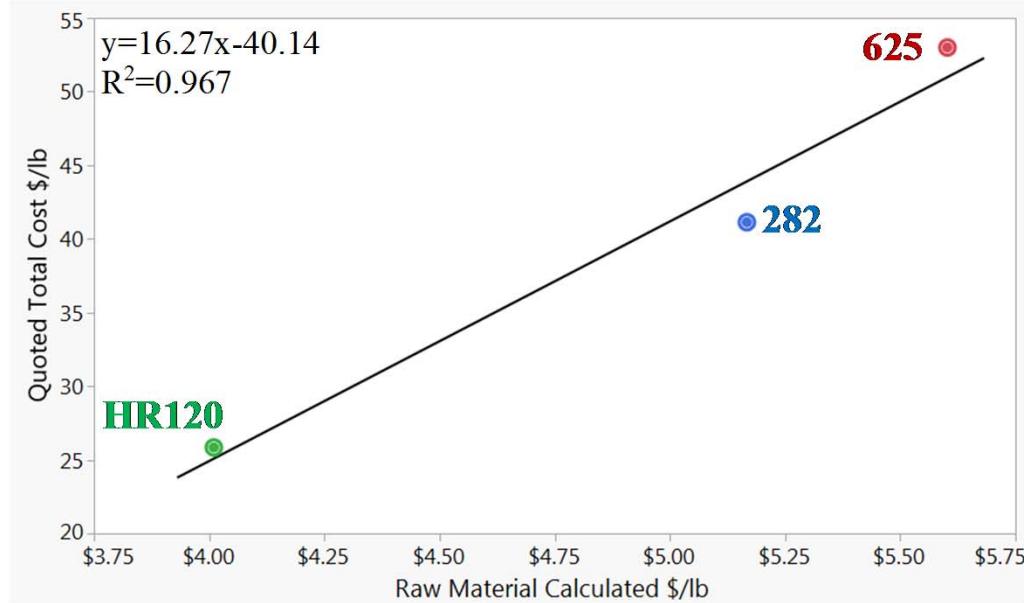
Identifying Candidate Alloys

Alloy	Category	Code Qualifications				Raw Material Cost (\$/Lb)	
		(Y, N)	ASME B31.1		BPVC		
			Category	Max T (°C)	Category	Max T (°C)	
API 5L	Carbon Steel	Y	Seamless Pipe and Tube (X65)	427			\$0.91
Grade 22	Ferritic	Y	Seamless Pipe and Tube (P22, T22, FP22)	593			\$1.04
Grade 91	Ferritic	Y	Seamless Pipe and Tube (P91, T91)	649			\$1.30
410	Ferritic	Y	Seamless Pipe and Tube (TP410)	371			\$1.23
E-Brite	Ferritic	Y	Seamless Pipe and Tube (TPXM-27)	343			\$1.75
304H	Austenitic	Y	Seamless Pipe and Tube (TP304H)	816			\$1.75
310S	Austenitic	N					\$2.37
310H	Austenitic	Y	Seamless Pipe and Tube (TP310H)	816			\$2.37
316L	Austenitic	Y	Seamless Pipe and Tube (TP316L)	816			\$1.83
316H	Austenitic	Y	Seamless Pipe and Tube (TP316H)	816			\$1.83
316FR	Austenitic	N					\$1.83
316LN	Austenitic	N					\$1.83
316	Austenitic	Y	Seamless Pipe and Tube (TP316)	649			\$1.83
347H	Austenitic	Y	Seamless Pipe and Tube (TP347H)	816			\$1.82
347HFG	Austenitic	N					\$1.82
AL-6XN	Super-Austenitic	Y	Seamless Pipe and Tube (N08367)	427			\$2.77
800H	Super-Austenitic	Y	Seamless Pipe and Tube (N08367)	816			\$2.64
600	Ni-Base Chromia-Forming	Y	Seamless Pipe and Tube (N06600)	649			\$4.18
617	Ni-Base Chromia-Forming	Y	Seamless Pipe and Tube (N06617)	816			\$5.38
625	Ni-Base Chromia-Forming	Y	Seamless Pipe and Tube (N06625)	649			\$5.60
690	Ni-Base Chromia-Forming	Y			BPVC, Sec II, Part D	650	\$4.04
230	Ni-Base Chromia-Forming	Y			BPVC, Sec II, Part D	900	\$5.86
282	Ni-Base Chromia-Forming	N					\$5.17
PE16	Ni-Base Chromia-Forming	N					\$3.43
718	Ni-Base Chromia-Forming	N					\$5.29
740	Ni-Base Chromia-Forming	N					\$6.27
740H	Ni-Base Chromia-Forming	Y			BPVC, Code Case 2702-1	800	\$6.18
HR120	Ni-Base Chromia-Forming	Y			BPVC, Sec II, Part D	900	\$4.01
214	Ni-Base Alumina-Forming	N					\$4.17
247	Ni-Base Alumina-Forming	N					\$9.06

✓ Corrosion Data

✓ Code Qualified

Elements	Raw Material Price July 2016 (\$/Lb)
Nickel	\$4.65
Cobalt	\$11.67
Molybdenum	\$6.99
Copper	\$2.20
Niobium	\$34.00
Iron	\$0.90
Chromium	\$3.78
Tungsten	\$13.00
Titanium	\$1.15
Manganese	\$0.75
Hafnium	\$75.00
Tantalum	\$59.88
Vanadium	\$8.77
Aluminum	\$0.75



For 3 inch – Schedule 160 pipe



Alloy Cost to Satisfy Strength Requirements

Minimum wall thickness calculation (Equation 7 in B31.1-2014):

$$t_m = \frac{PD_o}{2(SE + Py)} + A$$

t_m : Minimum wall thickness (inches)

P: Internal pressure (ksi) - **used 4.35ksi (30 Mpa)**

D_o: Outer diameter (inches) - **used 4 inches**

S: Allowable stress given as function of temperature (ksi) - **used values in code**

E: Weld joint efficiency - **used 1 (assumed seamless pipe no welds)**

y: used values from table 104.1.2

A: Additional thickness (corrosion allowance, etc.)

Cost of alloy per 1 ft length that satisfies the ASME code strength requirements:

$$\text{Cost} (\$) = \frac{\pi \times 12in \times [D_o^2 - (D_o - t_m)^2]}{1728 \text{ in}^3/\text{ft}^3} \times \rho_{\text{alloy}} \times \text{Cost}_{\text{alloy}}$$

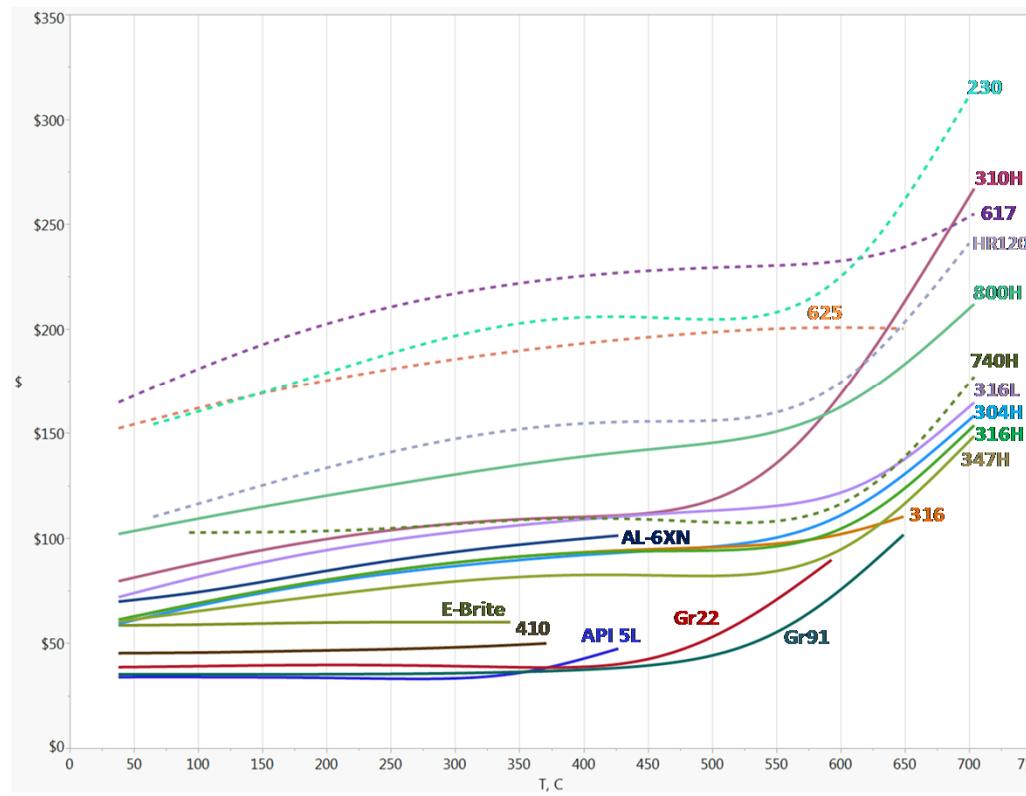
t_m : Minimum wall thickness (inches)

ρ_{alloy} : density of alloy in units of lbs/ft³

$\text{Cost}_{\text{alloy}}$: cost per lb of alloy based on raw material prices

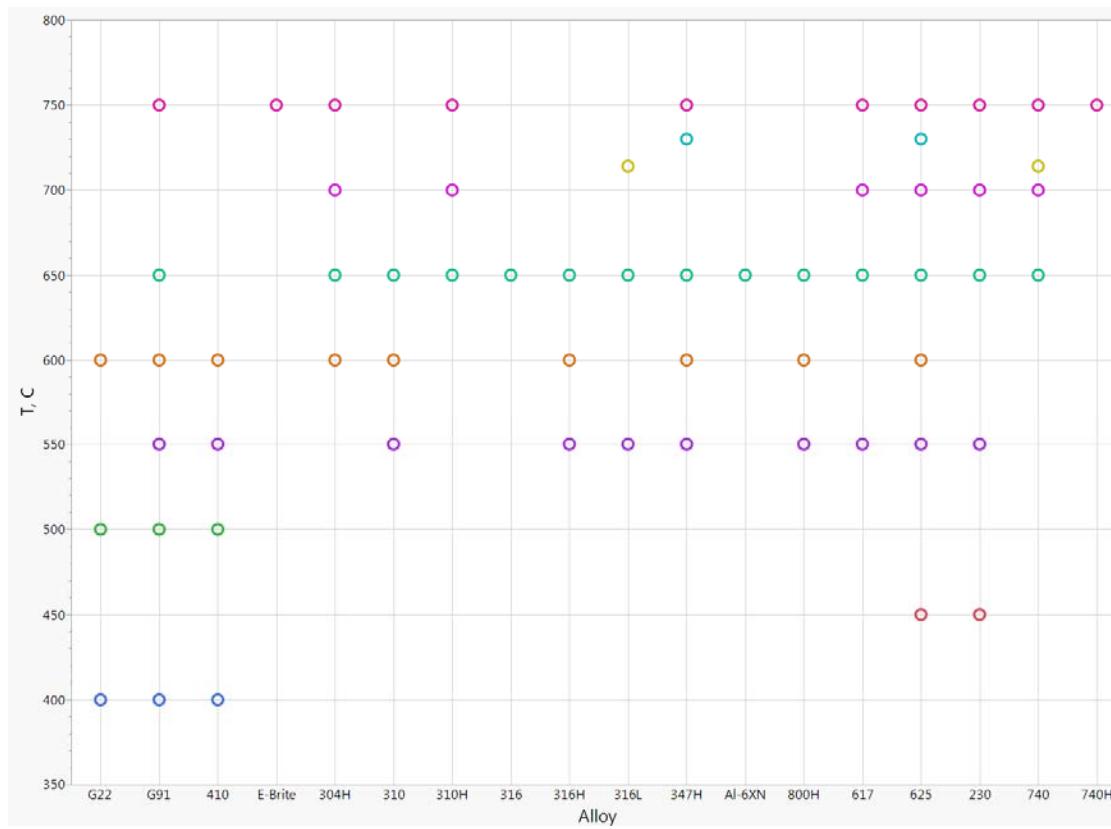


Alloy Costs (\$/ft) to Satisfy Strength Requirements

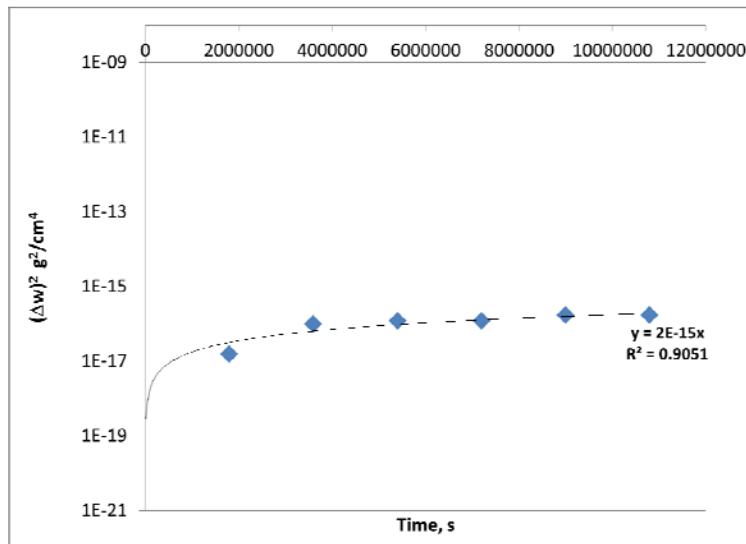




Available Alloy Corrosion Data (400-750°C, RG sCO₂, 200-250 bar)



Approach for Comparing Alloy Corrosion Rates



Parabolic fit to Cao's (2012) experimental data for 800H at 650°C

Assuming parabolic oxidation kinetics, the parabolic rate constant (k_p) can be calculated for each set of data

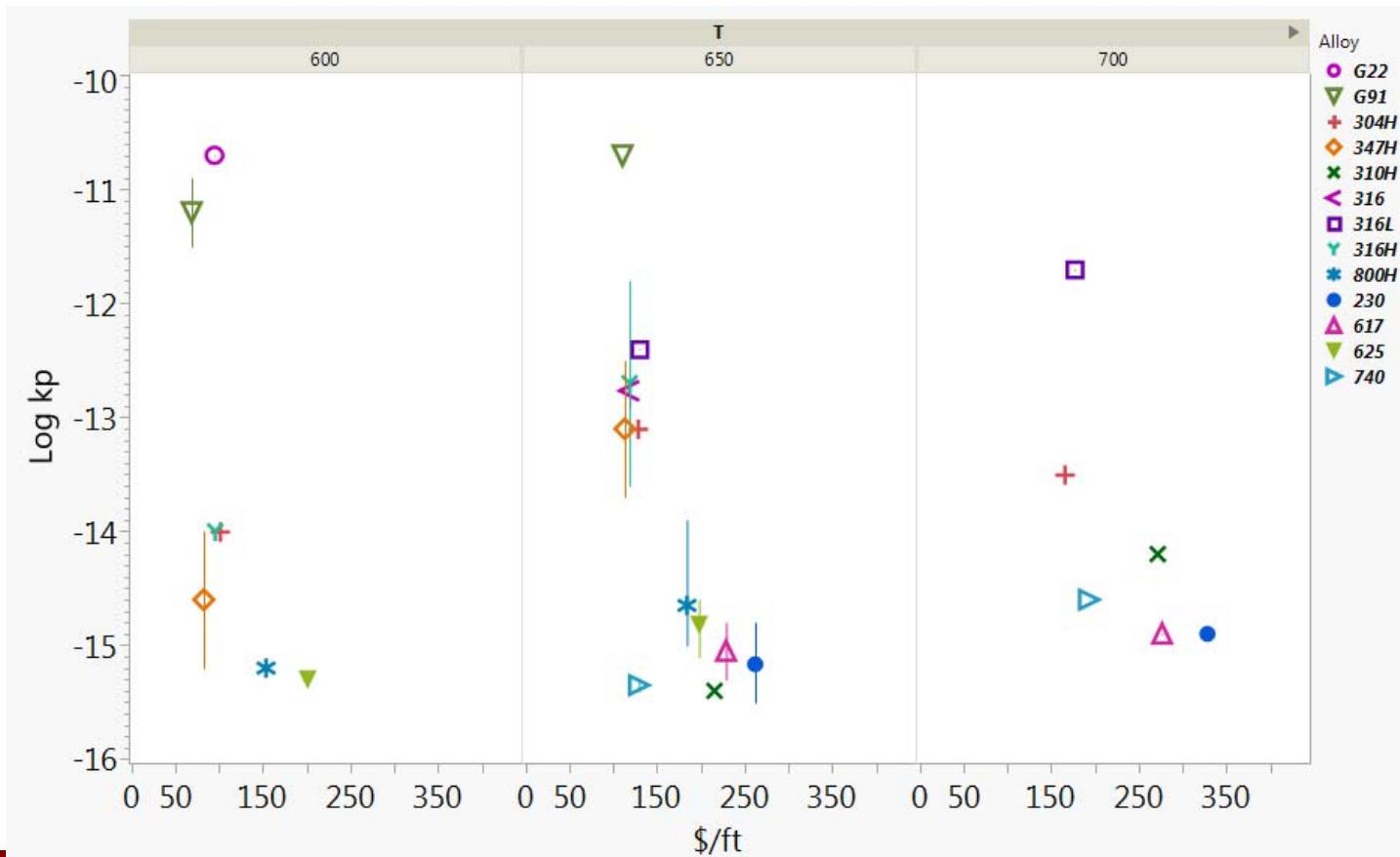
$$k_p = \frac{(\Delta m)^2}{2t}$$

Log k_p values are used as a corrosion rate comparison between alloys

Unable to accurately relate this back to alloy thickness requirements, which would be preferred

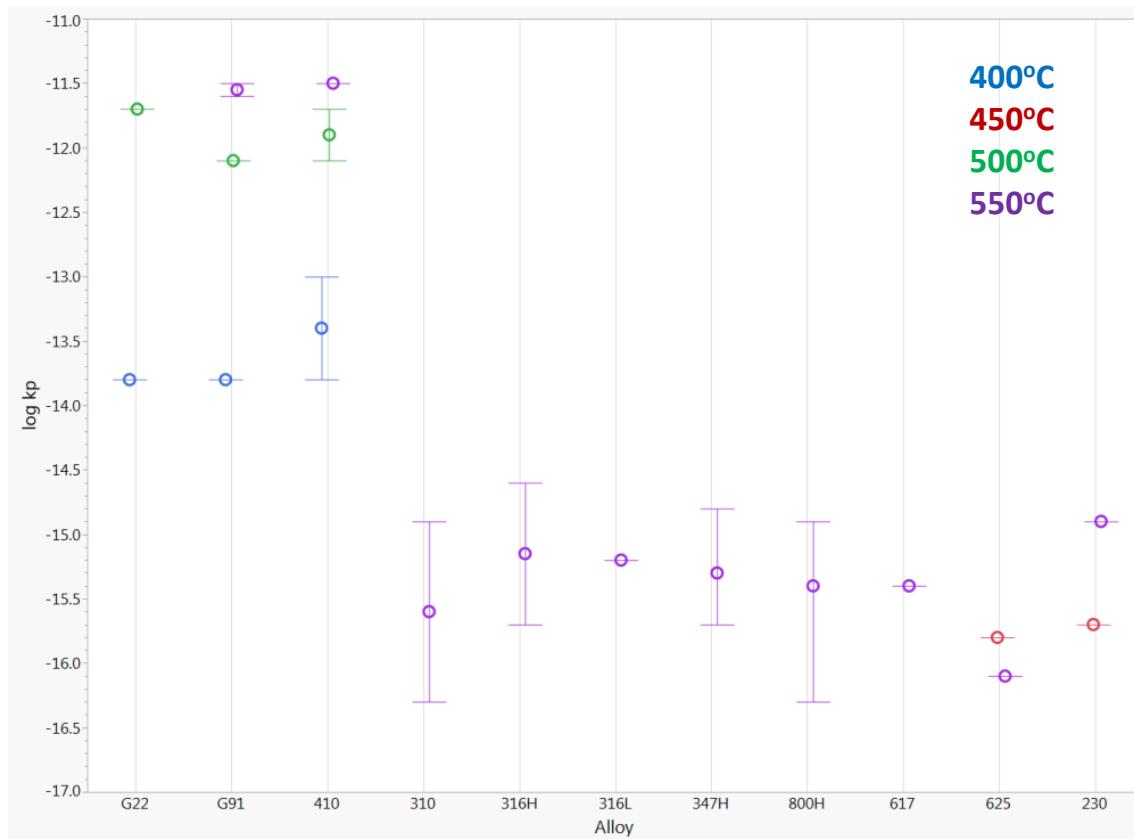


Comparing Alloy Corrosion Rates (600 – 700°C)



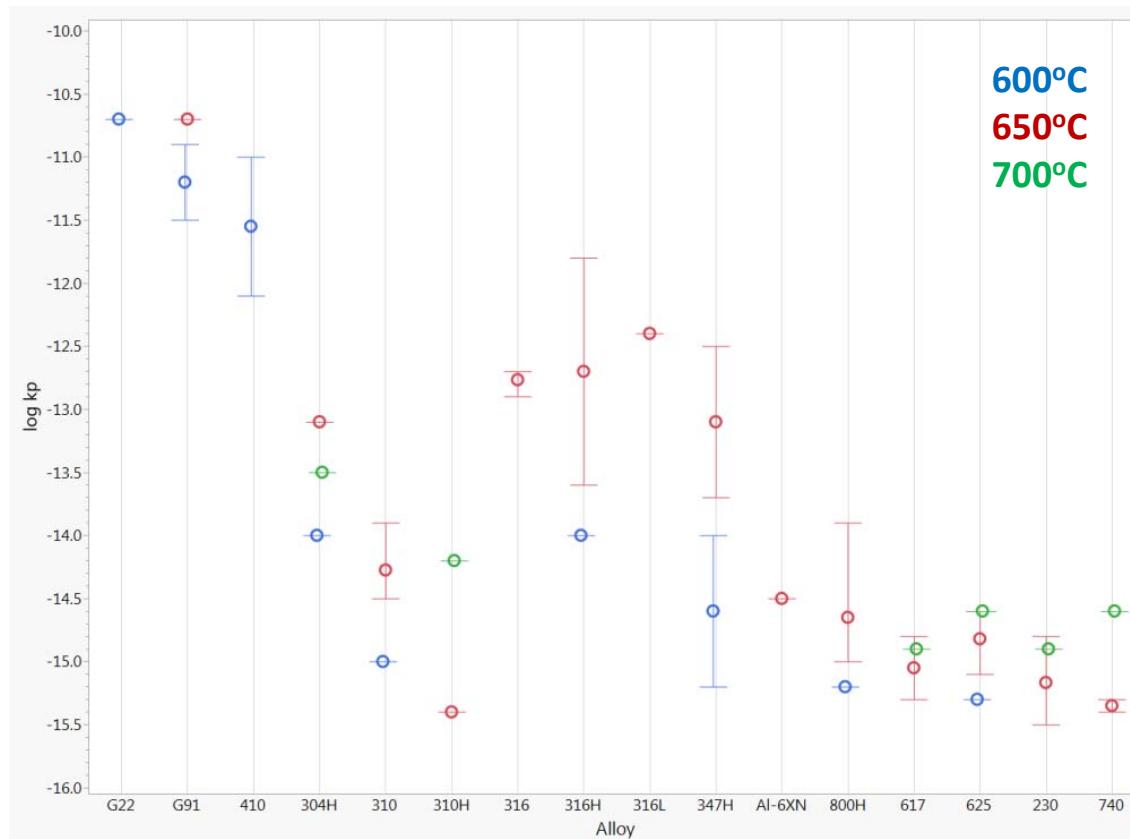


Comparing Alloy Corrosion Rates (400 – 550°C)





Comparing Alloy Corrosion Rates (600 – 700°C)





**400 to
550°C**

Alloy	T (°C)	Pressure (bar)	$\log k_p^A$ ($\text{g}^2 \text{cm}^{-4} \text{s}^{-1}$)	Time range (hours)	$\log k_p^B$ ($\text{g}^2 \text{cm}^{-4} \text{s}^{-1}$)	Time range (hours)	Reference
G22	400	200			-13.8	0-500	Pint 2016 ^[13]
G22	500	200			-11.7	0-500	Pint 2016 ^[13]
G91	550	200			-11.6	0-1000	Lee 2014 ^[14]
G91	550	250			-11.5	0-310	Rouillard 2011 ^[15]
G91	400	200			-13.8	0-500	Pint 2016 ^[13]
G91	500	200			-12.1	0-500	Pint 2016 ^[13]
410	400	200	-13.0	0-2000			Furukawa 2010 ^[16]
410	500	200	-11.7	0-2000			Furukawa 2010 ^[16]
410	550	200	-11.5	0-2000			Furukawa 2010 ^[16]
410	400	200			-13.8	0-500	Pint 2016 ^[13]
410	500	200			-12.1	0-500	Pint 2016 ^[13]
310	550	200			-16.3	0-1000	Lee 2014 ^[14]
310	550	200			-14.9	0-250	Kim 2014 ^[17]
316H	550	200	-14.6	0-3000	-15.8	0-1000	Lee 2015 ^[18]
316H	550	200			-15.7	0-250	Kim 2014 ^[17]
316L	550	250			-15.2	0-310	Rouillard 2011 ^[15]
347H	550	200	-15.4	0-3000	-15.7	0-1000	Lee 2015 ^[18]
347H	550	200			-14.8	0-250	Kim 2014 ^[17]
347H	550	200	-15.7	0-1000			Mahaffey 2014 ^[19]
800H	550	200			-14.9	0-250	Kim 2014 ^[17]
800H	550	200			-16.3	0-1000	Lee 2014 ^[14]
800H	550	250			-15.1	0-310	Rouillard 2011 ^[15]
800H	550	200	-15.3	0-1000			Mahaffey 2014 ^[19]
617	550	200	-15.4	0-1000	-15.1	0-200	Dheeradhada 2015 ^[20]
625	550	200			-16.1	0-1000	Pint 2014 ^[21]
625	450	200	-15.8	200-1000	-17	0-200	Mahaffey 2015 ^[22]
625	550	200	-16.1	200-1000	-15.2	0-200	Mahaffey 2015 ^[22]
625	550	200			-16.1	0-1000	Lee 2014 ^[14]
230	450	200	-15.7	200-1000	-16.8	0-200	Mahaffey 2015 ^[22]
230	550	200	-14.9	0-1000	-15	0-200	Mahaffey 2015 ^[22]

$\log k_p^A$ Derived by fitting through multiple points over the time range

$\log k_p^B$ Derived by fitting through a single point over the time range



**600 to
700°C**

Alloy	T (°C)	Pressure (bar)	$\log k_p^A$ ($\text{g}^2\text{cm}^{-4}\text{s}^{-1}$)	Time range (hours)	$\log k_p^B$ ($\text{g}^2\text{cm}^{-4}\text{s}^{-1}$)	Time range (hours)	Reference
G22	600	200			-10.7	0-500	Pint 2016 ^[13]
G91	600	200			-10.9	0-1000	Lee 2014 ^[14]
G91	650	200			-10.7	0-1000	Lee 2014 ^[14]
G91	650	207			-10.7	0-500	Tan 2011 ^[13]
G91	600	200			-11.5	0-500	Pint 2016 ^[13]
410	600	200	-11.0	0-2000			Furukawa 2010 ^[16]
410	600	200			-12.1	0-500	Pint 2016 ^[13]
304H	650	200			-13.1	0-500	Pint 2014 ^[21]
304H	700	200			-13.5	0-500	Pint 2014 ^[21]
304H	600	200			-14.0	0-500	Pint 2016 ^[13]
310	650	200	-14.3	0-2002	-14.7	0-502	Cao 2012 ^[24]
310	600	200			-15	0-1000	Lee 2014 ^[14]
310	650	200			-14.5	0-1000	Lee 2014 ^[14]
310	650	200			-13.9	0-250	Kim 2014 ^[17]
310	650	200	-14.4	0-2000			Firouzdar 2015 ^[25]
310H	650	200			-15.4	0-500	Pint 2014 ^[21]
310H	700	200			-14.2	0-500	Pint 2014 ^[21]
316	650	200	-12.7	0-3000	-15.1	0-502	Cao 2012 ^[24]
316	650	200	-12.9	0-998	-12.5	0-117	Olivares 2015 ^[26]
316	650	200	-12.7	0-3000			Firouzdar 2015 ^[25]
316H	600	200	-14	0-3000	-15	0-1000	Lee 2015 ^[18]
316H	650	200			-13.6	0-1000	Lee 2015 ^[18]
316H	650	200			-11.8	0-250	Kim 2014 ^[17]
316L	650	200			-12.4	0-194	Lim 2008 ^[27]
347H	600	200	-15.2	0-3000	-15.1	0-1000	Lee 2015 ^[18]
347H	650	200	-13.7	0-3000	-13.7	0-1000	Lee 2015 ^[18]
347H	650	200			-12.5	0-250	Kim 2014 ^[17]
347H	600	200			-14.0	0-500	Pint 2016 ^[13]
Al-6XN	650	207	-14.5	0-3000			Tan 2011 ^[13]
Al-6XN	650	200	-14.5	0-3000			Firouzdar 2013 ^[28]
800H	650	200			-13.9	0-250	Kim 2014 ^[17]
800H	600	200			-15.2	0-1000	Lee 2014 ^[14]
800H	650	200			-15.0	0-1000	Lee 2014 ^[14]
800H	650	207	-15.0	0-3000			Tan 2011 ^[13]
800H	650	200	-14.7	0-3000			Cao 2012 ^[24]
617	650	200			-15.3	0-500	Pint 2014 ^[21]
617	700	200			-14.9	0-500	Pint 2014 ^[21]
617	650	200	-14.8	200-1000	-13.9	0-200	Dheeradhaba 2015 ^[20]
625	650	200	-14.9	0-2995	-14.6	0-492	Firouzdar 2013 ^[28]
625	650	200			-15.1	0-500	Pint 2014 ^[21]
625	700	200			-14.6	0-500	Pint 2014 ^[21]
625	600	200			-15.3	0-1000	Pint 2014 ^[21]
625	650	200			-14.6	0-1000	Pint 2014 ^[21]
625	650	200	-14.9	200-1000	-14.3	0-200	Mahaffey 2015 ^[22]
625	600	200			-15.3	0-1000	Lee 2014 ^[14]
625	650	200			-14.6	0-1000	Lee 2014 ^[14]
230	650	200	-15.5	492-2995	-14.5	0-492	Firouzdar 2013 ^[28]
230	650	200			-15.2	0-500	Pint 2014 ^[21]
230	700	200			-14.9	0-500	Pint 2014 ^[21]
230	650	200	-14.8	200-1000	-13.9	0-200	Mahaffey 2015 ^[22]
740	650	200			-15.4	0-500	Pint 2014 ^[21]
740	700	200			-14.6	0-500	Pint 2014 ^[21]
740	650	200	-15.3	200-1000	-14.7	0-200	Mahaffey 2015 ^[22]

$\log k_p^A$ Derived by fitting through multiple points over the time range

$\log k_p^B$ Derived by fitting through a single point over the time range

After the ferritic alloys, 316H is the most susceptible to corrosion in CO₂



Alloy Specimen Mass Changes

