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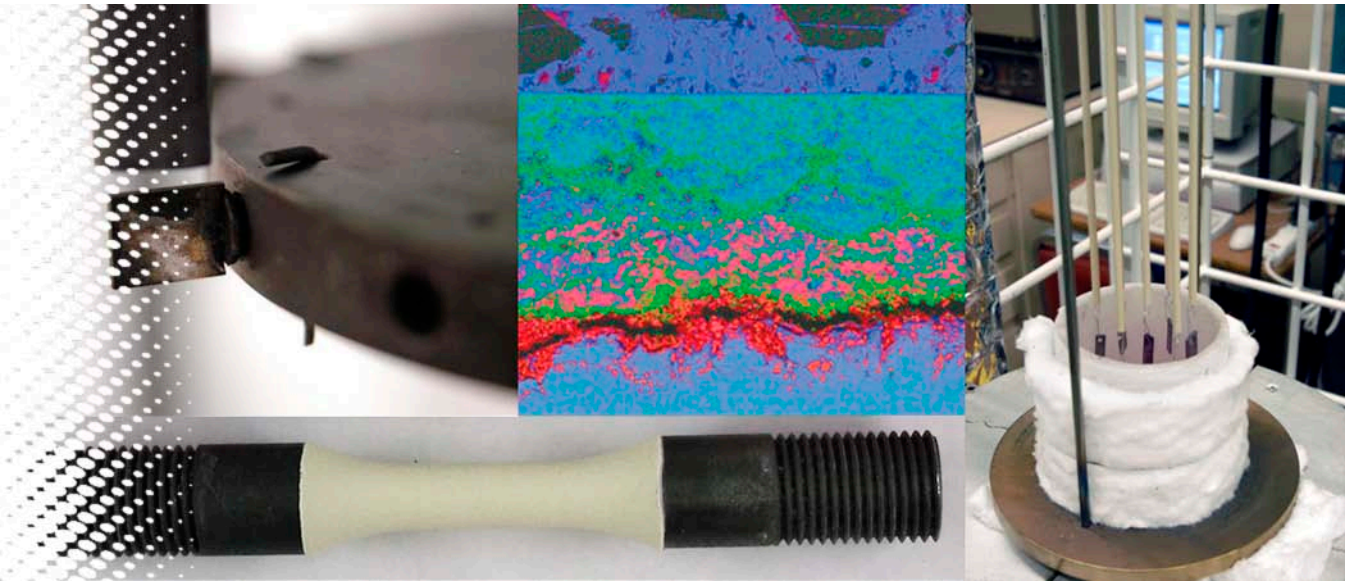


Materials Performance in USC Steam

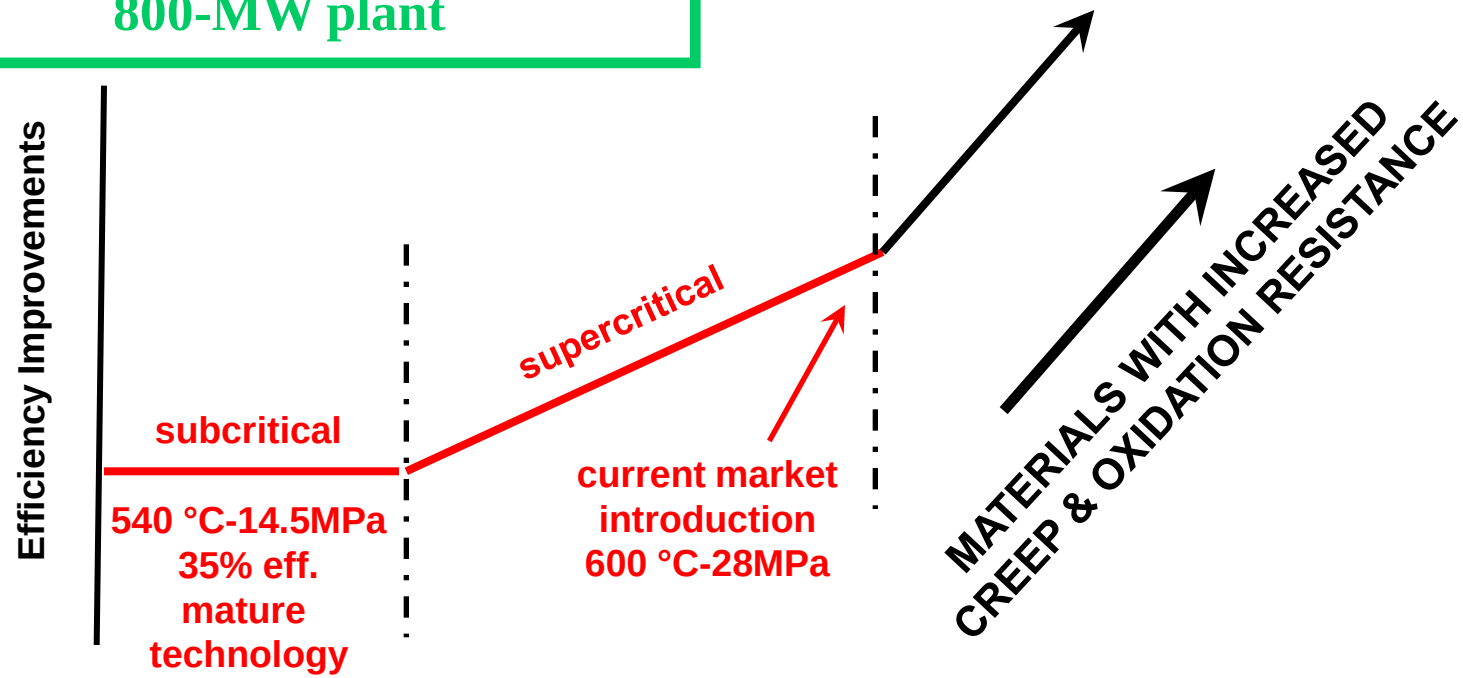
Gordon R. Holcomb, NETL
Joesph Tylczak, NETL
Rongxiang (Rachel) Hu, NETL and URS Corp

U.S. DEPARTMENT OF ENERGY

Increasing Efficiency

Each 1% increase in efficiency eliminates ~1,000,000 tons of CO_2 emissions over the lifetime of an 800-MW plant

US-DOE Advanced Power Systems:
46%-48% efficiency from coal generation
Steam condition: 760 °C - 35MPa
~ 5ksi



Subcritical: < 22 MPa
Supercritical (SC): > 22.1 MPa, 538 to 565 °C
Ultra Supercritical (USC): 565 to ~675 °C (advanced ferritic & austenitic steels required)
Advanced Ultra Supercritical (A-USC): > ~675 °C (nickel-base superalloys required)

Adapted from: Viswanathan, et al , 2005 and Swanekamp, 2002

Materials Performance in USC Steam

NETL Materials Development

- Steam oxidation resistance of cast alloys for USC steam turbines (FY10)
- Steam oxidation resource as more materials are developed (FY11+)

Last Years Focus

Pressure Effects on Steam Oxidation

- Unique capability close to coming on-line

Brief Update

Chromia Evaporation Issues

- Primarily a concern for rotating blades in HP turbine
- Further model and ramification development

Main Focus of Talk

A-USC Steam Autoclave

Construction Finished

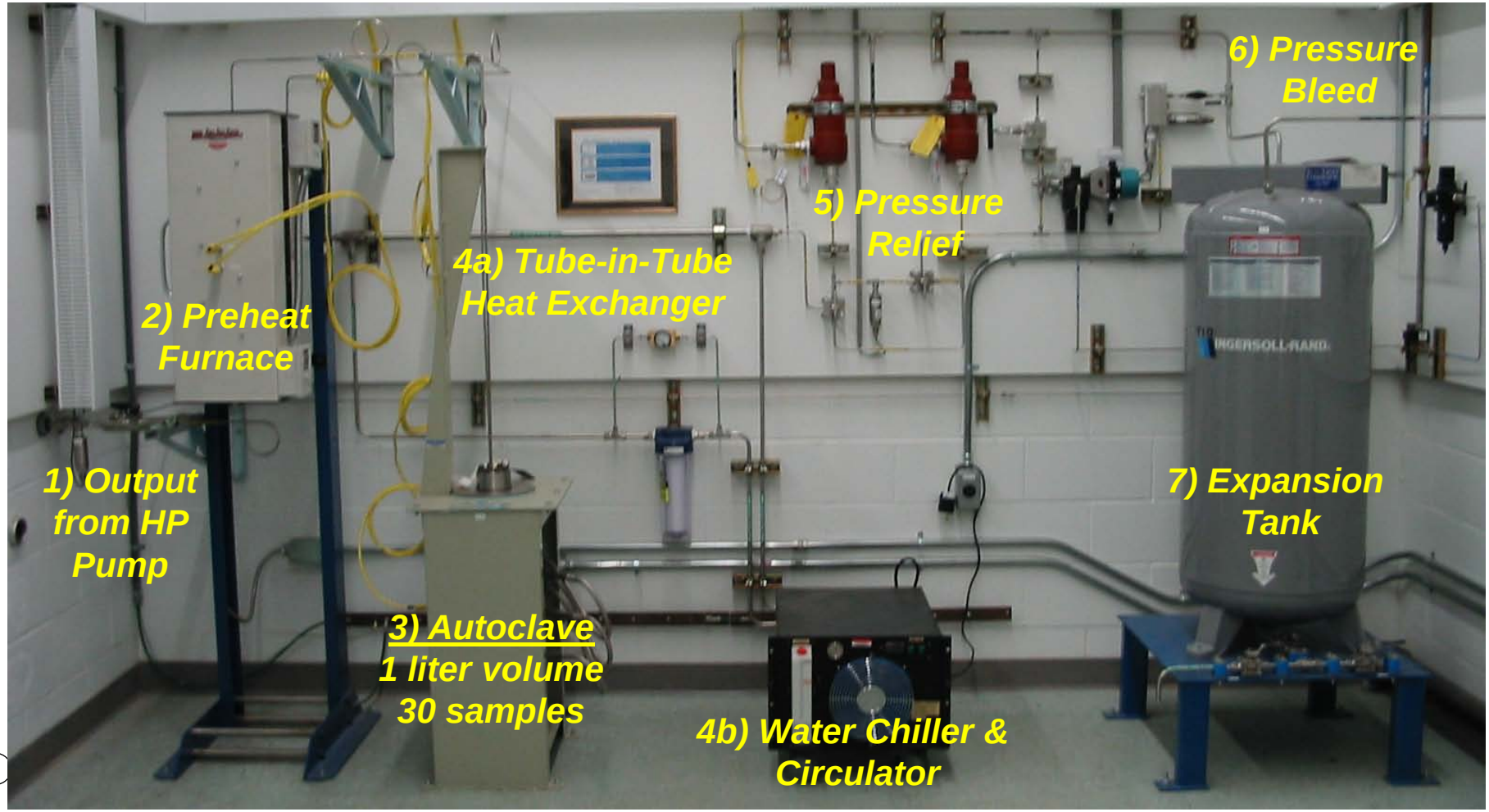
Current Status

- Control system checks
- Mechanical inspections and leak checks
- Final facilities approvals

Aim for Shakedown Activities this Summer

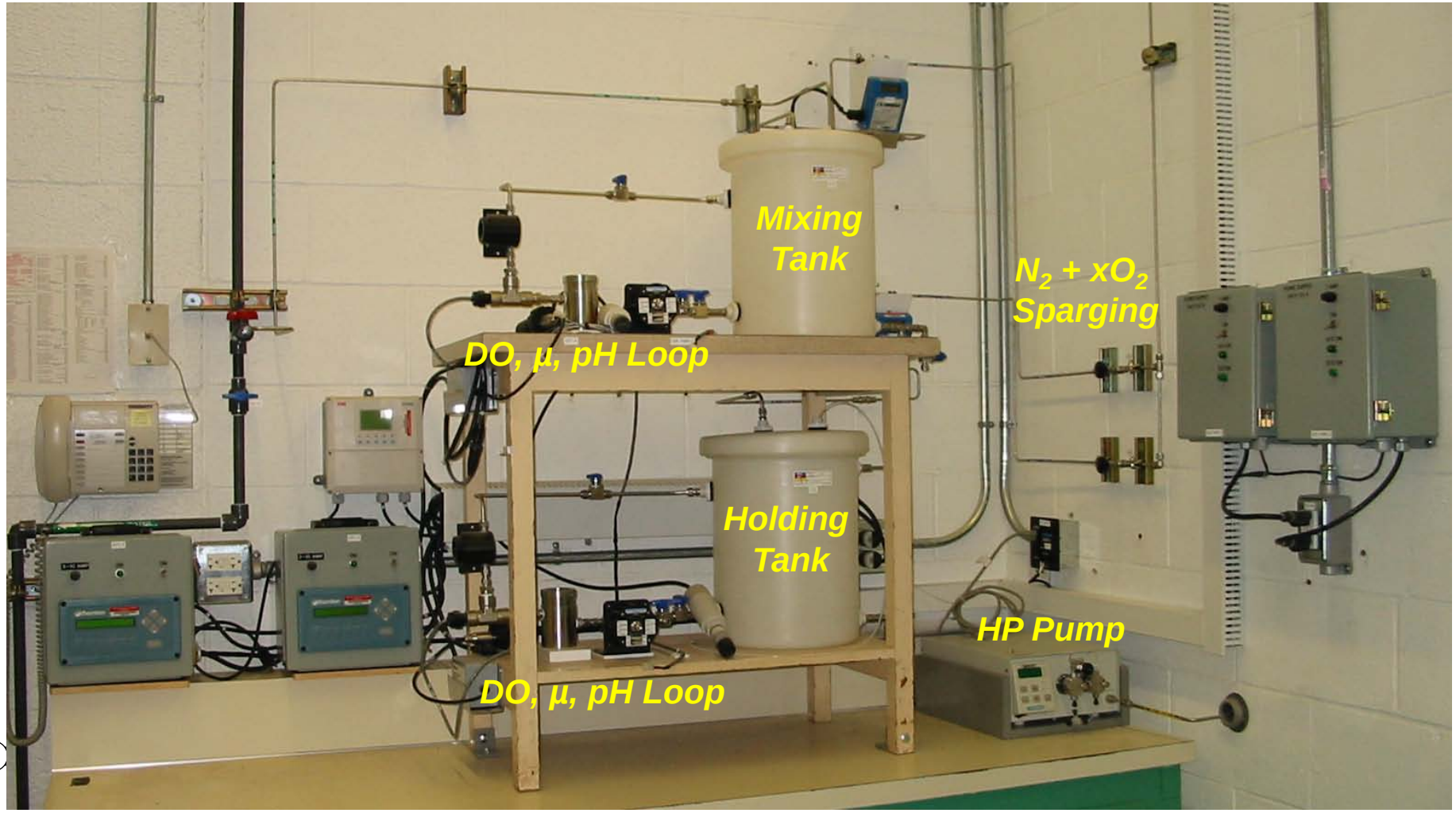
Dual Rated Flowing Steam A-USC Autoclave

- 5000 psig (34.5 MPa) at up to 704°C
- 3300 psig (22.7 MPa) at up to 760°C
- Haynes 230 used for autoclave and high T/P line material



A-USC Steam Autoclave Water Treatment

- *Two tank system*
- *Dissolved oxygen, pH, and conductivity*



Chromia Evaporation

Model Developed in Prior Years

- Brief overview

Current Tests to Further Examine Model

- Experimental status
- Results of work in progress
- Model implications

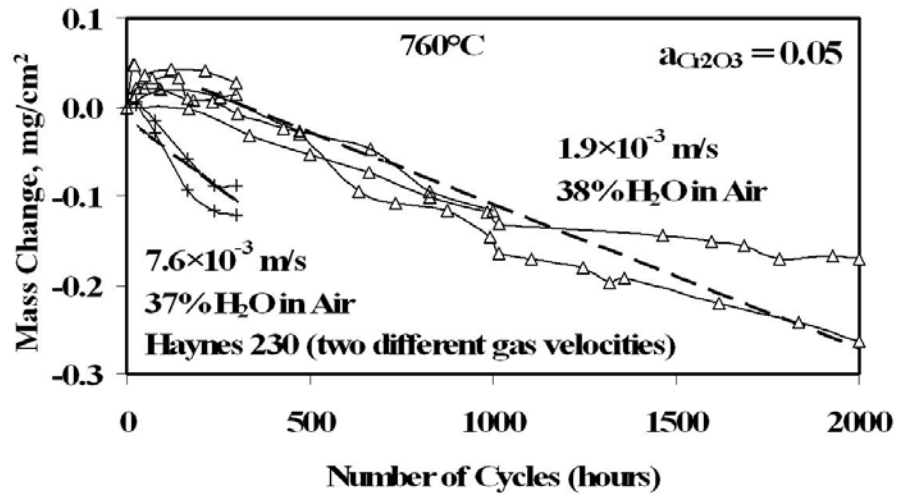
Upcoming Tests at Higher Velocities

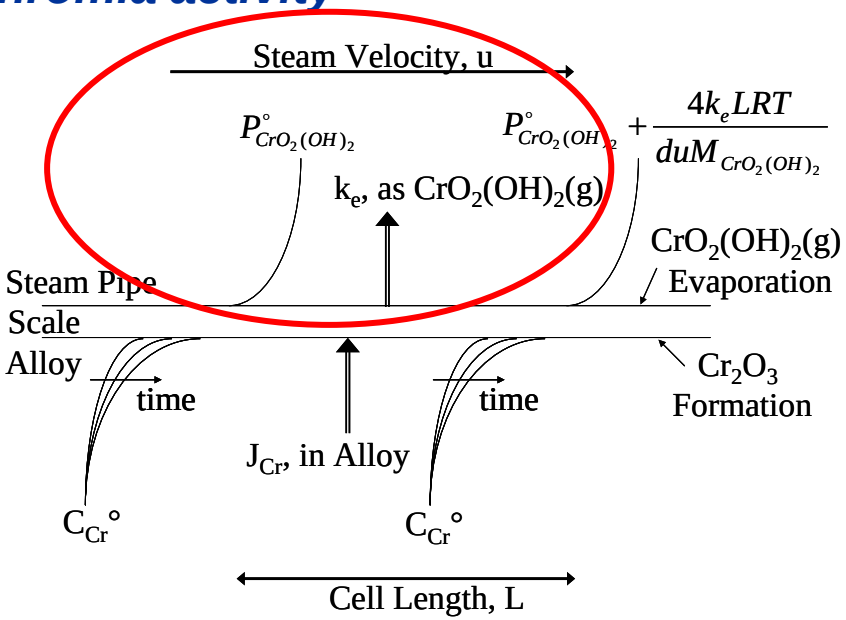
- Rotating disk experimental status

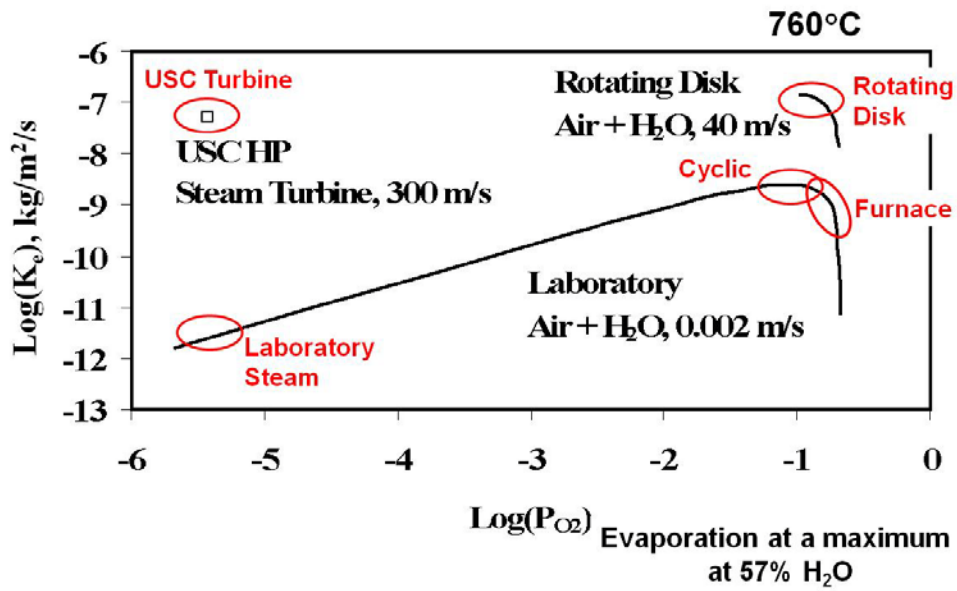
Chromia Evaporation Model—Brief Overview

$\frac{1}{2}Cr_2O_3(s) + H_2O(g) + \frac{3}{4}O_2(g) = CrO_2(OH)_2(g)$

- *Thermodynamics data from Opila (2007)*
- *Boundary layer model of surface evaporation*
- *$CrO_2(OH)_2(g)$ saturation in gas phase*
- *Cr diffusion and depletion in alloy*
- *Time to breakaway oxidation, t^**
- *Kinetics determines apparent surface chromia activity*



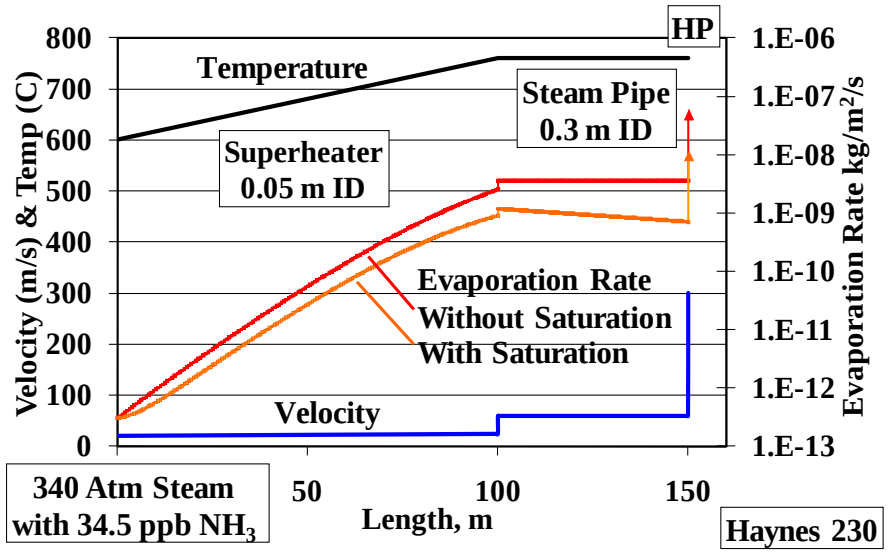


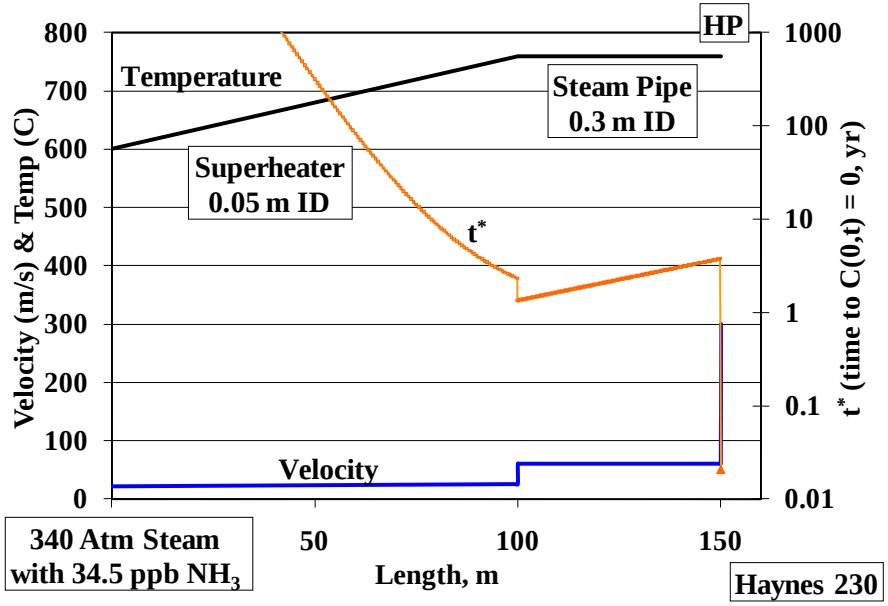


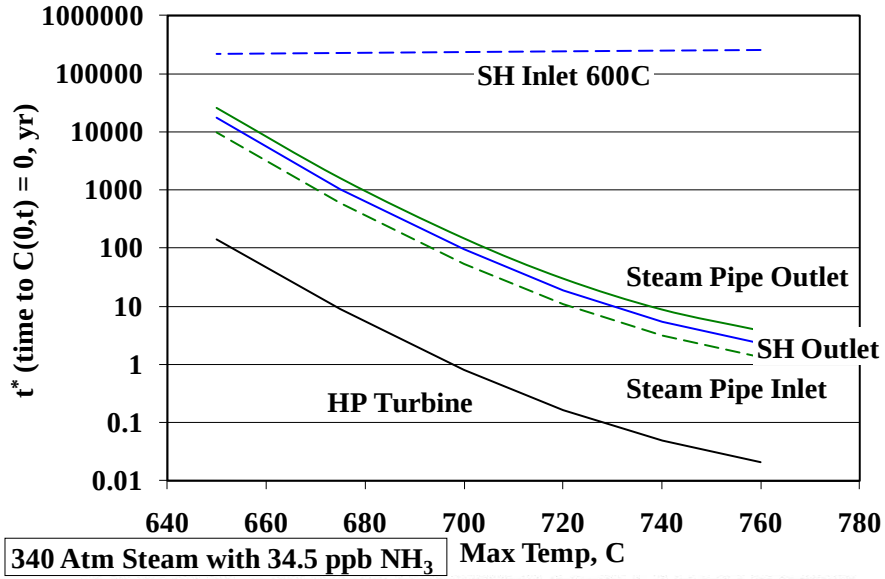
Holcomb, Journal of The Electrochemical Society, 156 9 C292-C297 2009.

Chromia Evaporation Model—Brief Overview

- ***Hypothetical Steam Path***
  - *Superheater, steam pipe, HP turbine*
- ***Chromia activity of 0.05***
- ***No issues below 650°C***
- ***Very rapid breakaway oxidation at HP turbine at 760°C***







Chromia Evaporation Follow-up

Model predicts significant issues at the highest temperatures, pressures, and steam velocities

- These are A-USC HP steam turbine conditions
- Warrants examining model assumptions and sensitivity

Speculation about steam turbine alloys

- As chromia leaves the surface, Mn and Ti oxides may concentrate and reduce chromia activity
- A reduction of evaporation with Mn & Ti alloy additions
- At higher evaporation rates—self correcting?

Chromia Evaporation Cyclic Tests

Chromia Evaporation Test Matrix

2000 hr, hourly cycles

Wrought H230, N263, H282, N105

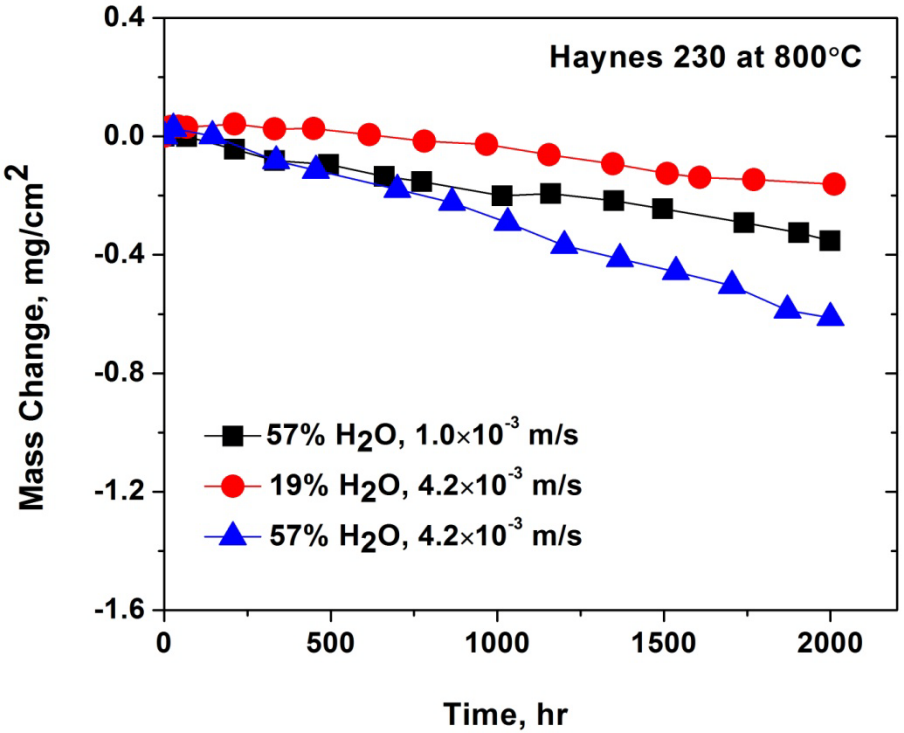
Cast & Homogenized N263, H282, N105

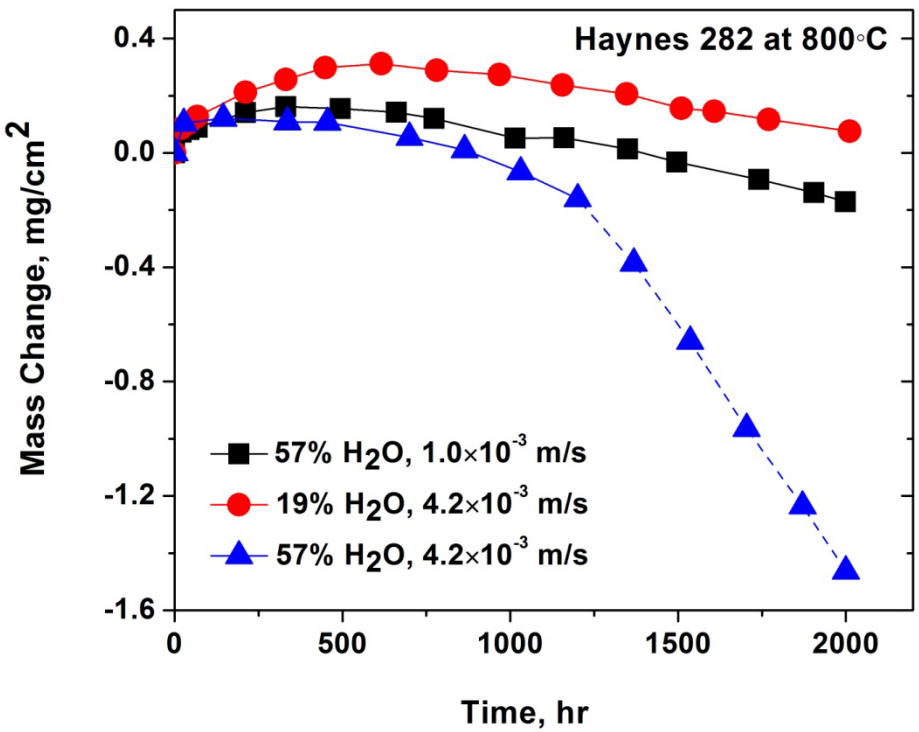
	Gas Velocity, cm/min	
$\%H_2O$	6.25	25.0
19%	760°C	760°C
	800°C	800°C
57%	760°C	760°C
	800°C	800°C

Completed Tests
Ongoing Tests

Alloy	Cr	Al	Ti	Mn
N105	14.85	4.70	1.10	0.50
C&H	14.61	4.43	1.10	0.51
N263	20.00	0.35	2.10	0.50
C&H	19.68	0.40	2.04	0.50
H282	19.50	1.50	2.10	0.25
C&H	19.22	1.44	2.08	0.24
H230	22.00	0.35		0.70

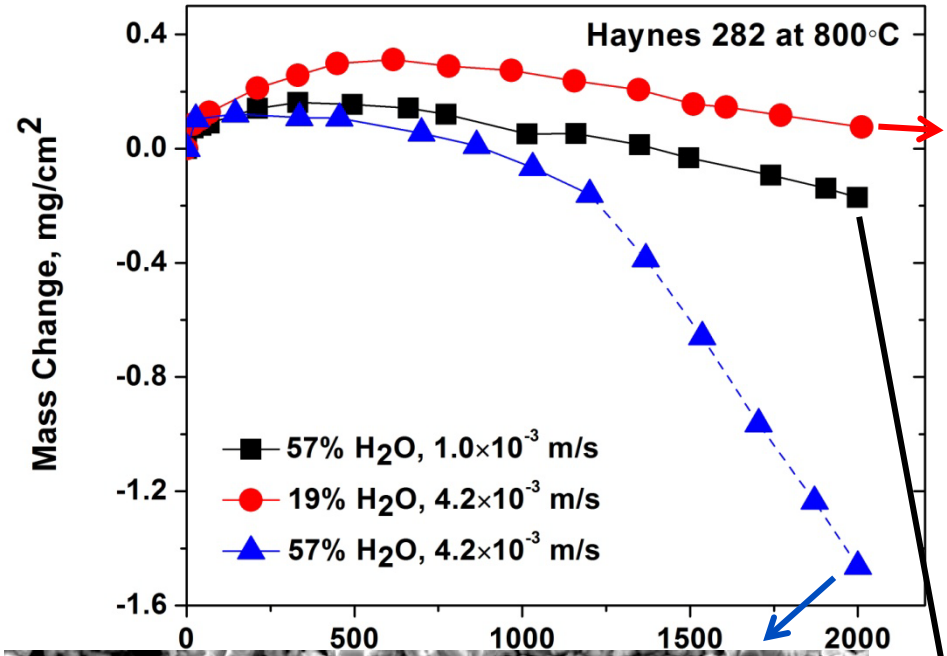
Cyclic Results

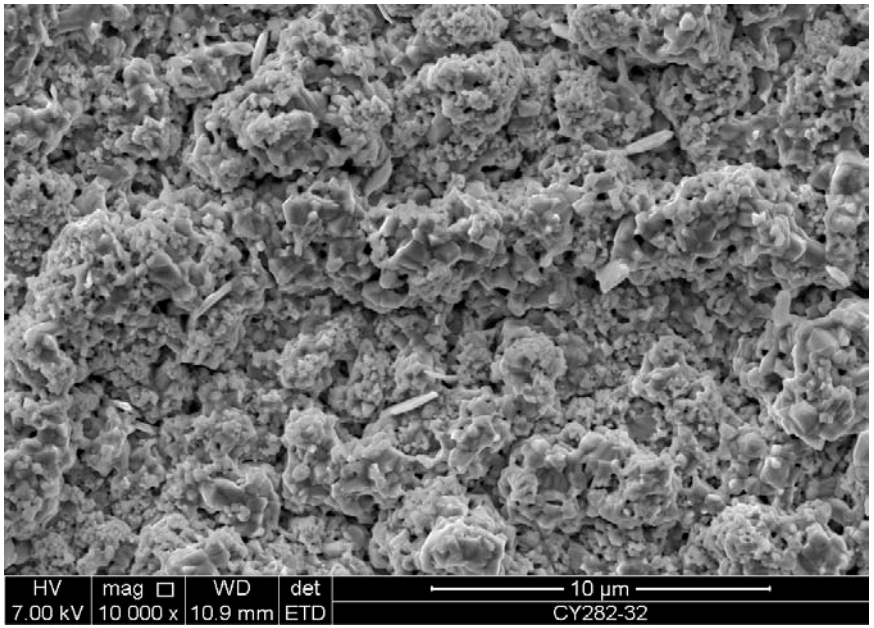


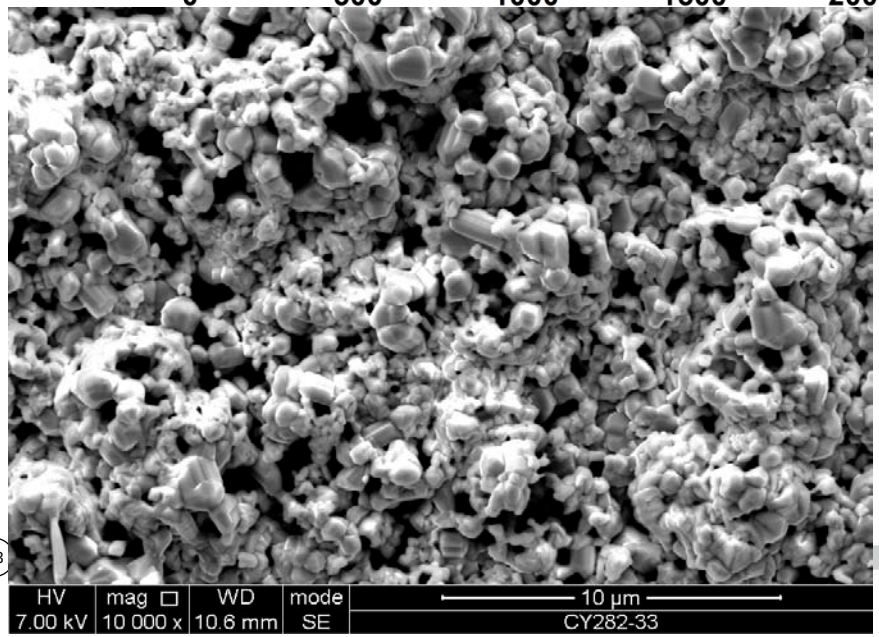


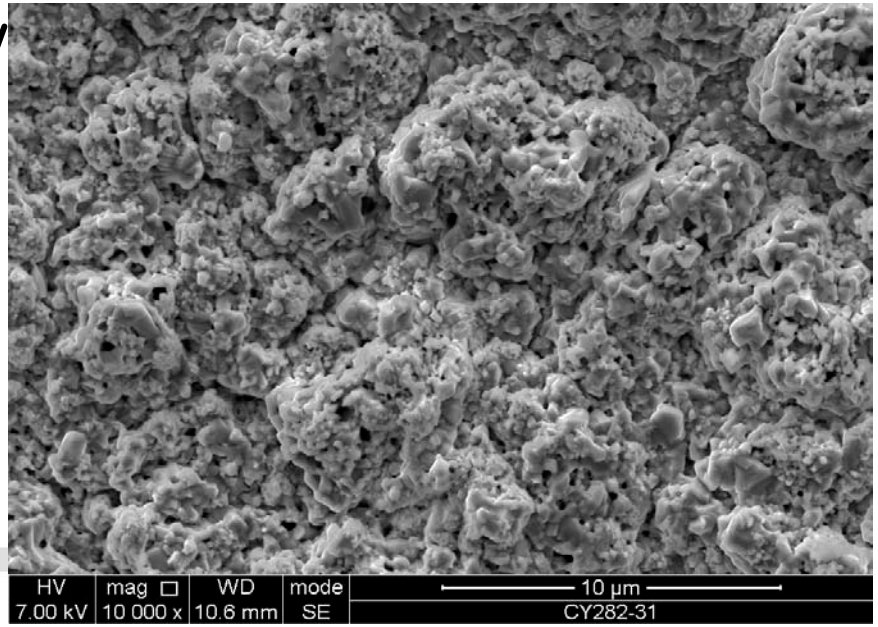
- ***Nimonic 263 showing too much spallation for evaporation analysis***
- ***Nimonic 105 showing alumina formation and no detectible evaporation***

Haynes 282 and Surface Structure

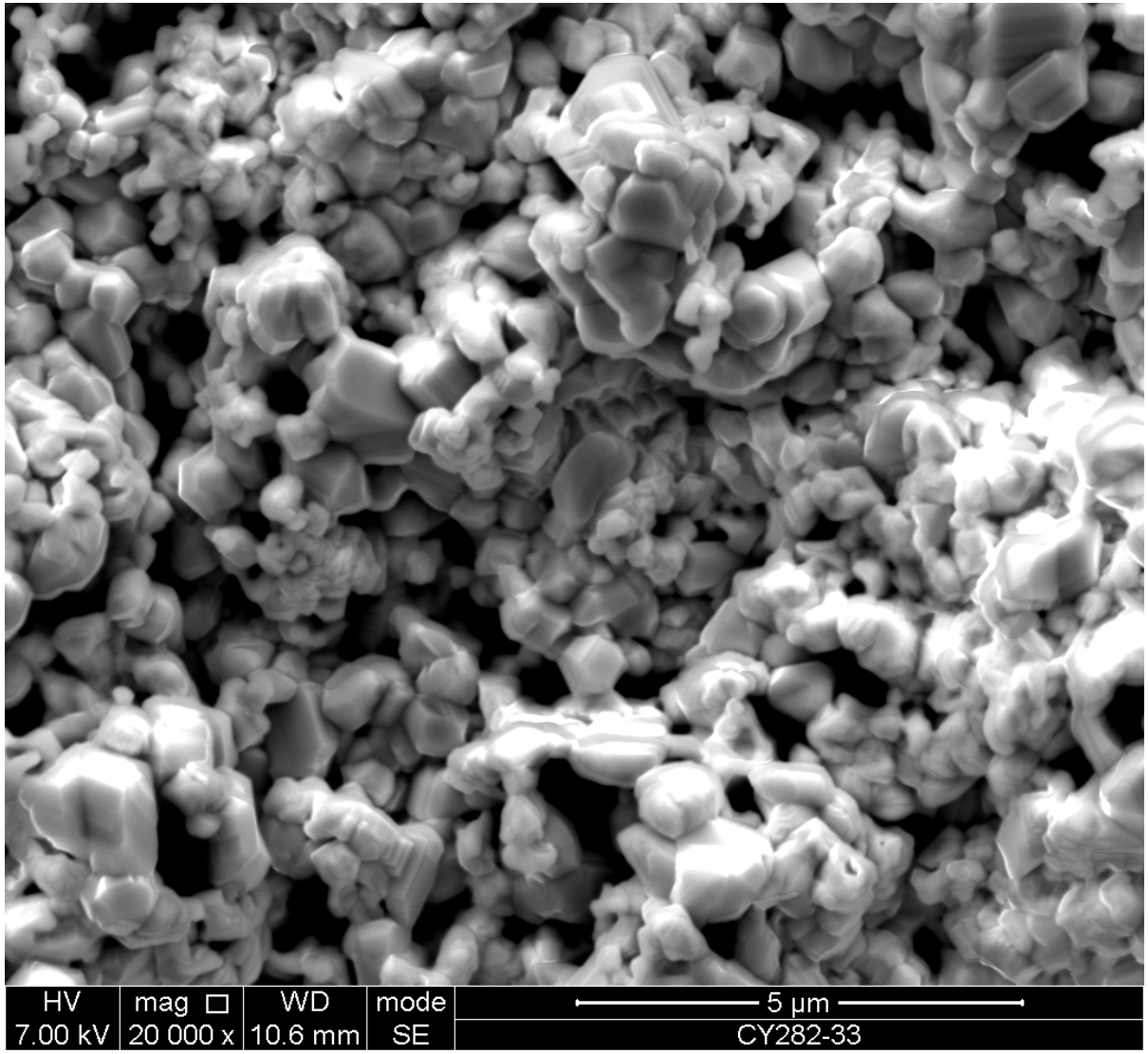








Elemental Spot Analysis—Spalled H282



- **Larger grains with flats rich in Ti and O**
  - TiO_2
- **Smaller grains rich in Cr and O**
  - Cr_2O_3
- **Localized TiO_2 not very useful in chromia evaporation protection**

Apparent Chromia Activities

Alloys, conditions, and results for cyclic oxidation tests in moist air. Gas flow rates are at temperature. $k_e[Cr_2O_3]$ is the evaporation rate on a chromia basis.

Alloy	T, °C	P_{H2O}	Flow Rate, m/s	k_e $[Cr_2O_3]$, kg/m^{2}s	Time Range, hr	Apparent a_{Cr2O3}
Haynes 230	800	0.19	4.2×10^{-3}	3.4×10^{-10}	200-2000	0.06
Haynes 230	800	0.57	1.0×10^{-3}	4.9×10^{-10}	24-2000	0.14
Haynes 230	800	0.57	4.2×10^{-3}	9.1×10^{-10}	24-2000	0.11
Haynes 282	800	0.19	4.2×10^{-3}	4.9×10^{-10}	600-2000	0.12
Haynes 282	800	0.57	1.0×10^{-3}	6.1×10^{-10}	500-2000	0.21
Haynes 282	800	0.57	4.2×10^{-3}	7.2×10^{-10}	125-1000	0.07

Increased flow rates

- ***Increased evaporation***
- ***Decreased chromia activity***

Increased water (from 19% to 57%)

- ***Increased evaporation***
- ***Mixed chromia activity results***

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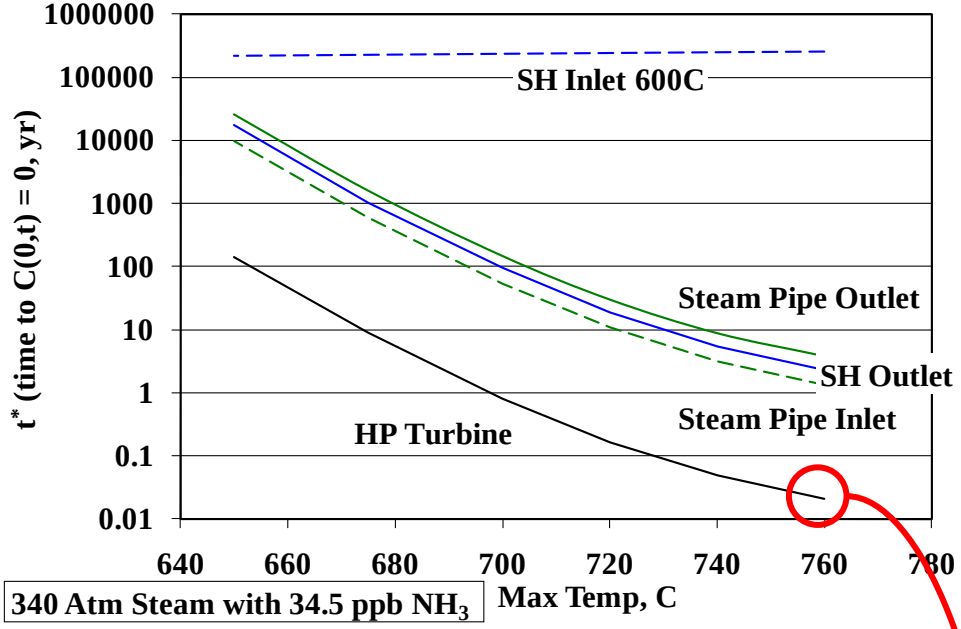
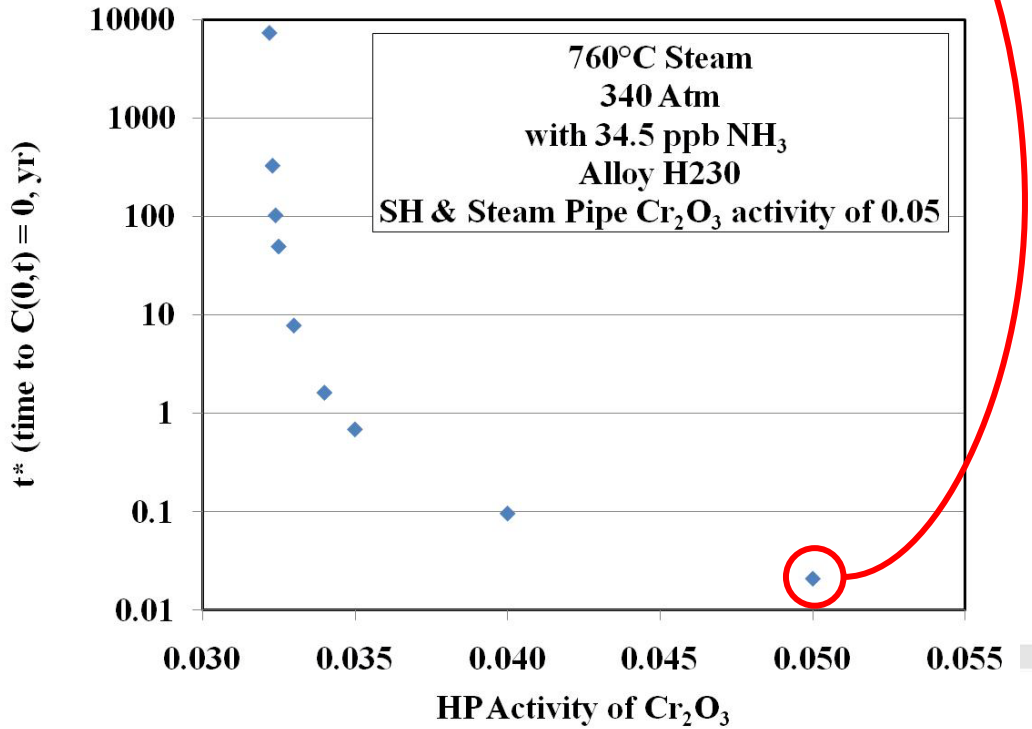
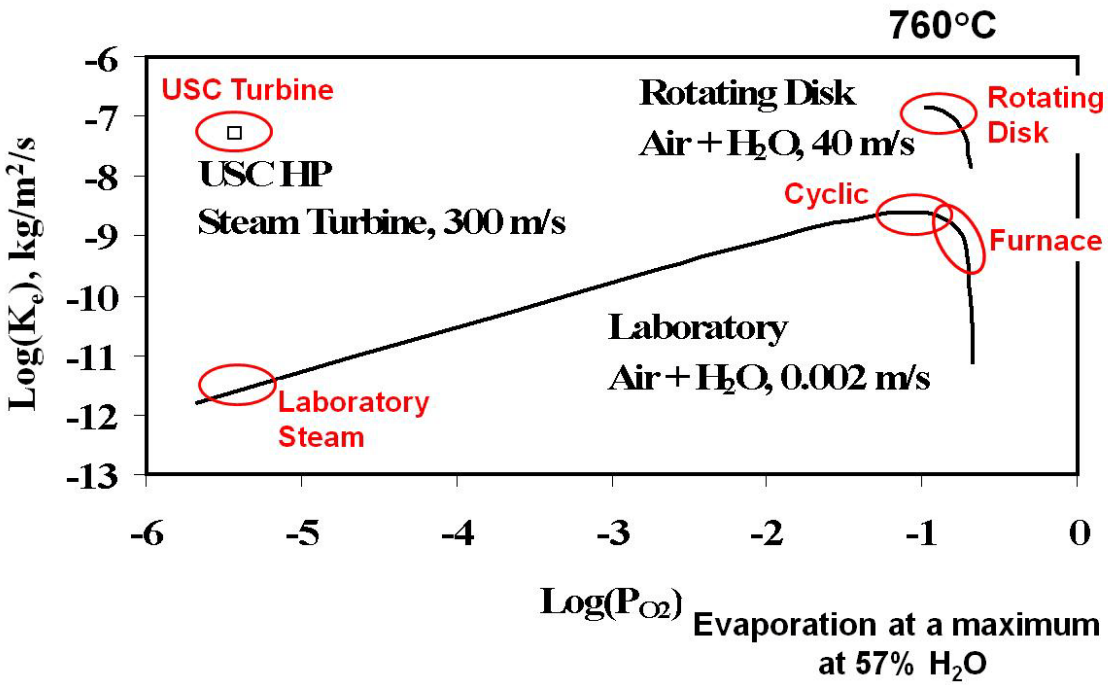
Model Sensitivity to HP Chromia Activity





- ***Upstream saturation lowers driving force for evaporation***
- ***Shows that t* is very sensitive to chromia activity differences***

Rotating Disk Experiments



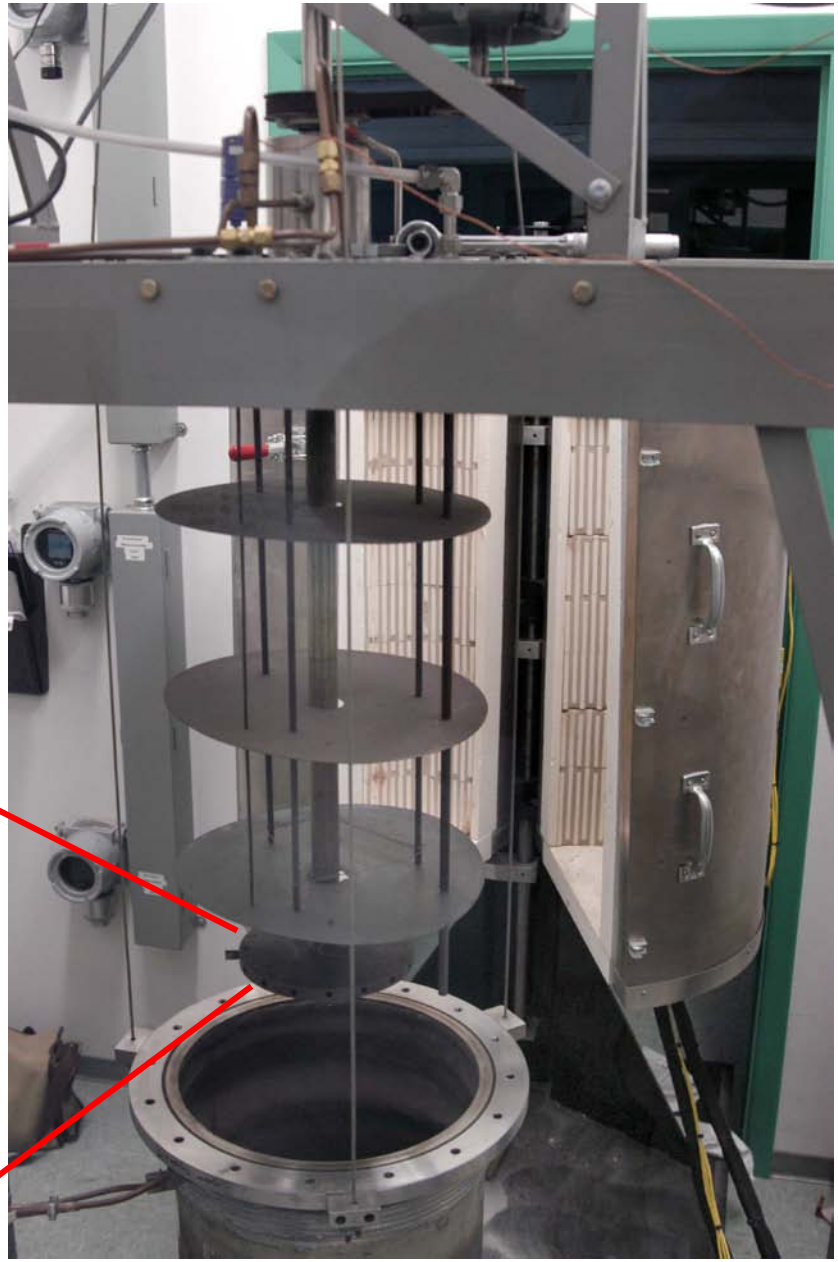
- *Want to examine kinetics and surfaces with more aggressive evaporation*
- *Turbulent flow*
- *Tests started this week*

Alloy	Fe	Cr	Ni	Co	Mo	C	Si	Ti	Al	B ppm	Mn	W	Other
H230	1.5	22	Bal	2.5	2	0.1	0.4		0.3	75	0.5	14	0.02 La
H282	0.75	19.5	Bal	10	8.5	0.06	0.075	2.1	1.5	50	0.15		0.15 Cu
I617	1.5	22	Bal	12.5	9	0.1	0.5	0.3	1.15	30	0.5		0.25 Cu

Rotating Disk

Modify a high temperature erosion rig for steam oxidation with up to 40 m/s relative velocity

Samples of H230, H282 and IN617 are machined



A-USC Implications (Conclusions)

Increased flow rates can lower chromia activity in alloys with Ti and Mn

- Reduced chromia activity reduces equilibrium $CrO_2(OH)_2(g)$ vapor pressures

Model is very sensitive to small decreases in chromia activity at the HP turbine

- Upstream partial saturation of the gas phase with $CrO_2(OH)_2(g)$ can become nearly or fully saturated at the HP turbine
- Can radically change breakaway oxidation times from less than a year to never happening

Thus even small chromia activity reductions from Ti and Mn additions can make evaporation issues self-correcting