SunShot
U.S. Department of Energy

CSP Program Summit 2016

Halide and Oxy-halide Eutectic Systems for High Performance High Temperature Heat Transfer Fluids

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Outline of this presentation

- Introduction
- Properties of ionic and covalent salts mixtures
- Figure of merit of the salts
- Future studies for heat transfer and enhancement
- Behavior of the corrosion of the salts to metals
- Tech transfer for commercialization of the HTF

Introduction

Objectives

Scientific and technical rational of using halide salts

Basic data about compositional salts

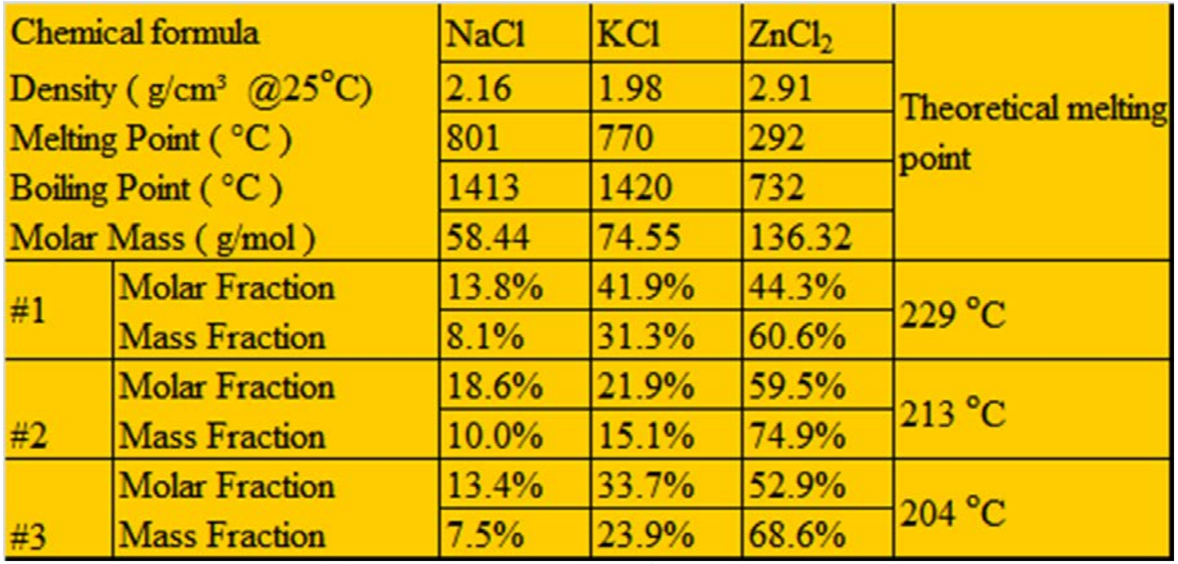
Three available eutectic compositions

The objective of this MURI project is to develop a heat transfer fluid (HTF) for concentrated solar power (CSP) systems with the use of mixtures of molten chloride salts covering a working temperature ranging from 250 °C to 800 °C or above. Target of properties of the fluid include: vapor pressure ≦ 1.0 atm at 800 ^{o}C, viscosity ≤0.012 Pa·s at 300 ^{o}C and ≤0.004 Pa·s at 600 ^{o}C, thermal conductivity ≥0.51 W/m·K, density ≤5400 kg/m^3, heat capacity ≥1.5 kJ/kg·K, and corrosion rate to a compatible metal ≤100μm/year.

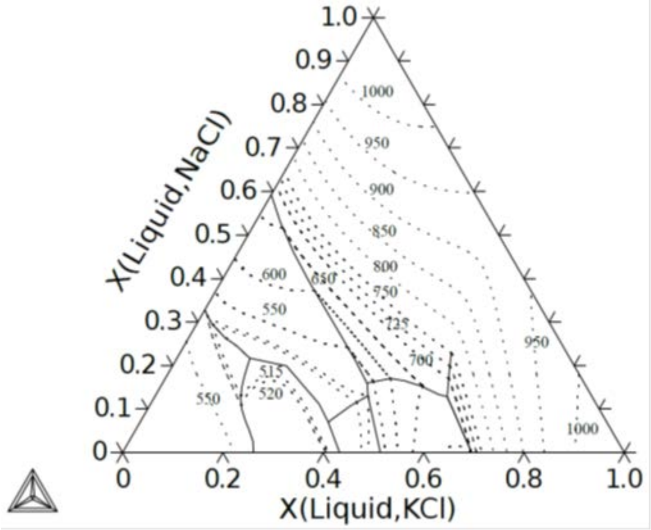
Scientific and technical rational of using halide salts

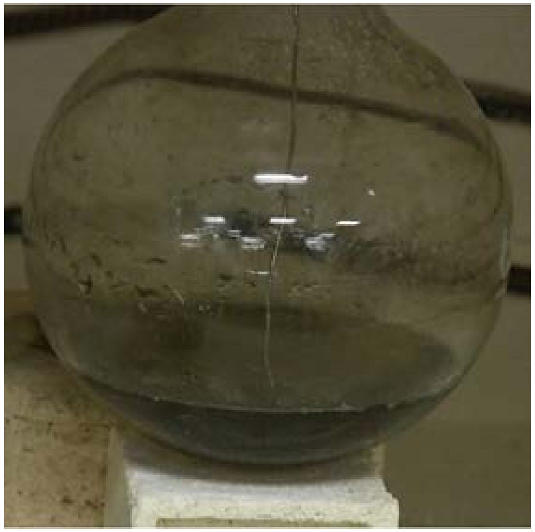
Three species of chloride salts have been chosen to make ternary eutectic salts. Among the three, NaCl and KCl are ionic salts with high thermal stability and high boiling temperatures; $ZnCl_2$ is a covalent salt with low melting point and also high thermal stability. Mixing of covalent and ionic species is driven at molecular level by the Lewis acid base reaction between these species. Mismatch of molecule size, shape, and bonding of species comprising the salt creates disorder leading to low melting; Lewis acid-base stabilization leads high boiling point. Metals making containers are mostly more noble than the metal ions (Na^+, K^+, Zn^{+2}) in the molten salt leading to low metal corrosion rates.

Basic data about compositional salts
Three available eutectic compositions



Chemical formula		NaCl	KCl	$ZnCl_2$	Theoretical melting point
Density (g/cm^3 @25°C)		2.16	1.98	2.91	
Melting Point (°C)		801	770	292	
Boiling Point (°C)		1413	1420	732	
Molar Mass (g/mol)		58.44	74.55	136.32	
#1	Molar Fraction	13.8%	41.9%	44.3%	229 °C
	Mass Fraction	8.1%	31.3%	60.6%	
#2	Molar Fraction	18.6%	21.9%	59.5%	213 °C
	Mass Fraction	10.0%	15.1%	74.9%	
#3	Molar Fraction	13.4%	33.7%	52.9%	204 °C
	Mass Fraction	7.5%	23.9%	68.6%	





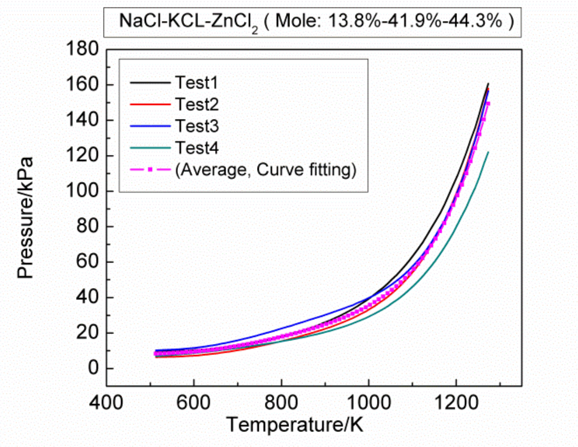
Properties of ionic and covalent salts mixtures

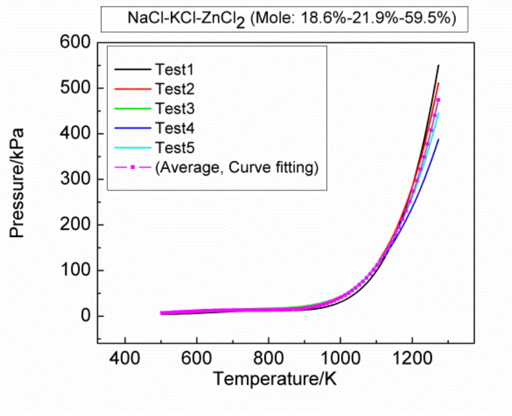
3.1 Experimentally obtained heat capacity	
Salt #1	$Cp=0.917 \pm 0.021$ kJ/kg K (95% probability)
Salt #2	$Cp=0.913 \pm 0.019$ kJ/kg K (95% probability)
Salt #3	$Cp=0.900 \pm 0.020$ kJ/kg K (95% probability)

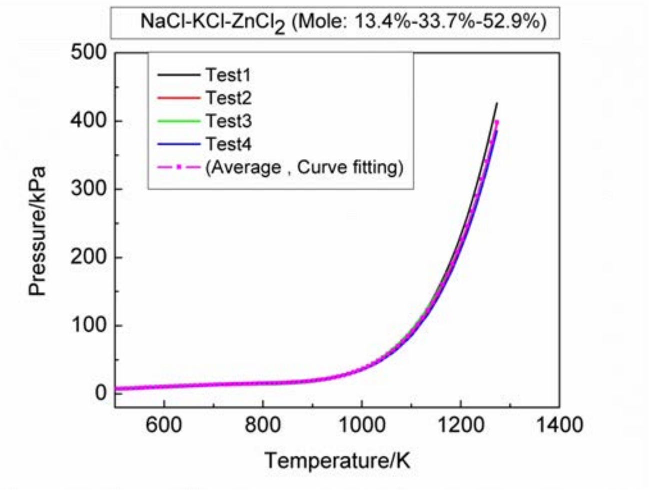
3.2 Experimentally obtained melting point	
Salt #1	$T_{mp}=199.3 \pm 1.6$ ^{o}C (95% probability)
Salt #2	$T_{mp}=198.7 \pm 0.7$ ^{o}C (95% probability)
Salt #3	$T_{mp}=210.3 \pm 1.2$ ^{o}C (95% probability)

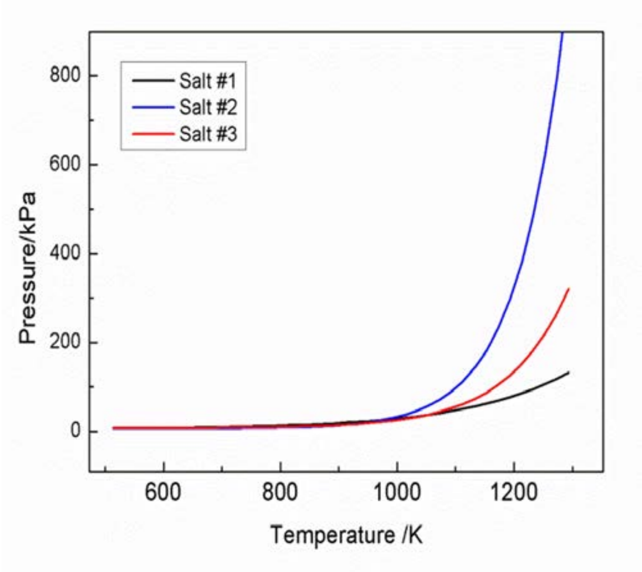
3.3 Experimentally obtained heat of fusion	
Salt #1	$\Delta H_{fu}=67.706 \pm 2.321$ kJ/kg (95% probability)
Salt #2	$\Delta H_{fu}=71.057 \pm 1.862$ kJ/kg (95% probability)
Salt #3	$\Delta H_{fu}=73.893 \pm 2.448$ kJ/kg (95% probability)

Vapor pressure





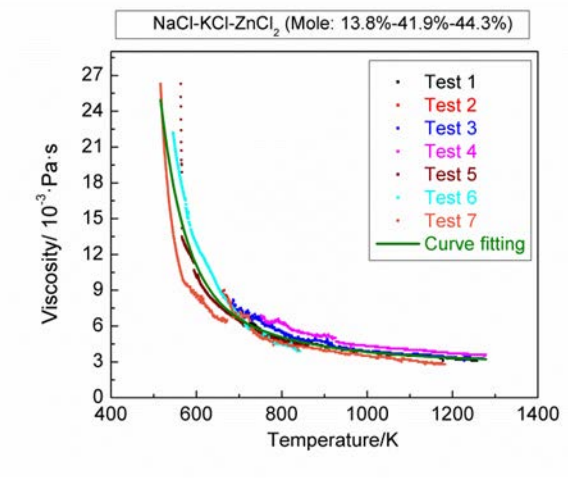


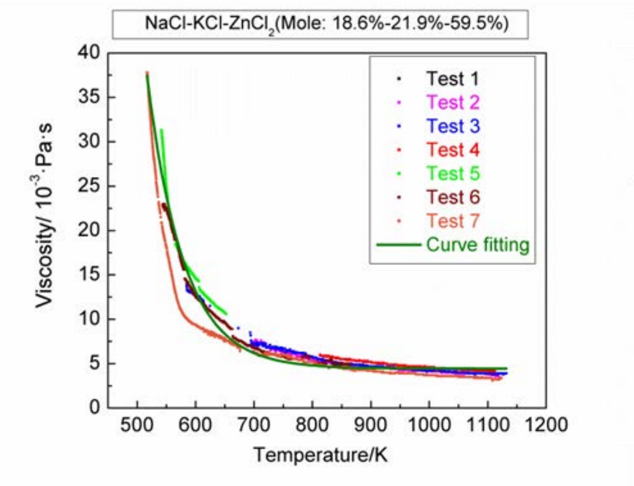


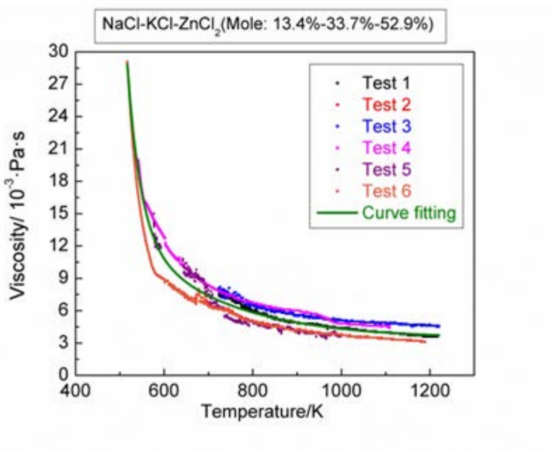
$$P = B_0 + B_1T + B_2T^2 + B_3T^3 + B_4T^4 + B_5T^5 \text{ kPa} \qquad (1)$$

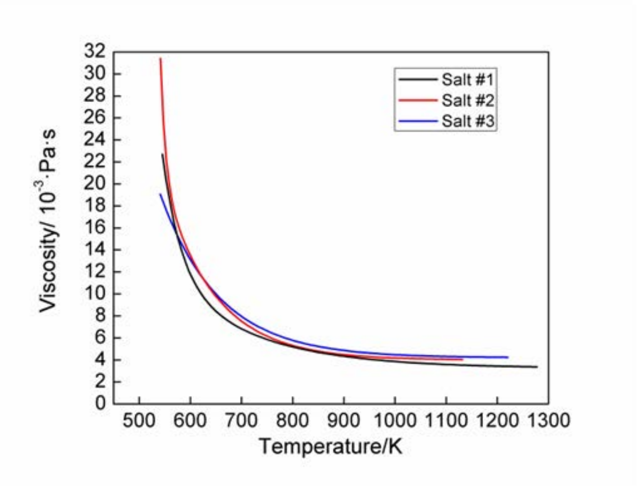
Coefficients in Eq. (1)	Salt #1	Salt #2	Salt #3
B_0	-224.95905	-74.06966	705.61094
B_1	1.80215	0.83241	-3.73013
B_2	-0.00546	-0.00365	0.00671
B_3	8.05463E-6	7.73152E-6	-3.79543E-6
B_4	-5.77404E-9	-7.67531E-9	-1.26977E-9
B_5	1.63798E-12	2.87387E-12	1.41533E-12
Uncertainty @ confidence of 95%	± 0.54 (kPa)	± 1.1 (kPa)	± 0.42 (kPa)

Viscosity





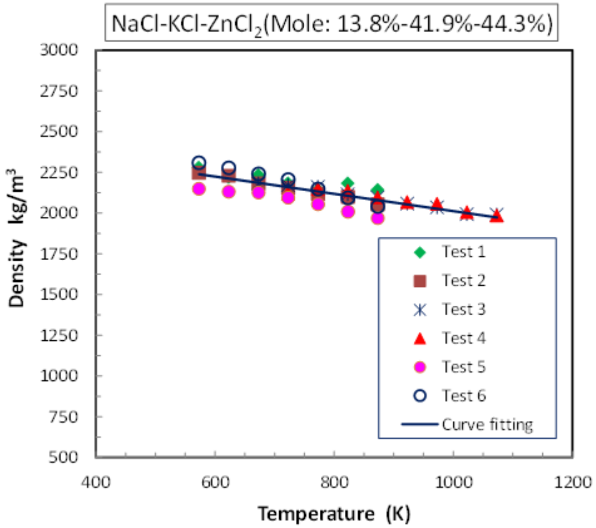


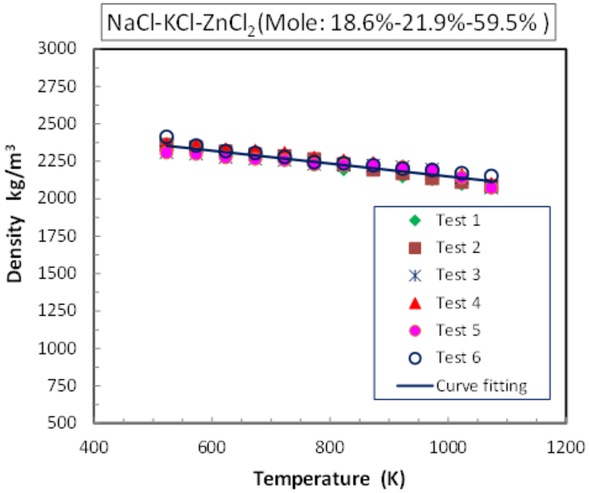


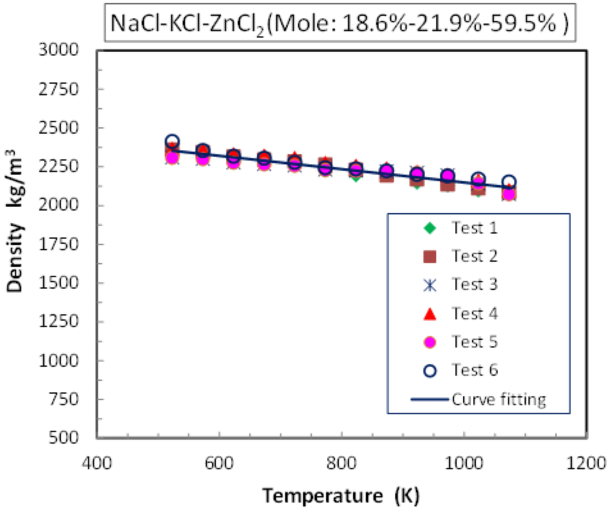
$$\mu = A\exp(-T/T_1) + B\exp(-T/T_2) + \mu_0 \qquad (\mathrm{Pa\cdot s}) \qquad (2)$$

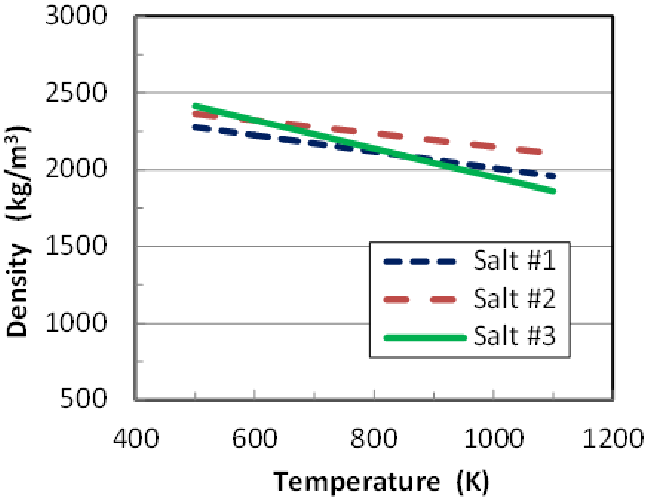
Coefficients in Eq. (2)	Salt #1	Salt #2	Salt #3
μ_0 (Pa·s)	2.97E-3	4.46E-3	3.41E-3
A (Pa·s)	152.3679	131.0731	0.12055
B (Pa·s)	0.05994	0	497613.0848
T_1 (K)	56.03143	62.36328	204.70939
T_2 (K)	235.78682	-	29.9169
Uncertainty @ confidence of 95%	± 1.31E-05 (Pa·s)	± 2.04E-05 (Pa·s)	± 2.68E-05 (Pa·s)

Density


NaCl-KCl-ZnCl$_2$(Mole: 13.8%-41.9%-44.3%)


NaCl-KCl-ZnCl$_2$(Mole: 18.6%-21.9%-59.5%)

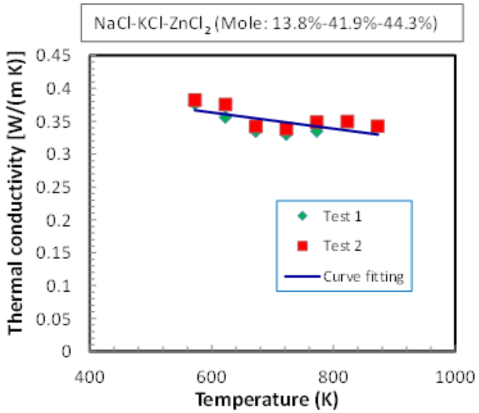

NaCl-KCl-ZnCl$_2$(Mole: 18.6%-21.9%-59.5%)

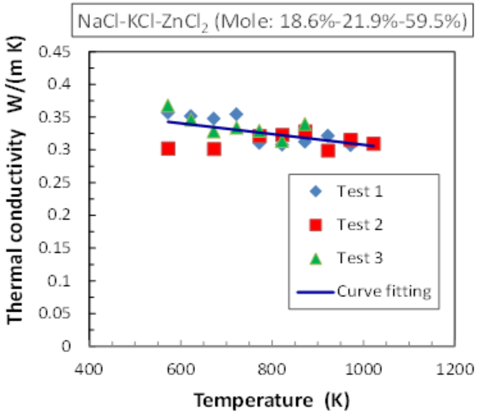


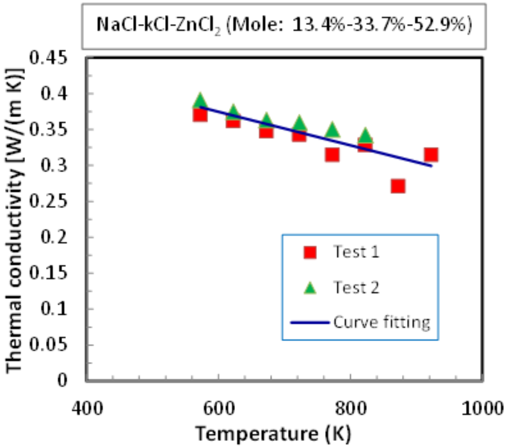
$$\rho = A_0 + A_1 T \qquad (\mathrm{kg/m^3}) \qquad (3)$$

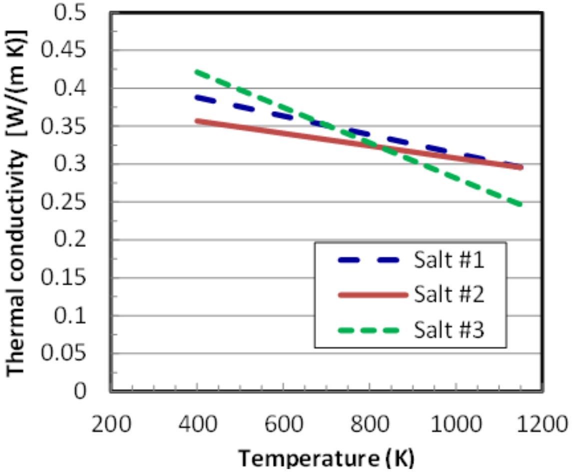
Coefficients in Eq. (3)	Salt #1	Salt #2	Salt #3
A_0 A_1	2.5417368449E3 -0.53018137763	2.5810897805E3 -0.43205969697	2.8783243363E3 -0.92630377059
Uncertainty @ confidence of 95%	±13.507 (kg/m^3)	±6.1726 (kg/m^3)	±20.2500 (kg/m^3)

Thermal conductivity







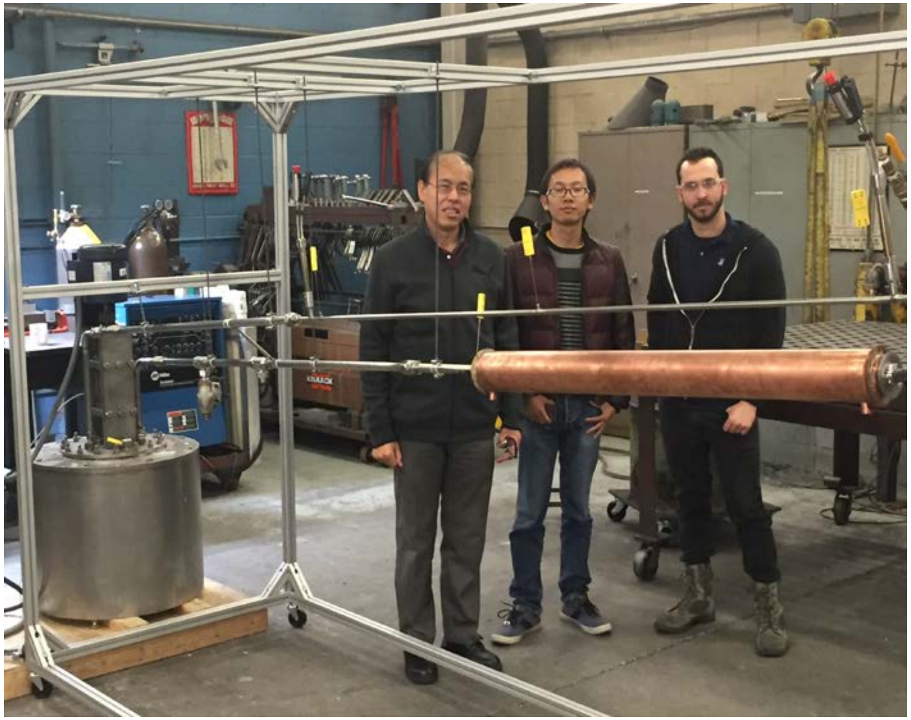


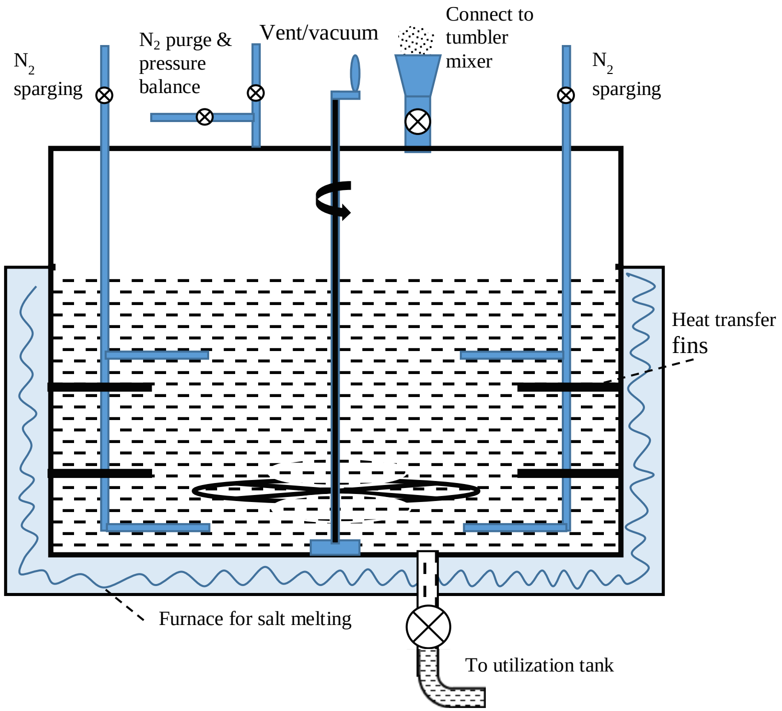
$$k = k_0 + k_1 T \qquad (\mathrm{W/m \cdot K}) \qquad (4)$$

Coefficients in Eq. (4)	Salt #1	Salt #2	Salt #3
k_0 k_1	0.43719611446 -1.2300724988E-4	0.38948756456 -8.1685567308E-5	0.51447164399 -2.3308636401E-4
Uncertainty @ confidence of 95%	±8.892E-3 (W/m·K)	±7.073E-3 (W/m_K)	±9.883E-3 (W/m_K)

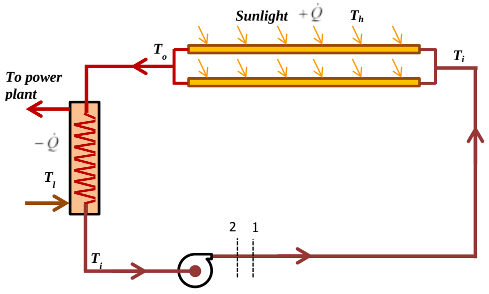
Test loop for heat transfer and corrosion under flow

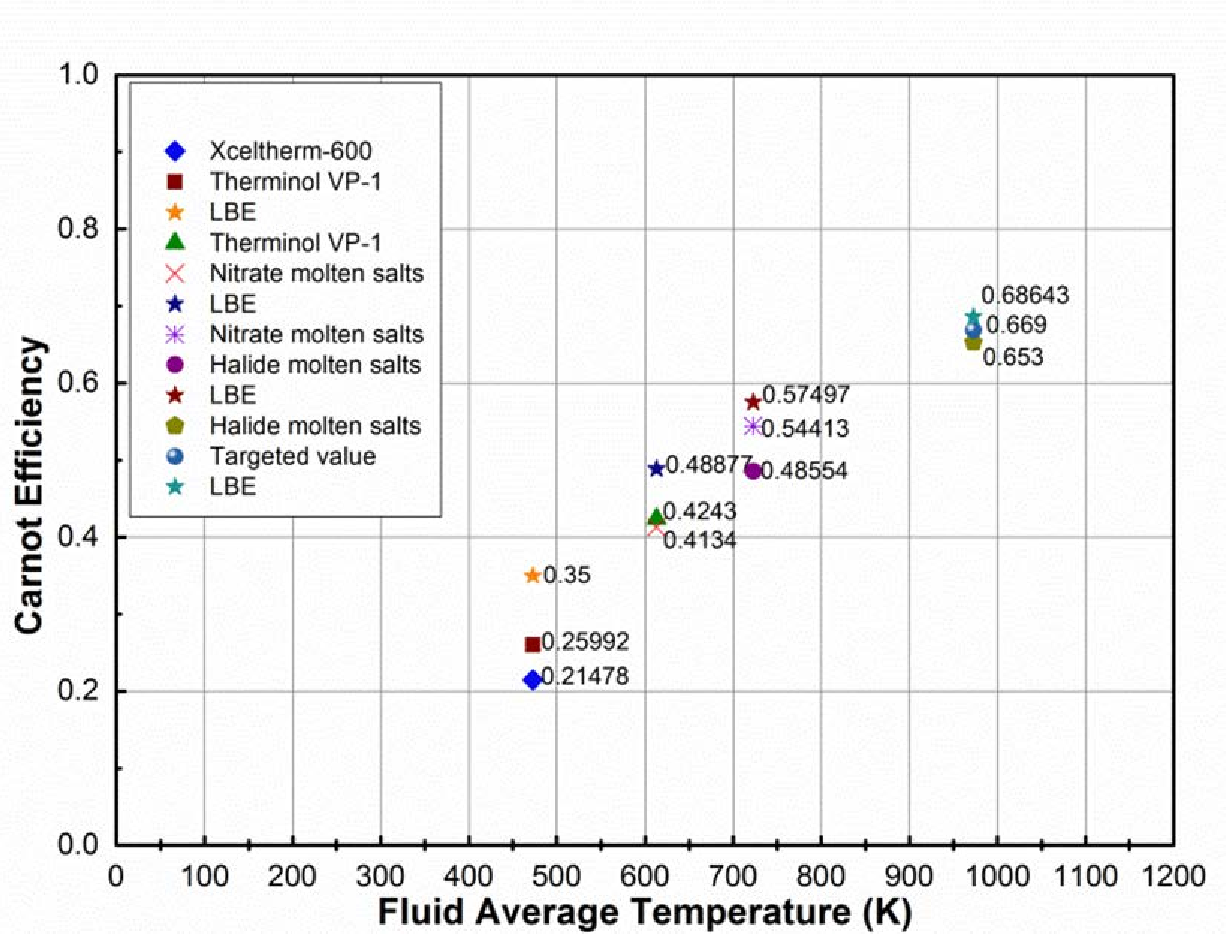
Salt melting and salt processing device





Heat transfer figure of merit





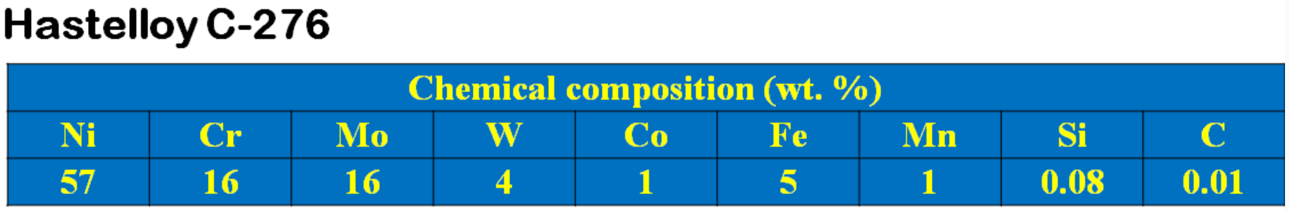
Corrosion rates of C-276 Hastelloy in ternary NaCl-KCl-$ZnCl_2$ molten salt

Molten salt during metal corrosion studied from 300 to 900 ºC

Aerobic - salt equilibrated with stagnant air or flowing dry or humidified air
Anaerobic - salt equilibrated with dry or humidified Argon; stagnant or flowing

Methods of determining Corrosion Rate (CR)

Gravimetrically - by weighing metal, immersing it in salt and reweighing
    Reliable standard method, but takes a long time (days to weeks) to do.
Electrochemically – by determining corrosion current of metal in salt in 3 electrode cell
    New method, takes a short time (minutes) to do; basis for a “state of health” (SOH) pipeline sensor.



Hastelloy C-276

Chemical composition (wt. %)								
Ni	Cr	Mo	W	Co	Fe	Mn	Si	C
57	16	16	4	1	5	1	0.08	0.01

Determining corrosion rate (CR) by Gravimetric method

Calculation of corrosion rate (CR)

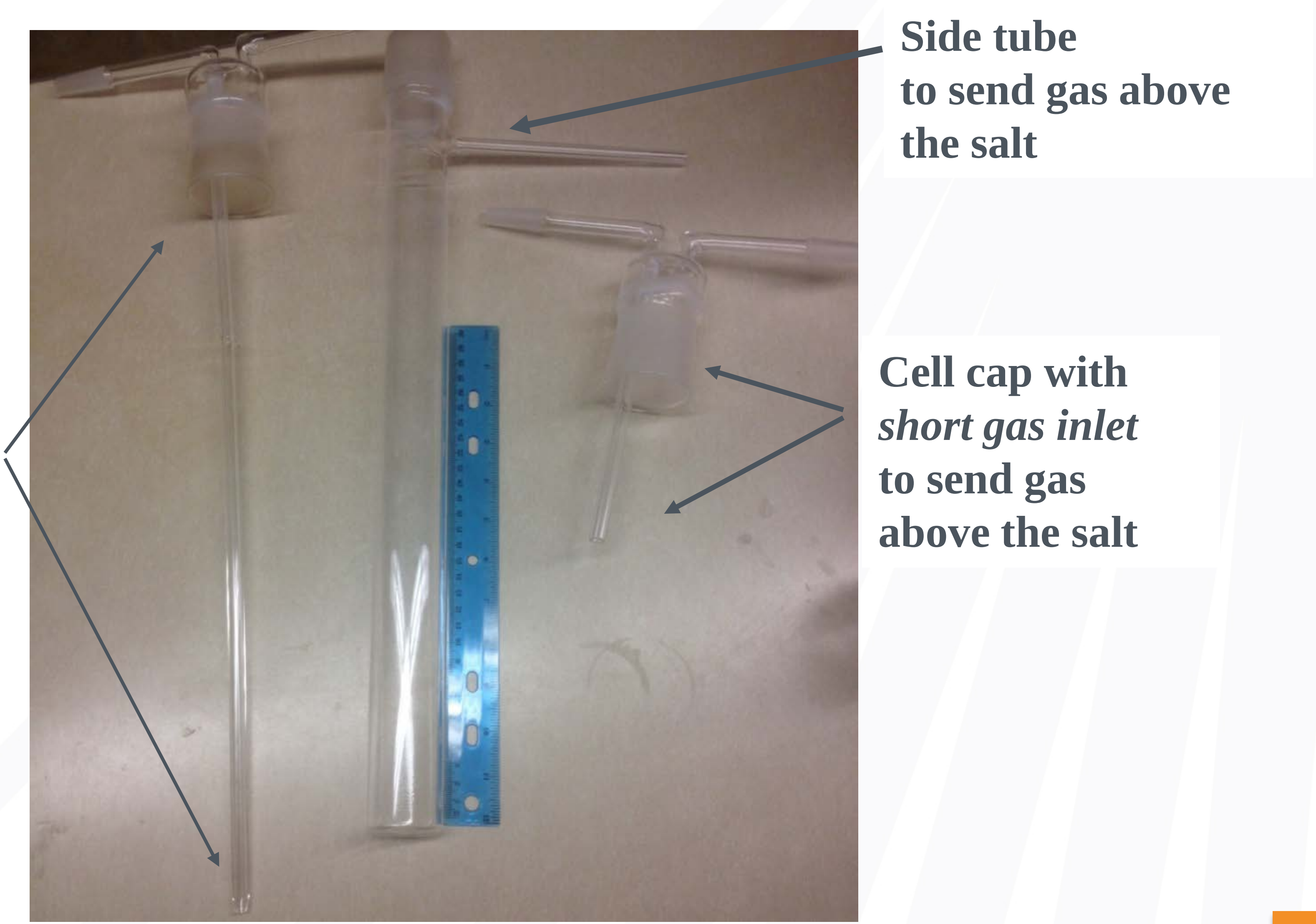
$$CR\ (\mu m/y) = \frac{365 * 10^4 * \Delta Wt}{\rho * A * T}$$

ΔWt is the weight loss in grams
ρ is density (g/cm^3) of the Hastelloy
A is the total immersed area in cm^2
T is the immersion duration in days

Procedure used for finding CR of metal with flowing gas in molten salt

- ~50 cm^2 of metal ground with SiC paper with 200 to 600 grit
- Degas salt using Ar sparging at 175 SCCM at 500°C for 1 hour
- Immerse metal in 300 gm of degassed salt
- Continue for 50 hours (2 days) at 800°C.

Quartz cell with two caps for controlling atmosphere during Gravimetric Corrosion Test

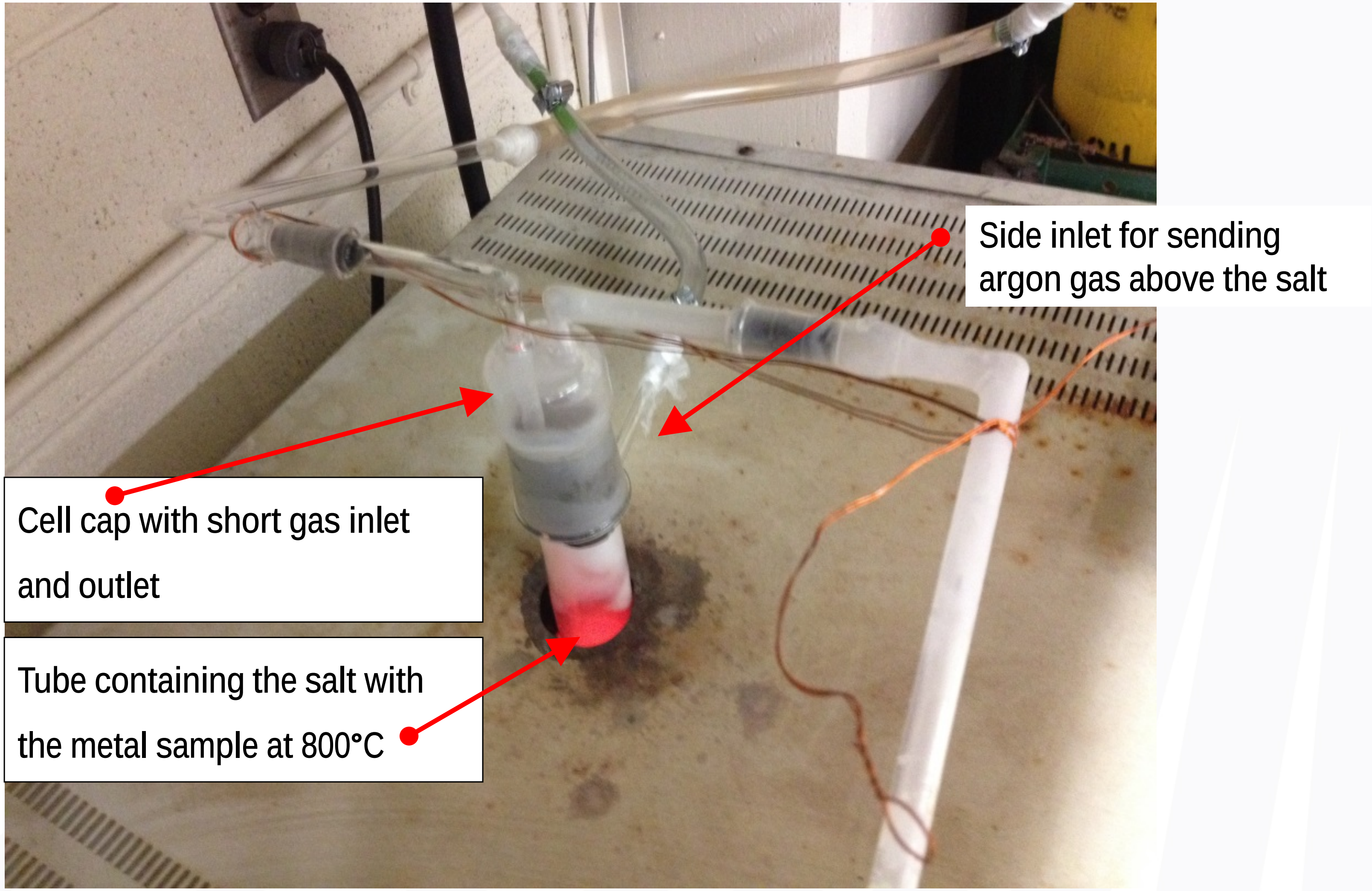


Side tube
to send gas above
the salt

Cell cap with
long gas inlet
to send gas
into (sparge)
the salt during
the initial
degassing of
salt

Cell cap with
short gas inlet
to send gas
above the salt

Quartz cell in the furnace

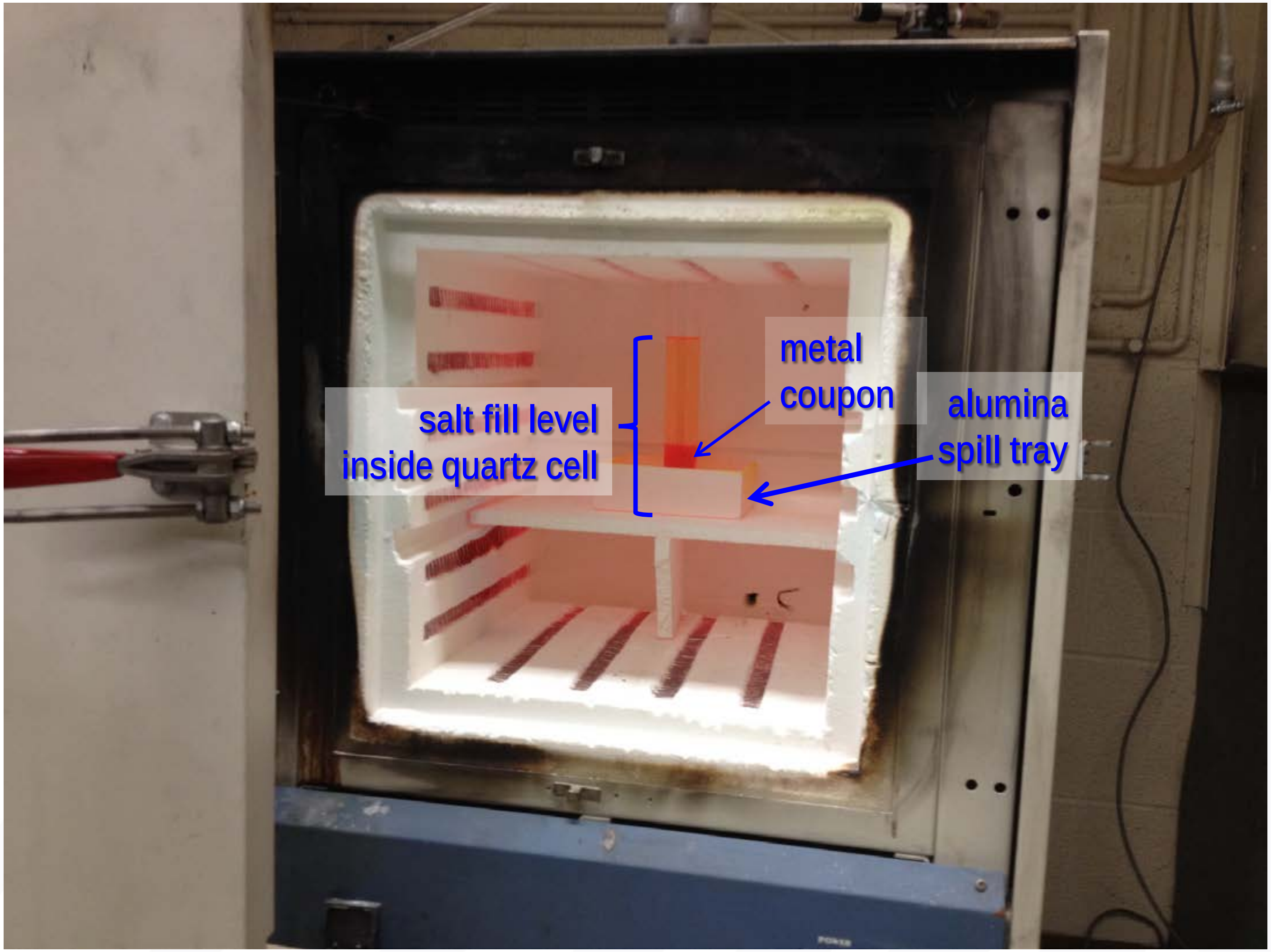


Side inlet for sending argon gas above the salt

Cell cap with short gas inlet and outlet

Tube containing the salt with the metal sample at 800°C

Quartz cell in the furnace

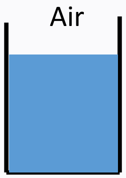


Results of 3 immersion tests

1. Aerobic (cell open to atmospheric air)

Corrosion rate = 1700 µm/year

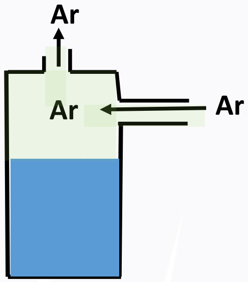
- high corrosion rate due to high flux of O_2 and water (oxidants) from air into salt at high temperature.



2. Anaerobic *without* initial degassing

Corrosion rate = 113 µm/year

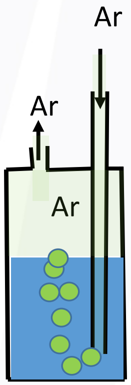
- corrosion rate decreased.
- lower corrosion rate because Argon blanket cut off air supply (oxidant flux) into salt
- CR still greater than 80 µm/y, the DoE target value for CR.



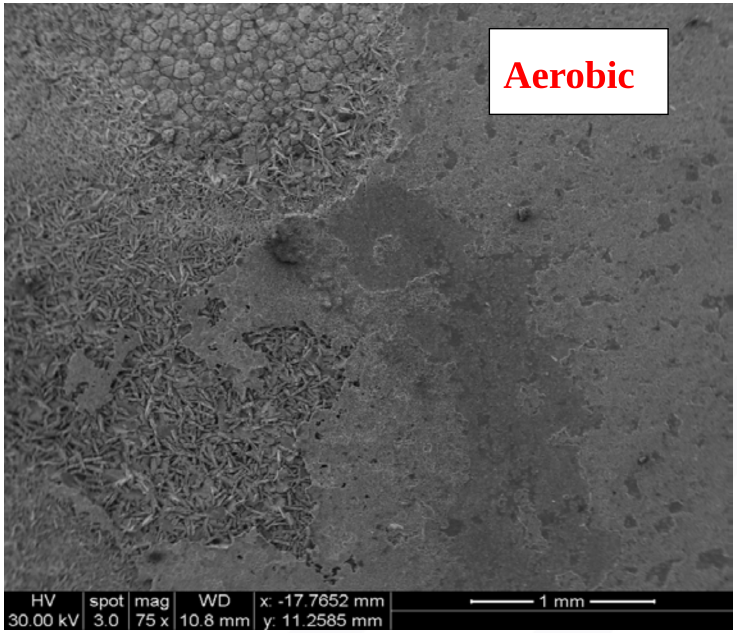
3. Anaerobic with initial degassing (1h Ar gas sparging at 500°C)

Corrosion rate = 53 µm/y

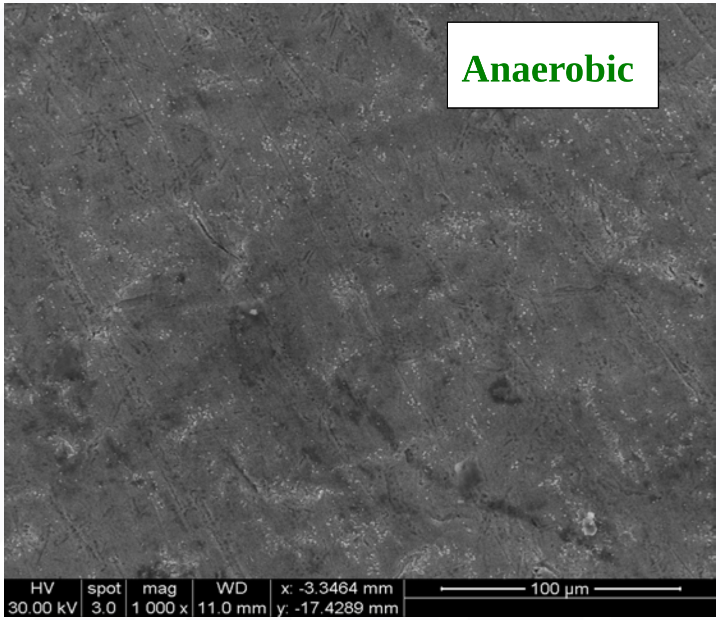
- *Corrosion rate of metal significantly decreased even more with sparging.*
- *CR now lower than the DoE target value (≤ 80 µm/y).*
- *Salt was effectively isolated from the atmosphere air.*
- *Air (O_2 and water vapor) in salt was displaced by Argon*
- *Attaining lower metal CR after sparging confirms the convection of the salt during the degassing process effectively removes H_2O and O_2 (the main oxidants from air) from the salt.*



Appearance of metal after exposure to aerobic and anaerobic molten salt at 800°C

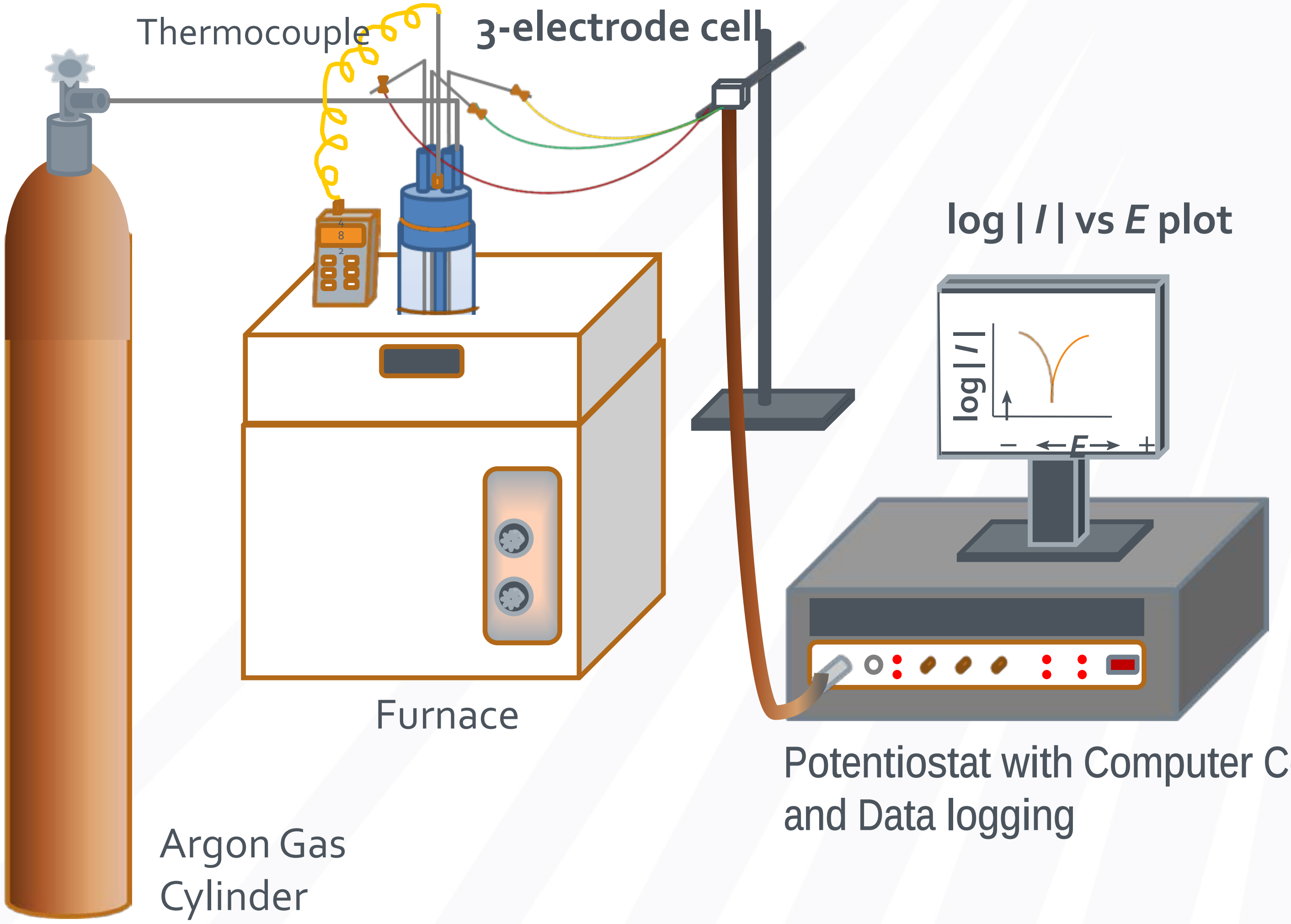


Higher corrosion rate in aerobic salt
More roughening of the metal surface



Low corrosion rate in anaerobic salt
Little roughening of the metal surface

Electrochemical corrosion test setup



Thermocouple

3-electrode cell

log | *I* | vs *E* plot

Furnace

Potentiostat with Computer Control and Data logging

Argon Gas Cylinder

Electrochemical corrosion tests

Analysis of E-chem data to find corrosion rate of Hastelloy C276

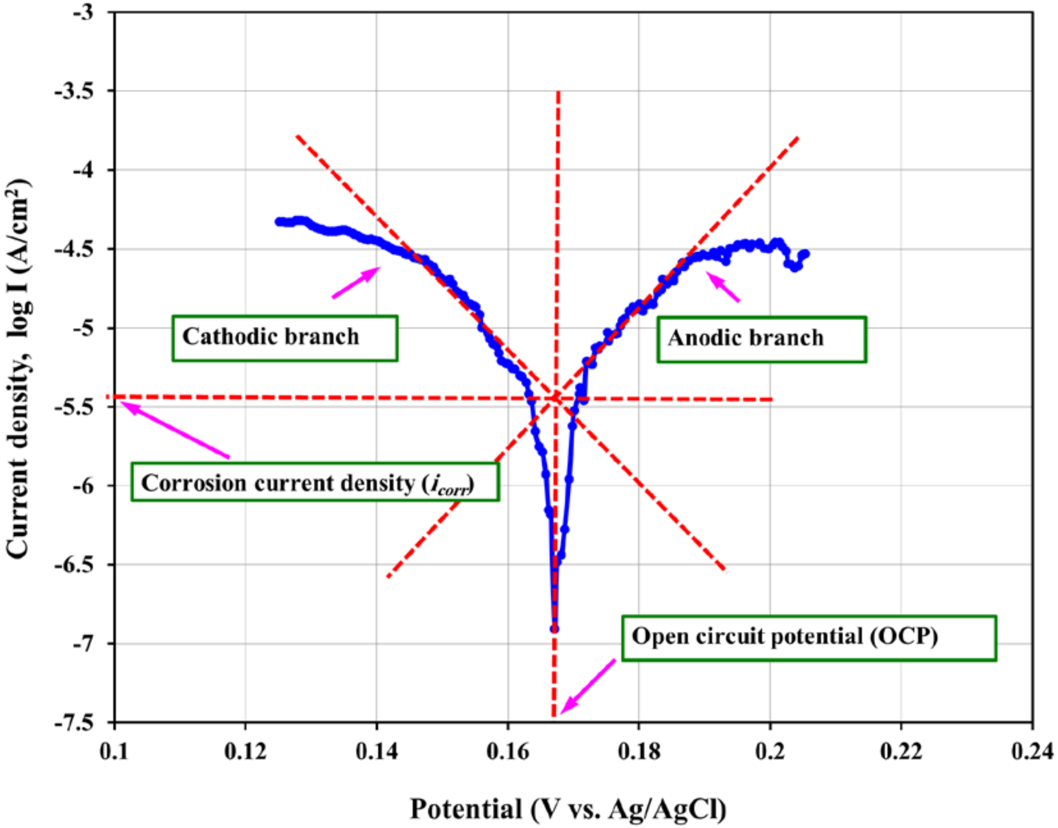
$$CR\ (\mu m/y) = k_1 \left[\frac{i_{corr} EW}{\rho}\right]$$

k_1 = 3.27 in µm g μA^{-1} cm^{-1} yr^{-1}
i_{corr} = corrosion current density in µA cm^{-2}
EW = equivalent weight (27.01 g/eq)
ρ = density (8.89 g cm^{-3})

Procedure for non-destructive Stern-Geary polarization test

- Metal wet polished to 600 grit SiC paper
- Salt degassed by Ar sparging at 175 SCCM at 500°C for 1 hour.
- Metal immersed in 150 gm of salt.
- Metal potential scanned from -30 mV vs OCP to +30 mV vs OCP at scan rate 0.2 mV/s
- Potentials measured vs. Ag/AgCl reference electrode.

Graphical estimation of parameters, i_{corr} and E_{corr} (OCP) needed to find the corrosion rate (*CR*)



$$CR\ (\mu m/y) = k_1 \left[\frac{i_{corr} EW}{\rho}\right]$$

where:

k_1 = 3.27 in µm g µA^{-1} cm^{-1} yr^{-1}
i_{corr} = corrosion current density in µA cm^{-2}
EW = equivalent weight (27.01 g/eq)
ρ = density (8.89 g cm^{-3})

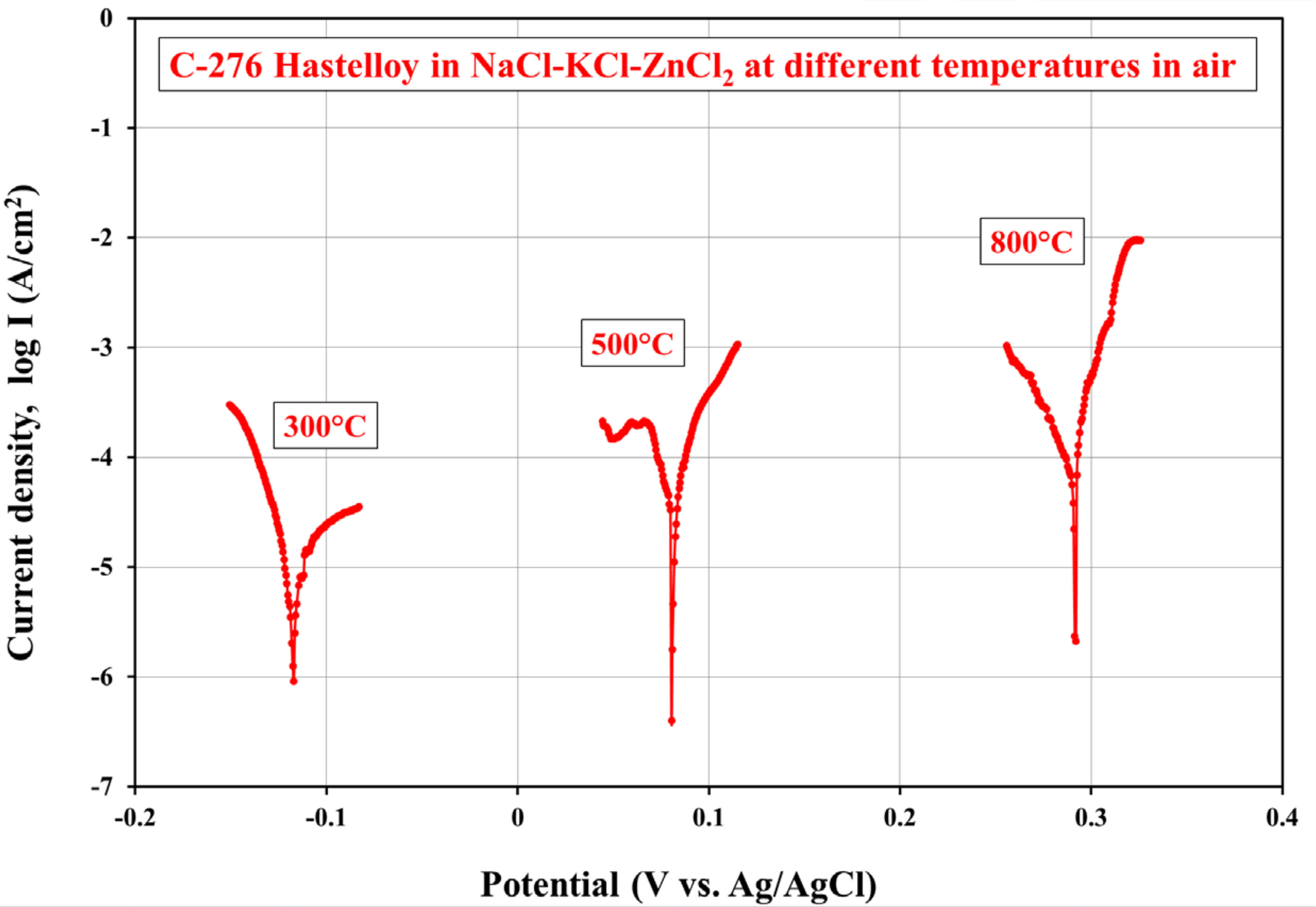
Reference Electrode and Cell
for Electrochemical determination of corrosion rates (CR)

Ag/AgCl (SSE)

Refference Electrode

Electrochemical cell

Typical data for finding corrosion rate of metal in salt at 3 temperatures by Electrochemical method



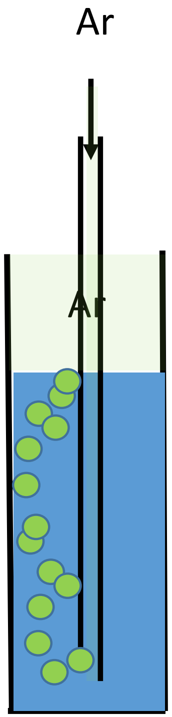
Corrosion rates for Hastelloy C276 in Na K Zn chloride salt

equilibrated with aerobic and anaerobic atmospheres & found by the Electrochemical Stern-Geary Method

Temperature (°C) / Atmosphere	Surface area for WE and CE	Corrosion potential, E_{corr} (V)	Corrosion current density, I_{corr} ($\mu A/cm^2$)	Corrosion rate , (µm/y)
300 …… Air	WE=17.5 cm2 CE=27.3 cm2	-0.115	5	49.7
500 …… Air	WE=17.5 cm2 CE=27.3 cm2	0.08	43.6	433
800 …… Air ↓	WE=17.5 cm2 CE=27.3 cm2	0.291 ↓	240	2380 ↓
300 … Argon	WE=14 cm2 CE=24.5 cm2	-0.08	0.795	7.89
500 … Argon	WE=14 cm2 CE=24.5 cm2	-0.057	1.86	18.5
800 … Argon ↓	WE=14 cm2 CE=24.5 cm2	0.166 ↓	3.16	31.4 ↓

As temperature increases, transport of oxygen, E_{corr} and CR increase.

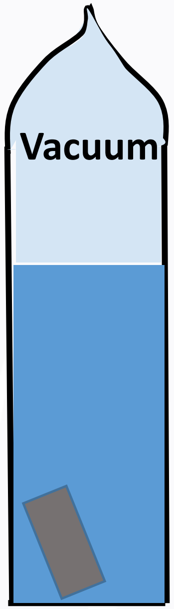
Long term gravimetric corrosion testing of metal in anaerobic molten salt sealed in a quartz tube and heated in a furnace



Sparging

Preparation of Sample in molten salt

- Sparge molten salt at 500 °C with Argon gas in quartz tube for 1 hour
- Flow Argon gas over salt and insert metal
- Apply vacuum and back fill with Argon at 500 °C for 5 times
- Seal under vacuum



Sealed

O_2 or H_2O (or both) from air sustain corrosion
by accepting electrons from the metal

Anodic reactions in "local cell" corrosion mechanism

$$\text{M (Cr, Ni, and Fe)} \rightarrow M^{n+} + ne^-$$

Cathodic reactions in "local cell"

$$O_2 + 4e^- \rightarrow 2\,O^{2-}$$

and/or

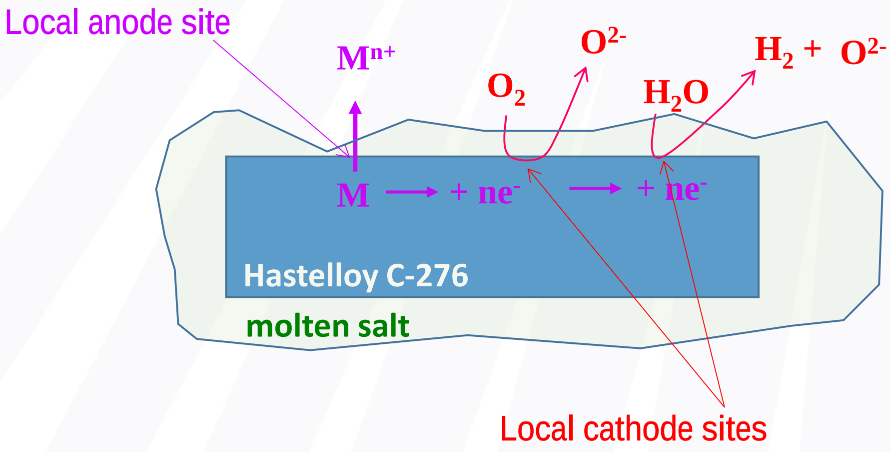
$$H_2O + 2\,e^- \rightarrow H_2 + O^{2-}$$

Charge balance reactions in molten chloride salt Na-K-Zn-Cl_4

$$M^{n+} + nNaCl \rightarrow M^{n+}Cl^-_n + nNa^+$$

$$2nNa^+ + nO^{2-} \rightarrow nNa^+_2O^{2-}$$

Schematic diagram of **"local cell"** mechanism



Can the ternary chloride salt, itself, oxidize Hastelloy metal ??

Composition of ternary chloride salt is Na-K-Zn-Cl_4

13.40mol%	33.70%	52.90%

Composition of Hastelloy C-276 is

	Ni	Co	Cr	Mo	W	Fe	Mn
Wt%	57	1	16	16	4	5	1

From Table of Reduction potentials, E

$E_{Al, K, Na, Zn, Cr}$ (molten salts) << E_{Fe} (stainless, carbon steel) < E_{Ni} (Hastelloys)

Less Noble → More Noble

Only possible interaction between salt and metal is Zn^{+2} in salt *might* oxidize Cr^0 metal in the Hastelloy because the reduction potential vs NHE of

Zn = - 0.76 V (slightly less Noble)

Cr = - 0.74 V (slightly more Noble)

Does Zn^{+2} ion oxidize Cr metal in Hastelloy C276 ?

Only by one of the following two reactions?

$$3\ Zn^{+2} + 2\ Cr^{0} \rightarrow 3\ Zn^{0} + 2\ Cr^{+3}$$

$$Zn^{+2} + Cr^{0} \rightarrow Zn^{0} + Cr^{+2}$$

If Zn^{+2} ion oxidizes Cr metal, then Zn metal should form

To answer this question, Hastelloy C-276 coupons were studied by

- **EDS spectroscopy,**
- **XRD scattering and**
- **XPS spectroscopy.**

The 3 Hastelloy coupons were: *1 pristine* Hastelloy C276 coupons and *2 more such coupons corroded* in anaerobic ternary Na-K-$ZnCl_4$ molten salt (mp 204°C) and sealed in quartz. These are designated sample 1 (S1), sample 2 (S2) and sample 3 (S3) where

- Sample 1...is *pristine* as received Hastelloy C-276 wet polished to a mirror finish with1200 SiC paper; rinsed with DI water and acetone.
- Sample 2...is *corroded* by taking the pristine as received sample 1 and sealing with Na-K-Zn ternary in quartz for 4 weeks at 800°C
- Sample 3...is *corroded* by taking the pristine as received sample 1 and sealing with Na-K-Zn ternary in quartz for 1 week at 900°C

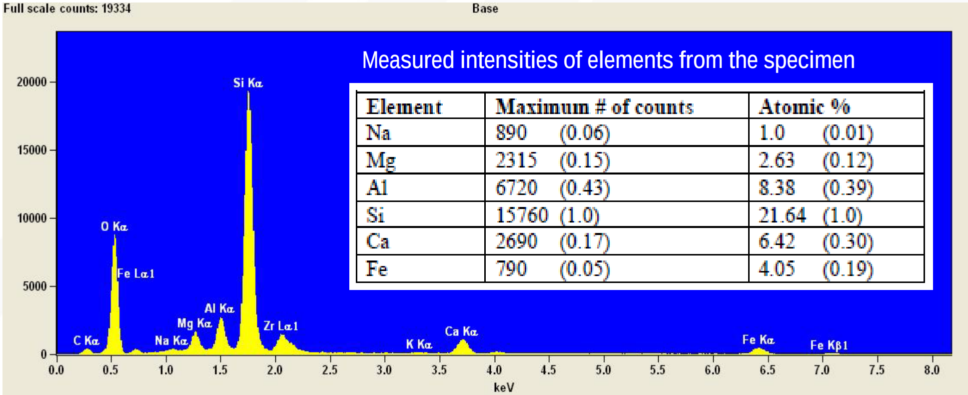
First: Is there Zn present in any form (ionic or metallic) ?
EDS was used to answer this first question.

EDS cross section studies of Hastelloy C276

Energy Dispersive Spectroscopy (EDS) allows identification of elements present backscattering electrons and relative proportions (atomic % or wt%).

Cross section analysis polish surface through a material and examine microscopically with with energy dispersive x-ray analysis (EDX) or with x-ray photoelectron spectroscopy (XPS) to give a spatial mapping of the composition of the material.

Initial EDS analysis an X-ray spectrum from the entire area scanned by an SEM to give an image of a specimen and the corresponding X-ray spectra.
The Y-axis in the X-ray spectrum shows the number of X-rays received by the detector (counts) and the X-axis shows the energy level of those counts which is characteristic of a particular element.

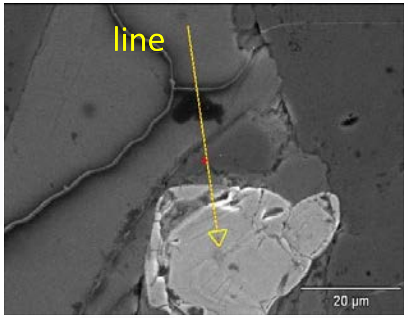


Measured intensities of elements from the specimen

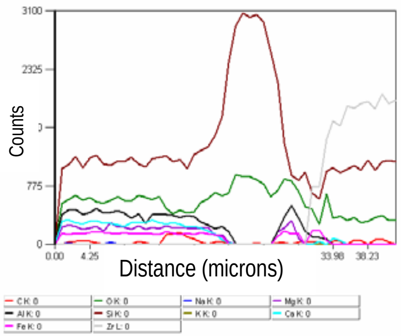
Element	Maximum # of counts	Atomic %
Na	890 (0.06)	1.0 (0.01)
Mg	2315 (0.15)	2.63 (0.12)
Al	6720 (0.43)	8.38 (0.39)
Si	15760 (1.0)	21.64 (1.0)
Ca	2690 (0.17)	6.42 (0.30)
Fe	790 (0.05)	4.05 (0.19)

Elemental mapping is spatial mapping of an element by having the electron beam follow a line along an image to plot the relative proportions of elements on that line.

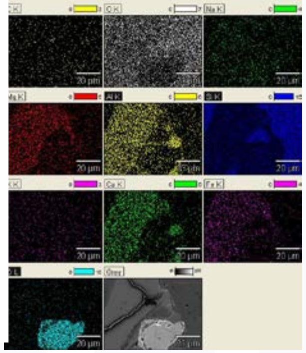
The Specimen



Line map of elements in a specimen



2D map of elements in a specimen



EDS analysis of Composition of Hastelloy C-276 after 1week in ternary salt at 900C

Element Line	Wt.%	Wt.% Error	Atom %	Atom % Error
O K	0.00	± 0.00	0.00	---
Na K	3.37	± 0.28	8.90	0.74
K K	0.03	± 0.02	0.05	0.03
Cr K	6.95	± 0.05	8.11	0.06
Mn K	0.26	± 0.03	0.29	0.03
Fe K	4.72	± 0.06	5.13	0.06
Co K	1.41	± 0.06	1.46	0.06
Ni K	51.73	± 0.15	53.52	0.16
Zn K	11.14	± 0.16	10.35	0.15
Mo K	17.98	± 0.70	11.38	0.44
W L	2.41	± 0.40	0.80	0.13
	----------		----------	
Total	100.00		100.00	

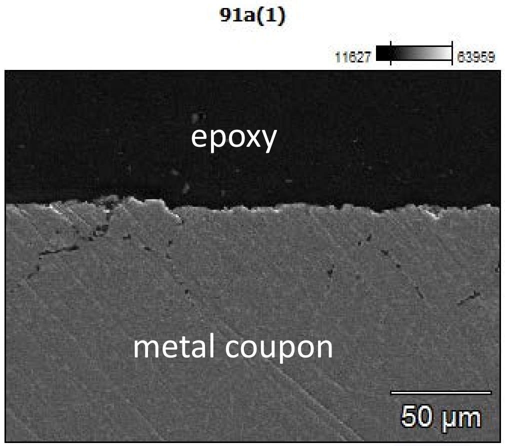
Composition of Hastelloy C-276

	Ni	Co	Cr	Mo	W	Fe	Mn
Wt%	57	1	16	16	4	5	1

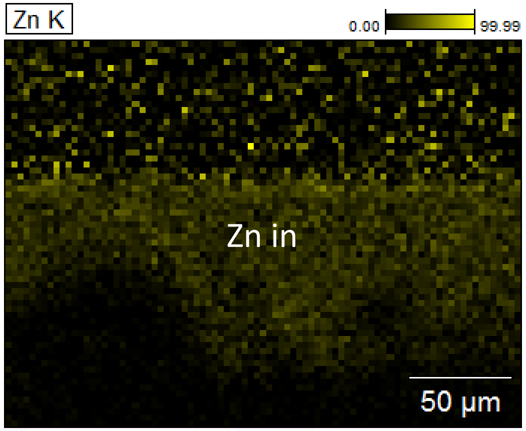
Clearly after exposure, the Hastelloy coupon lost Cr and zinc is present

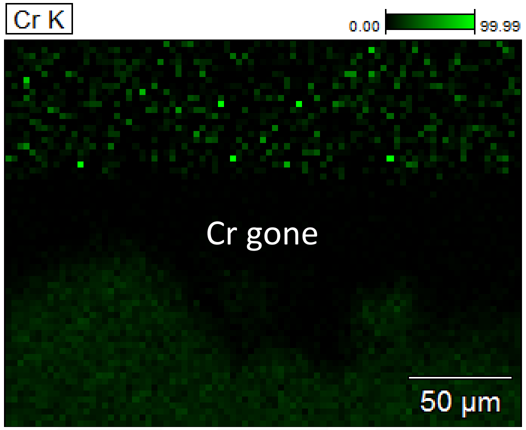
Does this mean Zn^{+2} oxidized Cr in the Hastelloy ?

EDS cross section of Hastelloy C-276 in ternary salt at 900C for 1week



Data Type: **Weight %**
Image Resolution: 512 by 384
Image Pixel Size: 0.49 µm
Map Resolution: 256 by 192
Map Pixel Size: 0.98 µm
Acc. Voltage: 30.0 kV
Magnification: 500
Weight % mode





After EDS work, where do we stand ?

EDS cross section studies showed that there is a lot of Zn in Hastelloy C276 when it is corroded in anaerobic ternary salt Na-K-Zn molten salt at 900°C for 1week

Is this Zn seen by EDS metallic Zn showing one of the following reactions occurs?

$$3\,Zn^{+2} + 2\,Cr^{0} \rightarrow 3\,Zn^{0} + 2\,Cr^{+3}$$

$$Zn^{+2} + Cr^{0} \rightarrow Zn^{0} + Cr^{+2}$$

Or is this ionic zinc from the Na-K-Zn-Cl_4 salt??

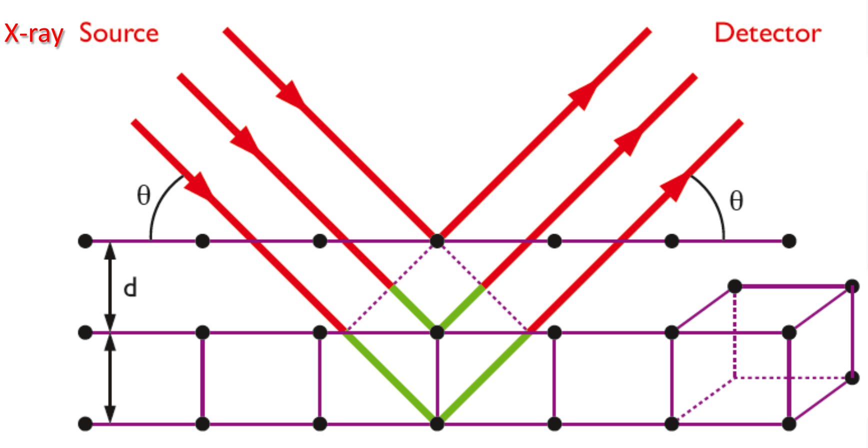
EDS does NOT distinguish Zn metal from Zn ion.

A valence specific tool is needed to answer this question. like

- X-ray diffraction (XRD) by identifying crystal peaks, or
- X-ray photoelectron spectroscopy (XPS) which is sensitive to the valency (metallic or ionic) of a metal , like Zn.

X-Ray Diffraction (XRD)

X-rays with a wavelength, λ, in the range of interatomic distances (0.1-10 Å) are used to the study of *crystalline materials.*



- Schematic representation of diffraction of X-rays in a crystalline material.
- Bragg's law is satisfied when the pathlength difference of the X-rays (indicated in green) is equal to n λ.
- The diffraction angle Θ is half the angle between the incident and diffracted X-rays.

The depth of XRD sampling ranges from a few micrometers to a few hundred micrometers.

SEM of two sides of the Hastelloy C276 coupon

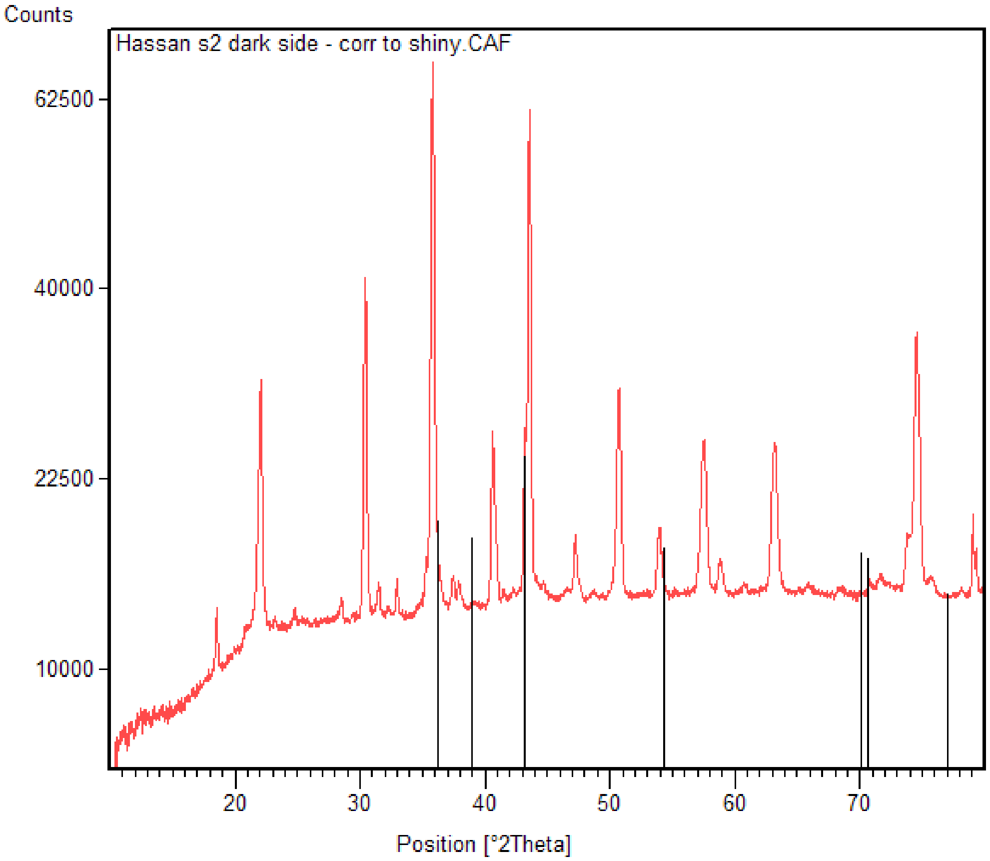
- exposed to anaerobic ternary molten chloride salt in sealed quartz tube at 900^{o}C for 1 week
- one side of the coupon is typically darker than the other
- the different optical appearance of the 2 different sides corresponds to NO DIFFERENCE in the XRD or XPS spectra observed from these 2 sides
- "dark side" and "light side" is just a convenient way to keep track of which side is being studied

This side is designated **"light side"**

This side is **"dark side"**

XRD of Sample 2 Hastelloy C-276 corroded in ternary Na-K-$ZnCl_4$ salt

polished (mirror finish @1200 SiC then sealed in anaerobic Na-K-Zn ternary for 4Weeks at 800C



Note:

The theoretical XRD Zn metal peaks (in black)

DO NOT MATCH the observed experimental XRD peaks (in red**)**

After XRD work, does Zn^{+2} oxidize Cr metal in Hastelloy?

Facts

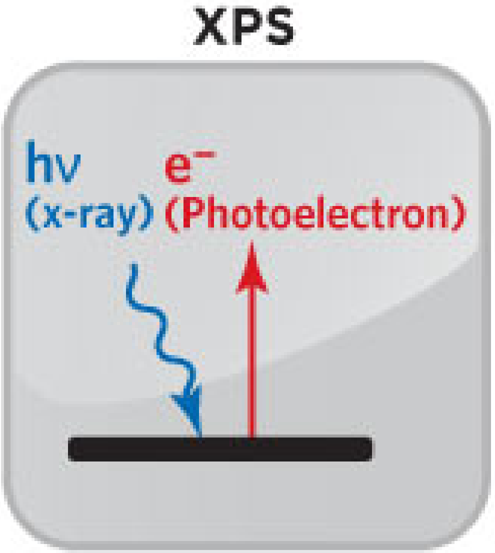
- The Hastelloy C276 coupon corroded in anaerobic Na-K-Zn ternary in quartz for 4Weeks at 800C is only 10 microns thick
- The depth of penetration of X-rays during XRD measurements ranges from a few micrometers to a few hundred micrometers,
- So from the XRD spectra we know that *there is no crystalline metallic Zn^0 in the Hastelloy C-276 coupons corroded in anaerobic ternary Na-K-$ZnCl_4$ salt sealed in quartz for 4Weeks at 800C*
- Similar results found for Sample 3 the coupon sealed with Na-K-Zn ternary in quartz for 1Week at 900C

Conclusions

- **XRD showed there was no crystalline metallic Zn^0 found in all of the corroded coupon**
- But what if the Zn metal is amorphous?
- Need a valence specific tool like XPS which is a surface spectroscopy which can “see” a crystalline or amorphous sample and give the valency of elements

X-ray Photoelectron Spectroscopy (XPS)

Is used to determine quantitative atomic composition and chemistry with a sampling volume that extends from the surface to a depth of approximately 5-7 nanometers.

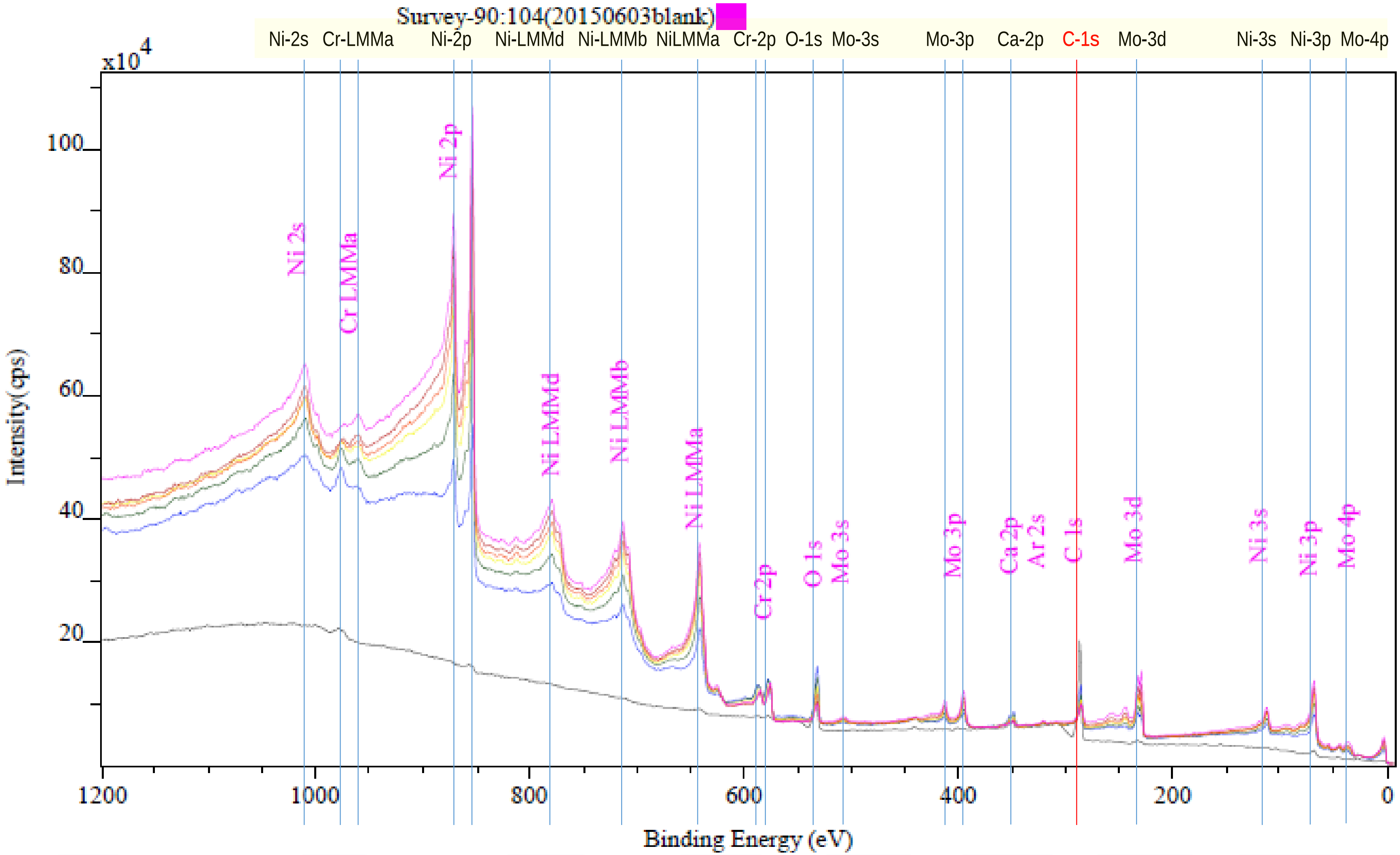


- XPS can be used to characterize crystalline and amorphous materials on a surface.
- XPS provides information on the chemical state of the detected elements, can distinguish between metallic (Zn^o)and ionic (Zn^{+2}) forms of the element zinc.
- XPS works by irradiating a sample with monochromatic x-rays, resulting in the emission of photoelectrons and Auger electrons whose energies are characteristic of the elements.
- Analysis of the Auger electrons is needed to distinguish between metallic (Zn^o)and ionic (Zn^{+2}) forms of the element zinc (Zn).

PRISTINE WITH NASCENT OXIDE

XPS of Hastelloy C276 polished 1200 grit washed DI water and acetone

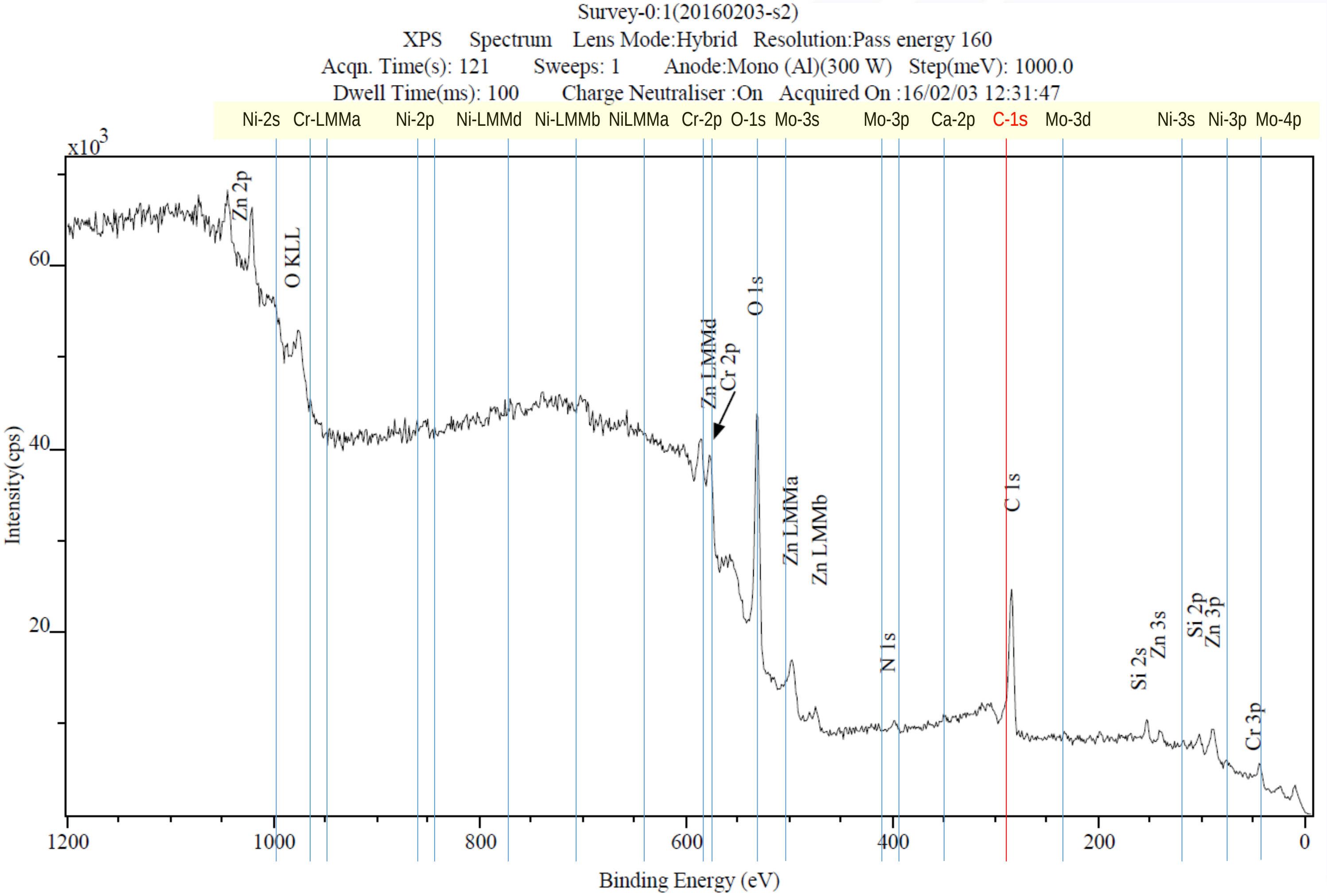
vertical lines showing XPS peak assignments of pristine alloy with native oxide



Corrosion layer NORMAL TO SURFACE

XPS Hastelloy C276 1200 grit corroded in Na-K-ZnCl4 at 800°C 4 weeks

vertical lines for pristine alloy & native oxide ; no match this spectrum of corrosion layer seen with no Zn metal



Survey-0:1(20160203-s2)

XPS Spectrum Lens Mode:Hybrid Resolution:Pass energy 160

Acqn. Time(s): 121 Sweeps: 1 Anode:Mono (Al)(300 W) Step(meV): 1000.0

Dwell Time(ms): 100 Charge Neutraliser :On Acquired On :16/02/03 12:31:47

CROSS SECTION of corrosion layer on Hastelloy C276 metal polished and no sputtering

XPS of 1200 C276 corroded in Na-K-ZnCl4 ternary at 800°C for 4 weeks

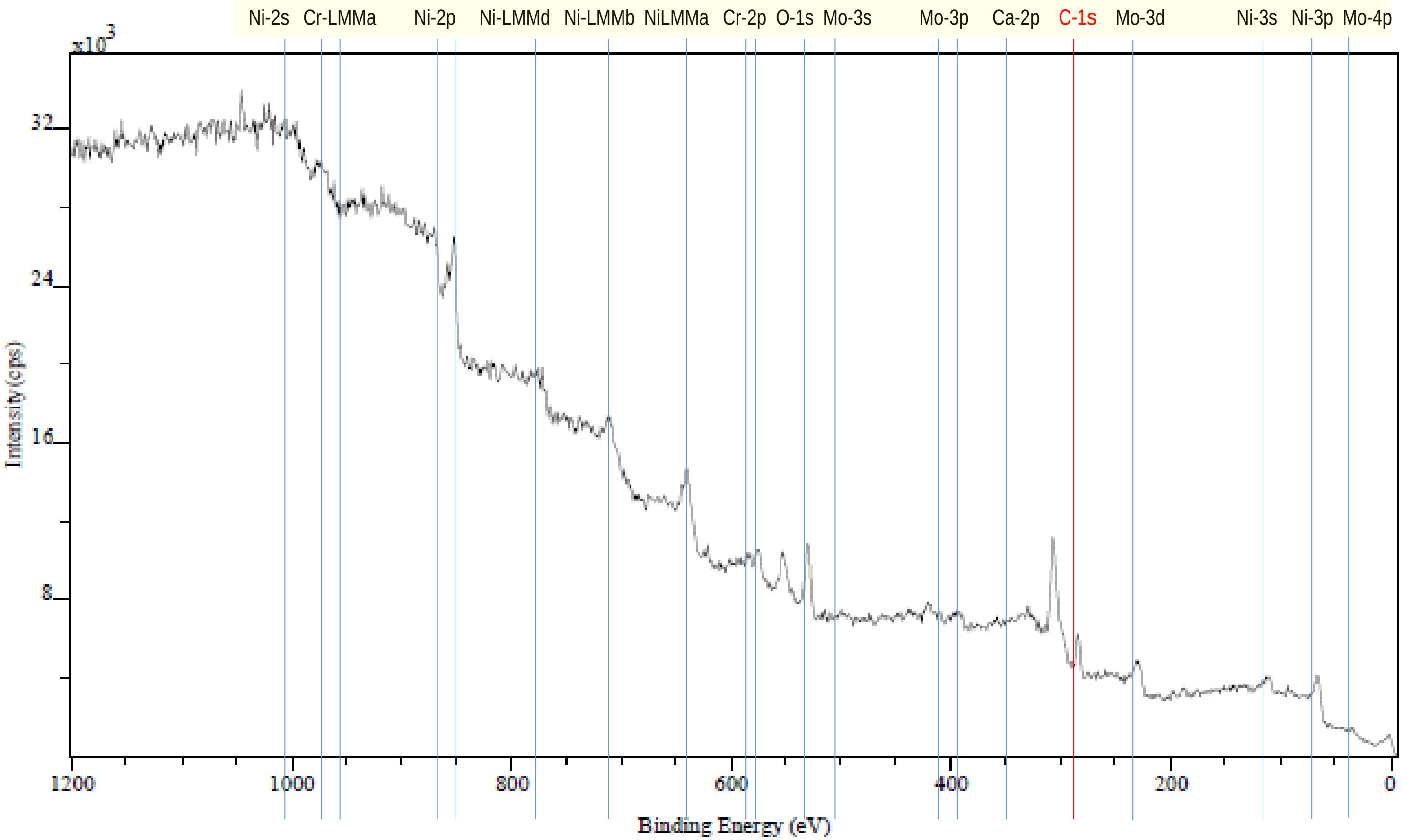
vertical lines showing for pristine alloy with native oxide ; partial match for corrosion layer on metal with no signal for Zn metal observed anywhere in cross section

Survey:4(20160324Hassan-xsect2-0)

XPS Spectrum Lens Mode:Hybrid Resolution:Pass energy 160

Acqn. Time(s): 241 Sweeps: 1 Anode:Mono (Al)(300 W) Step(meV): 1000.0

Dwell Time(ms): 200 Charge Neutraliser :Off Acquired On :16/03/24 09:43:56



Conclusion from XPS of Hastelloy C276 coupons

XPS conclusions

I. XPS sampled 2 to 4 nm beneath the surface of the corrosion layer on Hastelloy C276 coupons

II. The corroded Hastelloy 2 to 4 nm thick surface shell only contains homogeneous metal-oxide; **no zinc metal** or alloy metal

III. The corroded Hastelloy cross section contains homogeneous metal-oxide and alloy metal; **no zinc metal**

IV. XPS inconclusive since Zn-ion may be converted to zinc metal during sputtering needed to remove nascent oxide

Detailed conclusions are:

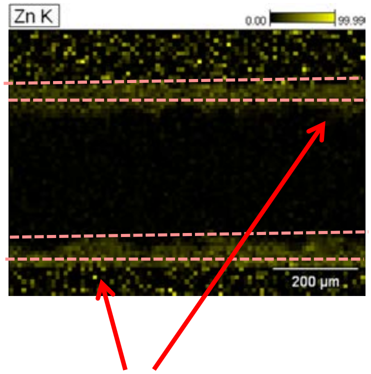
- **to know there is no zinc metal** in the corrosion layer nor in the bulk Hastelloy C276 metal, need to do one of two things:
  1. XPS sampling of a cross section,
     - if no zinc metal seen this is a *TRUE POSITIVE* Zn^{+2} can not oxidize Cr metal in Hastelloy
  2. XPS depth profiling
     - If no XPS peaks are found for zinc-metal in a coupon, then this test is a *TRUE NEGATIVE* test that zinc-ion does not oxidize chromium-metal in the Hastelloy C276.
     - if zinc metal is seen, this test is *NOT a TRUE POSITIVE* test telling that zinc-ion can oxidize chromium-metal in the Hastelloy C276, because sputtering can convert Zn-ion to Zn-metal giving a false positive.

Accelerated corrosion test at 900°C

Hastelloy C276 to 1200 grit and then corroded in Na-K-ZnCl4 ternary at 900°C for 1, 2 and 4 weeks

The anaerobic condition was made by sparging Ar gas in the salt for 1h at 500C and preserved by blanketing Ar gas above the salt during coupon immersion and afterwards then the mixture (salt + metal sample) was sequentially subjected to vacuum (millitorr) and Ar gas backfill (1 atm) 5 times. The quartz tube was melted to seal it while under vacuum, and then the metal in molten salt sealed in the quartz tube was transferred to an electric furnace at 900°C for 1, 2 and 4weeks. Then the EDS cross section was measured as shown below.

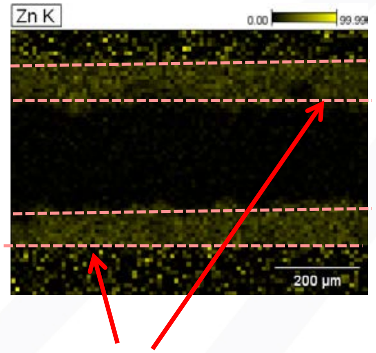
1 week



Surface corrosion layers

(~ 55 µm on each side)

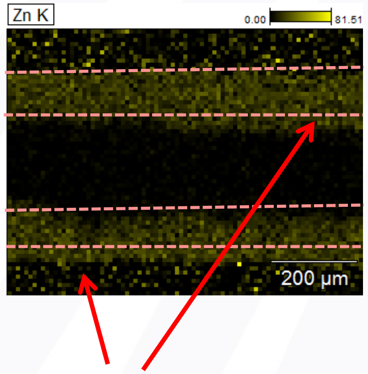
2 weeks



Surface corrosion layers

(~ 100 µm on each side)

4 weeks



Surface corrosion layers

(~ 125 µm on each side)

The rate of growth for the thickness of the corrosion layer is decreasing as time increases indicating the oxidant in the sealed tube is being depleted.

The decrease in the growth of the corrosion layer with time is consistent with the oxidant being water which is an impurity in the salt and NOT Zn^{+2} ion, which is present in the salt in large excess.

This test is being repeated and continue to 8 weeks to determine if growth of the corrosion layer stops when water is depleted from the salt.

Composition changes after accelerated corrosion at 900 °C for 4 weeks

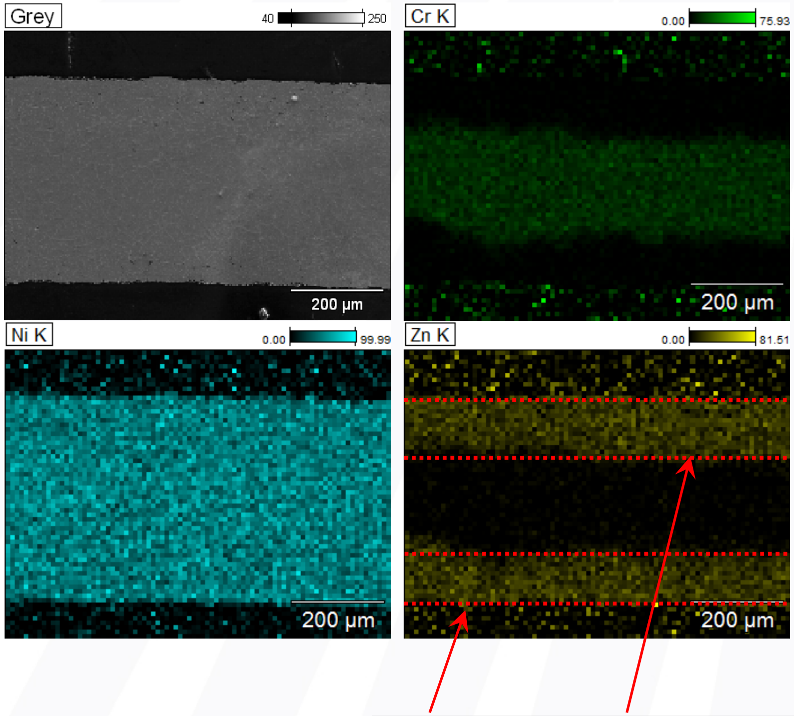
Accelerated corrosion testing at 900 °C shows corrosion process slows down in time indicative of depletion of oxidant, which is probably water not Zn ion, since water is an impurity Zn is present in a large excess in the salt.

Composition of Hastelloy C-276 is

	Ni	Co	Cr	Mo	W	Fe	Mn
Wt%	57	1	16	16	4	5	1

Element Line	Element Wt.%	Wt.% Error	Atom %	Atom % Error
O K	0.00	± 0.00	0.00	---
Na K	2.64	± 0.26	7.07	0.71
Cl K	0.05	± 0.03	0.08	0.05
K K	0.01	± 0.01	0.02	0.03
Cr K	7.75	± 0.05	9.17	0.06
Mn K	0.27	± 0.02	0.31	0.03
Fe K	4.86	± 0.03	5.36	0.04
Co K	1.47	± 0.06	1.54	0.06
Ni K	52.21	± 0.15	54.72	0.15
Zn K	10.13	± 0.15	9.54	0.14
Mo K	17.28	± 0.65	11.09	0.42
W L	3.31	± 0.22	1.11	0.07
	----------		----------	
Total	100.00		100.00	

Salt mass: 50 gm, Total exposed metal surface area = 23 cm^2, Duration: **4 weeks**
Corrosion rate = -89.36 μm/y (notice the negative sign)
This sample was lightly washed with DI water after experiment to remove salt layer stuck on the sample to prepare it for EDS work (NO sonication in HCl or DI water).

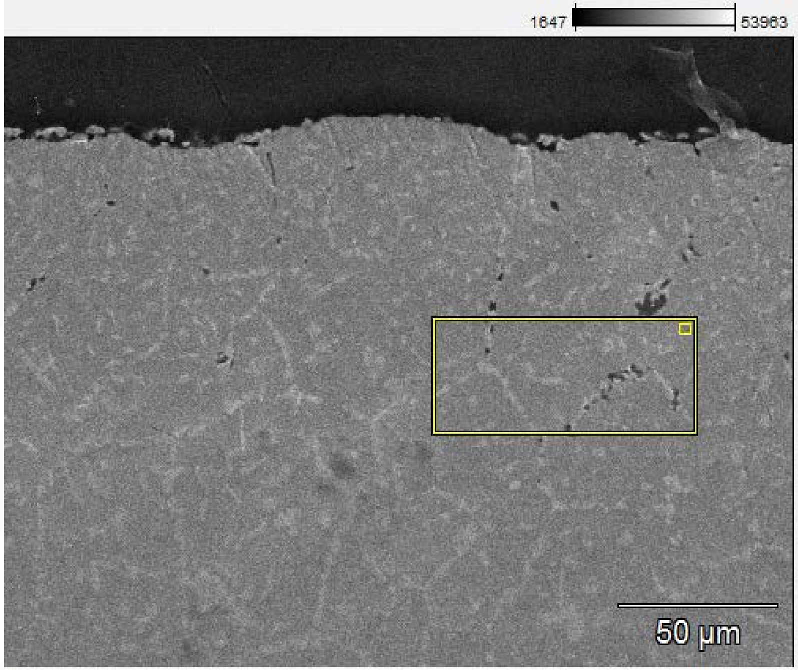


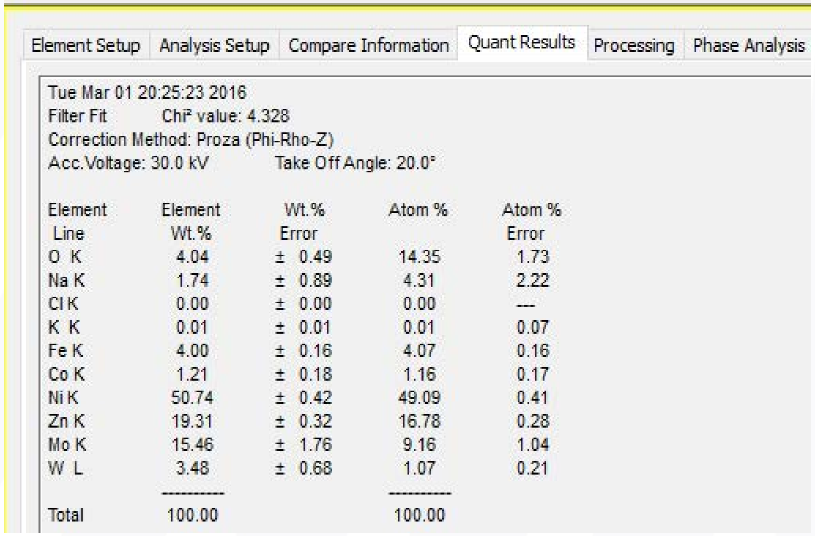
Zn surface layers (~ 125 μm on each side)

Presence of oxygen in corrosion layer in Hastelloy corroded in ternary salt at 900°C for 4 weeks

Analysis of the yellow line box in the SEM image which shows the presence of oxygen indicating Zn is a near stoichiometric oxide (AW of O is 16 and Zn is 65) in voids in grain boundaries of Hastelloy, which are not detected when taking large low resolution images.

Element Line	Element Wt.%	Wt.% Error	Atom %	Atom % Error
O K	**4.04**	**± 0.49**	**14.35**	**1.73**
Na K	**1.74**	**± 0.89**	**4.31**	**2.22**
Cl K	0.00	± 0.00	0.00	---
K K	0.01	± 0.01	0.01	0.07
Fe K	4.00	± 0.16	4.07	0.16
Co K	1.21	± 0.18	1.16	0.17
Ni K	50.74	± 0.42	49.09	0.41
Zn K	**19.31**	**± 0.32**	**16.78**	**0.28**
Mo K	15.46	± 1.76	9.16	1.04
W L	3.48	± 0.68	1.07	0.21
	----------		----------	
Total	100.00		100.00	





```
Tue Mar 01 20:25:23 2016
Filter Fit          Chi² value: 4.328
Correction Method: Proza (Phi-Rho-Z)
Acc.Voltage: 30.0 kV          Take Off Angle: 20.0°

Element    Element     Wt.%       Atom %     Atom %
 Line       Wt.%       Error                  Error
O  K        4.04      ± 0.49      14.35       1.73
Na K        1.74      ± 0.89       4.31       2.22
Cl K        0.00      ± 0.00       0.00       ---
K  K        0.01      ± 0.01       0.01       0.07
Fe K        4.00      ± 0.16       4.07       0.16
Co K        1.21      ± 0.18       1.16       0.17
Ni K       50.74      ± 0.42      49.09       0.41
Zn K       19.31      ± 0.32      16.78       0.28
Mo K       15.46      ± 1.76       9.16       1.04
W  L        3.48      ± 0.68       1.07       0.21
          ----------             ----------
Total     100.00                 100.00
```

Overall Conclusions about Corrosion of Hastelloy in Molten Salt

- Corrosion was monitored by conventional gravimetric method and a new electrochemical method (sensor); both methods give similar corrosion rates under similar conditions of metal in salt.
- Corrosion of metal used to contain the molten salt is a key issue and the corrosion rate is < 60 micron per year for Hastelloy C-276 in 13.4mol%NaCl–33.7mol%KCl–52.9mol% $ZnCl_2$ at 800ºC as required by the DoE
- Corrosion of Hastelloy C-276 in this molten salt is due to the presence of oxygen and water in the molten $NaKZnCl_4$ salt
- Heating and bubbling dry inert (N_2 or Ar) gas into the molten salt HTF dehumidifies and deoxygenates the salt.
- Residual water is particularly difficult to remove and accounts for corrosion of Hastelloy in nominally "dry anaerobic" salt up to 900 ºC.
- There is no direct evidence that Zn+2 ion in ternary molten oxidizes Hastelloy C276 metal at temperatures up to 900ºC
- Ternary 13.4mol%NaCl–33.7mol%KCl–52.9mol% $ZnCl_2$ salt appears suitable as a heat transfer fluid from a corrosion standpoint up to 900ºC.

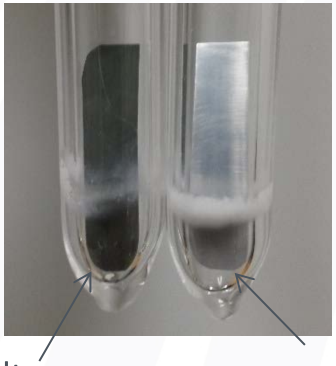
Studies on the corroded metal from Material

Corrosion Mechanism of Hastelloy C-276 exposed to $ZnCl_2$-based salts at 800°C:

- ***Objectives***: Establish the corrosion mechanism of Hastelloy C-276 exposed to $ZnCl_2$-based ionic salts at 800°C.

- All experiments are performed in ***anaerobic conditions***. Ultra high purity compounds used for all experiments. Coupon introduced in silica tube in glove box and sealed under vacuum.
- Thick Hastelloy coupon are used: 0.625mm thick as compared to 0.7 mm used in the flow loop
- Extent of corrosion characterized by EDS on sample cross section.

Coupons after exposure

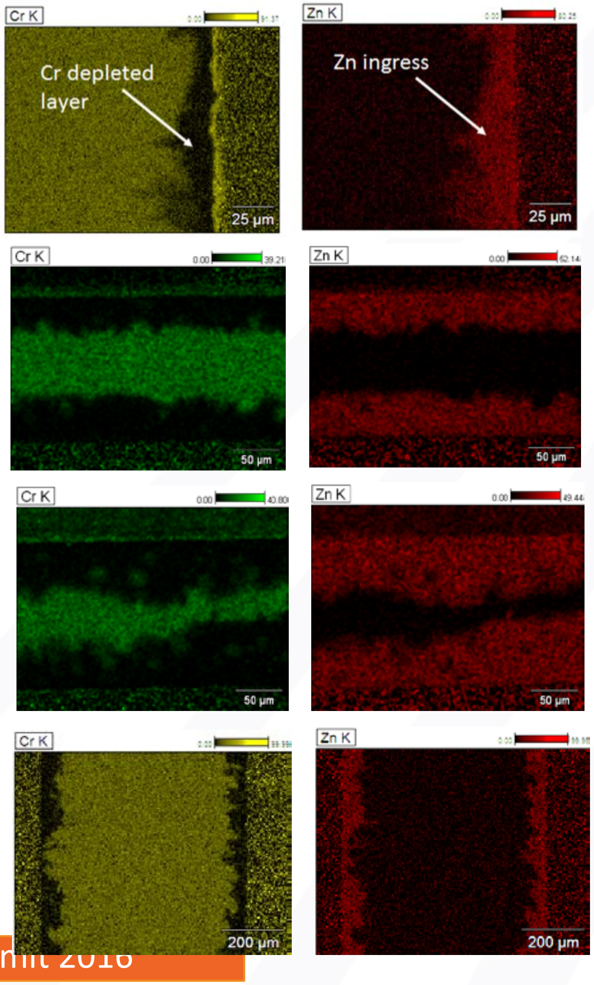


- Coupons held in melt at 800°C for 30 days.

Corrosion Mechanism of Hastelloy C-276 exposed to $ZnCl_2$-based salts at 800°C:

- *It is established that Zn substitute Cr in C-276 Hastelloy exposed to $ZnCl_2$-based salt at 800°C.*
- *The rate of corrosion increases with $ZnCl_2$ content as demonstrated by EDS mapping.*

EDS mapping



Salt Composition:	Corrosion Depth:
44.3% $ZnCl_2$	**20-40 µm/month**
50% $ZnCl_2$	**30-50 µm/month**
75% $ZnCl_2$	**40-60 µm/month**
100% $ZnCl_2$	**50-75 µm/month**

Corrosion Mechanism of Hastelloy C-276 exposed to $ZnCl_2$-based salts at 800°C:

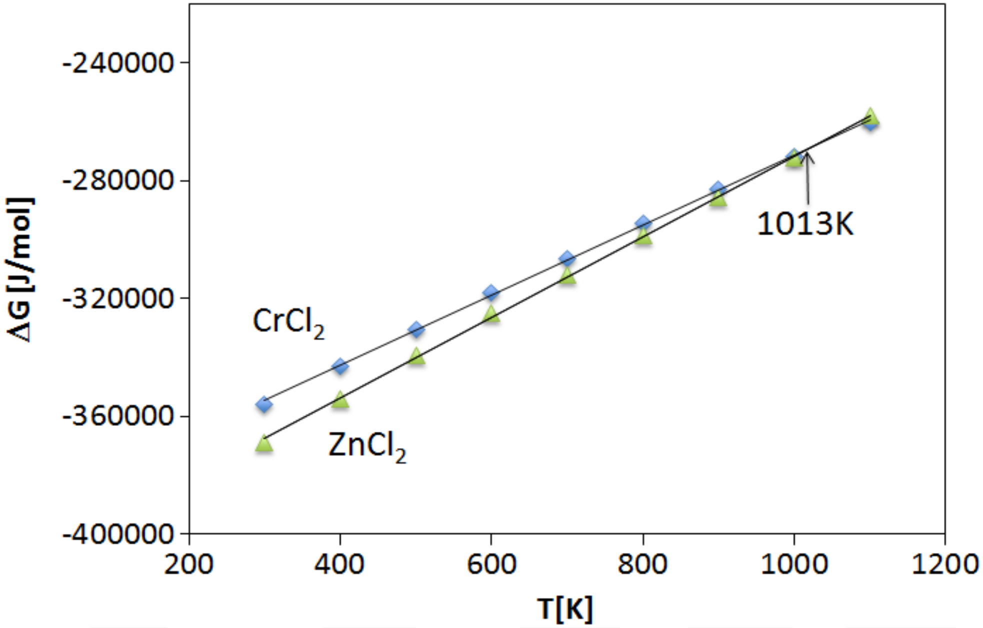
- ***Thermodynamic calculation provide theoretical corroboration of this process and predict that Cr is unstable against $ZnCl_2$ oxidation at temperature larger than 740°C.***

$Cr + ZnCl_2 \rightarrow Zn + CrCl_2$

$\Delta G_r = \Delta G_1 - \Delta G_2$

ΔG_1: $Cr + Cl_2 \rightarrow CrCl_2$

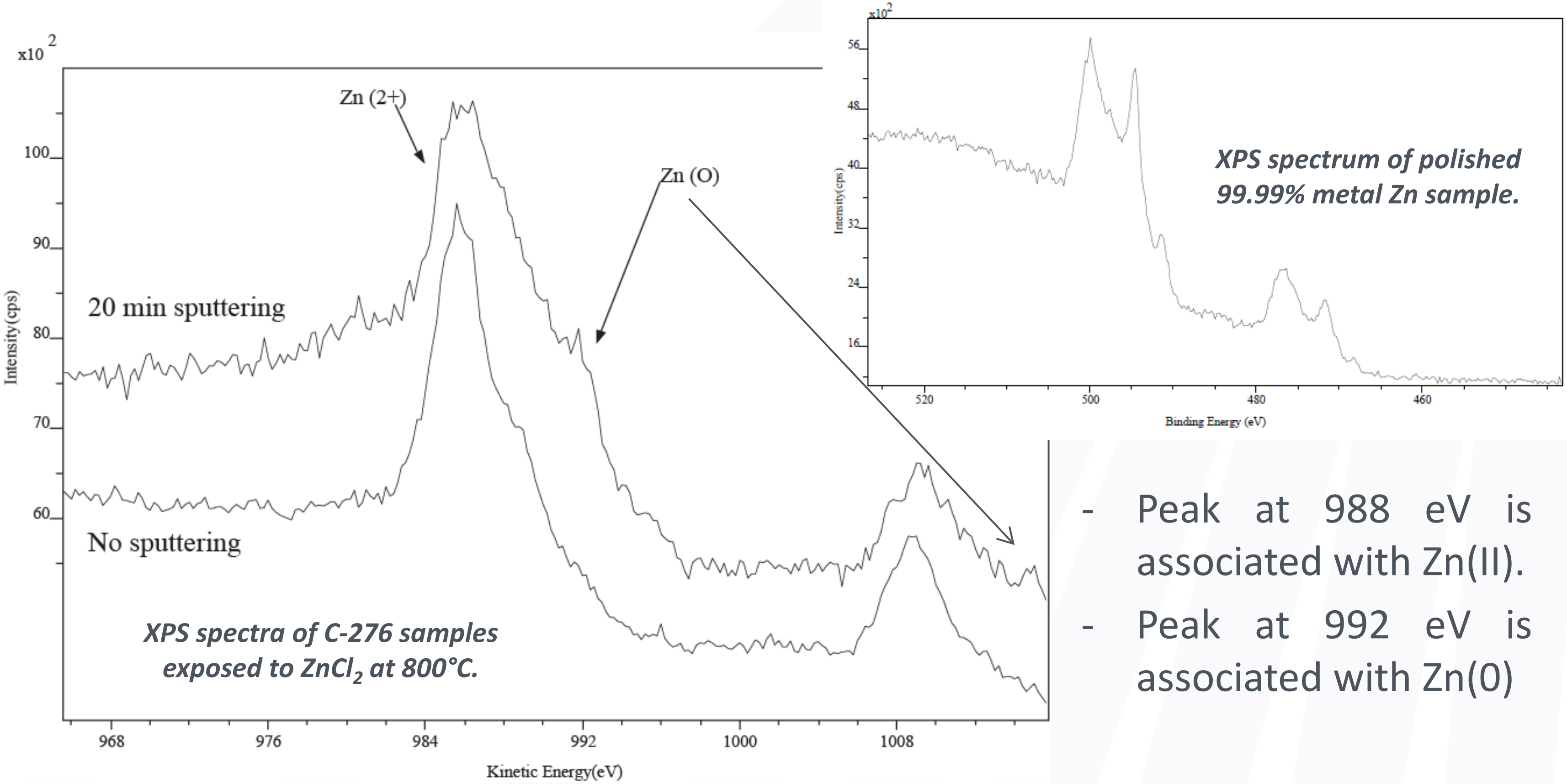
ΔG_2: $Zn + Cl_2 \rightarrow ZnCl_2$



- Ellingham diagram demonstrate that $ZnCl_2$ should be reduced by Cr at any temperature above 1,013 K (740°C) : $\Delta G_r < 0$

Corrosion Mechanism of Hastelloy C-276 exposed to $ZnCl_2$-based salts at 800°C:

- *Cr to Zn substitution mechanism involves Cr oxidation followed by Zn metal embrittlement.*
- *XPS indicates evidence for metallic Zn in C-276 exposed to $ZnCl_2$-based slats at 800°C.*



XPS spectra of C-276 samples exposed to $ZnCl_2$ at 800°C.

XPS spectrum of polished 99.99% metal Zn sample.

- Peak at 988 eV is associated with Zn(II).
- Peak at 992 eV is associated with Zn(0)

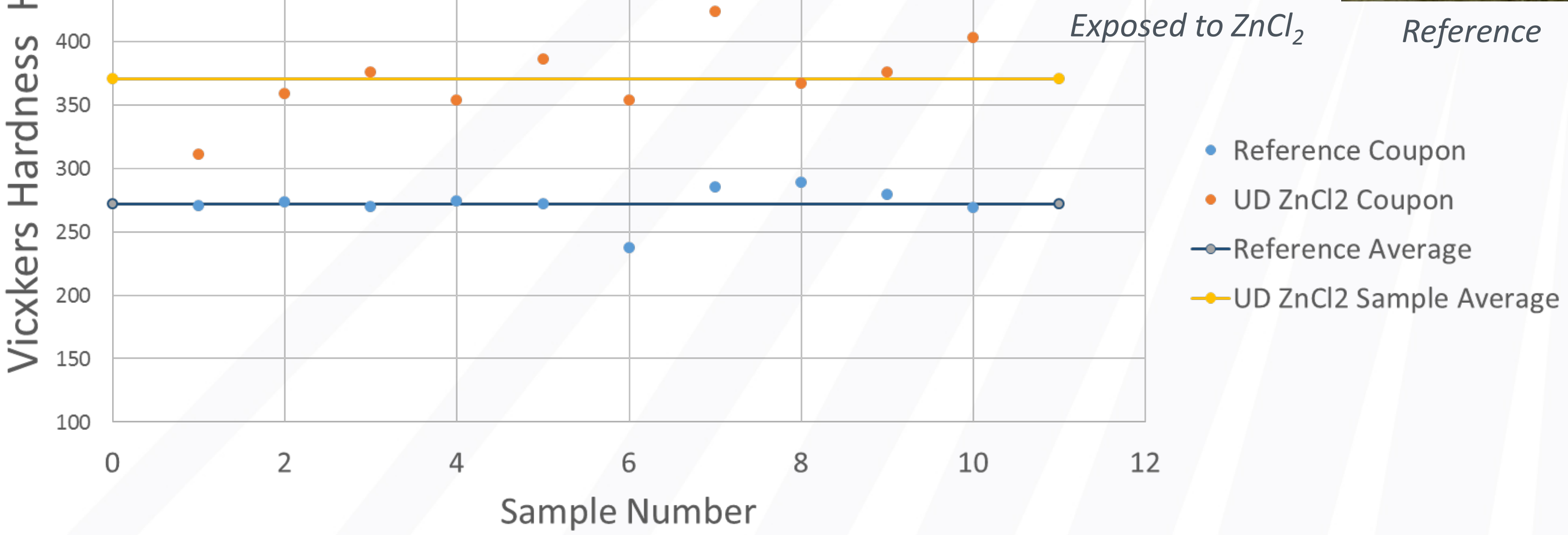
- *Measurement is complicated by the rapid oxidation of Zn metal surface in ambient atmosphere as demonstrated by spectrum of Zn metal 99.99%*

Corrosion Mechanism of Hastelloy C-276 exposed to $ZnCl_2$-based salts at 800°C:

- *Zn embrittlement leads to changes in mechanical properties of the alloys*
- *Exposed samples show increase in hardness characteristic of embrittlement that leads to decrease in fracture toughness.*
- *Tensile strength measurements will be performed as well.*

Exposed to $ZnCl_2$

Reference



Reference sample: Average = 271.94, St. Dev. = 13.11
UD ZnCl2 sample: Average = 370.69, St. Dev. = 29.01

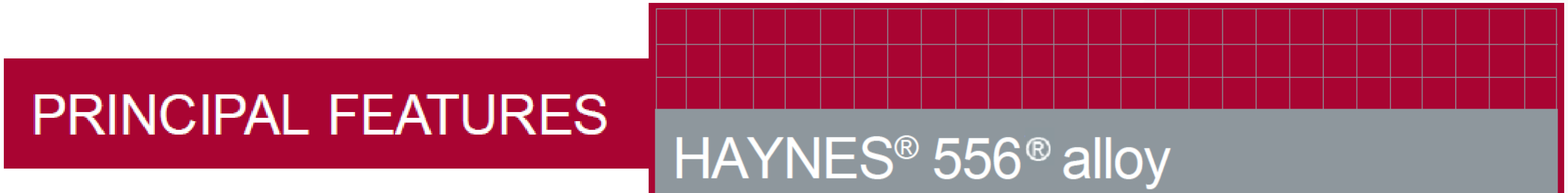
Corrosion Mechanism of Hastelloy C-276 exposed to $ZnCl_2$-based salts at 800°C:

Conclusions:

- *Hastelloy C-276 is not thermodynamically stable in molten salts containing $ZnCl_2$ at temperature of 800°C and above (confirmed by both thermodynamic calculation and EDS).*
- *In this range of temperatures Cr is oxidized while $ZnCl_2$ is reduced to metallic Zn which leads to Zn embrittlement (confirmed by XPS).*
- *Zn embrittlement leads to loss of mechanical properties of the Hastelloy.*
- ***Hastelloy is not a safe material for storage of $ZnCl_2$-based salts at temperature of 800°C and above.***

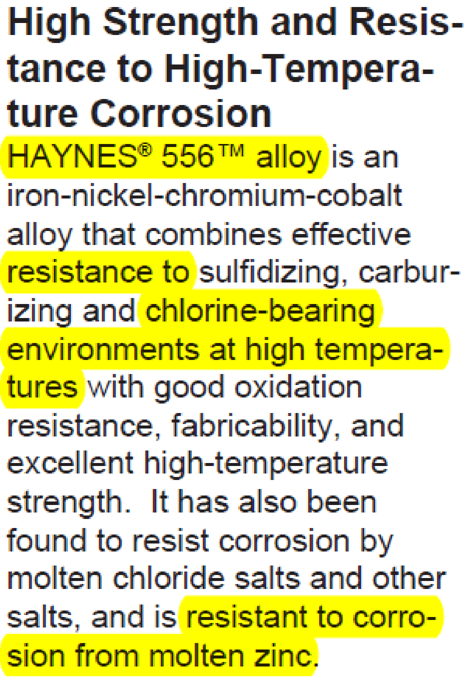
Remediation of Structural Alloy Corrosion Exposed to $ZnCl_2$-based salts at 800°C:

- *Since Zn embrittlement is the source of reduction in mechanical resistance on epotential remedial strategy involves the use of New Alloys preventing Zn embrittlement: Haynes 556*



PRINCIPAL FEATURES

HAYNES® 556® alloy



High Strength and Resistance to High-Temperature Corrosion

HAYNES® 556™ alloy is an iron-nickel-chromium-cobalt alloy that combines effective resistance to sulfidizing, carburizing and chlorine-bearing environments at high temperatures with good oxidation resistance, fabricability, and excellent high-temperature strength. It has also been found to resist corrosion by molten chloride salts and other salts, and is resistant to corrosion from molten zinc.

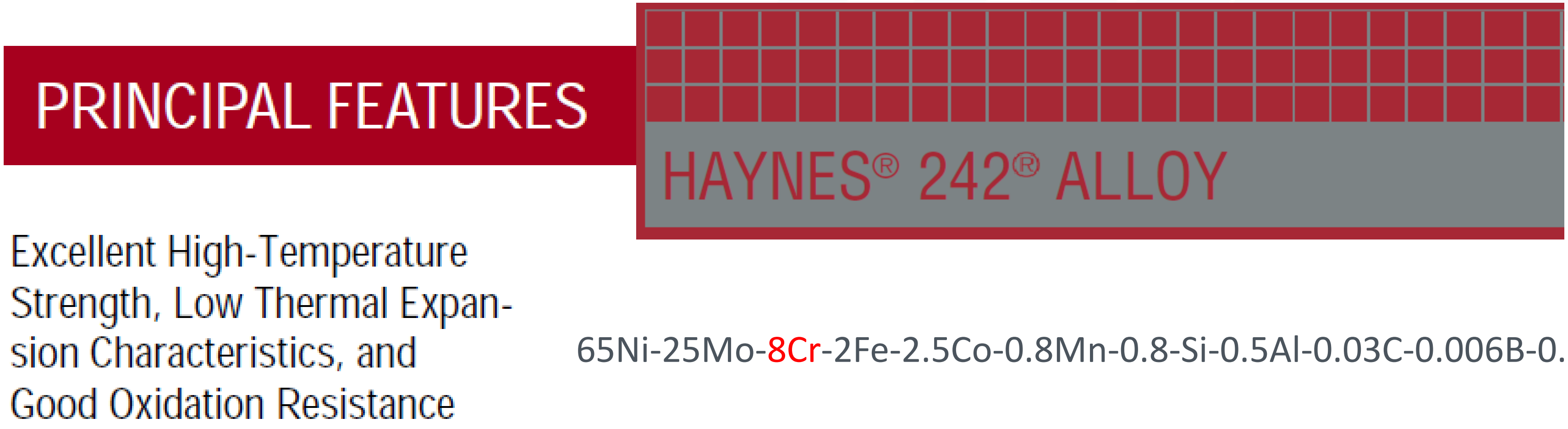
31Fe-22Cr-20Ni-18Co-3Mo-2.5W-1Mn-0.6Ta-0.4Si-0.2N-0.2Al-0.10C-0.02La-0.02Zr

- *Designed for high temperature operation up to 1175°C.*
- *Low Cr content.*
- *Resistance to Zn embrittlement.*
- *Resistance to chlorine environment at high temperature.*

- Currently being tested in $ZnCl_2$ at 800°C for 1 month.

Remediation of Structural Alloy Corrosion Exposed to $ZnCl_2$-based salts at 800°C:

- *Since Cr is the main element undergoing reaction with $ZnCl_2$ new alloys with low Cr content should reduce the Cr activity and consequently lower the reaction free energy.*
- *Lower free energy of reaction may enable operation above 800°C.*



PRINCIPAL FEATURES

HAYNES® 242® ALLOY

Excellent High-Temperature Strength, Low Thermal Expansion Characteristics, and Good Oxidation Resistance

65Ni-25Mo-8Cr-2Fe-2.5Co-0.8Mn-0.8-Si-0.5Al-0.03C-0.006B-0.5Cu

- ***Good oxidation resistance above 800°C***
- ***Low Cr content.***
- ***Resistant to halide environments***

- Currently being tested in $ZnCl_2$ at 800°C for 1 month.

Remediation of Structural Alloy Corrosion Exposed to $ZnCl_2$-based salts at 800°C:

- ***New alloys with Al content for formation of refractory Al_2O_3 passivation layer.***
- ***Insoluble and high density Al_2O_3 passivation layer should prevent diffusion of Zn^{2+} and alleviate corrosion.***

HIGH-TEMPERATURE A NEW ALLOY CONCEPT **HAYNES International**

HAYNES® HR-224® alloy

48.7Ni-27.5Fe-20Cr-3.8Al

- ***High temperature oxidation resistance.***
- ***Operation up to 982°C.***
- ***Al_2O_3 scale formation.***

HAYNES® 214® ALLOY

75Ni[a]-16Cr-4.5Al-3Fe-0.5Mn-0.2Si-0.1Zr-0.05C-0.01B-0.01Y

- ***High temperature oxidation resistance.***
- ***Operation up to 955°C.***
- ***Al_2O_3 scale formation.***
- ***Resistance to chlorine environments***

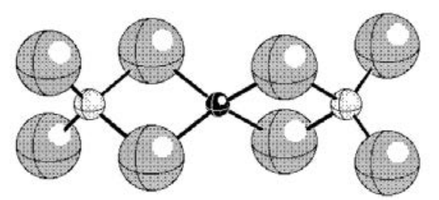
- Currently being tested in $ZnCl_2$ at 800°C for 1 month.

Remediation of Structural Alloy Corrosion Exposed to $ZnCl_2$-based salts at 800°C:

Complexation of Zn with $AlCl_3$:

- ***Addition of $AlCl_3$ to lower Zn chemical potential and raise free energy of reaction.***
- ***Complexation reaction generate product of lower energy: stabilizes Zn.***
- ***Lower free energy of reaction would permit to use Cr based alloys at temperature above 800°C.***

$AlCl_3$ is a Lewis acid that forms stable complex with $ZnCl_2$ such as $ZnAl_2Cl_8$. The presence of these complexes in the molten salt has been evidence by IR spectroscopy.



Stable complexes such as $ZnAl_2Cl_8$ will lower the chemical potential of Zn.

ADVANTAGES

- Cost reduction by 30-40%
- Lower vapor pressure
- Lower melting point

DRAWBACK

- $AlCl_3$ highly hygroscopic complicates CSP salt preparation. (*However, $AlCl_3$ is produced industrially at very low cost so effective preparation method must be available and could be leveraged for CSP salt production*).

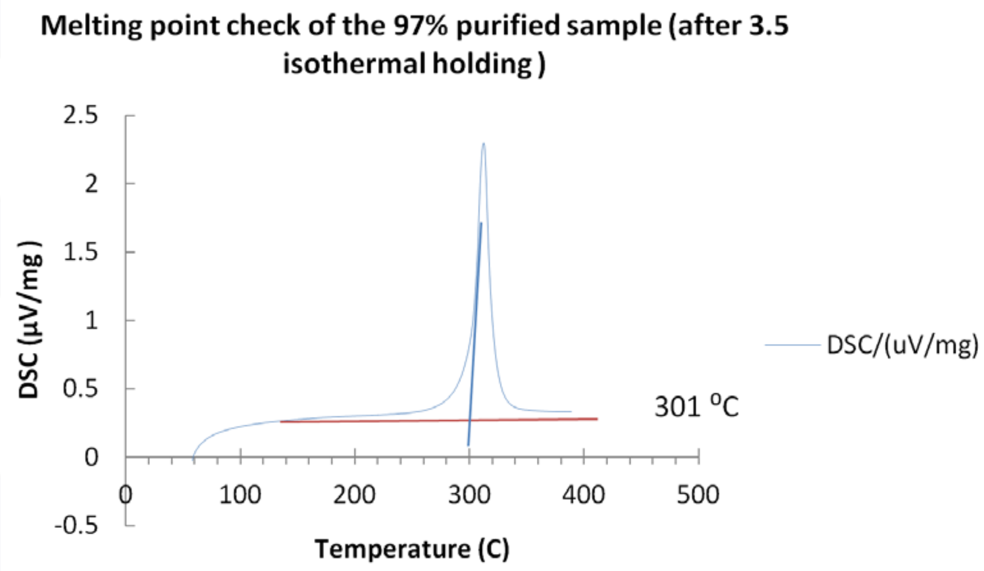
Remediation of Structural Alloy Corrosion Exposed to $ZnCl_2$-based salts at 800°C:

Conclusions:

- *Four approaches are currently being tested experimentally to alleviate corrosion of structural alloys in $ZnCl_2$ based salts:*
- *Use of novel alloys designed to prevent Zn embrittlement: Haynes 556.*
- *Use of novel alloys with low Cr content: Haynes 242*
- *Use of novel alloys producing Al_2O_3 passivation: Haynes 224 and 214*
- *Reduce chemical potential of Zn by complexation with $AlCl_3$ to reduce free energy of reaction and extend temperature stability range.*

Purification of industrial grade $ZnCl_2$:

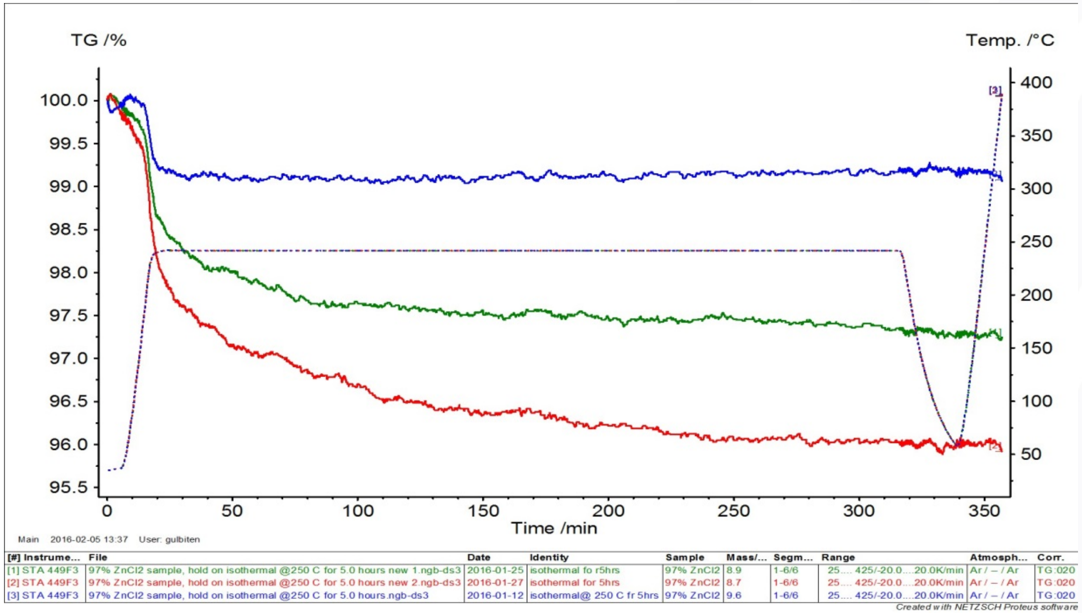
- ***Objectives***: Low cost $ZnCl_2$ contain significant amounts of water contamination and must be purified before use in CSP systems.
- ***Methods***: In order to simulate a process that is compatible with industrial CSP salt production, medium size samples of 97% $ZnCl_2$ (tens of g) are purified by heating at 250°C under an argon flow (10ml/min/cm^2) .
- ***Results***: Successful drying is achieved after 3.5 h.



- *Extent of purification is assessed calorimetrically by measuring the melting point of the purified ZnCl2 salts.*
- *The melting point is raised to the max level obtained previously under vacuum heating.*

Purification of industrial grade $ZnCl_2$:

- ***Objectives***: Low cost $ZnCl_2$ contain significant amounts of water contamination and must be purified before use in CSP systems.
- ***Results***: Purification time of 3.5 hours is consistent with mass loss plateau observed by gravimetry. It is also found that low cost $ZnCl_2$ are rather inhomogeneous and contain varying amount of water contamination.



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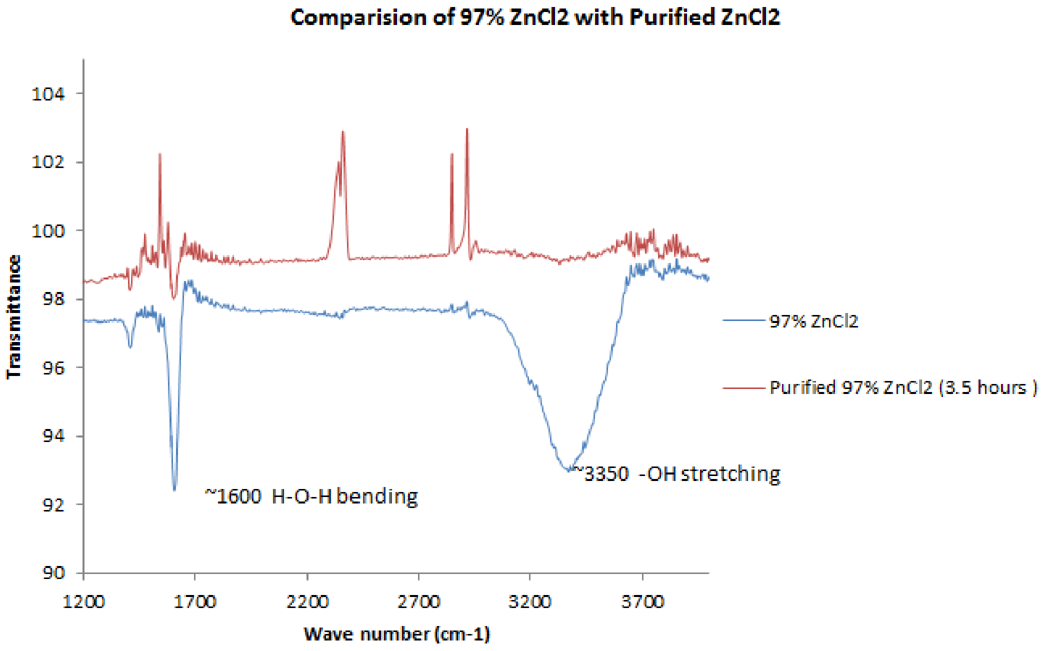
[#] Instrume...	File	Date	Identity	Sample	Mass/...	Segm...	Range	Atmosph...	Corr.
[1] STA 449F3	97% ZnCl2 sample, hold on isothermal @250 C for 5.0 hours new 1.ngb-ds3	2016-01-25	isothermal fo r5hrs	97% ZnCl2	8.9	1-6/6	25.... 425/-20.0....20.0K/min	Ar / – / Ar	TG:020
[2] STA 449F3	97% ZnCl2 sample, hold on isothermal @250 C for 5.0 hours new 2.ngb-ds3	2016-01-27	isothermal for 5hrs	97% ZnCl2	8.7	1-6/6	25.... 425/-20.0....20.0K/min	Ar / – / Ar	TG:020
[3] STA 449F3	97% ZnCl2 sample, hold on isothermal @250 C for 5.0 hours.ngb-ds3	2016-01-12	isothermal@ 250 C fr 5hrs	97% ZnCl2	9.6	1-6/6	25.... 425/-20.0....20.0K/min	Ar / – / Ar	TG:020

Created with NETZSCH Proteus software

- *Gravimetric measurement of 3 different samples of low cost $ZnCl_2$ from the same batch during isothermal treatment at 250°C.*
- *Significant variation in mass loss indicate inhomogeneity in water content within the same batch.*

Purification of industrial grade $ZnCl_2$:

- ***Objectives***: Low cost $ZnCl_2$ contain significant amounts of water contamination and must be purified before use in CSP systems.
- ***Results***: The nature of the contaminant, namely water is confirm spectroscopically by total attenuated reflectance FTIR. The OH bending and stretching bands are indicative of water.
- FTIR also confirms that the purification method is effective at removing water contamination.



- *FTIR spectra of low cost $ZnCl_2$ before and after purification by isothermal treatment at 250°C.*
- *3350 cm^{-1} and 1600 cm^{-1} bands are characteristic water modes.*
- *Positive peaks are artefact from incomplete flushing during background collection.*

Purification of industrial grade $ZnCl_2$:

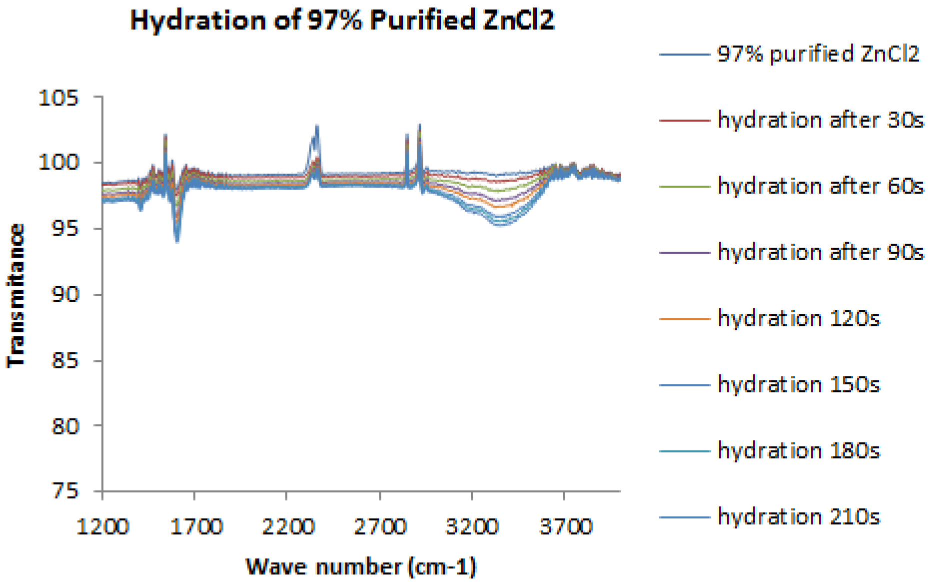
Conclusions:

- *Medium size purification test indicate that low cost $ZnCl_2$ containing water contamination can be effectively purified by heating at 250°C under inert gas flow in 3.5 hours.*
- *Thermal gravimetric analysis corroborate the drying kinetic and show evidence for inhomogeneity in low cost $ZnCl_2$ batches.*
- *FTIR spectroscopy confirms the nature of the contaminant and the effectiveness of the purification method.*
- ***Hydrated industrial salts can be effectively dried with a procedure compatible with large scale production.***

Kinetic of hydration of $ZnCl_2$:

- ***Objectives***: The kinetic of hydration of $ZnCl_2$ is of crucial interest for determining risks associated with air exposure during salt preparation and loading.
- ***Methods***: The kinetic of hydration of $ZnCl_2$ was quantified by monitoring the OH bending and stretching bands of water by total attenuated reflectance FTIR.

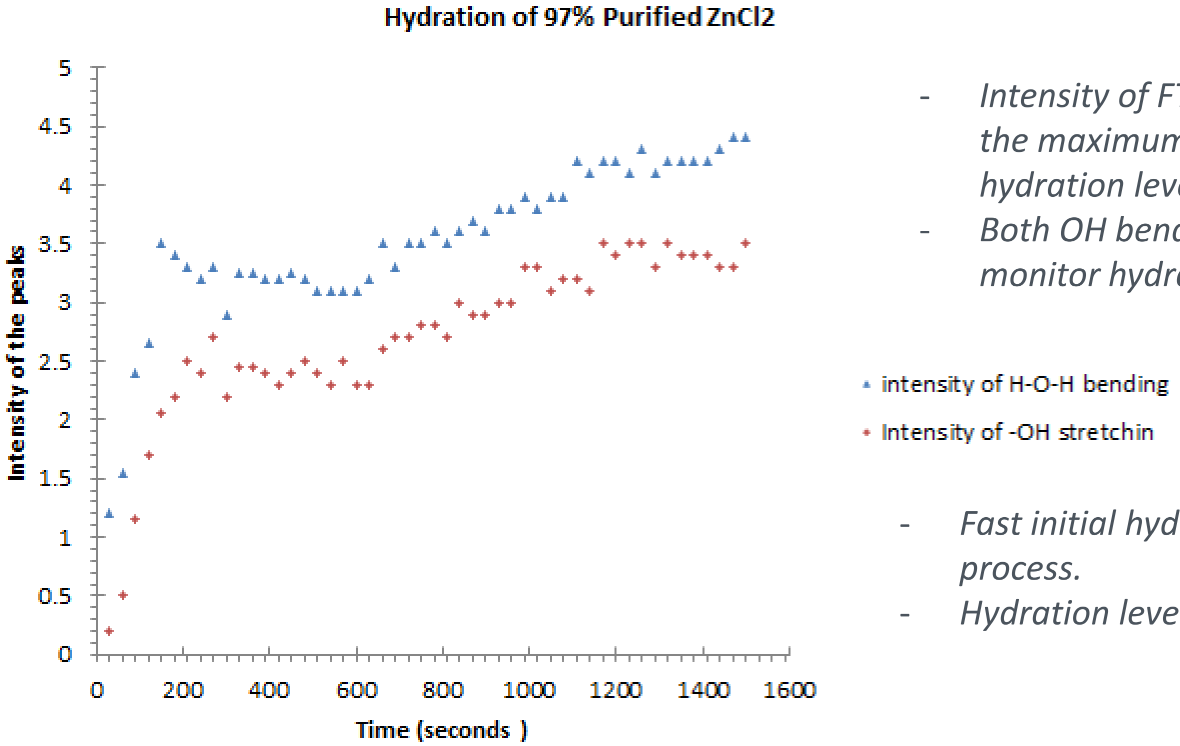
- *A sealed ATR cell previously loaded with $ZnCl_2$ in a glove box is opened to allow contact with air while time dependent FTIR spectra are collected.*



- *FTIR spectra of dried $ZnCl_2$ during the first 3 min of exposure showing growth of the water peaks.*

Kinetic of hydration of $ZnCl_2$:

- ***Objectives***: The kinetic of hydration of $ZnCl_2$ is of crucial interest for determining risks associated with air exposure during salt preparation and loading.
- ***Methods***: The kinetic of hydration of $ZnCl_2$ was quantified by monitoring the OH bending and stretching bands of water by total attenuated reflectance FTIR.



- *Intensity of FTIR absorption peaks with respect to the maximum transmission are used to quantify hydration level.*
- *Both OH bending and stretching modes are used to monitor hydration.*

- *Fast initial hydration step followed by slower process.*
- *Hydration level still increase after 30 min.*

Kinetic of hydration of $ZnCl_2$:

Conclusions:

- *$ZnCl_2$ hydrates rapidly within the first 3 min and then slow down.*
- *Quantitative hydration levels measured by spectroscopy will be determined by corroboration with STA.*
- *Longer exposure time will be performed to observe maximum in hydration.*