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Tritium Gas Stream Scrubbing using In-situ Reactive Materials

Paul Korinko, Simona Murph, and George Larsen

Tritium Focus Group Meeting

LANL Nov 3-5, 2015

SRNL-STI-2015-00597

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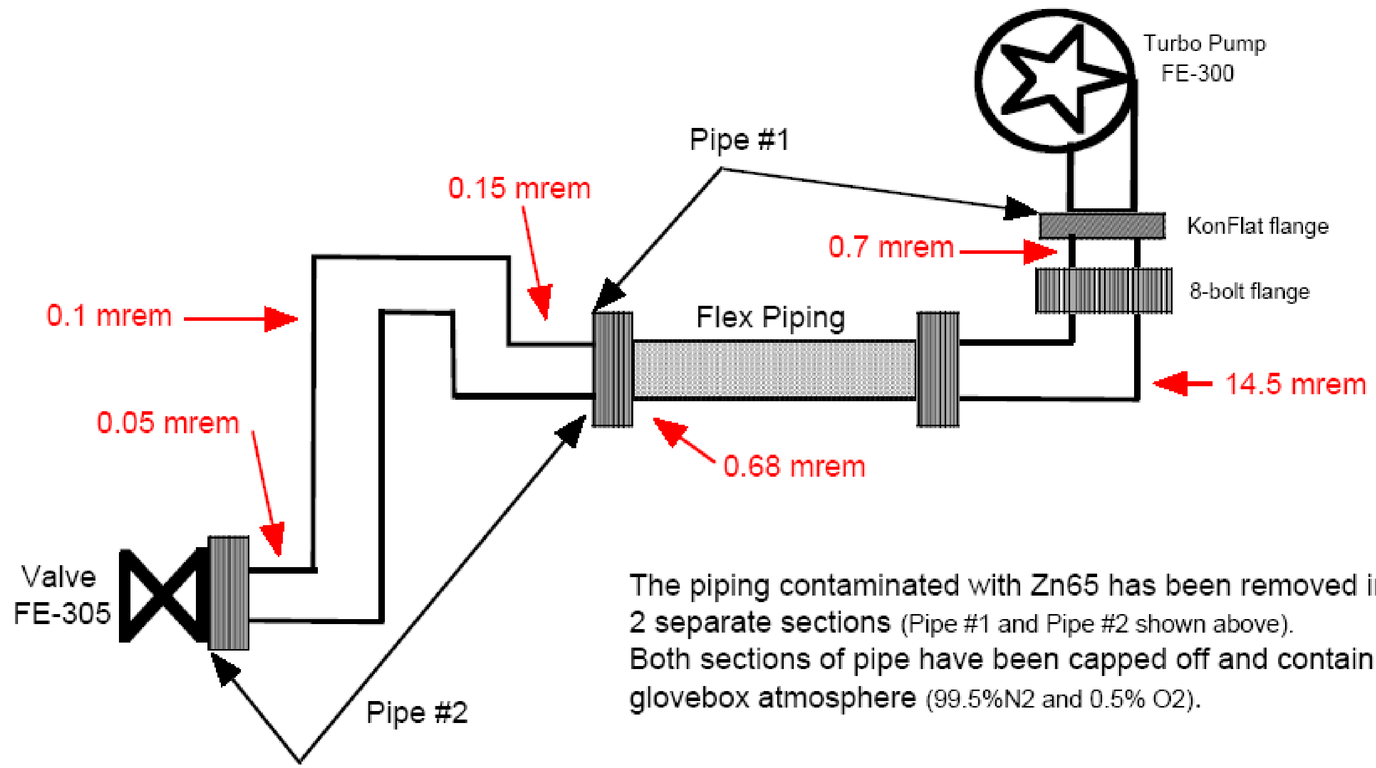
FLUOR • NEWPORT NEWS NUCLEAR • HONEYWELL

Tritium Production and Extraction

- **Tritium Producing Burnable Absorber Rods (TPBARs)**
  - Built to strict materials specifications
    - *Coatings, ceramics, metals, processes*
  - Meet NQA-1 requirements
  - Irradiated in a commercial light water reactor
  - Extracted at SRS in the Tritium Extraction Facility
  - Waste disposed on-site

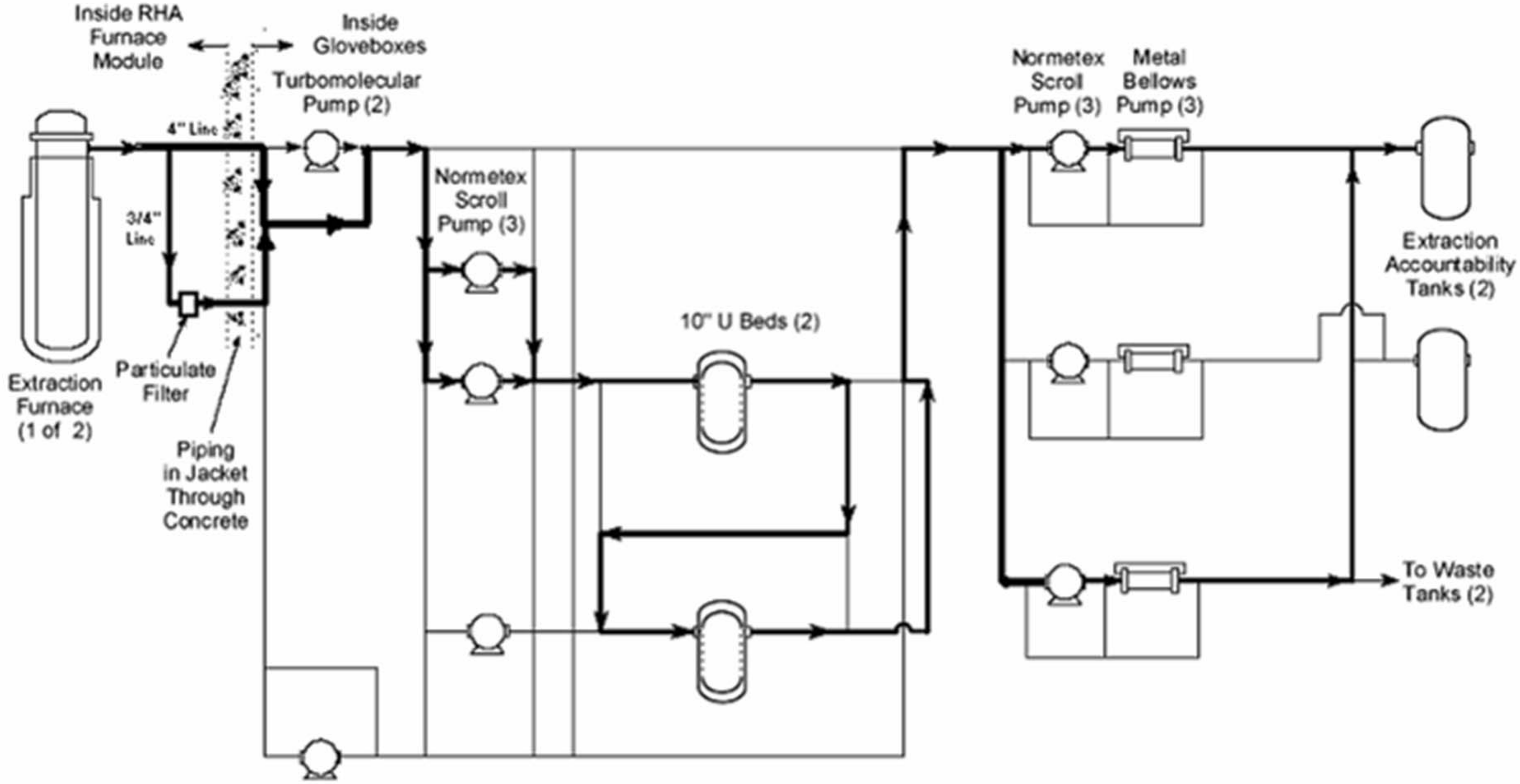
Contamination Measurements – First Full Extraction

Piping Contaminated with Zinc65 in Glovebox-500



The piping contaminated with Zn65 has been removed in 2 separate sections (Pipe #1 and Pipe #2 shown above).
Both sections of pipe have been capped off and contain glovebox atmosphere (99.5%N2 and 0.5% O2).

TEF Furnace Extraction System



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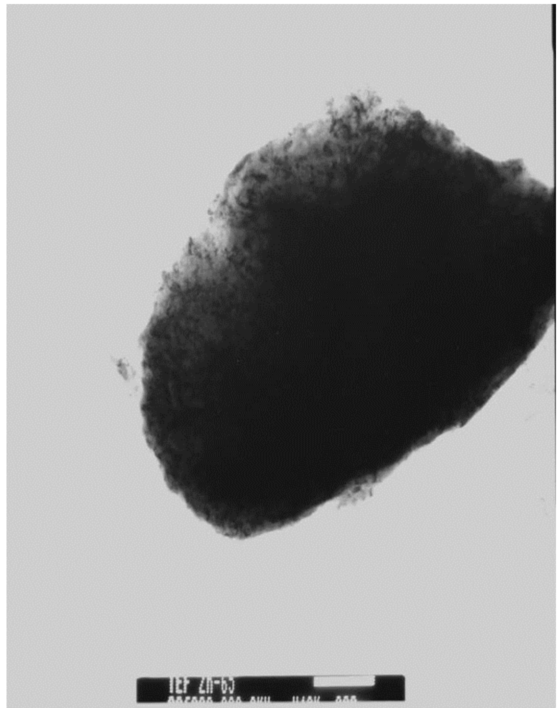
Zn Particle Morphologies

Agglomeration

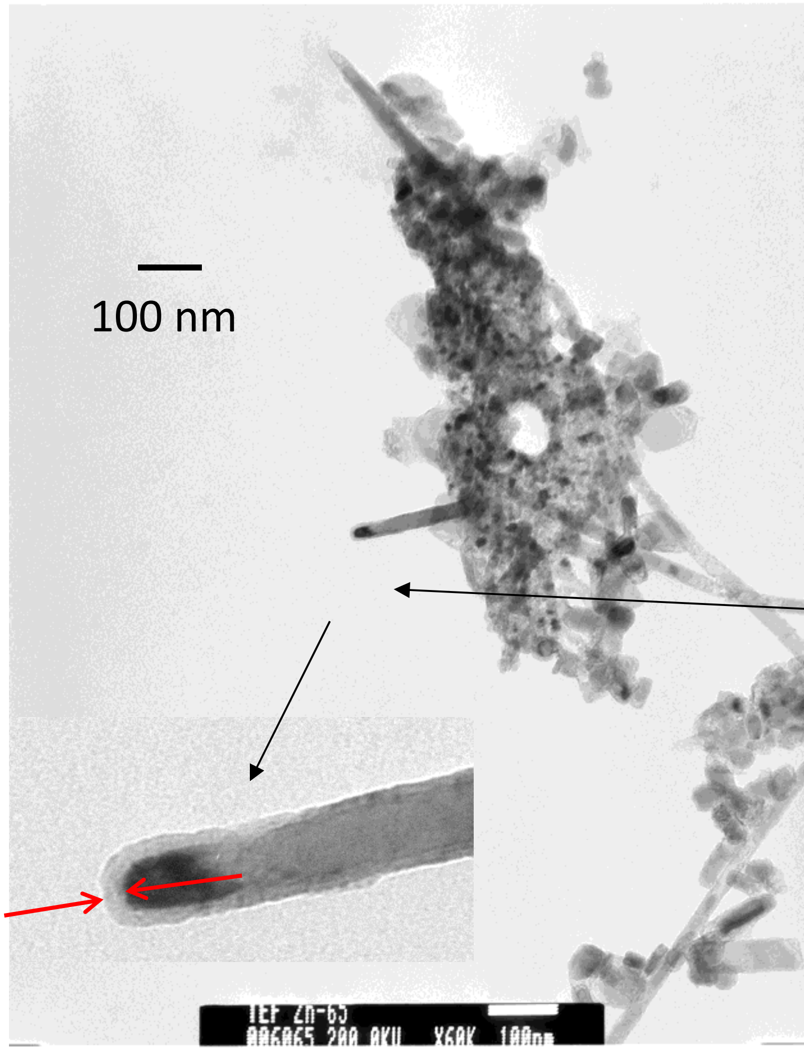


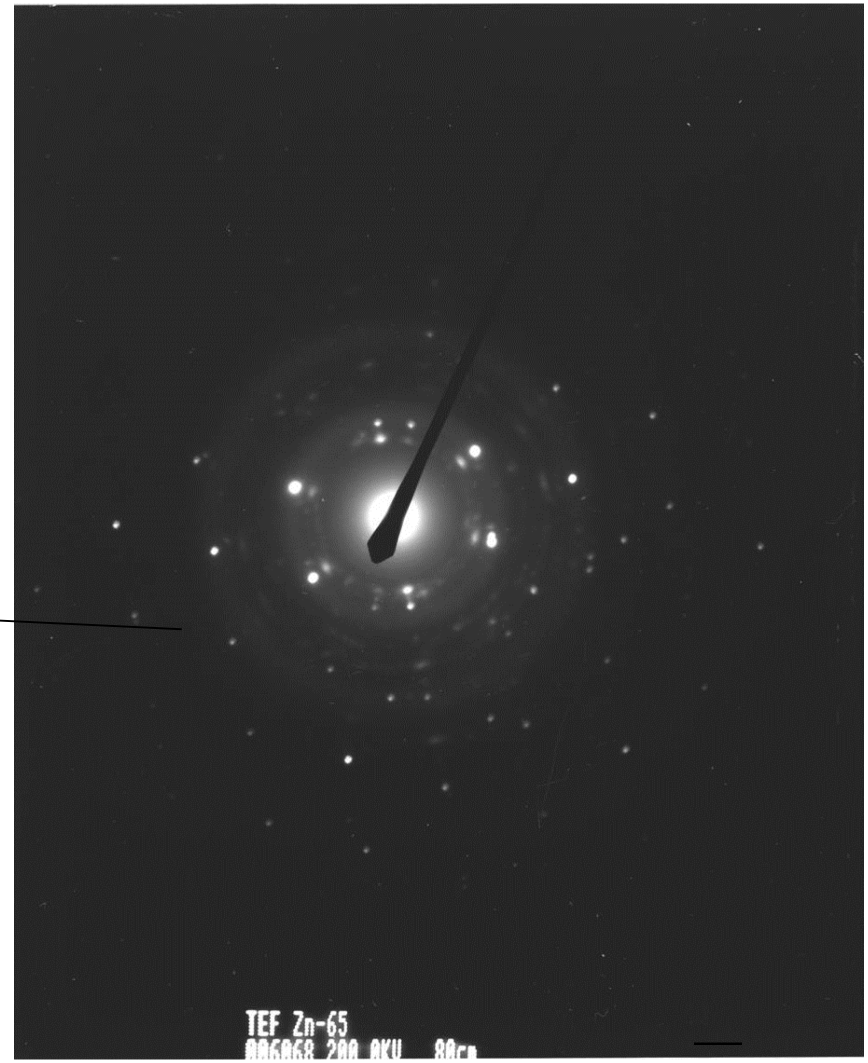
Bushy particles

Fibrous Agglomeration

Deposited as metallic zinc from vapor
Morphology is dependent on deposition conditions

Zinc Particle Characterization

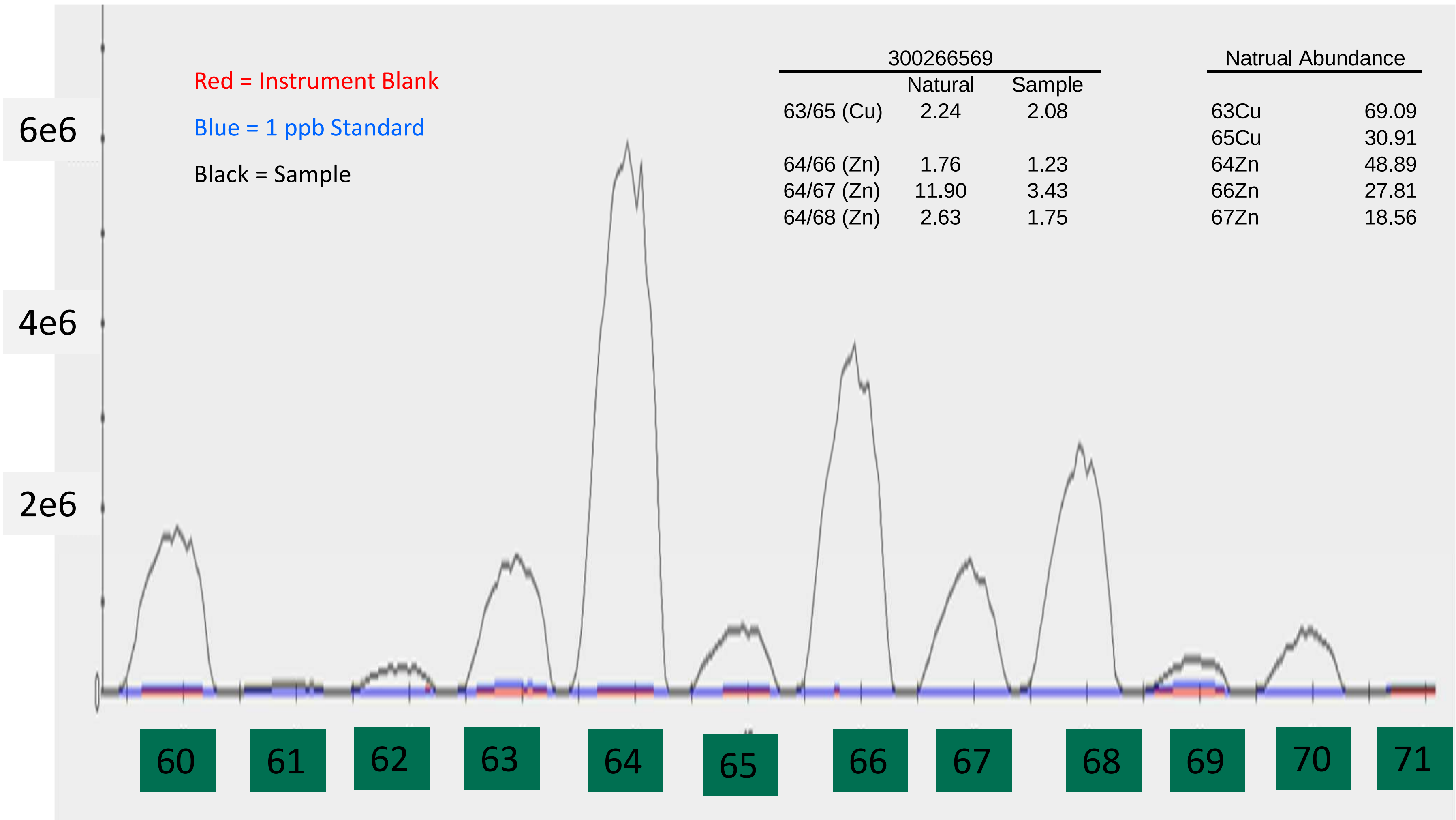




Oxide layer of 3 nm
(ghost on image)

Pattern shows Zn and ZnO 1123
habit plane

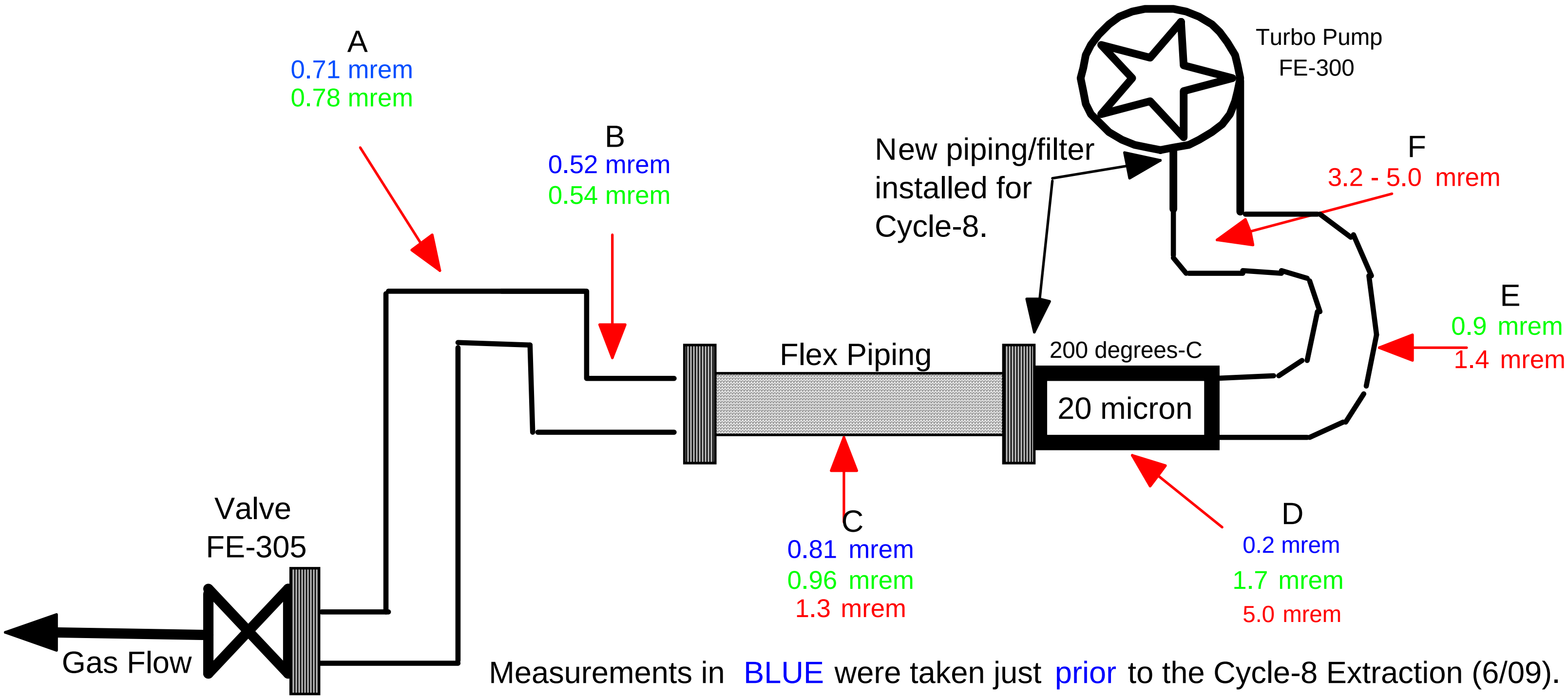
20 Micron Filter – Natural Zinc



	300266569	
	Natural	Sample
63/65 (Cu)	2.24	2.08
64/66 (Zn)	1.76	1.23
64/67 (Zn)	11.90	3.43
64/68 (Zn)	2.63	1.75

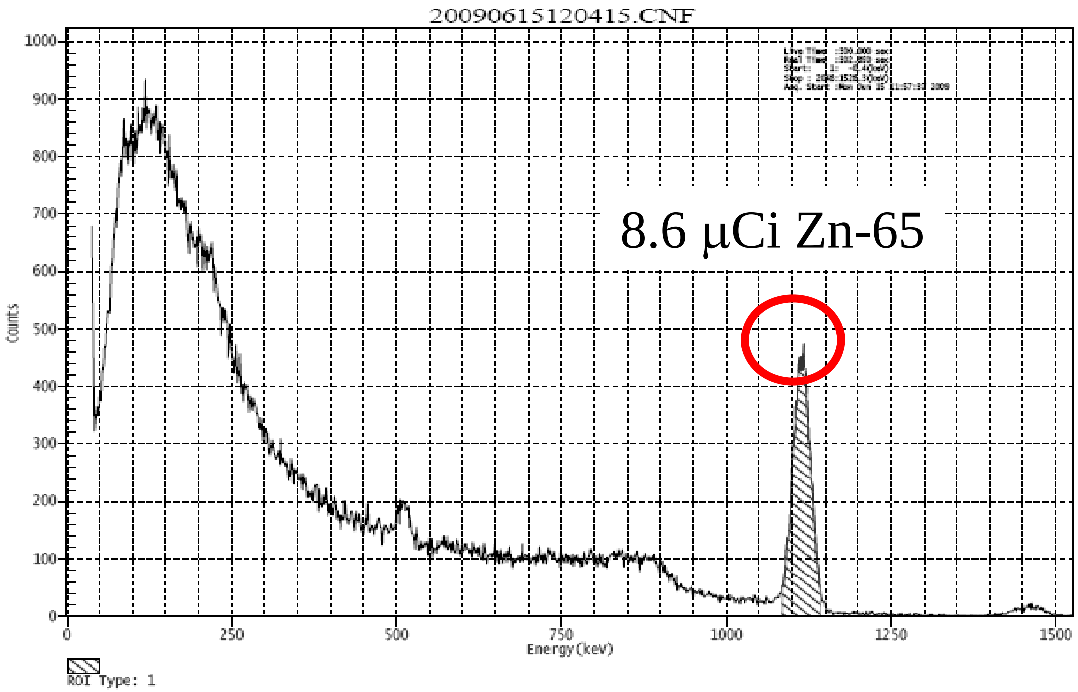
Natrual Abundance	
63Cu	69.09
65Cu	30.91
64Zn	48.89
66Zn	27.81
67Zn	18.56

Process Activation after Cycle 8 Extraction



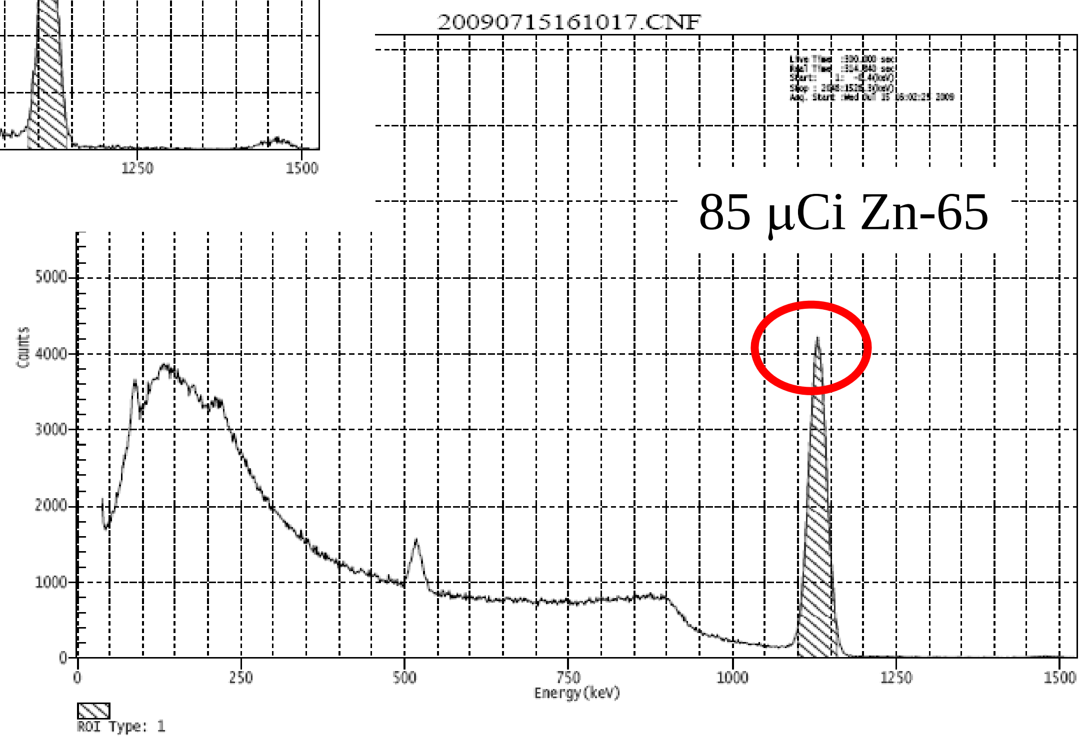
Measurements in BLUE were taken just prior to the Cycle-8 Extraction (6/09).
Measurements in GREEN were taken after the Cycle-8 Extraction w/ insulation (7/09).
Measurements in RED were taken after the Cycle-8 Extraction at contact (7/09).

Spectrum at 20 µm Filter



Before Cycle 8 Extraction

After Cycle 8 Extraction
10X increase in counts



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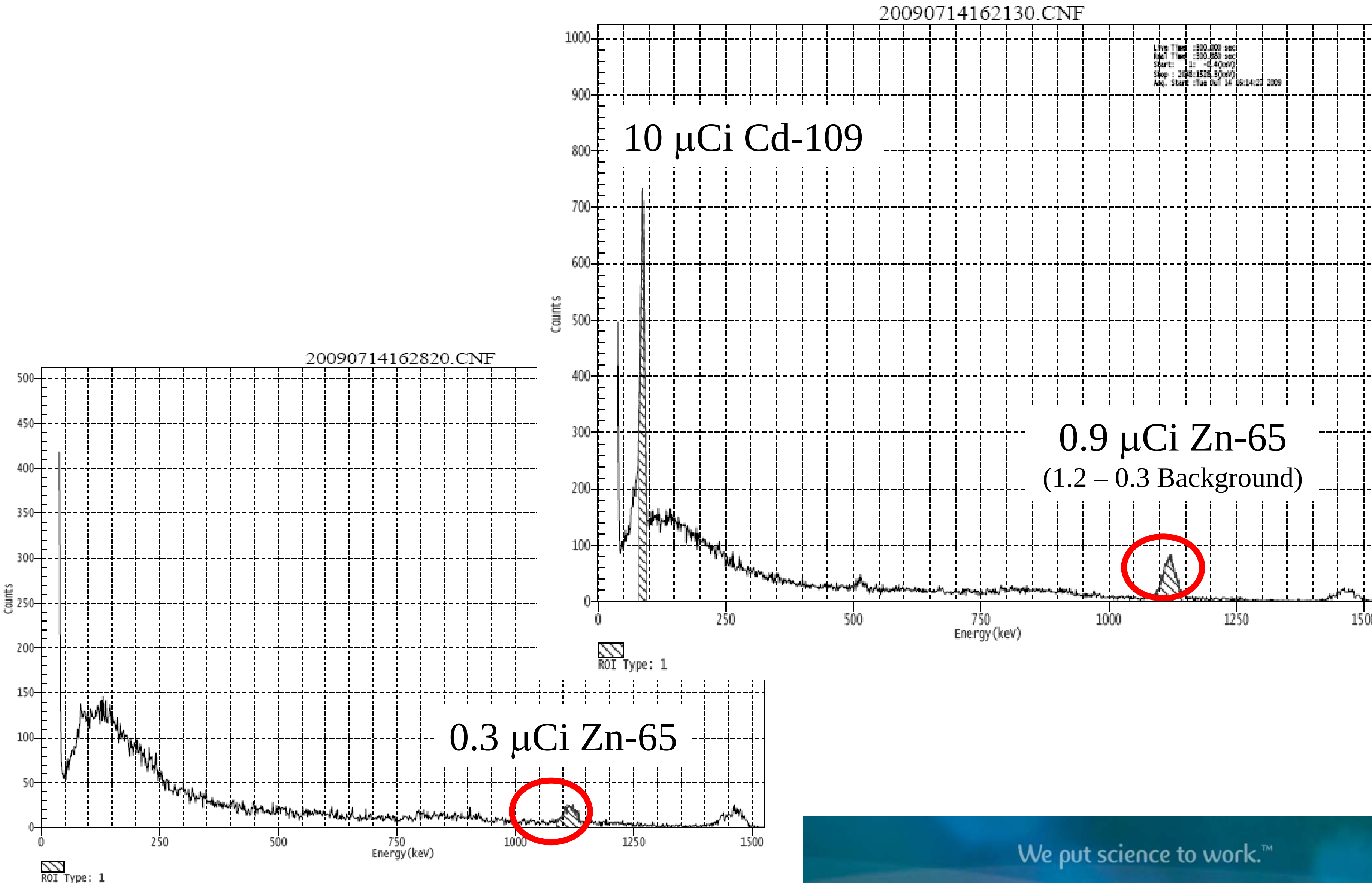
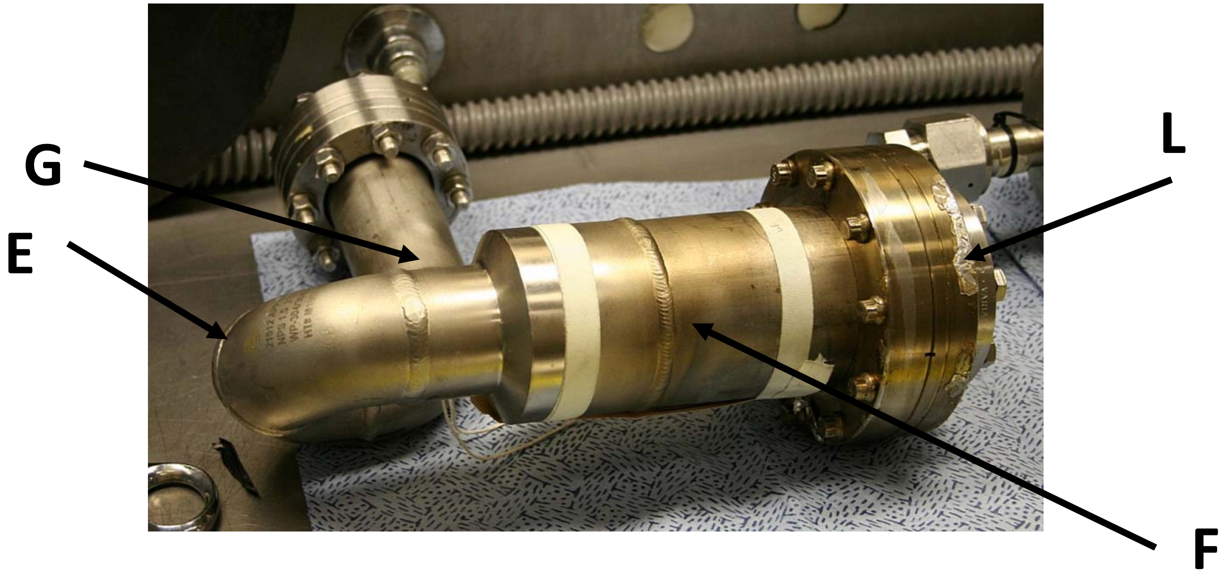
Spectrum from FE-530 Pump Filter (FLT-211) Removed from Process – 11 µm Filter Cy 6 & 7



Gamma Spectroscopy 20 µm Filter Cycle 8



Location	µCi
U-bend (E)	7 +/- 3
Filter and housing (F)	23 +/- 7
Flange on elbow (L)	< 2
Housing w/o filter element (F)	8 +/- 2
Elbow (G)	14 +/- 4

error ± 30%

Low Levels What's the Issue?

- Glovebox is designed for beta (tritium) not gamma
  - *It is difficult to detect / quantify*
- Personnel dose issue as extraction frequency increases
- Shielding opportunities are limited
- New waste stream created
- Prefer to dispose of all contaminants with the extracted TPBARs

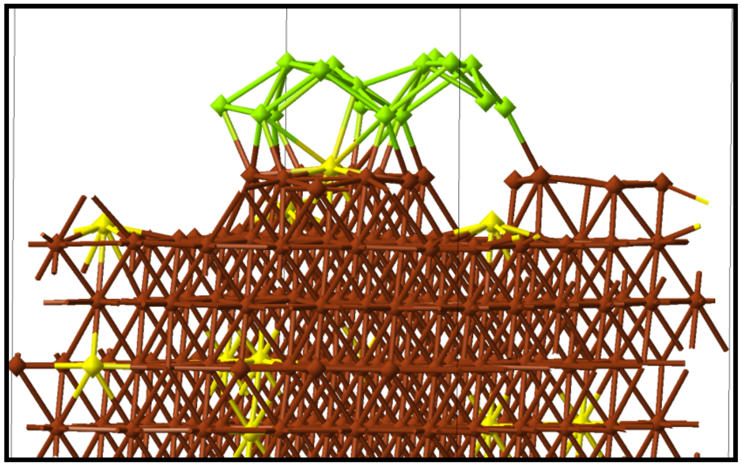
Methods to Contain Zn in Furnace Module

- **Physical trapping**
  - Cold trap
    - *Passive only*
    - *Deleted from original design*
    - *Not possible to reengineer*
- **Chemical trapping**
  - Non-reactive with hydrogen
  - Non-hazardous
  - Limited temperature range – Passive only

Chemical Material Trapping

Zinc Compound Forming	Radioactive, Reactive and Toxic	High Vapor Pressure	Hydride Forming	Remaining
Ag, As, Au, Ba, Ca, Ce, Co, Cr, Cu, Dy, Er, Eu, Fe, Gd, Ho, K, La, Li, Lu, Mn, Mo, Na, Nb, Nd, Ni, P, Pd, Po, Pr, Pt, Pu, Rb, Ru, S, Sb, Sc, Se, Sm, Sr, Ta, Tb, Tc, Te, Th, Ti, Tl, Tm, U, V, Y, Yb, Zr	As, Ce, Po, Pu, Te, Th, U, K, Na,	As, Ba, K, Li, Mg, Na, P, S, Sb, Sr, Se	Ag, Au, Ba, Ca, Ce, Cr, Dy, Er, Gd, Ho, K, La, Lu, Li, Mg, Na, Nb, Nd, Ni, P, Pd, Pr, Pu, Rb, Sm, Sc, Sr, Ta, Tb, Th, Ti, U, V, Y, Zr	Co, Cu, Mn, Mo, Pt, Ru

Calculation for Copper-Tin Alloy



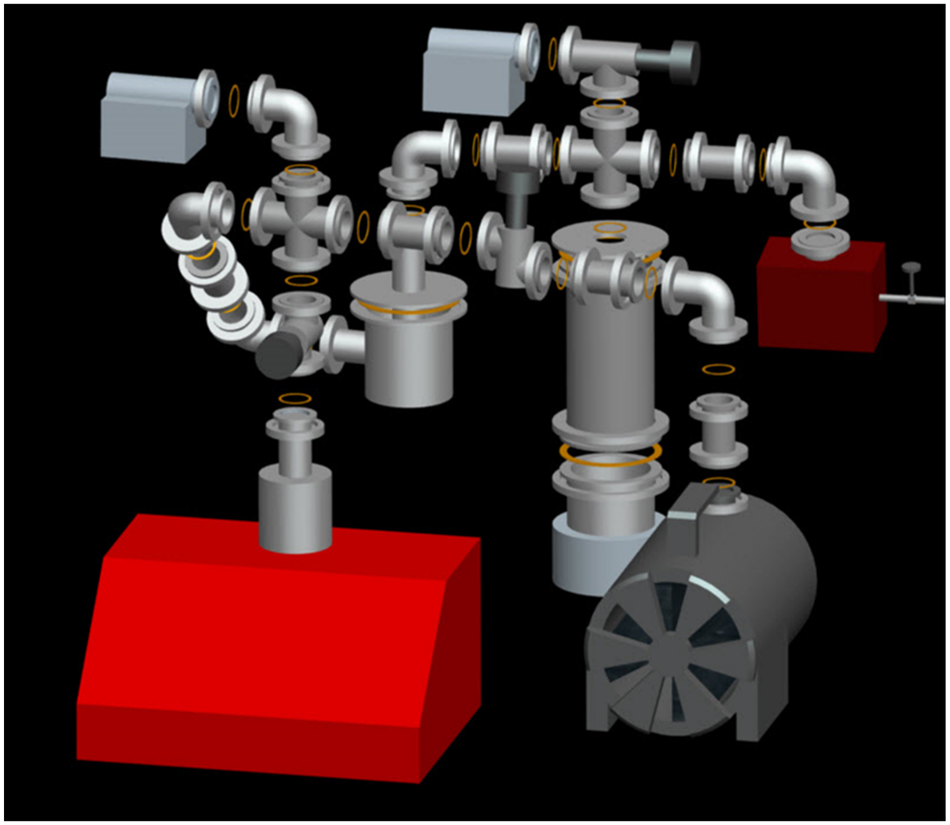
Preliminary results from the DFT modeling showing copper (rust) with tin (yellow) and zinc (green) deposits with the zinc preferentially depositing over the Sn when it is below the surface.

Courtesy: L. Roy

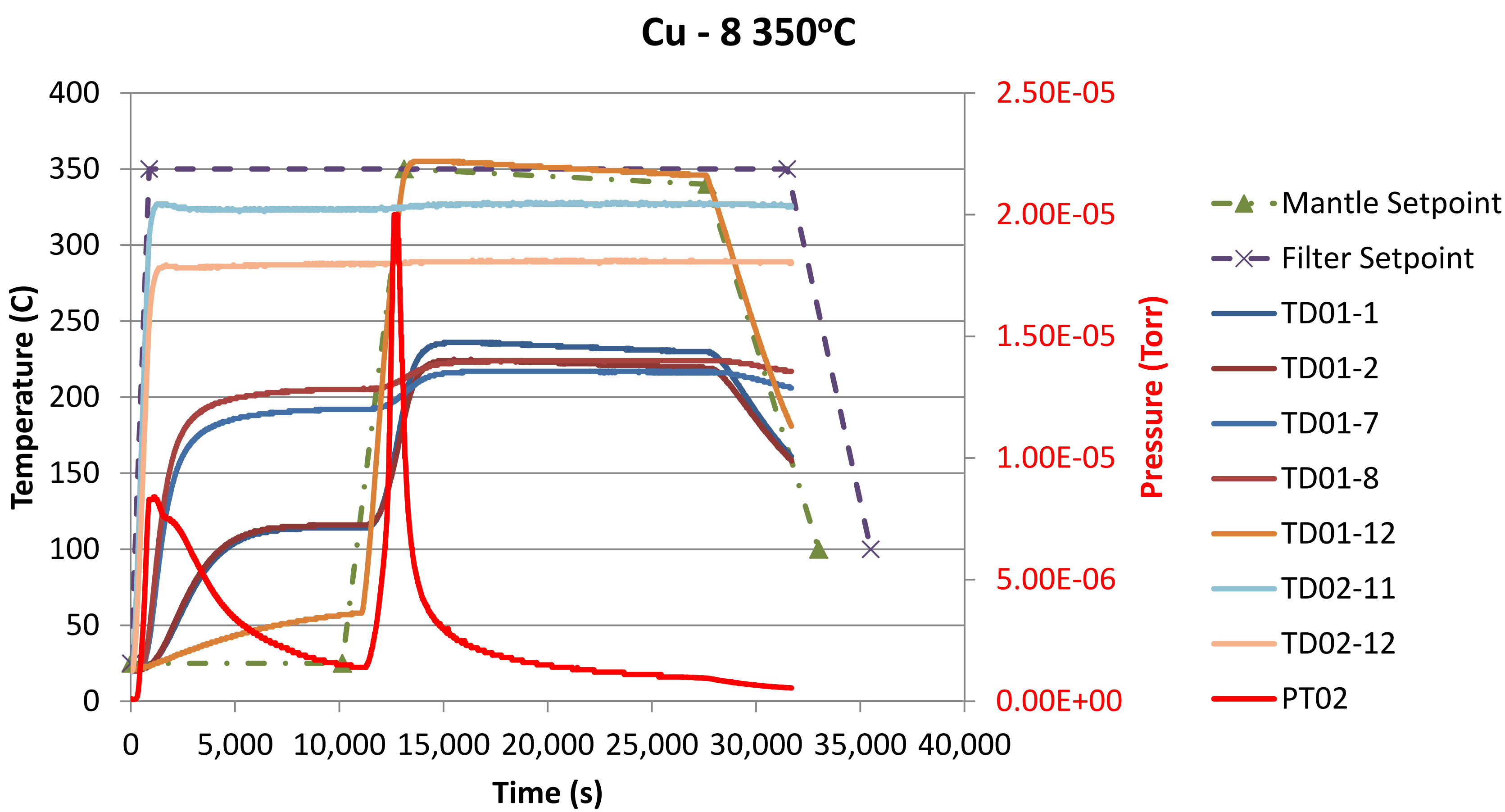
High Vacuum Zinc Deposition System

- **Design system for high vacuum with physical traps**
- **Utilize all metal seals**
  - Achieved 10^{-7} Torr
- **Conduct parametric testing**
  - Filter 250-500°C / 4 hours & Source 350°C
- **Test pure copper and bronze alloys**
  - PNNL comments suggest Sn additions may improve capture
- **Develop new materials if needed**
- **Determine stability**
- **Determine reactivity after simulated process**

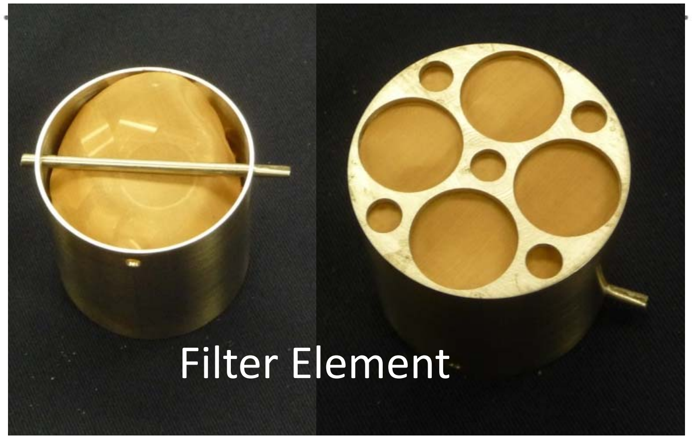
Zinc Deposition and Trapping System

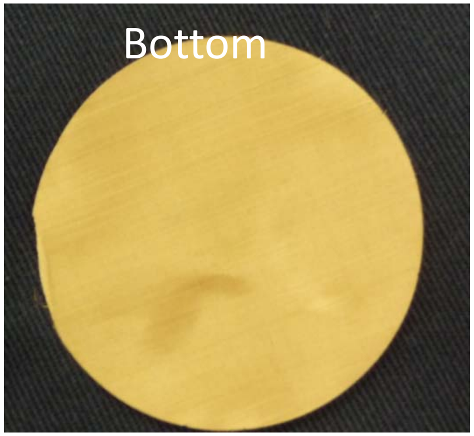


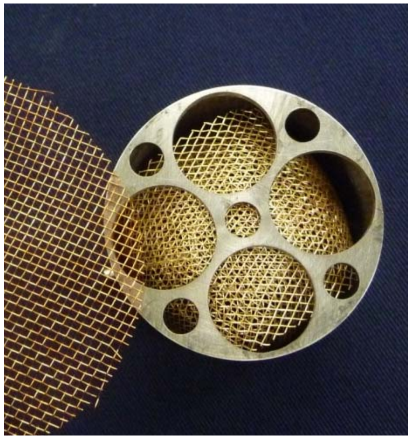
Reactive Zinc Capture on Copper

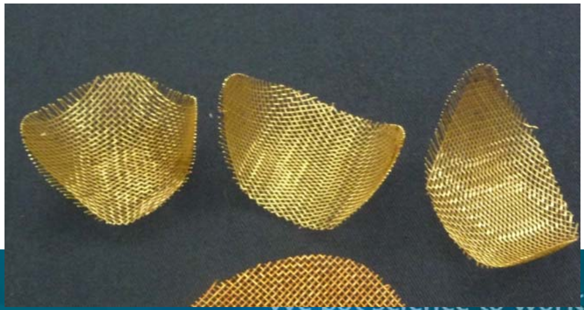


350°C Deposition

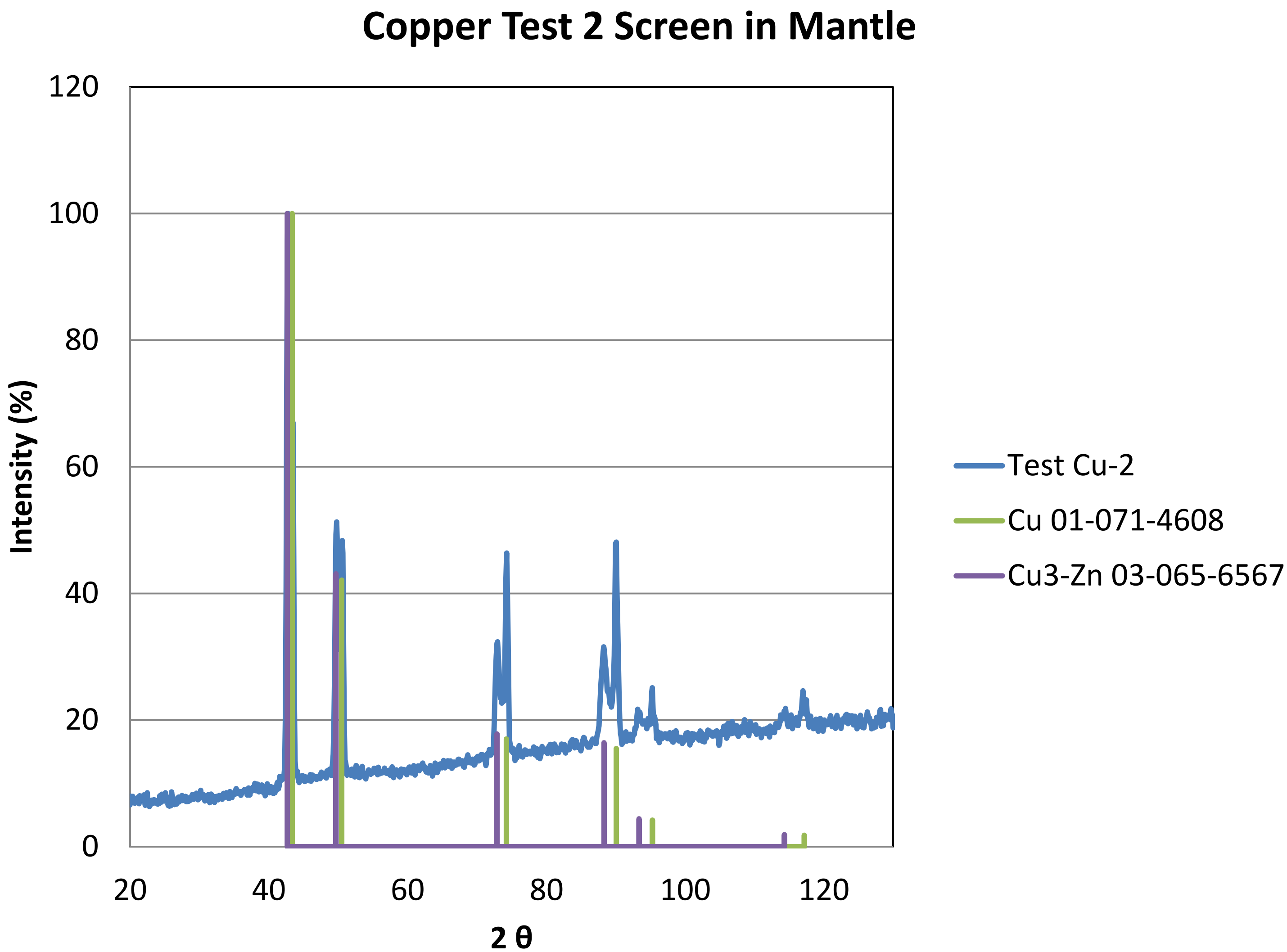




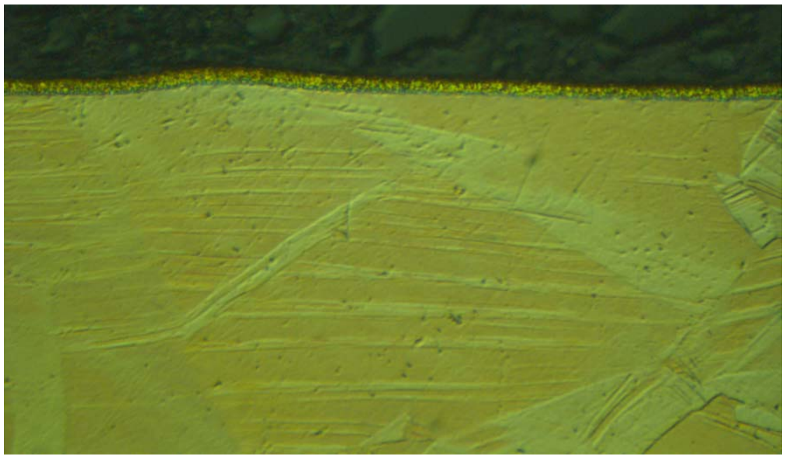


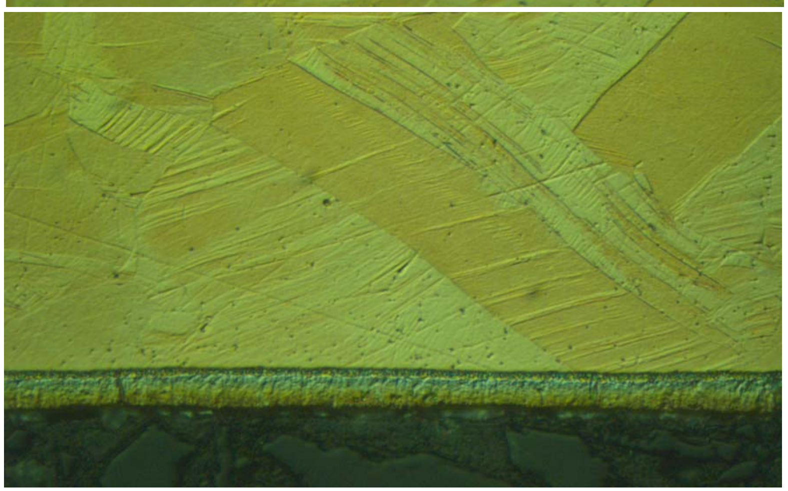


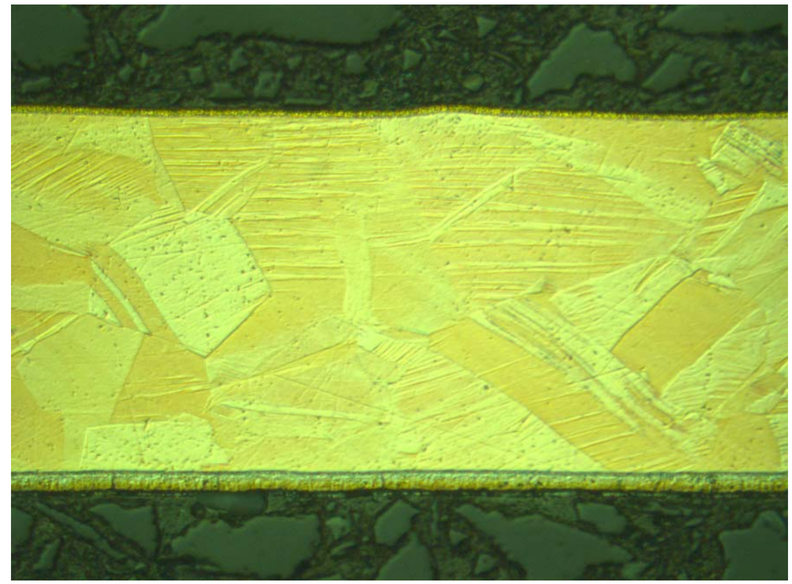
Copper Screen in Mantle Scoping Test



Br-2 Mantle Bronze Strip

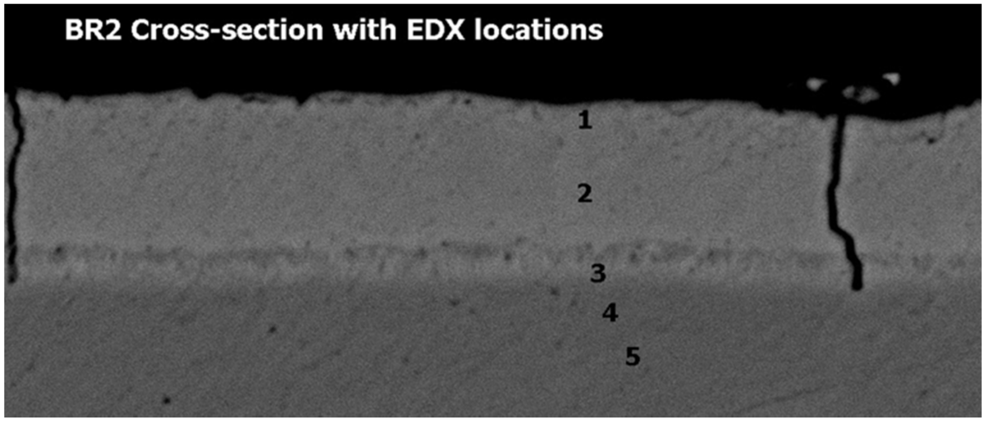




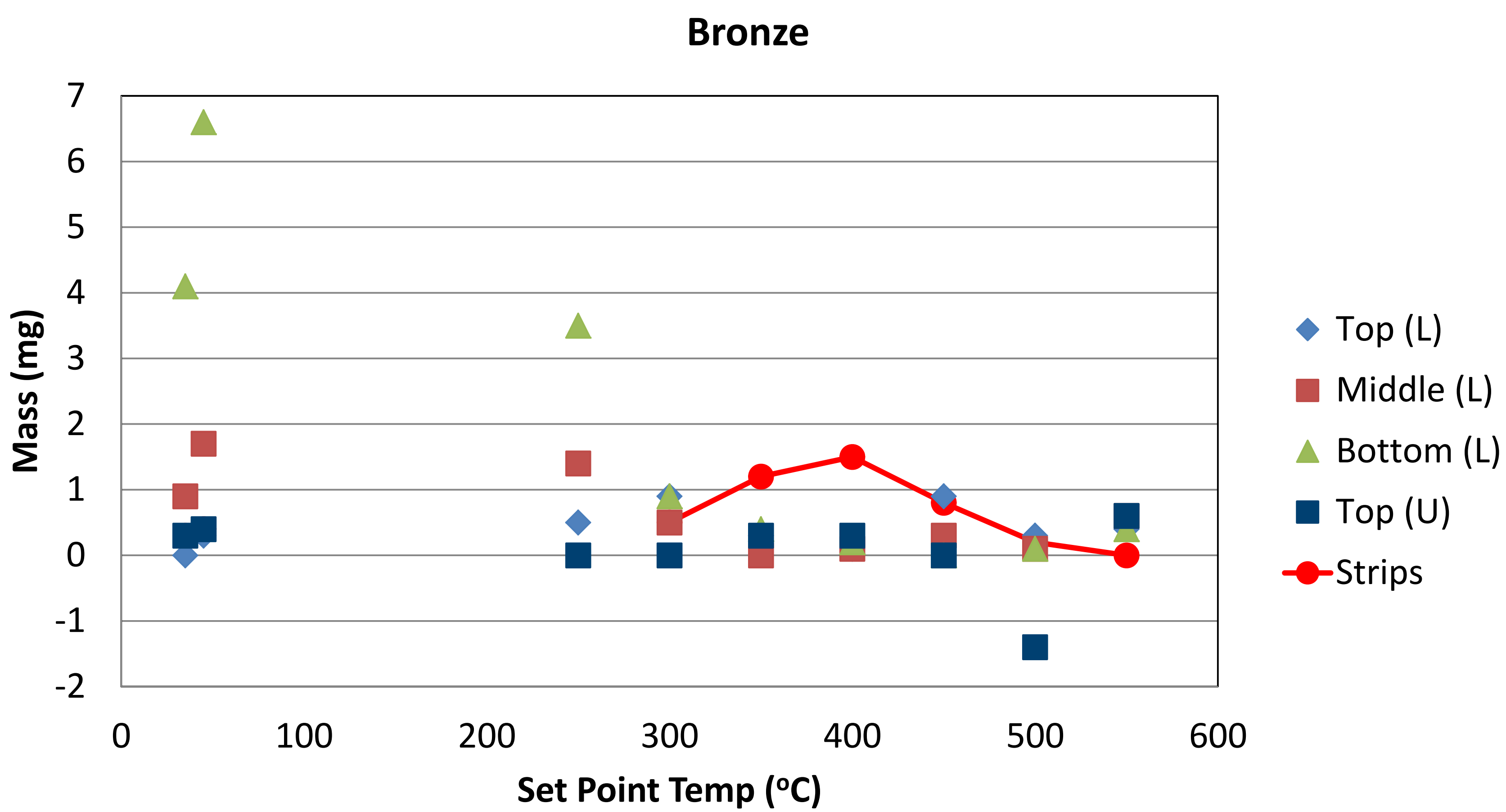


Deposit Chemistry

Location	W% Cu	W% Zn	W% Sn	Other
1	37.3	59.2	0	<4
2	39.3	60.0	0	<1
3	47.0	49.2	3.8	
4	83.3	10.9	5.6	<1
5	95.1	0	4.9	



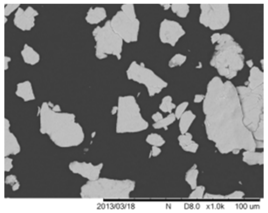
Summary Data Bronze

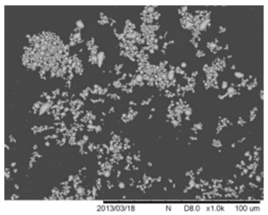


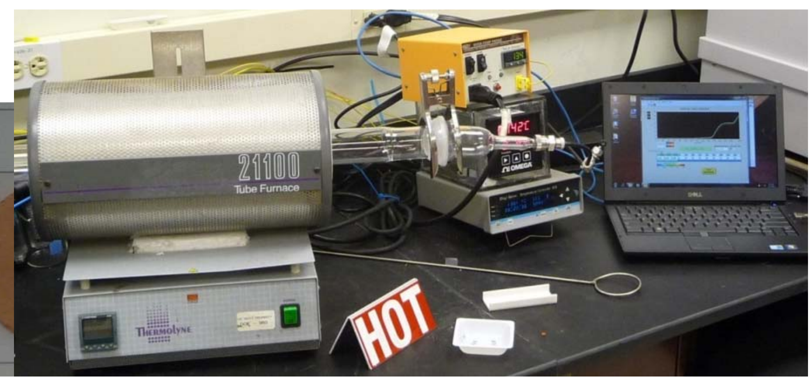
Commercial Products vs SRNL Prepared

- **Bronzes with 2-10% Sn**
  - Contain high phosphorous
  - May contain lead
  - Contain other undesirable alloying additions
- **Pure Cu and Sn Powder Metallurgy**
  - 0 – 30 w% Sn
  - No additional additives

Powder Processing Equipment

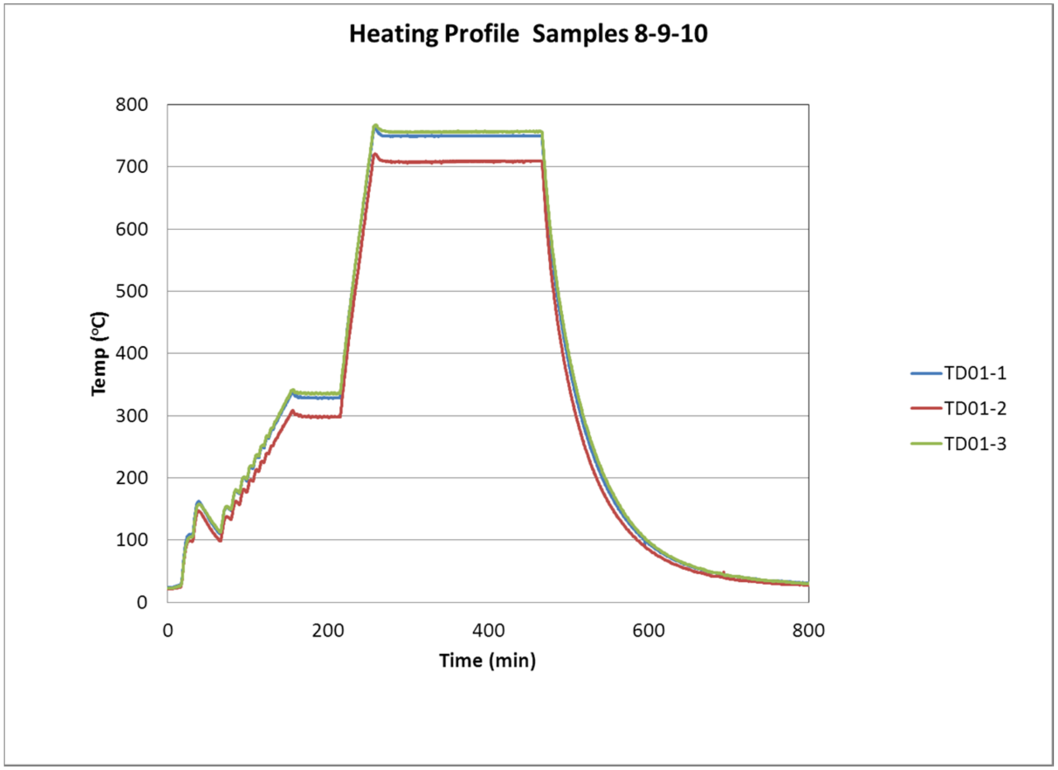


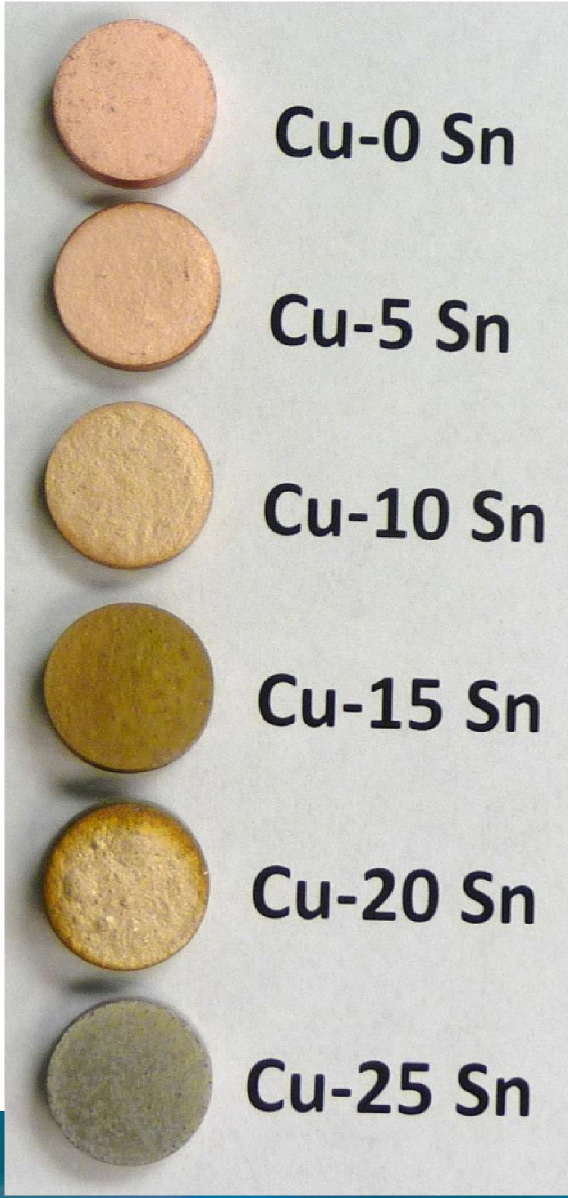




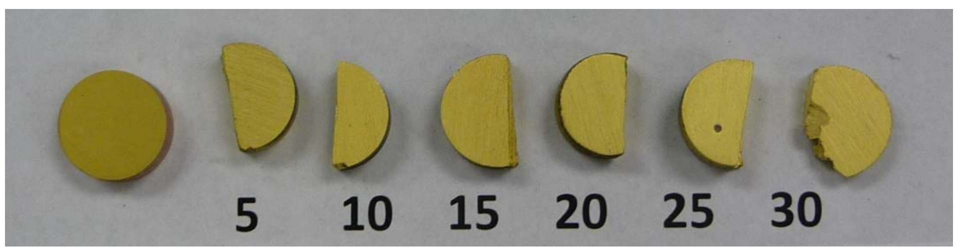
Solid State Sintered Pellets

- Mix elemental powders
- Compact in 13 mm die
- Sinter in Argon
- Characterize

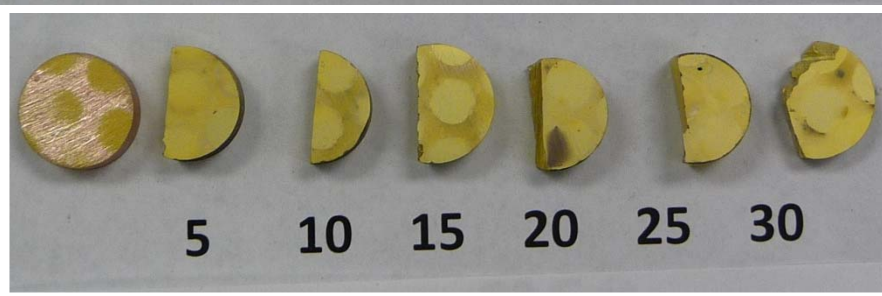




Bronze Pellets Before and After Zinc

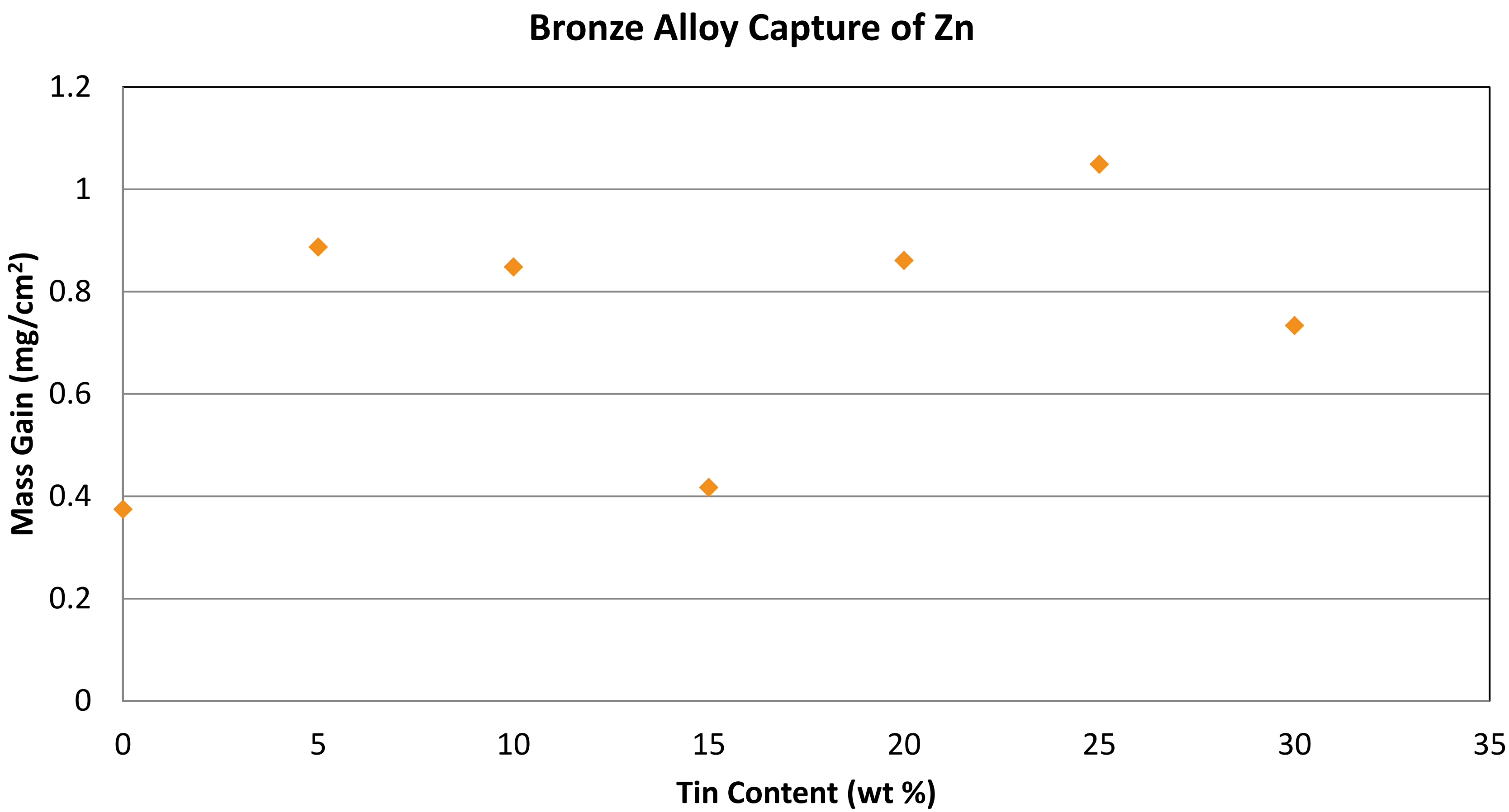


Bottom



Top

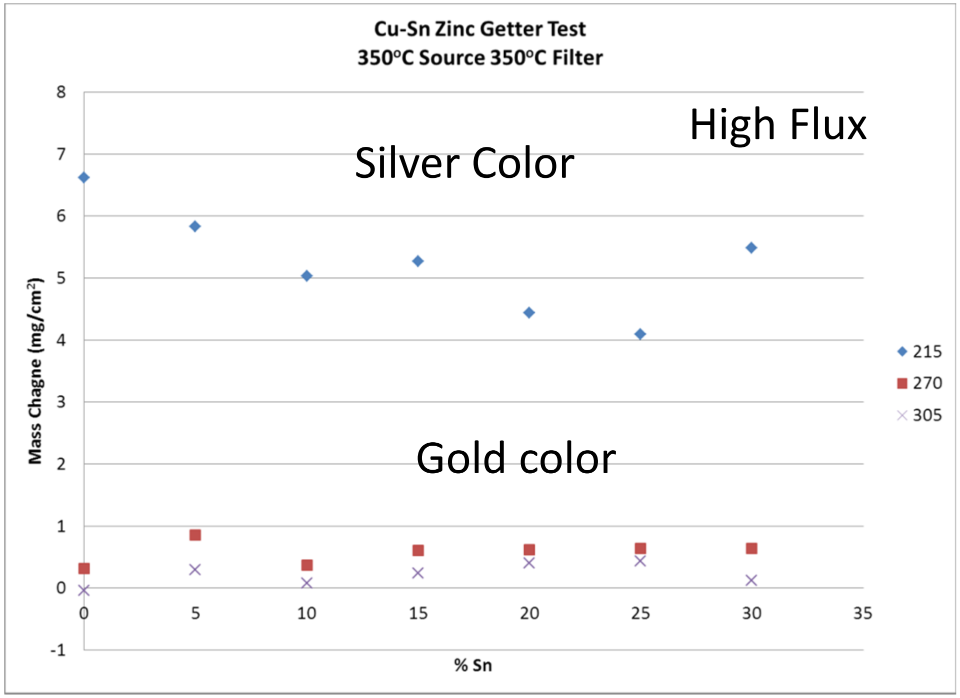
First Bronze Button Test

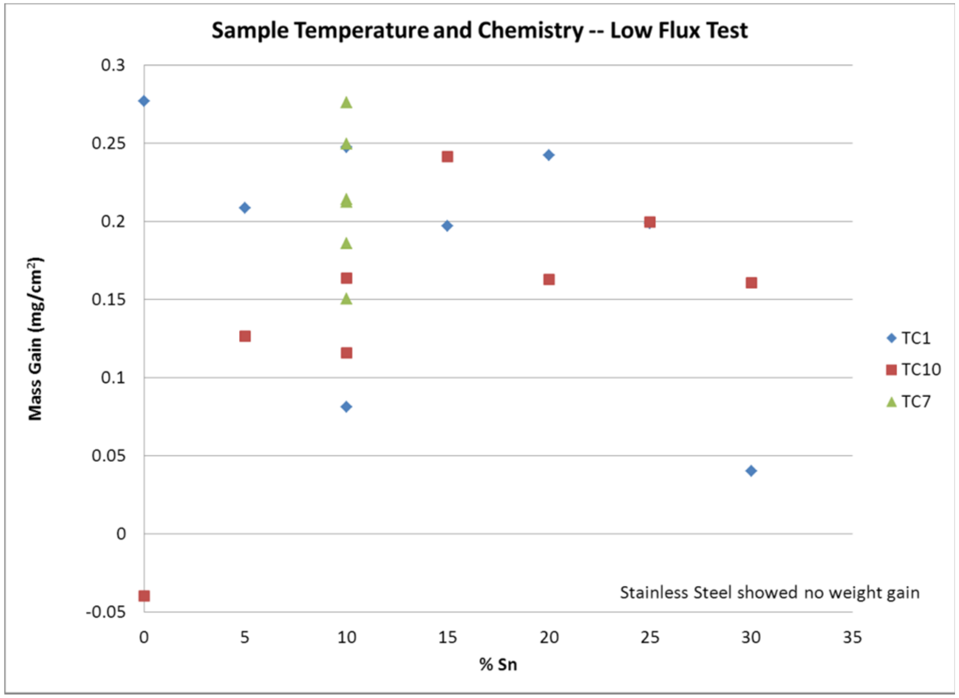


Solid State Sintered Cu-based Zinc Getters KorZincAlloy

- **Prepared 50 samples of various Sn content**
- **Tested high and low flux conditions for 0-30% Sn**
- **Determined**
  - Composition effects
  - Pure Cu less effective getter than alloys with Sn
  - Color change is good indicator of reaction
  - Sn changes morphology
  - Samples must be ground

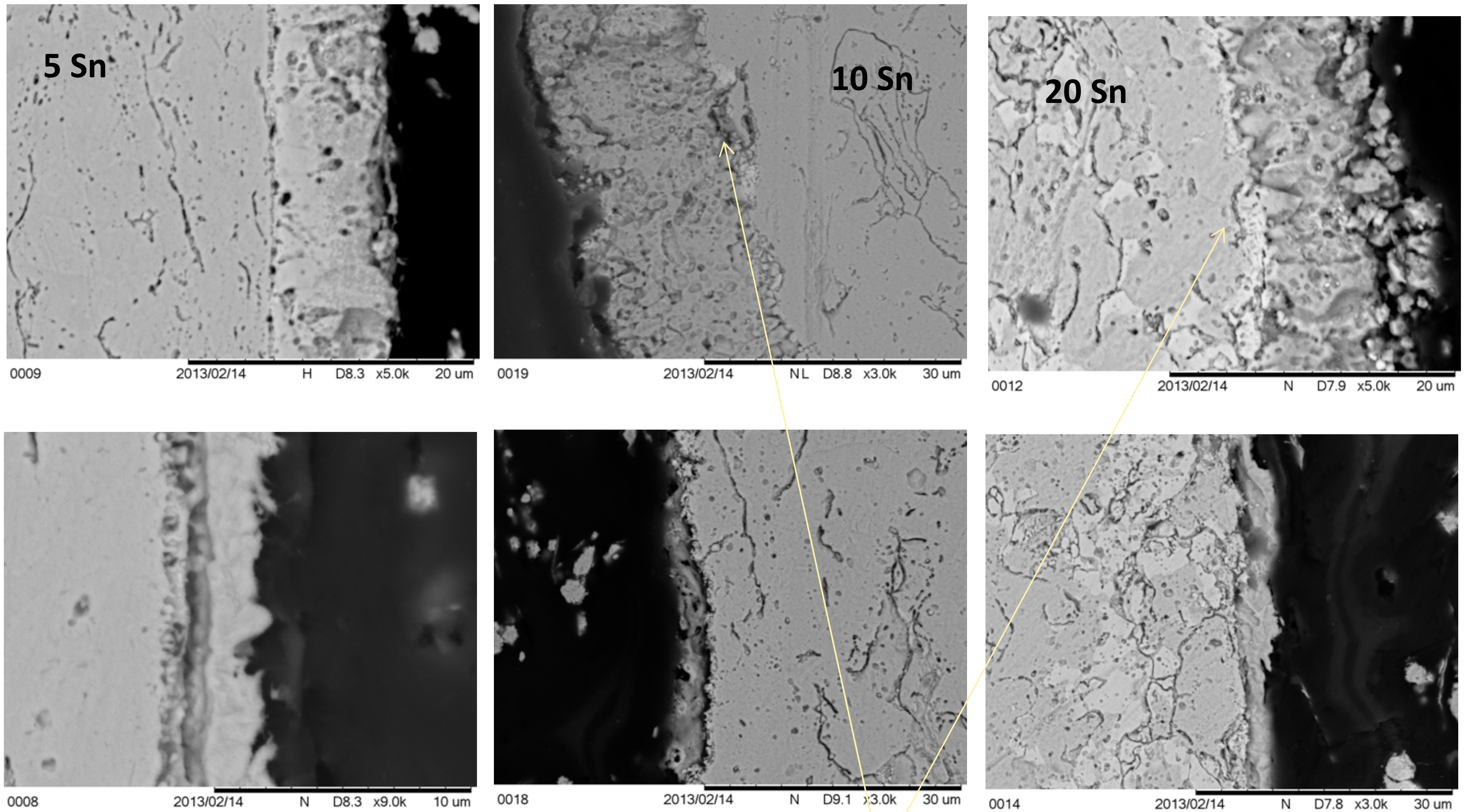
Solid State Sintered Cu-based Zinc Getters KorZincAlloy





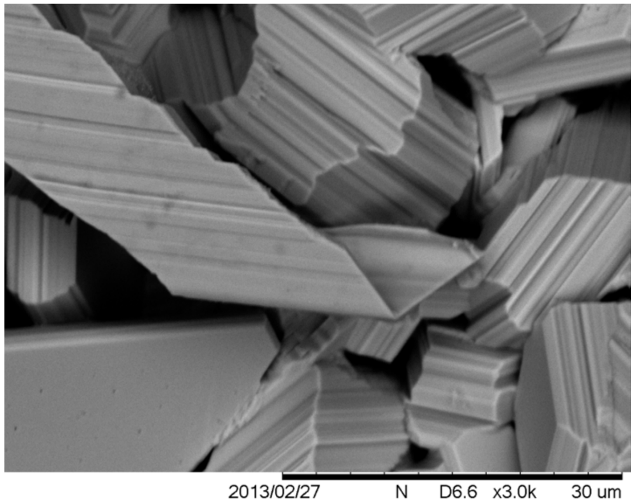
- Pure copper apparently has a small window of effectiveness
- There does not appear to be any systematic change of effectiveness with %Sn
- Sample position in the reactor dictates mass gain
- Low flux is still orders of magnitude higher than expected for TEF

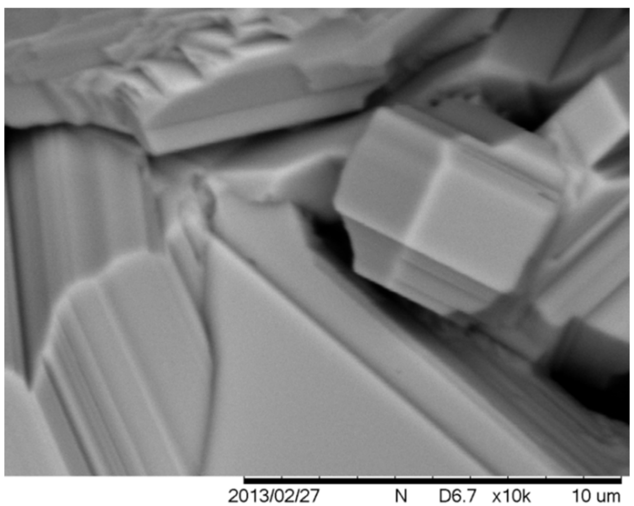
Zinc Deposit Characterization on KorZincAlloy



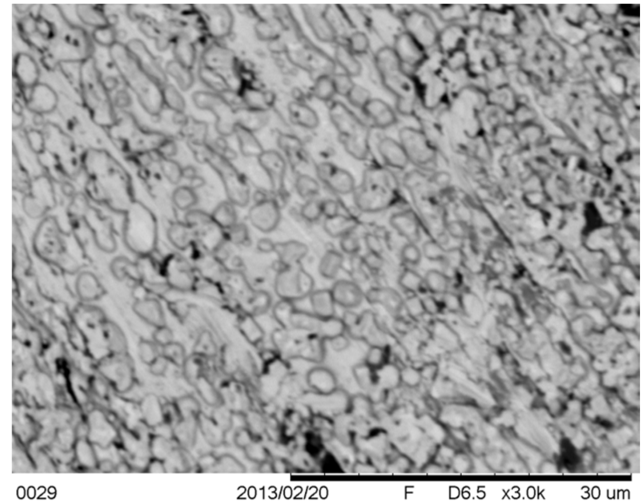
A Sn rich phase grows at the Zn/KZA interface – Cu outward diffusion

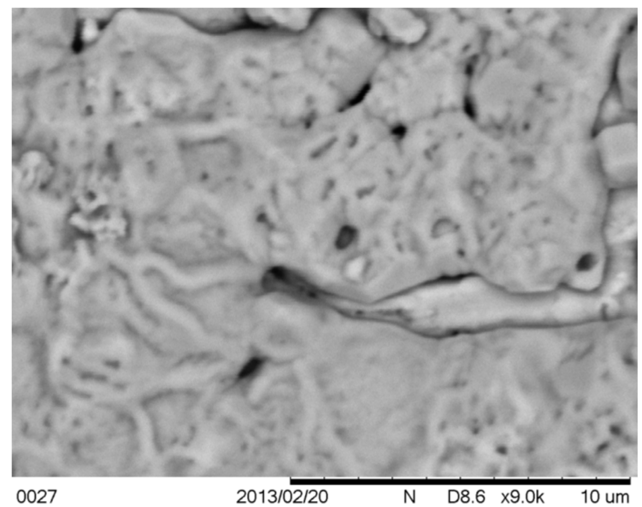
Zn Deposit Characterization





Zinc on Stainless Steel





Zinc on KZA 10
Moderate Flux Deposit with Geometric Shapes TC8

Extraction Gas Chemistry

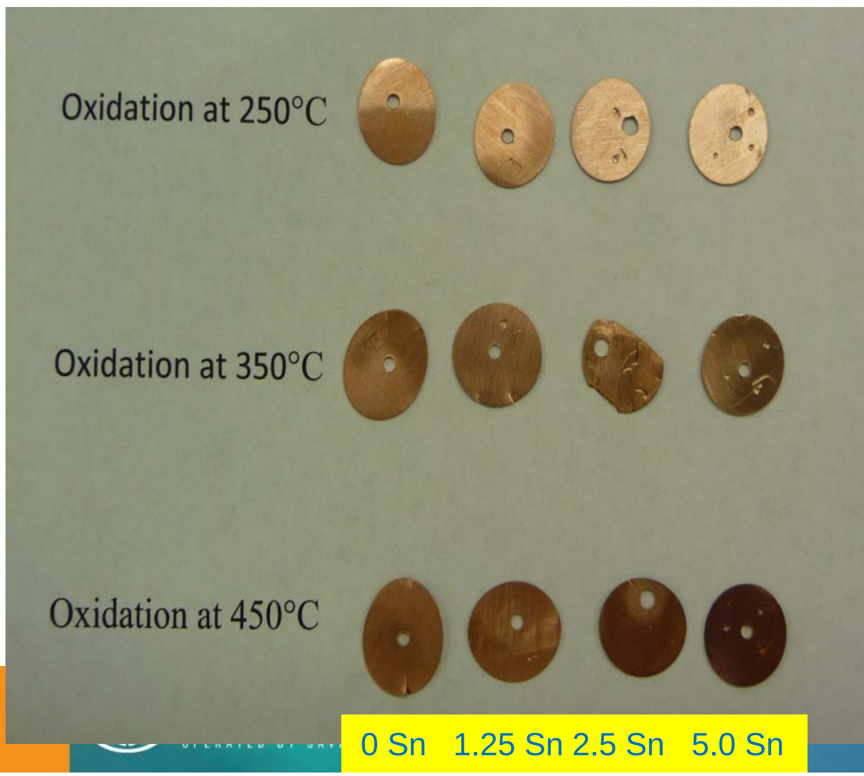
Species	Amount
Ar-37	.098 Ci 1 year after extraction
Ar-39	2.9 Ci after 90 days
T_2	60 moles
H_2	70 moles
He-4/He-3	18 moles
Q_2O (water)	40 moles of 130 hydrogen isotopes
CO	<0.1 moles
CO_2	<0.2 moles
CH_4	<0.1 moles
CH_3T	<0.1 moles

Oxidation – Reduction – Zincification Samples

Cu

Cu-2.5 Sn

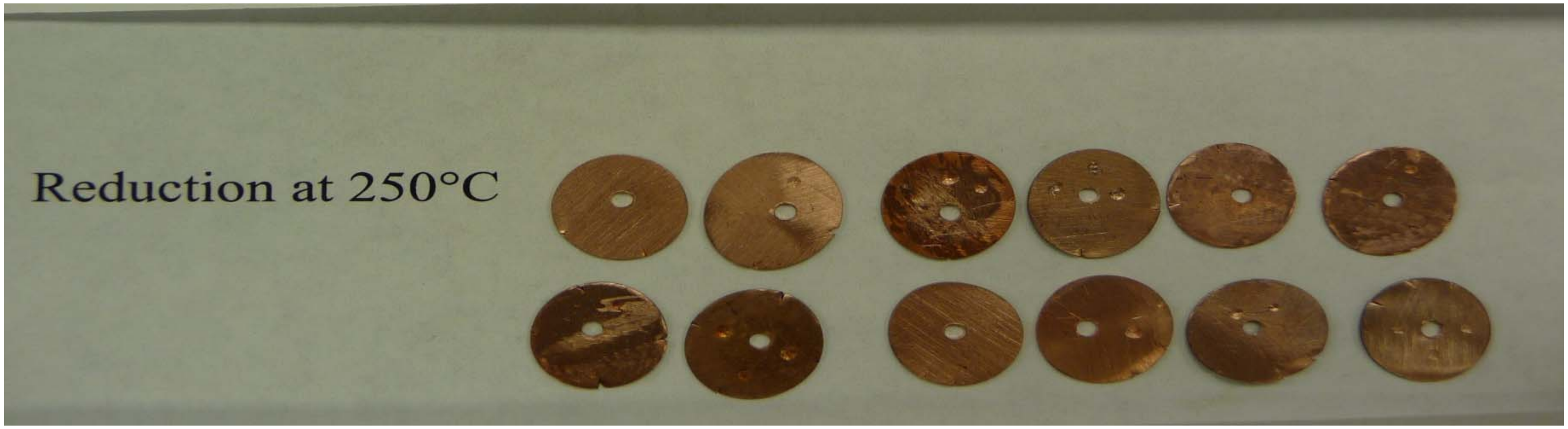
Cu-5 Sn



- **Oxidize at Low, Medium, & High Temps**
  - Ar + water
- **Reduce at Low, Medium, & High Temps**
  - Ar + H2 safegas
- **Zinc exposure at std 350/8 hours TC7 position**

H_2 - He Reduction Exposure

- Reduction exposures were conducted at 250, 350 and 450°C
  - Within each reduction exposure were samples that were oxidized at 250, 350 and 450°C
- 450°C Ox/250°C Red samples analyzed for oxygen reduction quantification



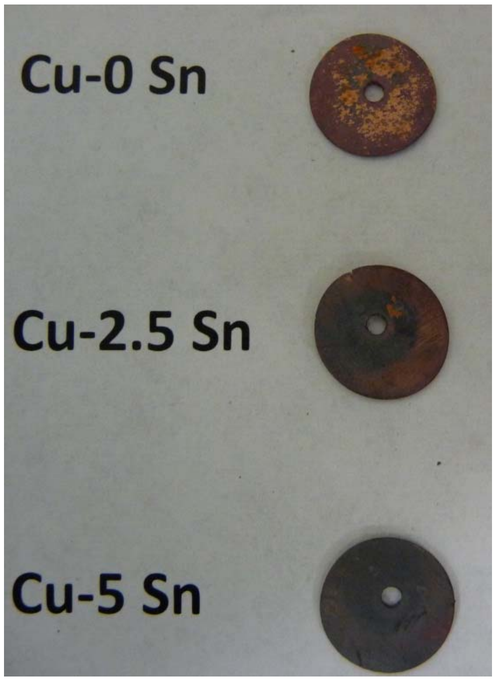
Oxidation Testing Results: SEM Analysis

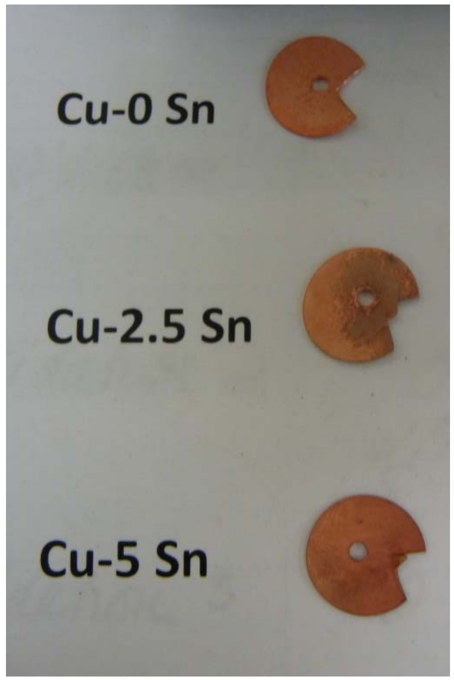
Comp.	Ox Temp	Cu (wt. %) as Ox	O (wt. %) as Ox	Sn (wt. %) as Ox
Cu 0 Sn	450°C	97.33	1.71	0.98
Cu 1.25 Sn	450°C	95.96	2.34	1.71
Cu 2.5 Sn	450°C	93.98	2.44	3.58
Cu 5.0 Sn**	450°C	55.19	2.35	3.05

Comp.	Red. Temp	Cu (wt. %) as Red	O (wt. %) as Red	Sn (wt. %) as Red	Δ O (wt. %)
Cu 0 Sn	450°C	98.68	1.32	0.00	0.39
Cu 1.25 Sn	450°C	96.23	1.80	1.97	0.54
Cu 2.5 Sn	450°C	96.64	1.21	2.15	1.21
Cu 5.0 Sn**	450°C	52.04	3.01	3.39	-.66

***Composition of Cu is lower due to Ta being included in the semi-quantitative analysis*

Surface condition of samples after Reduction

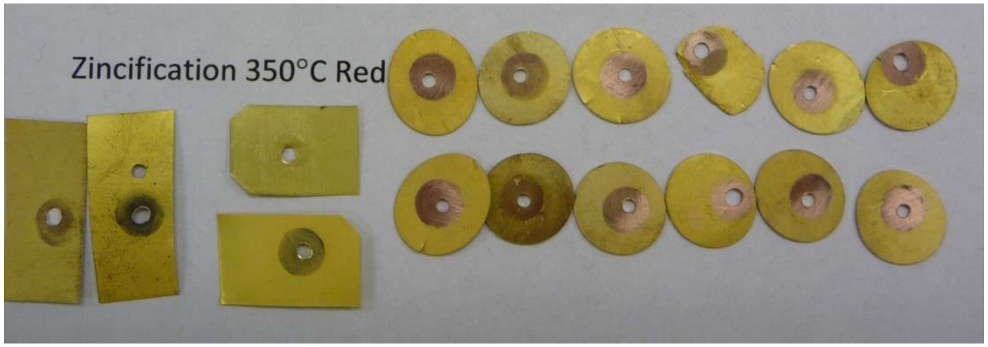


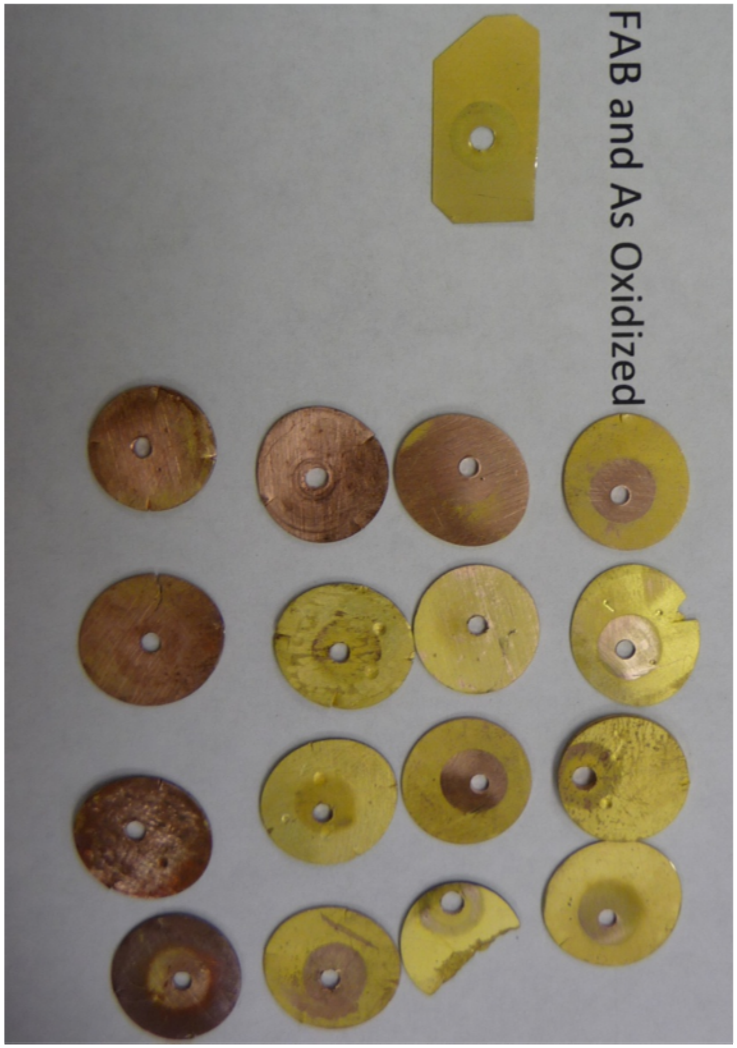


250°C

Heavily oxidized (HO) HO reduced 350°C He/H_2 450°C Red

Zinc exposed sample



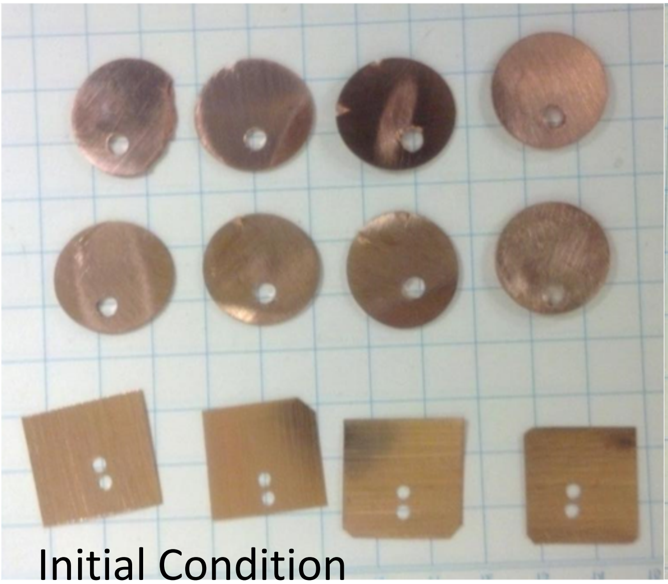


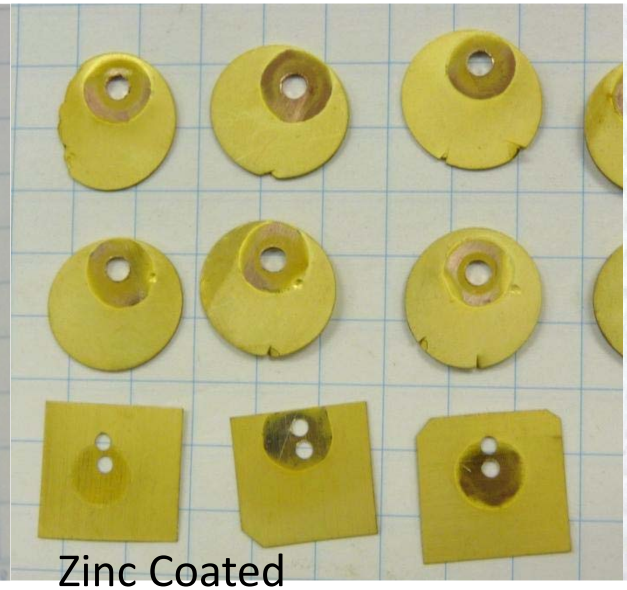
Zinc Weight Gain vs. Composition

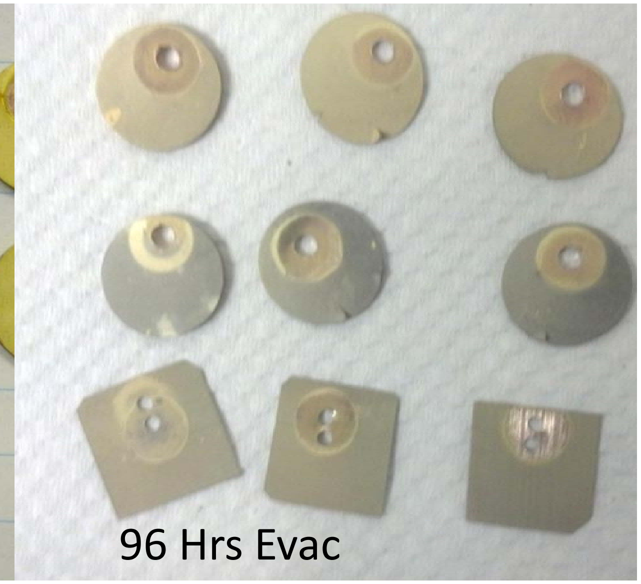
% Sn	Oxid 250	Oxid 350	Oxid 450	Ox450/ Red450	Ox350/ Red450	Ox250/ Red450	Ox450/ Red350
0	0.5	1.4	0.5	0.3	1.0	1.5	3.8
1.25	0.9	2.3	0.9	0.5	1.2	1.0	3.5
2.5	0.9	1.7	0.9	0.6	1.1	0.6	4.3
5	0.7	1.1	0.7	0.6	1.0	1.0	2.4

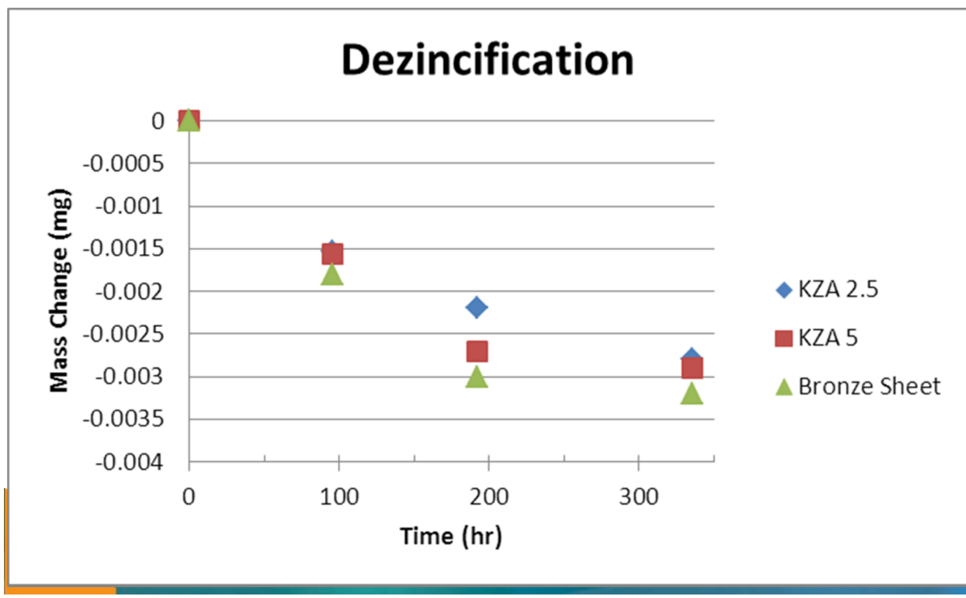
% Sn	Ox350/ Red350	Ox250/ Red350	Ox450/ Red250	Ox350/ Red250	Ox250/ Red250	As Fab
0.0	2.8	2.4	0.6	1.3	1.2	0.0
1.25	3.5	4.2	1.3	1.1	1.3	1.0
2.5	3.8	3.5	1.1	0.6	1.4	1.1
5.0	2.6	3.3	0.4	0.7	0.9	1.5

Dezincification of KZA vs Bronze Sheet



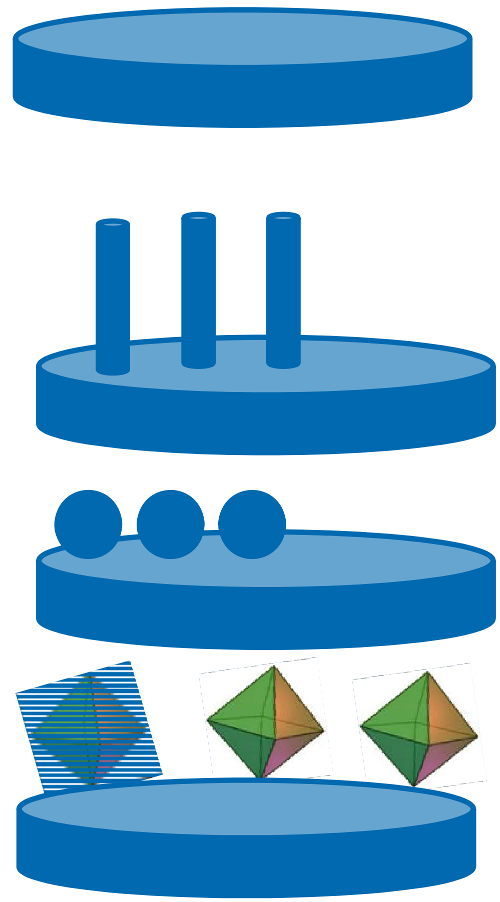






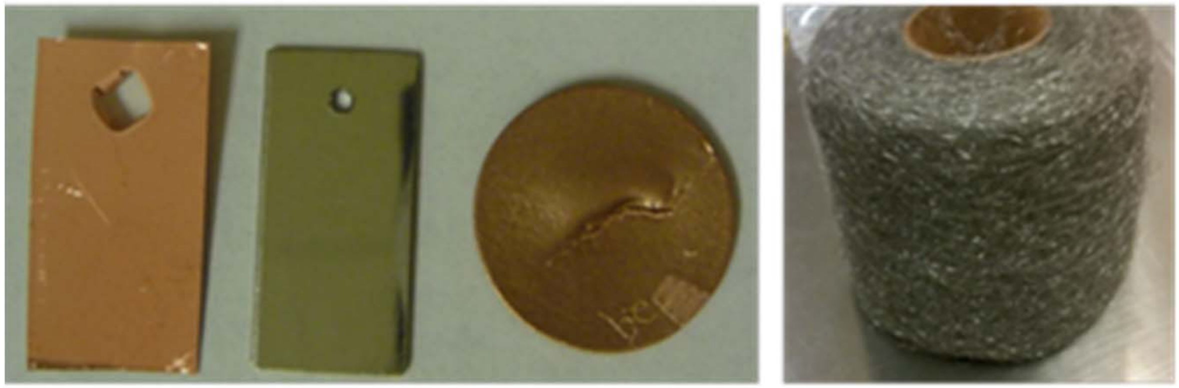
KZA vs Functionalized Materials

- **Why nanostructures?**
  - Provide higher surface area → provide additional "active" sites that will maximize Zn-65 capture and removal during the TPBARs processes.
  - More reactive than their bulk counterparts
    - May be able to use higher melting / vapor pressure materials at lower T_H
  - Properties depends highly on the size, shape, morphology and composition
  - Different shaped nanoparticles have different reactivities
  - Prepared by wet chemical processes → address scalability issues
  - Cost effective solutions



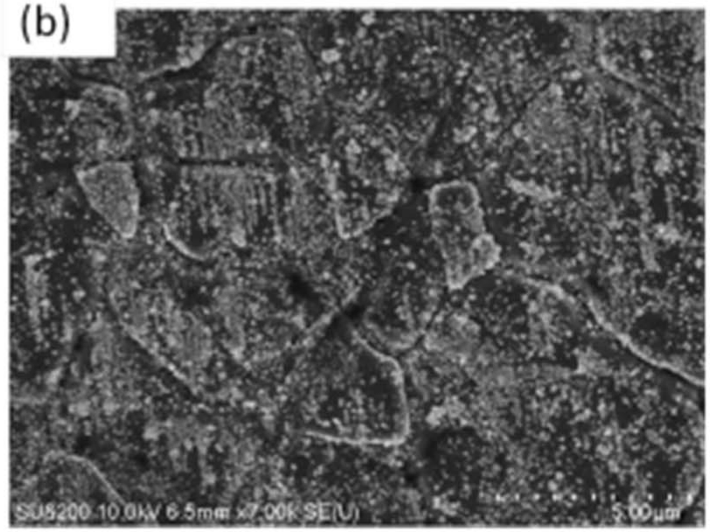
Preparation Procedure

Copper coupons | Stainless steel coupon | Bronze coupon | Stainless steel wool

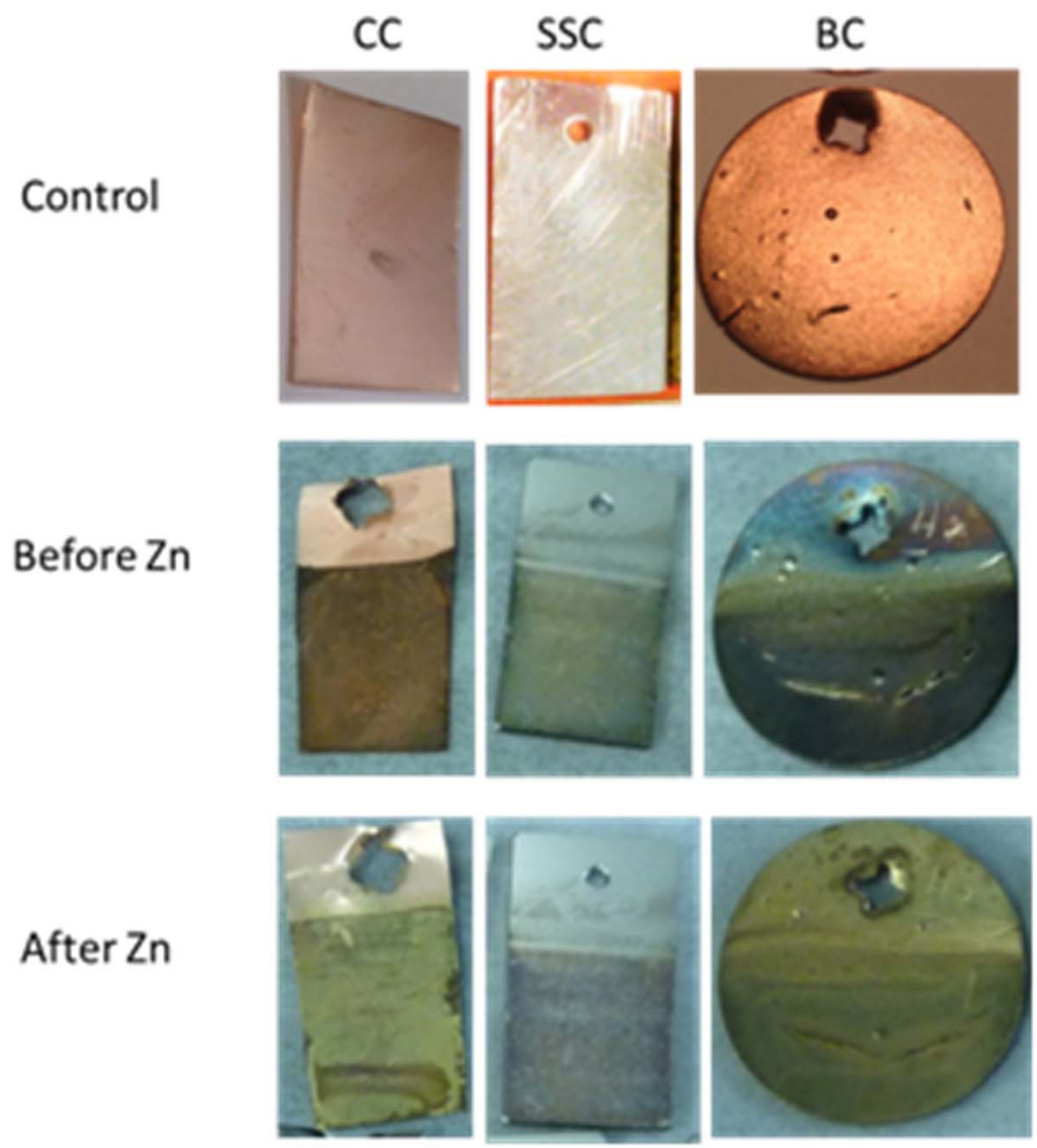


(a)

(b)

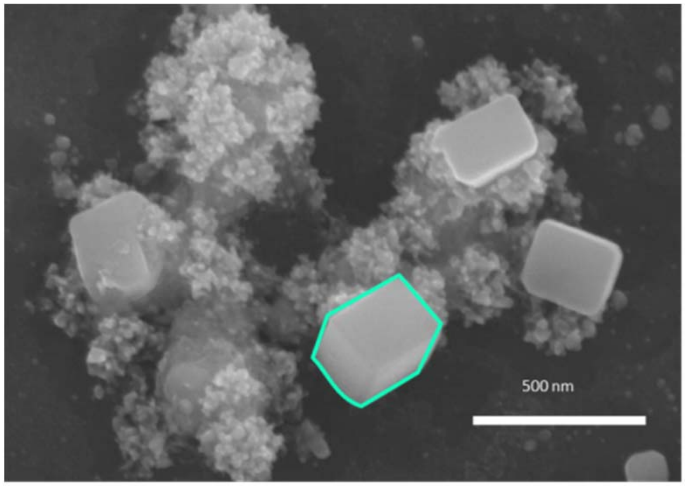


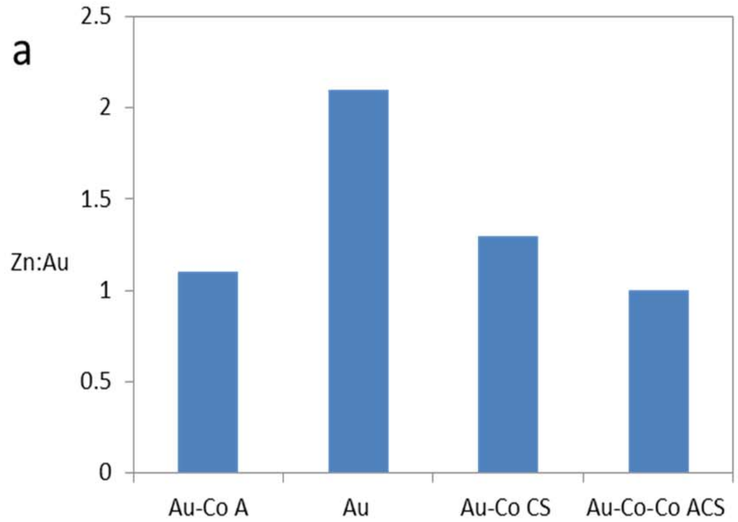
Supports Functionalized and Zn Exposure

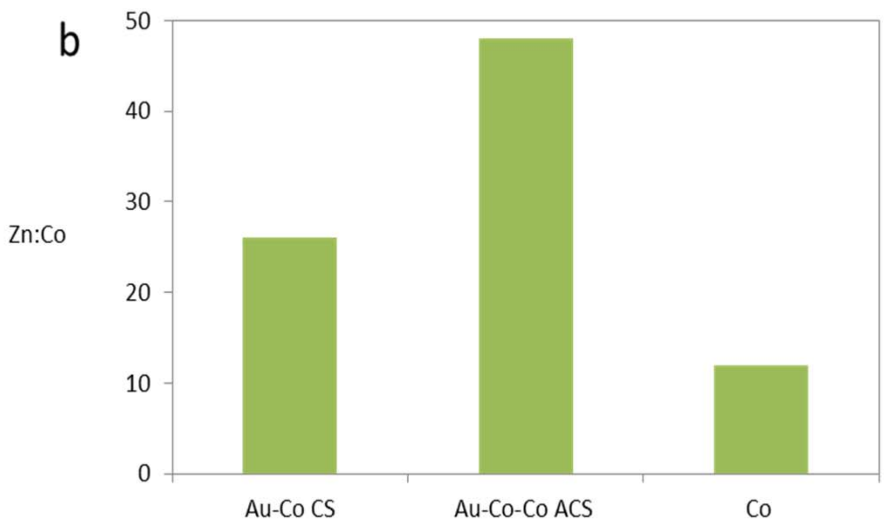


Materials screened
Co Nano-particles (Nps)
Au Nps
Au-Co alloyed Nps
Au-Co core shell Nps

Zn deposits "captured by Au-Co nanoparticles







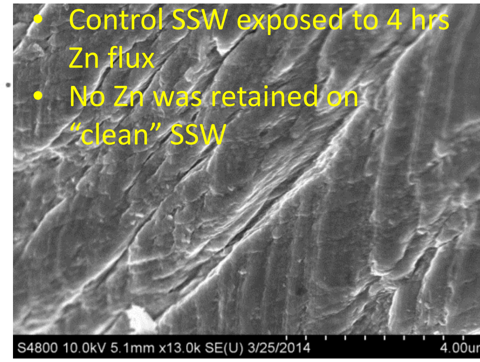
Saturation Experiments

- Previous studies conducted at 350°C after 4 hours Zn deposition experiments
- Elucidate the saturation hypothesis- conducted experiments at 1 hour and 30 min.

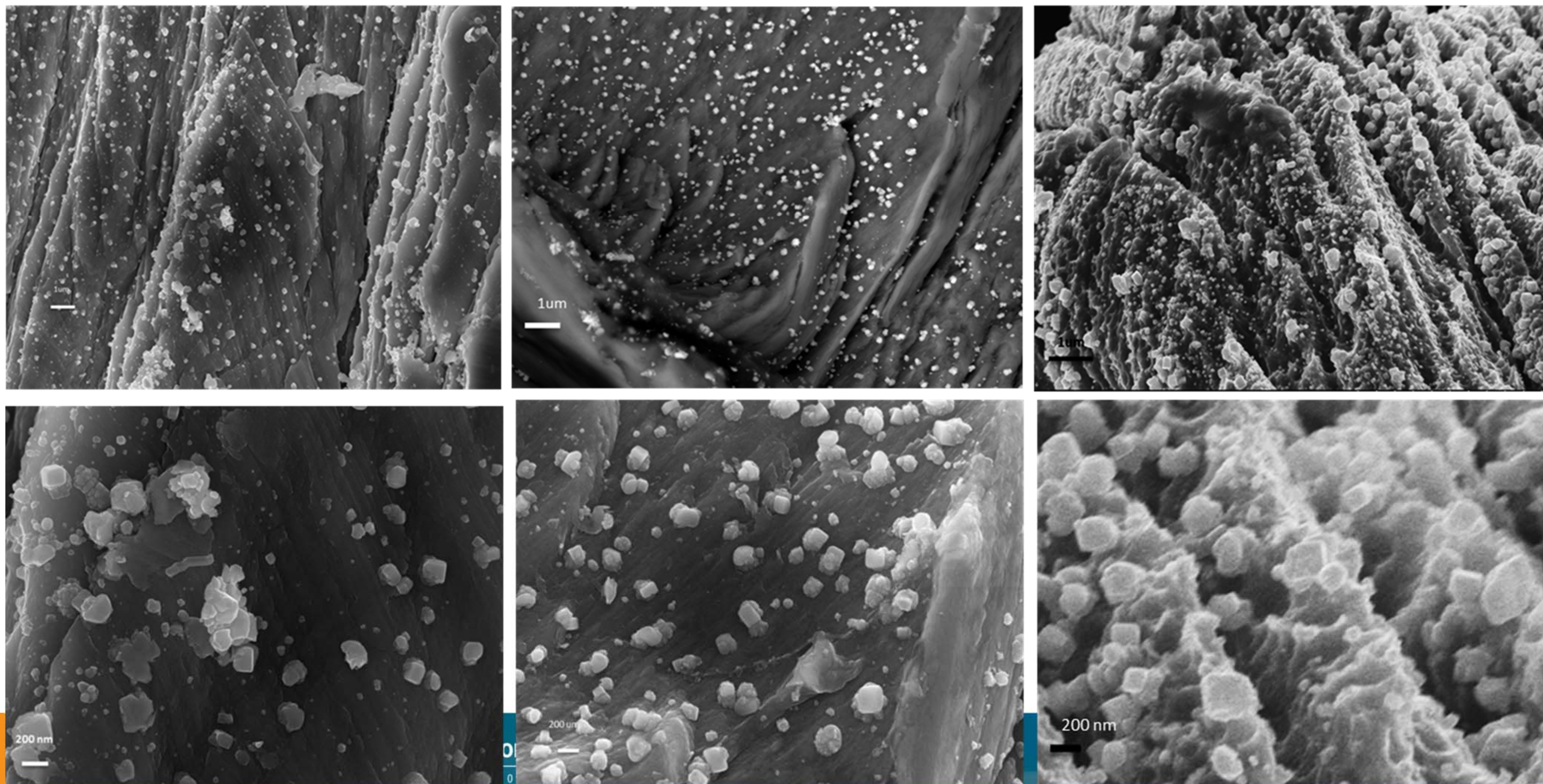
Control- No Nps | Au Nps -0.5 hrs Zn | Au Nps- 1hr Zn | Au Nps- 4hrs Zn

0 min → 1 hr → 4 hours

Au–Zn SSW Deposition

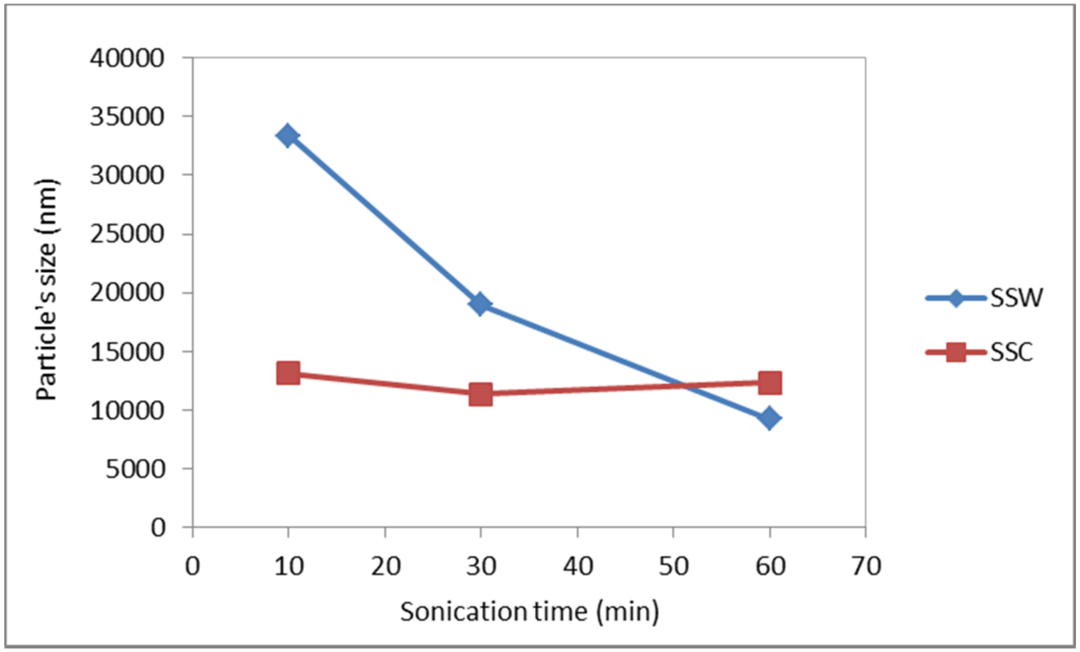


30 min | 1 hour | 4 hours

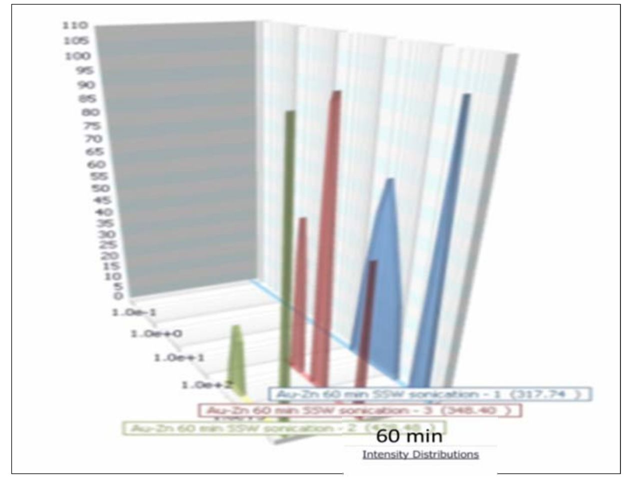


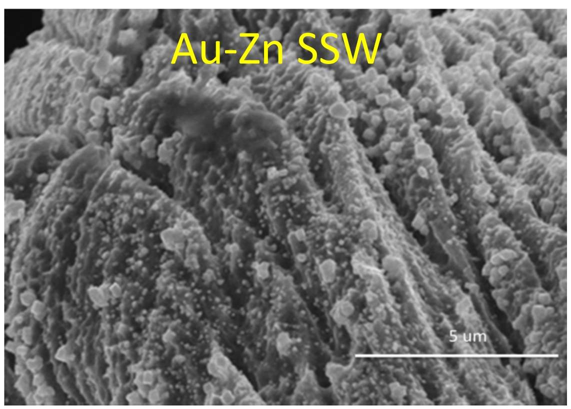
Dynamic Light Scattering Evaluation

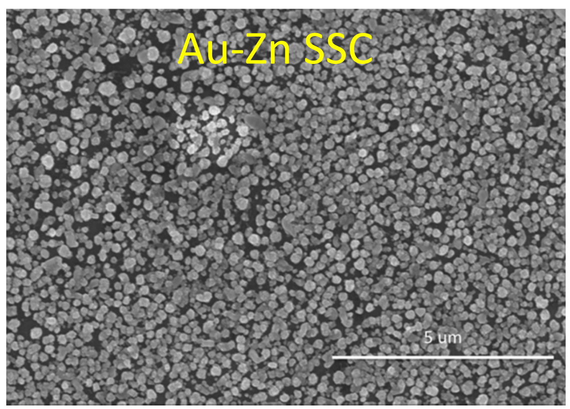
Relative abundance of population components



DLS: Relative Abundance of Population Components



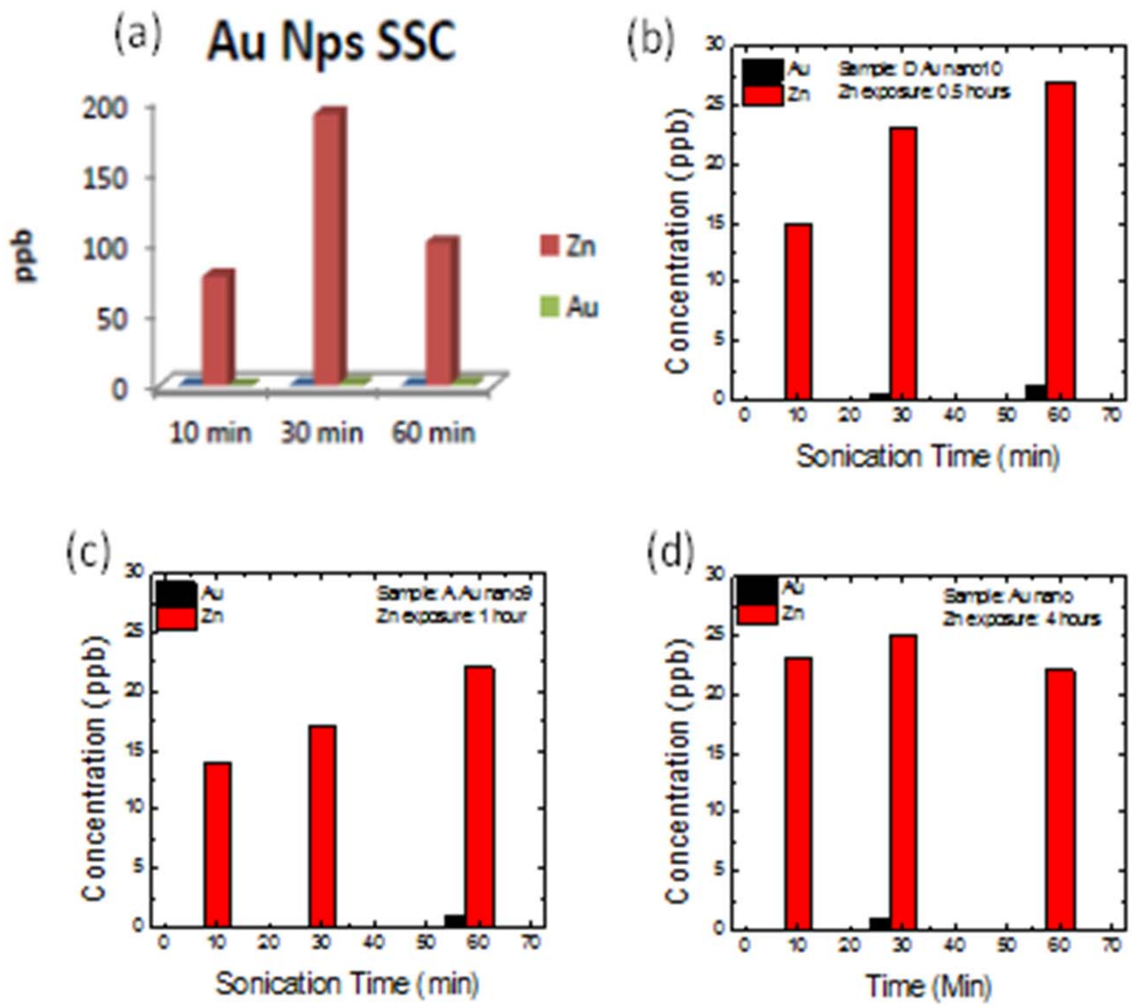




- Are particles being destroyed after 60 minutes sonication?

- SSW:
  - ✓ Different size particulate population sizes were produced
  - ✓ Larger particles were released at the beginning of the sonication experiments; smallest particulates were released after 60 minutes
- SSC:
  - ✓ Uniform particulate population were produced
  - ✓ Identical (almost) identical particulate sizes were removed after 10, 30 or 60 min experiments.

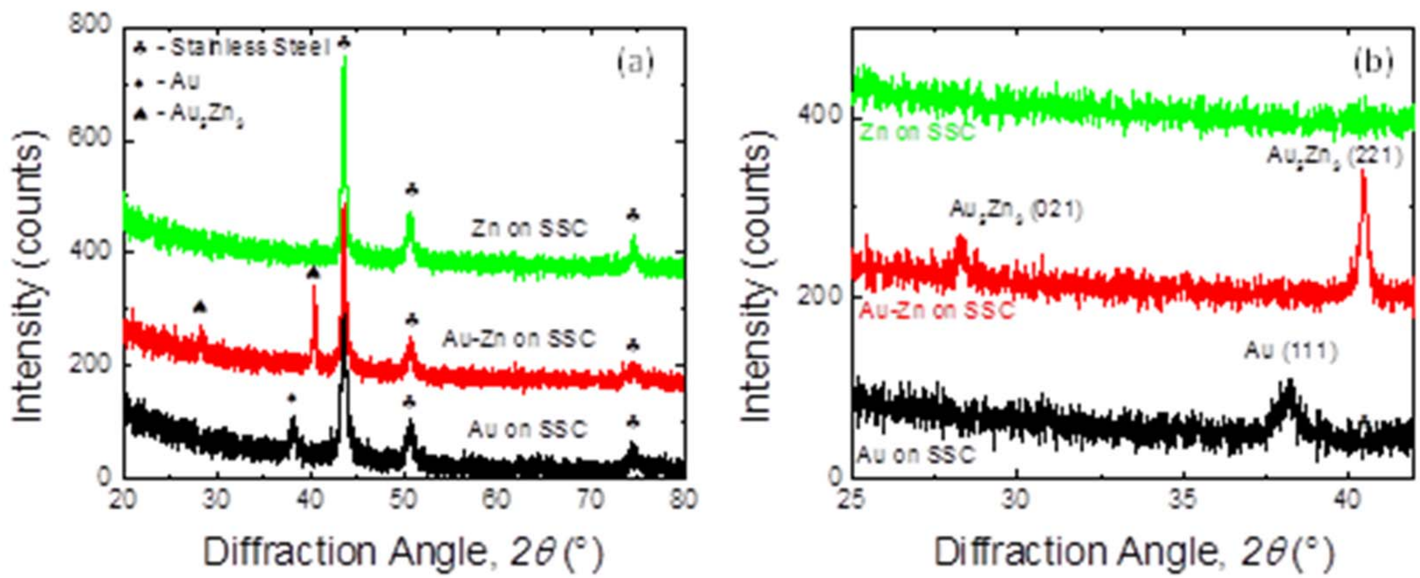
Improving and Characterizing Zn and Nanoparticle Adhesion



- ***the grit-blasted stainless steel coupons reduce the amount of Zn lost during sonication by almost an order of magnitude.***

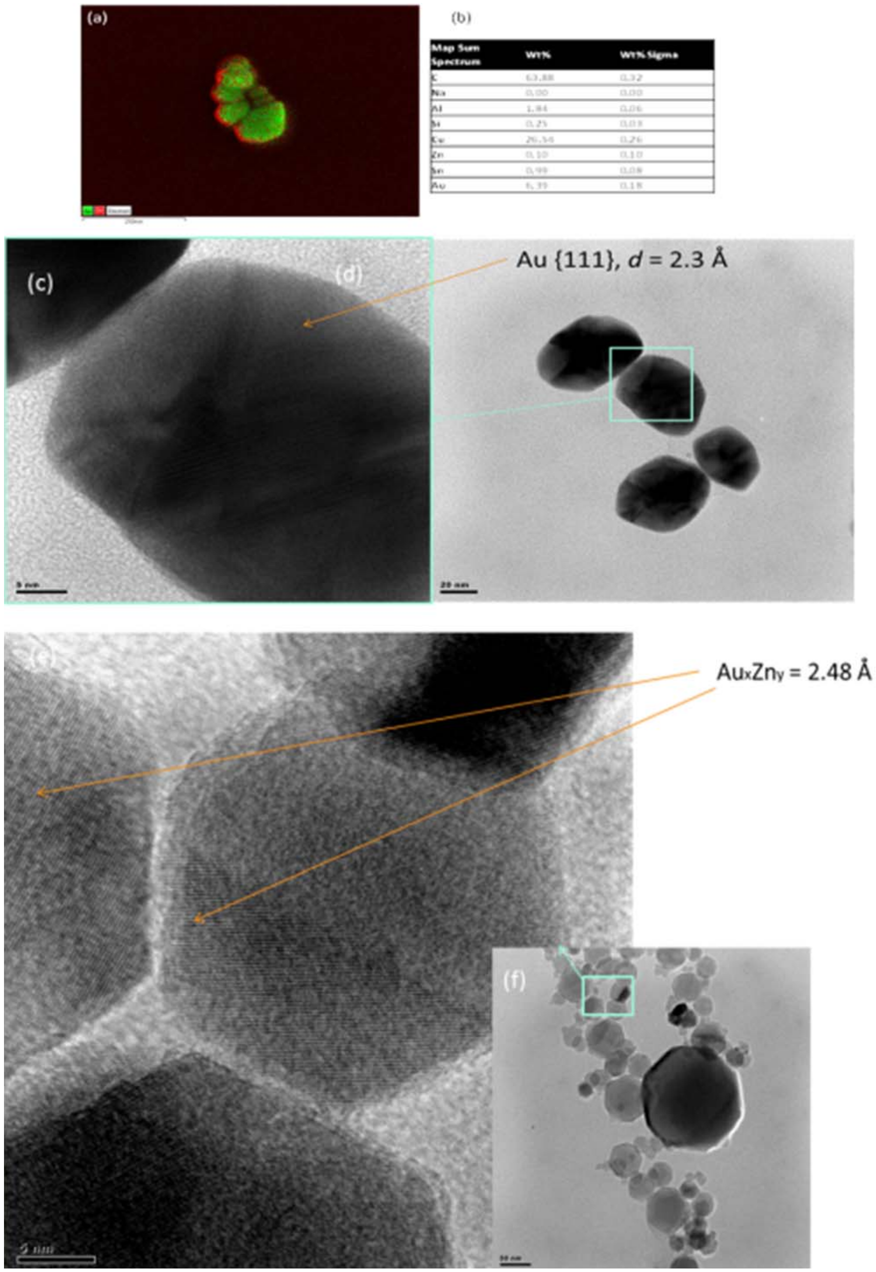
XRD Diffraction Data

AuNP on stainless steel coupon (SSC) getter, AuNP on SSC exposed to Zn vapor, and bare SSC exposed to Zn vapor.



These results confirm the alloying effect is occurring.

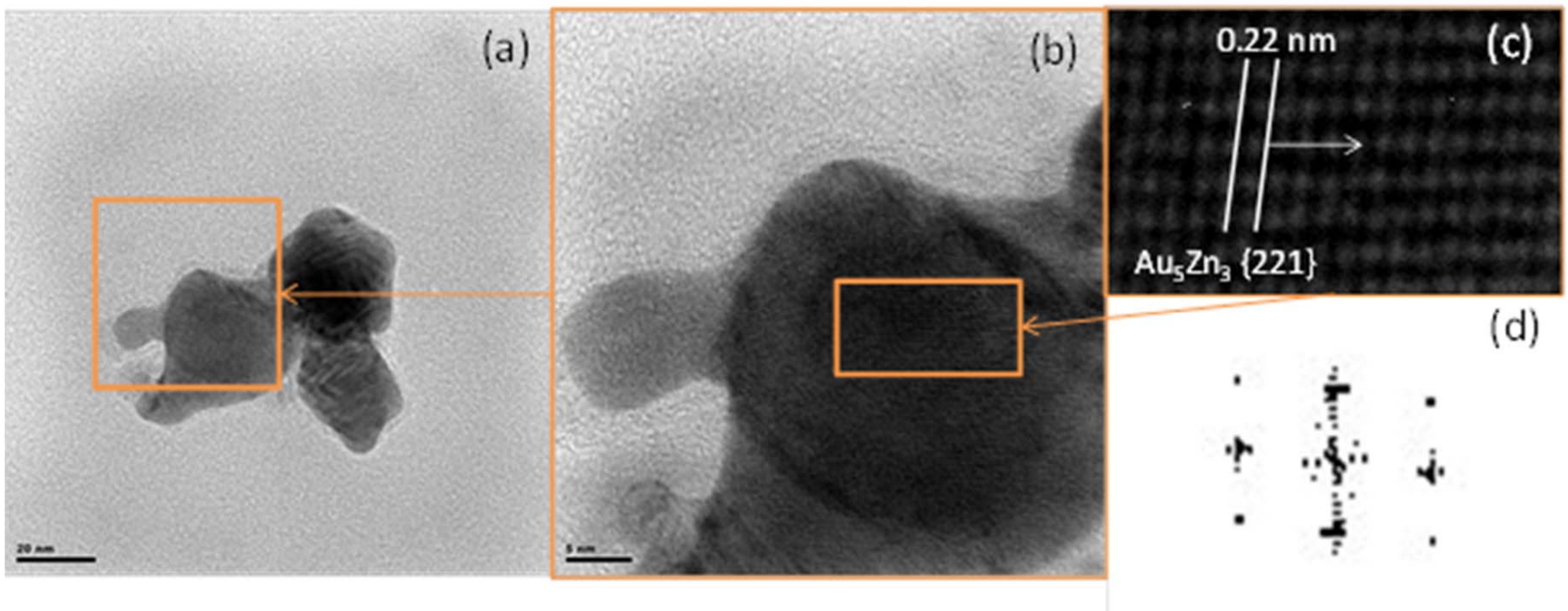
TEM of Zn particles



Map Sum Spectrum	Wt%	Wt% Sigma
C	63.88	0.32
Na	0.00	0.00
Al	1.84	0.06
Si	0.25	0.03
Cu	26.54	0.26
Zn	0.10	0.10
Sn	0.99	0.08
Au	6.39	0.18

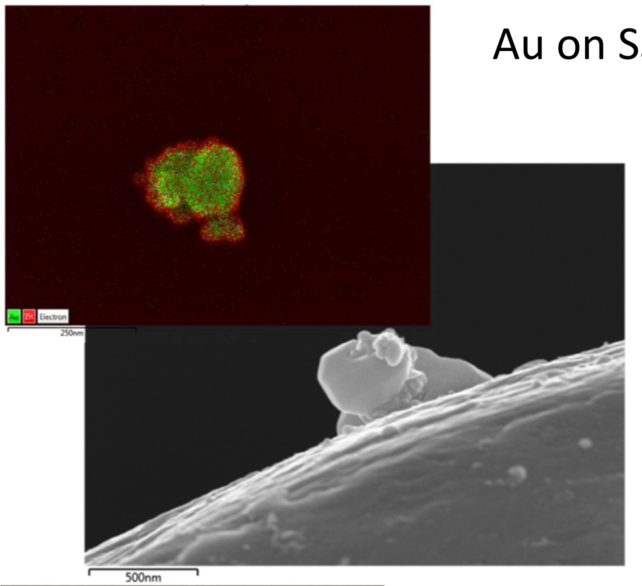
(a) EDX mapping of the sonicated nanoparticles showing the Au and Zn distributions. (b) Elemental analysis of the EDX mapping in part (a) showing the presence of Au and Zn. (c-f) Zoomed in and wide angle view of the sonicated nanoparticles obtained from TEM, showing the measured lattice spacings. (c,d) HRTEM and TEM images showing lattice information on Au; (e, f) HRTEM and TEM images showing different lattice information confirming alloying occurs.

HRTEM Studies

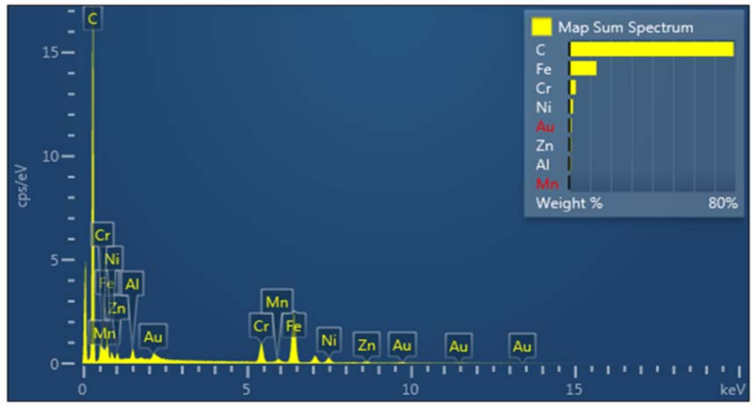


a)-(c) Progressively higher magnification TEM images of a sonicated Au_5Zn_3 nanoparticle; (d) FFT of the lattice fringes shown in (c).

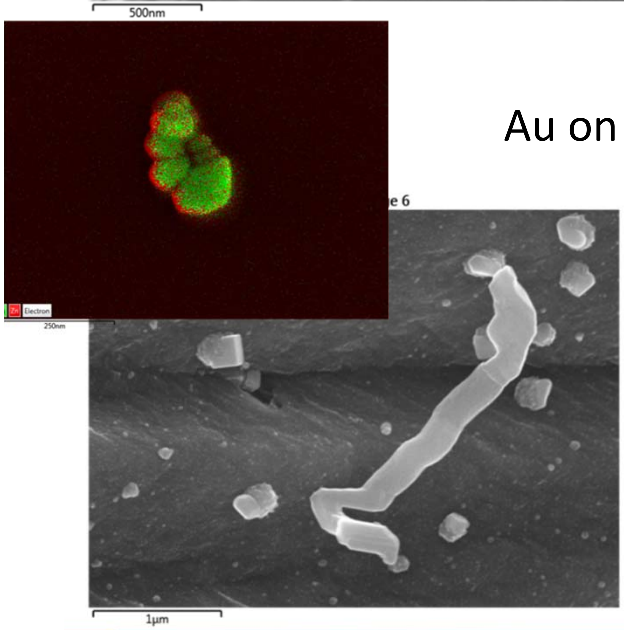
EDX and EDX Mapping Analysis



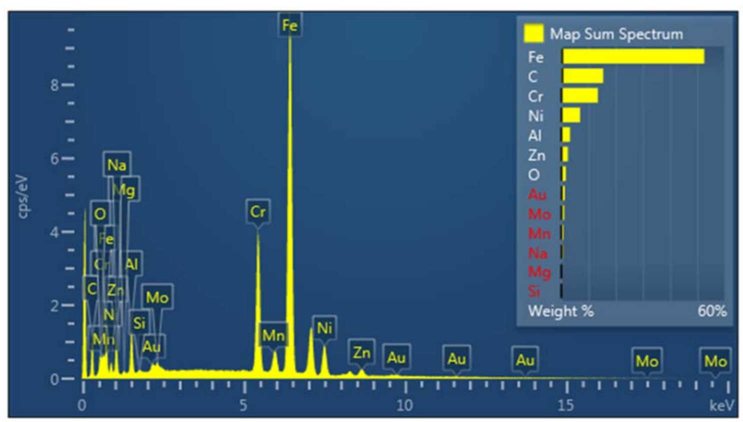
Au on SSW, Zn exposure: 30 minutes



Map Sum Spectrum	Wt%
C	79.13
Al	0.75
Mn	0.15
Fe	13.12
Ni	1.77
Zn	0.82
Au	1.00
Total	100.00

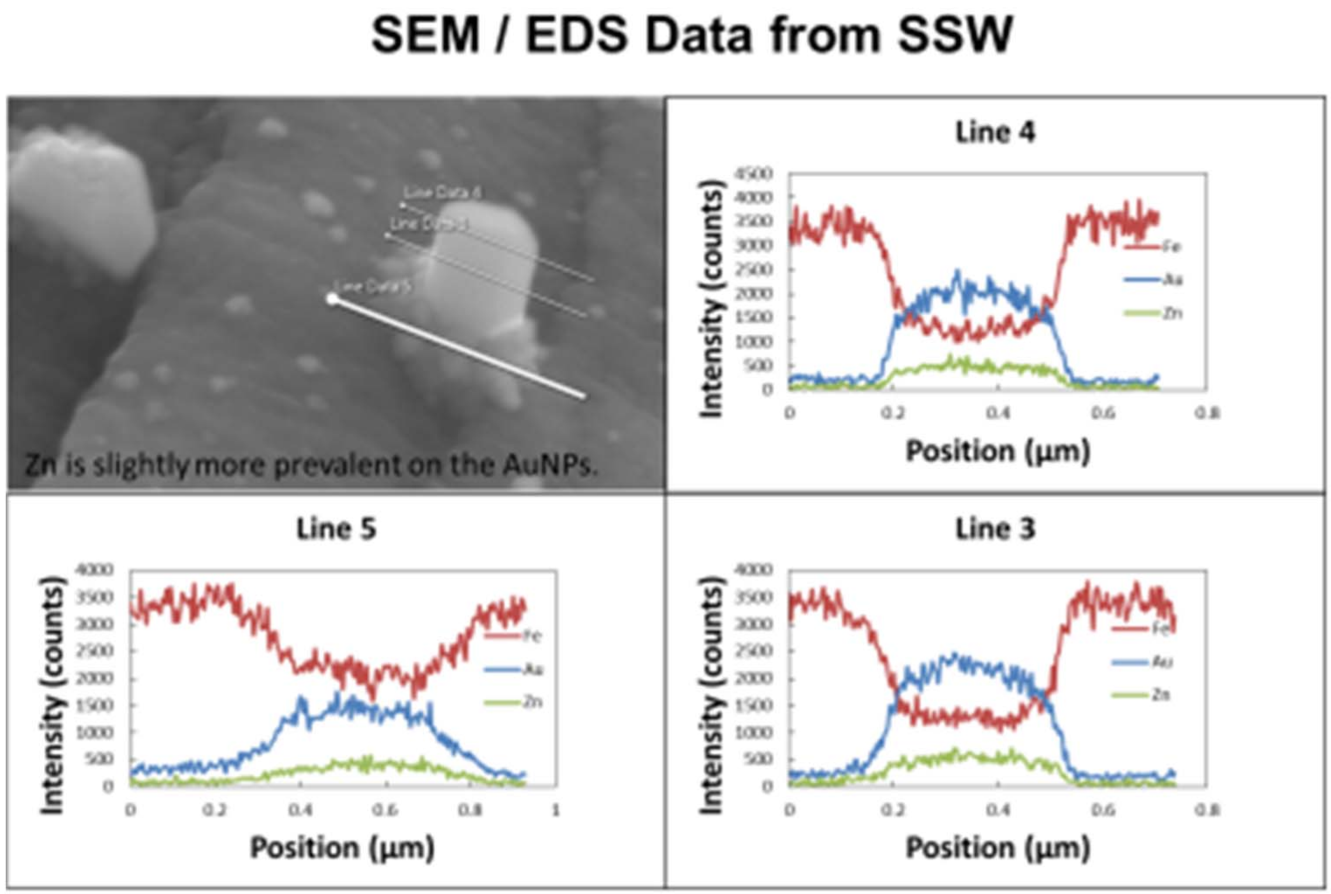


Au on SSW, Zn exposure: 60 minutes



Map Sum Spectrum	Wt%
C	15.45
Al	3.24
Mn	0.80
Fe	52.61
Ni	6.95
Zn	2.44
Au	1.31
Total	100.00

SEM Characterization of Nps on Stainless Steel Wool



SEM image and corresponding EDX lines scans of the AuNp getter surface showing the Au and Zn distributions.

Summary

- Zinc-65 found in GB 500 was from activated natural Zn
  - *Deposit morphology varied*
- Very few elements are compatible with TEF process
  - *Stable Zn compounds, stable hydrides, or volatile*
  - *Thermodynamic calculations used to cull the list*
    - Copper and cobalt based candidates
- Bronze captures Zn better than pure Cu and SS
  - *No systematic change in Sn to affect Zn*
  - *Commercial bronzes have undesirable alloying additions*

Summary

- PM bronze is effective at Zn capture
  - *The Sn changes the deposition characteristics from a regular geometric shape to a less well defined morphology*
    - Surface energy modification is expected cause
- PM bronze can be oxidized and reduced to remain effective as Zn getter
- Brass will decompose (dezincify) under high vacuum moderate temperature conditions
- An active zinc getter modification is recommended for testing in the system to determine feasibility

Summary

- All of the nanomaterials tested were effective as zinc getters.
- Various experimental conditions (different supports, NP composition, sizes, morphologies, different experimental parameters and surfaces substrates tested were evaluated revealing that Cu substrates and Au nanomaterials were the best at capturing Zn vapors.
- Deposition conditions affect the morphology, loading density, support geometry: planar vs. curved.
- The surface finish (rough vs. smooth) of the coupons greatly affects the adhesion of nanoparticles.
- Adhesion testing is highly dependent on support, Nps, experimental conditions

Summary

- The saturation effect during Zn deposition has been significantly reduced.
- The adhesion of the Zn deposits and nanomaterials has been improved by an order of magnitude over previous results.
- The composition of getters has been determined by XRD, and is found to be Au_5Zn_3.
- The most likely candidate for long term capture is a gold nano-particle. These particles alloy with the zinc vapors and form an intermetallic compound, which should be more stable than the simple alloying that occurs for the bronze to brass transition.
- Nanomaterials getters are found to alloy with the Zn vapor at a much lower temperature than their bulk counterparts, and thus, make better use of available thermal energy.
- Thermal coarsening is observed, which in addition to alloying, is expected to improve the stability of the captured Zn deposits over bulk materials.
- Nanomaterials can be cost effective due to thin surface treatment availability and ability for scaling up the solution chemistry developed:

Acknowledgements

- Donna Hasty and Bob Snyder for financial support through TEF Programs
- Katelyn Kessinger, Jonathan Baker, Melissa Golyski, Ansley Summer, Rebecca – Interns
- Craig Stripling laboratory support
- Michael Tosten TEM
- Adrian Medez-Torres SEM, Intern mentoring
- Tony Curtis SEM, Microscopy

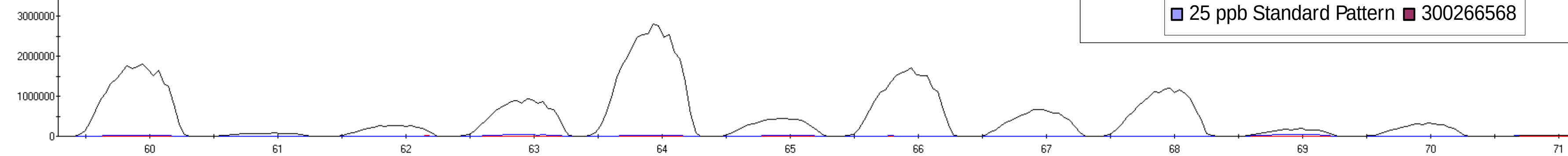
Backup Slides

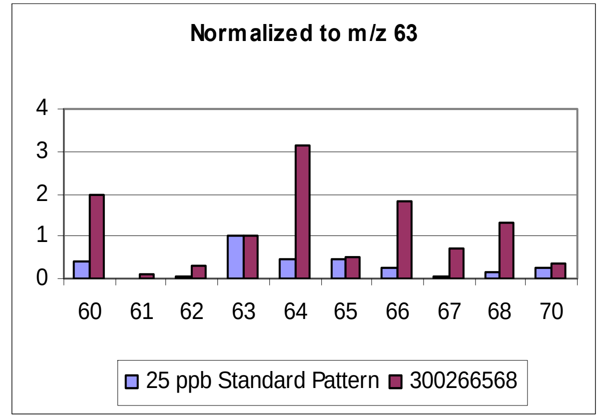
20 Micron Inside
300266568

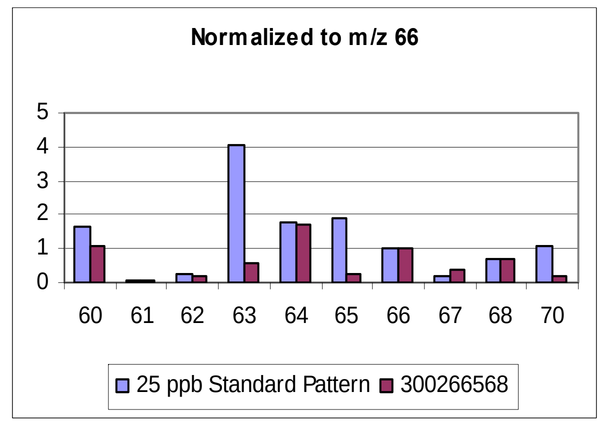
Red = Instrument Blank

Blue = 1 ppb Standard

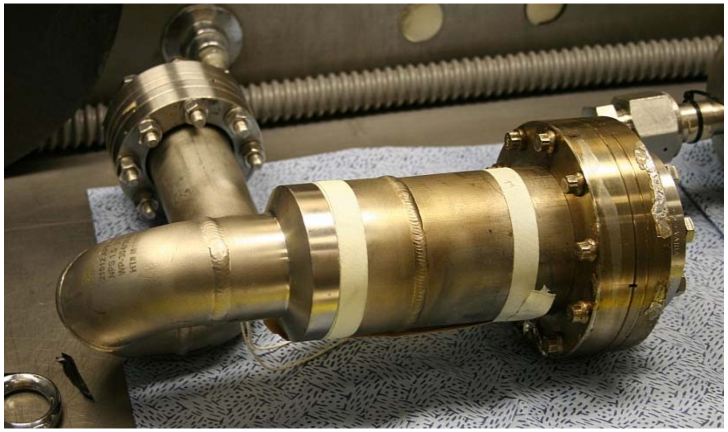
Black = Sample







Gamma Count – 20 µm Filter Smears – Filter Element

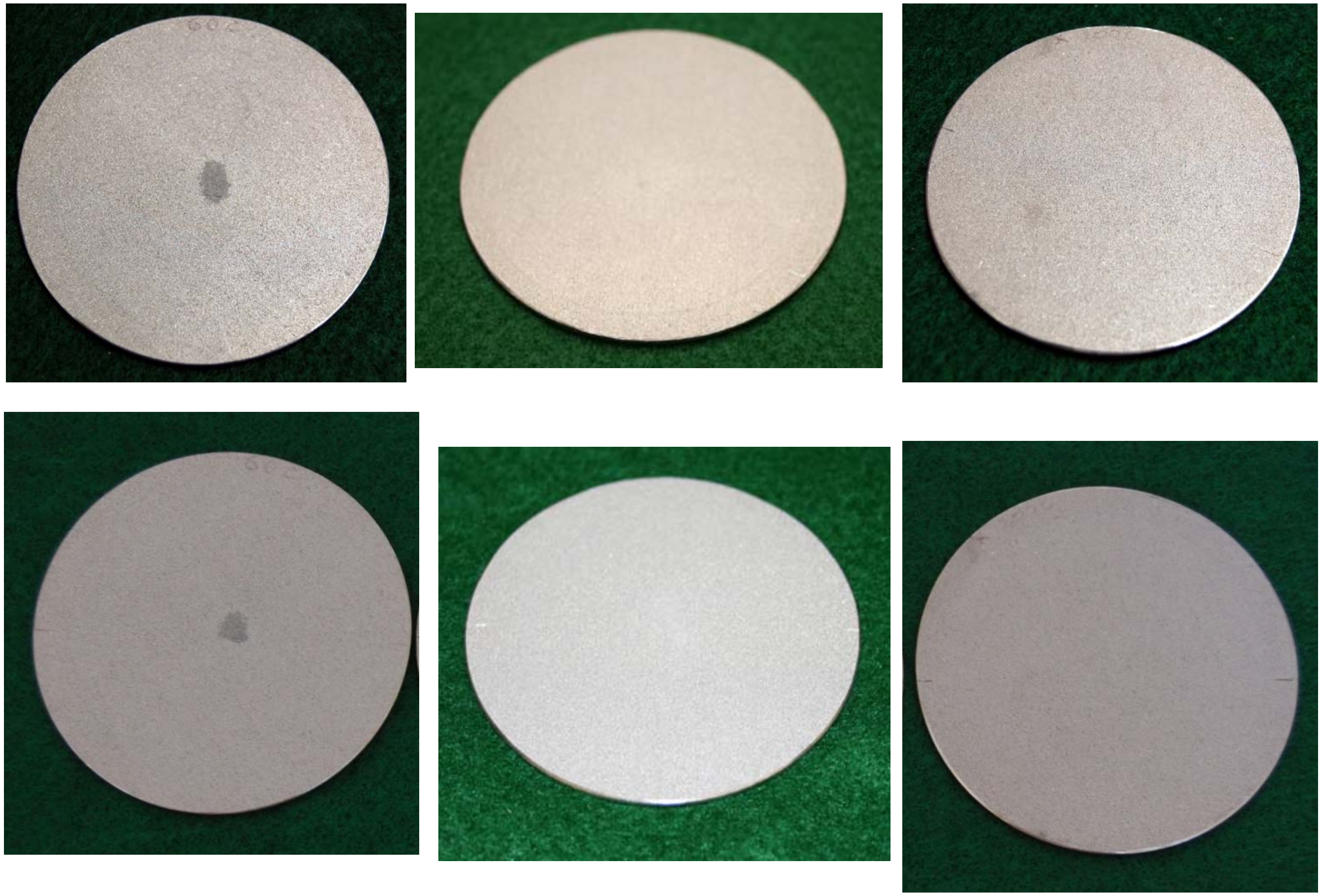


Sample	300267107	**20 µm Housing Smear**	**µCi**
Nuclide	Dpm/sample	1 Sigma Uncertainty	(0.5 Cd/Zn)
Zn-65	4.99E+04	5.00%	0.0225
Cd-109	2.55E+04	7.39%	0.0115
Sample ID	300266570	**Elbow**	
Nuclide	dpm/smear	1 Sigma Uncertainty	(3.7 Cd/Zn)
Zn-65	1.37E+04	5.00%	0.0062
Cd-109	5.05E+04	6.78%	0.0227
Am-241	2.22E+04	5.00%	0.0100

Using nominal size of piece and extrapolating it to the filter area indicates 43 µCi – same order of magnitude as Plant measurement (85 µCi) twice GS

Nuclide	dpm/smear	1 Sigma Uncertainty	**µCi**
Zn-65	<4.49E+02	MDA	NA
Cd-109	<1.13E+03	MDA	NA
Am-241	2.36E+04	5.00%	0.0106
Sample ID	300266568	**20 µm outside smear**	
Nuclide	dpm/smear	1 Sigma Uncertainty	(3 Cd/Zn)
Zn-65	5.18E+03	6.38%	0.0022
Cd-109	1.54E+04	8.79%	0.0069
Am-241	2.33E+04	5.00%	0.0105
Sample ID	300266569	**20 µm inside smear**	
Nuclide	dpm/smear	1 Sigma Uncertainty	(1.5 Cd/Zn)
Zn-65	5.52E+03	6.19%	0.0025
Cd-109	8.44E+03	12.3%	0.0038
Am-241	2.32E+04	5.00%	0.0105
Sample ID	300266925	**20 µm Filter Media**	
Nuclide	dpm/filter piece (~1cm^2)	1 Sigma Uncertainty	**(0.1 Cd/Zn)**
Zn-65	**1.33E+06**	**5.00%**	**0.5991**
Cd-109	1.11E+05	7.45%	0.0500

Filter Temperature Effects



As Deposited

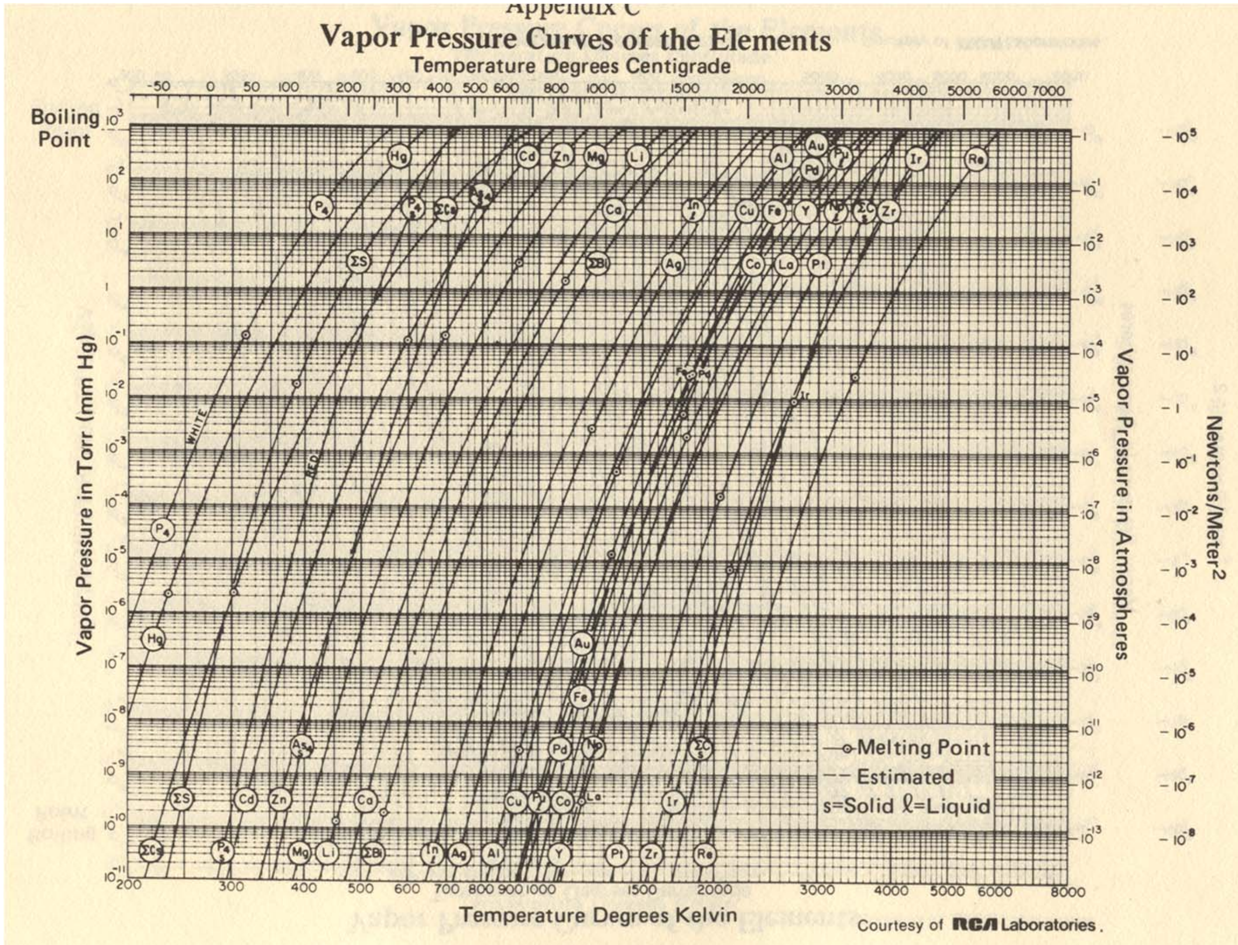
After Adhesion Testing

60^{o}C 3.8 mg   120^{O}C 1.6 mg   200^{o}C 2.6 mg

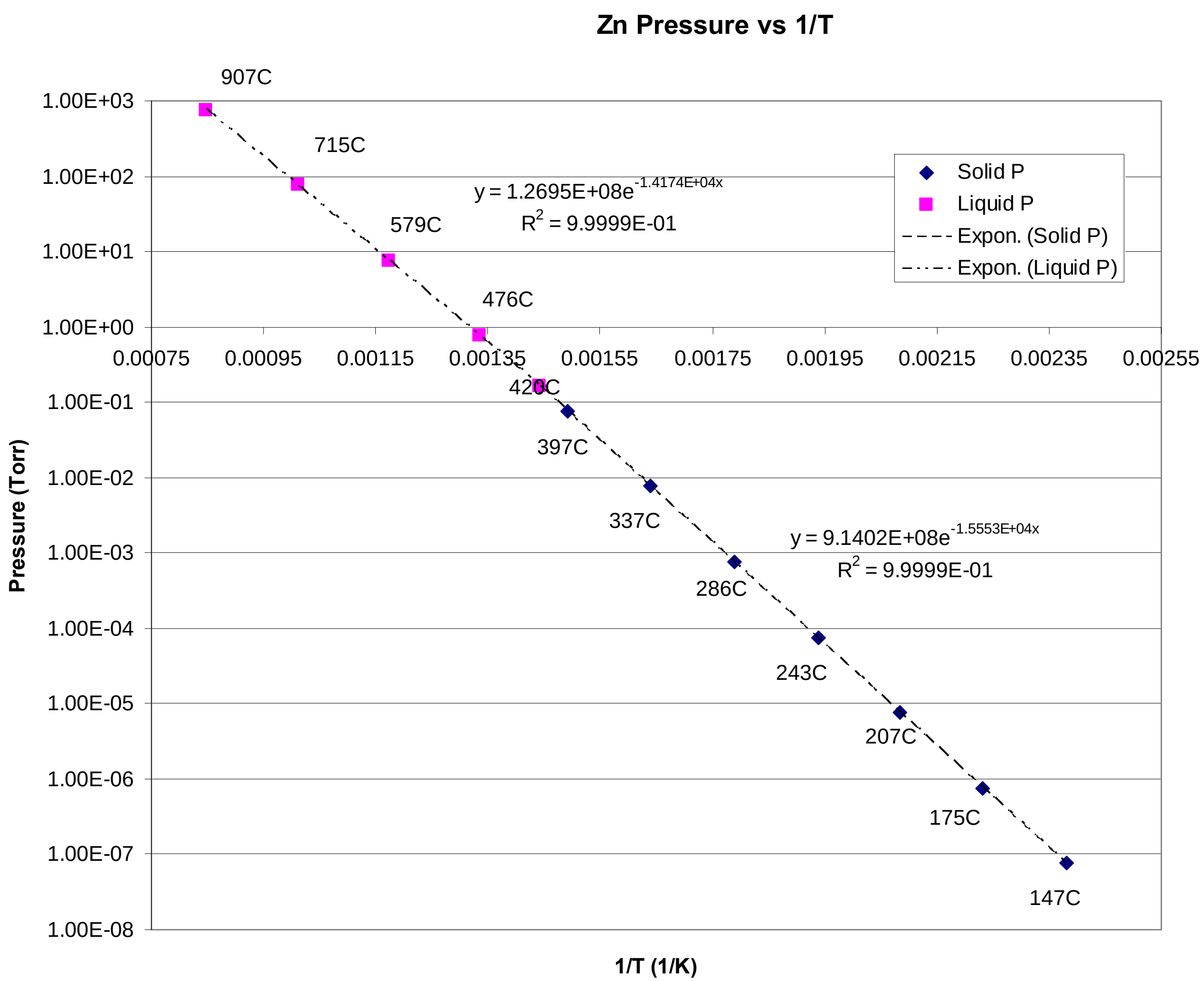
Half of the deposit on the 60^{o}C and 120^{o}C filter was removed after tape adhesion test

No material was lost from the 200^{o}C filter

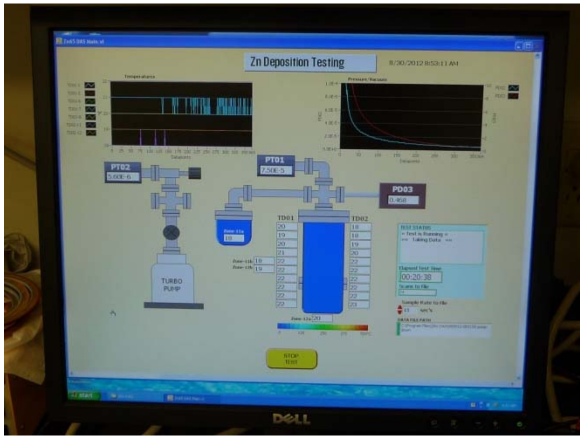
Vapor Pressure of the Elements



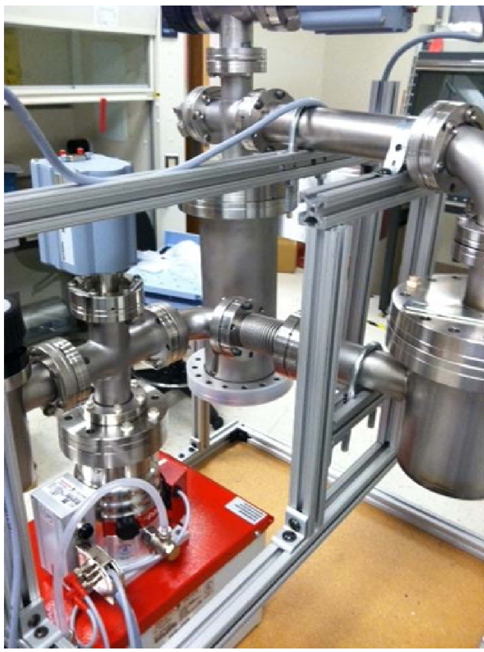
Predicted Zn Pressure

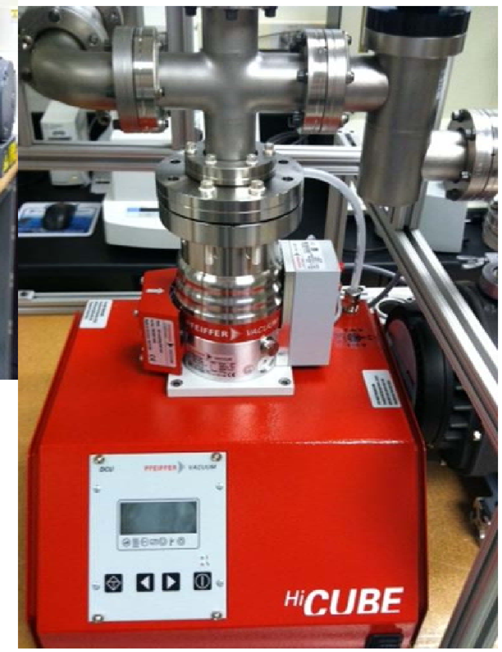


Experimental Set Up



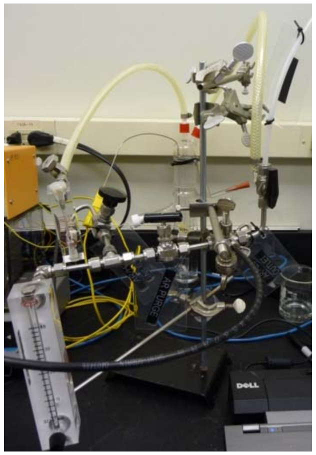
Apparatus Photos





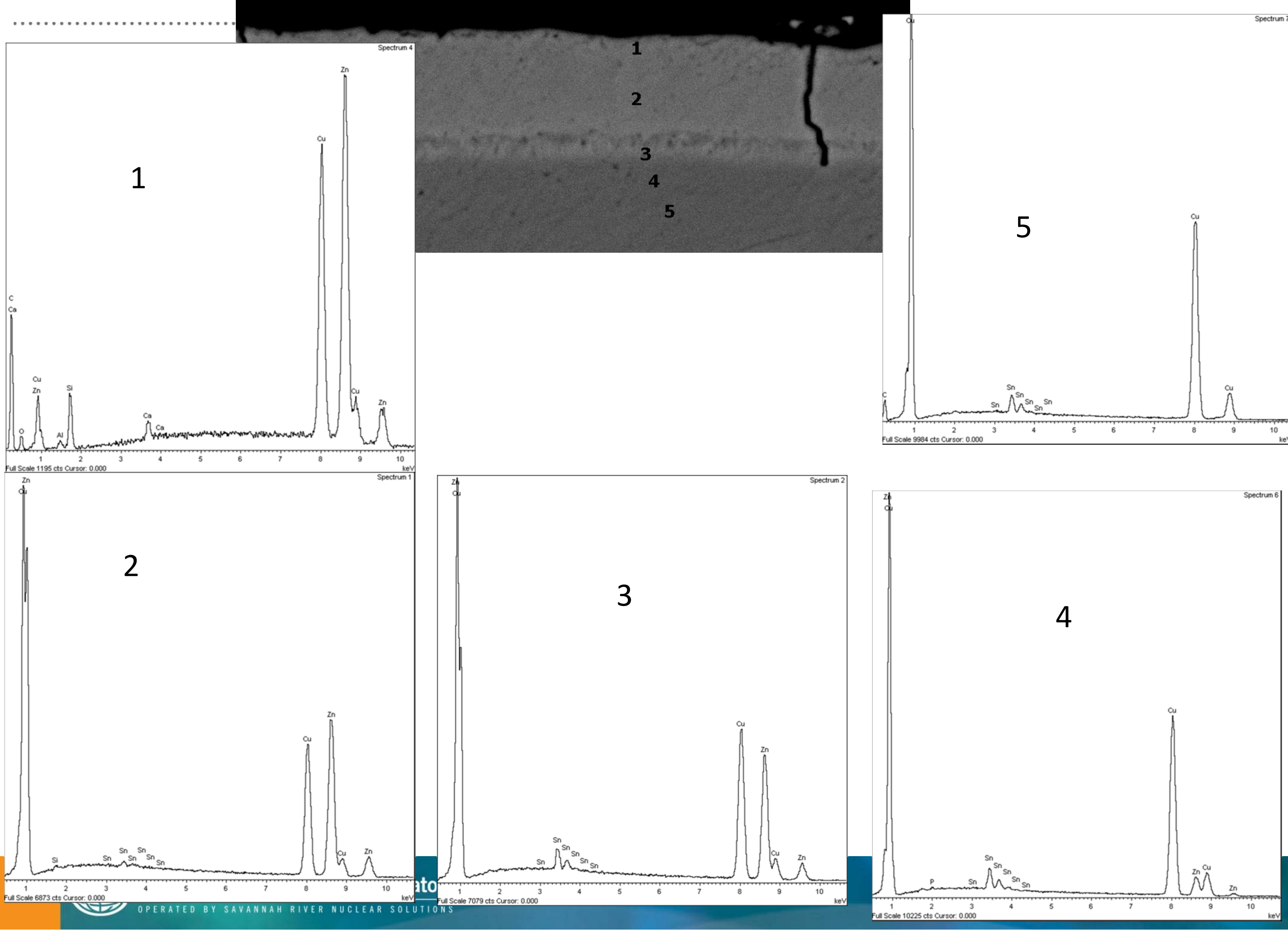
Apparatus Photos

Oxidation Exposure

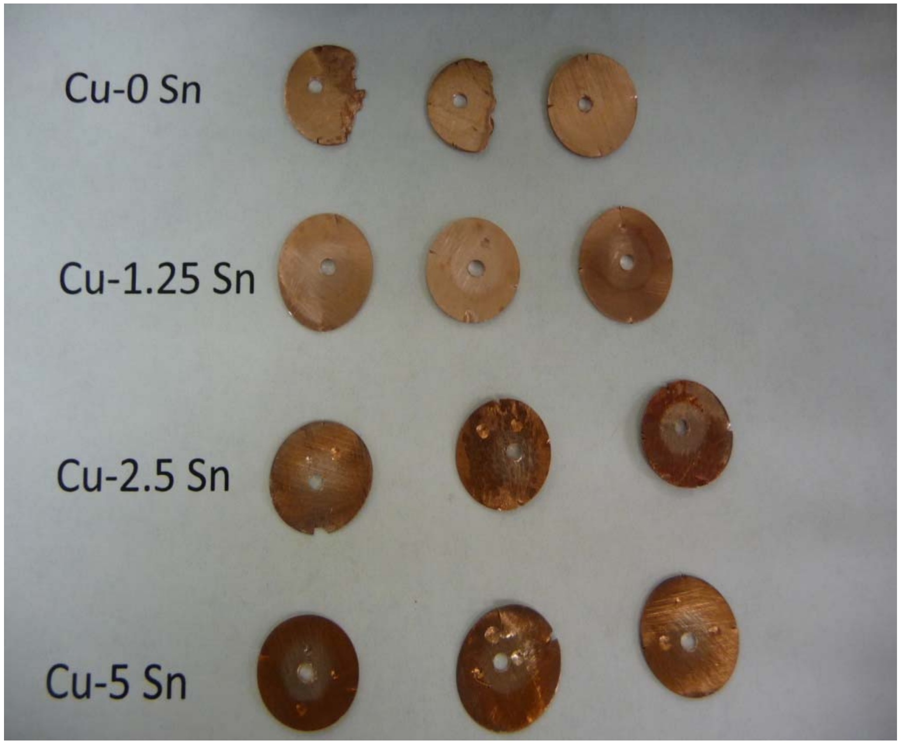


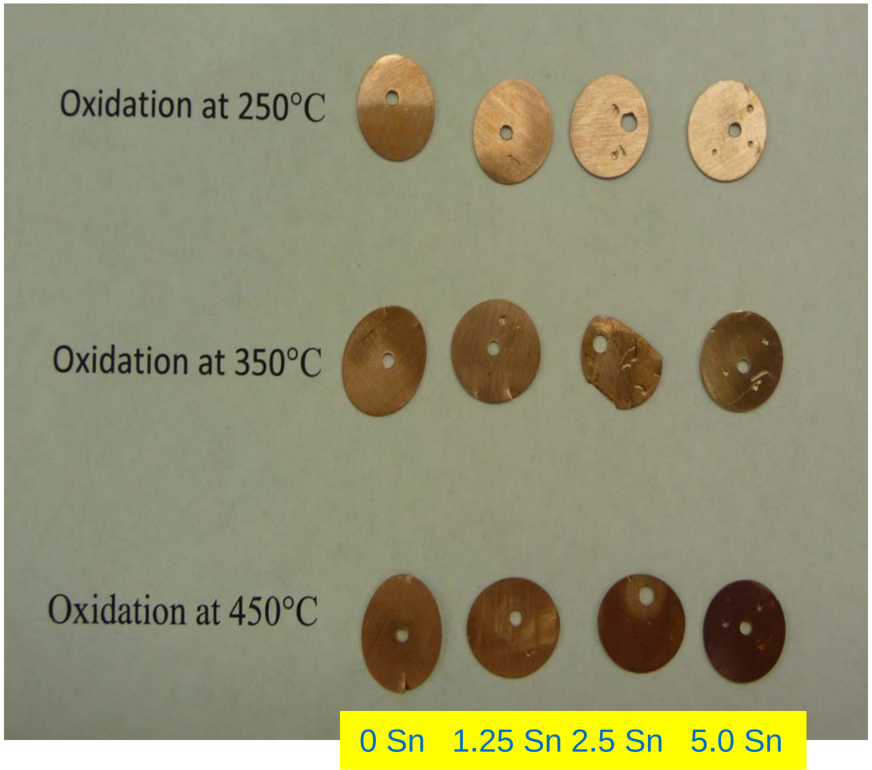
- A simple gas manifold was constructed to saturate argon purge gas with room temperature water vapor and used with the sintering furnace
    - *Flow conditions and test parameters were determined so air was displaced and only water vapor was introduced into the furnace*
- A two hour purge at 1 scfh was used to eliminate the air
- Water saturated Ar was introduced at 2 scfh
- Samples were heated to exposure temperatures of 250, 350, or 450°C and held for 12 hours
    - The MS measured the nitrogen, water vapor, oxygen, hydrogen and argon content during the exposure
        - *This information validated that the purge time and flow were sufficient to reduce the residual air to acceptable levels*
        - *This data showed qualitatively that water was being cracked over the surface of the samples as they oxidized*
- The as received and oxidized samples were examined using a scanning electron microscope (SEM) and x-ray diffraction equipment (XRD)

BR2 Cross-section with EDX locations



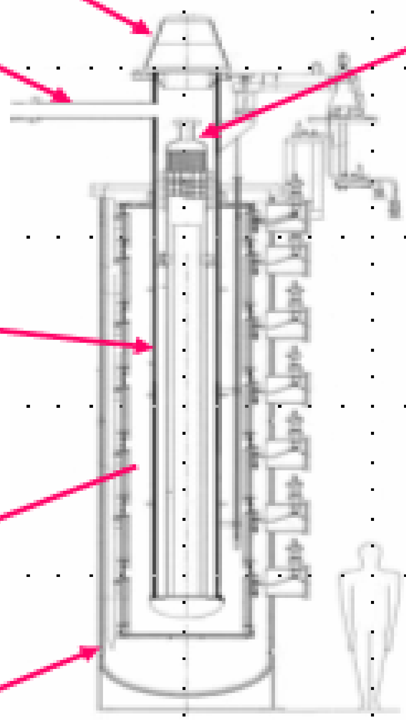
Oxidation Results





Left: Oxidation at 350°C
Right: Oxidations 250°C, 350°C and 450°C

Furnace Layout



Retort – extraction chamber
Cold Wall – exterior of furnace assembly
Annulus – volume between Retort & Cold Wall

Electric heater elements mounted in the Annulus

Overall height ≈ 25 feet

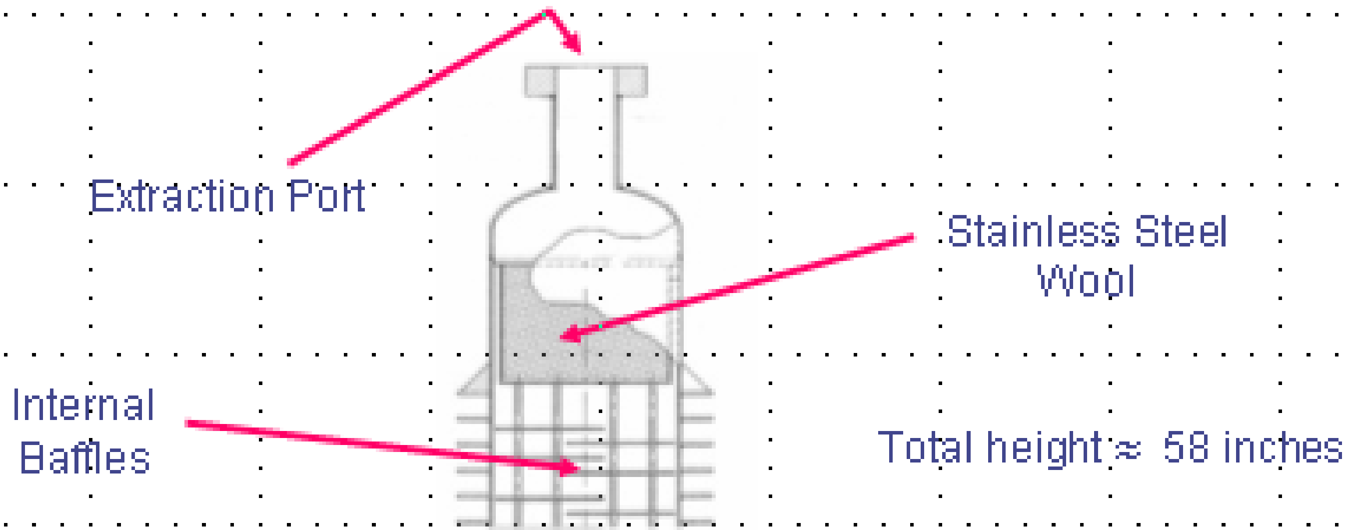
Cold Wall is cooled by Furnace Cooling Water System

Extraction Lid & Basket Filter

Bolts to extraction basket flange

Provides extraction gas outlet port & filter

- Torturous path & stainless steel wool
- Baffles provide reflective insulation (maintain lid < 350°C)
- Permits lithium contaminants to condense inside the basket



Zn Vapor Deposited on Stainless Steel