Project Update and Results of Analyses of Fine Particulates in Cleaned Coal Syngas and Its Combustion Products

University Turbine Systems Research (UTSR) Workshop
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Project Overview

- The University of North Dakota (UND) Energy & Environmental Research Center (EERC) and Department of Mechanical Engineering are working with Siemens Power Generation to test a new method for joining high-temperature alloys for use in advanced high-hydrogen-gas-burning turbines.
- Thin plates of oxidation- and spallation-resistant Kanthal APMT™ will be bonded to high-strength CM247LC and Rene® 80 using evaporative metal (EM) bonding.
- Bonded parts, with and without thermal barrier coatings (TBCs), will be tested for oxidation, corrosion, and spallation resistance.
- Gasifier sampling to determine appropriate corrosion conditions.

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Alloy Compositions

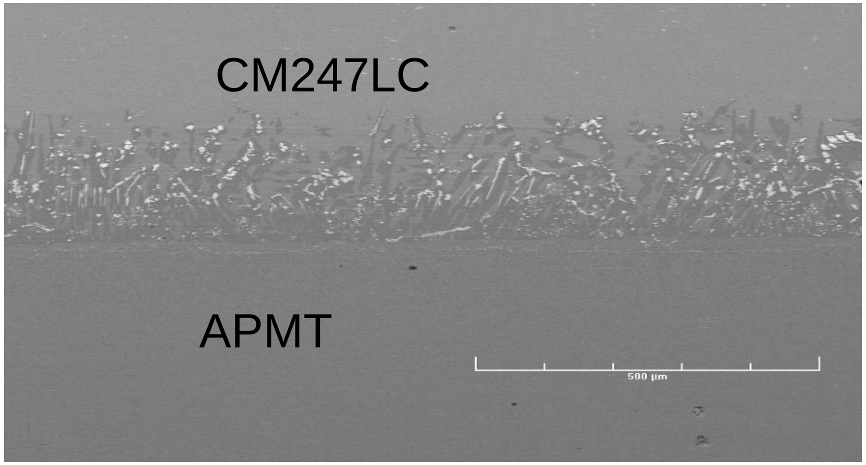
Composition of Kanthal APMT, wt% – Dispersion-Strengthened						
	Cr	Al	Mo	Mn	Si	Fe
APMT	22	5	3	0.4	0.7	Balance

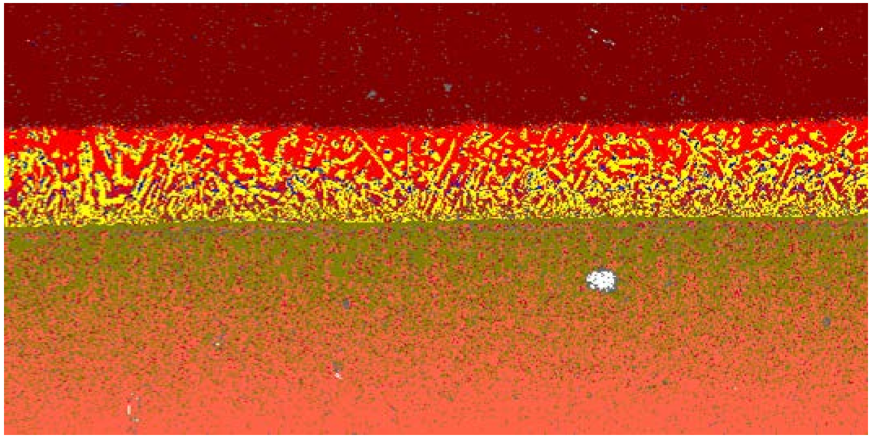
Composition of CM247LC, wt% – Gamma Prime-Strengthened													
	Fe	Ni	Cr	Al	Ti	Co	Mo	Ta	W	Nb	Hf	Mn	Si
CM247LC	–	Balance	8.1	5.6	0.7	9.5	0.5	3.2	9.5	0.1	1.4	–	–

Composition of Rene 80, wt% – Gamma Prime-Strengthened												
	Cr	C	Mo	W	Ti	Nb	Co	Al	B	Fe	Zr	Ni
Rene 80	14.2	0.16	4.0	4.1	5.1	0.03	9.4	3.0	0.02	0.10	0.04	Balance

Microstructure of EM Joints

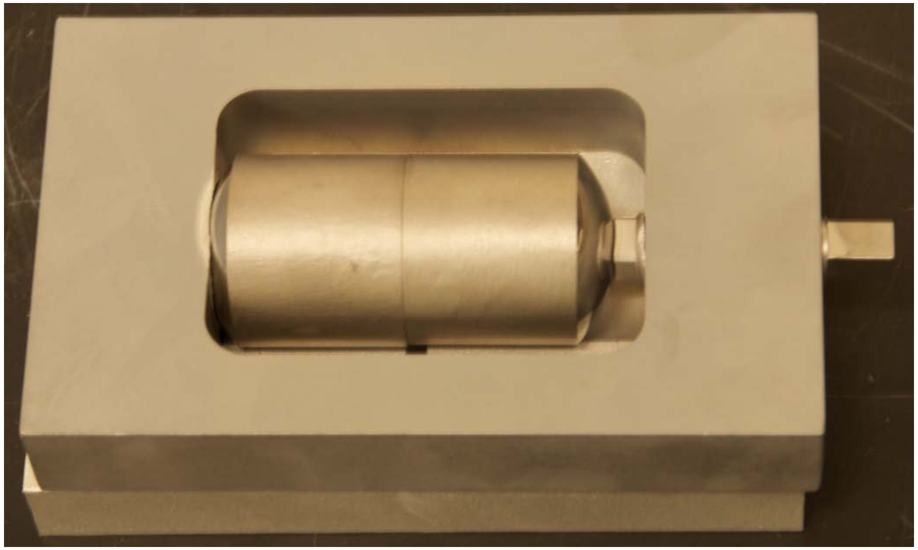
- Scanning electron microscopy (SEM) photo (top) and x-ray map (bottom).
- Needle growth and interdiffusion to create a joint stronger than the APMT.
- Nickel diffuses up to 700 µm into APMT.
- Iron diffuses 200 µm into CM247LC.





Articulated Clamping System

- Specimens are electrodischarge-machined to shape.
- Bonding surface is blasted with silica beads.
- Clamp is made from low-CTE metal (TZM molybdenum).
- Steel hemispheres (E52100) are used to articulate the pieces, which is necessary because of the thinness of the foils. Steel is used to facilitate modeling.
- Joints of APMT to CM247 and APMT to Rene 80.



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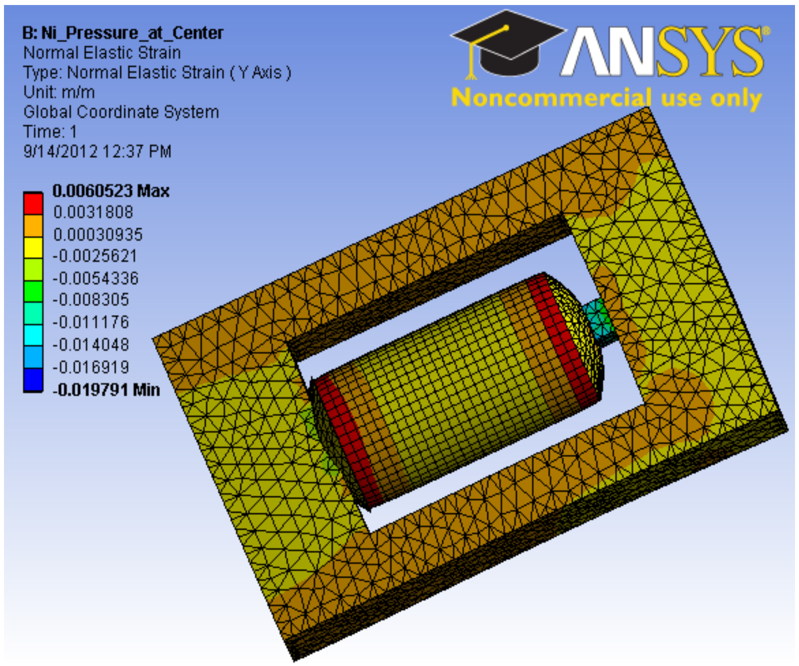
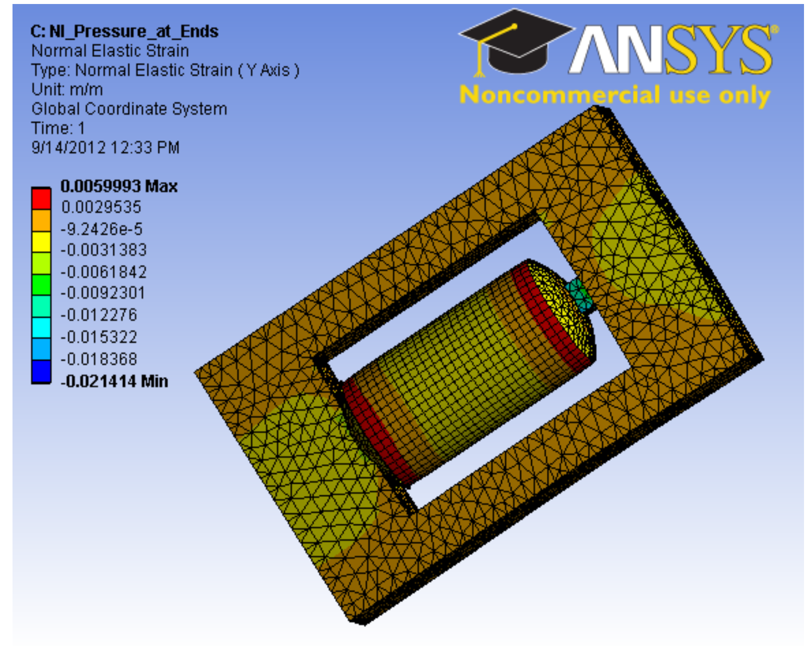
Stress modeling within the clamps



(a)



(b)

Comparison of strains in the bonding assembly when loads are applied at a) joint center or b) joint ends.

Stress Distribution at Bond Surface

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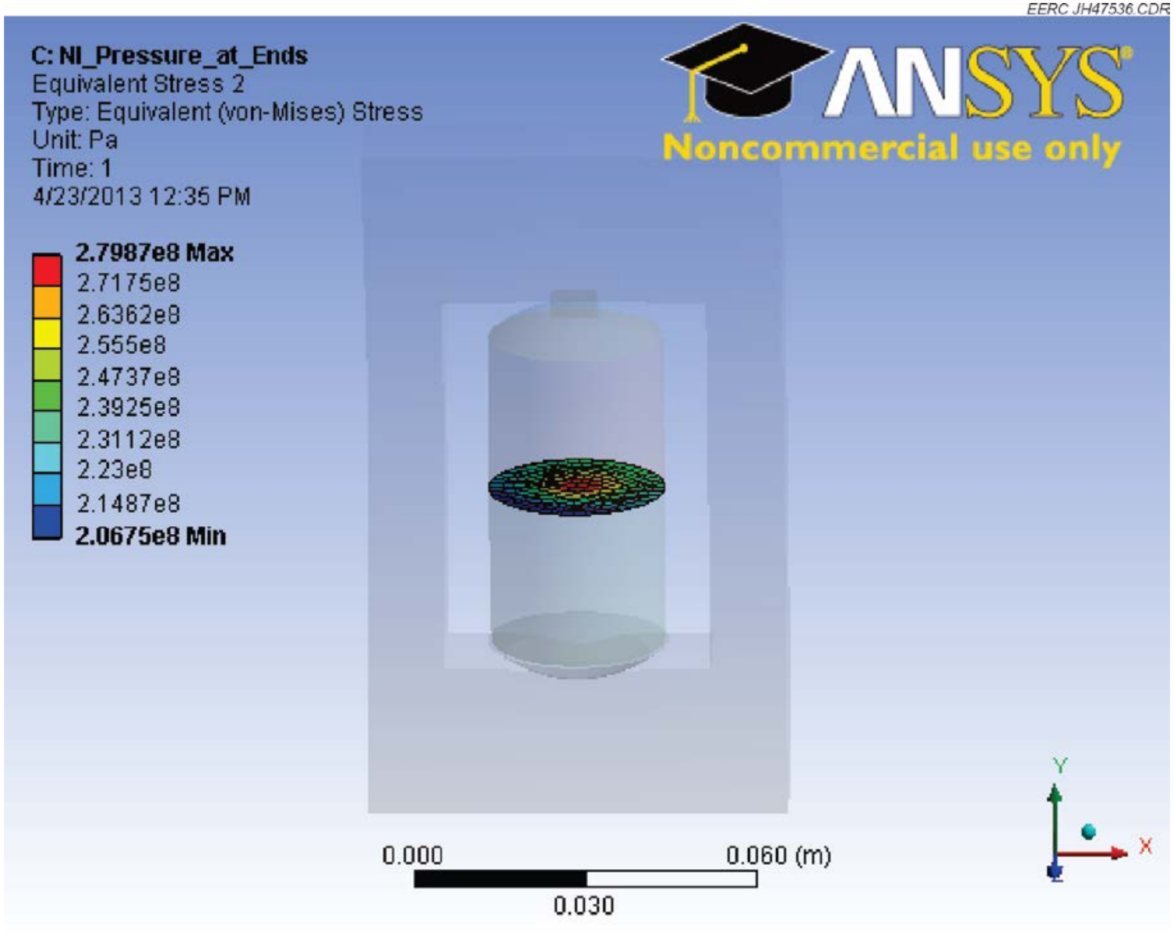

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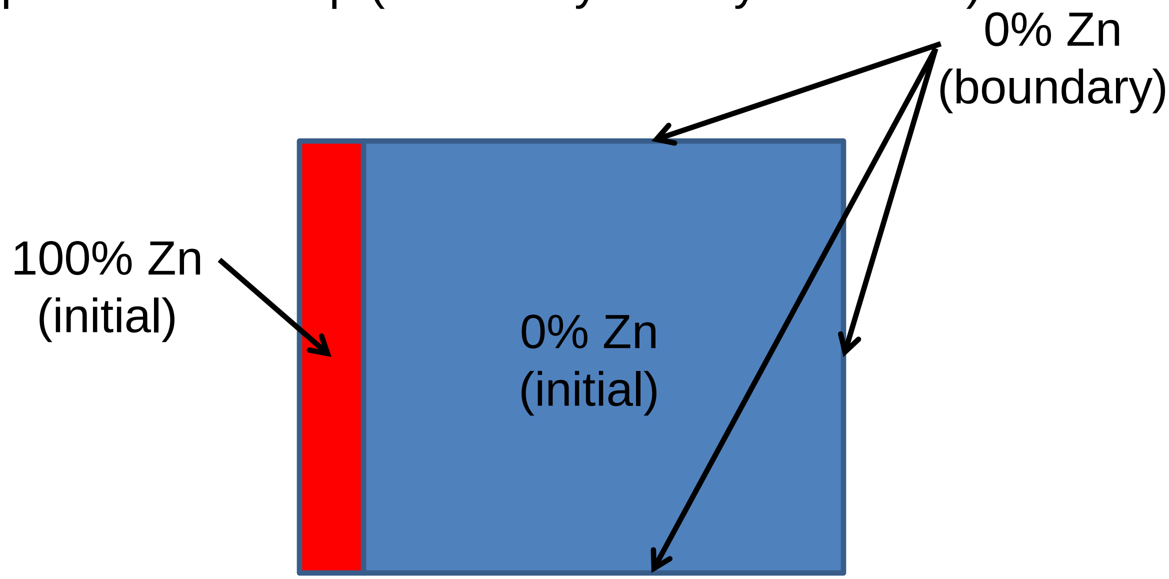
Diffusion Modeling

$$\frac{\partial C}{\partial t} = D\left[\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2}\right]$$

3-D Diffusion with Constant Diffusivity

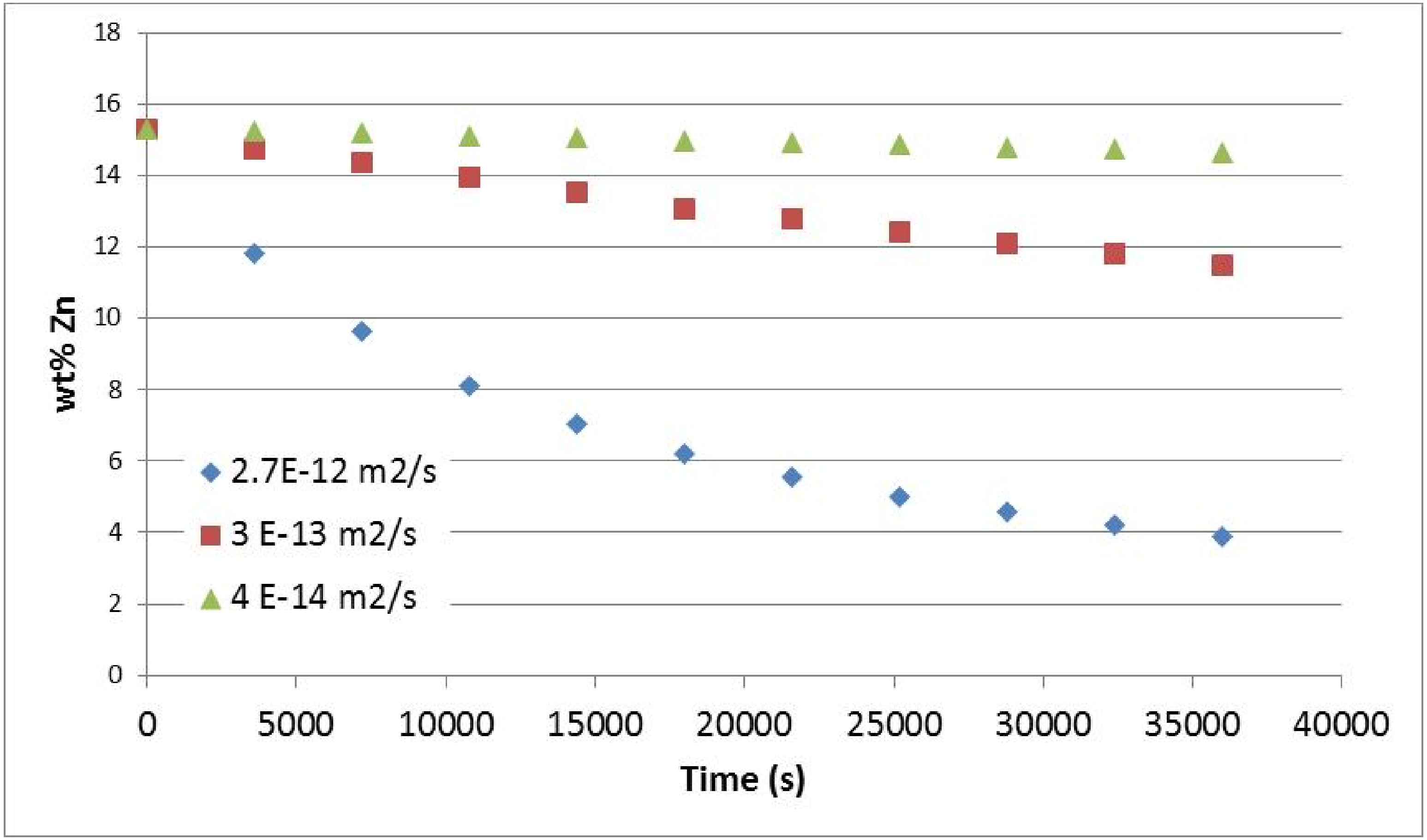
No analytical solution exists for the combination of initial and boundary conditions present in the experimental setup (midline symmetry assumed):



Diffusion Modeling

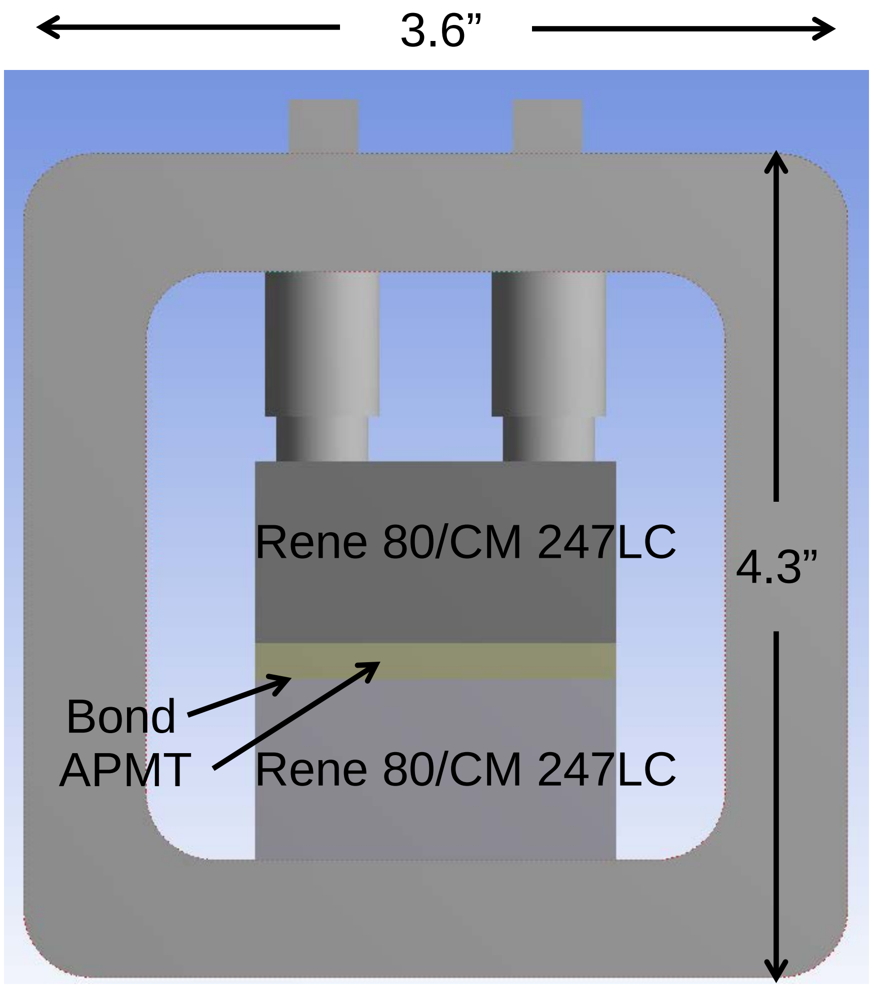
- A finite difference algorithm was implemented within MATLAB to solve the diffusion equation.
- The ‘hopscotch’ iterative solver was implemented to improve accuracy and computational efficiency.
- Algorithm assumes initial midline concentration of Zn, assumes constant diffusivity, uses a rectangular geometry and allows for different mesh size in each direction (x, y, z).

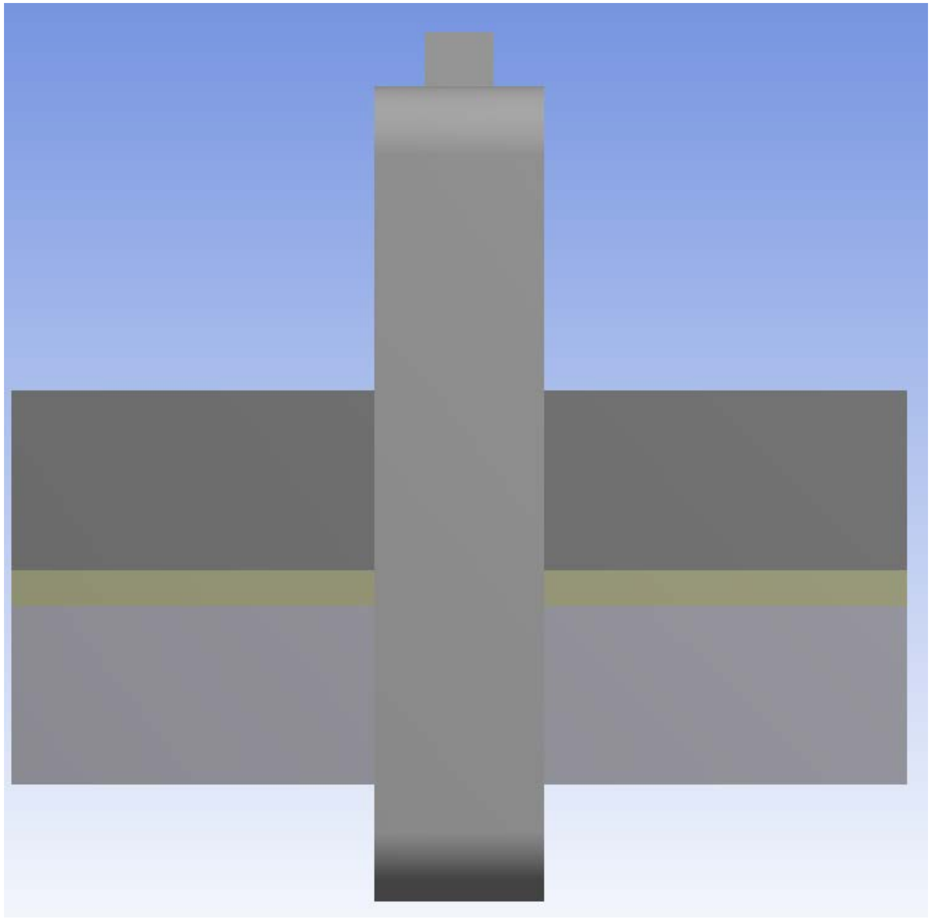
Diffusion Modeling



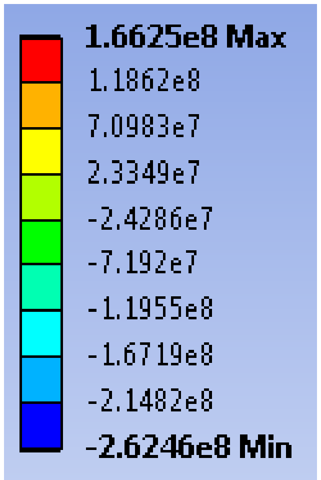
- ~15 wt% initial centerline composition for model
- D for Zn in APMT ~2.7 E-12 m^2/s
- D for Zn in Rene 80/CM 247 ~4 E-14 m^2/s

Joint Stresses

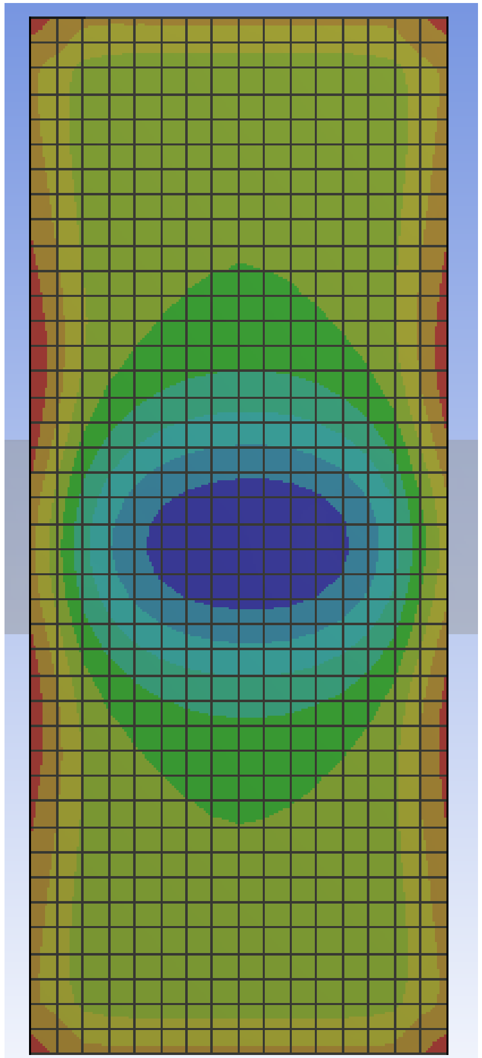


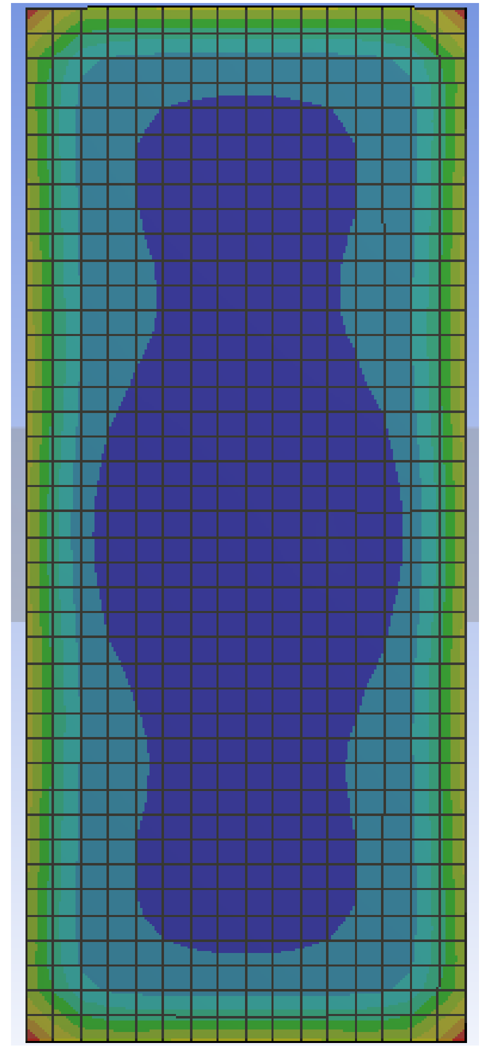


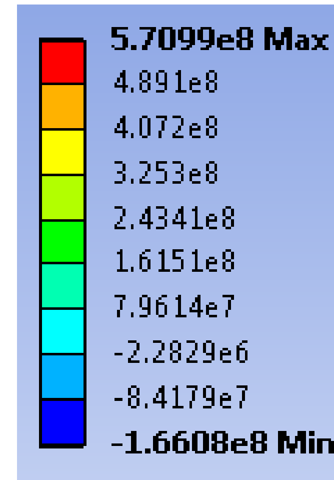
Joint Stresses (N/m^2)



Rene 80/APMT



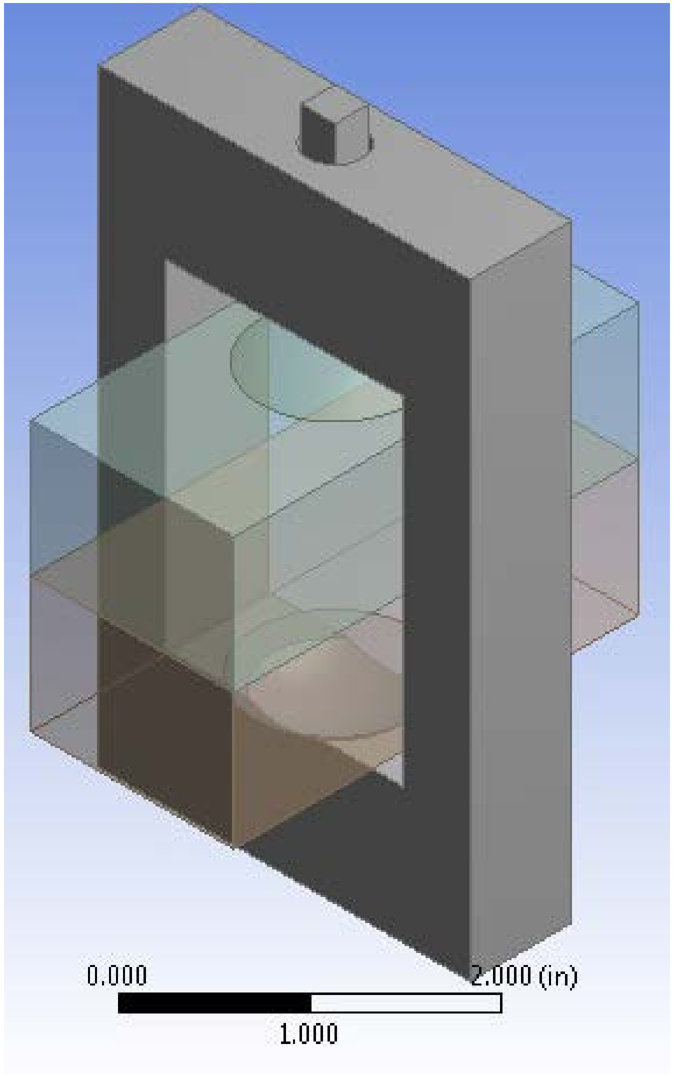




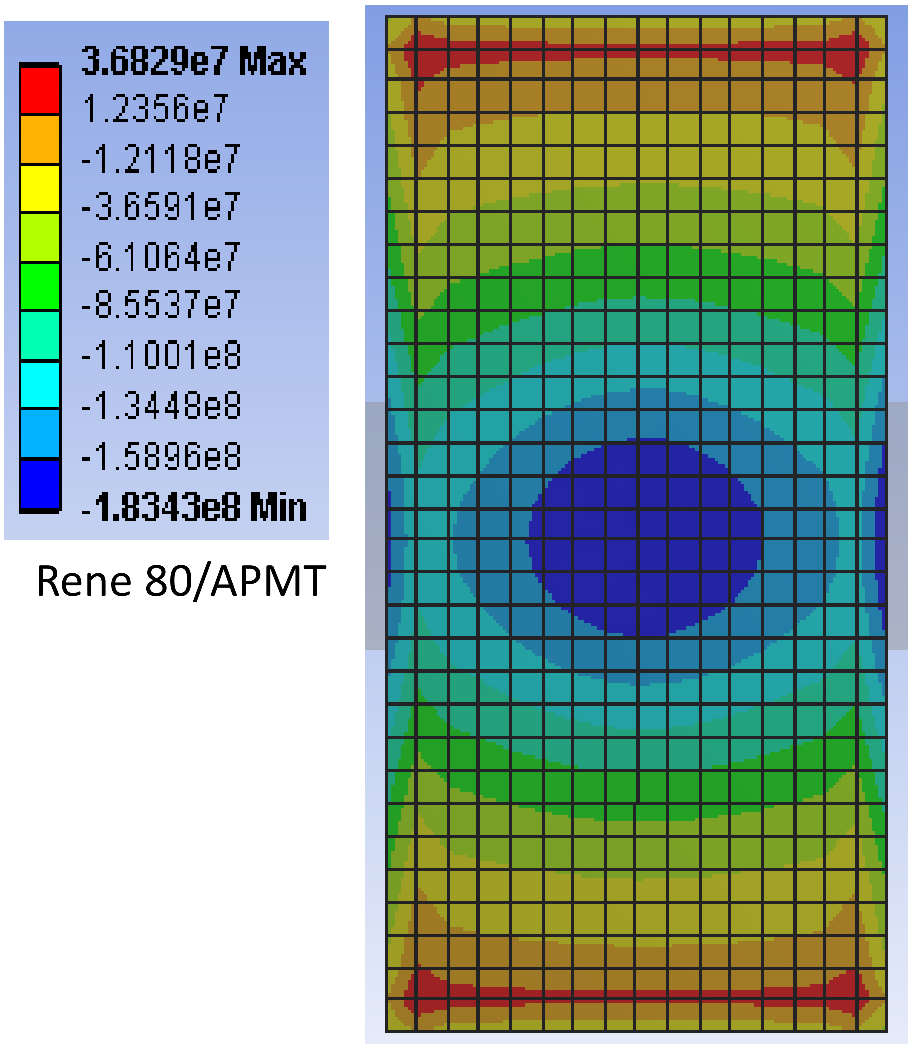
CM247LC/APMT

1200°C

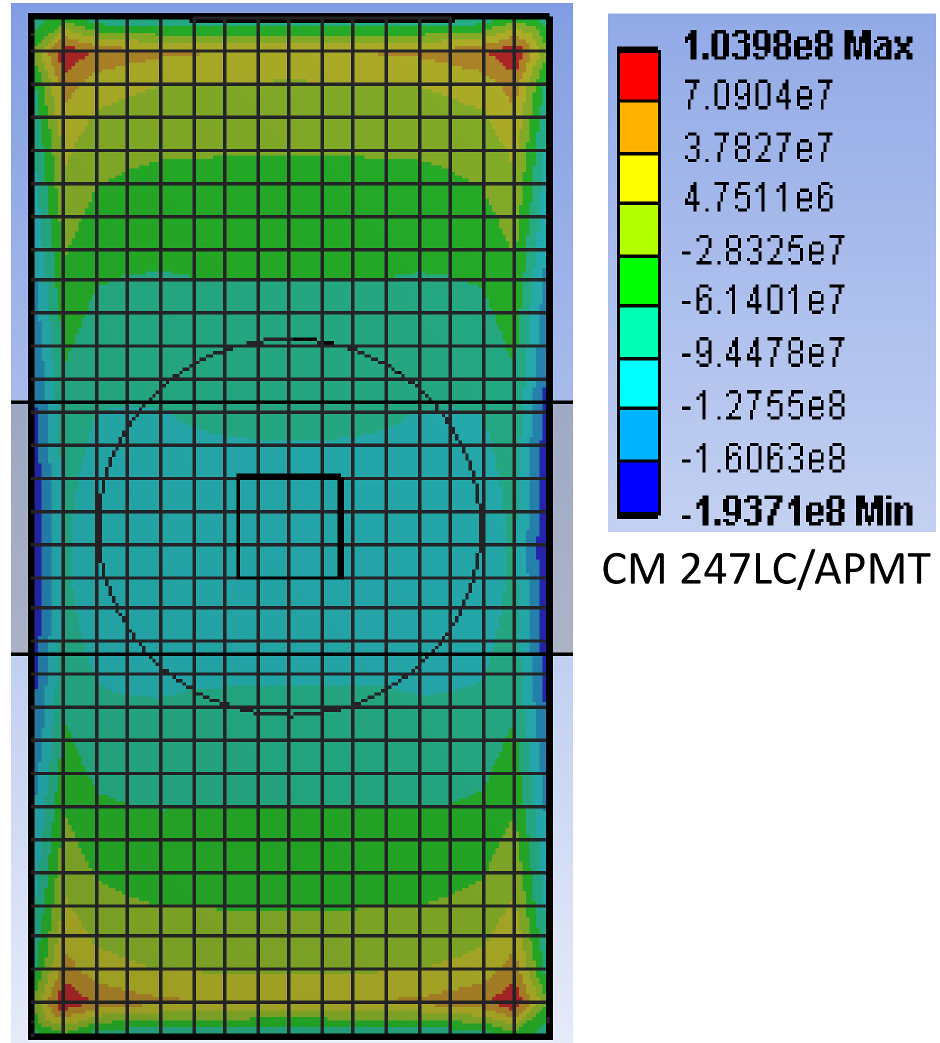
Joint Stresses



Joint Stresses (N/m^2)



Rene 80/APMT



CM 247LC/APMT

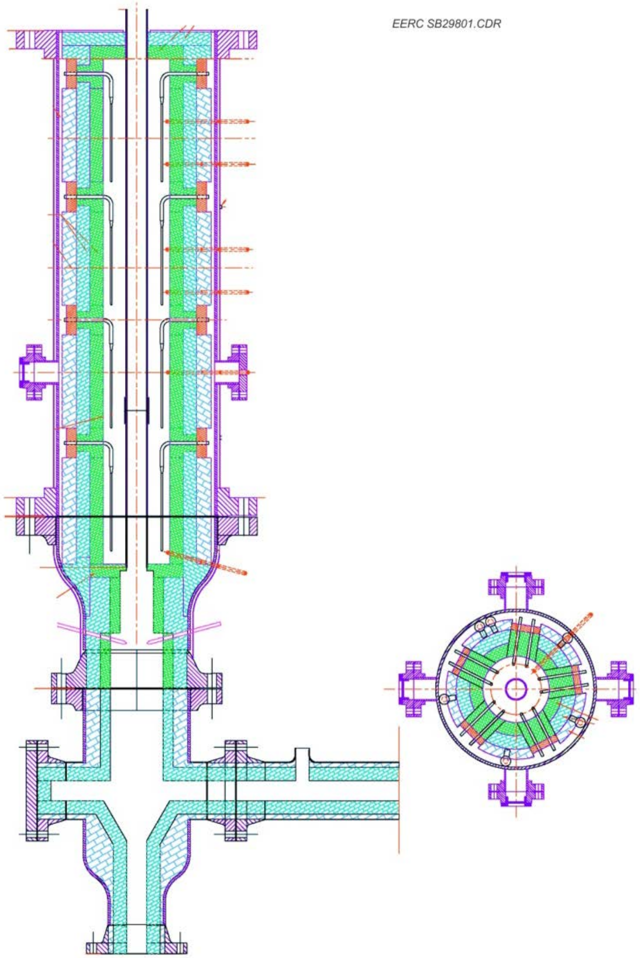
1200°C

Joint Stresses

- Regions of tensile stresses are likely artifacts of model boundary conditions (materials fixed across interface).
- Model convergence issues occurred when alternate interface conditions used (e.g., frictional boundary, springs, etc.).
- The steel hemispheres allow for joint articulation and have a larger area to reduce stresses in the bolt due to the lower yield stress of the steel compared to the TZM molybdenum.

Characterization of Combusted Syngas Contaminants

- Information to be used in designing later corrosion testing – contaminants will not be similar to gasifier fly ash.
- Collection of microcontaminants in combusted syngas created in two pilot-scale gasifiers.
- Analysis of captured microcontaminants by SEM.



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EERC Pilot-Scale Gasifiers

Entrained-Flow Gasifier (EFG)
1800°C, 300 psi

Fluid-Bed Gasifier (FBG)
800°C, 600 psi

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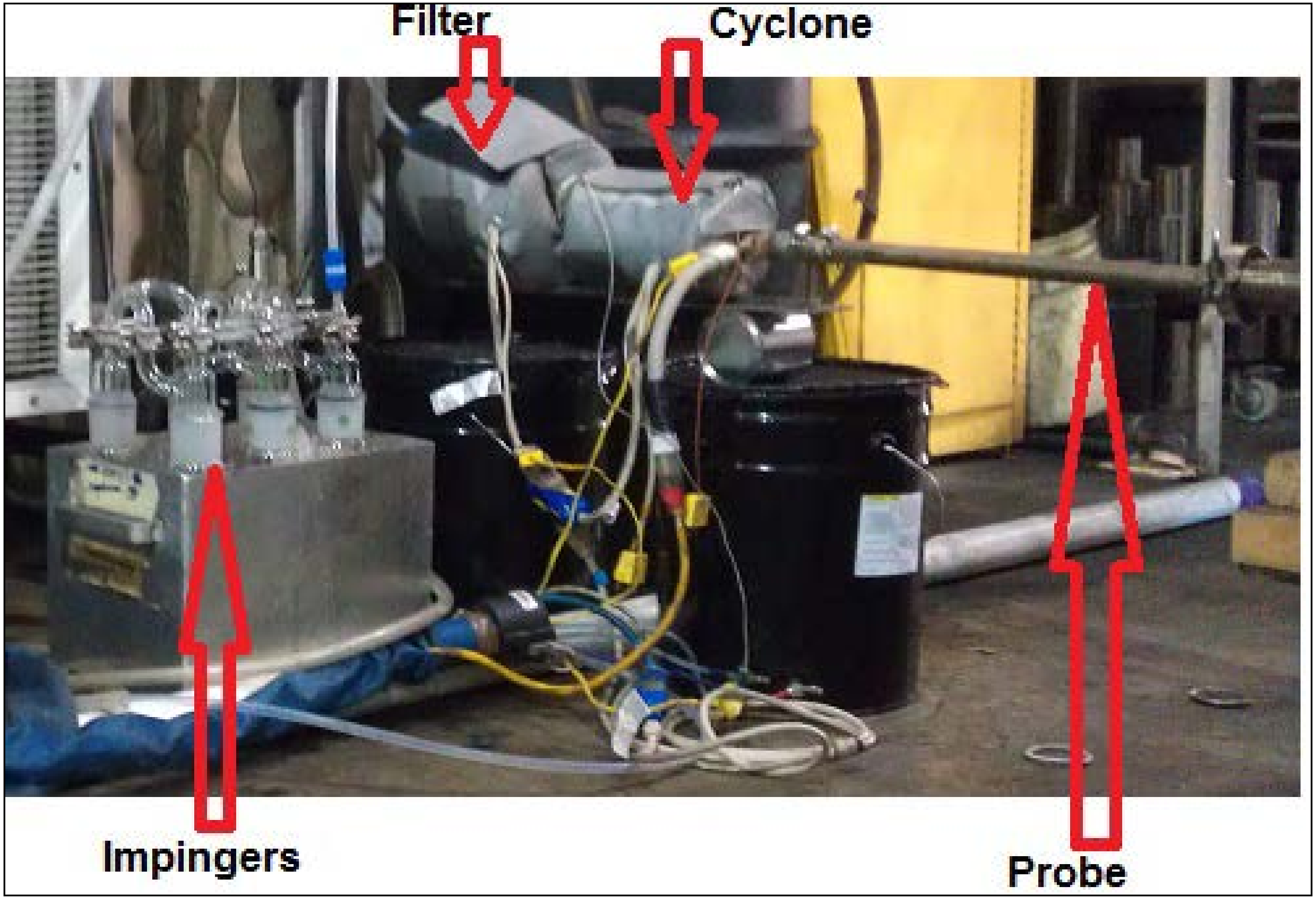
Sampling System



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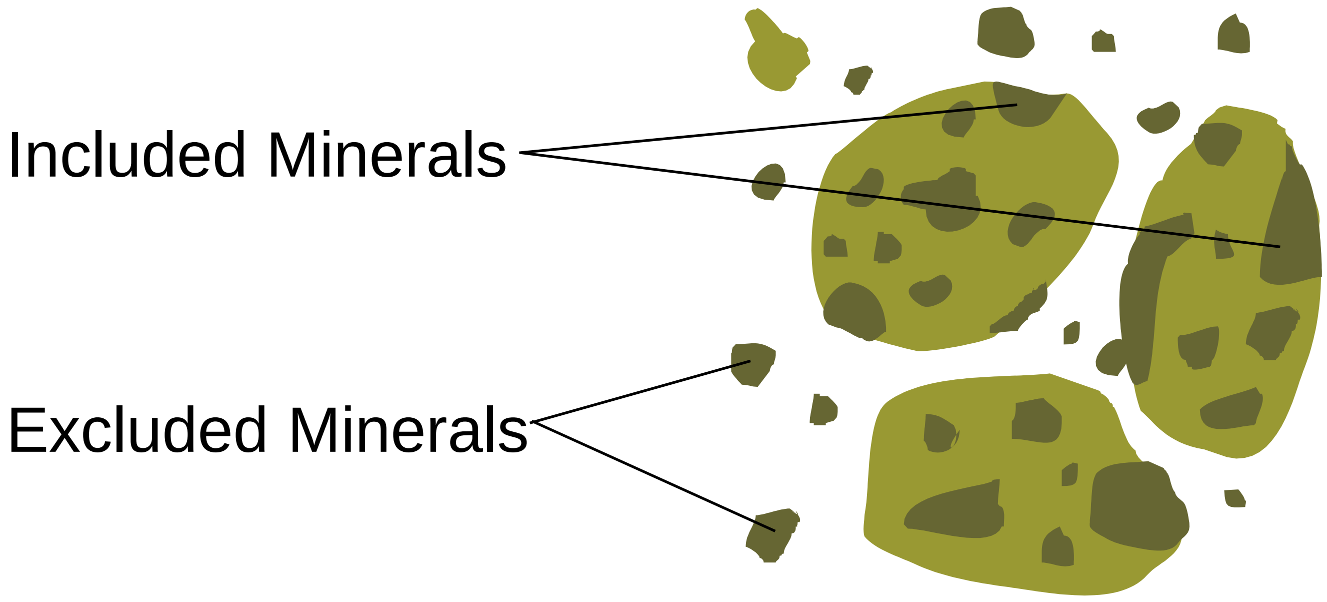
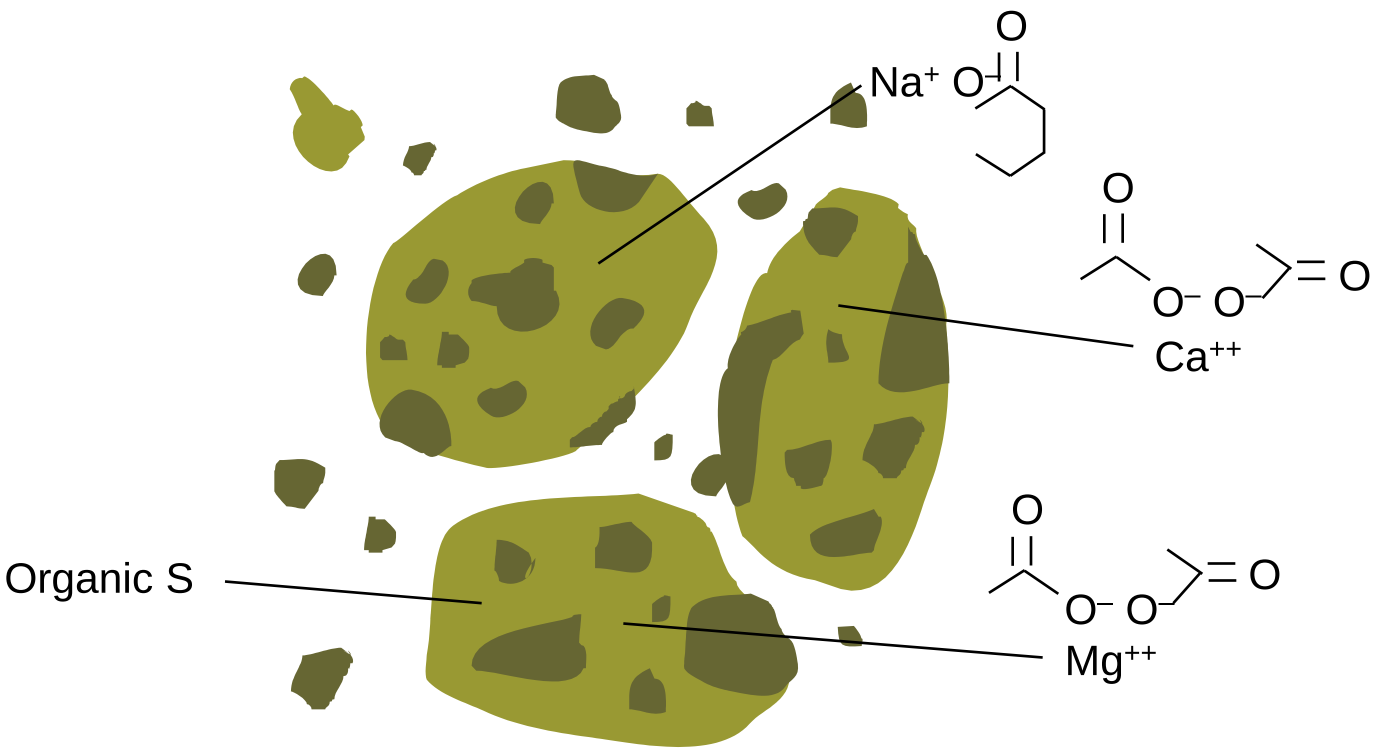
Inorganic Forms in Coal – Minerals



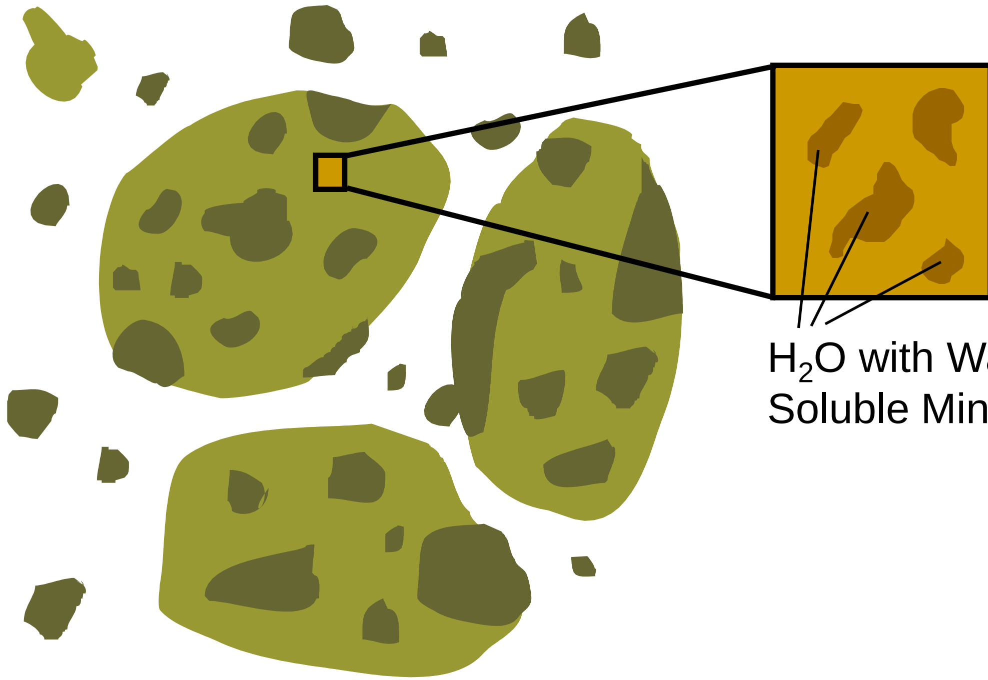
- Included minerals are contained within the carbon matrix of the coal.
- Excluded minerals are independent of the carbon matrix of the coal.

Inorganic Forms in Coal – Organically Associated



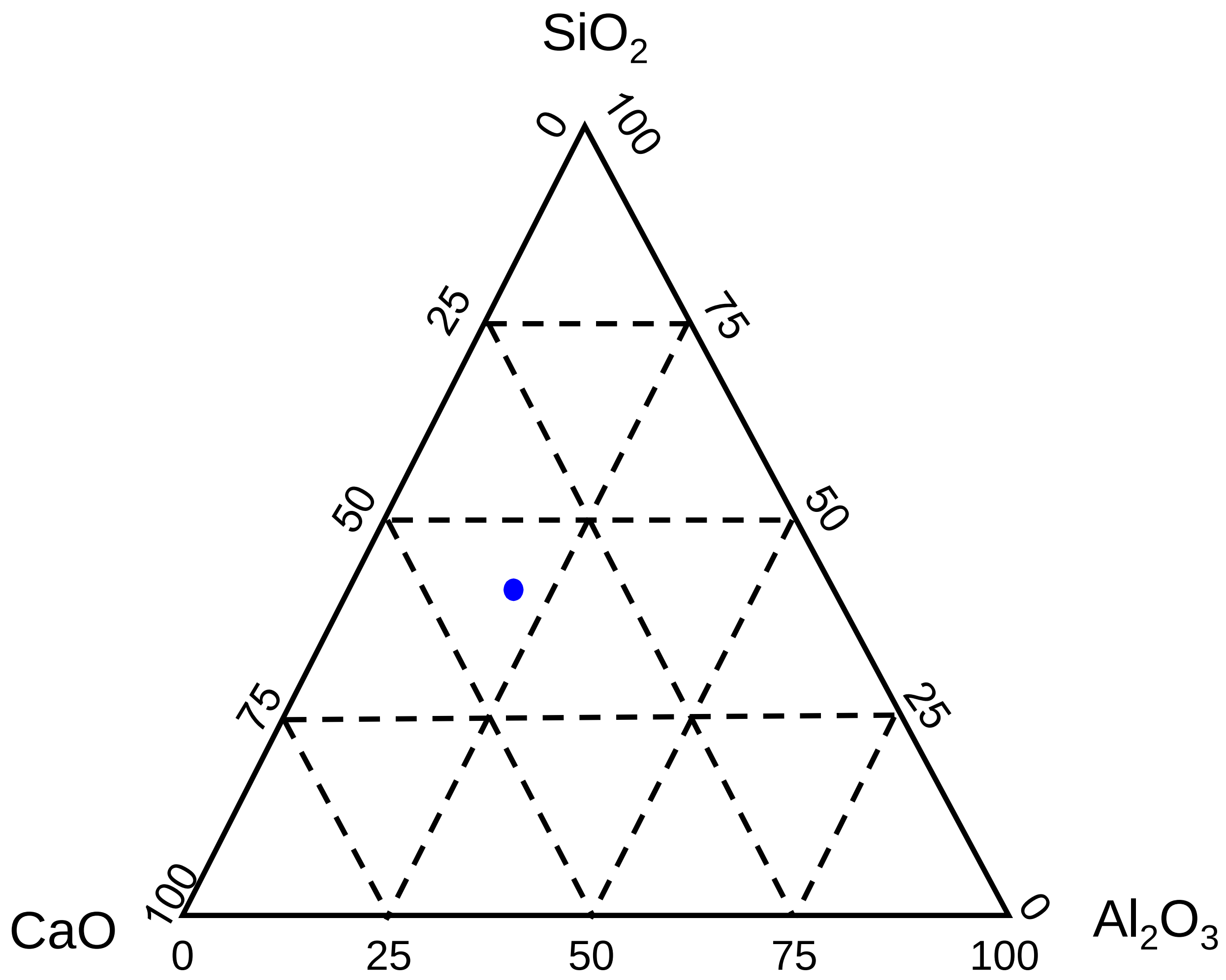
- Bound as salts of carboxylic acids.
- Organically associated sulfur.
- Coordination complexes Al^{3+} and Fe^{3+}.

Inorganic Forms in Coal – Fluid Matter

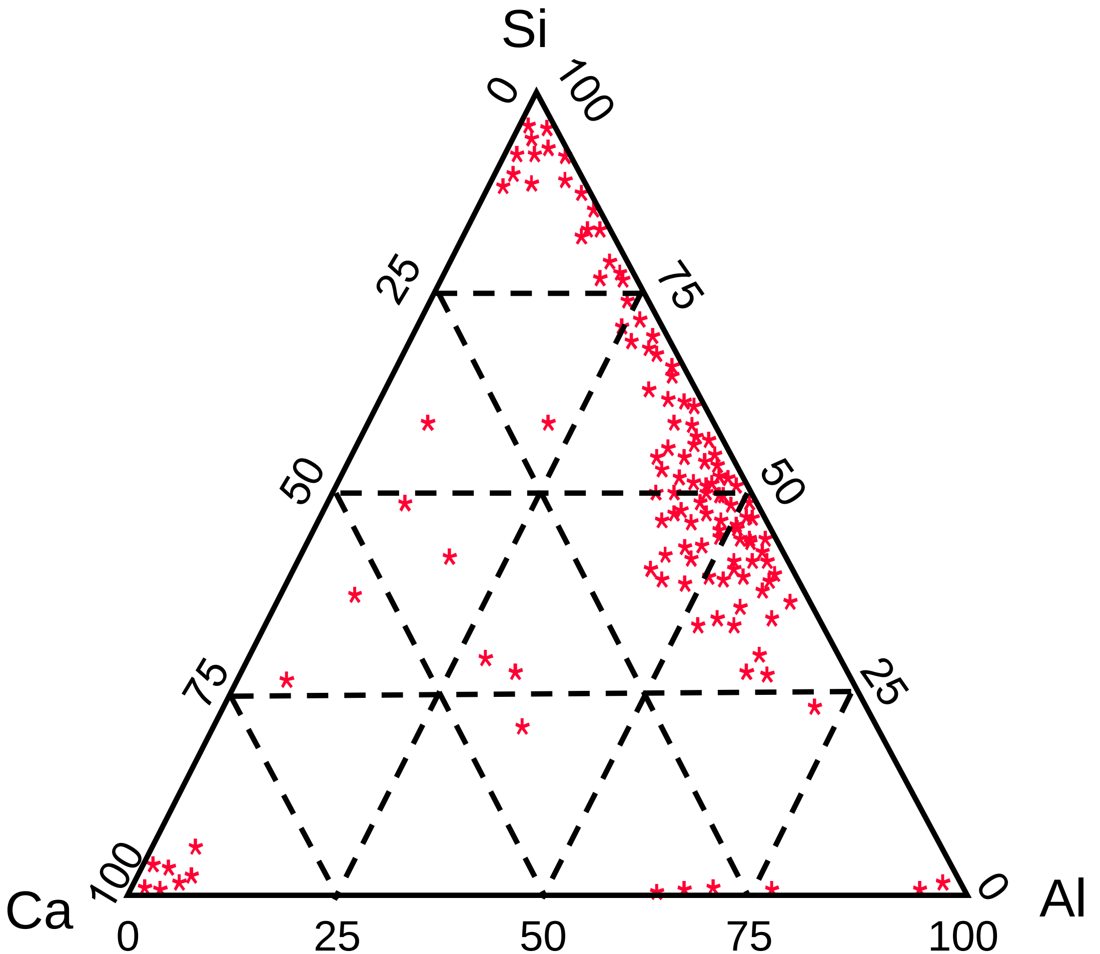


- Present in minor amounts.
- Na_2SO_4 and other soluble salts are the most common types.

Eagle Butte Coal Ash Composition

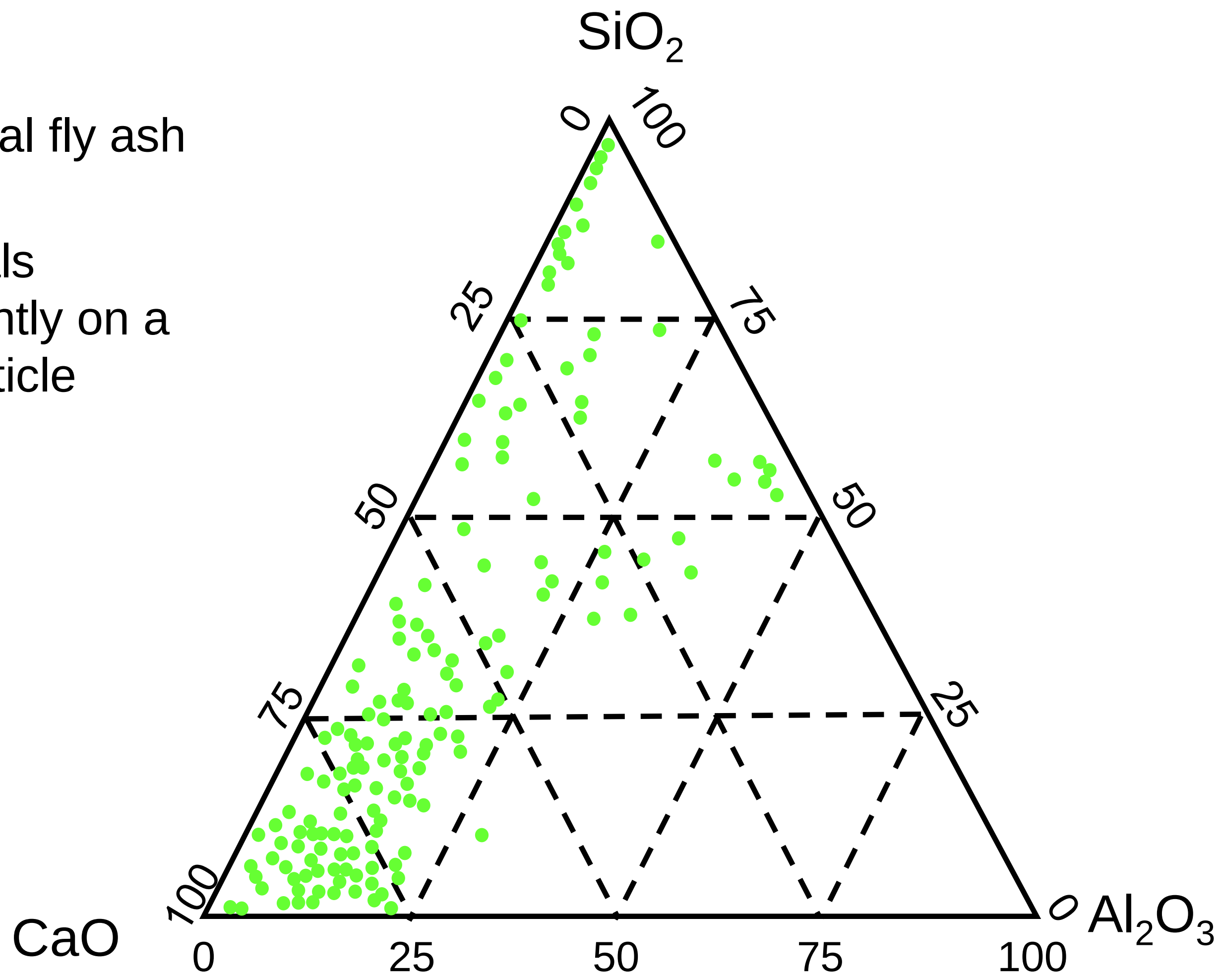


Eagle Butte Coal Mineral Compositions

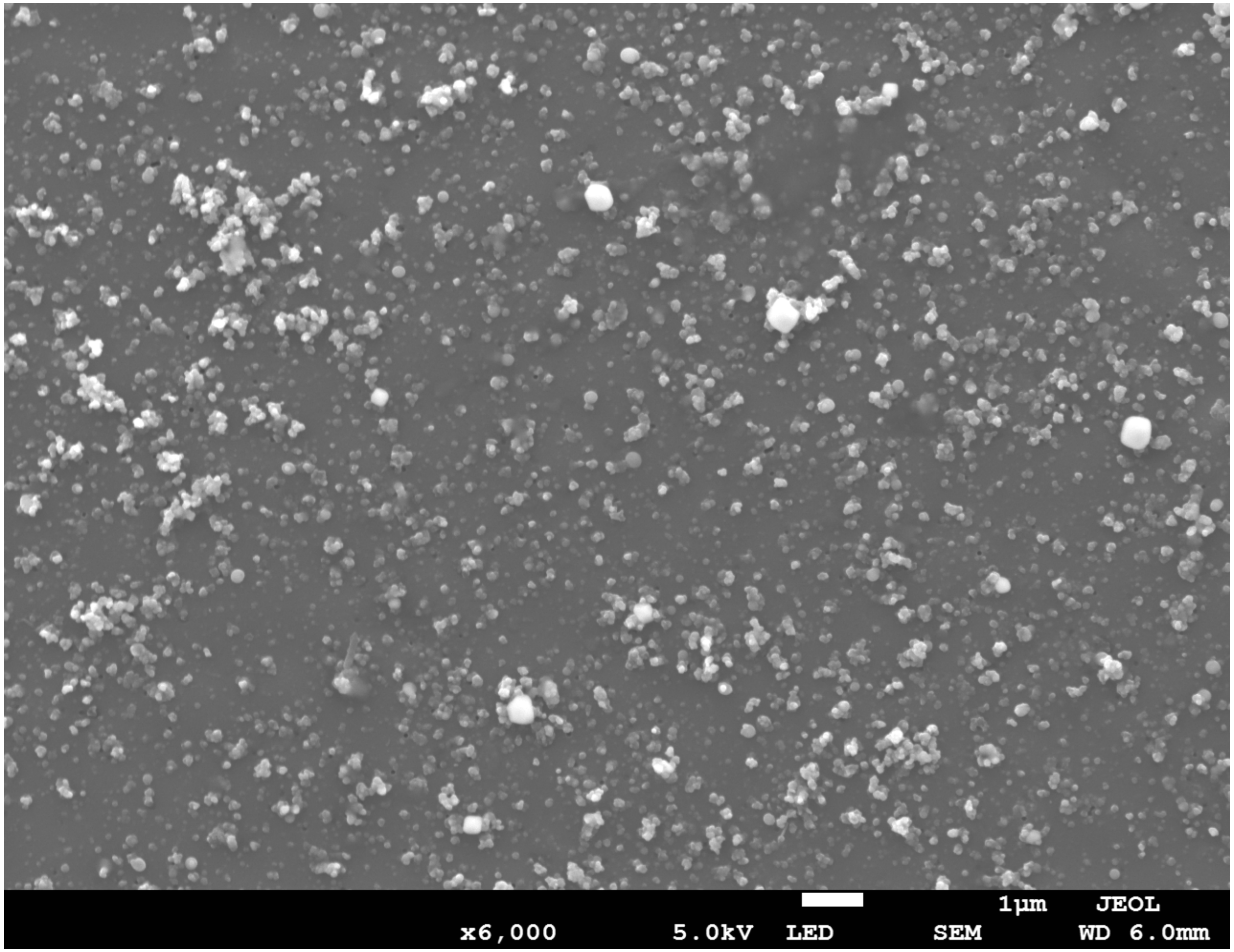


Advanced Technique Analysis for Eagle Butte Fly Ash

- Plot of individual fly ash minerals.
- Fly ash minerals behave differently on a particle-by-particle basis.



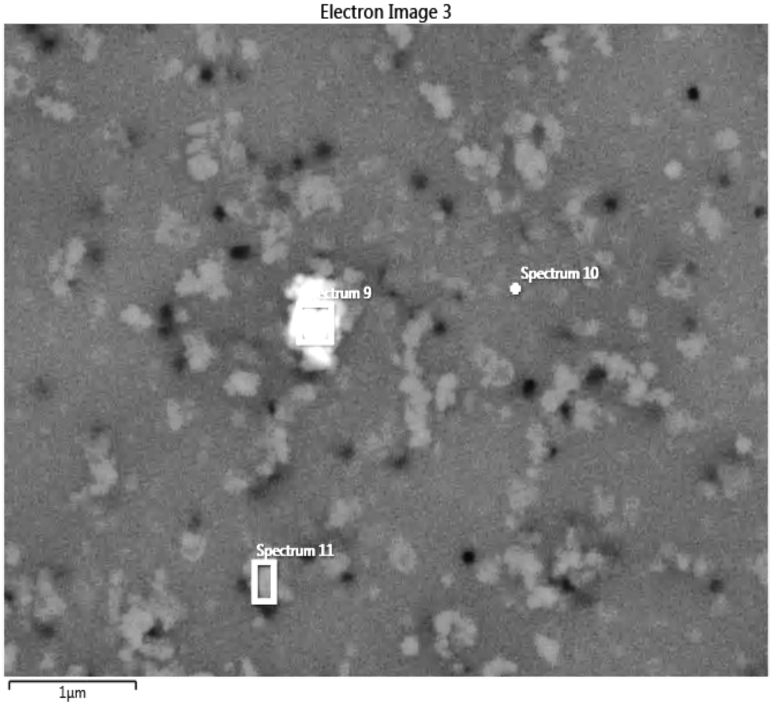
Thermal Oxidizer Inlet
FBG Firing Eagle Butte Coal (3/13/13)

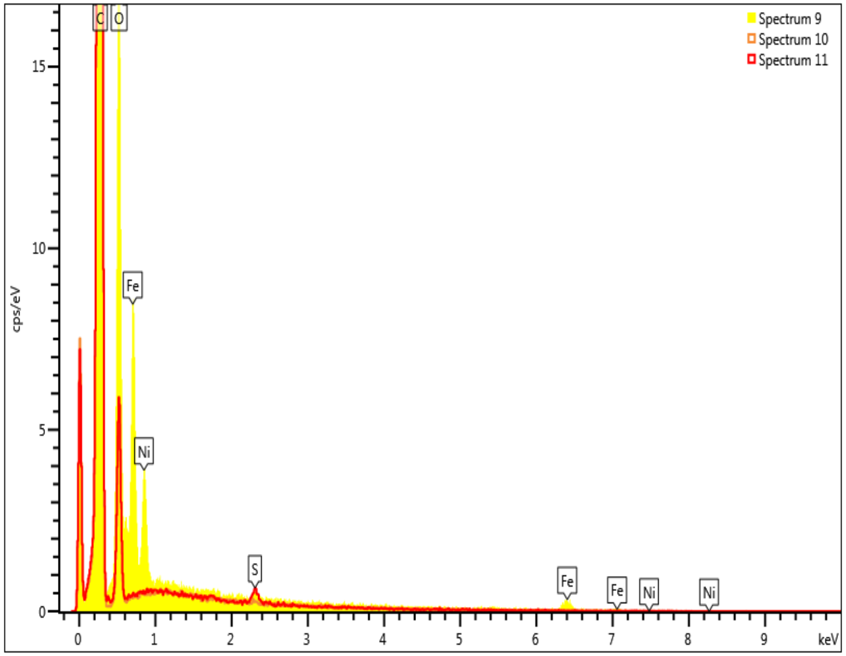


Thermal Oxidizer Inlet
FBG Firing Eagle Butte Coal (3/13/13)

Some larger flakes present

Flake composition is Fe oxide with some Na and S





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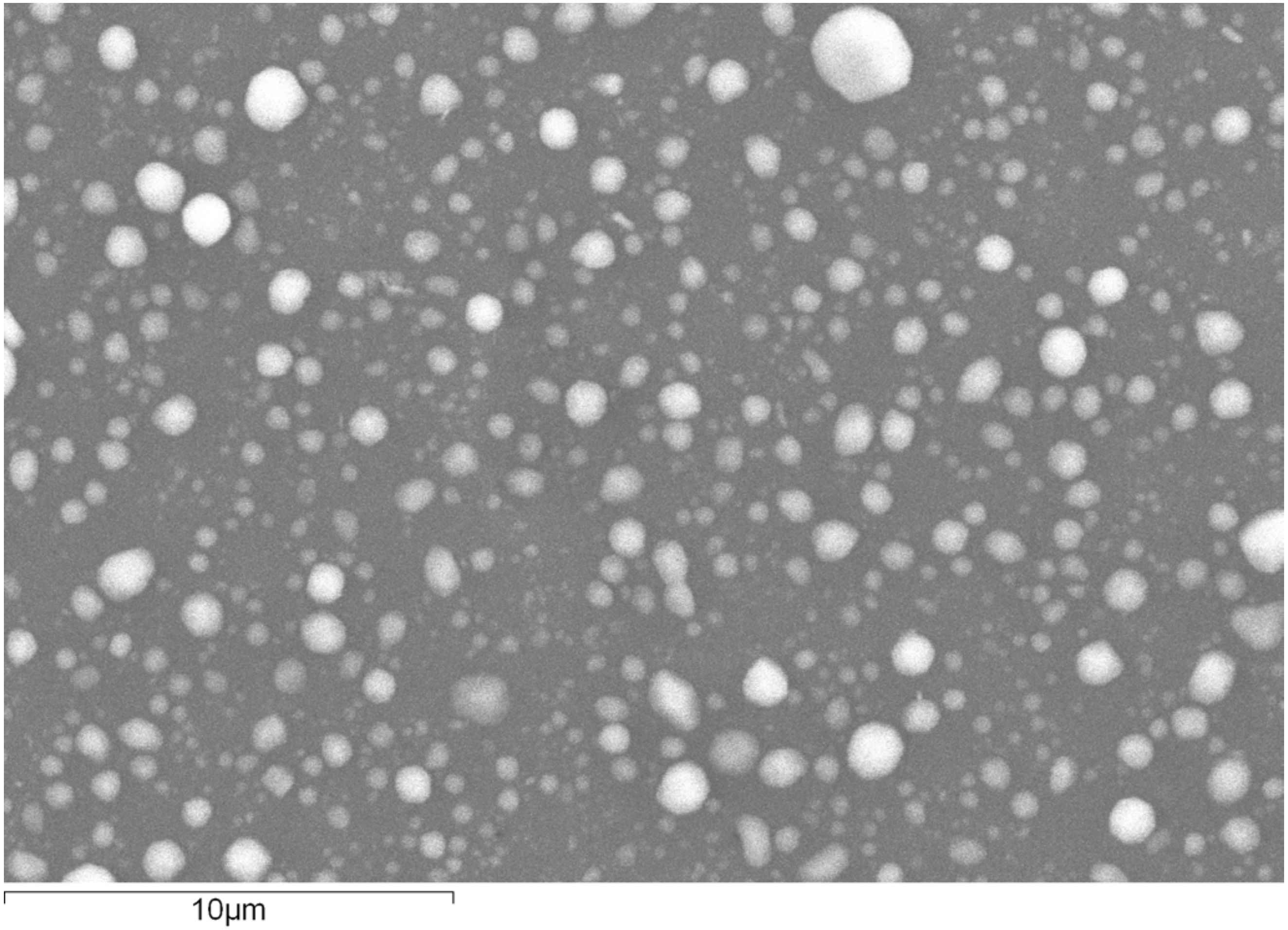
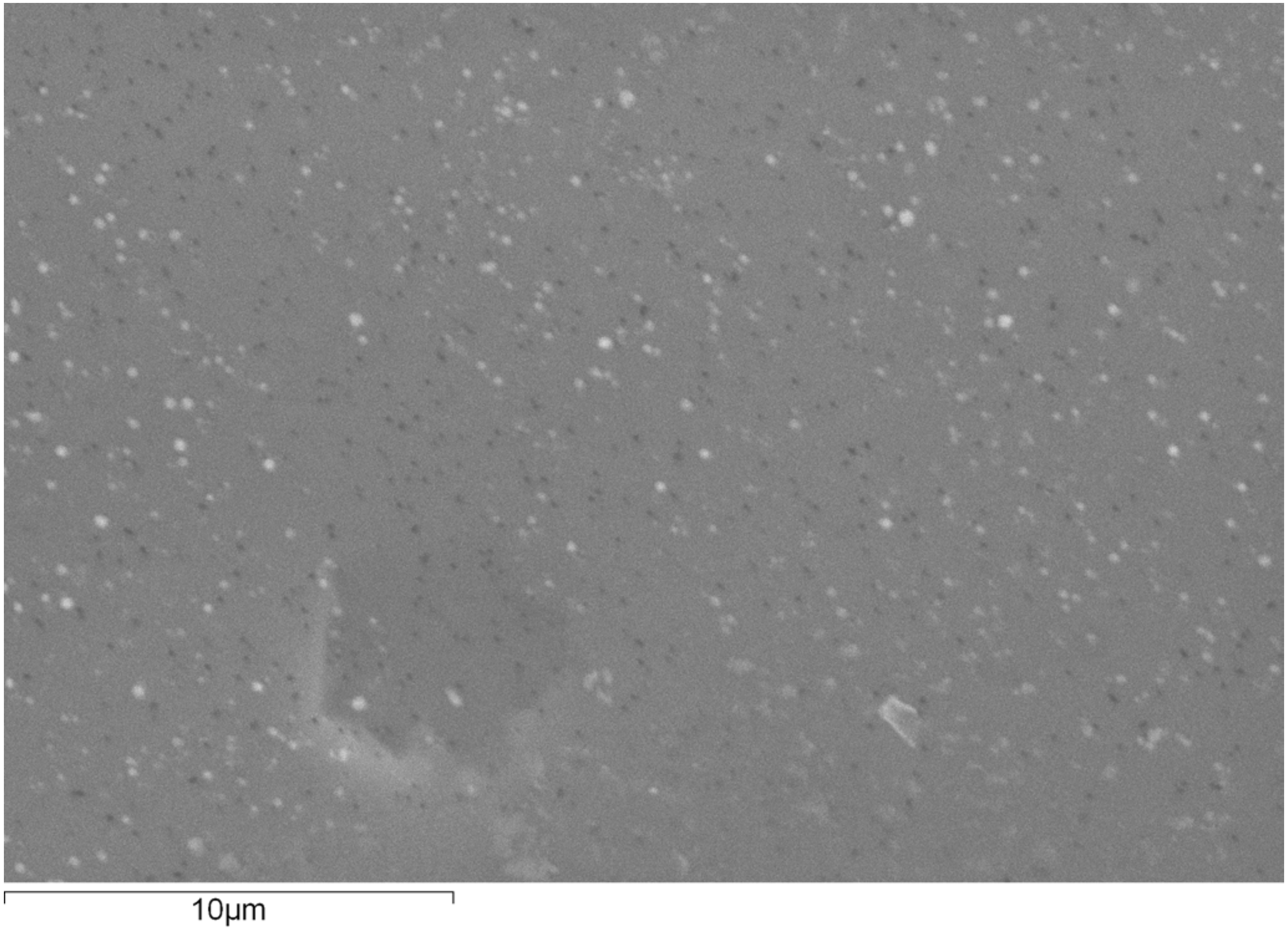
Thermal Oxidizer Outlet
FBG Firing Eagle Butte Coal (3/13/13)



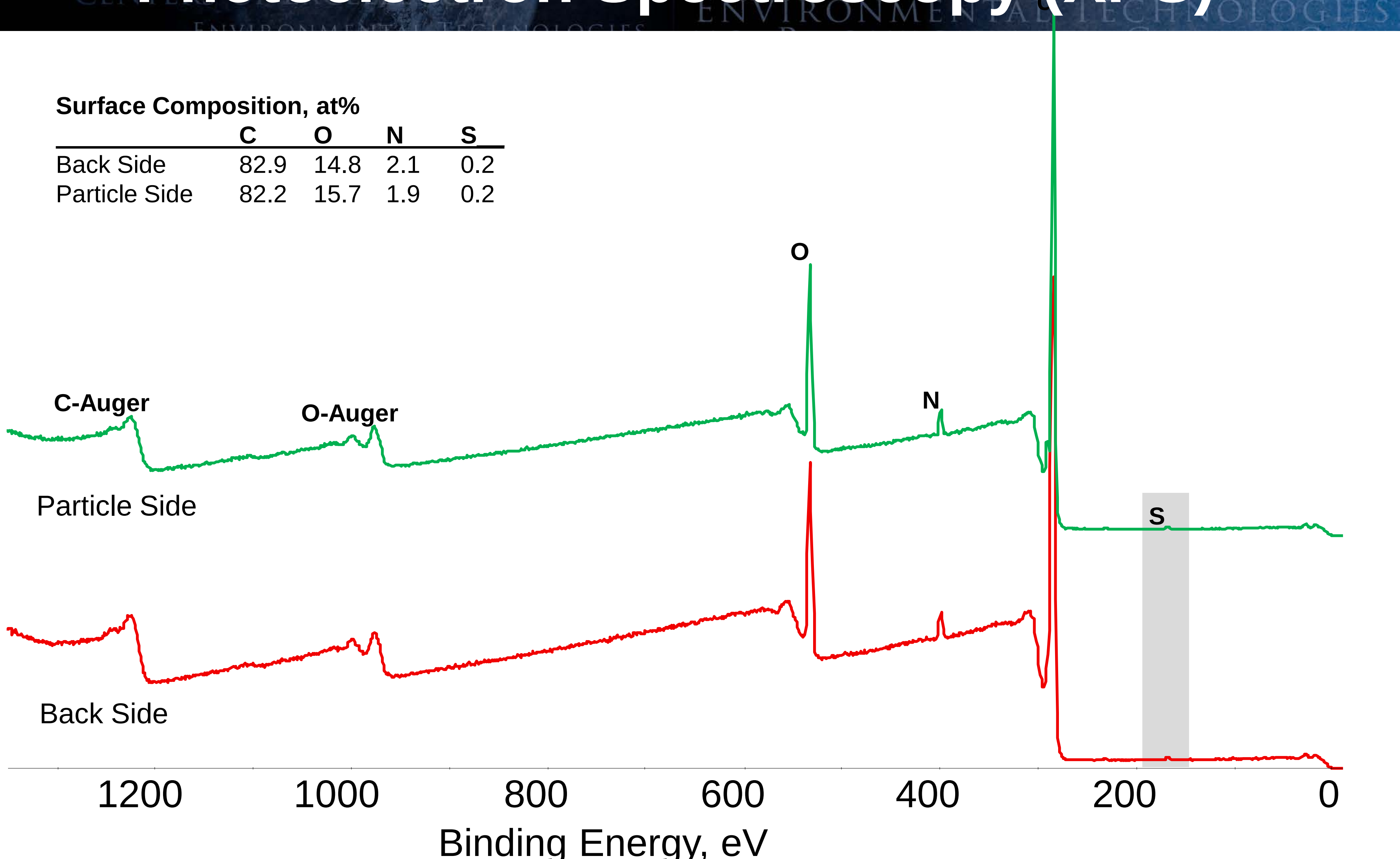
Thermal Oxidizer Outlet Natural Gas Firing (3/15/13)



FBG Syngas Filter Analyses by X-Ray Photoelectron Spectroscopy (XPS)

Surface Composition, at%

	C	O	N	S
Back Side	82.9	14.8	2.1	0.2
Particle Side	82.2	15.7	1.9	0.2

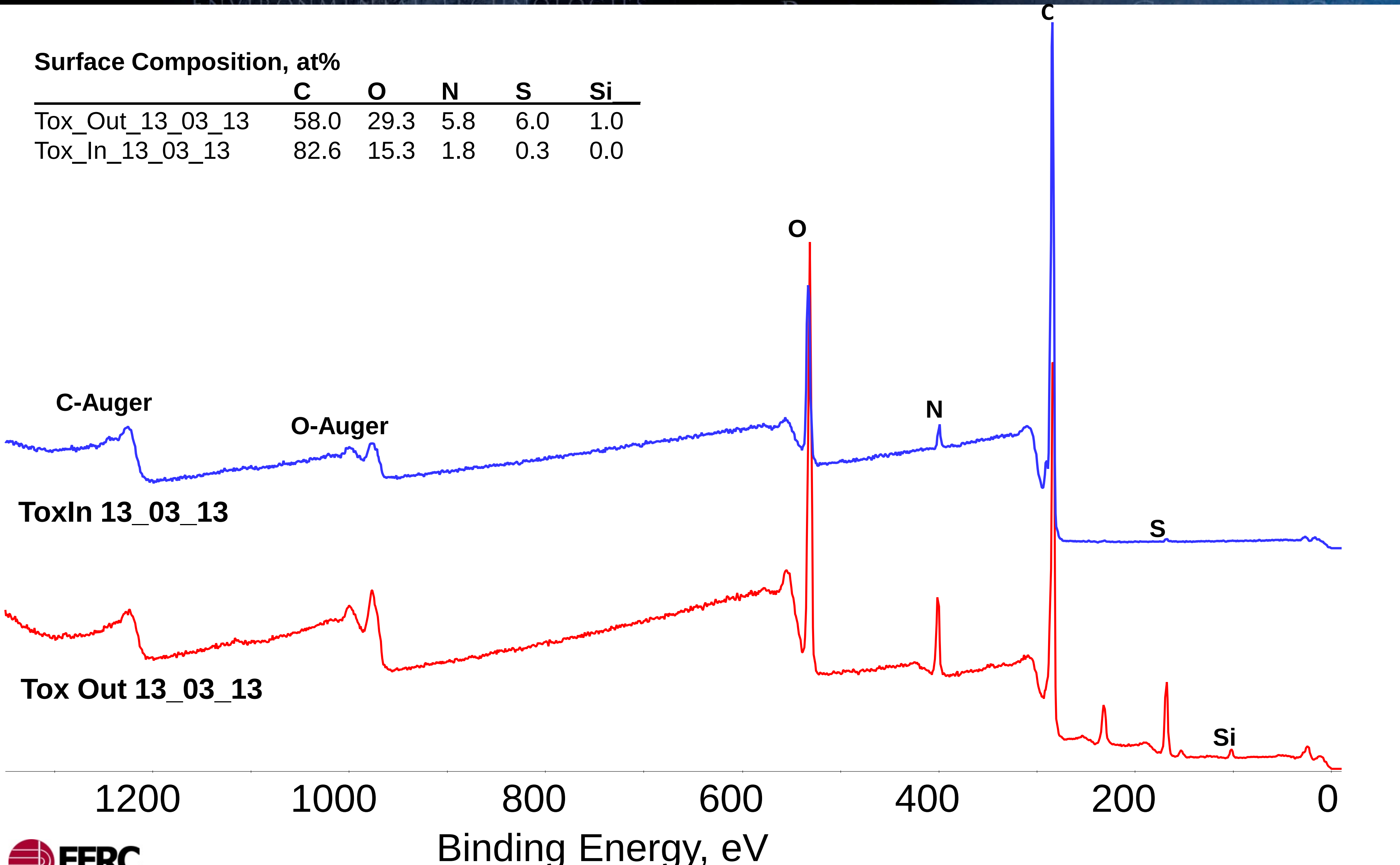


examined during visit

XPS Comparison of Syngas and Combusted Syngas Filters

Surface Composition, at%

	C	O	N	S	Si
Tox_Out_13_03_13	58.0	29.3	5.8	6.0	1.0
Tox_In_13_03_13	82.6	15.3	1.8	0.3	0.0



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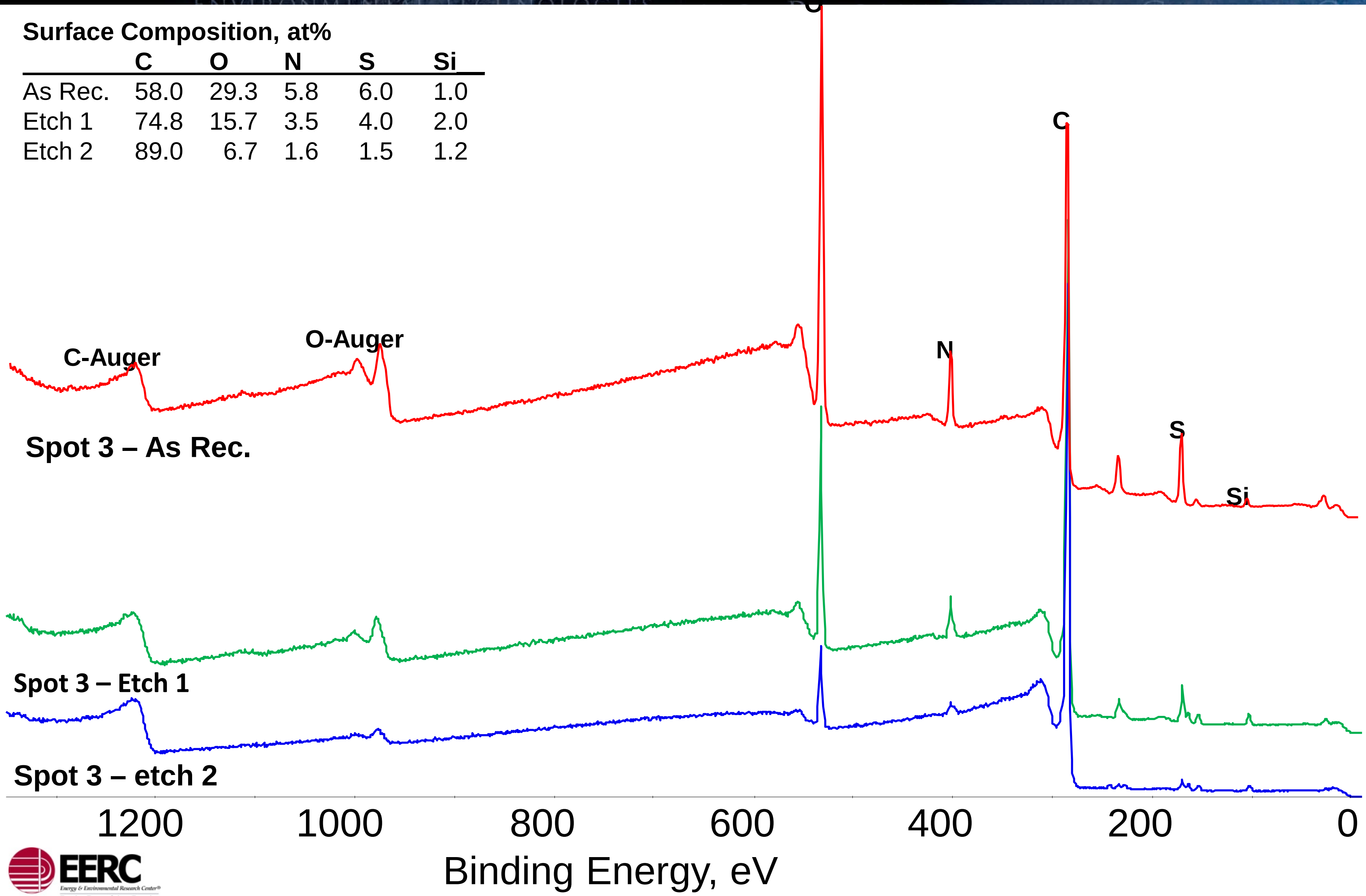
examined during visit

Effects of Ion Etching on Composition of the Combusted FBG Syngas Filter

Surface Composition, at%

	C	O	N	S	Si
As Rec.	58.0	29.3	5.8	6.0	1.0
Etch 1	74.8	15.7	3.5	4.0	2.0
Etch 2	89.0	6.7	1.6	1.5	1.2



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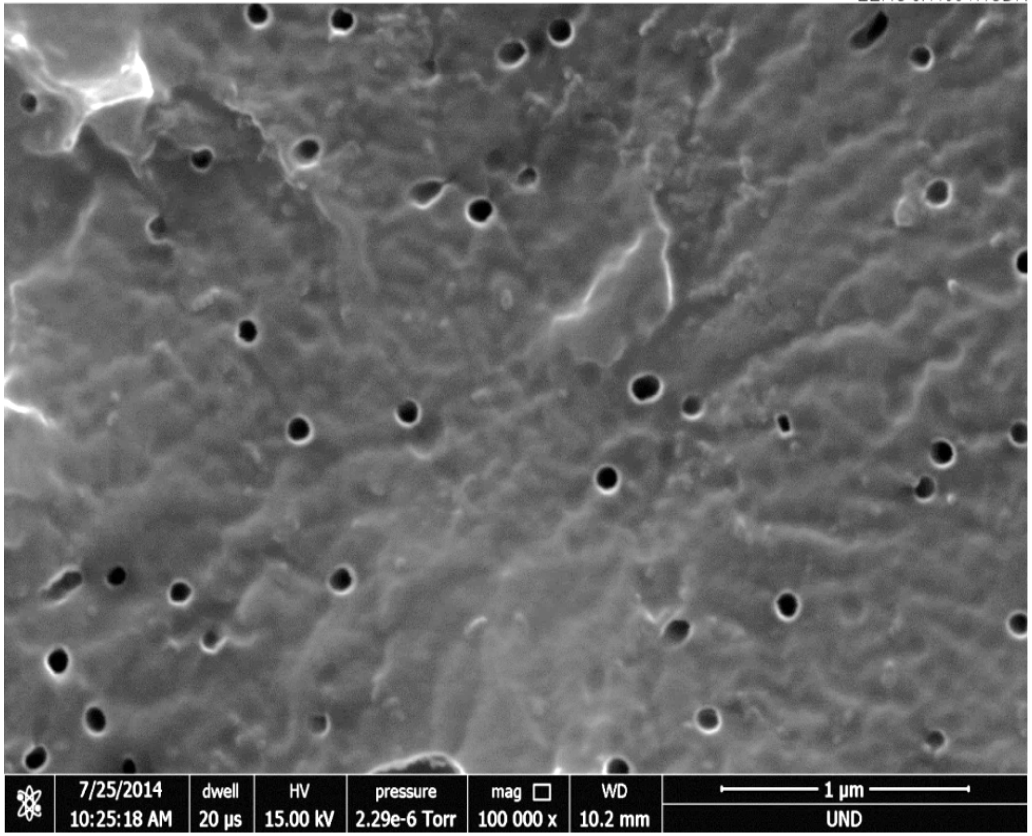
Results of FBG Particulate Analyses

- In the quenched syngas, the particulates are predominantly 0.1–0.5 µm in diameter.
- We were not able to get good energy-dispersive x-ray analyses of the small predominant particles.
- XPS shows that the average composition of the syngas particles is very close to that of the polycarbonate filter and is most likely carbonaceous soot.
- In the combusted syngas, the carbonaceous particles are more spherical than in the syngas and slightly larger, typically 0.2–2 µm.
- The combusted particles show more O, N, and S than the noncombusted particles.
- Ion etching shows that the increased O, N, and S were confined to the surface of the particles.

Thermal Oxidizer Inlet
Pressurized EFG Firing Antelope Coal (10/30/13)

- Particulate loading of 6.906 mg/m^3.
- Filter was heat damaged.
- Very little soot possibly because EFG produces much less tar.
- Particulate loading weight due to large flakes that had detached from the system walls.

EERC JH49947.CDR



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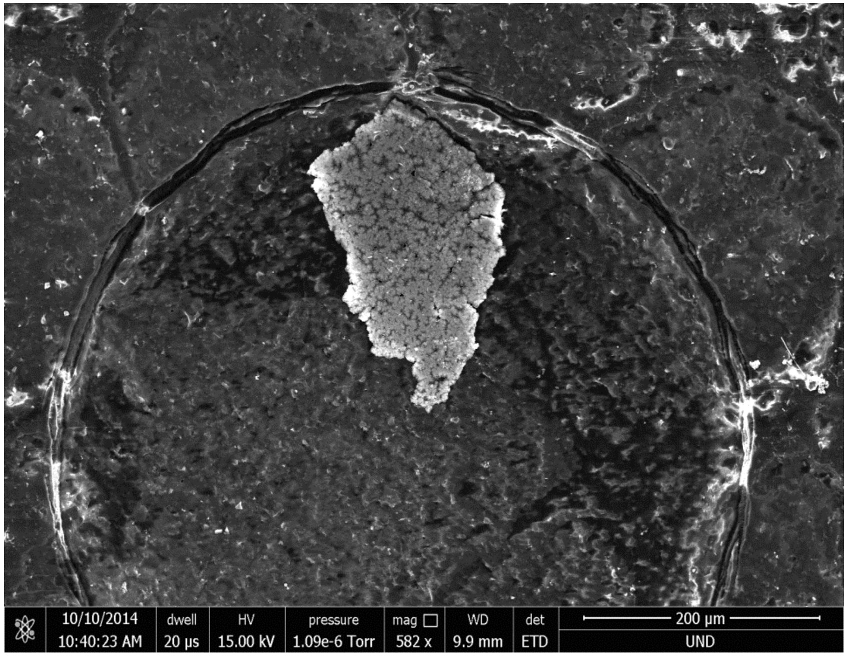
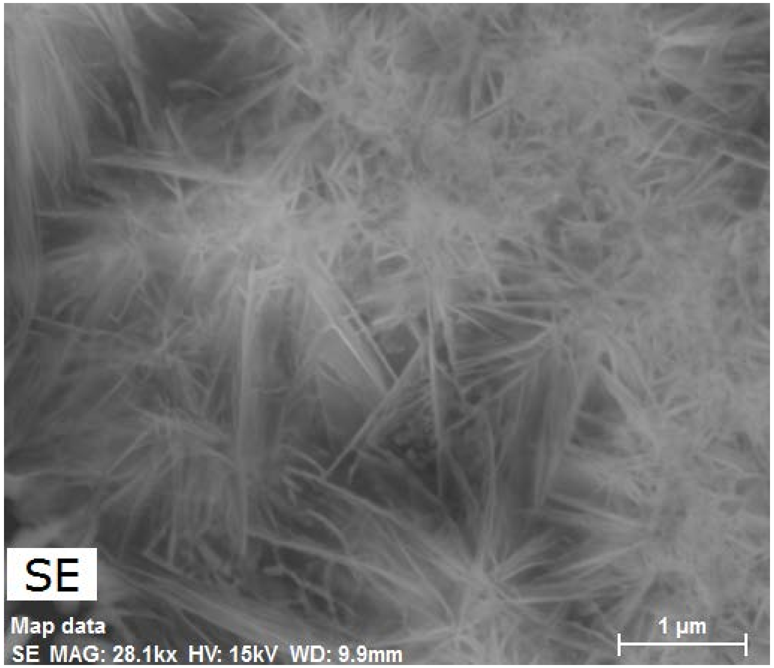
Thermal Oxidizer Inlet
Pressurized EFG Firing Antelope Coal (10/30/13)

Large flakes come from system surfaces.

Fe oxide with some C, Na, Cl, S, and Zn.





Thermal Oxidizer Outlet
EFG Firing Antelope Coal (10/29/13)

- Particulate loading of 0.808 mg/m^3.
- Particles are 0.1 to 0.3 microns in diameter.
- They are composed primarily of carbon with some oxygen and sulfur.

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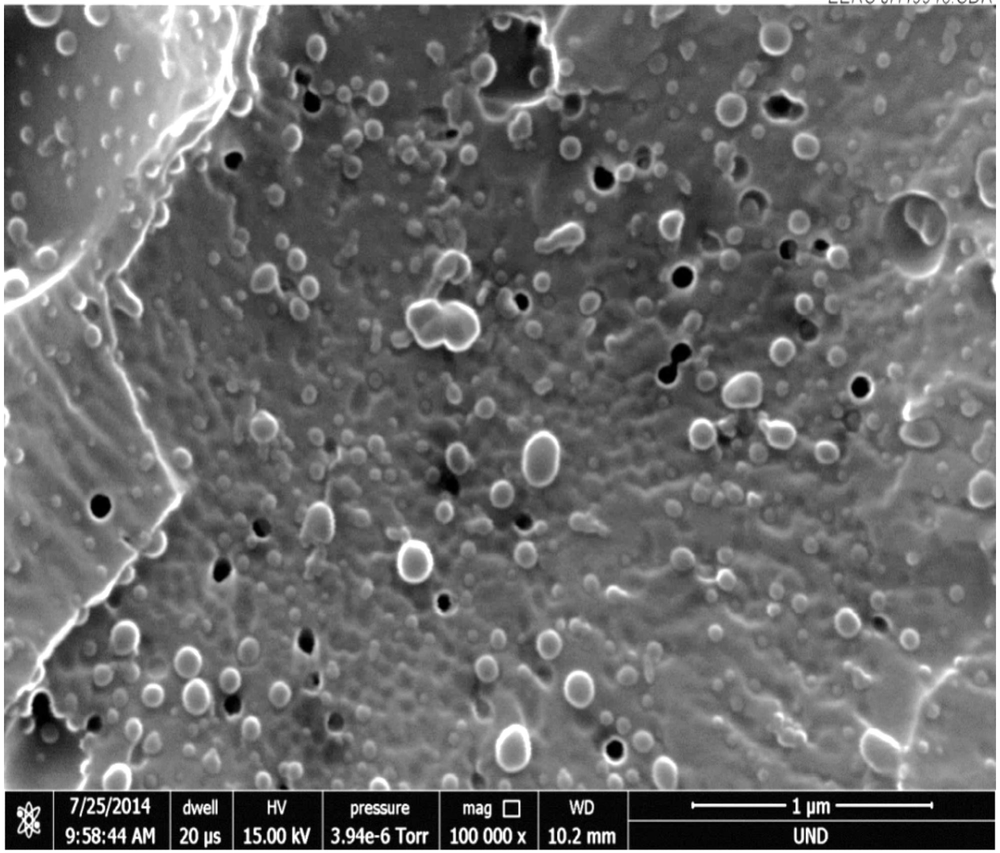

Thermal Oxidizer Outlet Firing Natural Gas (11/4/13)

- Particulate loading of 0.698 mg/m^3.
- Particles are smaller than when burning syngas but are still carbonaceous.

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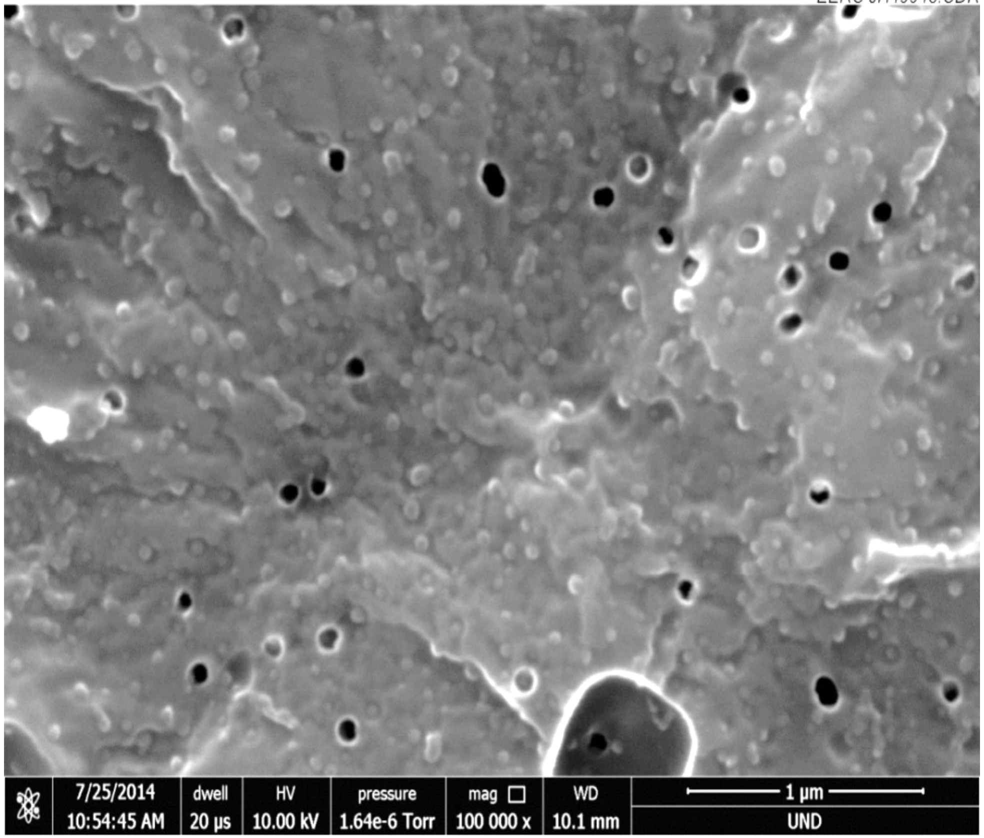

Results of EFG Particulate Analyses

- No submicron particulates were seen on the syngas filter either because the filter had softened or there is just less soot in an EFG.
- Flakes of iron oxide were collected from the syngas that came from system surfaces. They contained some C, Na, Cl, S, and Zn.
- Combusted syngas contained 0.1 to 0.3 micron soot particles.
- Some soot is collected even when burning only natural gas, but particles are smaller and fewer than when burning syngas.

Remaining Work

- Task 5 – Preparation of APMT-plated superalloy turbine parts
  - Use data from Tasks 2 and 3 to design clamping system and time–temperature heat treatment.

- Task 6 – Environmental testing of plated turbine parts
  - TBC coating and oxidation and spallation testing at Siemens Energy.
  - Corrosion testing at the EERC.

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- Josh Braband and Serges Tatsinkou Nguelo, graduate students in the UND Mechanical Engineering Department.

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