In-Operando Investigations of Refractory Materials Interacting with Ash/Slag from Mixed Feedstock Gasification

NATIONAL ENERGY TECHNOLOGY LABORATORY

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Disclaimer

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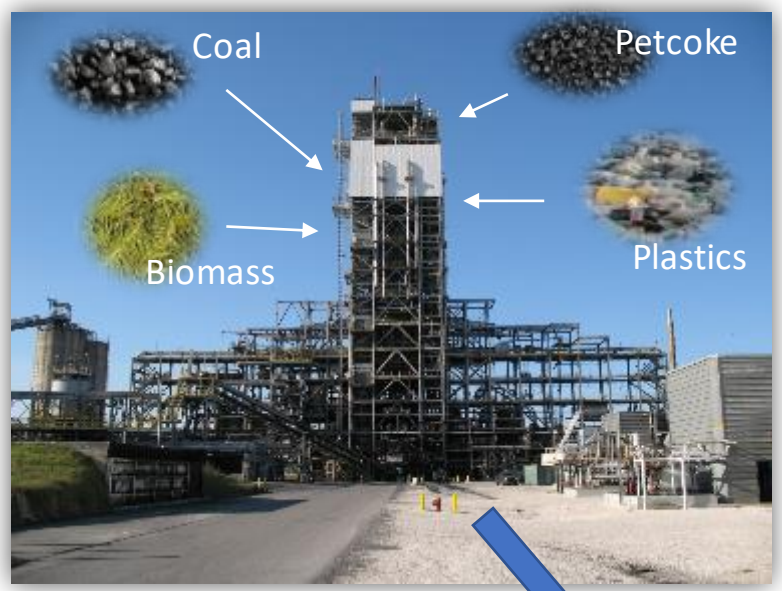
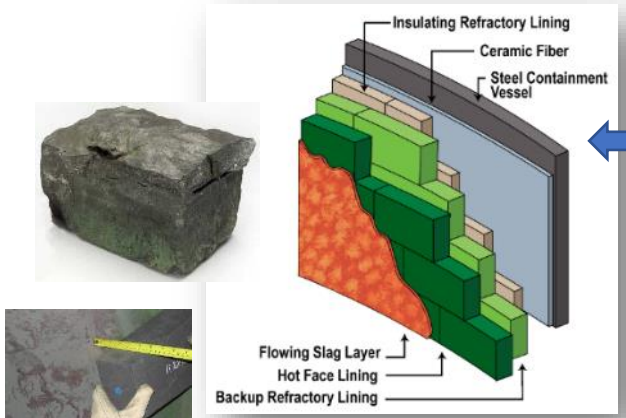
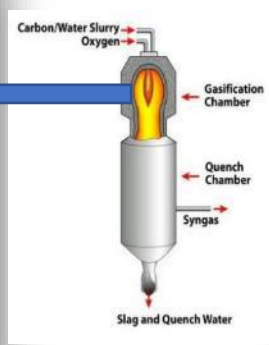
Research Objective

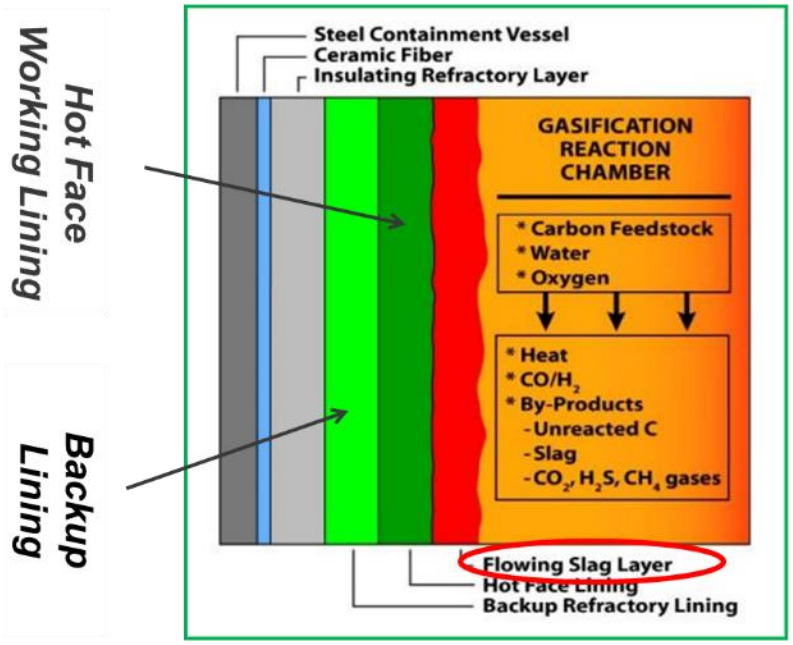
- To make **modular gasifiers** feasible, capital and operating costs need to be reduced to a level that is competitive with traditional power and fuel plants.
- **A limited refractory service life is a key barrier** to achieving the high online availability, energy efficiency, and successful commercialization of gasification technology.
- More feedstock options added to coal in programs at NETL:
  - 2008 – petcoke
  - 2019 – biomass
  - 2021 – plastics

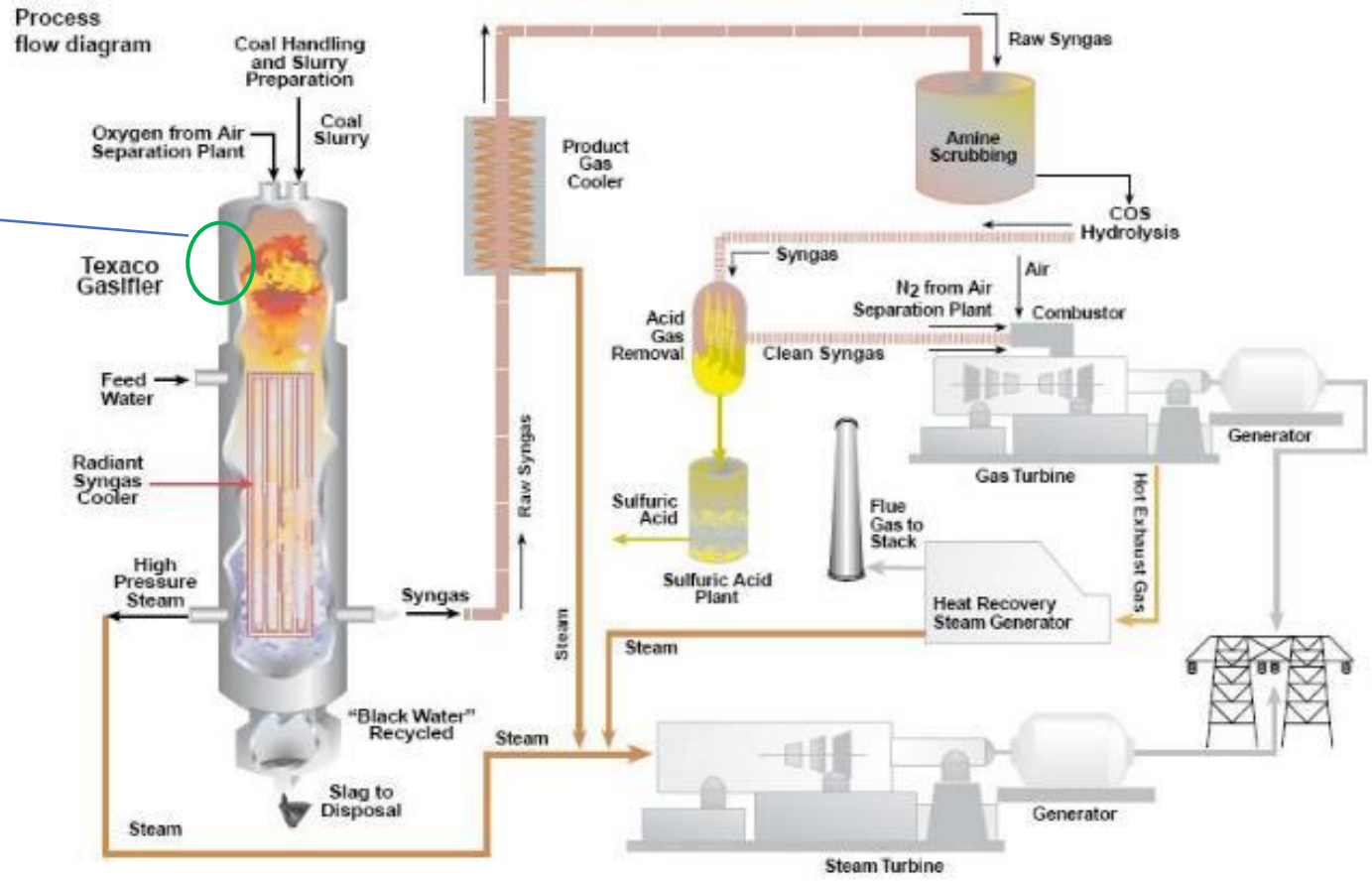






Gasification





- 1325 – 1575 °C
- 20 – 70 atm
- $10^{-4 \text{ to } -10}$ atm pp O_2
- Slag (70 – 300 t/d)
- Thermal cycling, etc.

Refractory Materials Identified for Coal/Biomass Ash

(1) V-CAST

	wt.%
Al_2O_3	70.9
SiC + C	18.1
SiO_2	7.5
TiO_2	1.4

Alumina based

(2) TUFF-FLO

	wt.%
Al_2O_3	60.3
SiO_2	28.4
SiC	4.4
TiO_2	2.0
CaO	1.9
ZrO_2	1.3
Fe_2O_3	0.9
others	0.8

Mullite based

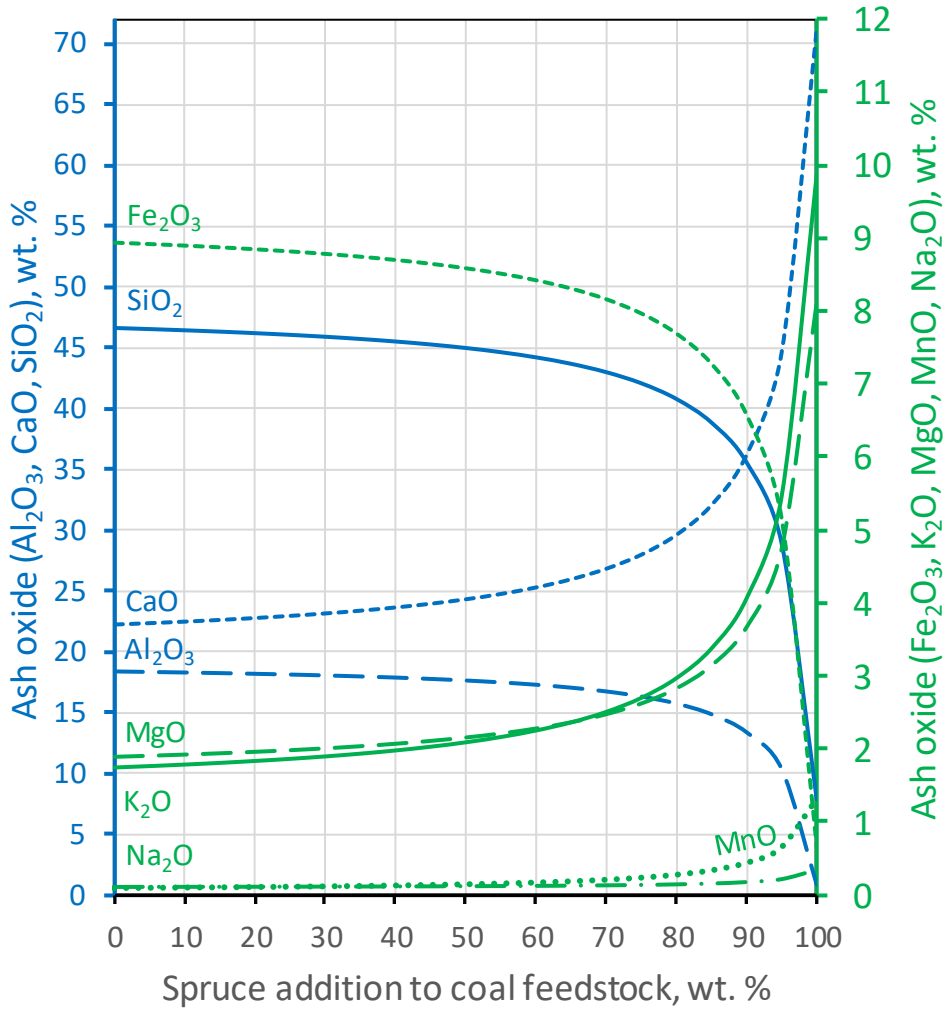
- Refractory materials and coupons were manufactured by ***Allied Mineral Products*** in collaboration with NETL.
- Compositions provided by Allied Mineral.

Ashes Considered in this Work

Ash chemistry (XRF)

(wt.%)	100% Coal (Usibelli)	100% Biomass (Spruce)	20% spruce – 80% coal
Ash contents	7	0.31	
SiO2	46.53	7.79	45.47
Al2O3	18.44	0.74	18.23
Fe2O3	8.93	0.65	8.9
CaO	22.27	71.19	23.28
MgO	1.88	8.12	1.98
K2O	1.74	9.87	1.89
Na2O	0.12	0.34	0.15
MnO	0.1	1.3	0.09
Total	100.00	100.00	100.00

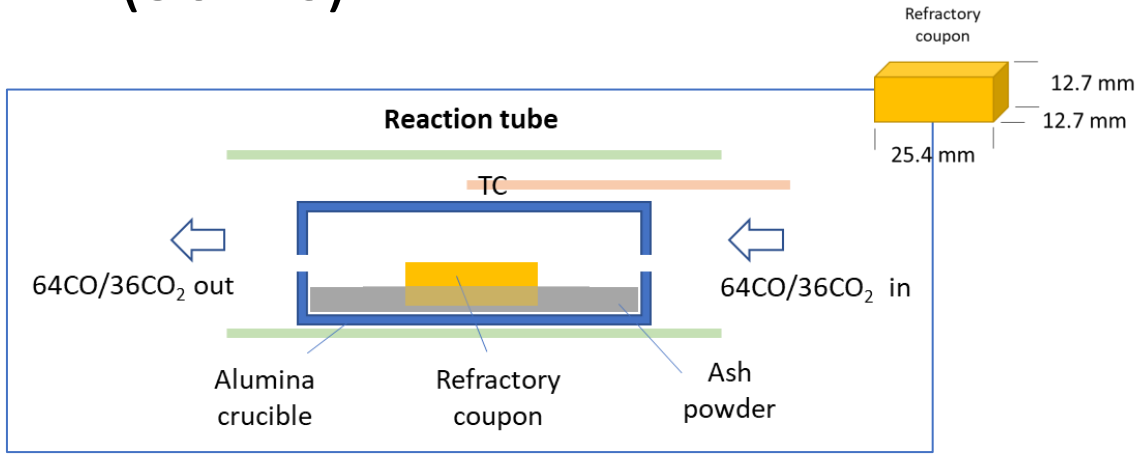
Coal: Usibelli coal data sheet, Usibelli Coal Mine, 2015
Spruce: J. Werkelin et al., Biomass and Bioenergy 35 (2011) 725-733

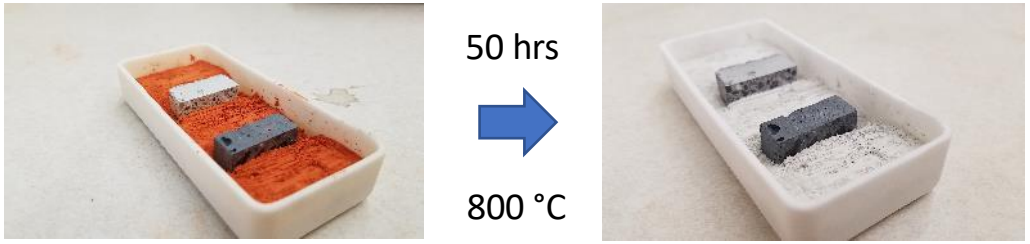


Experimental Techniques (this work)

1. Environmental HT confocal scanning laser microscope

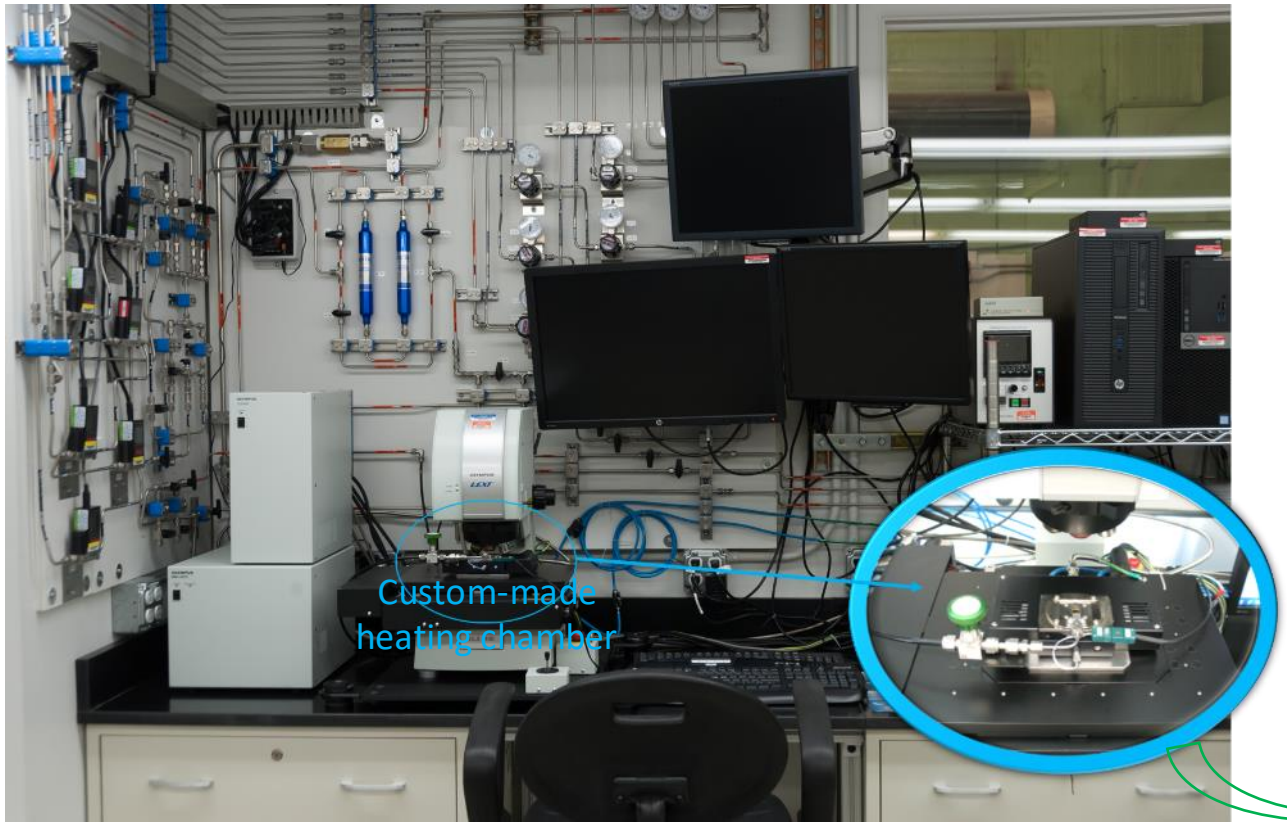
2. Extended exposure tests (50 hrs)

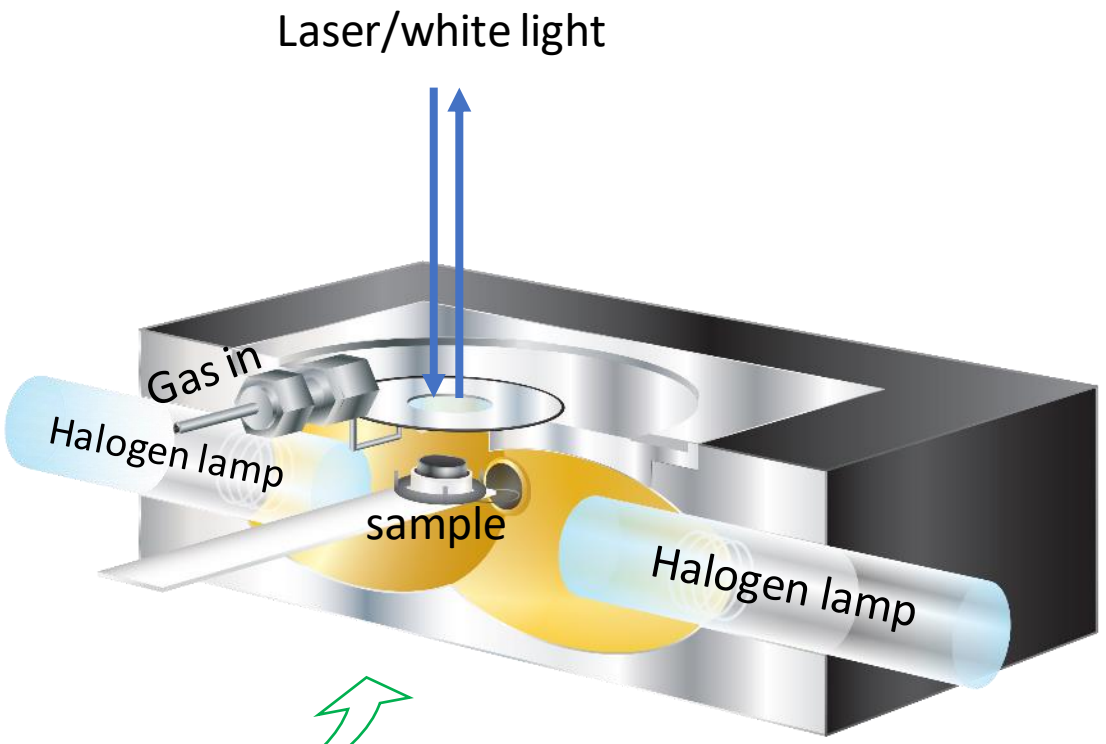




Firing Tests (In-Situ)

High temperature environmental confocal scanning laser microscope



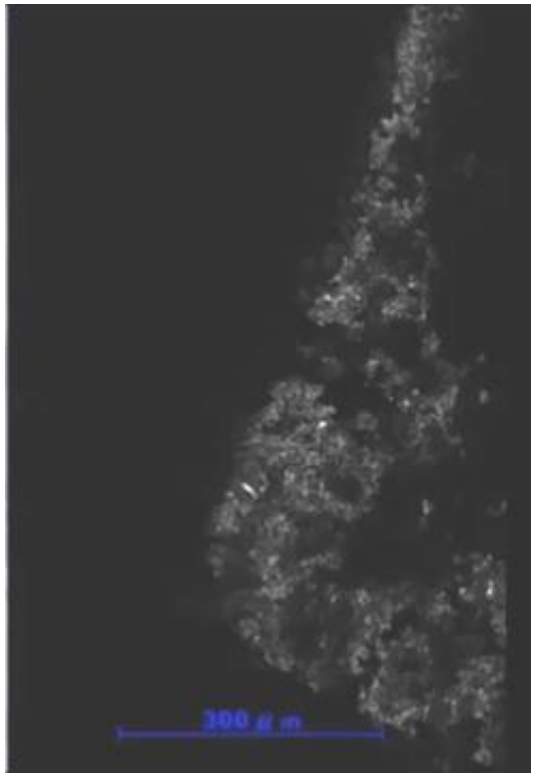


- Ash pre-fired at 800 °C
- 64%CO-36%CO_2
- One-hour exposure

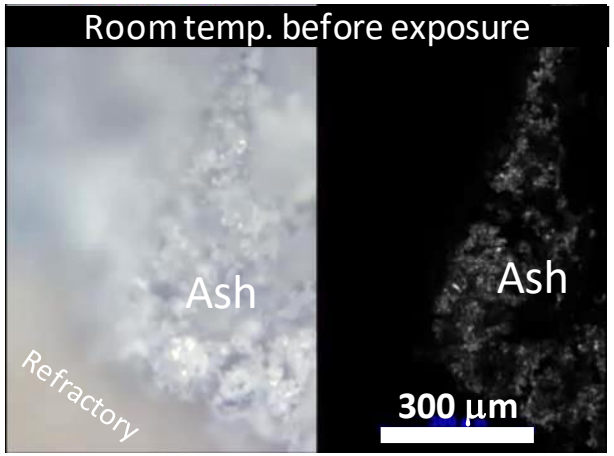
CSLM: V-CAST (100% Coal Ash) 800°C

Movie speed: 8x

White light



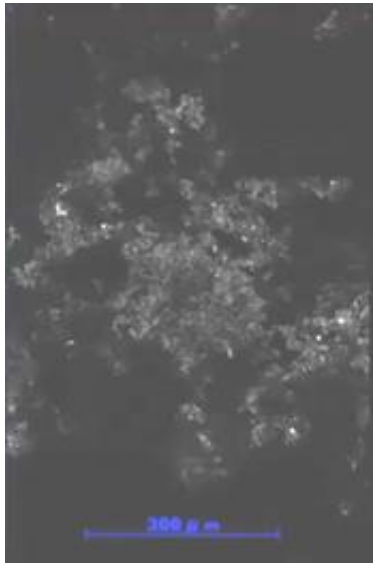
Laser



CSLM: V-CAST (100% Coal Ash) 1200°C

Movie speed: 8x

White light



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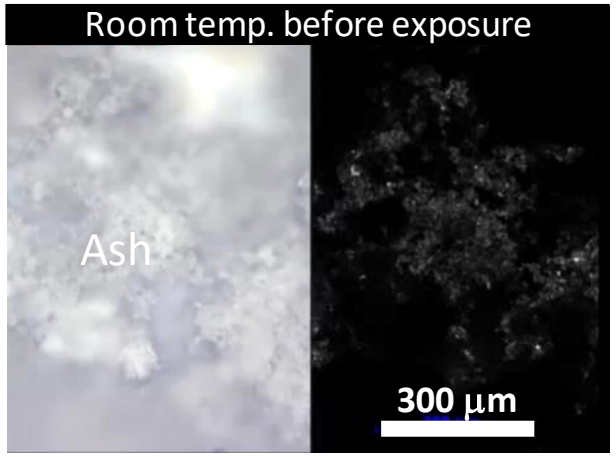
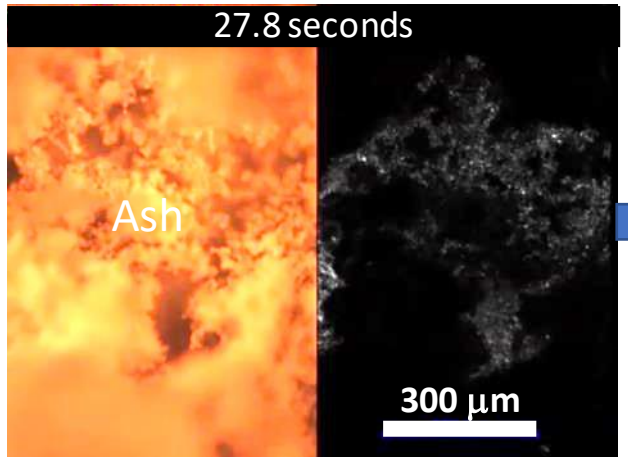
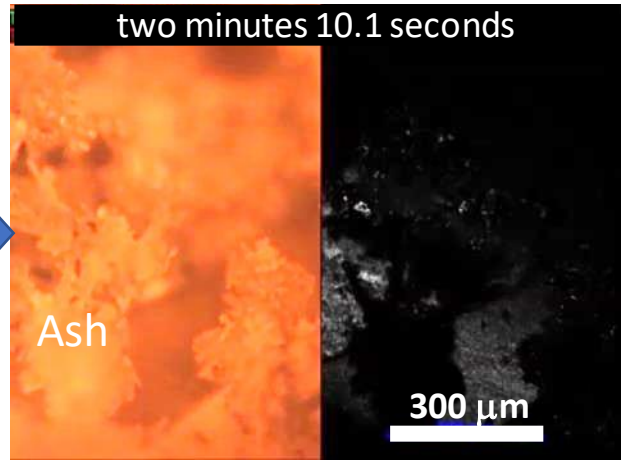
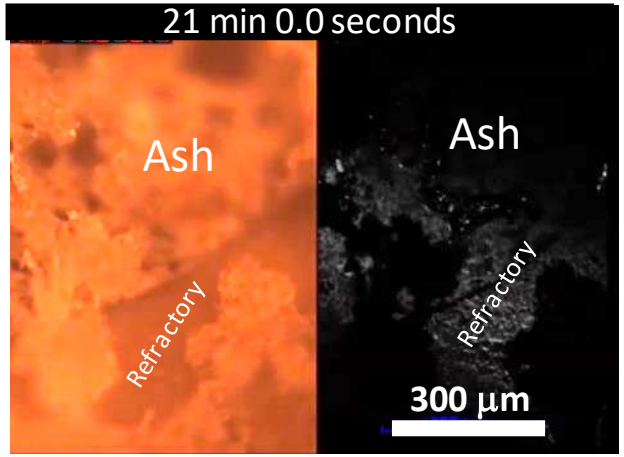


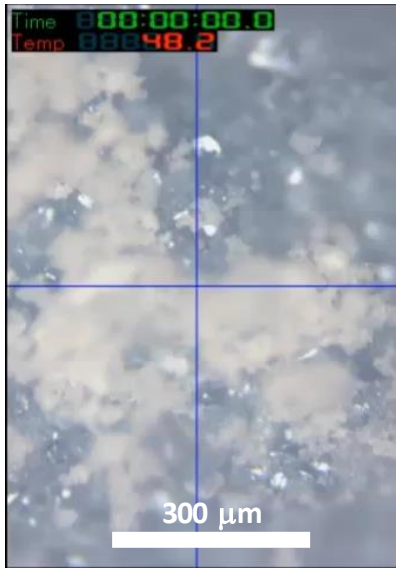






CSLM: V-CAST (100% Spruce) 1200°C

Movie speed: 8x



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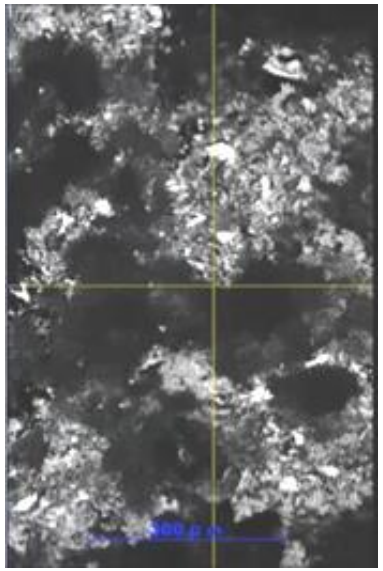

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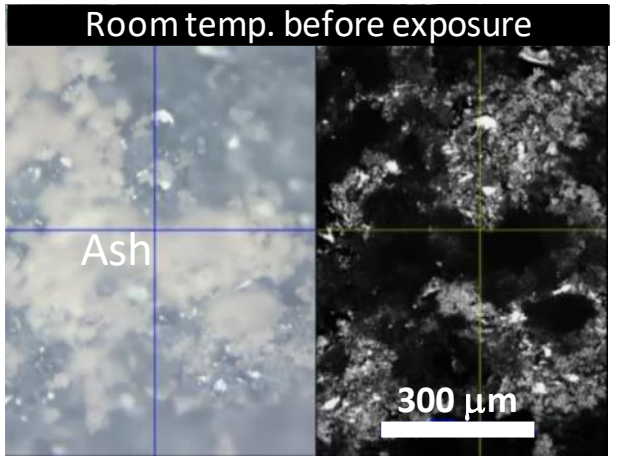
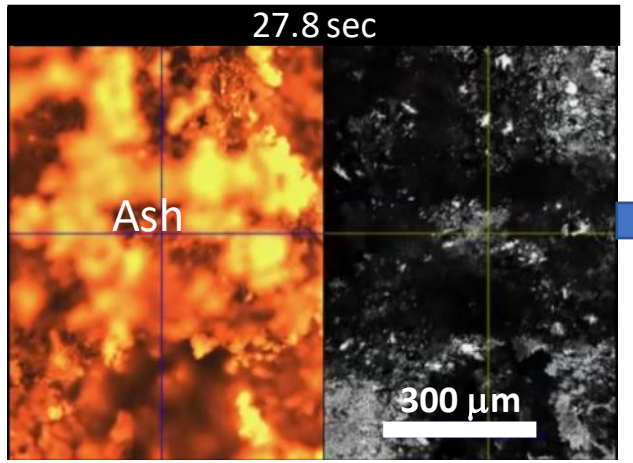
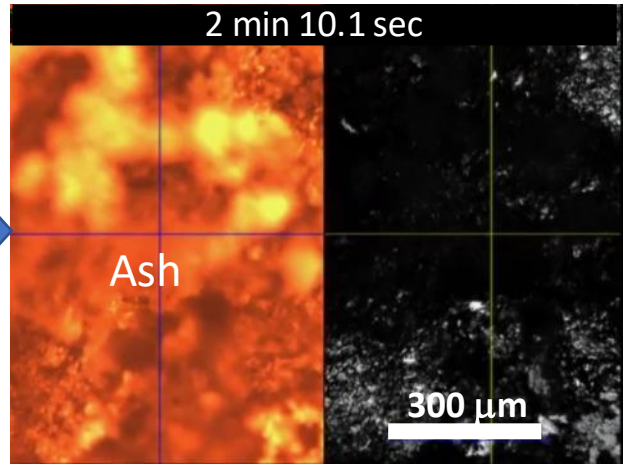
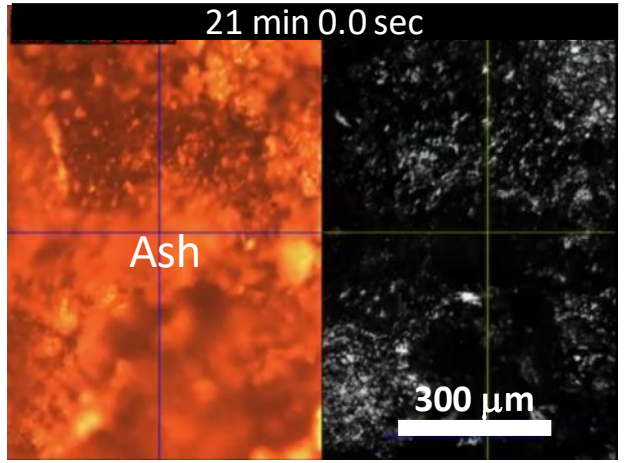


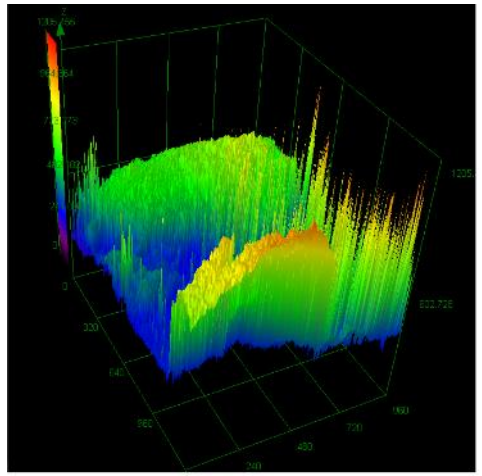




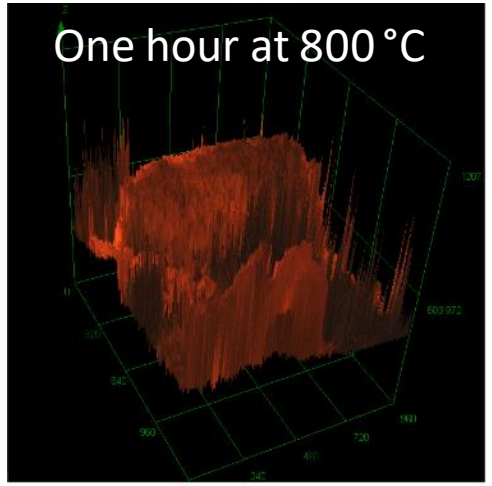


V-CAST (CSLM) (100% Coal Ash)

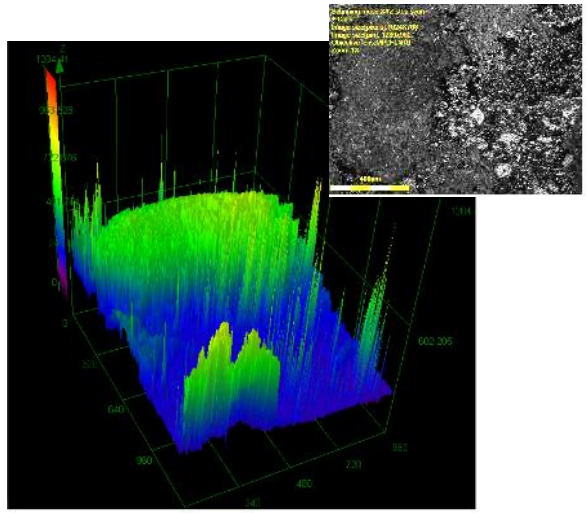
64%CO-36%CO2, 1 hr exposure

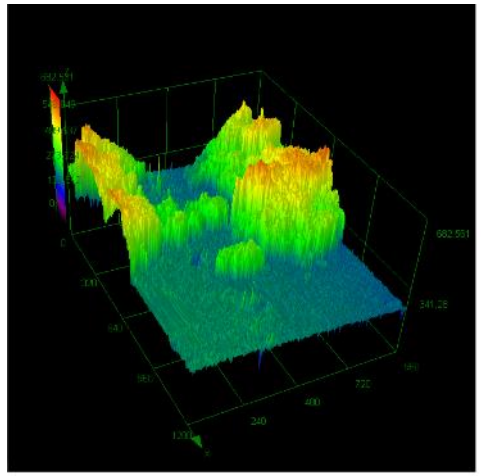


heating

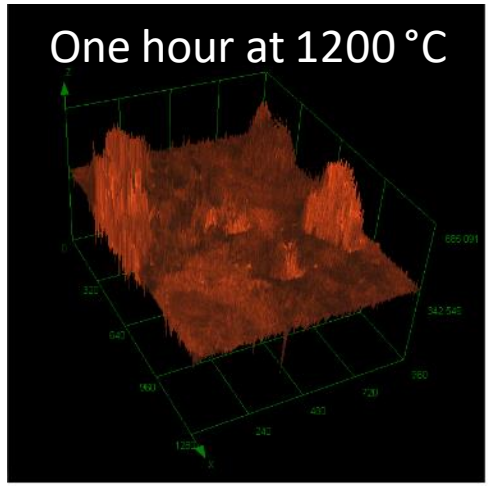


cooling

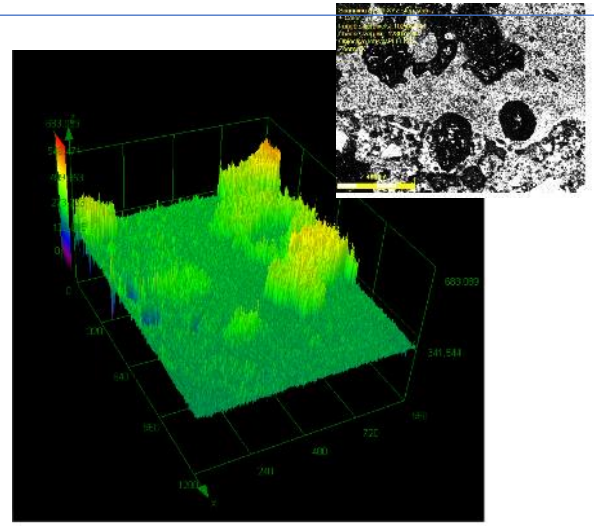




heating

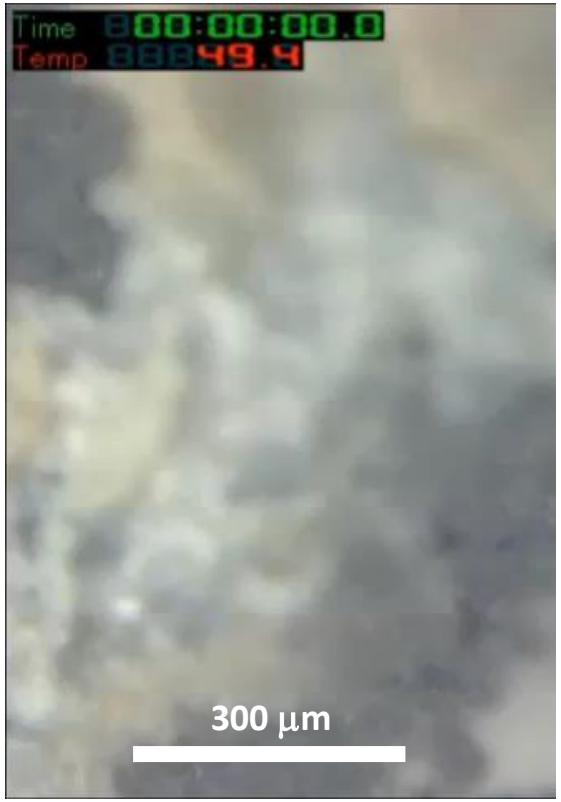


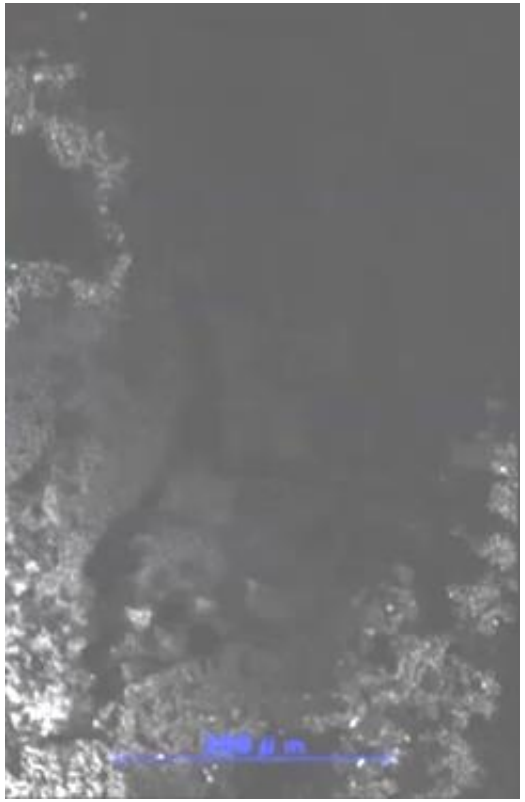
cooling



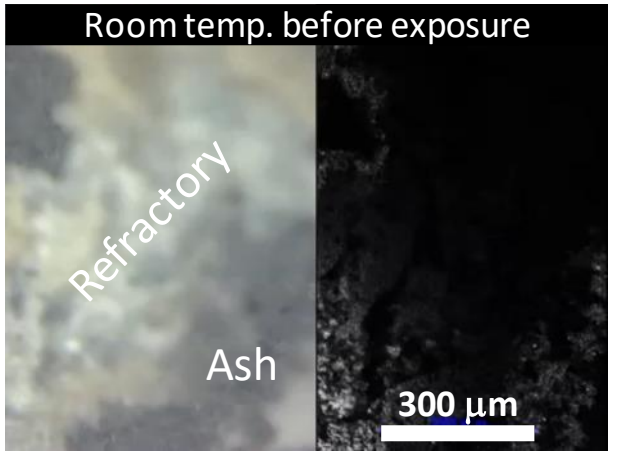
CSLM: TUFF-FLO (100% Coal Ash) 800°C

Movie speed: 6x



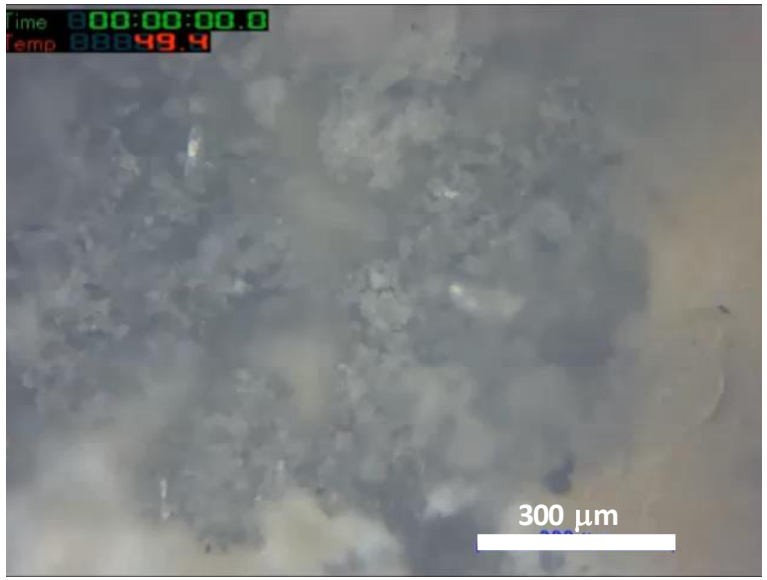


White light | ***Laser***



CSLM: TUFF-FLO (100% Coal Ash) 1200°C

Movie speed: 6x



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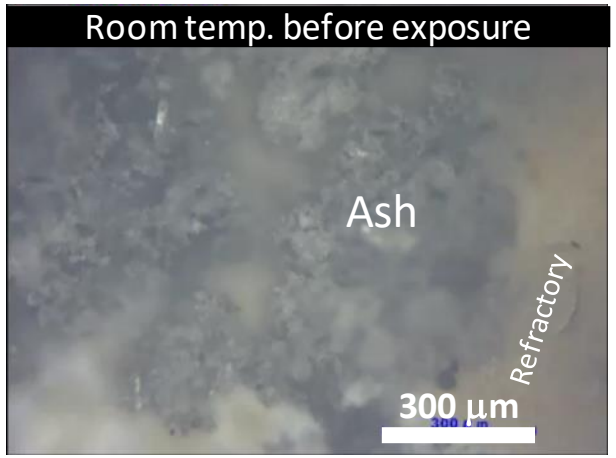
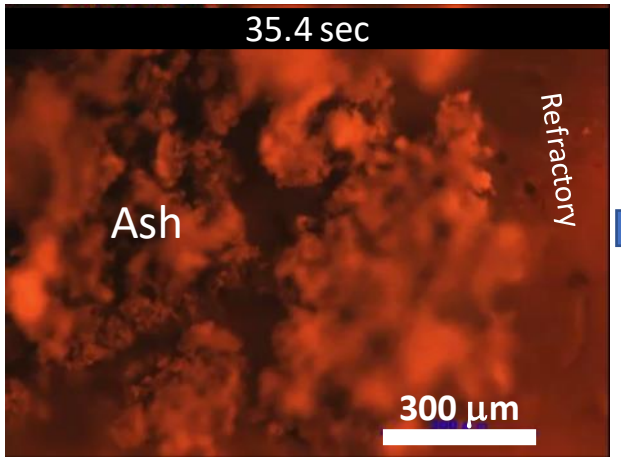
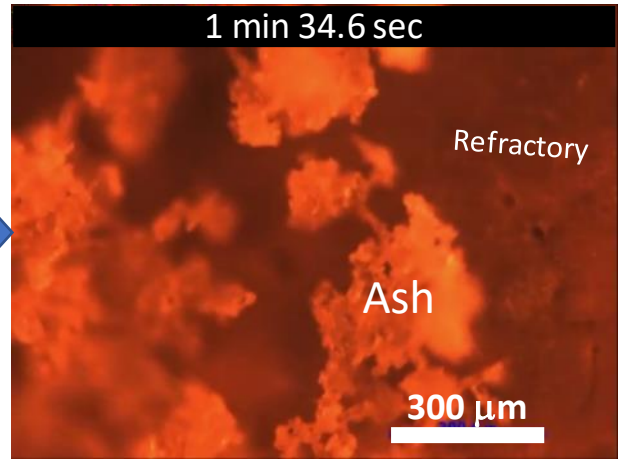
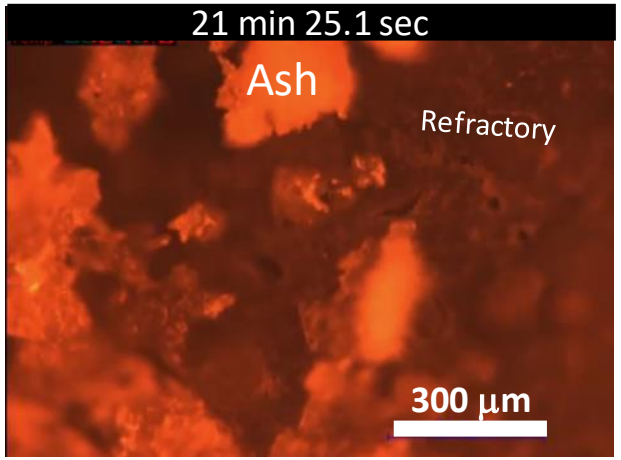


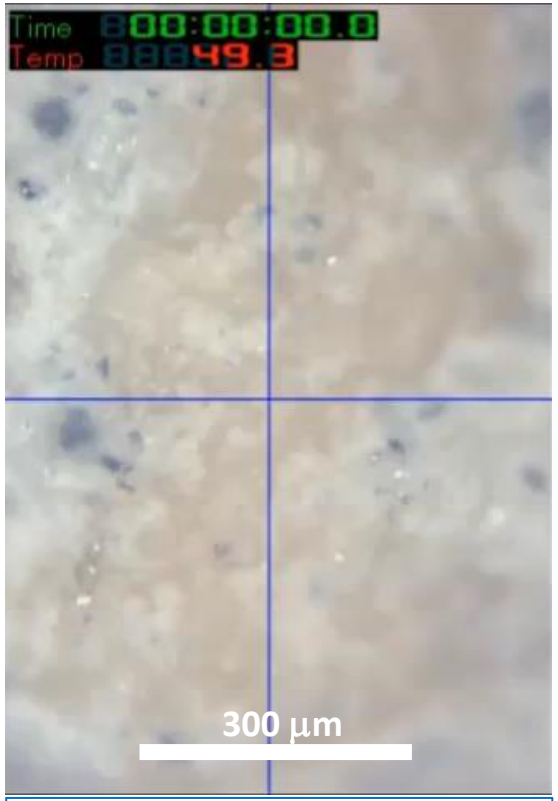






CSLM: TUFF-FLO (100% Spruce) 1200°C

Movie speed: 6x



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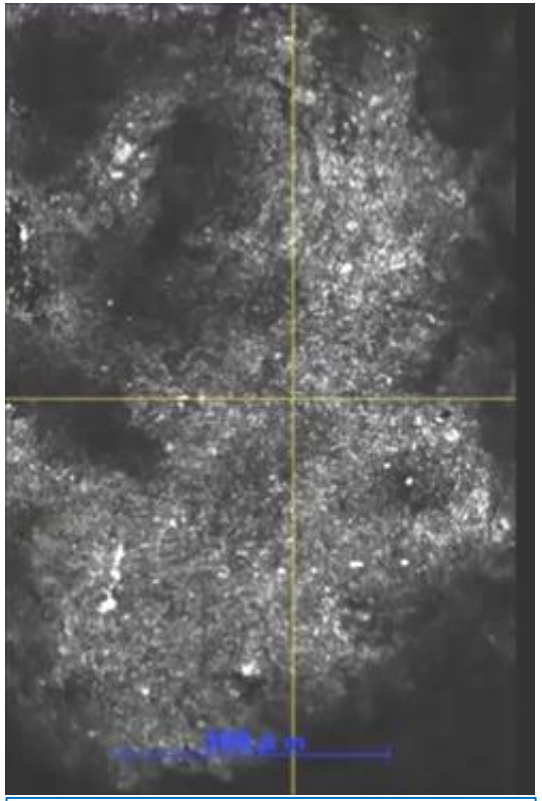
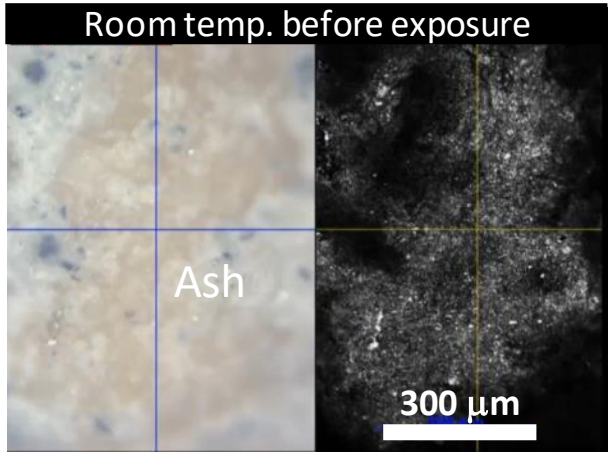
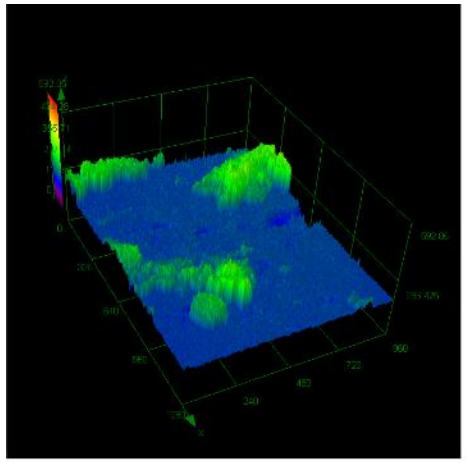


Laser

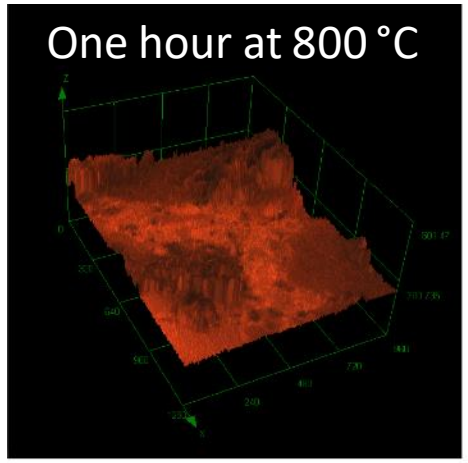


TUFF-FLO (CSLM) (100% Coal Ash)

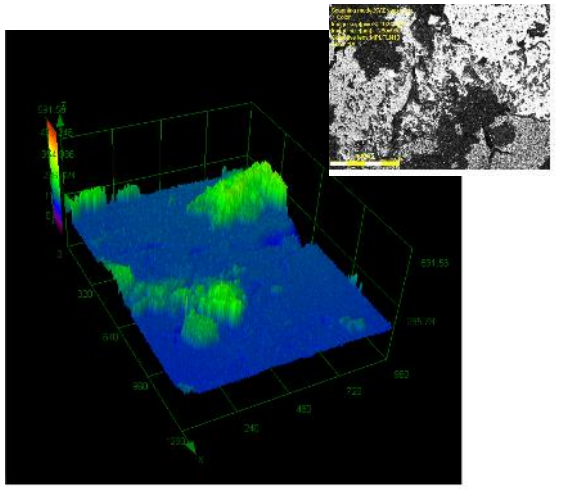
64%CO-36%CO2, 1-hour exposure

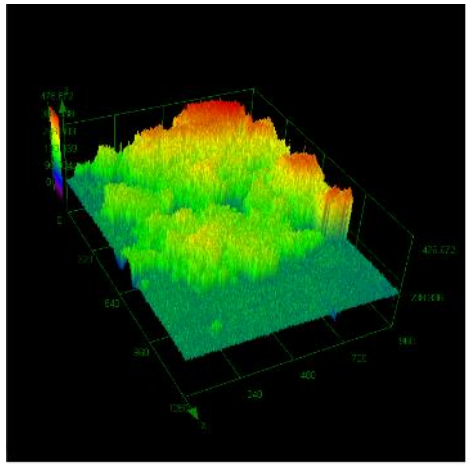


heating

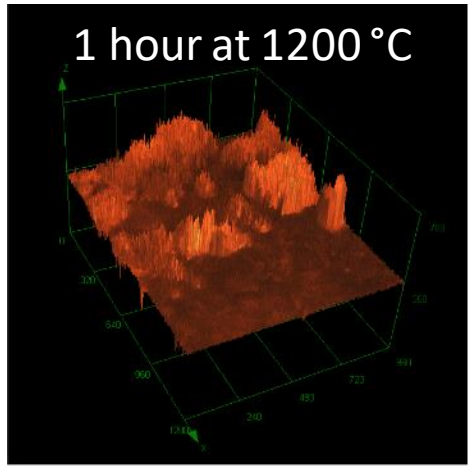


cooling





heating



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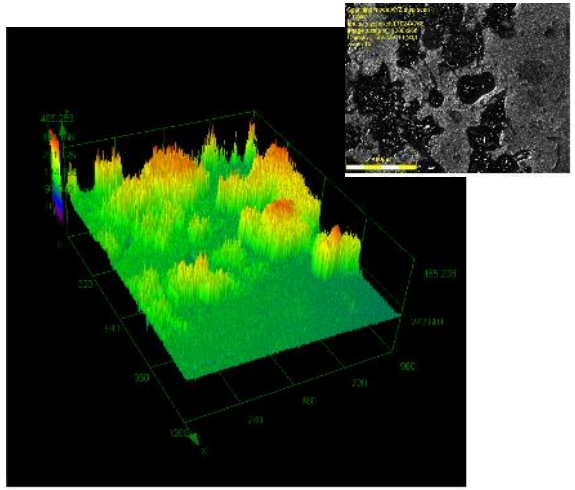
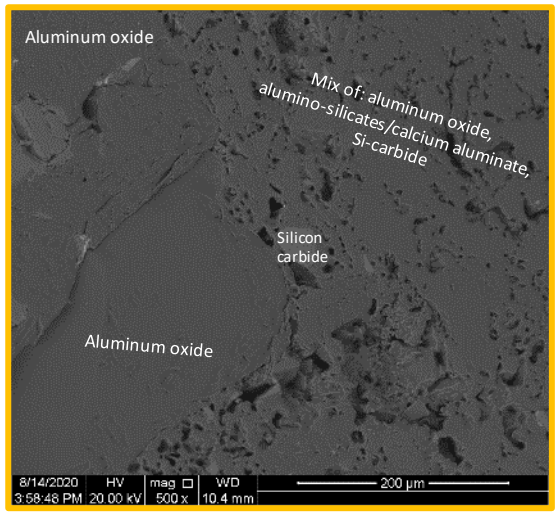


Extended Exposure: V-CAST (100% Coal Ash) 800°C

Before exposure

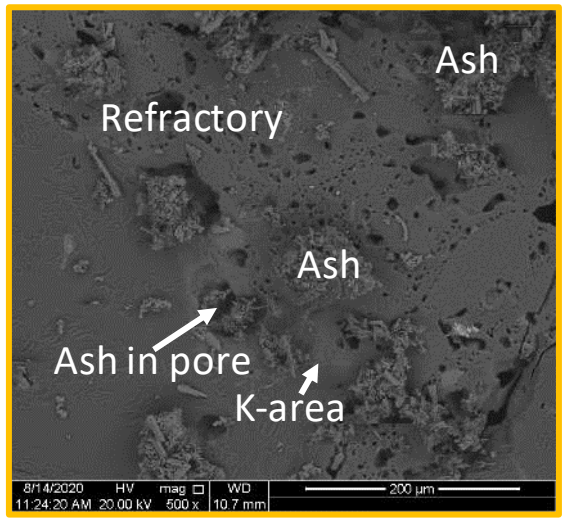
cross-section



- Micro-cracks and micro-pores.
- *Grains:* aluminum oxide.
- *Other phases identified:* alumino-silicates, calcium – aluminate, silicon carbide, Ti-oxide and some Si-oxide.

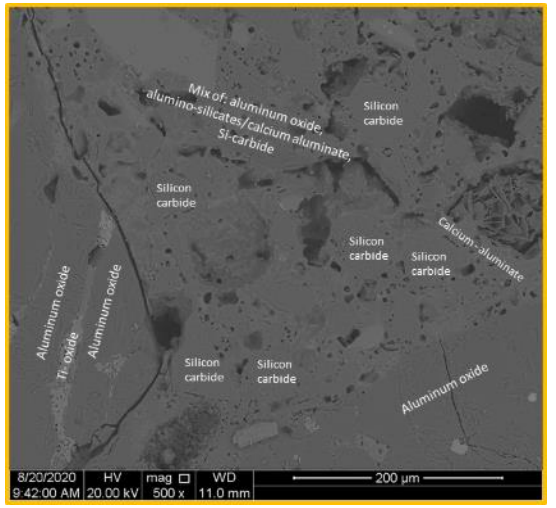
After exposure : surface

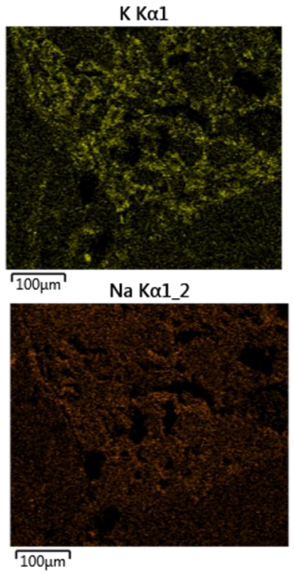
One hour



- Micro-cracks and micro-pores.
- Ash on refractory surface did not melt
- Minimal interaction with the refractory material.
- Minimal K (up to 0.7 at.%) on the surface.

50 hours



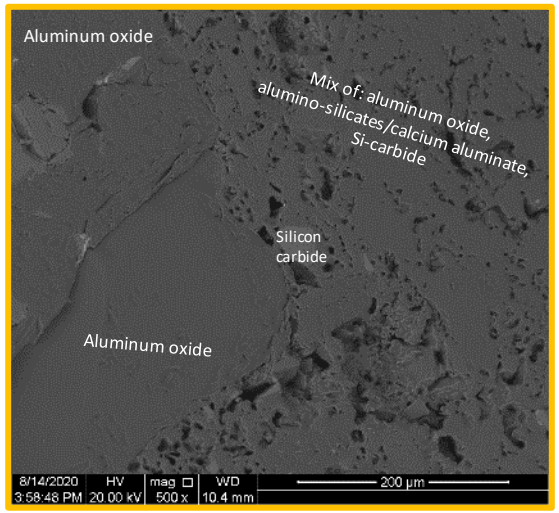


- Micro-cracks and micro-pores.
- Minimal Na and K elements were detected.

Extended Exposure: V-CAST (Spruce) 800°C

Before exposure

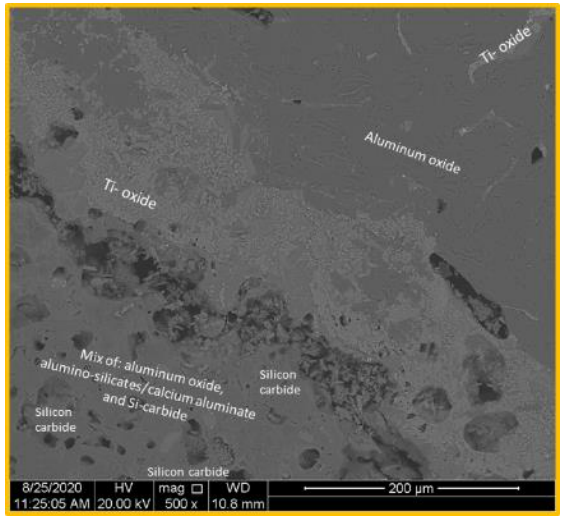
cross-section

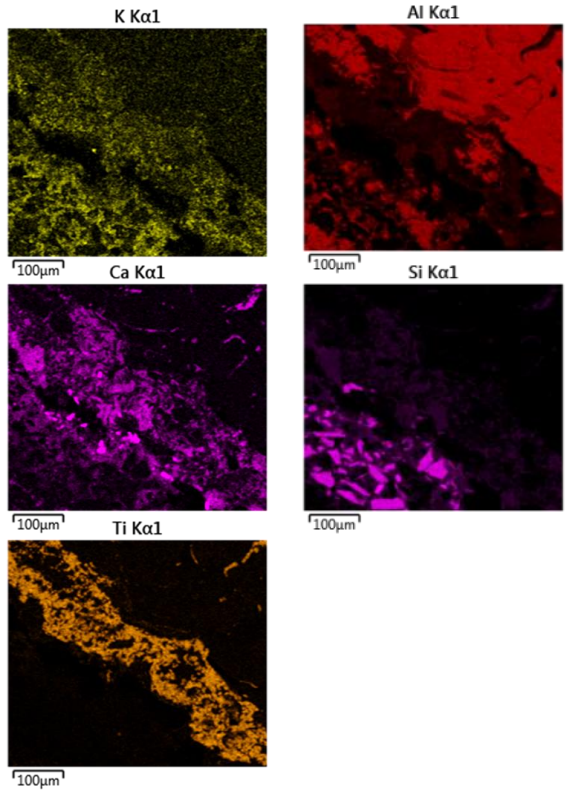


- Micro-cracks and micro-pores.
- *Grains:* aluminum oxide.
- *Other phases identified:* alumino-silicates, calcium – aluminate, silicon carbide, Ti-oxide and some Si-oxide.

After exposure: surface

80/20 coal/spruce





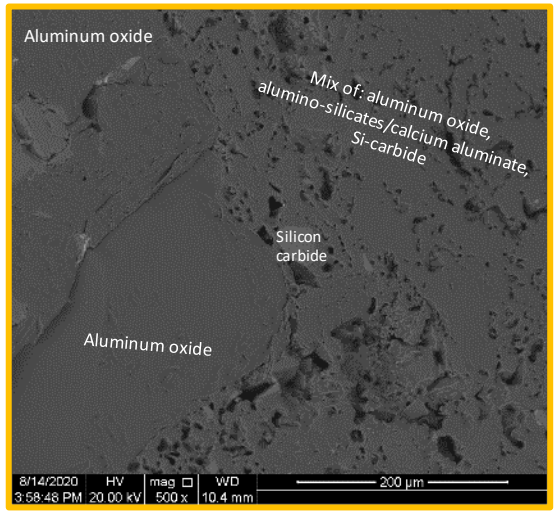
- Micro-cracks and micro-pores.
- Some Na and K elements were detected (up to 2 wt.%* each).

*based on the SEM-EDX points analyzed

Extended Exposure: V-CAST (Spruce) 800°C

Before exposure

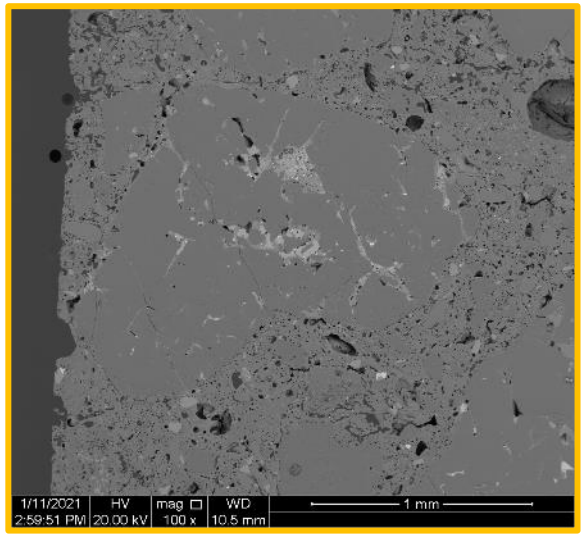
cross-section



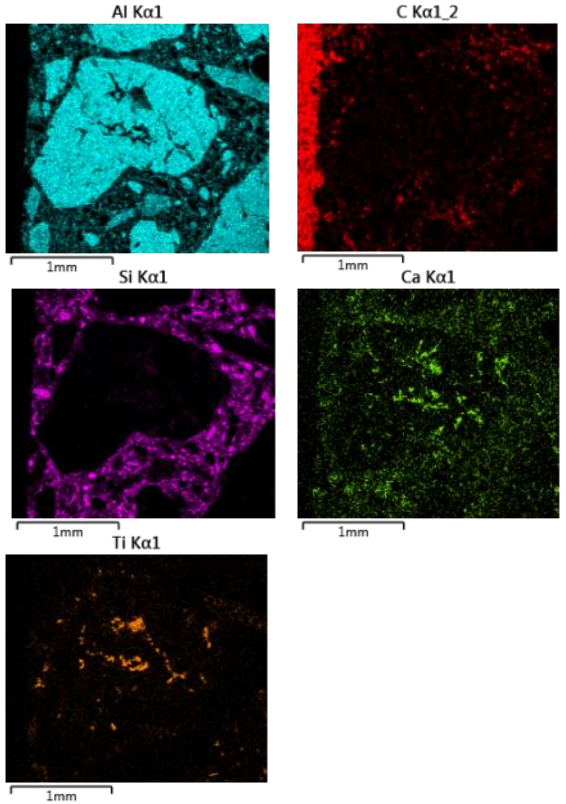
- Micro-cracks and micro-pores.
- *Grains:* aluminum oxide.
- *Other phases identified:* alumino-silicates, calcium – aluminate, silicon carbide, Ti-oxide and some Si-oxide.

After exposure: cross-section

80/20 coal/spruce



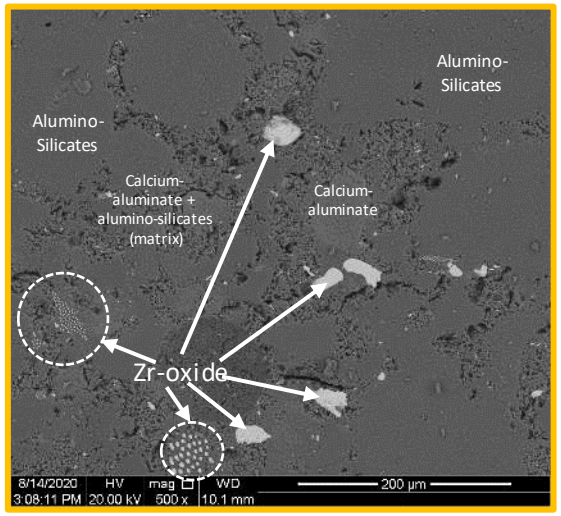
- Micro-pores.
- Na and K concentrations were below detection limit.



Extended Exposure: TUFF-FLO (100% Coal Ash) 800°C

Before exposure

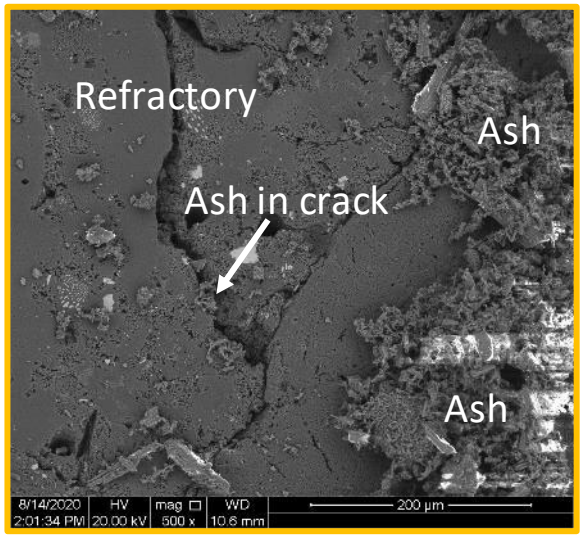
cross-section



- Micro-cracks and micro-pores.
- *Grains:* alumino-silicates.
- *Matrix:* calcium-aluminate + alumino-silicates with some Fe and Ti.
- *Other phases identified:* Silicon carbide, Zr-oxide, Ti-oxide.

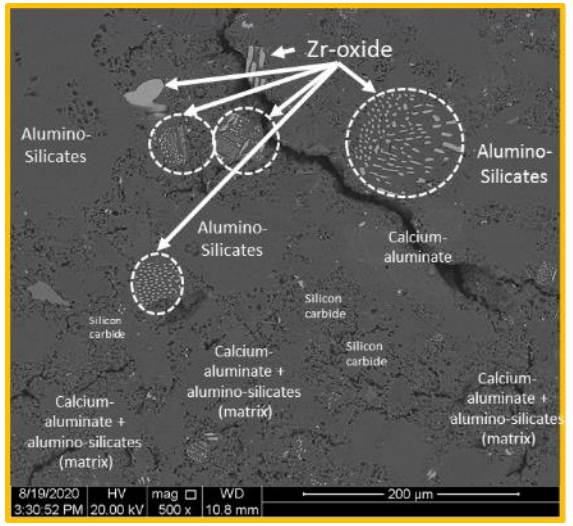
After exposure : surface

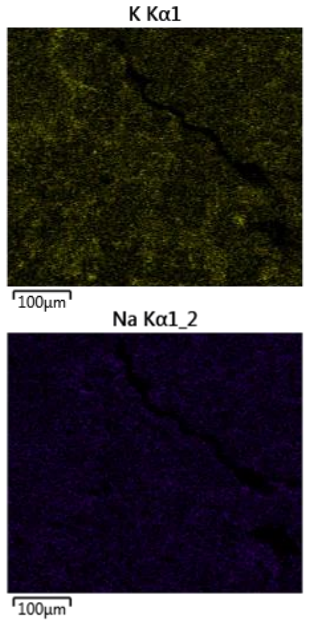
One hour



- Micro-cracks and micro-pores.
- Ash on refractory surface did not melt, indicating minimal interaction with the refractory material.

50 hours



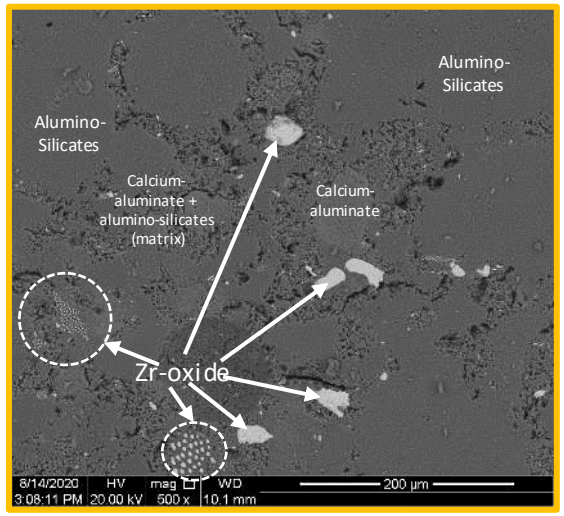


- Micro-cracks and micro-pores.
- Minimal Na and K elements were detected.

Extended Exposure: TUFF-FLO (80/20 Coal/Biomass) 800°C

Before exposure

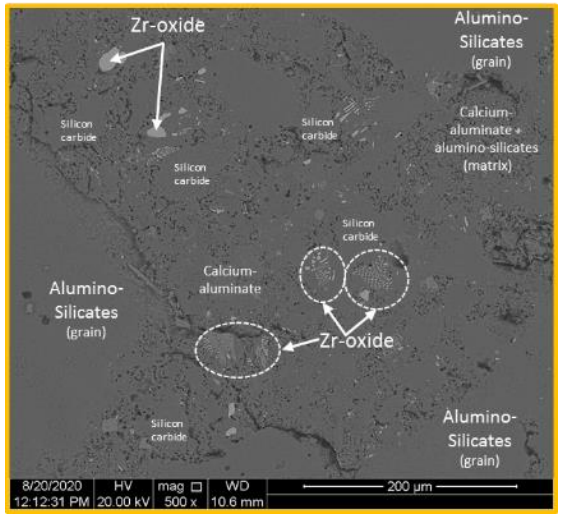
cross-section

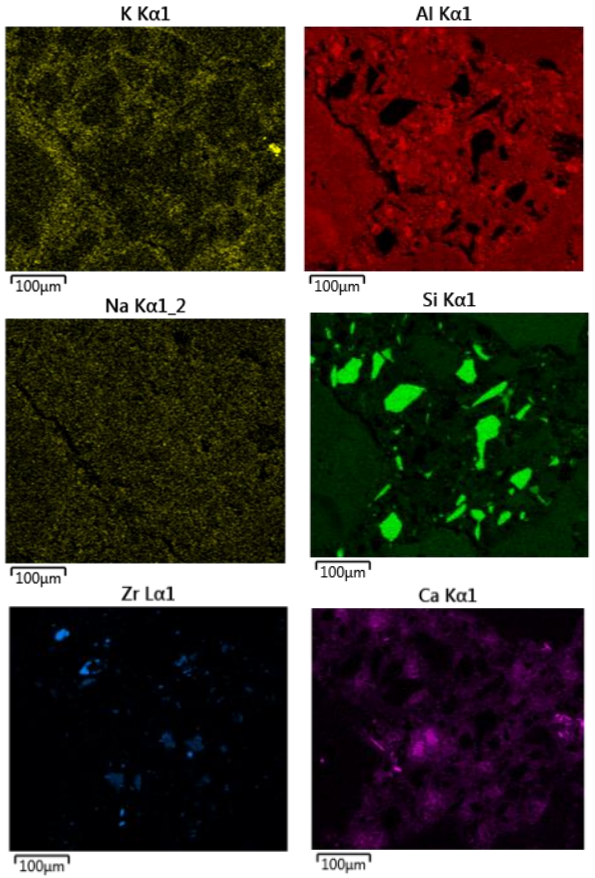


- Micro-cracks and micro-pores.
- *Grains:* alumino-silicates.
- *Matrix:* calcium-aluminate + alumino-silicates with some Fe and Ti.
- *Other phases identified:* Silicon carbide, Zr-oxide, Ti-oxide.

After exposure: surface

80/20 coal/spruce



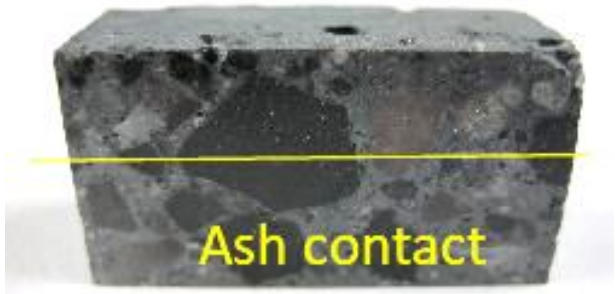


- Micro-cracks and micro-pores.
- *Grains:* alumino-silicates.
- *Matrix:* calcium-aluminate + alumino-silicates.
- *Other phases identified:* Silicon carbide, Zr-oxide, Ti-oxide.
- Minimal Na and K elements were detected.

Extended Exposure: Post Firing

100% coal

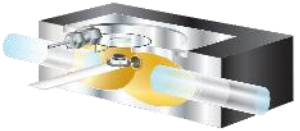
80/20
(coal/biomass)

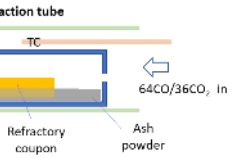


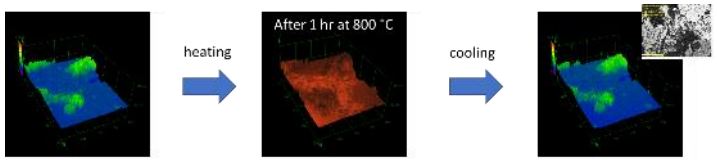
No apparent material degradation noted after 50 hours exposure to ashes at 800 °C.

Conclusion

- Alumina- and mullite-based refractory coupons were subjected to coal and biomass ash firing tests for one hour and 50 hours in a simulated gasifier environment.
- Confocal real time images exhibited no aggressive reactions on surface within a one-hour exposure.
- More alkalis (K and Na) found on surface and into refractory exposed to biomass ash; interactions with silicate especially in matrix components.
- Overall, no structural and chemical spalling was detected by alkali attack at 800 °C.







Acknowledgement

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