In-situ Analysis of Select Oxygen Carrier Materials Under Chemical Looping Combustion Conditions

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Introduction

- Chemical looping combustion (CLC) is an alternative concept for energy generation while enabling the high efficiency capture of CO_2 as a process byproduct.
- Various oxygen carrier materials are currently researched at NETL for CLC applications.

- ***Motivation***

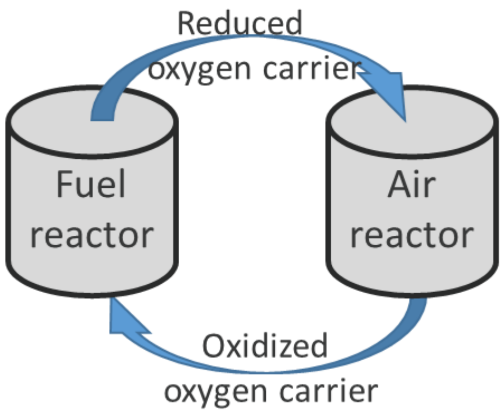
Oxygen carriers experience microstructural degradation during CLC redox exchange, leading to physical and chemical attrition. Materials improvement is needed.

- ***Objective of this work***

In-situ microstructural characterization of oxygen carriers during oxidation/reduction cycles to benchmark materials performance.

Chemical Looping Reactor at NETL Morgantown, West Virginia

Oxygen carrier - high temperature transition metal oxides.

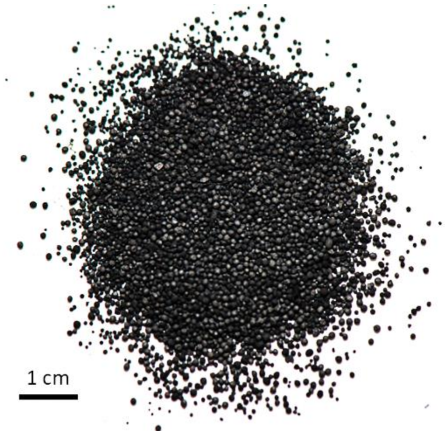


Materials (Oxygen Carriers) Studied in this Work

- NETL's Gen 2.0 (Cu/Fe spinel particles, supported on alumina)
- NETL's Gen 3.0 (Cu/Fe/Mn/Al spinel particles)
- Natural hematite (External material supplied from Canada)

NETL's Gen 2.0

NETL's Gen 3.0



Natural hematite

Materials (Oxygen Carriers) Studied in this Work

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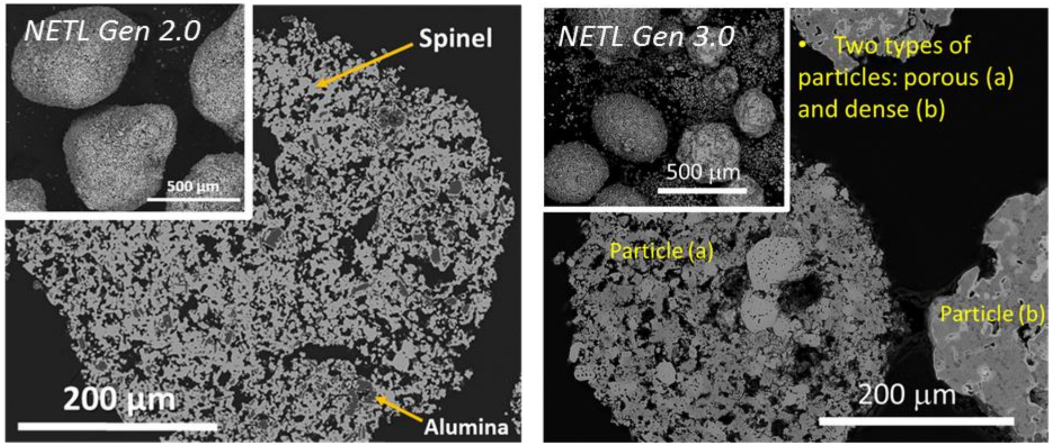
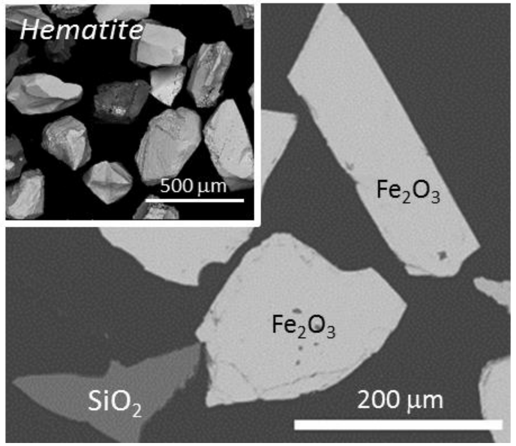
SEM: surface and cross-section morphology





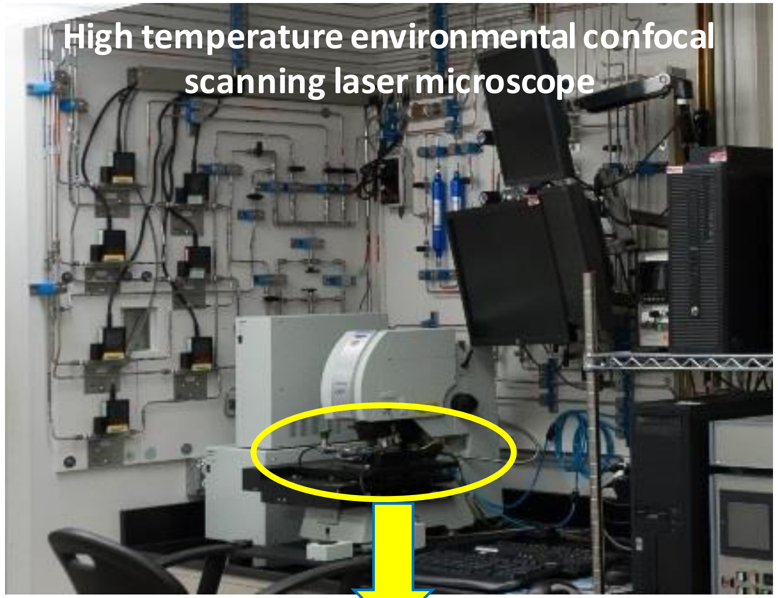
Chemical composition (XRF, mass%)

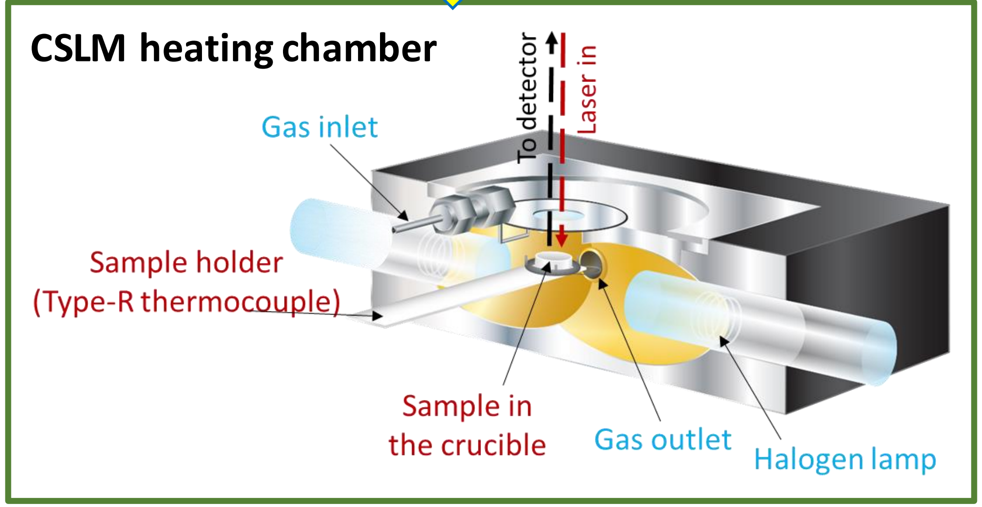
CLC material	Al_2O_3	CuO	Fe_2O_3	SiO_2	MnO
NETL Gen 2.0	33.9	34.2	31.9	-	-
NETL Gen 3.0	17.8	29.6	26.2	3.6	22.9
Natural hematite (Canada)	-	-	86.3	10.2	3.5

Crystalline phases (XRD)

CLC material	Identified crystal structures
NETL Gen 2.0	Spinel (Al rich), alumina
NETL Gen 3.0	Spinel (Cu, Mn rich)
Natural hematite	Hematite, silica

Experimental

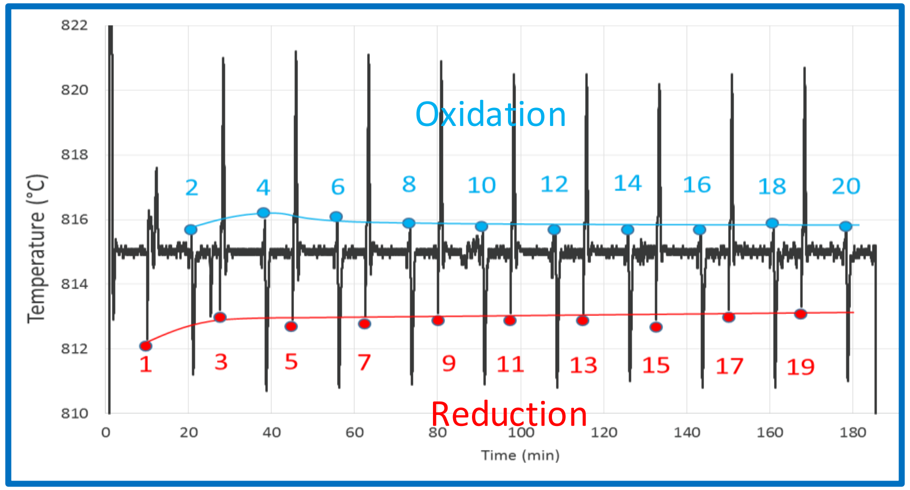




High temperature environmental confocal scanning laser microscope (CSLM)

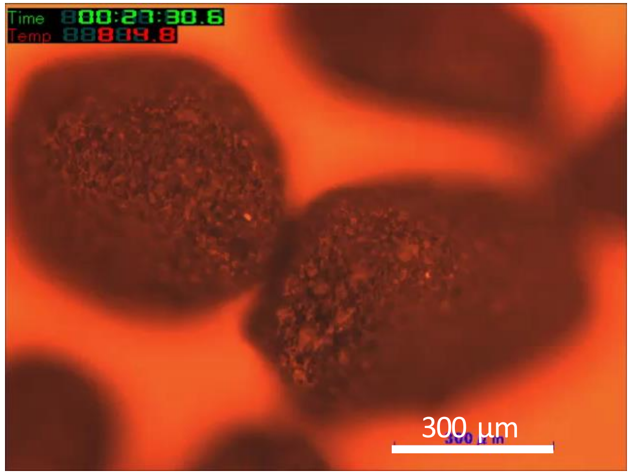
- Operation conditions standardized for benchmarking
  - 10 isothermal redox cycles (20 gas switches) at 800°C
  - Exposure lengths per cycle: 7.5 minutes in air and 10 min in 10 vol.% CO-Ar
  - **3D laser particle scans** at end of each exposure throughout entire cycles. (5 minutes each, 20 times per run)

Temperature profile (typical)



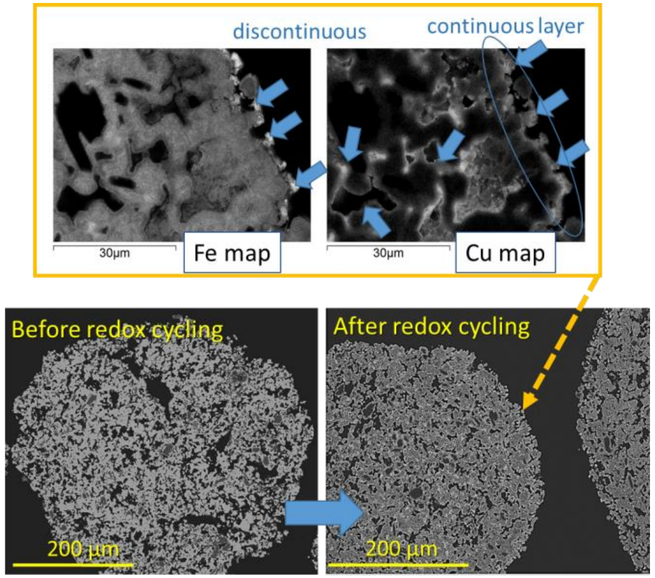
Results: NETL Gen 2.0

CSLM movie: Reduction (16x playback)



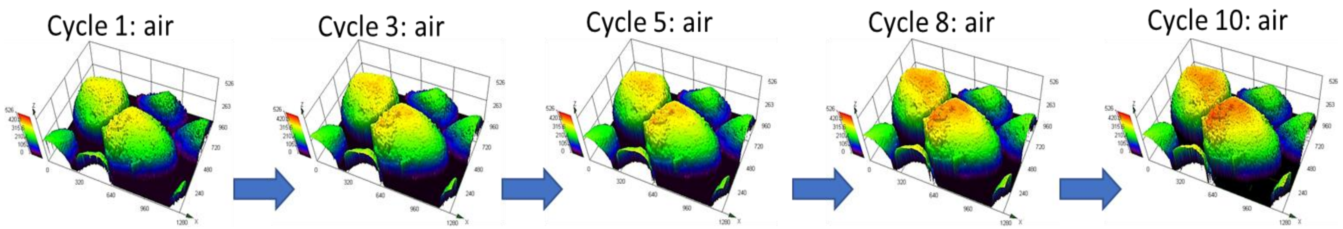
SEM analysis

After 10 redox cycles

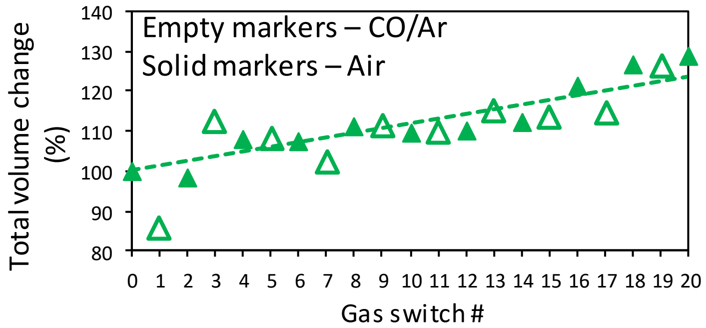


- Particles maintained structure well during present redox cycles.
- As redox cycles progressed, particles densified while porosity in inner grains increased.
- Elemental segregation of Fe and Cu led to outer layer formation around particles and inner grains.
- 3D laser scans indicated particles increased in volume over redox cycles.

3D CSLM high temperature maps: 800 °C



Volume change with cycles



Results: NETL Gen 3.0

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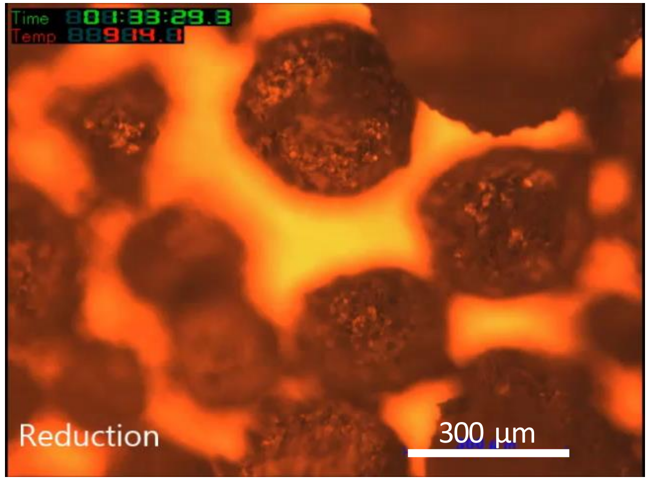
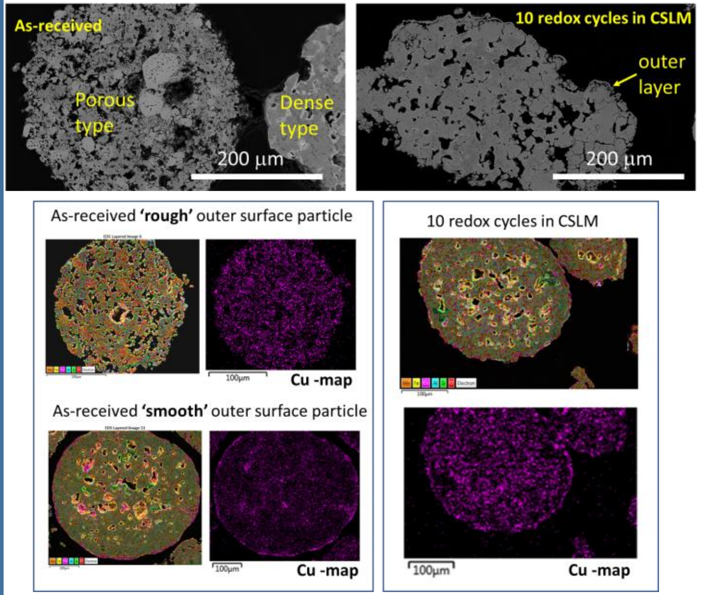
CSLM movie: Cycle 6 (20x playback)

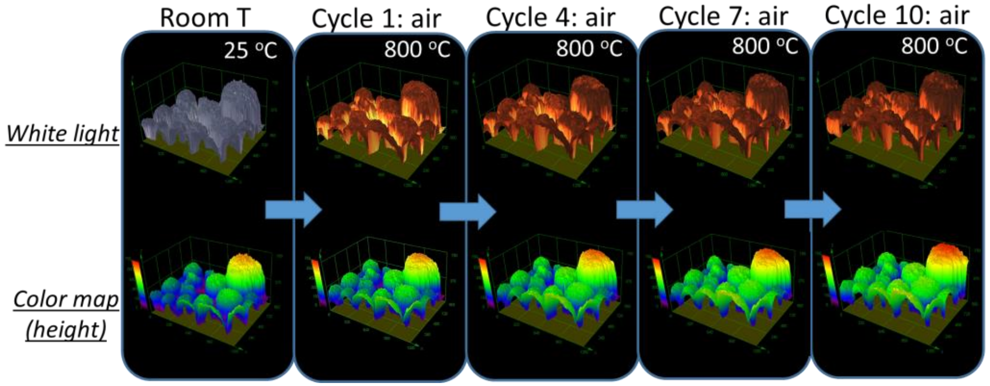


SEM analysis (Gen 3.0)

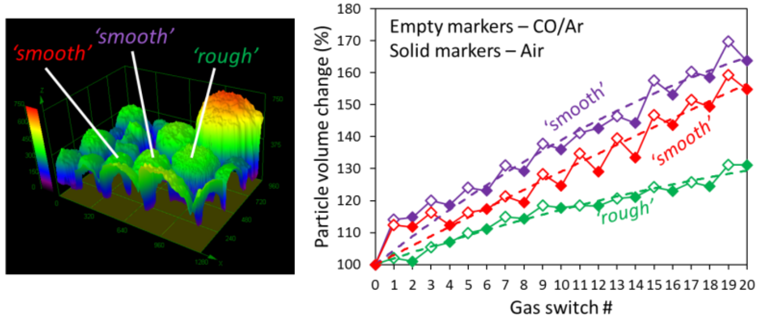


- In some particles, cracks were noted during oxidation after five redox cycles.
- In general, particles maintained their structure well during present redox cycles.
- As redox cycles progressed, particles densified while porosity in inner grains increased.
- Elemental segregation of Cu led to outer layer formation around particles and inner grains.
- 3D laser scans indicated particles increased in volume over redox cycles.

3D CSLM high temperature maps



Volume change with cycles

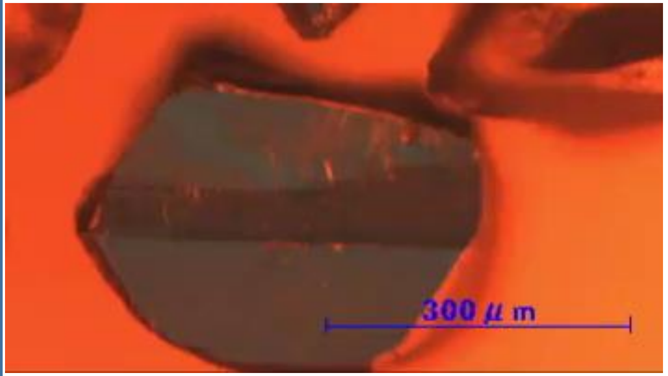


Zig-zag trend: decreases from reduction to oxidation, increases from oxidation to reduction.

Results: Natural Hematite

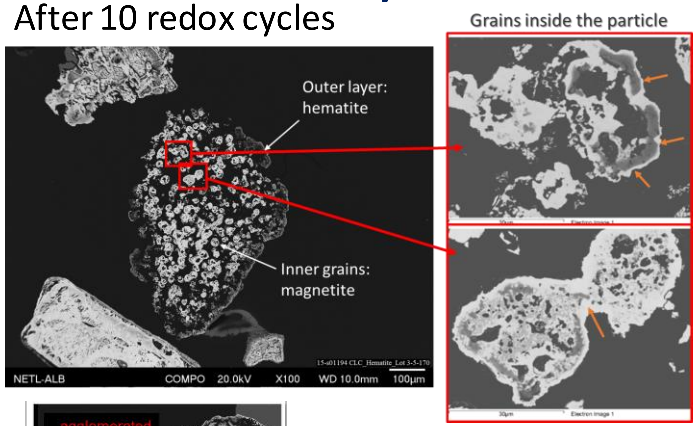
CSLM movie: Reduction (16x playback)

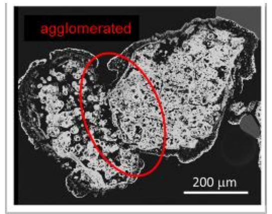
Directional surface reduction



SEM analysis

After 10 redox cycles

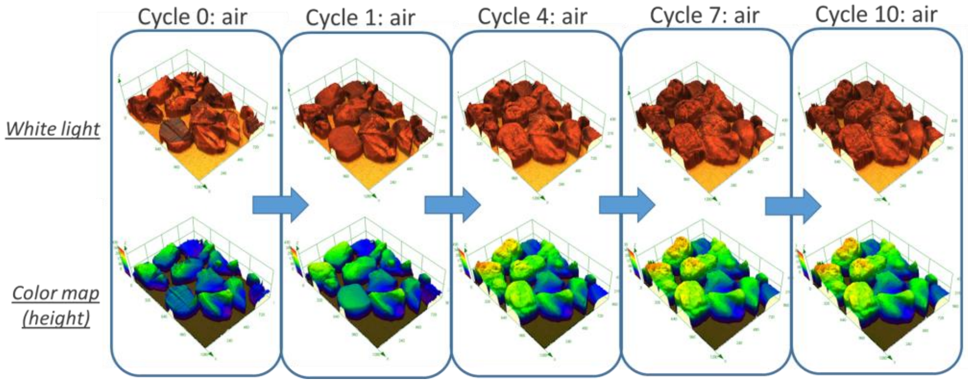




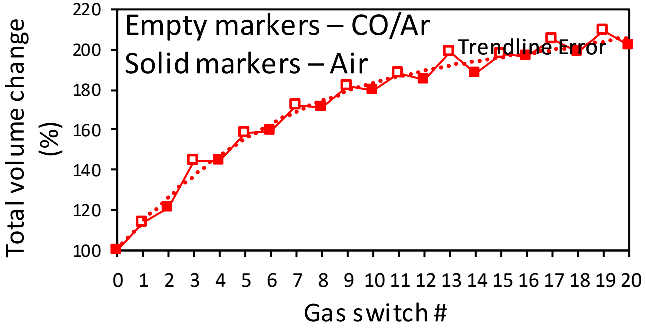
- Agglomeration

- Under redox cycling, directional surface reduction/oxidation resulted in a continuous product layer impacting radial diffusion kinetics.
- Interaction with neighboring particles, caused agglomeration by sintering.
- Sintering of inner grains inside the particle and outer layer formation around individual inner grains after 10 redox cycles.
- 3D laser scans indicated particles increased in volume over redox cycles.

3D CSLM high temperature maps: 800 °C



Volume change with cycles



Zig-zag trend: decreases from reduction to oxidation, increases from oxidation to reduction.

NETL's Gen 2.0 and Gen 3.0 vs. Hematite

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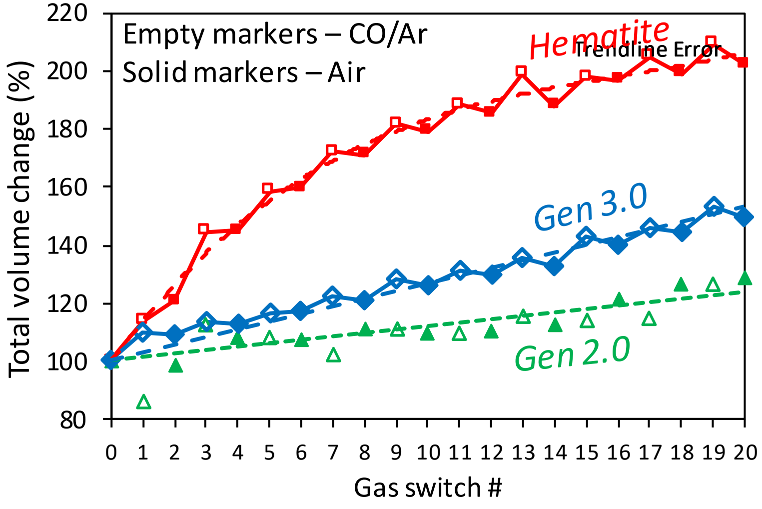
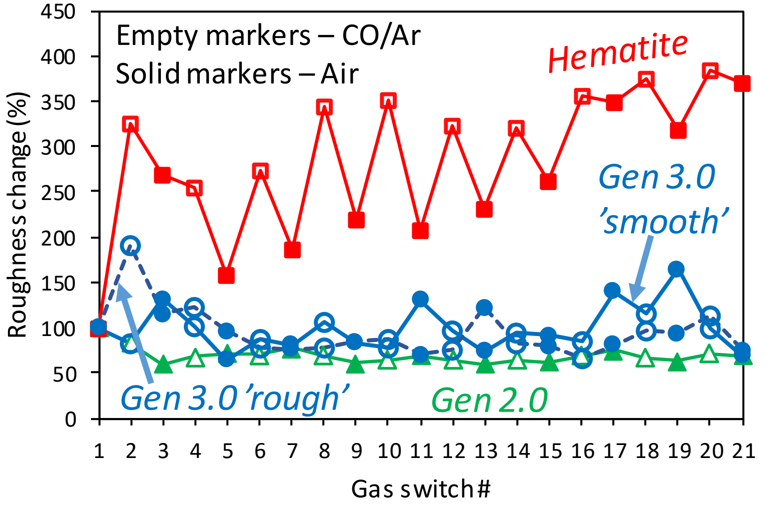
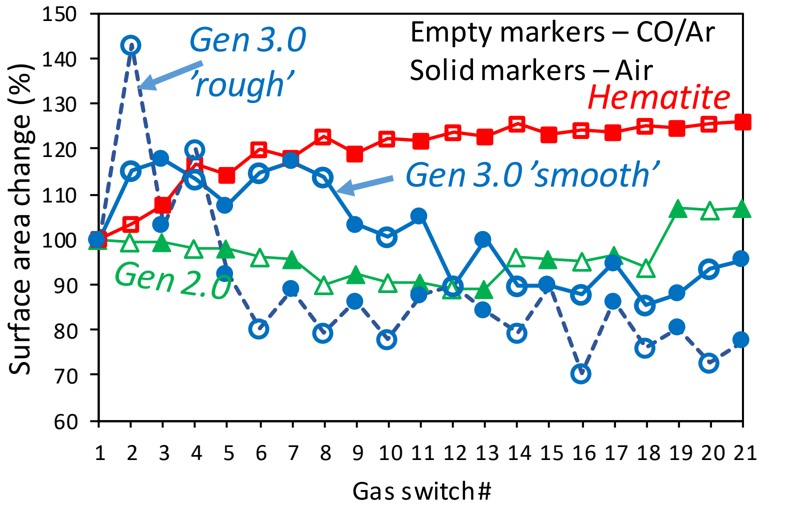
Volume change with cycles



Roughness change with cycles

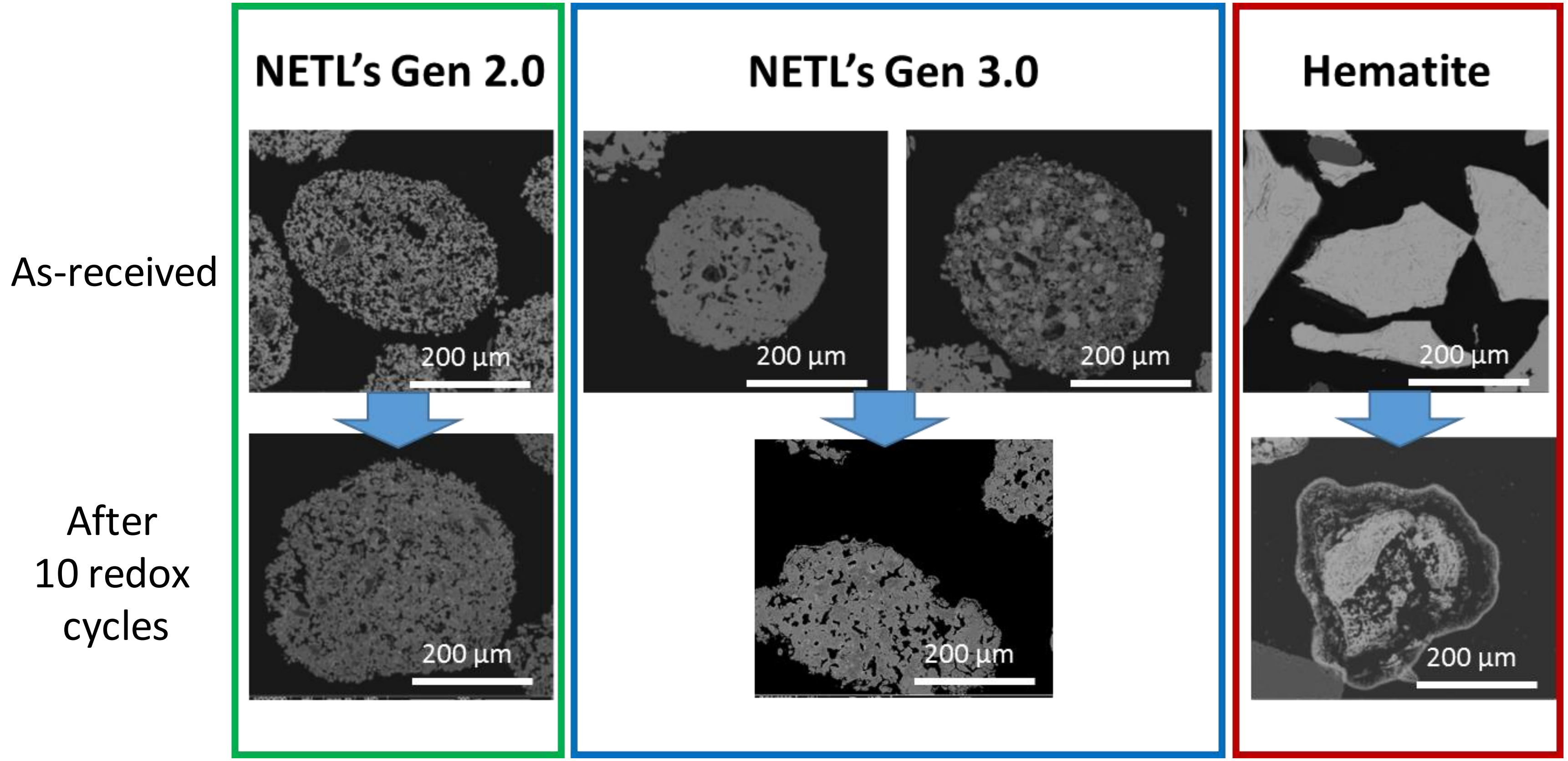


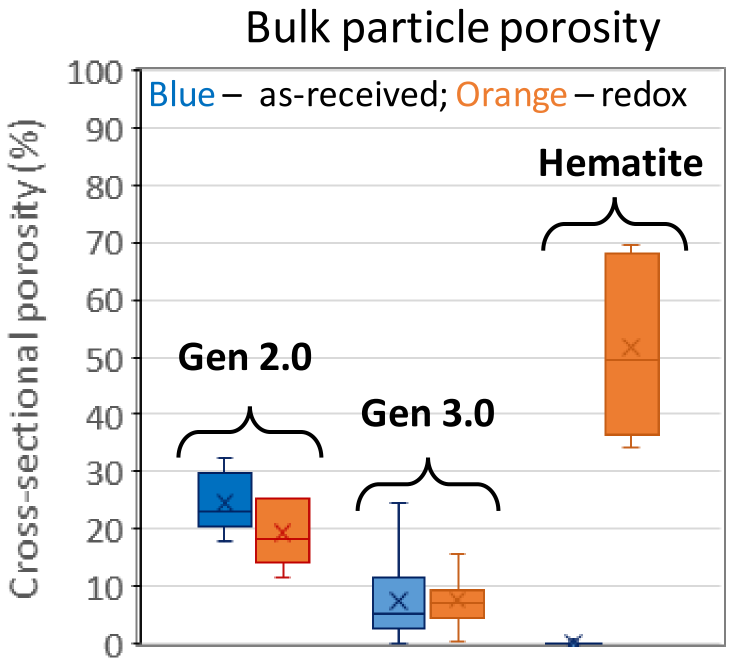
Surface area change with cycles



- **Volume after 10 redox cycles:** *NETL's G2.0* expanded by 28% compared to 50% for *NETL's G3.0* and 100% for *Hematite*.
- **Surface roughness after 10 redox cycles :** decreased in *NETL's Gen 2.0* by about 32% and in *NETL's G3.0 'rough'* and *'smooth'* particles by 25% and 30% respectively, while that of *Hematite* increased over 360%.
- **Surface area after 10 redox cycles :** increased in *NETL's Gen 2.0* by 7% compared to 26% for *Hematite*, while that of *NETL's G3.0 'rough'* and *'smooth'* particles decreased by 22% and 5% respectively.

Cross-Sectional Porosity (SEM-ImageJ): Bulk

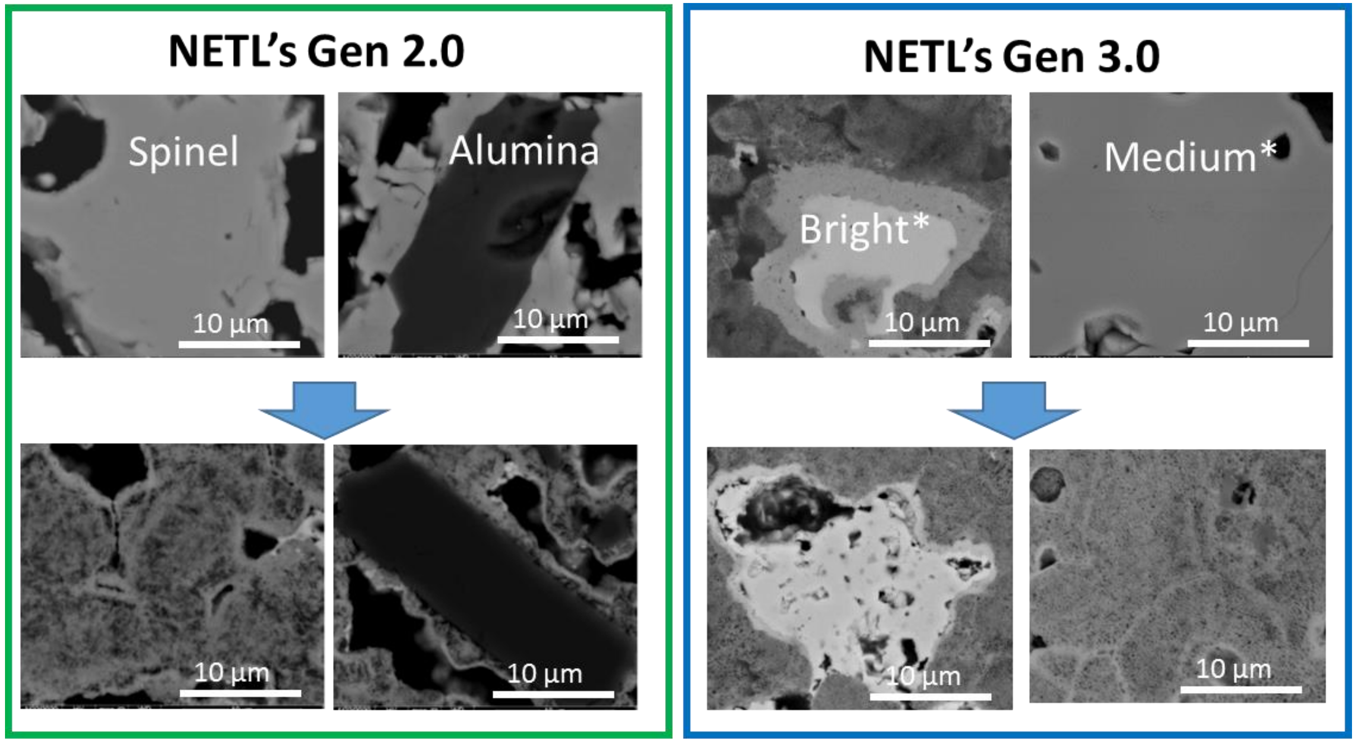




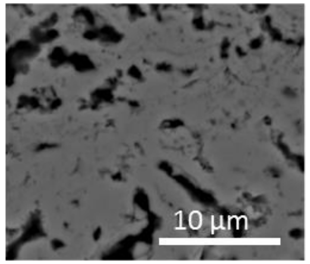
Cross-Sectional Porosity (SEM-ImageJ): Grain

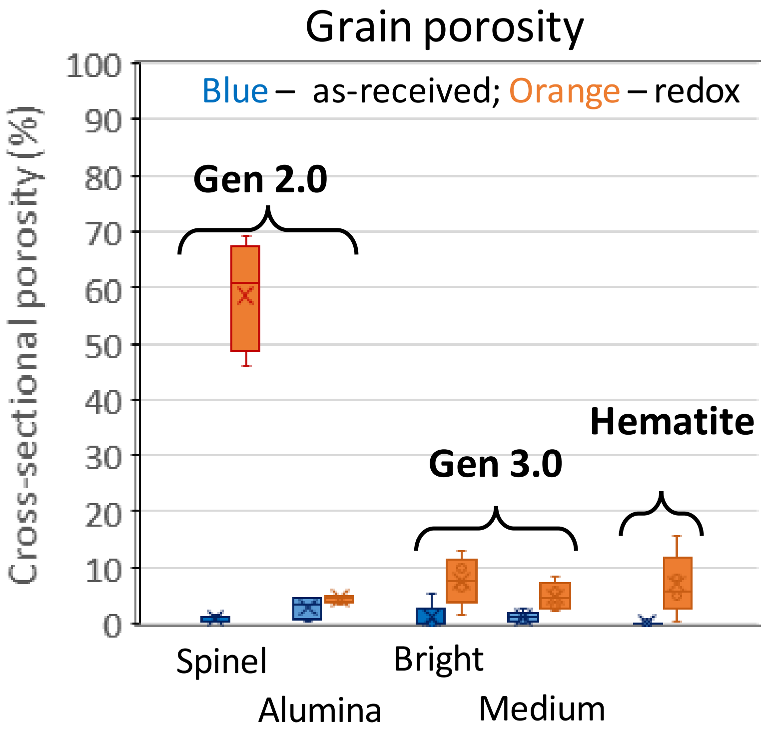
As-received

After 10 redox cycles



Hematite after redox





*Gen 3.0: 'Bright' – Cu-rich spinel; 'Medium' – Al-rich spinel

Conclusions

- Real time evolutions in microstructure, particle volume, surface area, and roughness obtained from the 3D laser scans were used as parameters to benchmark NETL's Gen 2.0, Gen 3.0 and natural hematite oxygen carrier materials performance under simulated redox cycles using CSLM.

- Particle volume expansion was noted over redox exposures for all materials. Particle surface area increased over redox exposures in Gen 2.0 and Hematite, while that in Gen 3.0 decreased.

- Particle surface roughness decreased over redox exposures in Gen 2.0 and Gen 3.0 due to sintering and surface morphology modifications, while that in hematite significantly increased. Roughness can be interpreted as an index of materials degradation.

- Continuous/discontinuous product outer layer formation around particles and inner grains impacted radial diffusion kinetics.

- NETL's Gen 2.0 and Gen 3.0 particles densified while porosity in inner grains increased. Major increase in bulk and grain porosity for hematite. Higher porosity created more internal passage for oxygen exchange.

- Hematite particle agglomeration was noted as early as the third redox gas cycle.

- Structural damage on the Gen 2.0 and Gen 3.0 particles after the redox exposures was minimal.

Acknowledgements

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