An analysis of in-situ phase changes occurring in natural hematite exposed to simulated high temperature redox gas cycling encountered in chemical looping

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**Technical Issue**
Oxygen carriers experience microstructural changes and degradation during CLC, contributing to attrition. Understanding of materials behavior is needed.

**Objective of this part of work**
Study in-situ microstructural characterization of hematite during oxidation/reduction cycles (no particle mixing).


More info on CLC: [https://www.netl.doe.gov/newsroom/labnotes/labnotes-archive/01-2014](https://www.netl.doe.gov/newsroom/labnotes/labnotes-archive/01-2014)
**Experimental Materials**

<table>
<thead>
<tr>
<th>Sample</th>
<th>XRF (mass.%)</th>
<th>XRD Identified crystalline phases</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe$_2$O$_3$</td>
<td>MnO</td>
</tr>
<tr>
<td>Natural hematite</td>
<td>86.27</td>
<td>3.51</td>
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</tbody>
</table>

**Natural hematite**
- Primary crystalline phase = hematite.
- Source = Wabush Mine, Newfoundland/Labrador, Canada
Experimental Test Procedures

HTC Confocal Scanning Laser Microscope - used to observe isothermal Redox gas cyclic exposures

- Temperature: 800°C and 1200°C
- Gas switched between synthetic air (oxidation) and 10 vol.% CO-90 vol.% Ar (reduction) at a flow of 50 ml/min
- Repeated 10 cycles - 20 gas switches (1 cycle = 7.5 min each for oxidation + 10 min each for reduction)
Natural hematite analysis (800°C)
Real time surface morphology change at 800°C

Reduction. Cycle 1: 10CO-Ar

Play back 8x
Gas switched at 11:00
Hematite: Overall change with redox cycles (real color)

800°C

Before redox cycles

Gas switch # 1 (CO)
Gas switch # 9 (CO)
Gas switch # 19 (CO)
Gas switch # 2 (Air)
Gas switch # 10 (Air)
Gas switch # 20 (Air)
Hematite: Overall change with redox cycles (topology map)

Before redox cycles

800°C

Gas switch # 1 (CO)

Gas switch # 2 (Air)

Gas switch # 3-8

Gas switch # 9 (CO)

Gas switch # 10 (Air)

Gas switch # 11-18

Gas switch # 19 (CO)

Gas switch # 20 (Air)
Agglomeration at 800°C

Before cycles
00:00:00

Cycle 3: 10CO-Ar
00:40:00

Cycle 6: 10CO-Ar
01:32:30

After 10 cycles: air
02:50:00

SEM (cross-section)
Crack formation at 800°C

- Before cycles: 00:00:00
- Cycle 4: air 01:05:32
- Cycle 6: air 01:40:20
- Cycle 8: air 02:15:26
- After 10 cycles: air 02:50:20
Inner grains in each particle \textbf{After 10 redox cycles at 800°C}

SEM-WDS analysis: cross-section

Grains inside the particle

Outer layer: hematite

Inner grains: magnetite

Note: Dark grey area is remaining silica-based polishing/epoxy

Sintering of inner grains inside the particle

Outer layer formation around individual inner grains
• Zig-zag volume change: decreases from reduction to oxidation, increases from oxidation to reduction – mainly due to hematite ↔ magnetite transitions (magnetite lattice > hematite lattice).

• Overall volume increase due to void formation.

Note: 3D scan in Air at 800° C was used as a reference 100% volume.
Surface area, Area, and Roughness Changes at 800°C

- **Surface area** = topography area (including bumps and dents – 3 D).
- **Area** = overall area without bumps and dents – 2 D.
- **Roughness** = difference in max. heights and pits over surface.

Increasing zig-zag trend with cycles
- Surface area increase (25%) > area increase (21%) \(\rightarrow\) due to the formation of **surface bumps and dents**.
- Overall roughness increase \(\rightarrow\) due to **structural breakdown/void formation**.

Note: 3D scan in air at room temperature before redox exposure was used as a reference for surface area and area.
Kinetics of surface phase transition at 800°C

(Cycle 2: 10CO-90Ar)

- Linear kinetics = interfacial
- Velocity = 0.99 um/sec

Phases calculated by thermodynamics. Confirmation by SEM-WDS.
Kinetics at 800°C

- **Delay** = incubation time required for the onset of phase transition after gas switch
- **v** = velocity of surface phase transition
- **P1** and **P2** = time required for complete visual surface phase transition of the selected particles 1 and 2.
Natural hematite analysis (1200°C)
Natural hematite - 1200°C

Reduction. Cycle 1 (10CO-Ar)

Play back 6x
Gas switched at 10:00

Surface became rougher. Particles moved.

Surface change ‘front line’

Delay about 6 min before the front line was noted.

Reduction. Cycle 3 (10CO-Ar)

Play back 32x
Gas switched at 45:00

Crack

Surface change

Delay about 45 sec before the surface change was noted.
Surface became darker and rougher. Particles moved, expanded, cracked.
Natural hematite, CSLM (1200°C)

Oxidation. Cycle 1 (Air)
- Delay about 45 sec. Surface brightened and became more rough.

Oxidation. Cycle 3 (Air)
- Delay about 45 sec. Surface darkened first and then brightened. Particles shrank.
Particle breakdown at 1200°C

Before cycles 00:00:00

Cycle 4: 10CO-Ar 00:57:30

Cycle 6: 10CO-Ar 01:32:30

Cycle 8: 10CO-Ar 02:07:30

Cycle 9: 10CO-Ar 02:25:00

Cycle 10: 10CO-Ar 02:42:30
Agglomeration at 1200°C

Before cycles 00:00:00

Cycle 2: 10CO-Ar 00:22:30

Cycle 3: 10CO-Ar 00:40:00

Cycle 6: 10CO-Ar 01:32:30

Cycle 9: 10CO-Ar 02:30:00

Just after 10 cycles: Air 02:50:00

300 µm
Volume change at 1200°C (color map)

Before redox cycles

Gas switch # 3 (CO)

Gas switch # 7 (CO)

Gas switch # 13 (CO)

Orange: 10CO-Ar
Blue: Air

Note: Quartz window fogged after gas switch 15
After the redox gas cycles at 1200°C

SEM-WDS analysis: cross-section

- The presence of interior magnetite implies 10 min reduction exposure was sufficiently long to induce phase transition at the center of the particle, at least at some point if not at later stages.
- At the last cycle, only surface grains transformed to hematite during 7.5 min air exposure.
Hematite surface change after redox exposures

(General groups of hematite particles)

Before redox exposure

White light images

After 10 redox cycles
800°C

Hematite surface turned reddish on cooling

Heavily sintered

After 10 redox cycles
1200°C
• Materials behaviors of natural hematite (Fe$_2$O$_3$) particles at 800°C and 1200°C were investigated under redox gas cycles (synthetic air and 10CO-90Ar) using HT-CSLM.

• During isothermal gas cycling, the hematite particles showed phase transitions across the surfaces corresponding to a hematite transforming to magnetite in 10CO-90Ar and magnetite to hematite when switching back to air (phases confirmed by SEM-WDS).

• In general, particle volumes, area, and roughness increased in transitioning to magnetite and decreased in transitioning to hematite, while, overall, all increased with cycles.

• Layering around the particles was noted but full transition to magnetite throughout the particle indicates hematite would be suitable for CL application if appropriately processed.
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