Raman Spectroscopy for the On-Line Analysis of Oxidation States of Oxygen Carrier Particles

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**Chemical Looping Combustion**

**Goal:** Combust fossil fuels in pure O$_2$ so as to generate pure CO$_2$ for storage.

**Conditions, including:**
- Temperatures: 800 °C – 1000 °C
- Pressure: ~ 10 atm
- Particles constantly moving

**Optimization of process requires ability to identify oxidation state**

“DOE/NETL Advanced Combustion Systems: Chemical Looping Summary,” July 2013, DOE/NETL
Oxygen Carrier Particles

This Project:
- $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$
- $\text{CaSO}_4$
- $\text{CuO}$

Desired properties include:
- High conversion efficiency
- High reactivity
- Low agglomeration
- Long lifetime
- Low cost
- Low environmental impact


Goal, Objectives, and Vision

Goal:
Develop a sensor for the on-line analysis of the oxidation state of oxygen carrier particles and demonstrate its feasibility.

Objectives:
(1) Set up and test a Raman spectroscopy system in combination with a pressurized high-temperature sample chamber.

(2) Optimize operating parameters of the Raman spectroscopy system and measure the high-temperature spectra of oxygen carriers.

(3) Develop an analysis procedure, including statistical modeling and multivariate calibration, for the interpretation of the Raman spectra.

Long-term Vision:
Monitoring system that can easily be integrated into different types of CLC systems and provide feedback for process control.
Raman Spectroscopy

- Widely used for the detection/identification of materials.
- Demonstrated for standoff/remote single-shot applications.

Widely used and proven technique.

https://www.sciaps.com/raman-spectrometers/, accessed 9/30/16
Raman Spectroscopy

Provides vibrational information unique to material.
Corrections for Raman Spectra

Raman spectra require various corrections.

Processing:
- **Instrumental transfer function**
  - Filters
  - Spectrometer
  - Detector
  - Other optical elements
- **Background**
  - Fluorescence
  - Blackbody
  - Cosmic radiation
  - Stray light
  - Laser fluctuation
- **Multi-peak fitting**
  - Peak position
  - FWHM
  - Peak area
Peak fitting provides important information for calibration models.
Raman Analysis

- Heat known materials (e.g., Fe$_2$O$_3$, Fe$_3$O$_4$) to high temperature (e.g., 800 °C, 900 °C, and 1000 °C) and measure Raman spectra.
- Perform Inverse calibration (determine composition and temperature):

  \[ x = \alpha_0 + \alpha_1 R_1 + \alpha_2 R_2 + \cdots + \alpha_h R_h \]
  \[ T = \beta_0 + \beta_1 R_1 + \beta_2 R_2 + \cdots + \beta_k R_k \]

- $x$: Composition (e.g., mol% Fe$_2$O$_3$)
- $T$: Temperature
- $\alpha_i, \beta_i$: fitting parameters
- $R_i$: subsets of the Raman parameters (frequency; FWHM; area)

**Yields T and x in the form of linear combinations of the Raman parameters.**

Using 355 nm instead of 785 nm reduces background by more than 5 orders of magnitude.

\[ I_\lambda = \frac{2hc^2}{\lambda^5 \left(e^{\left(\frac{hc}{\lambda kT}\right)} - 1\right)} \]
Blackbody Radiation - Fe$_2$O$_3$

Effects of blackbody radiation apparent using 532 nm excitation.
Envisioned Raman Spectroscopy Field Setup

- **Hot Metal Oxide**
- **Laser**
- **Telescope**
- **Spectrograph**
- **Detector**

Graph showing concentration (%) vs. time (sec) for different metal oxides, and temperature vs. time with markers for specific temperatures.
Initial Laboratory Setup

Calibration measurements on well-defined samples.
Investigation of OCPs

- **Calcium Sulfate Studies**
  - Pulsed/time gating approach successful for temperatures $>1000\,^\circ\text{C}$

- **Iron Oxide Studies**
  - Pulsed lasers generally not successful because of instability under intense light.
  - CW lasers have proved promising
CaSO$_4$ – High Temperature Measurements

532 nm

Characteristic Raman peaks observed above 1000°C.

CW, 100 ms

Single shot, long-pulse, 130 µs

Laser induced breakdown spectra (LIBS) observed using laser pulses of sufficient intensity.

Fe$_2$O$_3$/Fe$_3$O$_4$ – Challenges with Absorption

Ideally, we want high scattering and low absorption.
# Fe$_2$O$_3$ – Optimizing Light Intensity & Wavelength

## Using CW:

<table>
<thead>
<tr>
<th></th>
<th>360 nm**</th>
<th>532 nm*</th>
<th>633 nm*</th>
<th>785 nm*</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Intensity</strong></td>
<td>$\leq 10^6$ W/cm$^2$</td>
<td>$\leq 10^5$ W/cm$^2$</td>
<td>$\leq 10^5$ W/cm$^2$</td>
<td>$\leq 10^5$ W/cm$^2$</td>
</tr>
<tr>
<td><strong>Highest Temperature</strong></td>
<td>1050 °C</td>
<td>700 °C</td>
<td>400 °C</td>
<td>600 °C</td>
</tr>
</tbody>
</table>

*Using hematite powders (212 μm-600 μm)

**Light intensity only estimated, used densely packed powder

Light intensity must be low to avoid LIBS (creating an advantage for UV excitation).
**Fe₂O₃ – Comparison of Wavelengths**

Shorter wavelengths best for avoiding blackbody.
Fe$_2$O$_3$ at 1000 °C

Fe$_2$O$_3$ spectra at 1000 °C have been successfully collected using 360 nm and 532 nm excitation.

Benchmark high temperature spectrum.
**Reference Fe$_2$O$_3$ and Fe$_3$O$_4$ Spectra at RT**

Raman signatures of powders optimized prior to heating mixture sample.
Fe$_2$O$_3$/Fe$_3$O$_4$ Powder Mixture

**Fe$_2$O$_3$/Fe$_3$O$_4$ can be differentiated up to 600°C using CW 532 nm.**
Next Steps

- **Optimize Collection of Raman Spectra**
  - Further investigate UV Raman
  - Finalize selection of laser wavelength
  - Utilize lock-in amplifier with photomultiplier tube to minimize spectral noise/background

- **Test NETL Samples**
  - Collect reference spectra prior to heating

CuO-Fe$_2$O$_3$-Al$_2$O
Next Steps

- **Perform Multivariate Statistical Analysis**
  - Collect reference measurements for calibration
  - Test chemometric software for our analysis
  - Determine relative mole fraction of OCPs at a given temperature

Multiple linear regression (MLR) could be a useful chemometric technique for our analysis.

![Graph of Fe$_2$O$_3$ - 1000°C](image)

![PCA Analysis Example - Gel Ink Pens](image)

- **Blue gel inks**
- **Red gel inks**
Summary

- **CaSO$_4$**
  - Yields good spectra for both cw and low intensity pulses
  - Successfully measured spectra above 1000°C
  - LIBS observed with high intensity pulses

- **Fe$_2$O$_3$ and Fe$_3$O$_4$**
  - Shorter wavelengths and low intensity light ideal for avoiding LIBS and blackbody radiation
  - Benchmark Fe$_2$O$_3$ spectrum at 1000 °C achieved
  - Fe$_2$O$_3$/Fe$_3$O$_4$ Raman spectra collected up to 600 °C

- **Publications/Presentations**
Questions?

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