Development of Laser Induced Breakdown Spectroscopy Sensor for Molten Salt Reactor Off-Gas Stream

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MSR Workshop 2021
October 13th, 2021
We’re seeking to enable molten salt reactor (MSR) deployment by developing technology for off-gas analysis

- Quantify fission and activation products in off-gas system
- Monitor off-gas treatment component efficiency
What is laser-induced breakdown spectroscopy (LIBS)?

Laser ablation and optical emission collection

- Laser Power
- Laser Head
- Spectrometer
- Fiber Optic
- Focal lens
- Plasma
Why laser induced breakdown spectroscopy (LIBS)?

Elemental analysis via optical emission spectroscopy of laser induced plasmas

• Benefits:
  - Little to no sample prep
  - Useful for solid, liquid, and gas analysis
  - Typical sensitivities of ppm
  - Quasi-nondestructive (nanograms per shot)
  - Can be completely fiber optic based
Design Challenges

• Producing a surrogate aerosol stream
• Designing a measurement cell
A collision nebulizer was selected to generate aerosol stream for analysis

Aerosol particle sizes range from ~1-10 µm in diameter.
A sheath gas approach was used to contain aerosol stream during measurement
Sheath gas system successfully contained aerosol stream

Sheath gas is turned on and off repeatedly
A complete prototype aerosol measurement system was manufactured.
Aqueous aerosol monitoring system

• The three representative elements selected were Gd, Nd, and Sm
  – All act as neutron poisons in a reactor making their concentrations of interest to operators.
  – Concentrations ranging from 0 to 2000 ppm in liquid reservoir
  – 2000 ppm in reservoir ≈5 ppb in aerosol stream
Regression models were developed using a set of calibration samples

Sample 2 is Gd dominant
Sample 11 is Nd dominant
Sample 13 is Sm dominant
What is PLS regression?

Partial Least Squares Regression (PLS)
1. Matrices X and Y are decomposed into latent structures in an iterative process.
2. The latent structures corresponding to the most variation of Y ($u_i$) is explained by a latent structure in X ($t_i$) which explains it the best.

Note: the goal is to explain the most variance in Y, not necessarily X.
Predicted concentrations of validation samples match ICP-OES measurements
Performing a demonstration to show the measurement system’s capability to provide real-time monitoring

• Stock solutions pumped in/out of reservoir to nebulizer to allow real-time changes in concentrations
Initial concentration predictions leave room for improvement

The RMSE values were calculated to be 249, 108, and 99.8 ppm for Gd, Nd, and Sm, respectively.
A genetic algorithm is an optimization approach based on Darwin’s theory of evolution.

1. **Initialize**
2. **Population**
3. **Evaluation**
4. **Preserve Best Chromosomes**
5. **Crossover**
6. **Mutation**
7. **Terminate**

- $g = 0$
- $g = g + 1$
- $g = g_{max}$
A genetic algorithm was used to refine PLS feature selection.

Start, $g = 1$

Starting Population

Fitness Evaluation
$f_{best,g} = best$ score

$g = g + 1$

Yes, $f_{best,g} > f_{best}$ and $j = 0$

New Population
60% Children
30% New Genes
10% Retained Genes

New Population
90% New Genes
10% Retained Genes

No

Yes, $j_{max} = j_{max} + 10$ and $j = 0$

Yes, $g < g_{max}$?

End

Number of LVs

Gd: 5 → 4
Nd: 6 → 3
Sm: 9 → 3
Genetic algorithm filtered models showed dramatically improved results

The RMSE values were calculated to be 66.5, 89.2, and 75.3 ppm for Gd, Nd, and Sm, respectively.

This corresponds to a 73, 18, and 25% decrease in RMSE value from the previous model predictions.
Gaseous monitoring system

- The four representative elements selected were Xe, Kr, Cs, and Rb
  - Xe and Kr are expected to be large contributors to the off-gas loading
    - 0 to 10 g/h
  - Cs and Rb are the corresponding daughters of these gases
    - 0 to 2000 ppm
Krypton and xenon showed strong spectral responses

Collected LIBS spectrum of sample 7 containing 1.21 and 1.90 mol% of Xe and Kr and 2000 ppm Rb.
A closer look at collected spectra reveal strong gas peaks

Collected LIBS spectrum of a blank sample (sample 5) and sample 14 containing 1.21 and 1.90 mol% of Xe and Kr and 2000 and 1800.9 ppm of Cs and Rb.
Xe and Kr univariate models were developed

Univariate calibration models, dashed lines, comparing (a) 881.94 nm Xe I peak area and (b) 760.15 nm Kr I peak area response to changes to Xe and Kr mass flow rates, respectively.
Analytes in test samples were predicted using constructed models

*signifies a univariate regression model
The Kr concentration was successfully predicted in real-time

Model predictions for the concentration of Kr gas compared to converted flow meter measurements in systems where the gas flow rate is changed
In summary, we have demonstrated a LIBS capability for monitoring aerosols and gases.

- Our sheathed gas measuring system allows effective measurement of the sample stream while protecting optical components
- Multiple elements were simultaneously quantified in the two studies discussed
- A genetic algorithm was used to refine a quantitative model
- Both gases and aerosols were able to be monitored in real-time
Where is this project headed next?

- Future work involves completion of a molten salt aerosol test stand and integrating LIBS sensors with off-gas treatment systems.
Acknowledgments

**MSR Campaign Team**

- **NTD for Technology Development**: Patricia Paviet
- **NTD for MSR Licensing**: Jim Kinsey
- **Licensing Framework**: David Holcomb, Dave Luxat
- **Technology Development**: Kevin Robb, Jordan Massengale
- **Chemistry**: Jake McMurray, Mark Williamson, Toni Karlsson, Nathan Hoyt
- **Tritium**: Paul Humrickhouse
- **Thermophysical Properties**: Melissa Rose, Ryan Gallagher, Dianne Ezell, Marissa Monreal
- **Structural Materials**: Bruce Pint, Jim Keiser
- **Graphite**: Nidia Gallego
- **Advanced Material Development**: Sam Sham
- **Waste forms**: Brian Riley
- **Salt Spill**: Sara Thomas, Bill Ebert
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