Application of Laser Induced Breakdown Spectroscopy to Electrochemical Process Monitoring of Molten Chloride Salts

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Abstract. Techniques for in-situ, near real-time analysis of molten salt chlorides used in electrochemical fuel treatment processes face several challenges including atmospheric isolation, high radiation fields, corrosive environments and high temperatures. Therefore, techniques that can operate in a stand-off manner will have a definitive advantage for implementation in a fuel treatment facility. Laser induced breakdown spectroscopy (LIBS), an elemental analysis technique, is being pursued as a near real-time process monitor of various process streams. LIBS can operate at stand-off distances and has been used in other industries as a process monitoring technique. Argonne National Laboratory, as part of a multi-lab effort, is developing the technology to interface a LIBS spectrometer to an electrorefiner, which separates the actinides from the fission products in an electrochemical processing plant. Currently, all the optical components (focusing and collecting optics, power meter, etc.) are located on top of the electrorefiner above the heated zone. Design parameters include the ability to distinguish and quantify multiple actinide and lanthanide species, and operate near high-temperature zones in high radiation fields. The system requires little-to-no alignment after installation. Finally, a stand-off distance of approximately 0.5 meters (between the optics and the sample) is available to the system. The development and design of this system will be detailed. Results from testing with actinide samples in a glovebox environment containing a small electrorefining system will also be presented.

1. Introduction

Measuring actinide and fission product concentrations in electrochemical refining processes in near real time is a challenging technical goal. If met, it has implications on both process and plant management and may allow for decreased inspection requirements and higher plant throughput [1]. Thus, an electrochemical reprocessing plant can increase productivity and maintain tighter operational control by providing timely process information as part of the facility safeguards envelope.

However, process monitoring, in situ, poses considerable engineering challenges in electrochemical reprocessing plants. The active process streams have temperatures exceeding 500°C and are typically inside insulated devices in an inert environment. Generally, canyon or hot-cell style of construction would be used to shield the highly radiotoxic used fuel from the operations staff as well as maintaining the atmosphere [2]. Laser Induced Breakdown Spectroscopy (LIBS) was chosen as a potential process monitor as systems have been demonstrated to work at standoff distances where the electronic components have been remotely connected via fiber optics. Therefore, a production system could be fabricated to keep all sensitive components out of heated or radiation areas.

LIBS is a diagnostic technique that can perform qualitative elemental analysis via collection and identification of characteristic photon peaks. The response of these elemental emission lines is proportional to concentration, which allows the technique to be quantitative given a suitable calibration. LIBS has been used for quantitative analysis of solid [3], liquid [4], and gaseous [5] samples. The technique shares several operational aspects with atomic emission spectroscopy with the main difference being that LIBS uses a laser, rather than a radiofrequency coil, to create a plasma. In the process of generating the plasma, the laser pulse ablates the surface of the sample creating an ejection plume, which is then excited in the plasma. The excited atoms then relax to their ground states by emitting characteristic photons.

LIBS analysis is essentially non-destructive as only nanograms of material are removed from the sample during the analysis [6]. Generally, detection limits at the part-per-million level are achievable with commercial systems [7], usually by collection of multiple laser pulses [6]. Systems have been
developed that utilize standoff modes [8] and fiber delivery and collection [9]. All of these factors indicate that LIBS could be successfully adapted and integrated into an electrorefining system for process measurements.

2. LIBS system design

In order to be interfaced to a commercial-scale electrorefiner, the plant scale LIBS system must be able to meet several high level requirements. In a functional electrochemical reprocessing plant, the process stream will be isolated from the analyst by several meters, though heavy shielding and without detailed or articulate access to the stream. Therefore, to preserve the integrity and alignment of the optics and increase the operational lifetime of the system, all optics and other sensitive components should remain out of the heated zones. Similarly, the radiation sensitive components (i.e. the laser and spectrometer) must be moved out of the high radiation zone. Light collected from the plasma emissions must be routed via fiber optics. Light transmission to the process stream must then take place via fiber optics or through a system of mirrors and/or goniometers. Initial tests at Argonne indicated that focusing a laser at standoff distances (~400 mm) required a high incident laser power (>70 mJ) to reach irradiance levels sufficient to ignite a LIBS plasma. Large core fiber optic cables would be required to transmit these beams, which will prevent the laser from being focused at long distances. Therefore, the free beam approach has been pursued for the test system.

2.1. Design parameters for LIBS test system

The test LIBS system was constructed using Commercial Off-The-Shelf (COTS) components for the major functions, i.e. laser, spectrometer, detector, etc. The main technical challenge for the process scale system will be coupling COTS items to the electrorefiner (see above). Similarly, the test system must meet a similar set of requirements. The system must ignite a LIBS plasma at standoff distances of 450-500 mm using a free beam path laser. The plasma emissions must be collected with fiber optics and transferred to a spectrometer for analysis. The test system must be classified as a Class I laser system and be interfaced to a radiological glovebox while maintaining atmospheric integrity.

A test system that incorporates this set of design parameters will demonstrate, as a proof of concept, the feasibility of an open beam, standoff system. This system will also allow for bench scale tests of actinide-bearing eutectic salts to identify reliable spectral lines and estimate precision, accuracy and limits of detection.

2.2. Test system engineering

A Quantel-Big Sky laser head (CFR200) was selected for this project. The CRF200 is a pulsed, Q-switched Nd:YAG laser with maximum total power of 200mJ at 1,064nm. A motorized variable attenuator is mounted in the laser head to attenuate laser power between 2% and 100%. After the laser reaches the sample chamber (see below) a 10/90 beam splitter is used to sample the beam with a Coherent EnergyMax pyroelectric power meter.

A Czerny-Turner spectrograph (Andor, Shamrock SR-750-A, 0.03 nm wavelength resolution) was combined with an intensified CCD camera (Andor, iStar DH334T, 1024x1024 pixel chip) with a photocathode sensitive between 120 - 1100 nm for signal collection. The iStar has a built in Digital Delay Generator that controls the data acquisition and serves as the experiment master clock. The spectrometer is calibrated against a NIST traceable mercury vapor lamp.

To accommodate the open beam delivery method, fully enclosed beam tubes were manufactured to maintain the Class I certification. The beam tubes are composed of three primary components: a broadband mirror inside of a light-tight housing connected via a set of nested tube connectors and the sample chamber. The nested tubes allow for flexibility along the axis of the tube while maintaining a modular character. The sample chamber holds the laser focusing optic (500 mm plano-convex lens), with a fine control translation stage, the power meter and a polished silver parabolic collection optic.
The silver mirror maintains a constant focal point over the wavelength range for launch into the collection fiber. The beam tubes and sample chamber are shown in Fig. 1.

3. LIBS testing

3.1. Metallic standards

The first system test performed was an analysis of Inconel crucibles. Inconel has a well-defined chemical composition with several minor components. The number and density of emission lines would be comparable to any complex salt solution containing multiple elements (actinides, fission products, etc.). The Inconel crucible was tested at both room temperature and at a reference temperature of 450° C to ensure there were no thermal effects on the signal (Fig. 2).

The recorded full-width half-max of the Inconel peaks, which is a measure of the performance and resolution of the system, using the finest diffraction grating available, was approximately 0.2 nm. While this value is larger than values found in the literature, under the operating circumstances (long distance open beam propagation, small solid angle collection, etc.) the system performance was deemed acceptable. It should be noted that only minimal system optimization was applied at this point and that resolution and efficiency may increase after optimization.

3.2. Salt tests

Trivalent actinide chlorides (U, Np, Pu), with concentrations of up to 1.5 weight percent, in a eutectic mixture of lithium and potassium chloride were studied next, unfortunately with mixed results. The solid salts were optically opaque, which allowed for easy plasma formation on their surfaces. However, after multiple shots (up to 200), the laser bored a hole through the salt cake resulting in a loss of signal. During the first several dozen shots, significant contributions to the spectra corresponding to lithium and potassium could be seen (Fig. 3). No significant lines were assigned to any of the actinides during these tests.

FIG. 1. Left - External view of LIBS test system interfaced to glovebox. 1) Spectrometer and camera, 2) laser corner and beam tube, 3) glovebox feed through. Center - Cutaway rendering showing the operation concept of the sample chamber. Right - Finished sample chamber.
For the molten salt tests, the laser repetition rate was reduced to ~1 Hz. As each shot would create a small shock wave, this delay would allow the liquid salt surface to become quiescent prior to the next laser pulse. Concurrent to this, it was hypothesized that an incorrectly aligned laser would eject significant amounts of sample due to splashing. Therefore, clean eutectic samples were analyzed first.

It was observed that for thin layer samples, the signal intensity was inversely proportional to the thickness of the salt layer. This result indicated that the plasma was not forming at the surface of the sample, but was forming at the surface of the crucible (Fig. 4). When the covering salt layer was thin enough, standard LiCl/KCl lines were observed. Progressively thicker layers showed a decrease in the signal intensity.

Additional experiments are currently underway to re-focus the system to ignite a plasma at the molten salt surface. Once the system has been re-focused, titrations of all three actinide salts will be performed. These tests will determine the appropriate lines to monitor, their linearity and the detection limits of those lines.

4. Adaptation to plant scale

4.1. Proof of principle demonstration

The successful tests performed to date indicate that an open beam system would be able to be adapted for use in a commercial plant. All of the individual components worked as intended as part of a cohesive system. Successful tests of all scenarios, with the exception of molten salt samples (due to focus issues, see above), have been performed. The tests with the Inconel crucible show the system performs as expected with the appropriate resolution and sensitivity. The molten salt data will be collected in the near future to complete the testing and provide additional data on LIBS characteristics of actinide chlorides.
FIG. 3 - LIBS spectra of ~0.5 w/w% plutonium chloride in lithium potassium chloride eutectic at 20 C. All of the peaks in the spectrum have been identified as either Li or K. Inset: Salt cake with a hole produced by successive laser shots (indicated with arrow).

FIG. 4. Reduction in the 609 nm lithium peak based on salt level. The blue line (top) is signal generated with ~2 g of salt, the red (bottom) ~4 grams of salt. This reduction in signal is consistent with subsurface plasma generation.

4.2. COTS solutions

In order to adapt this system to an electrorefiner, more robust engineering solutions must be used to introduce the laser beam into the electrorefiner. In addition, the sample chamber must be redesigned to be more compact and rugged as well as being easy to install, service and replace. Commercially, advanced goniometer systems exist as COTS components, mainly for transmitting visible lasers as part of industrial robotic automation systems. These armatures could easily be adapted for IR lasers (such as a Nd:YAG) and used to bring the beam from a hot-cell penetration to the electrorefiner. The
sample chamber would have to undergo a re-design to minimize the footprint and allow easy coupling to the electrorefiner and the laser delivery system, regardless of type. A majority of the parts could indeed be COTS, though a custom housing would likely be required.

4.3. Challenges

As shown in our tests, the focus of the LIBS system is critical. Serious consideration must be given to reproducing the lens-to-sample distance for every data collection event. If the process tank level is continually changing, then there will be a continuum of spectral intensities available for identical samples, assuming a surface plasma is generated at all. Second, the ability to focus and align the system with minimal user input is a critical challenge that must be overcome to make this a practical technique. This point is further emphasized as the optical components in the sample chamber, especially the fiber optic cable, will have a limited lifetime in the processing environment due to radiolytic darkening. Therefore, as the components move toward a disposable model, ease of installation and alignment must be paramount.

5. Conclusions

A LIBS system was designed, constructed and evaluated for the potential to perform quantitative, real-time concentration measurements of actinides under molten salt reprocessing conditions. The ability to ignite a plasma and collect emissions at standoff distances using a free beam laser was demonstrated using an Inconel crucible. The ability to interface the system with an inert radiological glovebox was also demonstrated. The information gained from the design and demonstration of this system will be used to provide design specifications for a plant scale system. However, additional work is required to continue development of this technology for incorporation into a facility. Additional testing to study the fundamental LIBS spectra of the actinides is under way including identification of spectral lines, proportionality with respect to concentration, limits of detection and potential interferences. This data is required in order to provide a suitable calibration data set for quantitative data collection. An examination of the completed and planned research do not indicate the presence any substantive technological hurdles to implementing a LIBS-based accountancy system.

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REFERENCES


