Testing of a Microfluidic Sampling System for Pyrochemistry MC&A

Fuel Cycle Research & Development

Prepared for
U.S. Department of Energy
Fuel Cycle Options Campaign

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September 30, 2014

ANL-MPACT-093014

September 30, 2014

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Summary

This report describes recent progress in the development of high-temperature microfluidic systems for the sampling and analysis of electrochemical process salt. Microfluidic techniques enable production of micro-samples of molten or frozen salt for analysis by at-line and off-line sensors and detectors. The systems are under development for implementation in an electrochemical used fuel treatment facility as part of the material balance and control system. Electroanalytical and spectroscopic techniques are attractive candidates for improvement via high-throughput micro-sampling and analysis, which may reduce random statistical error associated with sampling inhomogeneity.

Two approaches to microfluidic droplet generation are being investigated. The first approach is based on microchannel droplet flows and on-chip droplet generation at a flow junction. The first generation microchip system used liquid heat transfer fluids as a carrier phase in molten salt droplet formation. The performance of these chips was inconsistent at process temperatures due to instability of the heat transfer fluid. To overcome this limitation, a second generation microchip was developed that uses argon gas as a carrier phase. The new chip will be evaluated in FY-15 to determine the absolute and relative phase flow rates required to achieve stable droplet flow.

The main project focus for FY-14 was on the development of a more robust and lower cost alternative to on-chip molten salt droplet generation. A new system based on pneumatic droplet generation was designed and fabricated. Preliminary testing of this pneumatic droplet generator with was carried out with water and molten salt. The results indicate that the pneumatic droplet generator would be ideal for spotting microanalytical samples onto a substrate for both at-line and off-line analysis. The pneumatic droplet generator may also have applications in at-line LIBS analysis or in the production of uniform frozen salt beads for off-line analysis. Preliminary feasibility testing for these droplet generator applications will be carried out in FY-15. Further characterization of pneumatic molten salt droplet generation using a high speed imaging system is also planned. Finally, methods of integrating the droplet generator with process equipment will continue to be explored with the long term goal of developing the new apparatus into a fully automated sampling system to replace the manual sampling protocol currently in use.

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Separation Matrix Generation for Reprocessing Used Nuclear Fuel

1. Introduction

Tracking the composition of salt as it moves through an electrochemical reprocessing facility is a difficult task because electrochemical material processing is done continuously at elevated temperatures while transfers involve discrete batches of used fuel or solids with adhered salts. Salt is recycled at several points within the process, making it difficult to relate changes in composition to specific processing operations. Particularly over long time steps, small differences or inhomogeneities may result in quantifiable changes in product output compositions. It is desirable to obtain an accurate and timely measure of the chemical and isotopic composition of the salt within the electrorefiner and through other operations in the facility to fully close the material mass balance.

The goal of this project is to develop a sampling system that will enable the accurate determination of the chemical and isotopic composition of the molten salt in an electrorefiner or adhering to cathode products or cladding wastes within a pyroprocessing facility. The system will ideally allow the combination of the best aspects of destructive analysis (high sensitivity, low measurement uncertainty, and high quantitative resolution) with the best aspect of non-destructive analysis (low sample loss, low processing impact, and rapid turnaround).

Practical safeguard difficulties associated with pyroprocessing include the absence of an input accountancy tank, high temperature processing, and batch-wise fuel addition and product harvesting coupled with synchronous dissolution and cathode deposition within the electrorefiner. In addition, salt is collected and recycled at several points within the cathode processing cycle, making it challenging to fully close the mass balance after the initial batch of fuel is dissolved. In addition, salt collected from processed cathodes may differ in composition from the balance of salt in the electrorefiner. Finally, inhomogeneity of salt/metal composition in the electrorefiner, while small, is non-zero.

2. Approach

Electroanalytical and spectroscopic techniques are attractive candidates for improvement through high-throughput sampling. Even the best analytical techniques can have issues with interfering signals, and variability arising from sample inhomogeneity must be addressed. Collection and measurement of a large number of samples, as is possible with micro-samples, can reduce the statistical error associated with more traditional sample collection methods. Sample purification will also improve sensor performance, and microfluidic systems are very adaptable to common purification techniques (e.g. solvent extraction[1]),

which can be automated at the micro-scale thus reducing the need for direct manipulation. Additionally, the small sample scale enables rapid sample cooling for contact with cooled detectors.

To meet the project's goals, and overcome some of the identified difficulties associated with pyroprocessing safeguards, we are developing high throughput microanalytical sampling systems that can be coupled to traditional, room-temperature analytical equipment. It may also be feasible to deploy remote optical microanalytical systems that can function at a distance from the sample. Microfluidic systems are micromachined fluidic networks operating at low Reynolds numbers. Low Reynolds numbers allow highly repeatable, deterministic flow.

We have previously demonstrated microfluidic systems capable of performing solvent extraction unit operations on lanthanides and actinides.[1] The microchip based-sampling system under development for pyroprocessing operations is an extension of this concept. Figures 1 and 2 show the microchip and droplet configurations for these aqueous microfluidic systems.

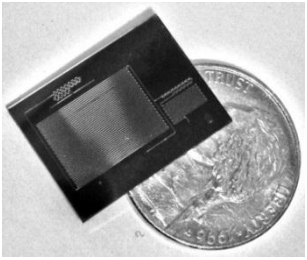


Figure 1 – An example of a microfluidic chip developed at ANL for aqueous solvent extraction.

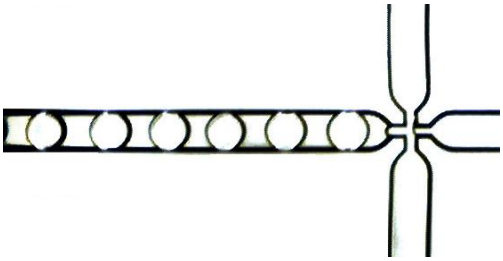


Figure 2 – An aqueous/organic emulsion generated in a microfluidic solvent extraction chip.

The microfluidic salt-sampling system may be deployed in a number of positions within the electrochemical reprocessing facility as shown in Figure 3. Microfluidic sampling systems may be deployed for analysis of process salt elemental composition in a single unit vessel or may be used to interface several process units with a single analytical instrument (Figure 4). Whether samples are collected from all of the locations noted in Figure 3 or from a subset, microfluidic-scale sampling enables interrogation of a large number of streams with relatively minimal impact on processing. One of the advantages of the droplet-based microfluidic approach is that the individual droplets are on the order of tens of nanoliters. Consequently, a large statistically significant number of discrete and consistent samples can be collected while the total quantity of material collected is on the order of milliliters.

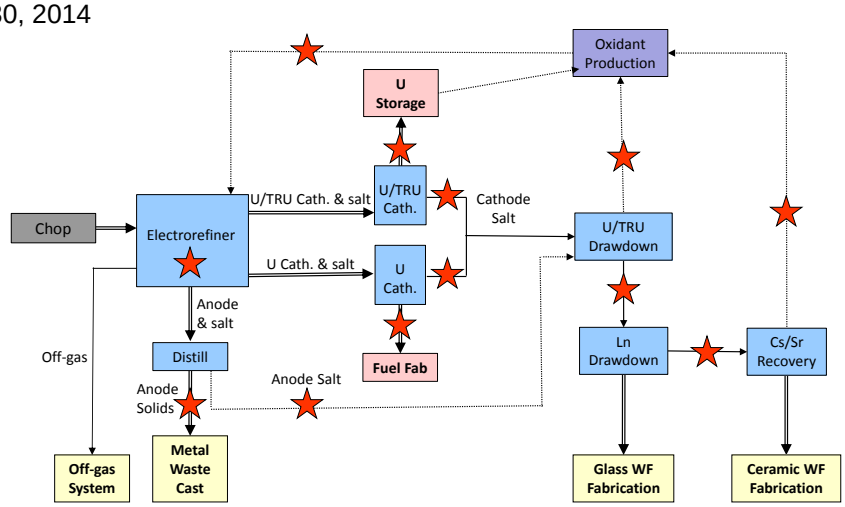


Figure 3 – A schematic of the electrochemical processing flow diagram with potential locations (stars) for salt sampling system to maintain a compositional mass balance.

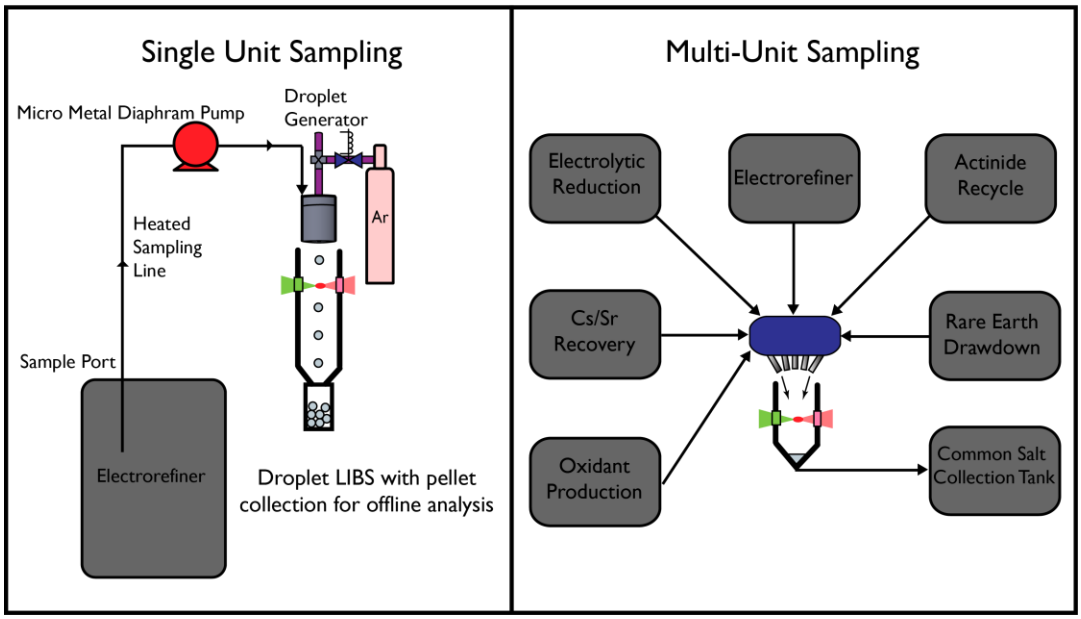


Figure 4 – Single unit and multi-unit microfluidic sampling - droplet laser induced spectroscopy examples.

3. Methods

High Temperature Fluorescent Imaging

Early FY-14 focused on improving the high temperature droplet chip imaging system and on screening different heat transfer fluids for use as a carrier phase in microchip molten salt droplet generation. To improve imaging and facilitate droplet microchip characterization

via automated image analysis, the high-temperature imaging system installed in FY-13 was modified in FY-14 to enable fluorescent imaging (Figure 5a). The modifications included a 150W metal halide light source with a 375 nm low pass filter and a removable emission filter on the long distance lens. The fluorescent imaging system is able to image the fluorescent fission products cesium and europium dissolved in molten salt samples. Examples of gas/molten salt flow imaged in brightfield and fluorescent mode are shown in Figure 5b and Figure 5c, respectively.

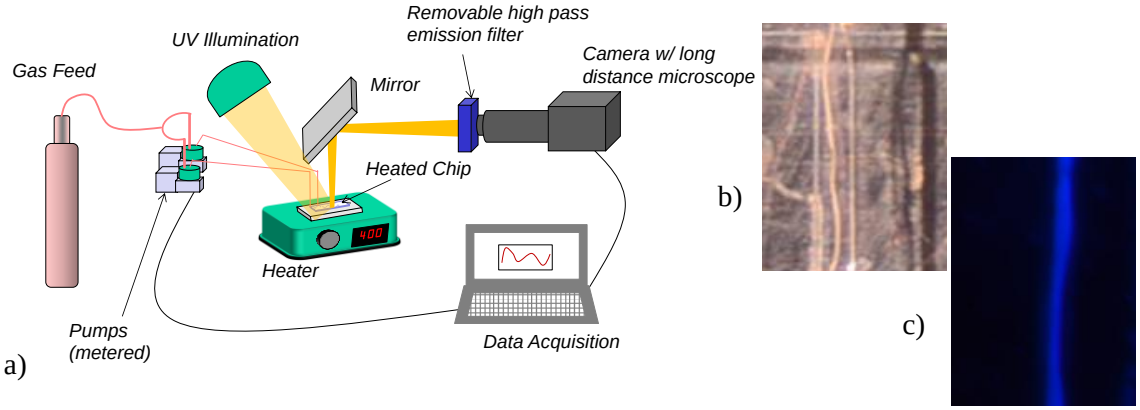
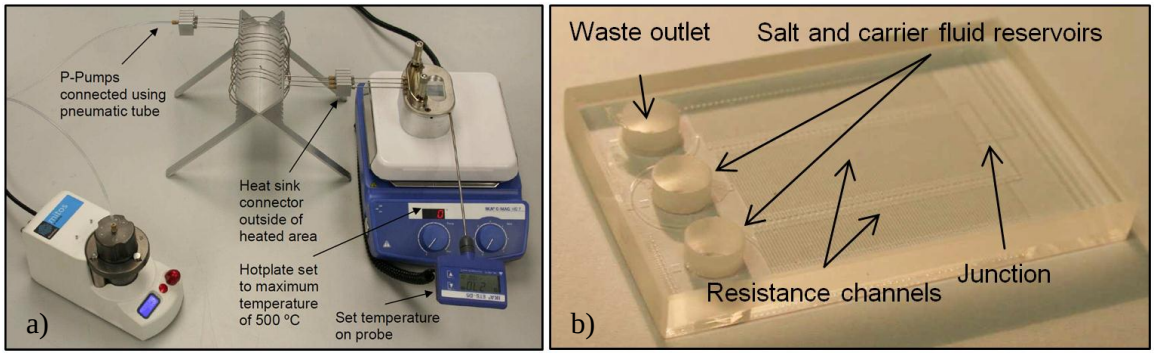


Figure 5 – (a) Fluorescent imaging set-up (b) Gas/LiI-CsI flow imaged in brightfield mode (c) Gas/Li-CsI flow imaged in fluorescent mode.

Constant pressure nitrogen pumps, a heat exchanger, a hotplate and a chip holder with a compression chuck interface comprise the molten salt microchip set-up pictured in Figure 6a. The first generation droplet chip is pictured in Figure 6b. This chip has reservoirs for salt and liquid carrier phases and long resistance channels to balance fluidic resistance so that droplets of molten salt form in the liquid carrier phase at a cross-junction.



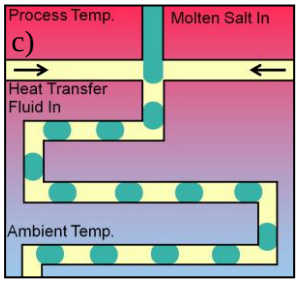


Figure 6 - (a) Microchip test set-up (b) Original droplet microchip (c) Molten salt droplet generation in liquid heat transfer fluid at a cross-junction.

Droplet Microchip

None of the heat transfer fluids under consideration for use as a liquid carrier phase were deemed robust enough for operation at process temperatures. The tested fluids tended to vaporize in the channel, particularly following the pressure drop at the flow junction. Due to this lack of temperature stability, three alternatives to the original droplet-chip design have been proposed: (1) a molten metal carrier phase, (2) an argon gas carrier phase, and (3) diluting with a lower melting salt to lower the melting point of the process salt. The argon gas carrier phase is being examined first because argon is stable at any temperature encountered in electrochemical processing and it does not introduce additional, potentially adverse, components to the process. The droplet chip was redesigned to accommodate a gas carrier phase and to address chip clogging issues that were experienced in the testing of the first generation droplet chip (Figure 7). To accommodate the gas carrier phase the droplet chip was redesigned to have a long and narrow high-resistance channel at the gas inlet to prevent back flow of the salt into the gas channel. Also, the new junction was optimized for gas liquid droplet generation. This included a transition from a cross junction to a T-junction. To reduce clogging and make the chip easier to clean out, the particle filter on the salt inlet was redesigned to be a single layer and the salt channel was widened. The new microchip is being fabricated by Dolomite Microfluidics in the UK. The original estimated lead time of 10 weeks has been extended to 15 weeks due to a mistake by the vendor.

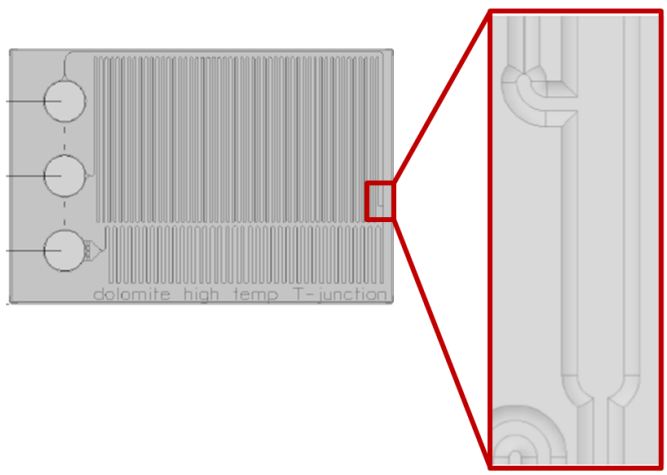


Figure 7 – New Gas-Liquid Droplet Chip with expanded view of T-junction.

Pneumatic Droplet Generator

Due to the problems encountered during testing of the first generation microchip (clogging, limited carrier phase options) and the long lead times and high cost ($20k per order of 4 chips)of quartz microchip fabrication, an alternative approach for generating large numbers of uniform micro-volume molten salt droplets was devised. This approach uses a high temperature pneumatic droplet generator, which was originally developed as a molten solder droplet dispensing technology by Ford Motor Company in the late 90's for the manufacture of printed circuit boards.[2] The specific molten salt droplet generator design is

based on molten metal dispenser designs by the Chandra group at the University of Toronto.[3, 4, 5] The prototype pneumatic molten salt droplet generator (Figure 8a) has a salt reservoir chamber, which is heated using a 275 W band heater. This chamber is connected to a pressurized gas supply through a normally closed solenoid valve (72P9DGM-N 24/DC, Peter Paul Electronics). When a pressure pulse is applied to the top of the reservoir chamber by opening the solenoid valve for a few milliseconds, a droplet is ejected through a small orifice on the bottom of the chamber. The gas from the pressure pulse escapes through a vent so that, ideally, only one droplet produced per pressure pulse. The prototype chamber takes a threaded orifice insert, so that the orifice size can easily be changed between experiments by swapping out orifice fittings (Figure 8b). While this design feature is efficient for testing purposes, the threads increase the potential for leaking and the high temperature thread sealant (Deacon 8875-Thin, Deacon Industries) required is a potential source of contamination. Therefore, once an optimal orifice diameter is chosen, the orifice mount will be redesigned as a compression fitting or, alternatively, the orifice will be directly laser machined into the chamber. This will make the unit more robust and suitable for process implementation. Because the pneumatic droplet generator is composed of commercially available stainless steel fittings and a simple stainless steel chamber and cap which are easily fabricated in-house (Figure 8c), the cost savings are substantial relative to the outsourced fabrication of the droplet chip. An additional anticipated benefit of this droplet generator compared to the droplet chip is a reduction or elimination of clogging problems due to the reduction of the microfluidic network to a single orifice. The droplet generator orifice is up to an order of magnitude wider than the microchannels in the first generation droplet chip design. This design feature will be particularly important for avoiding clogs when processing actual process salts, as these are expected to have some entrained solids.

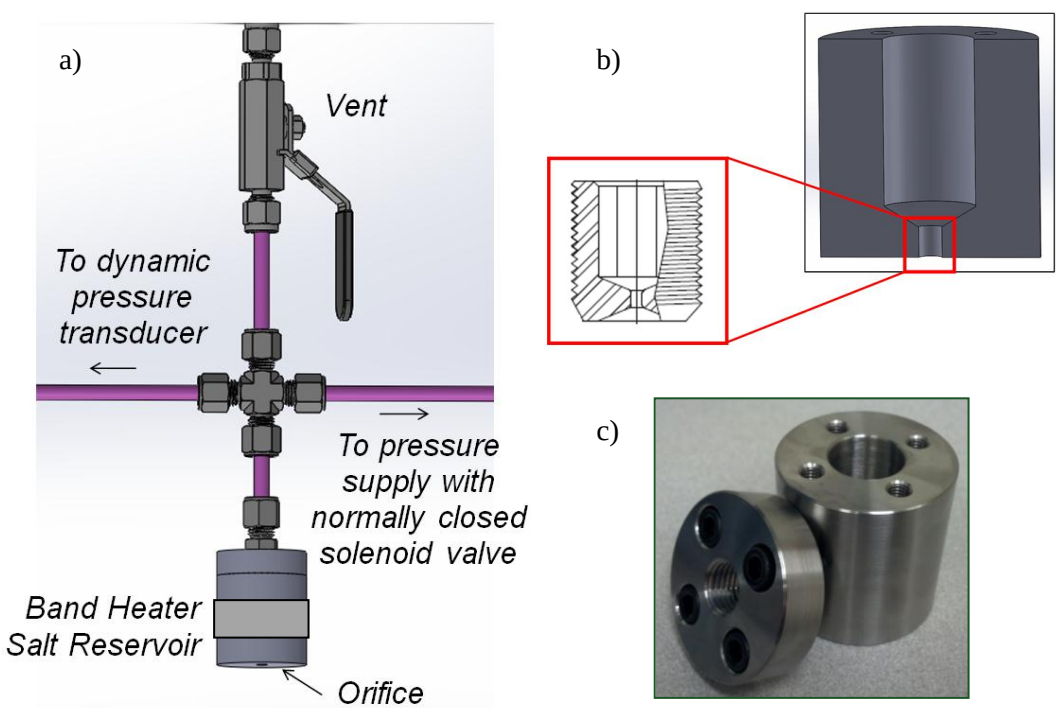


Figure 8 – Pneumatic Droplet Generator (a) Assembly (b) Cut-out view of chamber with threaded orifice insert (c) Chamber with cap.

In the pneumatic droplet generator, the chamber and exit vent act as a Helmholtz resonator. There is an initial pressure spike following the opening of the solenoid, and then the pressure oscillates as the gas exits through the vent (Figure 9). The ability to monitor droplet generation remotely and non-visually is important for this application, as the droplet generator will be operated remotely with limited access. Remote monitoring of droplet generation can be achieved by tracking the response of the dynamic pressure transducer, which is mounted opposite the pressure supply. The negative pressure at the first minimum in this oscillation acts to withdraw the liquid from the orifice, thus preventing the ejection of multiple droplets per pressure pulse. If the negative pressure is not sufficient, leaking is likely to occur. The initial pressure peak is also monitored during experiments to identify anomalies. For example, a blocked orifice due to incompletely melted salts will result in an increase in the height and width of the peak. If the chamber is empty, there is a shift in the peak (air, Figure 9).

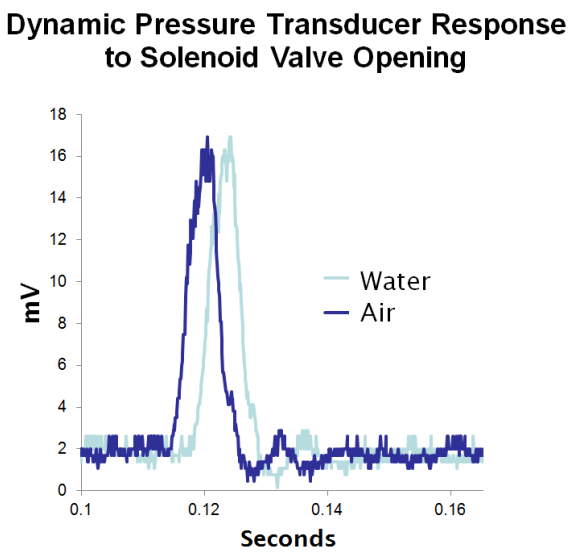


Figure 9 – Dynamic pressure transducer response to pressure pulse.

The current standard method for obtaining a molten salt sample involves inserting a threaded rod into the bulk salt. The salt will freeze on the rod as it is removed (Figure 10), then the rod is tapped against a surface to dislodge the salt. Obviously, a more accurate and automated technique will be required for an industrial scale pyroprocess. The pneumatic droplet generator is a good candidate to replace this manual protocol. If the molten salt droplets are allowed to freeze, they can be collected in a convenient pelletized and pourable form. The droplet generator can produce droplets of a specific particle size on demand which would allow exact sample metering, thus reducing waste relative to manual sampling approaches.

Figure 10 – Manual molten salt sampling.

4. Testing

High Temperature Fluorescent Imaging

Feasibility testing of the fluorescent imaging system was carried out. Two potential problems with molten salt fluorescent imaging are (1) the decreasing fluorescent intensity of fission products with increasing temperature and (2) the loss of intensity due to the long stand-off distance required for high temperature microscopy. It was determined that the fluorescent intensity of Eu decreases about 6.5% per 100°C increase in salt temperature, indicating that this phenomena would not be prohibitive to molten salt fluorescent imaging. Additional tests were carried out to determine if the fluorescent intensity was sufficient at the 40 mm stand-off distance used in the droplet chip experiments. It was determined that it is possible to fluorescently image both stationary and flowing LiI-CsI eutectic (used as a lower melting point surrogate for LiCl-KCl) with the system. However, in order to achieve the clearest images that are amenable to automated image analysis, the flow should be temporarily paused to allow longer exposure times.

Droplet Chip

After ruling out all candidate commercial heat transfer fluids for use as the carrier phase in the molten salt droplet chip (due to thermal instability above 350°C), the first generation chip was tested with an argon gas carrier phase. LiI-CsI (66 mol% lithium iodide and 34 mol% cesium iodide eutectic) salt in powder form was added to the microchip feed reservoir prior to placement in the holder assembly. The chip was carefully placed in the holder and sealed with a graphite gasket. The hot plate was heated to approximately 450°C to ensure a chip temperature above that of the melting point of the salt. Once the chip was at temperature and the salts had melted, pressure was applied to the salt inlet reservoir and to the second (empty) inlet reservoir. The resulting two phase flow regimes generated at the cross junction were imaged using the long distance fluorescent imaging system. Figure 11 shows three different phase configurations generated in this system. Systematic investigations with this chip were not completed due to chip clogging, potentially caused by salt back-flow into the inlet channels. The second generation droplet chip was designed with the goal of overcoming this clogging issue. Delivery of the new droplet chips is expected in early October 2014.

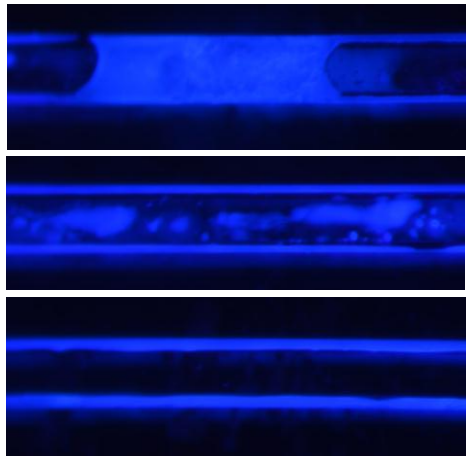


Figure 11 – Two phase flow regimes in the molten salt Droplet Chip. From top to bottom: slug flow, bubbly flow, annular flow.

Pneumatic Droplet Generator

Preliminary studies were conducted with the pnuematic droplet generator. The first studies used water, which is a good room-temperature analog for the molten salt (Table 1), and molten LiCl-KCl eutectic at 400°C. In both the water and molten salt trials, the average dispensed volume per pulse was determined by counting the number of pulses required to empty a known initial reservoir loading volume. In the water trials, it was found that there was not a statistically significant difference between the average dispensed volume per pressure pulse for a 3.0 mL initial loading volume versus a 1.5 or 0.5 mL loading volume. This indicates that the hydrostatic head does not have a large impact on dispensed volume, and therefore it is predicted that only basic control of the liquid level in the reservior chamber will be required to maintain consistent dispensed volumes. However, in the molten salt trials, reservior loading volumes greater than 2 mL resulted in poor performance and orifice blockage. The exact cause of the problem is unkown, but it could be caused by poor temperature control or incomplete melting of the salt. Due to this issue, the molten salt trials were carried out with initial loading volumes of 0.625 mL (1 g) of LiCl-KCl eutectic.

Table 1: Comparison of properties of molten LiCl-KCl eutectic and water[6]

Property	Water	Molten LiCl-KCl
Viscosity (cP)	1.00	2.10
Surface Tension (dyne/cm)	102	126.3
Density (g/cm^3)	1.0	1.62

In the molten salt trials, LiCl-KCl eutectic beads were poured into the reservior chamber before attaching the cap. The assembly was then heated to 400°C with a fluctuation range of ±15°C. Mineral wool pipe insulation (1.5” thickness) was used on the chamber to reduce heat loss and improve temperature control. Water droplets were collected on a glass slide, while molten salt droplets were collected either by spotting onto a metal surface or by plunging them into a heat transfer fluid. The operating parameters that were investigated in these preliminary studies are listed in Table 2.

Table 2: Experimental parameters for water and molten salt droplet generation

Parameter	Range Investigated	Working Range: Water	Working Range: Salt
Orifice material	Stainless steel, Sapphire	Sapphire	Sapphire
Supply pressure	5-50 psi	8 -15 psi	15 - 50 psi
Valve open time	11-18 ms	11-15 ms	11-15 ms
Orifice diameter	0.004”- 0.024”	0.006” - 0.018”	*0.014” and 0.016”
Initial fluid volume	≤ 6.8 mL	**≤ 6.8 mL	≤ 2.0 mL

*No other orifice diameters investigated. **Depends on orifice diameter and material.

Two different orifice types were investigated. One type was a threaded piece of stainless steel with the orifice laser machined into it (EIS-TE-190, EIS Inserts). The other was a small sapphire orifice that was swagged into a threaded stainless steel fitting (RB 82134 SS, Bird Precision). These orifice fittings are inexpensive at $5 each for the steel fittings and $40 each for the sapphire fittings. Leak testing results showed that the stainless steel orifices failed at lower reservior loading volumes and also had a higher frequency of leaking after a pressure pulse than the sapphire orifices. The better performance is due to the nonwetting properties (for both water and molten salt) of the sapphire material. For this reason, sapphire orifices were used in the majority of experiments. It should be noted that there may be a chemical compatability issue in the final aplication due to uranium reacting with the sapphire material. Alternative orifice materials being considered for the final application are cubic zirconia and glassy cabon. Orfices made from these materials are not commercially available. Both of these materials can be laser machined, however, so custom orifice fabrication should be possible. Several other materials have been used in molten salt applications where corrosion is an issue including hafnium nitride and berilium, but cost and/or ease of machinability may be issues for these orifice materials.

Figure 12 is a plot of peak pressure transducer response for a range of solenoid valve opening times and 2 different supply pressures. The 10 psi supply pressure gave consistent low peak response results across a span of solenoid valve opening times. Higher peak responses, such as those for the 20 psi pressure supply, correlated with the undesirable generation of multiple droplets. Overall, the shorter valve opening times gave the best results, so the system may benefit from a solenoid valve with a faster response time.

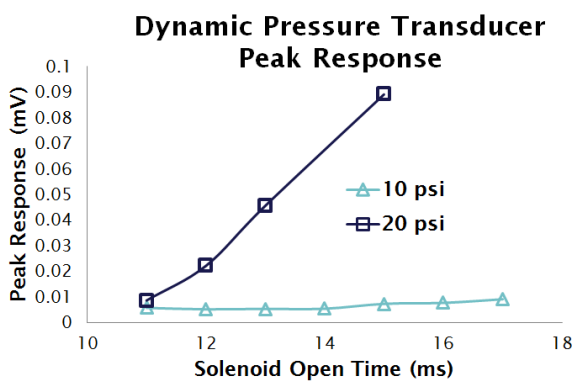


Figure 12 – Peak dynamic pressure transducer response.

A plot of average dispensed volume for 7 different orifice diameters is shown in Figure 13. The average dispensed volume was found to be very consistent across trials (n = 3, error bars = standard deviation). This indicates that the droplet generator would be good for spotting microanalytical samples onto a substrate (Figure 14 a).

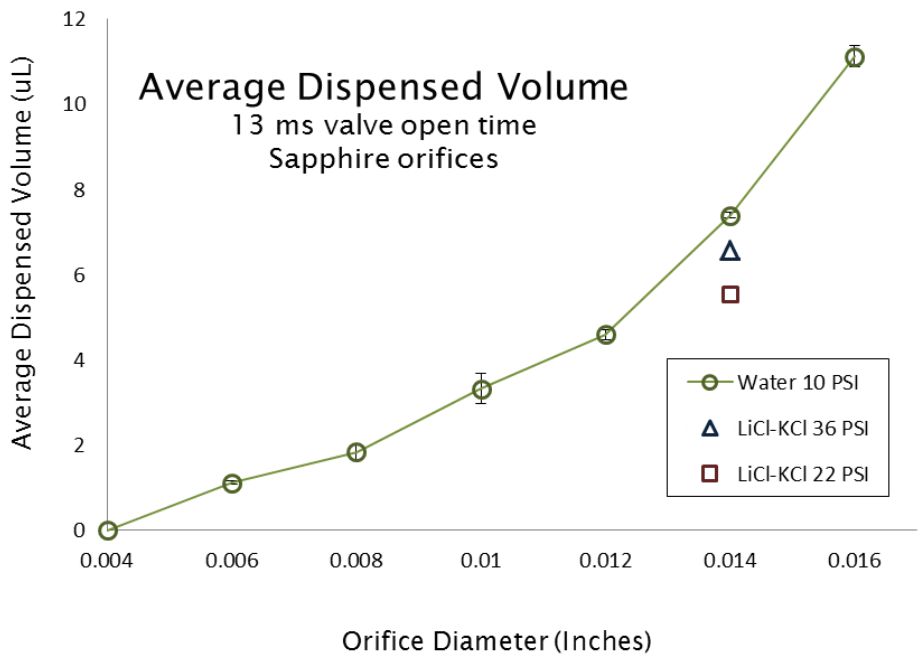


Figure 13 – Average dispensed water or molten salt volume per pressure pulse.

To analyze individual droplets, the ejected molten LiCl-KCl was quenched in commercial heat transfer fluid. Different heat transfer fluids were tested and it was found that the heat transfer fluid with the lowest surface tension (Duratherm S) was able to capture nearly spherical frozen droplets (Figure 14b). Uniform droplets for a given set of parameters were expected based on the results of the spotting studies, however, a size distribution was observed for droplets captured in the heat transfer fluid (Figure 14b). Based on the literature for molten metal droplet generation[3], it is believed that this is most likely caused by a consitently dispensed fluid volume shearing into two or more droplets as it exits the orifice. A newly installed high speed camera will allow a more thorough characterization of molten salt droplet generation in this system.

a)

b)

Figure 14 – (a) Salt droplet spotted onto steel pan. (b)Frozen salt droplets quenched in heat transfer fluid.

5. Future Directions

High speed imaging for pneumatic droplet generator characterization

The first key goal for the next fiscal year is to identify the operating parameters that result in single homogeneous droplets being produced from the pneumatic droplet generator. This will be accomplished by imaging each droplet as it is being generated using a new high speed camera (MotionXtra NX4-S1, Quantum Technologies) in combination with the existing long distance microscopy lens. Simple automated image analysis will be used for high throughput analysis of droplet production. This new imaging system will significantly accelerate the characterization of droplet generation in the pneumatic droplet generator by facilitating the screening of multiple parameters per run and by giving detailed insight into droplet generation. Droplet generation in the new gas-liquid droplet chip will also be investigated using both brightfield and fluorescent long distance microscopy.

Microfluidic sampling with spectroscopic analysis - microanalytical sample spotting

The second goal (and level 2 milestone) for the next fiscal year is to demonstrate microfluidic sampling with spectroscopic data. There are two approaches planned to accomplish this goal. The first approach is to use the pneumatic droplet generator to spot microanalytical samples onto a substrate (Figure 15). The envisioned final application would involve spotting samples onto a tape or laminate roll, followed by running the microanalytical samples through a detector bank with a variety of detectors. Roll-to-roll microsample processing has been used in pharmaceutical research, and it has great potential to facilitate high throughput process-salt sample analysis. In FY-15 different commercially available tape and laminate materials will be screened for this application. Material properties to be examined include surface geometry and structure for droplet containment, heat compatibility, and suitability as a substrate for different spectroscopic techniques. The size and quantity of droplets required for various spectroscopies will also be investigated.

Looking longer term, there are several different technologies available to seal the samples into the tape to facilitate removal of the samples from the inert environment to an on-site analytical lab or to an off-site regulatory lab. Well-developed technologies are available from the biotechnology industry for polymer and foil seals. These may be sufficient for on-site material transfers, although a custom engineered laminate material may be required to meet all the needs of the application, including temperature stability. For long term storage or off-site shipping of microanalytical samples, flexible glass tape with a laser sealed glass frit seal might be appropriate.

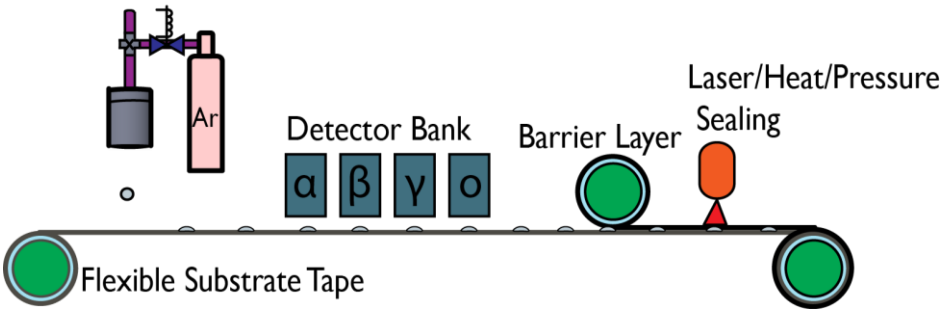


Figure 15 – Droplet generator for microanalytical sample spotting onto flexible substrate tape.

Microfluidic sampling with spectroscopic analysis - droplet LIBS

The second approach for demonstrating microfluidic sampling with spectroscopic analysis is related to the use of the droplet generator for droplet laser induced breakdown spectroscopy (LIBS). Some researchers have turned to inkjet printheads to generate droplet samples to interrogate via LIBS. This droplet LIBS is reported to avoid the shot-to-shot variation due to shock waves in a bulk liquid sample and to avoid splashing and bubble formation, which can cause quenching and shorter plasma lifetimes.[7,8,9] The pneumatic droplet generator could be used to adapt these droplet LIBS systems for use with high temperature molten salts (Figure 16). To begin testing the feasibility of this option, frozen salt droplets of varying sizes and elemental compositions will be generated on the pneumatic droplet generator and will be interrogated off-line using the LIBS apparatus at Argonne.

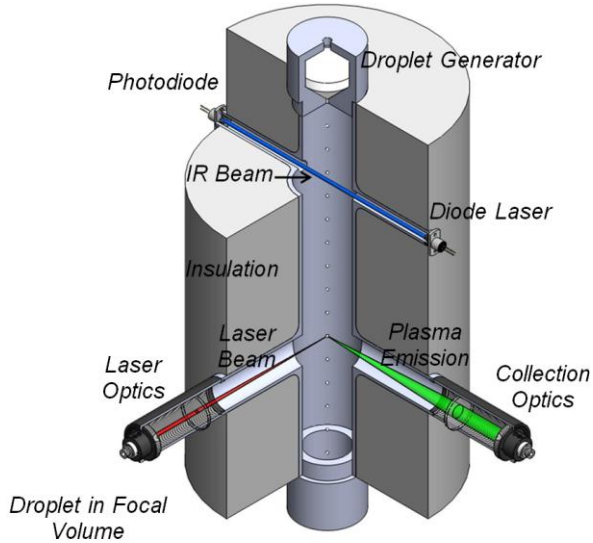


Figure 16 – Droplet Laser Induced Breakdown Spectroscopy – potential application for pneumatic droplet generator.

Integration of droplet generator with process equipment

The integration of the droplet generator with process equipment is not a trivial task considering that, currently, there is no technology available for pumping the small amounts molten salt required for this type of sampling. One potential solution is the development of a custom high-temperature solenoid operated microfluidic metal diaphragm pump. TCS Micropumps Ltd. (UK) is a world leader in micropump development, and has the design expertise to develop these pumps. They estimated a development cost of $33-50k and a production cost of $6k per order of 10 pumps. This type of pump would provide excellent flow control to feed molten salts from process vessels (such as the electrorefiner) to the droplet generator via heated sampling lines, or in any application requiring precise molten salt metering. A custom bellows or pneumatic system may also be suitable for preliminary field testing of the droplet generator.

6. Conclusion

Microfluidic techniques enable production of micro-samples of molten salt for analysis by at-line and off-line sensors and detectors for implementation in an electrochemical used fuel treatment facility as part of the material balance and control system. Microfluidics may reduce random statistical error associated with sampling inhomogeneity because a large number of uniform sub-microliter droplets may be generated and analyzed. Two approaches that apply microfluidic droplet techniques to sampling are being investigated based on (1) microchannel droplet flows and (2) pneumatic droplet generation.

The first generation microchip system used liquid commercial heat transfer fluids as a carrier phase in molten salt droplet formation. This system was able to form various two-phase flow regimes, including the desired droplet flow with lower melting point surrogates for pyroprocess salts. However, its performance was inconsistent at process temperatures due to instability of the heat transfer fluid. A second generation microchip using argon gas as the carrier phase has been created. This chip is expected to perform better at process

temperatures and will be tested in FY-15 to determine the absolute and relative phase flow rates required to achieve stable slug flow.

A high-temperature pneumatic droplet generator is also being developed, as a more robust and lower cost alternative to on-chip droplet generation. Preliminary testing of this pneumatic droplet generator with water and molten salt was carried out. The results indicate that the pneumatic droplet generator would be ideal for spotting microanalytical samples onto a substrate for both at-line and off-line analysis. The pneumatic droplet generator may also be suitable for use in a droplet LIBS system. Feasibility testing for both of these droplet generator applications will be carried out in FY-15. Further characterization of pneumatic molten salt droplet generation using a high speed imaging system is also planned. Finally, methods of integrating the pneumatic droplet generator with process equipment will continue to be explored with the goal of developing this new apparatus into a fully automated sampling system to replace the manual sampling protocol currently in use.

7. References

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