INL/CON-23-75403-Revision-0

Molten Salt Sampling Techniques and Analytical Approaches

November 2023

Changing the World's Energy Future

Janine N Lambert, Ammon N Williams, Toni Y Karlsson, Robert O Hoover, Jeff Sanders, Ken C Marsden, James A King

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Idaho National Laboratory
Idaho Falls, Idaho 83415

http://www.inl.gov

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Presented by Janine Lambert

Molten Salt Sampling Techniques and Analytical Approaches

Joint Project with MPACT & MRWFD in collaboration with INL & ANL

Introduction

- **Scope:** The Material Protection, Accounting and Control Technologies (MPACT) and the Material Recovery and Waste Form Development (MRWFD) campaigns have agreed to a joint activity to document the state of science for molten salt sampling and identify next steps with respect to addressing known shortcomings for both process control and Nuclear Material Accounting and Control (NMAC) purposes
- **Objectives:**
  - Document the current status of molten salt sampling techniques, results, & issues
  - Identify next steps to address deficiencies for process control and NMAC purposes

Investigated Molten Salt Sampling Techniques

- Skim sampling – rarely used
- Rod/dip sampling – currently used
- Dip sampling with a dip cup tool or Pipet –rarely used
- Suction Fine collector – no longer used
- Filtered sampling tubes – currently used in suction version
- Valve Core sampling – currently used in updated version
- Multi Level Sampler (MLS) – currently used

Skimming Technique (Skimmer, top sampler, etc)

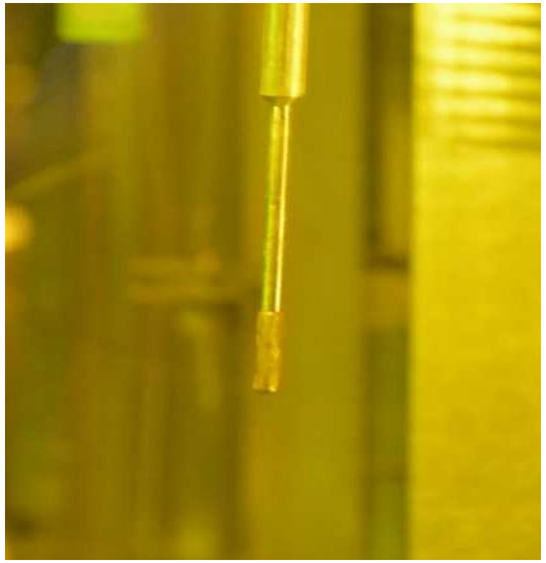
- Sample collected from the top surface of the salt
- Known surface area
- Design relies on salt freezing to the sampling device

- Pros:
  - Easy construction, reusable
  - Helps to understand the top layer that can form (‘crud’), used in 2019 JFCS ER
  - Qualitative and possibly quantitative data
  - reusable
- Cons:
  - Sensitive to elevation
  - When used with a temperature sensor, the response was too delayed to function
  - Some constituents more readily freeze than others
  - Hard to get exact depth

Rod Dip Samples

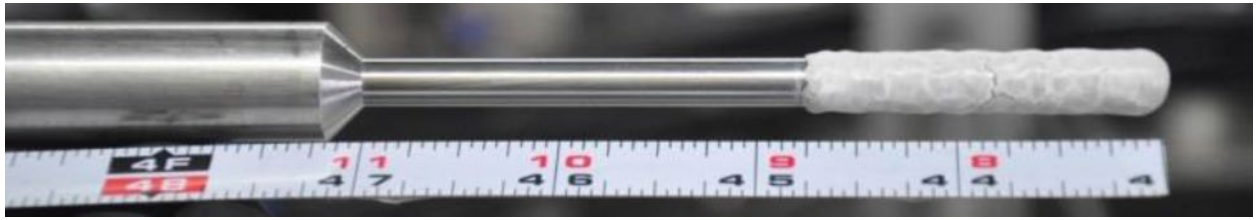
- Commonly used, cheap, easy for collection
- Stainless steel rod
  - Length sized to target a desired sampling depth
- Dipped into the salt bath and quickly removed
- Frozen salt on the rod is scraped off to collect a sample (0.25 - 0.75 g per sample)
- Different mixing & settling procedures before sampling have been explored
- Reusable – with a delay to allow for the rod to cool

Example of a dip rod



OR Salt

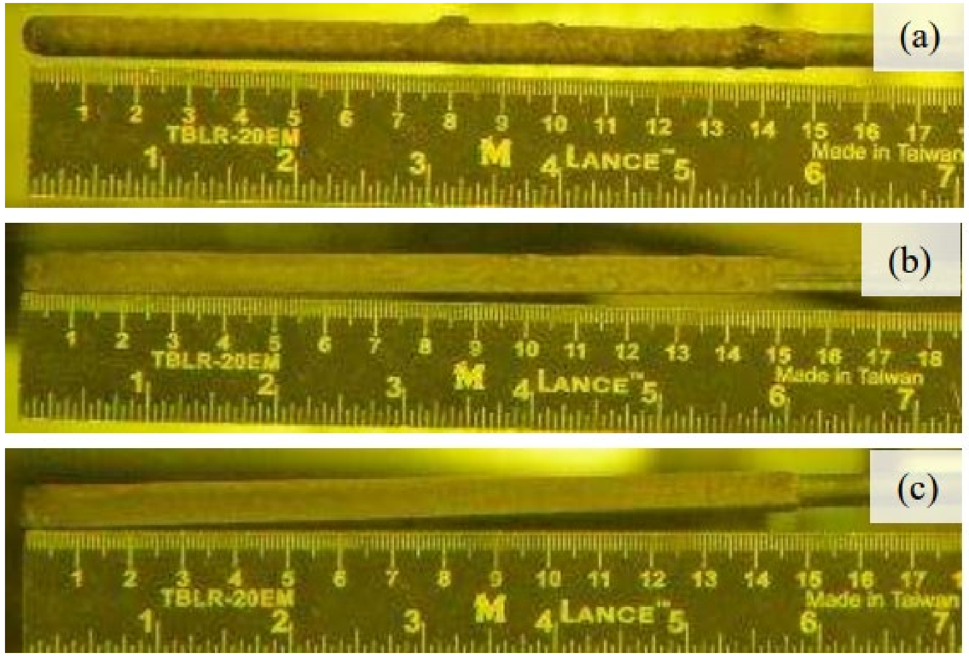
ER Salt



Sample from an Oxide Reduction salt

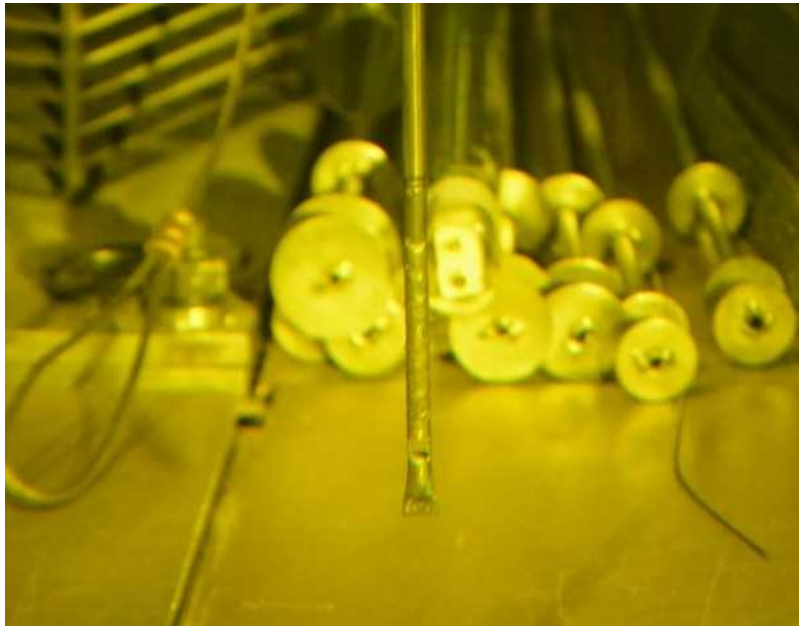
Rod Dip Issues

- The dip must be quick as otherwise, the rod becomes too hot and the salt melts off and back into the vessel
- Sampling is limited due to lack to homogeneity throughout the material
  - Some constituents more readily freeze than others
- Reproducibility and cross contamination are issues
- Sample is location specific and depth can vary
  - If the rod touches the bottom, additional debris are picked up



Dip Cup samples – Pre-Distillation Cadmium Products

- A hollow rod/cylinder with a small cup at the bottom was inserted into the molten cadmium in the ER
  - When the dip tool is removed, the small cup with cadmium inside is cut off and put in a sample container.
  - After the sample is removed, the rods are inspected for any remaining cadmium. If some is found, the rods are put back into the cadmium such that the remaining cadmium can drip back into the ER.
- This is commonly used, easy to operate and made from off-the-shelf parts
- Sometimes adapted slightly and called pipet method



Dip Cup/Pipet - Issues

- Difficult to reproduce
- Sampling depth can vary
  - Requires operators to measure depths each time
- If using pipet or similar device, it is non reusable

Suction Fine Collector

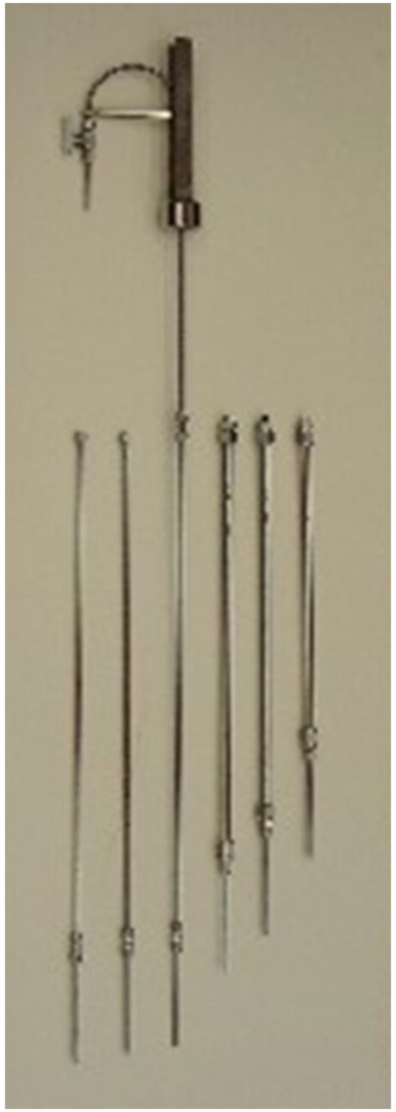
- Pros:
  - Collects fines along with salt by suction
  - Captured in a sacrificial tube which was then removed and sent for analysis
  - Provided qualitative data on the insoluble material at the bottom of the salt
  - Made from off-the-shelf parts

- Cons:
  - Samples are not quantitative
  - Does not work with large particles
  - Does not work with thick/dense slurries

Fines sample taken using a quartz tube. The area to the left is the part touching the bottom of the crucible.

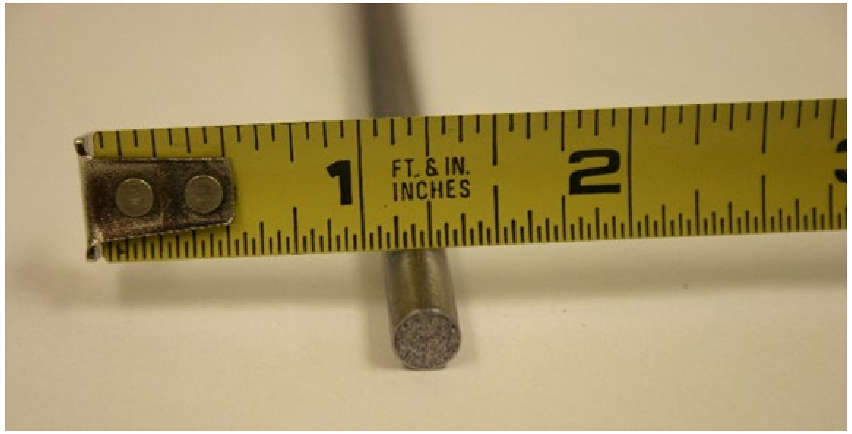
Filtered Sampling Approach

- Tantalum frit segments are attached to SS tubes
- Assemblies lowered into the salt vessel
- Salt and/or cadmium is drawn into the tube assembly through the frit using a slight vacuum applied to the tube
- Allows for a filtered sample
- Solids present in the salt or cadmium volume taken into the tube assembly will be trapped on or in the filter frit thus allowing for solids analysis



Salt sampling assembly

Tantalum filter tube for salt and cadmium sampling.



Tantalum filter frit.

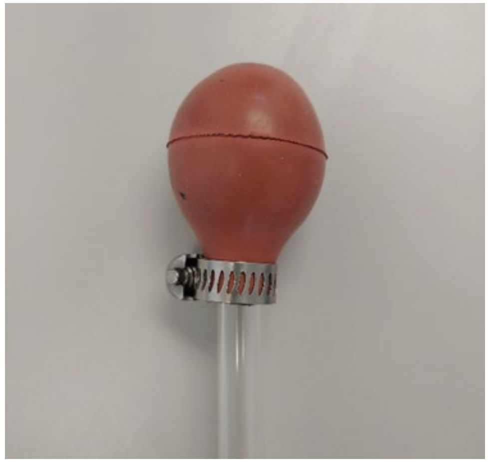
Filtered Samples Pros and Cons

- Difficult to determine what the frit will collect and the right size to do so
  - Should the frit be analyzed? The outer portion of the cut tube?
  - Lack of information on impurity particle sizes
  - A study at INL with TIMS measurements of filtered and unfiltered samples found that there was more variability with U sample results in filtered than unfiltered samples.
- Helps to avoid contamination of large particles which cause variability in samples
- Varying success depending on frit porosity
  - With finer frits, salt cannot flow through the sampler
  - With coarser frits, sat was able to flow but would quickly flow back out upon removal from bulk salt

Vacuum Assisted Salt Sampling

- Update to the previous filtration method
  - Pulling a small amount of vacuum to pull the salt sample through the frit
  - The quartz tube is then broken to retrieve the sample
  - Tried two methods:

- Rubber pipette bulb on top of sampler tube - Squeezed then released to create pressure difference

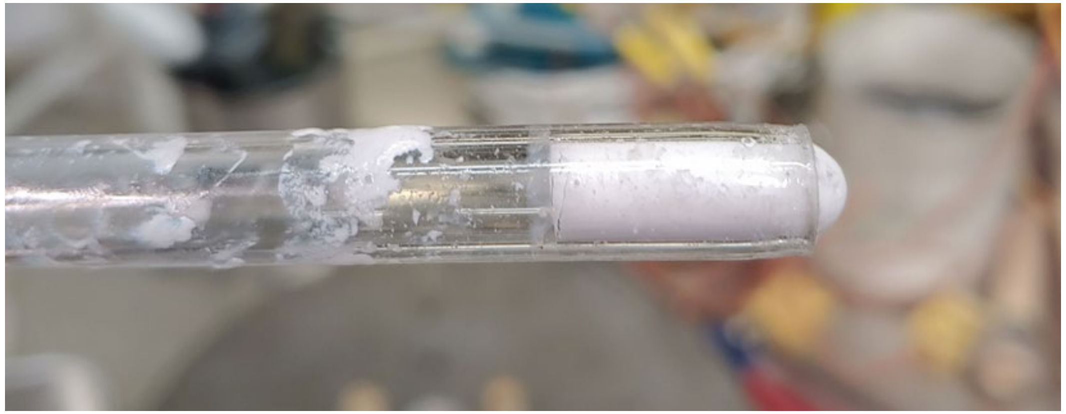


- Small piston pump on top of sampler tube -Tube is lowered into salt then the piston is extended which lowers the internal pressure of the assembly

Taken from INL/RPT-22-96252 by Robert Hoover et al.

Vacuum Assisted Salt Sampling Pros and Cons

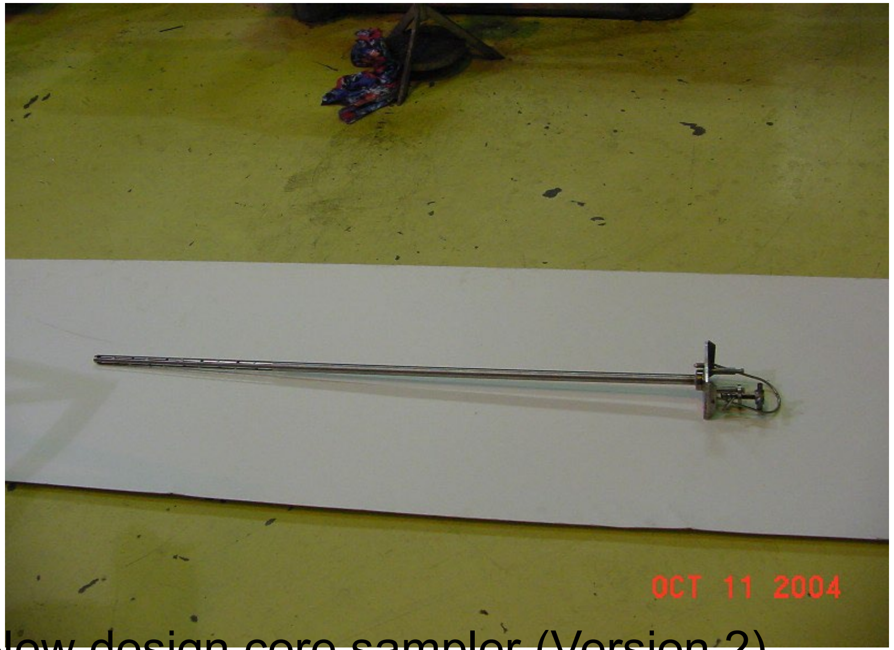
- Large amount of variability with pipette
  - Difficult to reliably seal the pipette to the tube
  - Leakage causing no salt to be pulled into sampler
- A piston vacuum assembly was successfully developed
  - Reliably and repeatably could pull salt through even the finest and stacked frits
  - Slight mod for manipulators in a hot cell



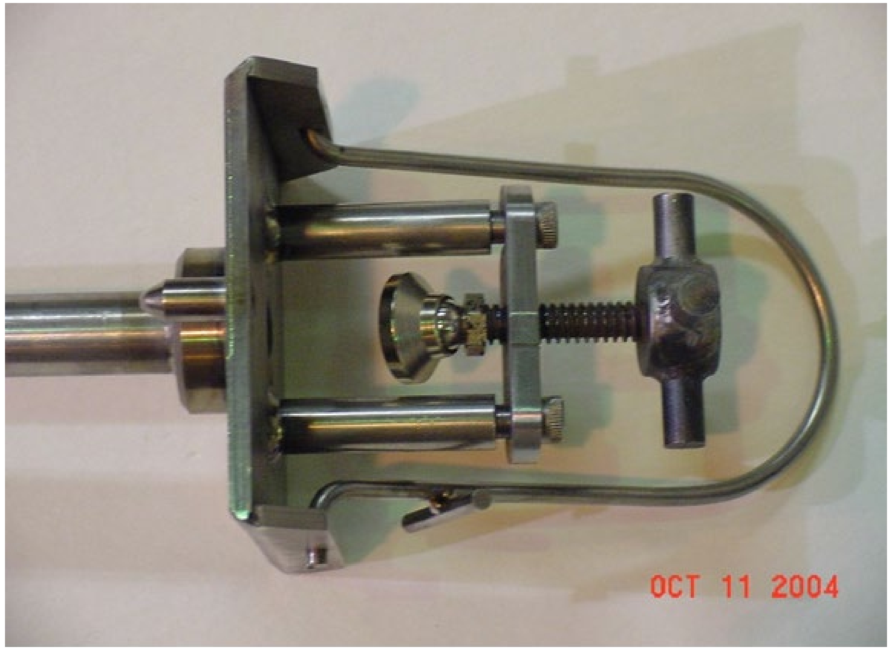
Taken from INL/RPT-22-96252 by Robert Hoover et al.

Core Sampler

- After the sampler has thermally equilibrated, the inner tube is forced down upon the end-cap and fit by an interference fit within the inner tube.



New design core sampler (Version 2)

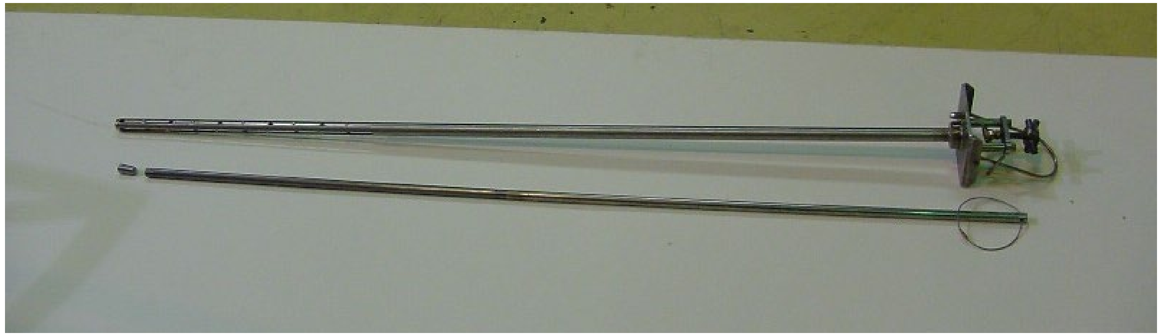


Core sampler swage fixture for new design core sampler.

From Close Tracking of Actinides and Fission Products in the Electrorefiner, INL, March 31 2005

Core Sampler

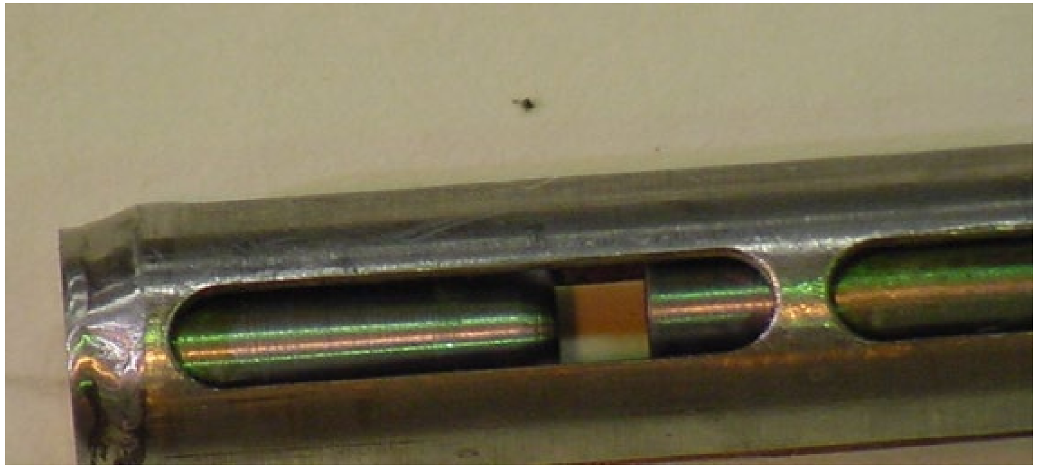
Outer and inner core sampler tubes with interference fit end cap.



New design core sampler inner and outer tubes with end-cap.

Core Sampler

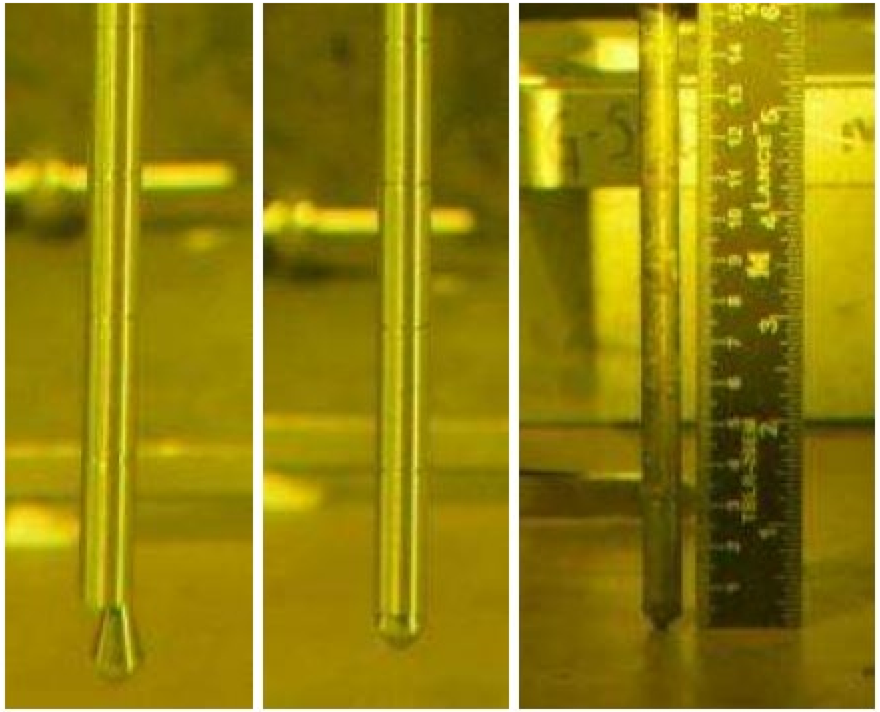
- The second and third core samples were successfully taken from the MK-IV ER during October of 2004.
  - Samples were taken at a temperature of $500^{O}C$ under an argon gas atmosphere.
  - Once the samples had been taken, the sampler tubes were disconnected from the sampler apparatus and the upper end of the tube was cut in order to decrease the length of the sample tube.

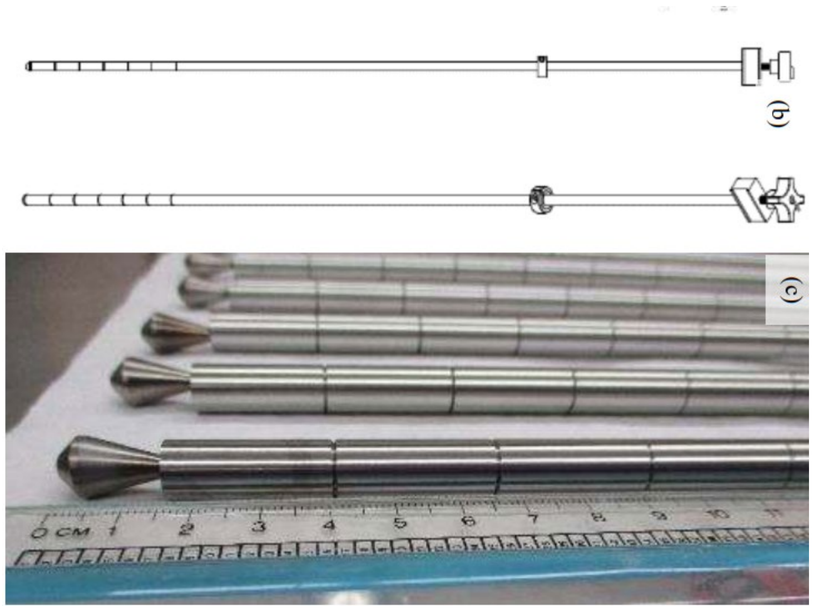


Inner sample tube within outer sample tube.

Core Sampler – Turn Knob Version

- A tube containing a valve that opens while lowering and closes before removal
  - Stops salt from slipping out as in old version
- The frozen sample is then cut into sections for analysis





Core Sampler Results and Issues

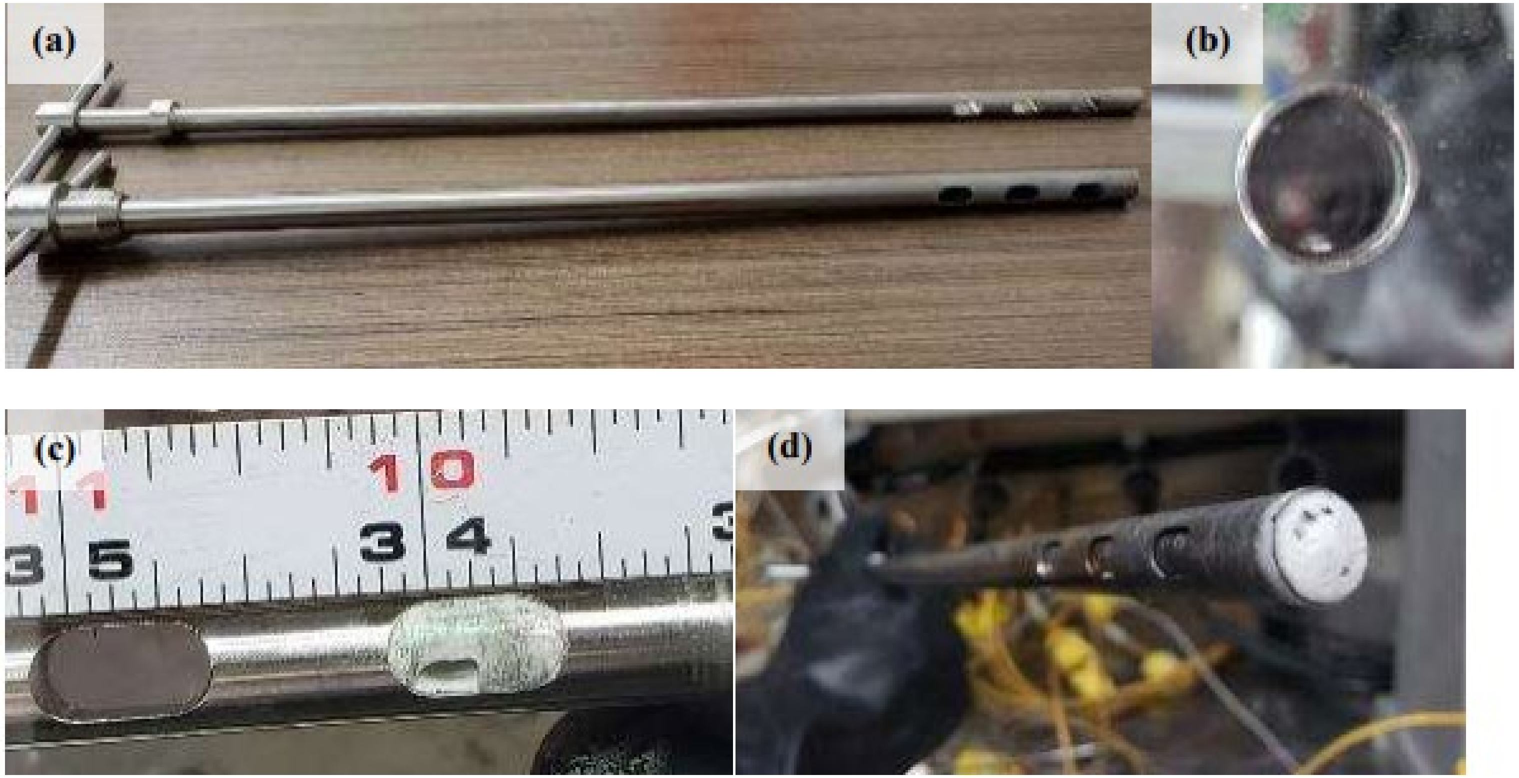
- First version failed
  - possibly due to a combination of a faulty design and/or solid material caught between the end cap and the sampler tube
- Handling with mechanical manipulators was rough and more rigid than in primary tests
- Density of salt caused multiple failures when removing the sample tube from the ER
  - Sample did not remain in the tube
- The turn knob version was mostly successful though some drops were lost

Multi Level Sampler (MLS)

- Composed of an inner rod with openings (sampling ports) at three heights (1, 3, and 5 inches from the bottom) and an outer tube with openings on one side
- When submerged it is initially closed so not salt can enter the chamber
- It is then opened by turning the inner tube 90 degrees to expose the sampling ports then turned back to close them before removal
- It saves time by collecting multiple samples at the same time
- Since the same heights are used, it reduces depth measurement errors
- It is easy to operate remotely and is mostly reusable

- Con: Can be difficult to remove samples if salt gets stuck between the two cylinders

MLS continued



Version of the MLS with chambered open end. Issues with salt buildup so future version will have smoother surface and better tolerance for the entire length of the inner rod and outer tube

MLS Results and Issues

- In preliminary tests it was shown to be reusable and retrieval of samples was simple
- However, in the ER it seized up on the second use and samples could not be retrieved
- Several modifications occurred but, in the end, handling it remotely was too complex and the sample was too hard to retrieve.

General Issues

- To stir or not to stir?
- Wait time for lab analysis or radiography
- Salt stratification due to varying densities and particle sizes
- Lack of homogeneity due to solid phase formation, stratification, sedimentation and/or suspension
- A top layer on the salt can form

Requirements For A Salt Sampling Device

- Effective in collecting samples throughout the container ie. Bottom middle and top, without disturbing the salt
- Should fit through a port or opening
- Made of materials that are resistant to corrosion and suitable for high temperature, remote handling
- Samples should be easy to remove from the device and weigh around 1-2g
  - should also fit in a standard sample holder
  - Samples should be retrievable with limited chance of contamination (e.g. from outer tube, manipulator, processing, etc.)
- If a sacrificial portion exists on the device, it must not contaminate the salt (for example: stainless steel, tantalum, or tungsten)

Future Work: FY24 and Beyond

- Continue to develop salt samplers
  - Specific depth
  - More robust
  - Easier to segment
  - Incorporation of filters
  - Fine collection
- Sampling parameters
  - Stirring
  - Settling time
  - Filtration
- Plan for non-static salt sampling?
  - In between runs
  - During ER operations?
- Address Deficiencies for Process Control and NMAC Purposes
  - Determine best way to collect samples from tubes
  - Minimize contaminants
  - Testing with surrogate insoluble impurities of known particle size