Development of solid materials for UF₆ sampling

FY16 Annual Report

Nuclear Engineering Division

About Argonne National Laboratory

Argonne is a U.S. Department of Energy laboratory managed by UChicago Argonne, LLC under contract DE-AC02-06CH11357. The Laboratory's main facility is outside Chicago, at 9700 South Cass Avenue, Argonne, Illinois 60439. For information about Argonne and its pioneering science and technology programs, see www.anl.gov.

DOCUMENT AVAILABILITY

Online Access: U.S. Department of Energy (DOE) reports produced after 1991 and a growing number of pre-1991 documents are available free via DOE's **SciTech Connect** (<http://www.osti.gov/scitech/>)

Reports not in digital format may be purchased by the public from the National Technical Information Service(NTIS):

U.S. Department of Commerce
National Technical Information Service
5301 Shawnee Rd
Alexandria, VA 22312
www.ntis.gov
Phone: (800) 553-NTIS (6847) or (703) 605-6000
Fax: (703) 605-6900
Email: **orders@ntis.gov**

Reports not in digital format are available to DOE and DOE contractors from the Office of Scientific and Technical Information (OSTI):

U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831-0062
www.osti.gov
Phone: (865) 576-8401
Fax: (865) 576-5728
Email: **reports@osti.gov**

Disclaimer

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor UChicago Argonne, LLC, nor any of their employees or officers, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of document authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof, Argonne National Laboratory, or UChicago Argonne, LLC.

Development of solid materials for UF₆ sampling

FY16 Annual Report

prepared by
Nicholas Smith, Joseph Savina, Andrew Hebden
Nuclear Engineering Division, Argonne National Laboratory

10/31/16

EXECUTIVE SUMMARY

A handheld implementation of the ABACC-developed Cristallini method, which captures uranium hexafluoride samples as an inert salt, was organized in FY17 and succeeded in demonstrating the handheld sampler concept with reactive hexafluoride gases. The Cristallini method relies on the use of a hydrated substrate to react the incoming hexafluoride resulting in the formation of a stable uranyl fluoride salt. The Cristallini method has been demonstrated as a facility modification installed near the sampling tap of a gas centrifuge enrichment plant. While very successful in reducing the hazards of uranium hexafluoride sample, the method still takes a considerable amount of time and can only be used in facilities where the apparatus has been installed; this arrangement generally prohibits the sampling of filled cylinders that have already exited the facility and have been deposited in the on-site tank storage yard.

The handheld unit under development will allow the use of the Cristallini method at facilities that have not been converted as well as tanks in the storage yard. The handheld system utilizes an active vacuum system, rather than a passive vacuum system in the facility setup, to drive the uranium hexafluoride onto the adsorbing media. The handheld unit will be battery operated for fully autonomous operation and will include onboard pressure sensing and flushing capability.

To date, the system concept of operations was demonstrated with tungsten hexafluoride that showed the active vacuum pump with multiple cartridges of adsorbing media was viable. Concurrently, the hardened prototype system was developed and tested; removable sample cartridges were developed (the only non-COTS component to date); and preparations were made for uranium tests and a domestic field test.

This work was funded by the National Nuclear Security Administration, Office of Defense Nuclear Nonproliferation Research and Development (NA-22).

CONTENTS

Executive Summary	i
Contents	ii
Figures.....	iii
Acronyms and Initialisms	iv
1. Summary Of Project	1
2. Task 1 – Evaluation of Substrate Materials	2
2.1. Identification of materials	2
2.2. Material testing	3
2.3. Results.....	4
3. Task 2 – Prototype Development.....	5
3.1. Prototype design.....	5
3.2. Substrate cartridges.....	6
3.3. Design and compaction.....	6
4. Task 4 - Field Testing	7
5. FY17 Outlook	8
6. Relevant references	9

FIGURES

Figure 1 - Tungsten Hexafluoride testing rig (right) and the initial implementation of the sampler (left).....	3
Figure 2 - Analysis of Tungsten hexafluoride deposition on alumina grit. Left - XRF spectrum showing the tungsten content at the top of the sample column (blue) and the bottom (red); Right - IR image of the top of the column during deposition showing the high localization of the reaction in the upper 1 cm of substrate.	4
Figure 3 - "Breadboard" configuration of the prototype sampler.	5

ACRONYMS AND INITIALISMS

ABACC.....	
.....	Brazilian-Argentine Agency for Accounting and Control of Nuclear Materials
ANL	Argonne National Laboratory
ANL-NE.....	Argonne Nuclear Engineering Division
COTS	Commercial off the Shelf
GCEP	Gaseous Centrifuge Enrichment Plant
HF	Hydrogen Fluoride
ICP-MS	Inductively Coupled Plasma Mass Spectrometer
IR.....	Infrared
NaF.....	Sodium Fluoride
UF ₆	Uranium Hexafluoride
WF ₆	Tungsten Hexafluoride
XRF.....	X-Ray Fluorescence

1. SUMMARY OF PROJECT

The goal of this project is to create a handheld implementation of the Cristallini method developed by the Brazilian-Argentine Agency for Accounting and Control of Nuclear Materials (ABACC). The method uses a passive vacuum system to drive uranium hexafluoride onto a hydrated alumina substrate; this causes the hexafluoride to react and form a stable salt. This stable salt is easier to transport due to the shipping regulations surrounding uranium hexafluoride. The main driver to create the handheld unit is to reduce the amount of sample collected using the Cristallini chemistry; reduce the time required to collect the sample; and extend the reach of the method to all uranium hexafluoride enrichment and storage/use facilities.

The project was organized into three separate tasks. The first task was to identify the likely materials to be used as the sampling substrate and test the various materials with tungsten and uranium hexafluoride. The second task was to create the prototype unit suitable for testing with uranium hexafluoride. Lastly, the third task was to perform an international field test; this task was eventually reorganized into a domestic field test concurrently funded by the Office of International Nuclear Safeguards (Safeguards Technology).

The project met its first milestone to test the system with a reactive hexafluoride on time during FY16. However, the milestone to test with uranium hexafluoride has shifted to October, 2016 due to delays in development of the prototype system. The uranium tests could have been completed sooner; however, the decision was made to preserve the ability to easily work with and alter the components required for the prototype rather than contaminate them to meet the original milestone timeline.

2. TASK 1 – EVALUATION OF SUBSTRATE MATERIALS

The first task was a key component of the project as the identification and testing of suitable substrate would be required to move forward with the project. A more comprehensive report on the material testing and evaluation can be found in the concurrent report “Cristallini Material Review and Selection” released as technical report ANL/NE-16/37.

2.1. IDENTIFICATION OF MATERIALS

The first task was focused on identifying and evaluating possible sampling substrates. A literature review was performed that identified a number of chemicals that are capable of adsorbing each of these gases with varying efficacy. Six different materials (or material types) were identified and will be tested.

- Alumina – the material of choice for commercial scrubbers and the existing Cristallini method. The reaction of hexafluorides in the presence of finely divided grit (50-100 mesh) *has not been studied to date* and therefore no reaction rate is known.
- Zeolites and Silicates – aluminosilicates that have high degrees of entrained water. In addition, the ability to tailor the chemistry of the zeolite to favor HF sequestration (e.g., by incorporation of calcium) without undue corrosion of the main structure could reduce the presence of fine silts observed in the Cristallini process.
- Sodium Fluoride – this material performs best at 50-120° C (absorbing ca. 1 g U per gram of NaF), though significant absorption may occur at room temperature. The solubility of the material increases the ease of recovery but may complicate the follow-on chemistry and the material is entrained as a UF₆ adduct rather than a uranyl salt.
- Activated Carbon – this material may become explosive with sufficient fluorination. Though this is not expected with the sample sizes under consideration, the hazard must be considered against any absorption benefit.
- Calcium or Magnesium Oxide – both materials are very good absorbers of UF₆ and free HF. Similar to sodium fluoride, the materials would likely be completely dissolved during recovery of the uranyl fluoride, though the resulting solution would be highly basic. These materials are also being investigated as an HF trap
- Calcium Carbonate – mainly being investigated as a free HF trap; the material may be able to directly sequester the hexafluoride gases.

All of the possible substrate materials were acquired and cataloged. An important consideration for the materials was their physical properties. Specifically, the hydration level was researched; the eventual recovery chemistry was examined; and materials were also tested under vacuum to ensure that the materials would not vapor lock. Lastly, commercially available, inexpensive materials were given priority.

The hydration level of the materials was hard to quantify for most materials without a disproportionate amount of effort. In most cases, a rough hydration level could be discerned from the certificates of analysis. Early indications show that the various sizes of alumina powder have very different dissolution and vacuum properties. For example, while one supply of fine grit alumina powder will readily vapor lock, a second batch with a similar grit but slightly different physical conformation readily evacuates. The dissolution chemistry evaluation, beyond the use of these materials in industry, eliminated several materials from

first round consideration. For example, magnesium oxide seemed to have good adsorption properties but would result in a highly basic sample upon recovery.

Analytical methods for each material considered were developed by the Argonne Analytical Chemistry Laboratory. This allowed for rapid analysis of the hexafluoride samples at collection. In addition, the Cristallini team developed methods for performing rough concentration screenings, if needed, based on x-ray fluorescence spectroscopy.

2.2. MATERIAL TESTING

The testing rig for WF_6 analysis was assembled late in the third quarter with final construction and commissioning in early July (Figure 1). Physical calculations were made to determine the appropriate conditions under which to collect the WF_6 as to simulate UF_6 conditions. The general concept used a series of substrate cartridges, each containing a known amount of substrate, which were exposed to the hexafluoride gas. The system used the same pump and vacuum gauges expected to be used in the uranium prototype. The cartridges were monitored with an infrared camera as the deposition reaction is very exothermic; samples were screened with a handheld XRF unit to determine tungsten content (Figure 2).

Figure 1 - Tungsten Hexafluoride testing rig (right) and the initial implementation of the sampler (left).

2.3. RESULTS

The testing rig was used to capture tungsten hexafluoride on multiple substrates. Generally, ~100-200 micron alumina powders performed well and captured test charges of 0.1 grams of tungsten hexafluoride. The total collection time was generally on the order of minutes (1-3); this is significantly faster than the original Cristallini method. The alumina samples showed no breakthrough of material to subsequent samples or to the system trap.

Samples were submitted to the ACL to determine total tungsten content via total dissolution of the substrates followed by ICP-MS analysis. In general, the medium grain alumina samples retained the predicted amount of tungsten and downstream samples showed no discernable tungsten deposits.

Figure 2 - Analysis of Tungsten hexafluoride deposition on alumina grit. Left - XRF spectrum showing the tungsten content at the top of the sample column (blue) and the bottom (red); Right - IR image of the top of the column during deposition showing the high localization of the reaction in the upper 1 cm of substrate.

3. TASK 2 – PROTOTYPE DEVELOPMENT

The design of the prototype was pursued to fulfill several design requirements. The following design requirements are enumerated here:

- The prototype needs to interface with the sample taps and valve connections found on UF₆ equipment.
- The device must be engineered in such a way as to protect the GCEP plant from external contamination.
- Cross contamination must be minimized/eliminated between samples to preserve their validity for safeguards declaration verification activities.
- The device should be completely self-contained and not rely on the site to provide any materials.
- The samples generated should be easy to package and hand carry.
- The device should not create a hazard for the operator or inspector.
- Each sample should be collected in less than 10 minutes.
- The device should be made of COTS components whenever possible for cost savings and modular maintenance.

A “breadboard” version of the prototype (non-compacted or housed) was assembled and functionally tested near the end of the fiscal year (Figure 2). The prototype will be tested with regard to operational parameters and the uranium campaign will commence in the first quarter of FY17.

Figure 3 - "Breadboard" configuration of the prototype sampler.

3.1. PROTOTYPE DESIGN

The initial design for the integrated device was started in the first quarter, including generating the design bases and concept of operation enumerated above. In general, materials of construction were limited to stainless steel, Monel or other high nickel alloys, and perfluorocarbon materials. High nickel alloys were found to better resist deposition of thin layers of reacted hexafluoride materials (as oxides or oxy-fluorides) on the wetted surfaces in comparison to stainless steel. While the stainless materials accumulate a small amount of material, the material does not participate in further reactions and is not a cross-contamination concern. In addition, the steel components can be disassembled and washed to remove

deposits. This behavior was seen during the tungsten campaign in some of the disposable plastic valves used and during the disassembly of the tungsten apparatus.

High nickel alloys and/or perfluorocarbon materials are being restrained to those components that are either hard to disassemble or clean (i.e., valves) or those that are readily available for a nominal surcharge. Teflon seated solenoid valves were selected for the system. These valves are normally closed, giving a fail-safe configuration, and can be remotely actuated for sample collection. Stainless steel versions will also be tested, though the potential of accumulating material in the valve is concerning at this point.

3.2. SUBSTRATE CARTRIDGES

The effect of water surface contamination inside the final device is a potential problem. Therefore, ways to minimize internal water (and thus potential cross contamination) were investigated. This information will be used during prototype testing if the internal cavities show signs of tungsten or uranium residues. Potential cross contamination is not a significant issue as any materials that react with surface moisture will not be able to be transported into the sampling device; only fresh gaseous material will be able make it to the sampler. A larger concern would be the clogging of the apparatus due to residue build up.

Several sample cartridges were designed over the course of the year. These designs varied in size and configuration as the prototype design evolved. Finally, a rigid sample cartridge was developed using self-sealing quick-disconnects that houses a charge of substrate compacted with polypropylene frits.

3.3. DESIGN AND COMPACTION

All components and designs are being directed to the Nuclear Engineering mechanical design department to facilitate the design and configuration of the prototype (to be assembled in early FY17). This department is responsible for the incorporation of the prototype design into an integrated unit, including battery compartments/charging ports; integrated controls and readouts; creation of a housing for the system. This housing, at least for the first few iterations, will likely be created via additive manufacturing to reduce costs and allow for rapid design changes.

4. TASK 4 - FIELD TESTING

Originally, the project was tasked with collaborating with an international enrichment facility, possibly via ABACC due to their involvement as the originator of the Cristallini method. However, the project was redirected to perform a domestic field test first. To that end, the field testing aspect was cross-funded through the Office of International Nuclear Safeguards for a field test near the end of FY17.

5. FY17 OUTLOOK

The project has been very successful to date; the proof of concept tests showed the basic viability of the technique and deposition tests have been promising. The uranium campaign is slated to start in October 2016 and last for the first two quarters of FY17. Concurrently, the prototype will be finalized and produced with an aim to test domestically by the end of the fiscal year. The project will terminate at the conclusion of the field test. At that point, the full design as well as physical prototype will be delivered (if desired) along with a complimentary project report. At this point, all milestones and deliverables appear to be reachable on schedule.

6. RELEVANT REFERENCES

1. Schuman, S. and N. Nutley, *Method of Recovering Uranium Hexafluoride*, U.S.P. Office, Editor. 1975, The United States of America as represented by the United States Energy Research and Development Administration.
2. Jury, S.H., *Recovery of Uranium from Gas Mixture*, in *osti.gov*, U.S.P. Office, Editor. 1954: United States.
3. Del Cul, G.D., et al., Some investigations of the reaction of activated charcoal with fluorine and uranium hexafluoride. *Journal of Fluorine Chemistry*, 2000. **101**(1): p. 137-148.
4. Schults, R.M., et al., *Sorbent Selection and Design Considerations for Uranium Trapping*. 1981, Oak Ridge Gaseous Diffusion Plant Oak Ridge, TN, USA.
5. Galdoz, E., et al., *UF₆ sampling method using alumina*. Annual Meeting Proceedings of the Institute of Nuclear Materials Management, 2008. **49**: p. 199/1-199/8.
6. Acute Exposure Guideline Levels (Aegls) for Sulfuryl Fluoride, E.P. Agency, Editor. 2008.

Nuclear Engineering Division

Argonne National Laboratory

9700 South Cass Avenue, Bldg. 205

Argonne, IL 60439

www.anl.gov

**U.S. DEPARTMENT OF
ENERGY**

Argonne National Laboratory is a U.S. Department of Energy
laboratory managed by UChicago Argonne, LLC