



Challenges and Solutions for Handling and Characterizing Alkali-Tc-Oxide Salts

Journal:	<i>MRS Advances</i>
Manuscript ID	Draft
Manuscript Type:	Regular Article
Date Submitted by the Author:	n/a
Complete List of Authors:	Weaver, Jamie; Washington State University, Chemistry; Pacific Northwest National Laboratory, Soderquist, Chuck; Pacific Northwest National Laboratory Washton, Nancy; Pacific Northwest National Laboratory, Gassman, Paul; Pacific Northwest National Laboratory Walter, Eric; Pacific Northwest National Laboratory Bowden, M.; Pacific Northwest National Laboratory Lukens, Wayne; E O Lawrence Berkeley National Laboratory McCloy, John; Washington State University, School of Mechanical and Materials Engineering; Pacific Northwest National Laboratory,
Keywords:	nuclear materials, nuclear magnetic resonance (NMR), Raman spectroscopy, extended x-ray absorption fine structure (EXAFS), neutron scattering



Challenges and Solutions for Handling and Characterizing Alkali-Tc-Oxide Salts

Jamie L. Weaver,^{1,2} Chuck Soderquist,² Nancy Washton,² Paul Gassman,² Eric Walter,² Mark Bowden,² Wayne Lukens,³ and John S. McCloy^{1,2,4}

¹*Department of Chemistry, Washington State University, Pullman, WA 99164, USA*

²*Pacific Northwest National Laboratory, Richland, WA 99352, USA*

³*Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA*

⁴*Materials Science and Engineering Program and School of Mechanical & Materials Engineering, Washington State University, Pullman, WA 99164, USA*

ABSTRACT

Though not often discussed explicitly in literature, sample handling and preparation for advanced characterization techniques is a significant challenge for radiological materials. In this contribution, a detailed description is given of method development associated with characterization of highly radioactive and, in some cases, hygroscopic oxides of technetium. Details are given on developed protocols, fixtures, and tooling designed for x-ray and neutron diffraction, x-ray absorption, Raman spectroscopy, magic angle spinning nuclear magnetic resonance, and electron paramagnetic resonance. In some cases, multiple iterations of improved sample holder design are described. Lessons learned in handling Tc compounds for these and similar characterization methods are discussed.

INTRODUCTION

Italian researchers Perrier and Segre first isolated technetium (element 43) in 1937 [1]. Since its discovery it has found extremely important uses in the medical field [2, 3], as well as interest in steel processing [4] and superconductivity [5]. It has been identified in the spectrum of stars [6, 7], which led to the discovery of solar production of heavy elements. In inorganic chemistry, it is the only non-transuranic unstable transition metal, sharing chemical properties with Re and Mn [8].

It is the radioactive nature of Tc, particularly the soft beta emitting ⁹⁹Tc, which has made analysis of the element and associated compounds challenging. Unlike most other transition

metals, the handling and analysis of Tc-bearing compounds is complicated and usually requires special permits and costly modifications to already expensive and often uncommon analytical instrumentation. Additionally, carefully planned procedures and experimental protocols usually require approval before work with the isotopes can be conducted. Experiments on Tc compounds, particularly some Tc oxides, can be further complicated by their strongly hygroscopic and friable natures. As a result of these challenges, only a small number of laboratories internationally are actively conducting research on ^{99}Tc .

There are some differences between ^{99}Tc and $^{99\text{m}}\text{Tc}$ radiation hazards that should be noted. ^{99}Tc does not pose a significant external radiation hazard, so shielding is not typically as important. Shielding from the ^{99}Tc beta particle can be provided by two layers of latex laboratory gloves, but these materials will receive a substantial dose and will break down over time. Typical laboratory glassware and plastic ware will also effectively shield beta radiation, though it will penetrate thin Kapton®. In contrast to the risk posed from external exposure, ^{99}Tc is an internal radiation hazard, and thus contamination control is critical. $^{99\text{m}}\text{Tc}$, on the other hand, is a gamma ray emitter, so the external radiation hazard is important while internal radiation hazard is not, so shielding is the important radiological control.

Although limited, Research on Tc is important. $^{99\text{m}}\text{Tc}$ is being produced daily for the radiopharmaceutical industry, and ^{99}Tc is a significant component of most nuclear wastes. Within the last few decades, there has been a significant increase in research efforts endeavouring to understand how best to store and dispose of Tc [9-17]. In conjunction with these efforts has been a push for advanced analyses of Tc-bearing materials using state-of-the-art equipment [13, 18-24]. X-ray absorption fine structure (XAFS) has been utilized to investigate the local structures of Tc in both crystals and soft matter. Neutron diffraction has provided insight into the effect of ligands on crystal field distortions, and solid-state nuclear magnetic resonance (NMR) has been used to clarify a half-century old debate on the oxidation state of fundamental Tc oxides.

Accompanying this research has been the development of methods on how to safely and properly prepare Tc samples for these instruments, and how to design sample environments that are durable (*i.e.*, “radiation hard”), prevent diffusion of water into the samples, and provide effective containment. These critical aspects of sample handling have generally not been described in research publications. Dissemination of this information is necessary, particularly as the Nuclear Energy Institute has estimated that 39% of the nuclear workforce (which has been primarily responsible for the creation of these methods) will be eligible for retirement by 2018 [25]. Determining optimal procedures and protocols takes years of research and development and sizeable budgets, and the lack of detailed documentation, coupled to loss of expertise, could drastically delay further research efforts in the field. The focus of this work is to document some of the development efforts on methods for handling and characterization of Tc compounds.

EXPERIMENTAL METHODS

Tc utilized in these studies was obtained from Oak Ridge National Laboratory. Processing, synthesis, and purification of alkali-Tc-oxide salts has been previously described [18]. Conversion of alkali pertechnetates to other alkali-Tc-oxides was completed under dry conditions, because the final compounds were determined to quickly absorb atmospheric water [19]. The reversion of the alkali-Tc-oxide compounds from the desired chemistry back to an alkali pertechnetate was accompanied by a change in color, from yellow to white. Therefore, a

cursory visual analysis of a compound could be made to determine if and at what step the Tc-containing sample had significantly reverted to its precursor form.

All samples were stored and loaded into sample holders under dry and inert conditions to avoid moisture-driven transformations. A layer of containment that was readily disposable was used during the handling and loading of samples into holders, as powders were friable and therefore a significant dispersion and contamination hazard. An inexpensive plastic glove bag filled with 99.99% N₂ gas (Linde) was placed inside a radioactive materials fume hood as the disposable containment (Figure 1). The bag was taped to the floor of the fume hood. Special sample holders and tools were designed to fit and be workable within the bag's dimensions. A set of primary and secondary gloves were required for fume hood entry. An additional set of gloves, a size smaller than the gloves integral to the bag, was placed over the bag gloves for better dexterity and more accurate and efficient sample handling.

All equipment that went into the glove bag was dried to the greatest extent possible. Tools and equipment that were conducive to heat treatment (beakers, spatulas, crucibles, mortar and pestle, and so on) were dried at >100°C for an hour or more, then taken into the bag while still warm. One set of tools was dedicated to preparing Tc samples, and were not used with other radioactive materials. This eliminated the possibility of cross-contaminating samples with additional radiation sources, which could complicate obtaining approval to transport samples to analytical facilities. All samples were pulverized into a free-flowing powder inside the glove bag, using a small ceramic mortar and pestle. To prevent mechanically-induced undesirable phase changes, pulverizing was performed with minimal force.

During the work, the inside of the bag and the surface of the equipment was periodically wiped with dry towels to control radioactive particles. Once samples were loaded and sealed into holders, all surfaces of the containers, reusable tools, and walls of the glove bag were repeatedly wiped with damp disposable towels to remove and check for unwanted radioactive contamination. Most Tc compounds produced in these experiments were water soluble, and could be easily removed from unwanted areas by a damp towel. Dry towels were less efficient at removing Tc contamination from surfaces. Whenever possible, Tc was recovered for recycling and use in later experiments. After swipes of an object showed no activity on a hand-held Geiger-Müller survey instrument, the object could be removed from the bag and placed in the fume hood.

After removal from the glove bag, hygroscopic samples were placed in a sealed container with a few grams of desiccant, such as molecular sieve. Samples that were to be sent out for analyses were removed from the holder and hood a few hours prior to being shipped, and were sealed in new plastic bags and checked by wet and dry swipes before being removed from the hood. A final layer of containment, and a final set of wet and dry swipes, was completed before sealing in a sturdy shipping box.

Sample holder materials and sealing compounds/methods were evaluated over the course of experimentation. Many common sealing compounds, such as certain types and brands of epoxy and most tapes, were found to be inadequate at keeping the holders water-tight. Some sealers, particularly two-part epoxies, were found to contain water which reacted with the samples, even if the adhesive was several centimeters away from the sample. In most cases, multiple layers of sealing materials and a minimum of two layers of containment were required. However, even these container materials often showed degradation with time and exposure to the Tc samples' moderate levels of radiation.

Sample holders were developed for the analysis of the hygroscopic alkali-Tc-oxides by XRD, neutron diffraction, XAFS, Raman spectroscopy, solid-state NMR, and EPR. Details are provided below on each analysis methods sample holder design.



Figure 1. Special sample holder filling containers (left) and glove bag plus multi-glove rad hood protocol (right)

Considerations for Non-dispersibility

Sample holders had to enclose and seal the radioactive samples, preventing dispersal into the environment. Although all samples were shipped overnight to non-local facilities for various analyses, the holders were often tested for longer-term containment ability. Often a sample would be loaded a few days to a few weeks prior to analysis, and then checked once or twice daily to ensure no material had leaked.

X-ray diffraction

Capillary XRD samples were loaded with crushed sample powders ($\sim 15 \mu\text{g}$) in the glove bag. The capillaries (Borokapillaren, 0.5 mm diameter, 0.01 mm wall thickness, Charles Supper Co.) were broken to length and sealed with Parafilm[®], which was capped with a layer of epoxy. This holder was then placed inside a Kapton[®] sleeve as a secondary containment and as protection for the fragile glass, and both sides of the sleeve were sealed shut with epoxy and covered with Kapton[®] tape. This method was useful for analysis by a microfocus diffractometer or facilities at synchrotron beamlines, where patterns can be obtained from relatively small specimens. The main challenge with using the capillaries was placing the statically charged radioactive particles inside the very small diameter capillary in sufficient quantity, particularly when performing the operation in a hood inside a nitrogen-containing bag used to keep out water. Once inside the glass capillary, water ingress was not a problem as long as the capping material did not contain water.

Other options for XRD include hemispherical top airtight specimen holders (Bruker) if water intrusion is a problem and a relatively larger amount of sample can be used. Placing Kapton[®] tape over standard powder holders only protects from atmosphere for short periods on relatively moisture-insensitive samples. Various other holder designs and related methods for XRD have been previously reviewed [26].

Neutron diffraction

Initial neutron diffraction analyses of alkali pertechnetate salts were conducted on samples sealed in a 1 mm thick-walled fused quartz tubes to ensure no breakage occurred during shipping and handling. The large diameter tube (~ 8 mm inner diameter) allowed 200-400 mg of sample to be loaded, resulting in typical sample activities of >1 mCi (>37 MBq). Loading was

completed by placing a smaller diameter glass tube into the holder, and tapping the powder sample through this tube and into the bottom of the sample holder. Loading the sample in this manner ensured that no powder adhered to the sides of the sample holder, the presence of which could interfere with the flame sealing procedure. The thick walls of the tubes made flame sealing the ends difficult, however, resulting in uneven glass ends. It was found that this caused excessive amorphous backgrounds in diffraction, particularly with small sample volumes. However, the background signature was easier to fit well, and thus resulted in lower chi-squared for the low volume, high background sample data fits [18].

In the second iteration, neutron diffraction samples were placed in 5 mm outer diameter amorphous silica NMR tubes (fused quartz, 0.38 mm wall thickness, Wilmad 509-PP-7QTZ); flame sealing to a final length of 25-50 mm proved easier due to decreased wall thickness. The tubes, once loaded following the same protocol as above, were slowly evacuated prior to being sealed. After a more thorough understanding of the effects and durability of epoxy for these kinds of samples was gained, it was decided that a better method of sample closure for the neutron diffraction experiments would be flame sealing. Flame sealing was performed with a propane-oxygen torch in a radiological fume hood. Care was taken not to heat the samples during sealing, and the tube was frequently checked to make sure it remained cool during the sealing process. Approximately 30 – 200 mg of the Tc compound was placed in each tube using a special tool which ensured particle size $<75\ \mu\text{m}$ (Figure 2). For the beamline used, filling the tube to a height of 8 mm was ideal to take advantage of the whole beam.

For neutron diffraction analysis, the powder-filled tubes were held between two rubber bars inside a metal sample holder frame (Figure 2), and the bottoms of the tubes, where the powder was located, were aligned to the neutron beam. Longer tubes were made for the second set of sample analyses to allow for better sample orientation within the diffraction chamber.



Figure 2. Neutron diffraction holders. First generation (left) and second generation (center); tool used to sieve the samples to $<75\ \mu\text{m}$ and also to load the NMR tubes (right).

X-ray absorption

XAFS samples were crushed powders that had been thoroughly mixed with boron nitride powder to achieve a necessary dilution ratio for XAFS analysis. The sample holder consisted of a dry metal or TeflonTM rectangular frame (2 x 2-4 cm) that had an oblong window ($\sim 3 \times 10\ \text{mm}$) in the middle. The frames were taped on one side, covering the hole and edges, with Kapton[®] (polyimide) tape, and the sample was loaded into the window until the window was filled. A second piece of Kapton[®] was then placed over the window to seal in the powder. Another layer of Kapton[®] was adhered on either side of the holder. The holders were smeared and counted to determine if any contamination was present. If contaminated, the holders were wiped down until no contamination was detected. The holder was heat-sealed inside a Mylar[®] (polyethylene

terephthalate) bag, which counted as secondary containment. These bags were then attached to a larger metal frame (typically aluminum) with the windows of the sample holders aligned to the windows of frame (Figure 3). Samples prepared this way could be measured in both fluorescence and transmission XAFS modes. Early versions of this procedure used Mylar®-backed tape to seal in the samples, but this material was found to contain too much water, and the samples decomposed after a few days of contact. Dilution of the samples with dry boron nitride and sealing with Kapton® helped mitigate water intrusion leading to decomposition in the short term. Typical radioactivity of each sample was $\sim 43 \mu\text{Ci}$ (1.59 MBq). This sample holder design was usable for analyses at multiple synchrotron x-ray beamlines (SSRL and APS).



Figure 3. X-ray absorption holders. Completed assembly (left) and loaded for beamline (right)

Raman spectroscopy

Confocal (microscopic) Raman analyses of synthesized technetium-containing glasses and oxides required their encapsulation in containers to prevent dispersal of radioactive particles. This was particularly important as the Raman spectrometer used was located in a facility which was not designated for radioactive materials, so samples had to be justifiably sealed sources.

A prototype sample holder was made from a polystyrene “membrane box” modified to present a silica window through which scattered Raman light could be collected (Figure 4). These boxes consist of two halves, each with a plastic membrane stretched across their inner surfaces. The boxes were inexpensive and were considered “one time use” containers. Membrane boxes (Ted Pella Inc.) were easily adapted to encapsulate the Tc- containing materials. The membrane boxes were machined on a lathe to remove a ~ 18 mm circular opening on one side of the two-piece box. A ~ 25 mm square quartz window was then epoxied to the outside surface of the membrane box to cover the opening on one side of the box. Attaching the silica window to the outside of the box allowed for a larger working distance on the inverted stage confocal Raman microscope. Once the epoxy had cured, the membrane was removed from the “window” side of the two-piece box. A ~ 12 mm circular Teflon™ washer, with approximately a ~ 3 mm central hole, was epoxied to the inside surface of the quartz window to create a well for the sample. This well was essential for ensuring there were enough particles within the viewing area of the confocal Raman microscope when using varying magnification microscope objectives. After the sample was placed in the center of the Teflon™ washer, a second silica window was epoxied to the top of washer, sealing the Tc between the two windows. The two halves of the membrane box were then sealed together with vinyl tape around the periphery.

Each assembled box and sample was placed upside down on the inverted stage microscope for analysis. The scattered Raman light was collected in a 180° backscatter geometry. Spectra were acquired from approximately 10 to 20 particles, or 10 to 20 spots on Tc-

containing glasses, and evaluated for consistency of spectral bands and band intensities before averaging [27].

The epoxy released water vapor as it cured, which made it unsuitable for a number of Tc compounds, as previously described. Also, samples containing relatively high levels of radioactivity, $\sim 50 \mu\text{Ci}$ (1.85 MBq), caused epoxy seals in membrane boxes to degrade within a few weeks. This led to a second design: a threaded metal sample holder which consisted of front and rear fused silica windows, an O-ring, a TeflonTM washer, a cylindrical housing, and a threaded compression plug (Figure 4). The samples were sealed by the threaded plug compressing the O-ring between the windows, which removed the need for use of adhesives or tape. To fill a mount, the front window was placed in the housing, then an O-ring was placed on the window, with a small TeflonTM washer inside the O-ring. The sample was then placed inside the TeflonTM washer using a special funnel that kept the rest of the housing clean. The rear window was then placed on the O-ring and the back was screwed on using the wrench. The sample contacted only the silica windows and the TeflonTM washer. No epoxy or tape was used, and the mount could be easily assembled in an inert atmosphere inside a glove bag. After the mount was assembled and moved from a controlled environment to ambient conditions, the O-ring prevented atmospheric moisture from intruding into the sample. The mount could be disassembled to retrieve and recycle the technetium compound inside. The mounts could be re-used indefinitely, with only O-rings needing replacement.



Figure 4. Raman spectroscopy holders. Generation one membrane box (left). Generation two tooling including metal housing with fused silica windows, washers, and housing back plug in exploded view (center), shown inside the carrying container with housing plug wrench and funnel (right). The completed Raman holder (right) is shown inside its TeflonTM carrying holder (cap removed) designed for secondary containment during transport and storage.

Nuclear magnetic resonance

For magic angle spinning (MAS), solid-state NMR experiments, $\sim 75 \mu\text{g}$ of powder ($\sim 100 \mu\text{Ci}$ or 3.70 MBq of radioactivity) were packed into a specially designed Torlon® (polyamide-imide) solid state-NMR insert (Figure 5) that fit into commercial 3.2 mm PENCIL style (Agilent or Revolution NMR) zirconia NMR rotors. The insert provided a strong, impact resistant secondary layer of containment for the Tc powders. This was a necessary feature to decrease the probability of sample dispersal as a result of a rotor “crash” during spinning at 18 kHz, where the zirconia holder can break. The inserts could be easily handled and cleaned (by placing in simmering water for a few hours). Cleaned inserts were found to contain no dispersible Tc on their surfaces nor material contamination on the inside, and could be reused multiple times before being discarded. Special reusable NMR tools (Figure 5) were designed to allow for careful incremental packing of the insert to prevent sample placement imbalances which are known to promote rotor crash in MAS NMR.

Previously used methods encapsulated radioactive powders in epoxy, thereby forming a solid, impact resistant plug. However, experiments conducted on Tc- and U-containing samples

impregnated in epoxy showed chemical reactions occurring over time (~ 2 weeks to several months), altering the oxidation state and/or ligand identity. The disadvantage of utilizing the Torlon® inserts is a significant decrease in sample volume relative to the epoxy method; the insert has an internal volume of 1.2 μl (equivalent to 1.2 mm rotor), while the epoxy pellet uses the entire 3.2 mm rotor volume of 22 μl , with a possibility of up to 80% wt/wt analyte loading in the pellet.

Electron paramagnetic resonance

Electron paramagnetic resonance (EPR) was performed using the NMR inserts as sample holders, ensuring that spectra for both techniques were collected on the identical sample. However, these spectra displayed a background arising from free radicals present in the Torlon® insert material. An alternative holder for EPR consisting of a 3.15 mm inner diameter FEP (fluorinated ethylene propylene copolymer) sleeve (Wilmad) that could be capped and sealed. This holder was subsequently used to obtain background-free spectra for comparison. In both cases, either the FEP tube or the NMR insert was subsequently inserted and sealed into a 5.0 mm outer diameter quartz screw-cap EPR tube (Wilmad), both as a second layer of containment and for compatibility with the Oxford Cryostat use in the experiments.



Figure 5. MAS-NMR tooling and sample holders (left) and final inserts for rotors (right)

DISCUSSION AND CONCLUSIONS

In all cases, several iterations of design and testing were necessary before an acceptable and radiologically durable sample holder for each analytical method was obtained. Dispersibility, adsorbed surface water content, radiation-hardness, and non-reactivity to sample materials needed to be considered for each material used in each holder. Because of the radioactivity of the samples, it generally took 3 to 5 times longer at each loading step (i.e., loading samples into holders and holders into instruments) than it would have required with non-radiological samples. This development process would have taken much longer if it were not for input and guidance provided by the radiation protection technicians, instrument scientists, sample environment support staff, and radioanalytical scientists who consulted and collaborated on this research.

ACKNOWLEDGMENTS

This work was supported by funding provided by the Federal Project Director of the Department of Energy (DOE) Waste Treatment & Immobilization Plant (WTP), under the direction of Dr. Albert Kruger. Additional funding was provided by DOE Offices of Nuclear Energy and Environmental Management through the Nuclear Energy University Program under the award DE-NE0008597.

A portion of this research was conducted at the Oak Ridge National Laboratory (ORNL) Spallation Neutron Source (SNS), proposals IPTS # 12371.1, 15451.1, and was sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. DOE. The authors greatly acknowledge the help of all the ORNL SNS staff, in particularly those associated with NOMAD beamline BL-1B, Jörg Neufeind, Mikhail Feygenson, and John Carruth. Portions of this work were supported by U.S. DOE, Basic Energy Sciences, Chemical Sciences, Biosciences, and Geosciences Division, Heavy Element Chemistry Program, and were performed at Lawrence Berkeley National Laboratory under Contract No. DE-AC02-05CH11231. Tc K-edge x-ray absorption spectra were obtained at the Stanford Synchrotron Radiation Lightsource (SSRL), SLAC National Accelerator Laboratory, which is supported by the U.S. DOE, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-76SF00515. This research used resources of the Advanced Photon Source (APS), a U.S. DOE Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. A portion of this research was performed using the Environmental Molecular Sciences Laboratory (Science theme # 48294), a DOE Office of Science User Facility sponsored by the Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory (PNNL). PNNL is operated by Battelle Memorial Institute for the U.S. DOE under contract DE-AC05-76RL01830.

We also thank Herman Cho, Andy Lipton, Vanessa Holfeltz, Gordon Thorogood, and many others for useful discussions. Also, we are significantly indebted to all the tool designers, engineers, and assemblers and radiological control technicians at all the facilities, without whom none of this work would have been accomplished.

REFERENCES

- 1 E. Segre and G. Seaborg, *Phys. Rev.* **54**, 772 (1938).
- 2 E. Deutsch, K. Libson, S. Jurisson and L.F. Lindoy, In *Progress in Inorganic Chemistry*, edited by S. J. Lippard, (John Wiley & Sons, Inc., 1983), pp. 75.
- 3 K. Schwochau, *Tchnetium: Chemistry and Radiopharmaceutical Applications*, (Wiley, 2000).
- 4 V.I. Spitsin, I.L. Rosenfeld, V.P. Persiantseva, N.N. Zamoshnikova and A.F. Kuzina, *Corrosion* **21**, 211 (1965).
- 5 T. Ishida and H. Mazaki, *Phys. Rev. B* **20**, 131 (1979).
- 6 I.R. Little-Marenin and S.J. Little, *Astronom. J.* **84**, 1374 (1979).
- 7 S. Goriely, In *Capture Gamma-Ray Spectroscopy and Related Topics*, edited, (World Scientific, 2013), pp. 326.
- 8 R.D.W. Kemmitt and R.D. Peacock, *The chemistry of manganese, technetium, and rhenium: Pergamon texts in inorganic chemistry*, (Pergamon Press, 1973).

- 9 M.C. Stennett, T.-H. Lee, D.J. Bailey, E.V. Johnstone, J. Heo and N.C. Hyatt, *MRS Adv.* **2**, 753 (2017).
- 10 D. Kim and A.A. Kruger, *J. Non-Cryst. Solids* **in press**, (2017).
- 11 C.Z. Soderquist, E.C. Buck, J.S. McCloy, M.J. Schweiger and A.A. Kruger, *J. Am. Ceram. Soc.* **99**, 3924 (2016).
- 12 J.J. Neeway, N.P. Qafoku, B.D. Williams, M.M.V. Snyder, C.F. Brown and E.M. Pierce, *Appl. Geochem.* **66**, 210 (2016).
- 13 W.W. Lukens, N. Magnani, T. Tyliczszak, C.I. Pearce and D.K. Shuh, *Environ. Sci. Technol.* **50**, 13160 (2016).
- 14 B.C. Childs, H. Braband, K. Lawler, D.S. Mast, L. Bigler, U. Stalder, P.M. Forster, K.R. Czerwinski, R. Alberto, A.P. Sattelberger and F. Poineau, *Inorg. Chem.* **55**, 10445 (2016).
- 15 D. Banerjee, D. Kim, M.J. Schweiger, A.A. Kruger and P.K. Thallapally, *Chem. Soc. Rev.* **45**, 2724 (2016).
- 16 I. Pegg, *J. Radioanal. Nucl. Chem.* **305**, 1 (2015).
- 17 S.A. Luksic, B.J. Riley, M. Schweiger and P. Hrma, *J. Nucl. Mater.* **466**, 526 (2015).
- 18 J. Weaver, C.Z. Soderquist, N.M. Washton, A.S. Lipton, P.L. Gassman, W.W. Lukens, A.A. Kruger, N.A. Wall and J.S. McCloy, *Inorg. Chem.* **56**, 2533 (2017).
- 19 J. Weaver, C. Soderquist, P. Gassman, E. Walter, W. Lukens and J.S. McCloy, *MRS Adv.* **2**, 525 (2017).
- 20 M.-S. Lee, W. Um, G. Wang, A.A. Kruger, W.W. Lukens, R. Rousseau and V.-A. Glezakou, *Nat. Commun.* **7**, 12067 (2016).
- 21 R.M. Asmussen, J.J. Neeway, A.R. Lawter, T.G. Levitskaia, W.W. Lukens and N.P. Qafoku, *J. Nucl. Mater.* **480**, 393 (2016).
- 22 J.O. Dickson, J.B. Harsh, W.W. Lukens and E.M. Pierce, *Chem. Geol.* **395**, 138 (2015).
- 23 C.Z. Soderquist, M.J. Schweiger, D.-S. Kim, W.W. Lukens and J.S. McCloy, *J. Nucl. Mater.* **449**, 173 (2014).
- 24 A.C. Buechele, D.A. McKeown, W.W. Lukens, D.K. Shuh and I.L. Pegg, *J. Nucl. Mater.* **429**, 159 (2012).
- 25 Nuclear Industry Workforce Getting Younger, Nuclear Energy Institute, www.nei.org (2015).
- 26 L.N. Squires, R.D. Mariani, T. Hartmann and J.R. Kennedy, *Adv. X-ray Anal.* **56**, 54 (2012).
- 27 P.L. Gassman, J.S. McCloy, C.Z. Soderquist and M.J. Schweiger, *J. Raman Spectros.* **45**, 139 (2014).