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Review

Review of multi-faceted morphologic signatures of actinide process materials for nuclear forensic science

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ABSTRACT

Particle morphology is an emerging signature that has the potential to identify the processing history of unknown nuclear materials. Using readily available scanning electron microscopes (SEM), the morphology of nearly any solid material can be measured within hours. Coupled with robust image analysis and classification methods, the morphological features can be quantified and support identification of the processing history of unknown nuclear materials. The viability of this signature depends on developing databases of morphological features, coupled with a rapid data analysis and accurate classification process. With developed reference methods, datasets, and throughputs, morphological analysis can be applied within days to (i) interdicted bulk nuclear materials (gram to kilogram quantities), and (ii) trace amounts of nuclear materials detected on swipes or environmental samples. This review aims to develop validated and verified analytical strategies for morphological analysis relevant to nuclear forensics.

1. Introduction

The microstructure and morphologies of nuclear materials have been studied since the 1960s [1]. In the decades that follow, most efforts focused on producing UO₂ with desirable densities for nuclear fuel in power reactors [2–5]. Many publications noted the physio-chemical connection between processing parameters, such as precipitation conditions, calcination temperature, and the starting material's composition to the resulting product's morphology. However, quantifying these features was the key limitation that prevented this signature from being used in nuclear forensics.

Unique morphological and microstructural features are found throughout the nuclear fuel cycle. The *first measurable uranium morphological signature* of process history is imparted following mining, extraction, and purification when uranium liquor is precipitated to compounds such as ammonium uranyl carbonate (AUC), ammonium diuranate (ADU), magnesium diuranate (MDU), sodium diuranate (SDU) and uranyl peroxide (UO₄) [6–9]. Calcination, or heating, removes water and oxygen from the precipitates, leaving behind an anhydrous uranium oxide including polymorphs of UO₃ or U₃O₈ [7,9, 10]. This calcination produces the *second measurable uranium morphological signature* while preserving features unique to the starting precipitate (i.e., AUC, UO₄, ADU, SDU, and MDU).

After calcination, the anhydrous U-oxide is fluorinated to uranium hexafluoride (UF₆) to enable enrichment of 235 U [6]. Fluorination removes the original morphological signatures. However, following enrichment, the product must be re-converted back to a U-oxide and is commonly reduced to the most common nuclear fuel, UO₂. UF₆ can be converted into UO₂ using dry or wet processing [11,12]. Both routes will yield the *third measurable uranium morphological signature*. This is often

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Received 21 July 2023; Received in revised form 10 October 2023; Accepted 11 October 2023 Available online 13 October 2023 0022-3115/© 2023 Elsevier B.V. All rights reserved. the final morphological signature prior to sintering of UO_2 into a fuel pellet for power production. It is possible that the sintered UO_2 fuel will retain microstructural signatures representative of the incoming UO_2 morphology; nonetheless, no studies have been published confirming correlations between the sintered fuel and the powdered UO_2 .

Like uranium, plutonium oxides have morphological signatures based on their precipitation and calcination history. The *first plutonium morphological signature* comes from its precipitation as plutonium peroxide, plutonium fluoride, or either the Pu^{II} or Pu^{IV} oxalate [13,14]. Subsequent calcination of the plutonium precipitates to PuO₂ yields the *second measurable plutonium morphological signature*. Like UO₂, it is possible that the sintered fuel retains microstructure features from the powdered PuO₂, but more research is needed to confirm this correlation.

As an alternative to oxide fuel production, the high purity uranium or plutonium-oxides can be converted to the metal *via* many processes, including electrochemical reduction [15], direct oxide reduction (DOR), or bomb reduction [9,13]. Once a metallic feedstock is acquired, metal processing may include further pyroprocessing, electrorefining, alloying *via* various casting methods, wrought processing, cold/hot rolling, or machining. Each process will yield *measurable morphological signatures* of the metal production history.

Once manufactured, uranium and plutonium metals are highly susceptible to corrosion through various mechanisms (hydrolysis, oxidation, and even hydriding). Their corrosion rates and products may be highly dependent on the starting metal itself, as well as the environmental conditions under which these materials are stored. These relationships provide *excellent opportunities for further measurable morphological signatures*.

Clearly, whether the product is an oxide, halide, or metal/alloy, unique morphological signatures can be incorporated based on the chemical and physical processing history. The purpose of this review is to document the most prominent morphological signatures to date and introduce best practices in SEM image collection as it relates to quantitative morphology. In addition, we discuss a set of data scientific approaches for quantifying particle morphology in SEM images including particle segmentation; supervised machine learning; unsupervised machine learning; and semi-supervised machine learning.

2. Identification of morphological signatures in uranium

2.1. Uranium oxides

Morphology has been used to characterize uranium oxides since the early work of Cordfunke et al. in the 1960s [1,16]. In these early studies, Cordfunke and Giessen noted that polymorphs of UO3 (alpha and amorphous) could be synthesized through the uranyl peroxide, and that each UO_3 had distinct morphologies [1]. Research for the next several decades continued to describe the morphological characteristics of U-oxides primarily as they related to uranium mining and nuclear fuels [17–24]. For example, Kim et al. performed a detailed evaluation of pH, ionic strength, reactant concentration, and reaction time on morphologies from uranyl peroxide [21], and Manna et al. probed the impact of using gaseous ammonia versus ammonium hydroxide on the morphologies of U-oxides from ADU [17]. Hence, it was well known that the UOC precipitation conditions would have a major impact on the morphology; despite this, it was the emergence of particle morphology in nuclear forensics investigations in the 2000s [25-32] that inspired the development morphology libraries and quantitative image processing [33].

In particular, an early use of morphology to support a nuclear forensics investigation in Australia noted that there was no quantitative data available to prove statistical significance [27]. In this case, the Australian Nuclear Science and Technology organization (ANSTO), assisted by Lawrence Livermore National Laboratory (LLNL), performed a detailed analysis of uranium powder recovered from a clandestine drug laboratory. The chemical and isotopic analysis revealed that the sample likely resulted from the Mary Kathleen Uranium Mine. Comparison of SEM images from the mine and unknown samples revealed similarity in grain size, but at high magnifications, different surface textures were observed that could not be quantitatively resolved between the two samples. These challenges in quantifying particle morphology were further chronicled in work by Plaue and Ho Mer Lin [34,35].

In 2019, Schwerdt et al. kickstarted the development of a uranium morphology library publishing a quantitative comparisons of the morphologies of UO_3 , U_3O_8 and UO_2 from UO_4 , ADU, AUC, MDU, and SDU (Fig. 1) [7]. Visually, the morphology of each processing route was distinct, and utilization of the particle segmentation and quantification software, Morphological Analysis of Materials (MAMA) [36], proved they were quantitatively different. With this baseline morphology established for U-oxides, research progressed to quantify how small differences (e.g., calcination temperature [37–39], production route [37], impurities [40,41], and solution thermodynamics [42]) could impact the final product morphology. Ultimately, while many factors can impact the morphology of the final products, the primary precipitation reaction used to produce the UOC is paramount. Other factors,



Fig. 1. Example morphological images UO_3 , U_3O_8 and UO_2 synthesized on the laboratory scale at the University of Utah. ADU = ammonium diuranate. AUC = ammonium uranyl carbonate. MDU = magnesium diuranate. SDU = sodium diuranate. UO_4 = uranyl peroxide (most commonly a schoepite phase is the precipitate). Full details on the synthetic conditions are available in Refs. [7, 38]. The image is reproduced from Ref. [102].

such as impurities, impart unique morphological features that can be traced to the inclusion of the anomaly [41]. Detection of these anomalies can further aid nuclear forensics investigations in identifying the processing history of unknown nuclear materials.

In the Australian nuclear forensics case, it is likely that the difference in observed morphologies had to do with how the samples aged. In a controlled laboratory study of aging U₃O₈ produced from ADU and AUC, different oxidation and hydration rates were observed, depending on the starting particle morphology [43]. In addition, an overall roughening of the surface features was observed that complicates the ability to perform quantitative assessments. An additional controlled laboratory aging study of amorphous UO3 found larger aging times, temperatures, and relative humidities caused particles sizes to increase and schoepite phases to form [44]. With further studies into aging mechanisms and their impacts on morphology, it will be possible to better relate real world samples to those produced in a controlled laboratory setting. In addition, further investigations are needed to understand the compounding impacts of different synthetic conditions, impurities, and aging. Despite these limitations, a solid foundation exists for justifying the use of morphology in future forensics investigations of uranium oxides.

2.2. Uranium fluorides

Uranium fluorides are encountered throughout various stages of the nuclear fuel cycle in the form of UF₄ from the hydrofluorination of UO₂; gaseous UF₆ generally from the fluorination of UF₄; and UO₂F₂ from the hydrolysis or deconversion of UF₆. Though these species are common in the nuclear fuel cycle, detailed investigations into the morphological signatures characteristic of these fluorides and their processing conditions have been limited. Early studies by Pickrell investigated the morphology of UF₆ hydrolysis products from gravimetric deposition in an aerosol chamber following the release of UF₆ into an airstream, concluding that increased relative humidity, concentration of UF₆, and growth time resulted in increased particle and agglomerate size [45,46]. In 2007, Kips reported similar observations from UF₆ hydrolysis reactions in a similar chamber and found well-separated, high-spherical particle shapes in high humidity hydrolysis conditions, and chainlike agglomerated particles in low humidity conditions [47]. A corresponding study in 2009 examined the morphology and fluorine composition of UO_2F_2 particles after 1 to 2 years of storage [48]. In 2015, Wagner et al. conducted an analogous morphologic study on the hydrolysis products of UF₆ deposited on carbon and aluminum conductive tape. The authors investigated the UF₆ and hydrolysis products under reduced pressure following introduction of ambient air into the storage vessel, and observed differing morphologies of the reaction products on the carbon versus aluminum tape [49].

In 2020, Cheng et al. used a scanning mobility particle sizer (SMPS) to investigate the growth-rate and size distribution of UO_2F_2 particles produced by gas-phase UF_6 hydrolysis in a custom-designed aerosol reactor with three extractive sampling ports along the column length. It was found that higher water molecule concentration produced greater numbered and larger UO_2F_2 particles. Further, one could precisely regulate the amount of water molecules to produce largely mono-dispersed particles [50]. In 2023, Jang et al. reported the particle size distribution of UO_2F_2 microspheres prepared in an autoclave using ammonium bifluoride and observed similar behaviors in the morphology and size-controlled particulates [51]. Other chemical degradation studies, though not primarily focused on morphology, have reported imagery of UO_2F_2 hydrates [52], UF_4 from stannous chloride and hydrofluoric acid precipitation [53,54], and commercially purchased anhydrous UF_4 [55,56].

2.3. Uranium metals

The synthetic preparation of U-metals was recently reviewed by Jang

et al. [57]. Briefly, U-metals are most commonly prepared through high temperature reactions (e.g., bomb reductions) using vacuum induction melting (VIM) into a mold or casting. Alternatively, U-metals can be prepared through electrochemical methods. Once made, the metals can be formed using rolling, deep drawing or swaging to achieve specific geometries, and impurities can be added to fine tune the properties of the metals. All of these process variables will impact the morphology of the final U-metal product.

For example, large castings often result in the formation of coarse, columnar grains that can be observed after macroetching the surface of the metal. Alterations to the grain structure can be achieved through heating between the α , β , and γ phases of the uranium. Athon et al. quantified how the morphological attributes of carbide inclusions varied as a function of metal cooling rate (Fig. 2) [58]. They observed a spectrum of spherical, faceted, acicular, rosette and dendritic shapes but in general, faster cooling rates resulted in finer carbide inclusions. Most recently, Olszta et al. monitored how carbide inclusion sizes and shapes incorporate, migrate, and transform during metal processing [59,60].

3. Identification of morphological signatures in plutonium

3.1. Plutonium oxides

While not as common as uranium oxides, plutonium oxides can be observed in the nuclear fuel cycle, primarily in feedstocks from reprocessing facilities which can be processed into standalone fuel or as mixed oxide fuel (MOX) for nuclear power. Despite being studied since the 1940's, there are still many unknowns regarding the Pu-oxygen system, and what has been published is often highly debated. The Pu oxygen system likely is comprised of four fundamental equilibrium phases [61]:

- 1 plutonium sesquioxide phases (Pu₂O₃),
- 2 hyperstoichiometric sesquioxide (PuO_{1.6+ δ}),
- 3 substoichiometric plutonium dioxide (PuO_{2-x}), and
- 4 stoichiometric plutonium dioxide (PuO₂).

Similar to U-oxides, the synthetic conditions used to make the various Pu oxides have a major impact on the morphology of the final product. In 1959, Francis and Sowden investigated the specific surface area and the particle sizes of PuO_2 prepared from Pu(IV) oxalate, nitrate, sulfate, iodate, and hydroxide [62]. For their oxalate reduction, Francis and Sowden calcined their oxalate at 500 °C. When heating the Pu oxalate from room temperature to 500 °C, they observed formation of a polymorph that could be broken down *via* grinding to a uniform distribution of particles. In contrast, they observed that placing the Pu-oxalate in a furnace already at 500 °C would decompose the oxalate and break up the polymorphs, presumably from the rapid escape of gases. The authors note that the microstructure of the PuO_2 is highly dependent on the preparation route of the Pu-oxalate and the calcination history [62]. The oxalate precipitation alone produced particles ranging from small and circular to large and square shaped.

Those initial observations by Francis and Sowden led to several additional studies qualitatively evaluating the impact of the synthetic conditions on the resulting PuO₂. Of note is a study by Doto and Peabody in which they were developing fuel pellets for the Fast Flux Test Facility [63]. In studying the Pu(IV) oxalate process, they evaluated the impact of the oxalate precipitation on the resulting PuO₂. They found that the rate of addition of oxalic acid and the concentration of the oxalic acid has a large impact on the resulting morphology. Too high of a concentration of oxalic acid would cause formation of numerous small crystals resulting in powders of high surface area, while low concentration of oxalic acid would result in incomplete precipitation and high filtrate loss. They expanded this study to evaluate the calcination temperature, time, and atmosphere on the production of PuO₂ in air yielded the



Fig. 2. SEM images of a polished U-metal surface showing different morphological features of carbide inclusions based on the processing conditions. This image is reproduced from Athon et al. [58].



Fig. 3. Representative images of PuO₂ produced using different precipitation and calcination conditions. Image is reproduced from Ref. [71] where there is also additional details on the synthetic conditions.

most complete reaction [63].

In 1984, Burney and Smith demonstrated that they could produce consistent PuO_2 particle sizes by extensively controlling the precipitation of the starting material, Pu(III) oxalate [64]. They calcined their Pu (III) oxalate at 735 °C for 2 h. in air. Likewise, they illustrated the impact of nitric acid concentration, Pu concentration, and oxalate concentration on the resulting morphology of PuO_2 [64]. Following these early studies, many additional articles were published over the next 20 years studying PuO_2 particle properties primarily for the production of mixed oxide (MOX) fuels [65–67].

In more recent years, a major design of experiment was developed to reevaluate processing conditions in the Pu oxalate system [68-70]. These studies focused on the impact of precipitation conditions during the conversion of plutonium nitrate to Pu(III) oxalate with subsequent conversion to PuO₂ (Fig. 3). 76 precipitations were carried out following a statistical design study that included plutonium concentration, nitric acid concentration, oxalic acid source, addition/digestion time, strike direction, and precipitation temperature as variables [71]. Several approaches have been applied to this data using feature distributions and outlines from MAMA-segmented and image textures with various inverse prediction models [70,72]. An alternative approach applied unsupervised machine learning for feature extraction and quantification from the PuO₂ particles, then simultaneously trained a model for parameter classification and clustering of similar particle morphologies [71]. The highest classification accuracies were seen for the oxalic acid source and strike direction parameters; the particle type distributions quantified from the clustering analysis showed which settings for each parameter resulted in more complex morphologies [71].

3.2. Plutonium metals

The synthetic preparation of Pu metal was reviewed by Clark et al. [13]. There are two main pyrochemical approaches to the preparation of Pu metal, reduction of halide (e.g., PuF4 and PuCl3) and oxide (e.g., PuO₂) compounds resulting from chemical separations. Their processing conditions are dictated by a need to produce pure Pu in high yield. Reduction of Pu compounds removes nonmetallic impurities (i.e., anion in the compound) from plutonium. Of these approaches, the direct reduction of oxide to metal has become the preferred route. Resulting metals can then be further purified through electrochemical processes such as molten-salt extraction (MSE) and electrorefining (ER). The purified Pu metal is often alloyed to stabilize the Pu delta phase followed by casting and forming processes such as rolling and machining operations. In operations at a production facility, we anticipate impurities from glovebox environments, pyrochemical process byproducts, and processing equipment such as crucibles. These impurities will be either trapped in the metal or form secondary phases. All of these process and chemical variables will influence the final morphology of the Pu metal product.

Unlike U-oxides, U-metals and even Pu-oxides, quantifying morphological features of Pu-metals is incredibly rare. While it is generally accepted that the processing parameters will impact the final Pu-metal morphology, much like that observed for the U-metals, the higher hazard of handling Pu coupled with its inclination to rapidly oxidize in the presence of any air or moisture, results in very limited facilities capable of handling these materials. Boehlert et al. published some of the early studies using an SEM with an electron backscatter diffraction detector (EBSD) [73,74]. To enable their analysis, they first used a scanning auger microprobe (SAM) to ion sputter the metal surface thus removing any existing oxidation layers. The samples were then vacuum transferred to the SEM, where they were able to probe the transformation behavior between the delta and epsilon phases. More recently, most studies have focused on three-dimensional analysis techniques for probing Pu metals to enable quantification of both the production and storage environments. These three-dimensional analyses are further described below.

4. Environmental swipe analysis

The U and Pu materials described above are focused on the analysis of bulk materials. This type of analysis is advantageous in a laboratory setting where the materials can be freshly prepared and analyzed with few limits on sample sizes. Collection of SEM micrographs from these bulk materials will surely aid in robust quantitative analysis as described below. These databases could also support the analysis of particles on environmental swipe samples; though additional research is needed, particularly in uncertainty quantification and out-of-distribution data analysis. Nonetheless, particle analysis is routinely applied on environmental swipe samples for materials accountancy at the International Atomic Energy Agency (IAEA)[75,76], and the extension of a bulk morphology library to environmental swipes could support the detection of undeclared nuclear activities.

Briefly, the environmental swipe program has been used by the IAEA for nearly 30 years [77]. Particles are collected on clean 10 \times 10 cm cotton swipes and sent for analysis within the IAEA Network of Analytical Laboratories (NWAL) [76]. Standard analysis includes radiation detection, x-ray fluorescence, SEM, and ultimately destructive analysis via mass spectrometry [78]. Unlike bulk particle analysis, there is often a limited number of particles observed on any given swipe. To concentrate the particles from the large cotton swipes onto an SEM stub, pieces of the original cotton swipe will be cut up and sonicated in an organic solvent such as heptane to suspend the particles in a liquid [76]. Centrifugation of the heptane suspension concentrates the particles enabling them to be pipetted and dried on an SEM stub [76]. Alternatively, vacuum impaction can be used to move particles from the swipe to an adhesive SEM stub [79] or when particles are concentrated in a smaller surface area such as a swipe from a hot cell, then an adhesive SEM stub can be used to collect samples directly from the swipe [76,80]. As discussed later, the preparation of samples for SEM analysis can impact the observed morphology.

5. Beyond two-dimensional morphological analysis

A great advantage of morphology analysis is the easy accessibility and non-destructive nature of using an SEM. This enables laboratories large and small to perform the analysis in a matter of hours. There are, however, situations where advanced analysis of morphological features is needed, and the following section highlights the potential of using focused ion beams and synchrotrons to support the analysis of particle morphologies.

5.1. Three-dimensional morphological analysis

Oftentimes, samples have been exposed to varying atmospheres which can alter the original morphology of the surface of interest. In efforts to probe both the original morphology and the storage atmospheres, three-dimensional morphological analysis is being performed. For example, Chung et al. characterized U and Pu metals using a focused ion beam scanning electron microscope (FIB-SEM) to build 3D morphologies that reveal entrapped morphological features within the bulk material (e.g., metal and oxides) and surface corrosion (oxide) layers that forms on metals [81]. Specifically, 3D microscopy enabled the acquisition of morphological features that cannot be measured using conventional 2D microscopy. As illustrated in Fig. 4, the 3D microscopy of a candidate Pu sample's internal morphology revealed the inclusion carbide phases, open pores, and Pu₆Fe. Building on these early results, Donald et al. was able to use FIB-SEM coupled with Auger Electron Spectroscopy (AES) to quantify oxide layers formed on Pu metal following storage in controlled atmospheres [82,83]. Hence, through 3D morphological analysis, source attributes and productions processes can be identified through the detection of impurity-based inclusions, and corresponding storage environments can be characterized through analysis of oxide layers.



Fig. 4. Example 3D microscopy within the bulk Pu metal, revealing detailed geometric and topological features related to processing. (A) Serial sectioning reveals microstructural features pinpointing the processing history; (b) 3D rendering shows detailed morphological variations within the bulk Pu. Red = carbide. Purple = Pore. Yellow = Pu_6Fe . Pu = transparent. Image is reproduced from Chung et al. [81].

5.2. Synchrotron morphological analysis

X-ray analysis from synchrotron-based sources can also be utilized to explore the chemical and molecular structure of an element of interest, using spectroscopic techniques, as well as the morphological distribution of these properties, using micro-focused spatially resolved spectroscopies. Synchrotron X-ray absorption spectroscopy (XAS) is highly sensitive to molecular structure around U, Pu, and impurities; it can also determine oxidation states, and can be monitored in bulk samples or applied to microscale particle mapping. EXAFS (Extended X-ray Absorption Fine Structure) spectroscopy is exquisitely sensitive to local molecular structure (i.e., distances, identities, and number of neighboring atoms) around metals and ions [84-86]. XANES (X-ray Absorption Near-Edge Structure) spectroscopy provides information on oxidation states and can be used to fingerprint the host phase. Both EXAFS and XANES can be measured from individual particles, and XANES is particular for chemical X-ray fluorescence imaging (XRF) [87–90]. In addition, the advances in utilizing High Energy Resolution Fluorescence Detection (HERFD) XANES optimizes the ability to map small changes between chemical states, such as variations in U and Pu oxidation state at the particle level [91]. Thus, the power of spatially resolved synchrotron techniques is to combine the imaging and spectroscopy to obtain a complimentary "chemical morphology" of sample particles with elemental and local structure information at the micrometer scale. An example of such efforts can be found in Pacold et al. where scanning transmission X-ray microscopy (STXM) was used to image and spectroscopically probe uranium particles [92].

The molecular structure around U, Pu, and impurity elements (e.g., Cl, Al, Cr, Fe, Ni, W, Zr), and their oxidation states transform during nuclear fuel synthesis and fabrication [87,93,94]. Each chemical processing step introduces another opportunity for the molecular environment around the U and Pu hosts to be altered (e.g., from fluoride to oxide form) and for impurities to be introduced or altered at the molecular scale, creating signatures that can be observed spectroscopically. These

molecular signatures provide a potential basis for identifying the origins of nuclear materials [95]. Thus far, studies utilizing the combination of these techniques have been limited to Pu- and U-contaminated environmental samples, rather than direct measurements of nuclear materials [87,96-100], although at least one study examined Pu in non-irradiated and irradiated MOX fuel samples [101]. In a study of soil samples from sites of B-52 bomber accidents involving nuclear weapons in Palomares, Spain and Thule, Greenland, morphology and elemental information from SEM-EDS analysis was complemented with μ-XAS, revealing the presence of U and Pu oxides [100]. In another study of actinide-contaminated sediments from a variety of locations, including the Hanford Site, Los Alamos, McGuire Air Force Base (Bomarc accident), Chernobyl and Mayak, the combined µ-XRF imaging/XAS approach showed the diversity of Pu and U local structures that may form. For samples from the Bomarc accident, where a missile carrying a nuclear warhead caught fire in 1960, the Pu and U distributions of two particles, indicated that one was a conglomerate of Pu-rich and U-rich oxide particles and the other was homogenized, suggesting that it was exposed to higher temperatures [87]. These results indicate that µ-XRF imaging/XAS may provide insight into the history of Pu and U materials via analysis of particles.

Although systematic studies of Pu in nuclear materials using μ -XRF imaging/XAS are not fully mature, a study of UO₂ fuel pellets [90] showed that there is an opportunity to apply these techniques to actinide materials processing, including Pu in addition to U. In that study, the distribution and local structure of impurities was also found to be valuable for providing processing history information. Indeed, impurities (e.g., Cl, Al, Cr, Fe, Ni, W, Zr), having different redox properties and/or occurring as reactor vessel erosion or corrosion products, can provide robust additional information not recovered from inspection of the major host phase element (Pu and U). However, because nuclear materials are generally considered to be 'pure' commercial products, the molecular structures around impurities have received little research attention. As a consequence, in spite of their tremendous potential for

use in forensics, trace molecular signatures remain underdeveloped in nuclear forensic science. Preliminary investigations show that combining spectroscopic and morphological analysis of impurities can provide signatures independent from the host phase that could be used to help identify corresponding chemical processes.

6. Collecting future morphological data for library development

Collectively, the studies reviewed above reveal that many processing conditions yield unique morphological features that can be readily probed, and have the potential to rapidly (within hours to days) reveal initial evidence into the process and storage histories of unknown nuclear materials. Confidence in the results relies on the data, and analytical procedures used to create the assessments. Generally, the data used to develop analytical methods and libraries should match future real-world data in its quality and diversity. Matching the quality and diversity of data is not only a task for current researchers; it also informs future procedures as best practices are discovered. Many lessons have already been learned to help the experimentalist collect data that most closely matches future real-world data and can be transferred amongst institutions and even individual instruments within institutions. Specifically, researchers have evaluated the data quality impacts of sample handling, imaging magnification, imaging detector, operator-chosen instrument settings, and instrument brands to reveal several useful tips for collecting SEM images that can be compared in a universal database [102].

One can taxonomize the lifecycle of an actinide into a "pre-possession" and "possession" phase – the first before the analytical team has control over the sample, the second while the analytical team has control. While many synthesis experiments and subsequent analyses have been performed in highly controlled settings with careful handling, during "pre-possession," rough handling and exposure to a variety of different atmospheres is to be expected. Therefore, highly controlled syntheses and analyses can be used to uncover chemical and physical mechanisms creating morphologies, but additional evaluations into the stability and lifetime of these morphological signatures is needed.

Starting at the "possession" stage, the analysis team has full control over a sample, and therefore sample preparation, imaging, and analysis processes can be highly specified, leading to best practices. It is beneficial to highly specify the sample preparation and imaging settings to extract the best signatures from each sample. Many mounting processes have been reported in the literature including the dusting of powdered materials onto the SEM stub [7], vacuum impaction [79], and the utilization of slurry mounts [14,76,103]. We have found that it is best to mount the sample using only a dusting of the particles onto the SEM

stubs, as this prevents any alternation of the existing morphology. Nonetheless, many laboratories have radioactivity limits for handling samples in electron microscopes and in those cases, slurry mounts from organic solvents can help reduce the mass and radioactivity of the sample on the SEM stubs [14]. Slurry mounting is a process of mixing a small quantity of powdered materials, usually a few mg, in a few milliliters of a volatile organic such as hexane or methanol. From this slurry, a few microliters can be pipetted onto an SEM stub thus resulting in a 1000-fold reduction in total mass on the SEM stub. While valuable from a radiation protection perspective, the slurry mounts do have the potential to alter the original morphology (Fig. 5), and more studies are needed to quantify these impacts.

With the samples mounted for SEM analysis, micrographs should be collected across a range of magnifications (ca. 10,000-100,000x). In a study by Nizinski et al. they found that the agglomeration of U₃O₈ particles produced from the AMEX and DAPEX processing of a U-ore results in unique morphologies [40]. Nonetheless, these agglomeration differences are only observed at lower magnifications. If the images had only been collected at only 100,000 magnification, then the materials would have appeared very similar, both being comprised of monodispersed particles that are well-rounded and somewhat spherical (Fig. 6). The reverse in also true. Ditcham et al. probed the morphology of UOCs from the Beverley, Ranger and Olympic Dam mines in Australia. At lower magnifications (30,000x), the morphologies appeared slightly different, but at 100,000x, the unique morphologies were readily visible [104]. Clearly, capturing SEM images that span low to high magnification is essential for reliably quantifying morphological features in nuclear forensics.

Similarly, it his highly beneficial to collect images using secondary electron (SE) and backscattered electron (BSE) detectors when available. SE imaging enables capturing more complex surface textures while BSE imaging is better at highlighting Z contrast (proton density) based on the material's elemental composition. For example, Fig. 7 shows a side-by-side comparison of materials processed through UO_2F_2 and imaged using both SE and BSE detectors [11]. The SE image revealed an abundance of surface texture. Nonetheless, the BSE image had a prominent dark spot which appeared to be an ordinary particle on the SE image. Further investigation of the dark region with energy dispersive spectroscopy (EDS) revealed a higher concentration of fluoride ions. Using both SE and BSE imaging, complementary results could be acquired to identify the morphology and inclusion of impurities which alter the morphology.



Fig. 5. Comparison of sample mounting procedures on the observed morphology (unpublished). Both images are from a washed UO_4 which was calcined to U_3O_8 then reduced to UO_2 . The sample on the left was dusted onto the SEM stub while the sample on the right was dispersed onto an SEM stub using an isopropyl alcohol (IPA) slurry. Both samples were imaged using the same SEM, magnification, and detector.



Fig. 6. Samples of U_3O_8 processed from a carnotite ore using either a DAPEX or AMEX process [40]. The U_3O_8 from both processing routes appears very similar at 100,000 magnification. Nonetheless, at 25,000 magnification, further clarity can be observed in discriminating the morphological uniqueness of the samples. This illustrates the importance of collecting SEM images at multiple magnifications.



Fig. 7. Comparison of SEM images collected using SE (a) and BSE (b) detectors. The BSE detector reveals a large dark spot that would not be visible using only SE imaging. Further characterization of the dark spot by EDS indicates this is an area of high fluoride concentration. Hence, BSE and SE imaging provide unique aspects into the morphology and collecting both can help reveal why some unique morphological features are observed. Image is modified from Ref. [11].

7. Robust quantitative analysis

Advanced data analysis and machine learning methods are key technologies for comparing and understanding what we know and what we can measure– about an unknown interdicted sample against a growing library of samples that have been collected with (and without) known process history. As we have observed, the immense variety, variation, and complexity of microstructural and morphological signatures associated with materials of interest poses a significant challenge. Extraneous variation must be reduced as much as possible through standards and protocols in sample collection, preparation, and measurement. Even under the best of circumstances, matching measurements from unknown samples to reference library measurements and/or predicting process history from measurements, with high level of confidence is a formidable undertaking.

The highly challenging task of attributing a sample to a process or entity requires an accurate and unbiased analytical methodology. In general, this task can be split into four components:

- a) Quantitative description of a given morphology.
- b) Option of fusion of additional data with the quantitative description.c) Inference of a property of the sample, given the quantitative description.
- d) Use of the inferred properties by an analyst.

Understanding morphological analysis in these terms allows the researcher to associate new developments with their location in the pipeline, and aids interoperability and the innovation of advanced techniques.

Developing unbiased and information-rich descriptions of images and image sets lies at the core of morphological analysis. The ideal quantitative description is *consistent* (i.e., it does not change between different analysts), *information-rich* (i.e., it captures all relevant information about the morphology), *inexpensive* (i.e., it requires little analyst intervention and feasible computational effort to compute) and characterizes the *associated uncertainty*. Despite recent advances, we are yet to see optimal representations and general-purpose methods that can meet all these criteria. Moreover, for nuclear forensics, the optimal representation must be understandable to a subject matter expert, as well as defensible through statistics and explainable in expert testimony.

In Fig. 8 we show some example images that span just some aspects of the morphological signature space. On the left, images exhibit distinct particles whose size and shape result from known physical and chemical processes that forensics experts use to determine process history. On the right, images have a more amorphous nature and physical structures that are hard to identify and describe, even by an expert. Real-world samples can be expected to lie somewhere between these two extremes. The overarching goal is to balance the use of both physical and statistical explanations. Four methods currently exist for performing this task (Fig. 9):

- a) User guided taxonomic description: a lexicon of qualitative descriptors was developed [105] and a set of best practices on how descriptors should be assigned. This lexicon increased the consistency with which descriptors were assigned and allowed for the discrete quantification of morphologies into a broader hierarchy. These descriptions are known to be inconsistent across analysts, and require an analyst to manually label images. The best practices were designed to be easily incorporated into the forensic expert's analysis workflow, and a prototype was implemented in the Morphological Analysis of MAterials (MAMA) analysis software [106]. This is an active area of research in the international nuclear forensics community, and we anticipate any advances to be similarly incorporated into the MAMA software.
- b) User guided segmentation: The particle size distribution is a revealing signature for particle provenance. Recognition of this fact motivated prior investments in user-guided image segmentation and quantification [107,108]. These tools enable the expert user to define and more easily delineate particles and other structures of interest within an image. This measurement, while interpretable by design, incurs a high analyst time-cost due to the laborious labeling, and only measures the outline of desired structures, providing no description of the surface of the particle.
- c) *Supervised segmentation:* Several researchers have created automated segmentation techniques to retrieve the benefits of User Guided Segmentation at a lower cost. Ly et al. worked towards detecting and

segmenting visual particles segmentation [109]. Ly et al. modified a neural network architecture called U-Net to better suit the characteristics of the uranium oxide SEM images. They applied the model to SEM images of U_3O_8 calcinated at different temperatures to obtain segmentations of fully visible particles and retrieved accurate outlines of particles for use in inference. While faster and less biased than User-Guided segmentation, automated segmentation still requires user-guided segmentation to create a training set, and, like user-guided segmentation, does not efficiently use all data in the image [110].

d) *Full image quantification*: Recent advances in machine learning and computer vision have enabled quantitative analysis of full images. These techniques, which use large training sets of images to learn optimal operations to quantify an image holistically, whether through hierarchical representations of image textures (as in convolutional neural networks) or full image feature mixing (as in visual transformers). Strong results exist for quantifying images with these methods, including using an autoencoder paradigm such as a vector-quantizing variational autoencoder from Pacific Northwest National Laboratory (PNNL) in Ref. [111], or using a supervised paradigm as in several convolutional neural networks created at the University of Utah in Ref. [112].

8. Optimal fusion of additional data

While image processing can create information rich descriptors of a sample's morphology, for each sample, there exist other data with information about its process and aging history. To make use of the other information, a process must be developed to fuse that data into the already quantified image data. In general, there are two disparate types of data fusion that can benefit quantitative analysis of samples, those of the same modality and those from other modalities.

Given the priority of SEM imagery for morphological signature characterization, there is a clear priority for the fusion of secondary electron SEM with backscattering SEM as we see in Fig. 8. As noted previously, backscattering imaging can reveal morphological characteristics not visible in secondary electron imaging. As we are collecting both in our imaging campaigns, we are well positioned for combining these analytically for a new morphological signature that can impact early in a nuclear forensic analytic timeline.

Because the highest costs in the analysis are incurred before imaging, usually the analyst receives more than one image, and within each image, there exists more than one particle from the given sample. These images may represent the same particles from the sample at different magnifications or imaging parameters or may include other particles from the sample. Therefore, the quantitative analysis of a single particle, or even a single image, does not fully describe the distribution of particles in the sample. This requires methods to combine these multiple particle representations into a holistic sample description.

In nuclear forensics, data is sparse in the sense that samples are expensive to create, so we are limited in the breadth of the sample types



Fig. 8. Morphological signatures manifest in a wide variety of different image features including particles, grains, and texture. Images are modified from Refs. [81,102].



Fig. 9. Morphological features can be realized using a suite of techniques including taxonomic descriptors, user guided segmentation, supervised segmentation, and full image quantification through supervised or unsupervised machine learning. The benefit of each technique depends on the features observed in the SEM images and the total number of images available for processing. For example, discrete particles are easy segment, but complex textures may be better processed through taxonomic descriptors and full image quantification. In addition, taxonomic descriptors are easily applied to a few images, but full image quantification with machine learning requires 1000's of images for training. Ideally, a combination of analysis techniques should be utilized to enable full quantification of the particle features. Images were modified from Refs. [39,109,112,115].

we can create in a given time. If we were to obtain samples from an unknown source, likely those samples are also limited in quantity. Ideally, we take advantage of all the information available on a sample. These can be as simple as the weight, volume, or substrate of the sample or may come from advanced analytical techniques, such as synchrotron analysis and other spectroscopic measurements. These provide information that may inform or augment the information in each image, and therefore an optimally information-rich representation would also include these findings. To fully exploit all the available information on small numbers of samples, this requires the development of fusion methods to combine all sample measurements from different modalities.

With a holistic quantitative description of a sample, methods to infer the properties, process history, aging, or provenance of a sample are then required. The inference step can be one of many tasks: previously studied tasks are: (1) the classification of a single image or particle to a given process history, (2) the efficient indexing and search of images by similar morphology, and (3) generating synthetic images to be indicative of other, unrealized process histories.

8.1. Classification

Ly et al. employed a linear classifier to determine calcination temperature of a given SEM of U_3O_8 using pixel area and perimeter of automatically segmented particles in that image as input [48]. Meanwhile, many works [31,52,53,57] utilized the powerful predictive capability of convolutional neural networks (CNNs) to directly discover relevant features captured in SEM images for discerning processing history, such as synthetic pathway, impurity, etc., without relying on hand-selected features of segmented particles. For instance, Ly et al. developed a multiple-input single-output (MISO) CNN-based model that takes as input 10,000x, 25,000x, 50,000x, and 100,000x magnification images of the same sample to perform classification [112]. As shown in Fig. 6, pairs of materials might be undistinguishable at one magnification but distinct at other magnifications. The MISO model captures all relevant features for classification without introducing user bias for magnification selection. In applying the MISO model to a 12-way classification problem (U_3O_8 , UO_3 , and UO_2 each from 4 different starting materials), they showed classification accuracies exceeding 96 %. Additionally, other work leveraged synthetic SEM images to further improve the classification perform of CNNs. Ly et al. developed a synthetic image generation framework that leverages SEM images from pure samples to artificially create images of mixed samples at various mixture ratios, which are then used to supervize the training of a mixture identification model [113].

While classification is a powerful method that can indicate the process history of common processing routes, statistical nuances exist. In a forensic setting, we anticipate that real-world samples could be different than those seen in a traditional lab. It is impossible to generate a classifier for all possible process histories. As a consequence, classifiers constructed for nuclear forensics have been tasked to classify 90 % of declared routes with 90 % accuracy. Other routes are directed to different methods of analysis. Classification has a known problem with over-confidence in predictions and under-performance on out-ofdistribution (OOD) data. OOD refers to the situation where the new observation is drawn from a different distribution than the system was trained on. To solve the over-confidence problem, work at PNNL provides calibrated probabilities to be associated with each supervised prediction. This allows an analyst to see not only the predicted synthetic route on a new image, but also the probability that the prediction is correct [114].

Recent work published in *Chemometrics* and *Intelligent Laboratory Systems* [102] implemented image classification models that were trained with uniformly-acquired SEM images of pure, unaged uranium oxides from different synthesis routes. The trained classifiers were then used to make predictions on micrographs that were out-of-distribution from the training dataset with respect to material process history (e.g., solution of precipitation, calcination conditions), data collection parameters (e.g., image scale, SEM used for imaging), or a combination of several factors to evaluate the extent to which these models were able to generalize OOD data. It was revealed that classifiers were sensitive to specific scanning electron microscopes and the beam voltages used to collect the images. Certain changes to material process history, such as aging in various atmospheres or chemical impurities, led to lower classification accuracies than other changes, such as the solution of precipitation. While classification is powerful, and speaks directly to desired forensic results, its drawbacks demonstrate the need for research and development of alternative inference approaches and analytic tasks.

8.2. Indexing and searching

Once micrographs are encoded into suitable feature vectors, they can be used in various downstream tasks. One of the most useful is *imagebased search*, and this enables the forensic expert to use a sample image as a query to find matches (or similar images) in a larger reference library. Image-based search is a valuable tool in the forensic analyst's toolbox, especially in the case of unseen morphologies, and has been explicitly requested by several end users. Looking forward, we expect that an image-based search capability could expand to include the full spectrum of quantification methods. Other analyses are also possible, such as change detection for aging studies, detection of specific oxides within mixed samples, and anomaly detection. A larger suite of machine learning techniques should be developed and leveraged for morphological analysis.

8.3. Synthetic data generation

The full space of possibilities for the creation of actinides is prohibitive to experimentally generate, and therefore it is impossible to create a comprehensive database for comparison of morphologies. While that is mitigated through some of the inference tasks above, such as classifying only those routes which are declared, and doing a closer inspection on any sample, not from those routes, there is also the possibility of creating synthetic data to close any gaps in extant databases. Work at PNNL has enabled the inclusion of physical models for enlarging the available dataset. Concretely, the outline of particles from a physically based Monte Carlo Potts model of UOC calcination can be used as input to a generative neural network to generate synthetic micrographs which have the appropriate particle size, shape, and distribution. This data has been shown to be helpful for training supervised segmentation model, especially in the low-data regime [58].

9. Conclusions

It is evident that unique morphological signatures can be imparted in U and Pu materials based on the chemical and physical processing histories. SEM analysis provides a rapid and readily accessible means to measure these morphological signatures. Statistical and computer vision techniques have enabled the characterization and use of these signatures in quantitative, verifiable, and validated interpretation pipelines. Analysis of impurities as well as oxidation and hydration can bring additional insights into the processing and storage histories. Developing morphology as a signature in nuclear forensics is best served through a partnership of experiment and data analysis methodological development. To be effective, we need morphological image libraries for unknown materials. Ideally for the support of robust, verified, and validated material identification methods, these libraries are as comprehensive as possible with quantifications through image segmentation, textural analysis, taxonomic descriptions, or full image quantification and including provenance of materials. While great strides have been made in the development of these libraries, these would ideally be created across the collaboration of many institutions. We offer a standardization of sample mounting procedures and imaging across a full range of magnifications (10,000–100,000) to foster the library development and support the data scientific tools being developed for analysis. It is our hope that this review helps to chart the path for future research and collaboration into the use of particle morphology to identify processing history of U and Pu materials.

CRediT authorship contribution statement

Luther W. McDonald: Conceptualization, Writing - original draft, Writing - review & editing, Funding acquisition. Kari Sentz: Conceptualization, Writing - original draft, Writing - review & editing, Funding acquisition. Alex Hagen: Conceptualization, Writing - original draft, Writing - review & editing, Funding acquisition. Brandon W. Chung: Conceptualization, Writing - original draft, Writing - review & editing, Funding acquisition. Cody A. Nizinski: Writing – original draft, Writing - review & editing. Ian J. Schwerdt: Writing - original draft, Writing review & editing. Alexa Hanson: Writing - original draft, Writing review & editing. Scott Donald: Writing - original draft, Writing - review & editing. Richard Clark: Writing - original draft, Writing - review & editing. Glenn Sjoden: Writing - original draft, Writing - review & editing. Reid Porter: Writing - original draft, Writing - review & editing. Matthew T. Athon: Writing - original draft, Writing - review & editing. Tolga Tasdizen: Writing - original draft, Writing - review & editing. Vincent Noel: Writing - original draft, Writing - review & editing. Samuel M. Webb: Writing - original draft, Writing - review & editing, Funding acquisition. Arjen Van Veelen: Writing - original draft, Writing - review & editing. Sarah M. Hickam: Writing - original draft, Writing - review & editing. Cuong Ly: Writing - original draft, Writing - review & editing.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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Data availability

Data will be made available on request.

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