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Characterization of the Internal Surfaces of Two Emptied 30A UF₆ Storage Cylinders

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MANAGED BY
MARTIN MARIETTA ENERGY SYSTEMS, INC.
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

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**CHARACTERIZATION OF THE INTERNAL SURFACES
OF TWO EMPTIED 30A UF₆ STORAGE CYLINDERS**

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for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-84OR21400

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ABBREVIATIONS AND ACRONYMS

ANSI	American National Standards Institute, Inc.
Ar	argon
C	carbon
CB	center back
CF	center front
cpm	counts per minute
cps	counts per second
Cs	cesium
CT	center top
Cu	copper
DOE	U.S. Department of Energy
EDXA	energy dispersive x-ray analysis
EB	end front (specimen mislabelled)
ET	end top
F	fluorine
Fe	iron
HAZWRAP	Hazardous Waste Remedial Actions Program
HP	Health Physics
IH	Industrial Hygiene
K-25 Site	Oak Ridge K-25 Site
m	meter
μm	micrometer
NDA	Non-Destructive Assay
Np	neptunium
O	oxygen
Pb	lead
ppm	parts per million
ppb	parts per billion
SEM	scanning electron microscope/microscopy
Tc	technetium
UF ₄	uranium tetrafluoride
UF ₆	uranium hexafluoride
XPS	x-ray photoelectron spectroscopy
XRD	x-ray diffraction
²³⁵ U	uranium-235
²³⁸ U	uranium-238

EXECUTIVE SUMMARY

The U.S. Department of Energy is currently involved in research and development of recycle efforts associated with all environmental restoration and cleanup activities. Among these activities are the decontaminating and decommissioning of facilities and scrap material no longer used or tracked for future needs. Among such materials at the Oak Ridge K-25 Site (K-25 Site) are excess Model 30A uranium hexafluoride (UF_6) cylinders. There are an estimated 700 empty 30A cylinders at the K-25 Site that have been designated scrap. These cylinders were used for storage and transportation of UF_6 from the early 1950s through the mid-1980s, with most of them having been put out of service in the mid-1970s.

The Offices of Environmental Restoration and Waste Management have formed a team to examine preliminary information necessary for recycling scrap cylinders. The Office of Environmental Restoration and the Office of Technology Development have provided guidance and funding for this effort to be carried out at the K-25 Site. Martin Marietta Energy Systems, Inc. (Energy Systems), personnel from the Hazardous Waste Remedial Actions Program, K-25 Technical and Program Support divisions have implemented activities for a radiological and materials analysis on two 30A UF_6 cylinders to determine and evaluate contaminants and residue that may exist in the cylinders.

Samples were cut out of the cylinders, and the internal surfaces were examined using nuclear spectroscopy, optical microscopy and standard metallographic techniques, scanning electron microscope/microscopy, energy dispersive x-ray analysis, x-ray photoelectron spectroscopy, and x-ray diffraction. Both cylinders contained significant amounts of uranium with 1–2% ^{235}U . There were indications of trace amounts of fission and transuranic products, but their presence could not be confirmed. Examination of the cylinders showed variations in internal scale thickness and morphology and surface chemistry between the cylinders, with one cylinder showing significant amounts of U-oxides uniformly distributed amidst a relatively thin Fe-oxide scale and the other showing a much thicker scale with pockets of green U-fluoride compounds in the recessed areas near the ends of the cylinder, which tend to be relatively harder to get cleaned. The differences between the cylinders suggest that the entire population of the cylinders cannot be characterized by the examination of a few samples and that a careful and thorough examination would be needed to provide a detailed and complete characterization of the internal surfaces of the cylinders.

The results did indicate that radiation meter surveys on external surfaces of the cylinders provide a fair idea of the extent of contamination and, combined with visual observations, may provide a rough method of separating the cylinders on the basis of expected internal contamination. In addition, within experimental limits, the contamination did not appear to penetrate the base metal and was restricted in the oxide layers, which varied from a thickness found in a new cylinder (up to 10 micrometers) to ten times that value. Decontamination could perhaps be achieved with an acid rinse which removes the scale layers. However, before removal of scale layers, a careful, higher resolution study of the scale/base metal interface area would have to be made to accurately ascertain the extent of penetration of contamination.

This information will help provide input for strategic decision making in economic benefits and cost that may be accounted for with recycling efforts. Various technologies can be evaluated and preselected based on understanding and basic knowledge of existing internal contaminants and their minimum and maximum concentrations. The results of this study will also provide metallurgical information for cylinders still in use at DOE's Portsmouth and Paducah sites. This information can provide guidance for the future storage, rinsing, and transportation of the cylinders for the Uranium Enrichment area.

CHARACTERIZATION OF THE INTERNAL SURFACES OF TWO EMPTIED 30A UF₆ STORAGE CYLINDERS*

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ABSTRACT

Before any cylinders used for storage of uranium hexafluoride (UF₆) can be decommissioned, all chemical and metallurgical changes that may have occurred in the cylinder walls during storage need to be well characterized and understood. However, there is little direct information available in this regard, and this study was conducted to obtain initial data on changes that may have occurred in cylinders because of long-term contact with UF₆.

Two 2.5-ton cylinders, which had been emptied of UF₆ and rinsed, were selected based on the extent of residual radioactivity, as judged from sweeps of a field survey meter over the outside surfaces of a batch of cylinders. A videoprobe was used to record the appearance of the internal surface of the selected cylinder. Sections of the cylinders representing various levels of residual radioactivity were cut out using a 6 in. diameter hole saw. These sections were further characterized by nuclear spectroscopy to identify the radionuclides present. Pieces were cut from the sections, mounted in taper section, and metallographically examined to characterize near-surface changes, including those resulting from surface corrosion from the moisture present in the washed cylinders. X-ray diffraction was used to further identify the various phases present, both in the corroded surface layers and in the immediate subsurface areas. Samples were examined using scanning electron microscopy and energy dispersive x-ray analysis to examine the morphology and chemical nature of surface residues relative to the various levels of residual radioactivity measured. X-ray photoelectron spectroscopy was used to examine the very-near surface layers. The results from the various techniques are discussed and compared to one another, and these results are interpreted in terms of their overall impact on decommissioning processes.

*Research sponsored by the U.S. Department of Energy, Office of Technology Development under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

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1. INTRODUCTION

The potential decontamination and recycling of uranium hexafluoride (UF_6) cylinders necessitates characterizing and understanding the nature and extent of contamination and resulting changes of the internal surfaces to permit safe handling for reuse or recycling. There is little radiological, chemical or microstructural information available on the state of internal surfaces of UF_6 cylinders. Further, the internal surfaces are not expected to be uniformly affected by UF_6 storage because of different local conditions: the bottom of the cylinders have a heavy concentration of nonvolatile daughter fission products, the general lower regions have intimate contact with solid UF_6 , and the upper regions are most exposed to the vapor phase. Therefore, one may expect different degrees of residual contamination and associated changes in various parts of the cylinder. A reasonably accurate microstructural/radiological map needs to be developed before cylinder reuse, recycle, or salvage. This study, the first ever of its nature, was undertaken to provide initial information of this type by examining samples cut out of two excess cylinders that had been emptied of UF_6 and rinsed. Areas of concern to be addressed included whether the rinsing process provided sufficient decontamination, the nature of contaminants left behind, and the extent of penetration of residual contamination into the cylinder surfaces.

The cylinders examined were model 30A cylinders, nominally 30 in. in diameter and 81 in. long, designed to hold 2.5 tons of UF_6 .^{*} A detailed history of the individual cylinders is not available. Approximately 700 empty cylinders and 200 cylinders containing UF_6 are stored at the Oak Ridge K-25 Site (K-25 Site) and were in use from the early 1950s through the mid-1980s, although most of them were put out of service in the mid-1970s. A large proportion of the cylinders were obtained from around 1951 to 1952 from government surplus and had been used previously as chlorine cylinders. These cylinders were cleaned, refitted with valves, and pressure tested before being put into UF_6 service. The cleaning process consisted of rinsing out the cylinders with small amounts of water (by rotating them on a horizontal axis) until the water rinsed clean. The cylinders were then steam dried and examined with a borescope before revalving and pressure testing. The cleaning process would typically be completed within an 8-h shift.

Most of the cylinders were used in lease service for supplying domestic and foreign commercial customers, typically shipping out with UF_6 and returning empty (except for residual heels). These cylinders would go through the cleaning process after every shipment, with one cylinder typically seeing 3-4 cleaning cycles in a year. This was done because the customers used oil-lubricated pumps to evacuate the cylinders, and oil contamination and possible reaction with UF_6 was always a possibility. Some of the cylinders were used at the K-25 Site for intraplant transportation of UF_6 normal feed material. This feed material could have contained various fission products including technetium (Tc)-99 from recycled U-oxide fuel from the Hanford Site. These cylinders were probably not cleaned except for the initial cleaning for conversion from chlorine service. In the early days, the 30A cylinders were

^{*}The historical information described here was provided by Ken Ziehlke, Bill Pryor, and Joe Dykstra, consultants, K-25 Site; and John Keith, K1066-J Cylinder Yard manager, K-25 Site. Some information on cylinder handling and cleaning can also be obtained from "Uranium Hexafluoride—Safe Handling, Processing and Transporting," Conference Proceedings, May 1988, edited by W. D. Strunk and S. G. Thornton, CONF-80558, Oak Ridge Gaseous Diffusion Plant, 1988.

probably used for storage of UF_6 tails (which was later refed). These cylinders may have stored the material for several years before being emptied and may have been cleaned 2–3 times in their service life. In addition, some of the cylinders stored at the K-25 Site do not belong to the U.S. Department of Energy (DOE), and these may have been used for other purposes, including storing reactor returns and normal UF_6 feed. Their history is unknown. The empty, rinsed cylinders are likely from the earliest batch of cylinders, initially used for chlorine service. These were decommissioned in the mid-1970s when a change in American National Standards Institute, Inc. (ANSI) specifications disallowed the use of cylinders that had been previously used for chlorine service.

2. EXPERIMENTAL DETAILS AND RESULTS

As described above, the UF_6 cylinders examined were chosen from previously filled 30A cylinders, which had been subsequently emptied and rinsed and stored in K1066-J yard. Initial screening of the cylinders was done by technicians of the Non-Destructive Assay (NDA) group of the Technical Division. An Eberline ESP general purpose radiation survey instrument with a sodium-iodide (NaI) detector was swept along the external surfaces of the cylinders to measure the count rate. A total of 17 cylinders in two rows were surveyed, and the results are presented in Table 1. The typical count rates measured were between 300–500 counts per second (cps), about the same as background levels in the area. One of the cylinders (No. 300071) showed an unusually high count rate (up to 2000 cps) and was selected for detailed examination. A second cylinder (No. 77252) with a count rate around 350 cps was also selected, with a third cylinder (No. 51363) having a count rate around 500 cps selected as a back-up. The measurements also showed that the count rates were not uniform around the cylinders, often tending to be higher on the heads and near the ends of the cylinders.

Before cutting samples out of the cylinders, the internal surfaces of the three selected cylinders were visually examined using a borescope attached to a video camera. The borescope was introduced through a rubber-stoppered hole originally containing the cylinder valve. A technician from Industrial Hygiene (IH) monitored the air in the immediate vicinity of the hole inside and outside the cylinder and did not detect any hydrogen fluoride (HF), indicating that no reactive products remained inside the cylinders. The borescope was sheathed in an aluminum tube to prevent possible contamination inside the cylinder. Figure 1 shows technicians recording the observations.

Cylinder 300071 showed large amounts of heavy scale, typically gray or brownish in color, and had significantly pitted areas. The scale had a layered appearance and seemed to have built-up over time. Cylinder 77252 was relatively clean with no evidence of built-up scale. The light brown surfaces seemed to be uniformly oxidized. The edge between the head and cylinder body was clearly visible, unlike in cylinder 300071. Cylinder 51363 had an appearance in between that of the two other cylinders. Heavy scale was present but looked more like large crystallites rather than the layered appearance in cylinder 300071. All three cylinders also appeared to be significantly wet, although no pools of water or other liquids were observed. This wetness was observed on the borescope sheath on withdrawal. Cylinder 300071 appeared to be the wettest, although this could not be confirmed. Videotapes of the observations are available for viewing.*

The borescope probe was surveyed by a Health Physics (HP) technician upon withdrawal from each cylinder and showed no contamination in each case, in spite of the probe often having had scraped against the internal surfaces during the observations. This probe indicated that no significant removable contamination was present in the cylinders.

Riggers used a forklift with a cylinder-lifting attachment (Fig. 2) to move cylinder 300071 to a clear location in K1066-J yard to minimize interference from background radiation, and the cylinder was again carefully surveyed radiologically by an NDA technician (Fig. 3) to identify the most desirable areas from which to obtain samples. The cylinder was surveyed at approximately a dozen points along its length at each of six different circumferential locations. A schematic of the results is shown in Fig. 4. The highest count

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rates were measured near the extreme ends of the cylinders. The count rates varied from a low of 530 cps to a high of 2200 cps, compared to a background of 230–260 cps. Based on these measurements, four locations were identified from which to cut coupons, as indicated in Fig. 4. These locations were the highest count region near the top end of the cylinder [specimen end top (ET)], halfway down the cylinder at the same end [specimen end front (EB) (specimen was mislabelled)], and two areas at the front and back near the center of the cylinder showing low (600 cps) and high count (1100 cps) specimens [center front (CF)] and [center back (CB)] respectively. Note that with respect to this study, "top" refers to the top of the cylinder in its stacked position, as opposed to the generally used definition of being the position corresponding to the valve location. As the cylinders were stacked, the valve plug was located at the 9 o'clock position in cylinder 300071 and at the 2 o'clock position in cylinder 77252.

The four locations were spectroscopically surveyed using gamma-ray spectroscopy to gain detailed information on the nature of the isotopic species inside the cylinder. In addition, neutron and gamma-ray quantitative measurements were used to estimate the amount of total U and U-235 (^{235}U) present in the cylinder. Figure 5 shows the quantitative measurements being performed, the results of which are shown in Table 2. The neutron measurements were made by placing the detector at two locations 18 in. from either end of the cylinder whereas the gamma-ray measurements were made with the detector in the center of the cylinder and at two other positions 12 in. from either end of the cylinder. The detector-to-cylinder distances corresponded to the optimum spacings for the two measurement methods. The neutron quantitative estimates were significantly higher than the estimates from the gamma-ray measurements. The neutron detector samples a larger volume than the gamma-ray detector, and it was felt that a significant amount of the difference in estimated U content could be explained because of overlap of sampled volume in the case of the neutron measurements and incomplete sampling in case of the gamma-ray measurements. A reasonable assumption, therefore, is that the U content can be approximated to be in between the two estimates (i.e., around 5500 grams or 12 lb). This suggests that the rinse process for cylinder 300071 was not highly efficient.

Six inch diameter coupons were then cut out of the four locations using hole saws. All cutting operations on the cylinders were done by personnel from the K-25 Site Maintenance Division. To control contamination, the cylinder was placed on a plastic sheet to catch debris from the cutting operation. Samples of scale material that fell off during the cutting operation were also collected. Two coupons were also cut out of the top of cylinder 77252 (10 o'clock position with respect to the valve), one at the end near the head (specimen ET) and the other near the middle of the cylinder length [specimen center top (CT)]. Cylinder 77252 was not moved from its storage position before cutting nor was any spectroscopy performed on the two locations of the cuts. The cutting operation was recorded on videotape and is available for viewing.* Figure 6 shows an example of a just-completed cutting operation.

HP surveys of the inside-facing surfaces of the six coupons from the two cylinders showed a high level of activity, with beta-gamma readings varying between 9000–750,000 cpm as listed in Table 3. These levels of contamination were significantly higher than measurements from outside surfaces of the cylinders had indicated. Gamma spectroscopy was used to examine the inside surfaces of the coupons to identify and quantify the radioisotopes present and compare the results with the external measurements. The results are summarized in Table 4. Both external measurements and measurements on the inside

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surfaces of the coupons from cylinder 300071 showed 1–2% ^{235}U in the samples. However, the external results are more closely grouped and do not show the same ranking as the inside surface measurements. The smaller range of values for the external measurements can be attributed to sampling adjoining areas of the cylinder during the measurements, which tended to average out the results. Signals for external measurements were significantly stronger than data from the individual coupons, again because larger sampling areas were available. Signals from coupons of cylinder 77252 were at or below the detection limits, as was coupon CF300071. The inside surface measurements ranked the ^{235}U content of the coupons in the same order as the HP measurements of activity (Table 3) except for reversing the order of CB300071 and ET300071 at the high end. The accuracy of the data is expected to be approximately $\pm 20\%$, with the external measurements being more accurate because of the stronger signal strength.

As shown in Table 4, small amounts of neptunium (Np)-237 and cesium (Cs)-137 [in parts per million (ppm) and parts per billion (ppb) respectively] were also detected in the external measurements and on some of the coupons of cylinder 300071, with generally good agreement between the two sets of measurements. Again, accuracy would be expected to be higher in the external measurements. Transuranic or fission products were not detected on the coupons from cylinder 77252, in agreement with the generally lower level of activity observed. However, this lack of detection could also be a result of the weaker signal from the coupons.

Figure 7 shows examples of the 6-in. circular coupons, most of which had a uniform brown/grey appearance, except for coupons ET300071 and EB300071 that had areas with green and white deposits on one side. In both cases, this side of the coupon was closest to the head of the cylinder. Coupons from cylinder 77252 [Figs. 7(d) and 7(e)] showed significantly less scale and fewer corrosion products than coupons from cylinder 300071 [Figs. 7(a), 7(b), and 7(c)], in agreement with earlier observations from the borescope video recordings.

Smaller samples for analysis by scanning electron microscope/microscopy (SEM), x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS) and metallography were cut out of the 6-in. circular coupons using a band saw. One set of samples was used from each large coupon except for ET300071 and EB300071. In these cases two sets of samples were examined (one from the "green" area and one from the remainder of the coupon). Each sample was numbered, and its position on the coupon documented (e.g., sample ET300071-1 refers to sample no. 1 cut from the green deposit area of coupon ET300071). Figure 8 is a set of macrographs of samples cut from the large coupons. Also included is a macrograph of a sample cut from a new 48-in. storage cylinder, which is made of a steel of chemical composition similar to that of the 30A cylinders (A 285 steel) but with a finer grain structure. As Fig. 8 shows, samples from cylinder 77252 are closer in appearance to the sample from the new cylinder than to the thick scale-covered samples from cylinder 300071.

Samples from each of the coupons were examined in an SEM equipped with an energy dispersive x-ray analysis (EDXA) unit, as shown in Fig. 9. SEM/EDXA observations showed sample areas with varying amounts of U on the surface as well as different morphologies of the scale layers. Figure 10(a) is a micrograph from sample ET300071-2, similar in appearance to the sample shown in Fig. 8(a), and Figs. 10(b) and 10(c) are U and iron (Fe) x-ray maps respectively of the area in Fig. 10(a). As can be seen, most of the viewing area is U-rich except for the particles right of the center in Fig. 10(a). These particles are low in U and are Fe-rich, indicating that they may be pieces of Fe-oxides. In other areas, however, U and Fe seem to be uniformly distributed. The green areas in coupon ET300071 were U-rich, as can be seen from the EDXA spectra shown in Figs. 11(a) and 11(b) obtained from the green deposit

area marked "a" and the brown scale area marked "b" in Fig. 8(a). The green material could be a uranium-fluorine (F) compound, but the presence or absence of F could not be confirmed in either of the areas, because while F could be detected by using the EDXA detector in the windowless mode, the F peak overlaps with Fe, and identification by EDXA is not possible.

In contrast, areas of the coupon ET300071 away from the green area showed a distinctly different surface morphology, as shown in Figs. 12(a) and 12(b) (sample ET300071-11). The deposit is powdery looking and is made up of relatively fine particles [see Fig. 12(b)]. The EDXA spectra in Fig. 13, obtained from the entire area of Fig. 12(a) shows a relatively low U concentration, implying that this area of the specimen is mainly covered with Fe-oxides.

Figure 14 shows SEM micrographs and x-ray maps from sample EB300071-3, which also showed green deposits [similar to Fig. 8(c)]. Figures 14(a) and 14(b) show that the scale layer appears to be a relatively smooth compaction of fine grains covered with a network of cracks. The x-ray maps show discrete U- and Fe-rich areas, but as Figs. 14(a) and 14(b) show, there appears to be no distinct morphological differences between these areas. In Fig. 14(b), for example, comparison with the x-ray maps shows that the top left-hand quadrant is significantly more U-rich than the rest of the micrograph. Yet the area looks similar to the adjoining U-poor areas, suggesting that scale composition cannot always be deduced by the appearance of the scale alone.

Figure 15(a), from sample EB300071-11 [similar to Fig. 8(d)] away from the green deposit shows a powdery scale layer somewhat similar to sample ET300071-11 (see Fig. 12). The EDXA spectra from this area, shown in Fig. 15(b) shows that any U present is below the detectable limits (about 1%).

Figures 16(a) and 16(b) show two areas from coupon CB300071. In Fig. 16(a) (sample CB300071-6) a powdery deposit is observed. EDXA spectra from this area showed no U. In contrast, the area seen in Fig. 16(b) (sample CB300071-10) is composed of more compacted and smoother areas. EDXA spectra from this area showed a moderate amount of U, similar to Fig. 11(b). However, U and Fe x-ray maps did not identify discrete Fe-rich or U-rich areas.

Figures 17(a) and 17(b) show two areas from specimen CF300071-3. Once again, the powdery deposit areas [Fig. 17(a)] showed no detectable U, whereas the more compacted deposits [Fig. 17(b)] had a moderate amount of well-distributed U.

Results from cylinder 77252 contrasted with the observations described above for cylinder 300071. Figures 18(a) and 18(b) from sample ET77252-4 show a powdery deposit similar to that seen on samples from cylinder 300071. However, unlike those cases where the EDXA spectra were essentially pure Fe, relatively large amounts of U were observed in these deposits. Figures 19(a) and 19(b) show EDXA spectra from the areas marked in Fig. 18(b). The particle in Fig. 18(b) has a relatively high U content whereas the underlying substrate is significantly more Fe-rich. Most of the particles showed similar spectra. The spectra in Fig. 19 also showed small amounts of copper (Cu) and several other elements which could not be conclusively identified. Possibilities include bismuth, cadmium, Cs, indium, polonium, antimony, tin, Tc, and tellurium, among others. Because of peak overlaps, an independent means of confirming their presence would be required, and time constraints did not permit the exploration of these possibilities.

A somewhat different morphology is seen in Fig. 20, from sample CT77252-4. Several areas of collections of needle-like crystallites like those seen covering most of Fig. 20 were observed on the sample. These areas were U-rich [Fig. 21(a)] and often adjacent to areas that were Fe-rich [Fig. 21(b)].

The relatively high U content seen in spectra from cylinder 77252, in spite of the relatively low activity (see Tables 2 and 3), are not surprising in light of the NDA measurements (see Table 4) that showed little or no ^{235}U in cylinder 77252 but a small but significant amount in cylinder 300071. Because the more active ^{235}U produces significantly more gamma radiation than U-238 (^{238}U), it is not surprising that HP measurements show more gamma activity in cylinder 300071 (because of the ^{235}U) whereas EDXA results show comparable, if not higher, U concentrations (mostly, if not all, ^{238}U) in cylinder 77252.

Samples of scale material that fell off during the cutting of the coupons were also examined in the SEM. Figure 22(a) shows needle-like crystallites seen on the surface, confirmed to be U compounds by the U x-ray map in Fig. 22(b) and the Fe x-ray map in Fig. 22(c). A detail of the area in Fig. 22(a) is shown in Fig. 22(d). The more equiaxed particle aggregates were found to be significantly more Fe-rich than the acicular crystals.

To examine the scale layers, samples from each of the coupons were metallographically mounted at an inclined angle as tapered cross-sections and polished and etched. The taper magnified distances in the thickness direction, making it easier to examine the scale, as shown schematically in Fig. 23. The samples were mounted at a taper angle of approximately 8° , giving a taper magnification of approximately 7:1. In other words, while viewing the samples along the taper, dimensions equivalent to those directly beneath the surface (in a "normal" cross section) were magnified by a factor of 7. Figures 24(a) and 24(b) show optical micrographs from coupons CT77252 and ET300071. The scale is significantly thicker in the latter case, although the thickness varied considerably. There are regions of CT77252 where the scale is very thin or even nonexistent. This difference between the cylinders was observed in all other samples and was consistent with visual and SEM observations. There were no significant differences in scale thickness between samples taken from the end of the cylinders (ET and EB) and samples taken from the middle of the cylinders (CB, CF, and CT). Figure 24(c) shows a micrograph from the coupon from the new 48-in. cylinder. A significant scale is also evident in this case. Measurement from optical micrographs showed that scale thickness varied between 5–100 micrometers (μm) for cylinder 300071 (typically around 30 μm) and 0–10 μm for cylinder 77252 and the new cylinder. The cleaning practices used on the 30A cylinders may have been responsible for forming or modifying scale deposits on the internal surfaces. The new 48-in. cylinder was not subjected to such vigorous cleaning but was exposed to water during hydrotesting and then air-blast dried.

The taper-sectioned samples were also examined in the SEM. The EDXA x-ray detector was used in the windowless mode to detect lighter elements—especially F and oxygen (O). However, F could not be identified because of overlap of the F peak with Fe L x-ray peaks, present in all areas of all samples.

Figure 25(a) shows a taper sectioned sample from coupon ET300071, from an area away from the green deposit and with a somewhat thinner scale. The darker contrast scale layer is clearly observable. The U x-ray map in Fig. 25(b) shows that U is fairly uniformly distributed throughout the thickness of the scale. However, this was not always the case. Figure 26 shows another example from the same sample along with U, O, and Fe x-ray maps. The entire scale clearly contains uniformly distributed O and Fe. However, the concentration of U is nonuniform in the scale and is at or below the detection limit in several areas. Sampling in the spot mode showed that U concentrations often dropped significantly as the Fe underlayer was approached; the reverse was never observed. U was not observed in the base metal layers.

Figure 27 shows a micrograph and an O x-ray map from a sample of coupon CF300071. No U was detected in the scale region, and the entire scale is evidently composed of oxides of

Fe. Examination of the scale area shows areas where the scale is evidently not as densely packed as other areas or where it is comprised of a conglomeration of fine particles. Similar observations were made in sectioned samples of CB300071 and EB300071.

Figure 28 shows an SEM micrograph and corresponding U x-ray map from coupon CT77252. Similar observations were made from coupon ET77252. The darker contrast scale layer seen in cylinder 300071 was not observed in cylinder 77252. The U x-ray map shows that U is distributed throughout the scale layer. However, sampling from various spots in the scale showed that U concentrations often dropped to below detection limits before the Fe underlayer was reached, as seen in samples from cylinder 300071. Unlike cylinder 300071, U was always observed in some part of the scale on coupons CT77252 and ET77252.

XPS analysis was used to more accurately examine the chemistry of the very-near surface layers. Since the sampling depth is a few atomic layers compared to several μm for the SEM/EDXA, the information obtained would complement the results described above. For XPS analysis, a small piece was cut out of each sample if the surface had been directly examined by SEM, with the remaining piece of the sample reserved for XRD. Figure 29 shows the samples being examined on the XPS instrument.

Samples ET-11, ET-2, CF-3, EB-3, CB-6 from cylinder 300071 and ET-4 and CT-4 from cylinder 77252 were examined, in addition to a sample from the new 48-in. cylinder. The new cylinder showed a surface chemistry of carbon (C) (probably from surface contamination), Fe, O, and small amounts of Cu and F. The source of F and Cu is unknown. All other samples showed C, Fe, O, F, and U. In addition, sample ET300071-2 showed a small amount of lead (Pb), and both samples from cylinder 77252 showed Cu. During SEM observations, Cu had also been observed in the EDXA spectra [see Figs. 19(a), 19(b), and 21(a)] but not Pb. Time constraints did not permit investigation for the source of these species. In each sample, the area examined was sequentially sputtered using an argon (Ar) ion gun for various intervals of time up to a total of 106 min. Periodic surveys of the sputtered area were taken to monitor the change in chemistry with depth into the scale layer. Sputtering is a relatively slow process, and the total amount of material removed was probably in the range of 0.1–0.5 μm , still well within the scale layer in all samples. The results of the depth profiles are shown in Table 5, where the concentrations are reported relative to Fe (direct quantitative composition estimates are not possible on the instrument used). Figure 30 shows the data plotted as a function of sputtering time for U, O, and F. In all cases, concentration decreases with depth, as would be expected as the Fe underlayer is approached. However, a significant amount of the elements is still present at the end of the sputtering, reflecting the relatively shallow layer of material removed. Highest U concentrations were consistently observed in the two samples from cylinder 77252 and sample EB300071-3. Fluorine concentrations were also the highest in sample EB300071-3 but were generally on the lower side in the two samples from cylinder 77252. There were no sharp differences in O concentrations, though in a few cases, surface O levels exceeded Fe concentrations. The high F in sample EB300071-3 may have come from the green deposit found in this area of the coupon. The deposit was also present on coupon ET300071-2, but XPS results did not show significantly more F than from the sample cut from an area away from the green deposit (sample ET300071-11). The relatively small XPS beam (about 1 mm square) may have sampled an area away from the green deposit in sample ET300071-2. Again, time constraints did not permit comparison of different areas of the sample.

All samples that had been examined in the SEM (see Figs. 10–18) were also examined by XRD to identify the compounds present on the internal surfaces. These were samples CF-3,

CB-6, CB-10, EB-3, EB-11, ET-2, and ET-11 from cylinder 300071 and samples ET-4 and CT-4 from cylinder 77252. The x-ray beam samples a roughly 1 in. square area to a depth of a few μm , so that a good average representation of the coupons would be obtained. Figure 31 shows a run being set up on the x-ray diffractometer.

Some difficulties were encountered in interpreting the data because of sample surface conditions, especially from samples of cylinder 300071. The rough, uneven scale gave rise to a significant amount of peak broadening and noise in the data, making identification difficult, especially since the diffraction patterns were fairly complex. Significantly better patterns were obtained from the smoother surfaces of cylinder 77252, and identification was relatively complete. To aid the identification process in samples of cylinder 300071, parts of the scale that appeared to be most representative of the sample (e.g., green deposit areas, if present) were scraped off and mounted on an aluminum slide. This more uniform distribution of particles produced a "cleaner" pattern, simplifying the identification process. In spite of this production of a "cleaner" pattern, questions about the patterns from cylinder 300071 could not be completely resolved. Figure 32 shows examples of diffractometer patterns from solid and powder samples from EB300071-3 and from the solid sample ET77252-4.

Table 6 lists the compounds identified in the various samples. The compounds are listed in the observed order of intensities, proportional to the relative concentrations in the irradiated area. All samples showed significant amounts of Fe-oxide/hydroxide compounds. In agreement with the other experimental observations, the oxides were often the predominant component in cylinder 300071 (thick scales) and the minor component in cylinder 77252 (thin scale). In cylinder 77252, although the predominant peaks are those of Fe from the underlying steel, a significant amount of U-oxides are present on the surfaces. In contrast, U-oxides could not be identified in most of the samples from cylinder 300071. Scrapings from samples EB300071-3 and ET300071-2, both with green deposits, showed evidence of hydrated uranium tetrafluoride (UF_4) salts. Uranium compounds could not be conclusively identified in the other samples from cylinder 300071. This lack of certainty supports to some extent the SEM/EDXA observations described earlier that not all areas of these samples showed U peaks. However, because the x-ray beam samples the entire area, any U compounds present should have been detected. The representation of U compounds in many of the unidentified diffraction peaks may be present because of the intermingling of U compounds to form intermediate phases. The data may be further convoluted because of peak shifts from sample surface conditions, as mentioned earlier.

3. DISCUSSION

The various analytical results described in Sect. 2 contain significant information that was unavailable before this study. Apart from general identification of substances one may expect to find on the internal surfaces of cleaned UF_6 cylinders, the results clearly demonstrated cylinder-to-cylinder differences, as well as differences depending on location within one cylinder. This is the kind of information needed before decisions on salvage/recycling operations can be made.

The two cylinders in this study showed differences in all aspects of the examination process. Compared to cylinder 300071, cylinder 77252 showed significantly lower radioactivity but a more uniform distribution (and probably greater amount) of residual U compounds, lower amounts of ^{235}U , and a cleaner looking surface with a thinner, more uniform oxide scale. In terms of all the cylinders initially surveyed, cylinder 77252, which had a count rate around 350 cps, appears to be more typical of the population because most of the cylinders gave a count rate of 300–500 cps on the survey meter. Cylinder 300071 was the only cylinder with a count rate greater than 1000 cps, and may be deemed to be a "worst case" example (one reason for choosing cylinder 370001 for the study).

The metallographic and SEM data also showed clear differences in the nature of the Fe-oxide scales formed on the internal surfaces of the two cylinders. The scale in cylinder 77252 was little different than that of the scale on the new cylinder, except for containing significant amounts of U-oxides. The scale in cylinder 300071 was often 10 times as thick as the thicker areas on the new cylinder. This indicates that significant corrosion/oxidation of the scale occurred in cylinder 300071. As described earlier, spot mode EDXA analysis in the scales of both cylinders showed that U content often decreased to below detectable limits before the underlying steel was reached. This area could probably be identified as the initial scale present on the cylinder when it was new. The more interesting observation was that in areas where U was detected in the scale, U concentration was always highest at the surface and decreased continuously from the surface into the underlayers. This is interesting especially with the thick scale in cylinder 300071. A reasonable assumption is that such a thick scale was not present in the cylinder when new and that significant oxidation had occurred. XRD data clearly showed that Fe-oxides were the major constituent of the scale in cylinder 300071. If the scale had grown because of uniform corrosion of the steel after the cylinder had been emptied and rinsed, either the residual U compounds should have been detected at some distance beneath the surface (if scale growth occurred at the surface) or there should have been a greater U-free area at the base of the scale (if oxidation and scale growth had occurred at the scale/base metal interface). Note also that all samples from cylinder 300071 also showed areas of thick U-free scale. This implies that discrete U-rich areas were present on the surfaces of the as-emptied cylinder, and the corrosion-induced growth of the scale occurred by incorporating the U, with the scale either growing through or around U-rich islands. Finally, it must also be noted that XPS data showed U in all samples examined. XPS is considerably more surface and concentration sensitive than EDXA, and the XPS observations indicate that small amounts of U are probably fairly uniformly distributed on the surfaces. However, only a relatively small area is analyzed, and the results from one analysis cannot be expected to be representative of the entire coupon. (For example, note that XPS results showed that the relative U concentration in sample ET300071-2 was among the lowest of all samples, contrary to all other results.)

The SEM observations also showed that it was not always possible to relate the major constituents of scale (whether mainly Fe-oxides or significant amounts of U) by its appearance. In cylinder 300071, scales with a powdery appearance were predominantly Fe-oxide whereas smoother, compact scales tended to be more U-rich (see Figs. 11–17). However, exceptions were observed, in which portions of the compact scales were found to be essentially Fe-oxides (see Fig. 14). In cylinder 77252, powdery looking scales contained both Fe and U. Although evaluation of the nature of a scale layer based on its appearance would be useful, these results suggest that such a judgment would not be generally possible.

Another SEM/EDXA observation with interesting implications was that in no case was U (or any other element apart from Fe) detected in the base metal beneath the scale layer. This shows that during the life of the cylinders, there was no significant diffusion or penetration of the cylinder contents into the steel container, although more sensitive XPS measurements at the interface may have shown some evidence of this. (Such measurements were not done because it would have taken an inordinately long time for the XPS instrument to sputter down from the surface to the scale/base metal interface. A special cross-sectioned XPS sample would have to be prepared.) Note that some of the coupons were cut from the top (as stacked) regions of the cylinders, corresponding to a 3 o'clock position for cylinder 300071 and a 10 o'clock position for cylinder 77252 if the valve were at the top—positions which would have had minimal or no contact with the solid cylinder contents during normal use. There were no significant differences in the distribution of U between coupons from the high position and those from lower areas of cylinder 300071 (corresponding to the bottom of the cylinder with respect to the valve position, regions in intimate contact with the cylinder's solid contents). Both coupons from cylinder 77252 were from the top region of the cylinder, yet showed significant amounts of U in the form of U-oxides. Higher activities had not been observed in other areas of the cylinder, suggesting that the residual contents of the cylinders were redistributed during the rinse operations. However, there is also evidence that UF_6 condenses on the steel surfaces from the vapor phase, and may, therefore, lead to a more uniform U distribution on the internal surfaces of the cylinder.

The observation that there appeared to be no significant U penetration into the base metal also has interesting implications from a decontamination and decommissioning viewpoint. Because U and other associated compounds were found to be restricted to the scale layer, effective decontamination would be achieved by the removal of the scale layer, which appeared to be typically around 10–25 μm (0.5–1 mil) thick and about 100 μm (4 mils) thick in the worst case. This could perhaps be achieved by an acid rinse. Note, however, that if such an approach is considered, a careful examination (perhaps by XPS) of the scale/base metal interface would have to be conducted in order to accurately ascertain that there is indeed no U penetration into the base metal (the current assessment is based on SEM/EDXA observations, which should be accurate for detecting about 1% U to within 2–3 μm of the base metal/scale interface).

Not all of the data could be clearly and completely interpreted. Even though cylinder 300071 gave much higher counts than cylinder 77252 at all locations, no U compounds (or those of other radioactive elements) could be identified in the XRD patterns from coupons from the center of the cylinder. SEM/EDXA data have shown areas in these coupons with no detectable U along with areas with moderate amounts of U. Uranium could possibly be contained in small amounts of U compounds distributed around the cylinder, contributing to the several unidentified XRD peaks from these samples, as described earlier. Many of the peaks partially matched the patterns of several U-oxide and U-fluoride compounds.

The XPS and EDXA data also need further corroboration, although the main results are clear and self-consistent. The sources for the small amounts of Pb and Cu observed in some of the samples were not confirmed nor were there positive identifications for some of the minor constituents detected by EDXA (e.g., see Fig. 19). The unidentified peaks seen in the XRD patterns could not be matched with compounds containing the possible elements in the EDXA spectra (see Figs. 19 and 21). EDXA also suggested that one of the unidentified peaks could be Tc, the existence of which is a possibility since at least some 30A cylinders were used for reactor recycles as well as normal UF_6 feed. However, it does not seem reasonable to expect levels of Tc that would show up on an EDXA spectrum (0.5–1%). A careful chemical analysis would be required to identify the minor constituents seen in the EDXA spectra. Technetium is a beta emitter and could not be detected during the gamma spectroscopy measurements.

The nuclear spectroscopy data estimated trace amounts of Np and Cs (in parts per million and parts per billion respectively). Neptunium was not detected by any of the other analytical techniques. Although Cs was a possibility in some of the EDXA spectra, independent confirmation is needed. In addition, for an element to be detected by EDXA, its concentration in the matrix must typically be at least a fraction of 1%—far from the ppb estimated by nuclear spectroscopy. Further, XPS analysis, which is far more sensitive than EDXA, did not pick up Cs in any of the samples. This indicates that to fine tune the identification process and completely identify all the minor constituents, a significant amount of careful analytical work will have to be done. The need to do this will have to be balanced against the extent of detail required for such information. One option is to exhaustively analyze one coupon from each cylinder.

Cylinder 300071 also showed distinct differences between various regions of the cylinder. The two coupons cut from near the end of the cylinder showed green deposits not observed in any of the other coupons. In both cases, the green areas were on the sides of the coupons closest to the end of the cylinder. The construction of the 30A cylinders leaves a significant circumferential crevice around the heads at either end of the cylinder. These recessed, partially protected areas would be more likely to retain cylinder contents after the rinsing operations. The initial radiation meter surveys showed that activity increased significantly towards each end of cylinder 300071 (see Fig. 4). Activity in other parts of the cylinder was also higher than in other cylinders. Evidently in this case, the rinsing operation was not thorough and left behind a significant amount of the cylinder contents.

The discussion in this document reflects the level of difficulty encountered in trying to characterize a population of cylinders based on the examination of one or two cylinders. As a general conclusion, the cylinders cannot be qualified based on the results of this study. A significant piece of information that is lacking is a history of the cylinders examined. Variability in case of cleaning may relate to cylinder history, number of use cycles, size and nature of the heel, and quality control associated with cleaning practices (i.e., who cleaned the cylinder). Efforts to obtain past-use data were unsuccessful, and available information suggested that all data were destroyed when the cylinders were removed from service. Such knowledge would have provided a means of fine tuning the analysis process. The significant differences between cylinders 300071 and 77252 in both visual appearance and surface chemistry support a conclusion that the two cylinders had disparate histories.

On the other hand, the relatively close agreement between external and inside-surface NDA measurements is encouraging. To a first approximation, measurements on external cylinder surfaces provide a means of separating cylinder populations based on levels of activity observed, since these measurements correlated well with the contamination levels observed

inside the cylinders (although the data are from only two cylinders). As explained earlier (see Table 1), the external count rate on cylinder 77252 was typical of the 17 cylinders surveyed, whereas that from cylinder 300071 was significantly higher, with the latter showing greater ^{235}U concentration. In addition, the external measurements on cylinder 300071 were also successful in identifying the more highly contaminated recessed areas near the heads at the ends of the cylinder.

The standby cylinder selected for this study, cylinder 51363, had an external count rate similar to cylinder 77252 (500 cps and 350 cps respectively). However, visual (borescope) observations on cylinder 51363, which was not examined further, showed a scale quite different from that on cylinder 77252, implying potential differences in chemistry/contamination. This indicates that the count rate alone is not enough to characterize the cylinder's contents and that further analysis needs to be performed. In other words, an external survey using a general-purpose radiation meter can give a gross idea as to the level and distribution of contamination in a cylinder, but detailed information can only be obtained by cutting the cylinder open. Note also that the accuracy of NDA measurements will degrade quickly with "cleaner" cylinders (such as cylinder 77252) as the signal strength approaches that of the background.

Using information from this study, a statistical sampling of the cylinder population would probably have to be made in order to ascertain the types and extent of contamination present in the emptied cylinders. Examination of the sampled cylinders would provide a data base of the residues present while also validating the extent to which external surveys could be used to separate and qualify cylinders. Such information could then be used to strike a balance between economic and technical considerations during decision-making processes.

4. SUMMARY AND CONCLUSIONS

The internal surfaces of two emptied 30A UF₆ cylinders were examined in detail in terms of surface appearance, scale morphology, and surface chemistry with the goal of establishing the level of contamination in the cylinders and evaluating the feasibility of using the data to characterize a larger population of cylinders.

The results indicate that the cylinders contained significant amounts of residual U with 1–2% ²³⁵U, as estimated using nuclear spectroscopy. The amount of total U in one of the cylinders (cylinder 300071) was estimated to be on the order of 5500 g (12 lb). External surveys using a general purpose radiation meter were able to successfully separate the cylinders in order of internal contamination and to identify areas with differing levels of contamination within a particular cylinder.

Coupons were cut from the cylinders and the internal surfaces were examined in detail, using XPS, SEM/EDXA, and XRD. These results showed variations in scale thickness and morphology and surface chemistry between the cylinders. Cylinder 77252 showed significant amounts of U-oxides uniformly distributed amidst a relatively thin Fe-oxide scale. Cylinder 300071 showed a much thicker scale with pockets of green U-F compounds in the recessed areas near the ends of the cylinder, suggesting that the rinse operation had not been thorough. Although scale morphology could often be associated with its major constituents (Fe and/or U), there were enough deviations that an appearance-based scale identification process was not possible. The thick scale observed in cylinder 300071 suggested that significant oxidation may have occurred after the cylinders were put out of service, an idea supported by borescope observations that the insides of the cylinders were wet.

To the limits of SEM/EDXA measurements (0.5–1% in concentration and 2–3 μm spatial resolution), U was found to be restricted in the internal scale layers, which varied from a thickness found in a new cylinder (up to 10 μm) to ten times that value. For decontamination purposes, removing the scale layer, perhaps with an acid rinse, may be enough. Before this, a careful, higher resolution study of the scale/base metal interface area (perhaps by XPS) would have to be made to accurately ascertain the extent of contamination.

There was no independent confirmation of the presence of small levels of Np and Cs that had been observed by nuclear spectroscopy, nor was there any confirmation for the presence of Tc, the possible existence of which was indicated in EDXA spectra.

Careful and thorough examination of a few small samples would be needed to provide a detailed and complete characterization of the internal surfaces of the cylinders. External NDA measurements combined with visual observations may provide a grossly accurate means of separating the cylinders on the basis of expected internal contamination. This statement needs to be confirmed by developing a data base of observations of the type described in this report, and it suggests that a compromise may have to be reached between economic and technical considerations before qualifying cylinders for salvage or reuse.

5. ACKNOWLEDGMENTS

The contributions of those people who made the completion of this project possible, are greatly appreciated. They include Bill Davis, who assisted with borescope observations; Gerry Marsh, who assisted with metallography; Dr. Bob Stephenson and Dianna Vail, who set up and ran the XRD experiments; James Harrison, who performed the XPS experiments; Dr. Ron Brandenburg of the NDA group, who arranged for the nuclear spectroscopy measurements and analyzed the results; and Jackie Harris and Sondra Bush, who performed NDA measurements. Finally, thanks also to Ken Ziehlke, who provided a wealth of useful historical and processing information and reviewed this manuscript.

FIGURES

Fig. 1. Technicians recording the view inside an empty 30A UF₆ cylinder using a borescope and a video recorder. At the stage shown, the plug at the end of the cylinder has been removed, the air sampled and passed by Industrial Hygiene and Health Physics personnel, and the probe has been inserted into the cylinder.

KAMET93-00176

Fig. 2. Forklift with cylinder lifting attachment moving cylinder 300071 to a clear area in 1066-J yard for Non-Destructive Assay measurements and cutting of coupons.

K/MET93-00186

Fig. 3. Non-Destructive Assay technician conducting an external radiological survey on cylinder 300071 using an Eberline ESP survey instrument.

Fig. 4. Results of a survey on cylinder 300071 using a hand-held radiation meter, showing radiological activity (in cps) observed at various locations. The cylinder is shown schematically in elevation in its storage position with the cylinder valve hole in the 9 o'clock position. Numbers in parenthesis refer to areas on the rear of the cylinder. Locations from where coupons were cut are marked "ET," "EB," "CF," and "CB."

Fig. 5. Non-Destructive Assay technician conducting external quantitative gamma spectroscopy measurements on cylinder 300071.

K/MET93-00207

Fig. 6. A just-completed hole saw cut. The coupon is contained within the hole saw blade.

K/PH93-6693

Fig. 7(a). Photographs of 6 in. diameter coupons immediately after cutting operation. Note the green deposits on samples ET300071 and EB300071. In both cases the edges with the green deposits were closest to the end of the cylinder.

K/MET93-00211

Fig. 7(b). Photographs of 6-in. diameter coupons immediately after cutting operation. (Continued)

Fig. 7(c). Photographs of 6 in. diameter coupons immediately after cutting operation. (Continued)

Fig. 7(d). Photographs of 6 in. diameter coupons immediately after cutting operation. (Continued)

KMET93-00214

Fig. 7(e). Photographs of 6 in. diameter coupons immediately after cutting operation. (Continued)

(a)

(b)

Fig. 8. Micrographs of samples cut from the 6 in. diameter coupons. For coupons ET300071 and EB300071, samples were cut from both the green deposit areas and from areas without the deposit. Coupons are identified by the following: (a) ET300071-3, (b) ET300071-12, (c) EB300071-2, (d) EB300071-10, (e) CB300071-9, (f) CF300071-5, (g) ET77252-3, (h) CT77252-5, and (i) new cylinder.

(c)

(d)

Fig. 8. Micrographs of samples cut from the 6 in. diameter coupons. For coupons ET300071 and EB300071, samples were cut from both the green deposit areas and from areas without the deposit. Coupons are identified by the following: (a) ET300071-3, (b) ET300071-12, (c) EB300071-2, (d) EB300071-10, (e) CB300071-9, (f) CF300071-5, (g) ET77252-3, (h) CT77252-5, and (i) new cylinder. (Continued)

(e)

(f)

Fig. 8. Micrographs of samples cut from the 6 in. diameter coupons. For coupons ET300071 and EB300071, samples were cut from both the green deposit areas and from areas without the deposit. Coupons are identified by the following: (a) ET300071-3, (b) ET300071-12, (c) EB300071-2, (d) EB300071-10, (e) CB300071-9, (f) CF300071-5, (g) ET77252-3, (h) CT77252-5, and (i) new cylinder. (Continued)

(g)

(h)

Fig. 8. Micrographs of samples cut from the 6 in. diameter coupons. For coupons ET300071 and EB300071, samples were cut from both the green deposit areas and from areas without the deposit. Coupons are identified by the following: (a) ET300071-3, (b) ET300071-12, (c) EB300071-2, (d) EB300071-10, (e) CB300071-9, (f) CF300071-5, (g) ET77252-3, (h) CT77252-5, and (i) new cylinder. (Continued)

(i)

Fig. 8. Micrographs of samples cut from the 6 in. diameter coupons. For coupons ET300071 and EB300071, samples were cut from both the green deposit areas and from areas without the deposit. Coupons are identified by the following: (a) ET300071-3, (b) ET300071-12, (c) EB300071-2, (d) EB300071-10, (e) CB300071-9, (f) CF300071-5, (g) ET77252-3, (h) CT77252-5, and (i) new cylinder. (Continued)

KMET93-00514

Fig. 9. Samples being examined on the SEM/EDXA instrument.

(a)

(b)

(c)

Fig. 10. (a) Secondary electron (SE) image from sample ET300071-2 showing surface morphology and loose Fe-oxide particles with corresponding (b) U x-ray map and (c) FE x-ray map.

Fig. 11. EDXA spectra obtained from (a) area of green deposit, marked "a" in Fig. 8(a) and (b), area marked "b" in Fig. 8(a).

Fig. 12. SE image of sample ET300071-11, away from the green deposit on the coupon, showing a different surface morphology; (b) is a higher magnification of the area marked in (a).

Fig. 13. EDXA spectrum obtained from the area shown in Fig. 12(a).

Fig. 14. (a) Area of sample EB300071-3 (with green deposit) showing a smooth, compacted scale layer covered with cracks (SE image); (b) detail of area marked in (a); (c) uranium x-ray map of area shown in (a); (d) iron (Fe) x-ray map of area shown in (a).

(c)

(d)

Fig. 14. (a) Area of sample EB300071-3 (with green deposit) showing a smooth, compacted scale layer covered with cracks (SE image); (b) detail of area marked in (a); (c) uranium x-ray map of area shown in (a); (d) iron (Fe) x-ray map of area shown in (a). (Continued)

Fig. 15. (a) Area of sample EB300071-11 (away from green deposit) showing a powdery scale (SE image); (b) EDXA spectrum obtained from (a).

(a)

(b)

Fig. 16. SE images from two areas from coupon CB300071 showing (a) powdery scale in sample CB300071-6, which had no detectable U, and (b) relatively compact scale from sample CB300071-10 with moderate amounts of U.

Fig. 17. SE images from two areas from sample CF300071-3 showing (a) powdery scale with no detectable U and (b) relatively compact scale with moderate amounts of U.

Fig. 18. SE image from sample ET77252-4 showing a powdery surface deposit; (b) is a higher magnification of the area shown in (a).

(a)

(b)

Fig. 19. (a) and (b) EDXA spectra from the upper and lower boxes respectively marked in Fig. 18(b).

Fig. 20. SE image from specimen CT77252-4 showing U-rich needle-like crystallites.

(a)

(b)

Fig. 21. (a) and (b) EDXA spectra from spots marked 1 and 2 respectively in Fig. 20.

Fig. 22. (a) SE image of sample of loose scale from cylinder 300071, collected during the cutting operation; (b) and (c) uranium and Fe x-ray maps respectively of (a); (d) higher magnification of area marked in (a).

(c)

(d)

Fig. 22. (a) SE image of sample of loose scale from cylinder 300071, collected during the cutting operation; (b) and (c) U and Fe x-ray maps respectively of (a); (d) higher magnification of area marked in (a). (Continued)

Fig. 23. Schematic showing the geometry of a taper-sectioned sample. Note how the scale thickness is magnified on the taper compared to a "normal" perpendicular cross section (by a factor of 7 for the 8° taper angle used).

Fig. 24. Optical micrographs from taper-sectioned samples showing scale layers: (a) CT77252, (b) ET300071, and (c) new cylinder. Note that the scale bar in the vertical direction (along the taper) represents one-seventh the dimensions shown for the horizontal direction.

Fig. 24. Optical micrographs from taper-sectioned samples showing scale layers: (a) CT77252, (b) ET300071, and (c) new cylinder. Note that the scale bar in the vertical direction (along the taper) represents one-seventh the dimensions shown for the horizontal direction. (Continued)

Fig. 25. (a) SE image of taper-sectioned sample ET300071 (away from green deposit area) showing darker contrast scale layer; (b) U x-ray map of (a). Note that the scale bar in the vertical direction (along the taper) represents one-seventh the dimensions shown for the horizontal direction.

Fig. 26. (a) Another area from sample ET300071; (b), (c), and (d) U, O, and Fe x-ray maps of (a). Note that the scale bar in the vertical direction (along the taper) represents one-seventh the dimensions shown for the horizontal direction.

(c)

(d)

Fig. 26. (a) Another area from sample ET300071; (b), (c), and (d) U, O, and Fe x-ray maps of (a). Note that the scale bar in the vertical direction (along the taper) represents one-seventh the dimensions shown for the horizontal direction. (Continued)

Fig. 27. (a) Se image from taper-sectioned sample CF300071 with (b) oxygen (O) x-ray map of (a). Note that the scale bar in the vertical direction (along the taper) represents one-seventh the dimensions shown for the horizontal direction.

Fig. 28. (a) SE image from sample CT77252. Note absence of darker contrast scale; **(b)** uranium x-ray map of (a). Note that the scale bar in the vertical direction (along the taper) represents one-seventh the dimensions shown for the horizontal direction.

Fig. 29. Samples being examined on the XPS instrument.

Fig. 30. XPS depth profiles showing change in concentration (relative to Fe) of (a) U, (b) O, and (c) fluorine (F) as a function of sputtering time.

Fig. 31. X-ray diffractometer being set up for a scan.

Fig. 32. X-ray diffractometer patterns obtained from (a) EB300071-3, solid sample; (b) EB300071-3, powder scraped from scale; and (c) ET77252-4, solid sample. Note the large number of unidentified peaks in traces from solid sample EB300071-3. The large aluminum (Al) peaks in (b) are from the Al substrate on which the scraped powder was mounted.

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TABLES

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Table 1. Results of radiation meter surveys on external surfaces of 17 empty 30A UF₆ cylinders in K1066-J yard

Cylinder no.	Row	Position	Count rate (cps)
A404	G	Bottom	500
24265	G	Bottom	500
39394	G	Bottom	450
26831	G	Bottom	400
37198	G	Bottom	500
51363	G	Top	500
25051	G	Top	500
30798	G	Top	500
?	G	Top	500
31191	G	Top	750
300071	D	Bottom	2000
23168	D	Bottom	300
3750	D	Bottom	250
25549	D	Bottom	450
77252	D	Top	350
78506	D	Top	600
A1495	D	Top	300
Background	—	—	300–500

Table 2. Neutron and gamma spectroscopy estimates of the U content of cylinder 300071 from measurements on the external cylinder surface

	Position	U (g)	²³⁵ U (g)	Enrichment (%)
Neutron	1	7080 ± 1630	119 ± 27	
	2	2560 ± 1520	43 ± 26	
	Total	9640	162	
Gamma	1	563.5 ± 16.9	15.5 ± 0.2	2.75
	2	363.3 ± 16.3	9.3 ± 0.17	2.56
	3	346.4 ± 16.3	11.4 ± 0.22	3.29
	Total	1273.2	36.2	2.84

Table 3. Results of Health Physics surveys on coupons cut from cylinders

Coupon no.	Beta-gamma reading (cpm)
CB300071	212,105
CF300071	45,240
EB300071	361,495
ET300071	732,550
ET77252	10,720
CT77252	9,110
Scale sample	218,755

Table 4. Results of gamma spectroscopy on external and internal surfaces of cylinders 300071 and 77252

Coupon/position	% ²³⁵ U	Np/Total U	Cs/Total U
<i>External measurements (before cutting)</i>			
ET300071	1.61	6.14×10^{-6}	13.36×10^{-10}
EB300071	1.76	4.35×10^{-6}	13.9×10^{-10}
CB300071	1.6	7.21×10^{-6}	3.98×10^{-10}
CF300071	1.75	1.76×10^{-6}	5.3×10^{-10}
<i>Measurements on individual coupons</i>			
ET300071	1.47	7.16×10^{-6}	3.63×10^{-10}
EB300071	1.18	1.07×10^{-6}	1.92×10^{-10}
CB300071	2.09	2.75×10^{-6}	15.55×10^{-10}
CF300071	1.07 ^a	<i>b</i>	1.35×10^{-10a}
ET77252	1.07 ^a	<i>b</i>	1.25×10^{-10a}
CT77252	<i>b</i>	<i>b</i>	<i>b</i>

^aInstrument at detection limit.^bBelow detection limits.

Table 5. Results from XPS depth profiles on coupons from cylinders 300071 and 77252.
Element concentrations are relative to that of Fe (Fe = 1)

Sample no.	Sputter time (min)	C/Fe	O/Fe	F/Fe	U/Fe	Pb/Fe	Cu/Fe
ET300071-11	0	0.688	3.267	0.585	0.445		
	1	0.105	0.82	0.157	0.12		
	16	0.034	0.551	0.144	0.069		
	46	0.026	0.494	0.125	0.029		
	106	0.011	0.457	0.113	0.04		
CF300071-3	0	0.153	1.134	0.125	0.467		
	1	0.051	0.775	0.109	0.3		
	16	0.015	0.646	0.096	0.333		
	46	0.016	0.59	0.097	0.319		
	106	0.009	0.551	0.09	0.285		
EB300071-3	0	0.196	0.704	1.34	1.724		
	1	0.076	0.436	0.09	1.129		
	16	0.029	0.33	0.594	0.877		
	46	0.024	0.345	0.543	0.909		
	106	0.018	0.345	0.528	0.951		
ET300071-2	0	0.228	0.844	0.271	0.408	0.081	
	1	0.081	0.487	0.208	0.286	0.056	
	16	0.034	0.384	0.161	0.255	0.037	
	46	0.022	0.327	0.136	0.211	0.031	
	106	0.018	0.321	0.123	0.198	0.025	
CB300071-6	0	0.131	0.902	0.08	0.034		
	1	0.042	0.697	0.084	0.028		
	16	0.014	0.517	0.06	0.022		
	46	0.012	0.489	0.057	0.024		
	106	0.016	0.912	0.11	0.025		
ET77252-4	0	0.322	1.219	0.087	0.321		0.123
	1	0.123	0.779	0.091	0.358		0.134
	16	0.052	0.585	0.067	0.302		0.102
	46	0.037	0.508	0.062	0.346		0.235
	106	0.025	0.494	0.058	0.418		0.071
CT77252-4	0	0.343	1.323	0.169	0.938		0.11
	1	0.147	0.898	0.177	0.84		0.132
	16	0.097	0.779	0.149	0.941		0.105
	46	0.096	0.639	0.134	0.885		0.106
	106	0.088	0.593	0.108	0.881		0.106
New cylinder	16	1.856	0.648	0.032			0.106

Table 6. Compounds identified from x-ray diffraction patterns of coupons from cylinders 300071 and 77252

Specimen no.	Compounds identified (in order of relative concentration)
ET300071-2, solid	Fe, UO ₂ , Fe ₃ O ₄ /Fe ₂ O ₃ , <i>b</i> , <i>b</i>
ET300071-2, powder ^a	UF ₄ 0.75H ₂ O, UF ₄ H ₂ O, Fe ₃ O ₄ /Fe ₂ O ₃ , <i>b</i>
ET300071-11, solid	Fe ₃ O ₄ /Fe ₂ O ₃ , <i>b</i> , Fe, <i>b</i> , <i>b</i>
ET300071-11, powder	Fe ₃ O ₄ /Fe ₂ O ₃ , <i>b</i>
EB300071-3, solid	Fe, <i>b</i> , <i>b</i> , <i>b</i>
EB300071-3, powder	UF ₄ 0.75H ₂ O, UF ₄ H ₂ O, Fe ₃ O ₄ /Fe ₂ O ₃ , <i>b</i> , <i>b</i>
EB300071-11, solid	Fe ₃ O ₄ /Fe ₂ O ₃ , Fe, UO ₂ , <i>b</i>
EB300071-11, powder	Fe ₃ O ₄ /Fe ₂ O ₃ , <i>b</i>
CB300071-6, solid	Fe ₃ O ₄ /Fe ₂ O ₃ , Fe, <i>b</i> , <i>b</i>
CB300071-6, powder	Fe ₃ O ₄ /Fe ₂ O ₃ , <i>b</i>
CB300071-10, solid	α-FeO(OH), Fe, <i>b</i>
CB300071-10, powder	α-FeO(OH), Fe, <i>b</i>
CF300071-3, solid	Fe ₃ O ₄ /Fe ₂ O ₃ , α-FeO(OH), <i>b</i>
CF300071-3, powder	Fe ₃ O ₄ /Fe ₂ O ₃ , α-FeO(OH), <i>b</i>
ET77252-4, solid	Fe, UO ₂ , Fe ₃ O ₄ /Fe ₂ O ₃
CT77252-4, solid	Fe, U ₄ O ₉ /UO ₂ /UO ₂ 0.5UO ₃ 10.5H ₂ O, Fe ₃ O ₄ /Fe ₂ O ₃
New cylinder, solid	Fe, Fe ₃ O ₄ /Fe ₂ O ₃ , <i>b</i>

^a"Powder" refers to scrapings from surface scales.

^bUnidentified compounds.

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