WORKER PROTECTION IMPLICATIONS OF THE SOLUBILITY AND HUMAN METABOLISM OF MODERN URANIUM MILL PRODUCTS IN THE U.S.

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Abstract—This paper presents an analysis of the implications of some recent studies performed to characterize uranium products from modern uranium recovery facilities important for worker protection. Assumptions about the solubility (related to the molecular species being produced) of these materials in humans are critical to properly assess radiation dose from intakes, understand chemotoxic implications, and establish protective exposure standards (airborne concentrations, limits on intake, etc.). Recent studies, as well as information in the historical professional literature, were reviewed that address the issue of solubility and related characteristics. These data are important for the design of programs for assessment of both chemical and radiological aspects of worker exposure to the products of modern uranium recovery plants (conventional uranium mills and in situ recovery plants; i.e., ISRs). The data suggest strongly that the oxide form produced by these facilities (and therefore, product solubility) is related to precipitation chemistry and thermal exposure (dryer temperature). Given the peroxide precipitation and low temperature drying methods being used at many modern uranium recovery facilities in the U.S. today, very soluble products are being produced. The dosimetric impacts of these products to the pulmonary system (except perhaps in case of an extreme acute insult) would be small, and any residual pulmonary retention beyond a month or two would most likely be too small to measure by traditional urinalysis sampling or the current state-of-the-art of natural uranium in vivo lung counting techniques. Uranium recovery plants should revisit the adequacy of current bioassay programs in the context of their process and product specifics. Workers potentially exposed to these very soluble yellowcake concentrates should have urine specimens submitted for uranium analysis on an approximately weekly basis, including analysis for the biomarkers associated with potential renal injury [e.g., glucose, lactate dehydrogenase (LDH) and protein albumen]. Additionally, implications for compliance with current U.S. Nuclear Regulatory Commission (NRC) regulations (e.g., 10 CFR20) are discussed. NRC, the applicable Agreement State agencies, and licensees need to recognize the importance of the uranium chemotoxicity versus dose relationship in the interest of worker protection. Health Phys. 107(5):403–409; 2014

Key words: bioassay; chemical toxicity; safety standards; uranium

INTRODUCTION

Uranium mills and similar uranium recovery facilities [e.g., those using in situ recovery (ISR) techniques] have operated in the United States for over 50 y. Historically, these facilities produced a uranium concentrate generically referred to as “yellowcake,” although these products have demonstrated a wide range of color variation including yellow, green, brown, and black. This color variation has been attributed to the range of uranium oxide species produced by these facilities. The variability of molecular speciation in these products has been shown to have significant implications for radiation and worker health protection programs as related to both the potential radiotoxicity (radiation dose) and chemotoxicity (renal system impact as a heavy metal) resulting from internal exposure (via inhalation or ingestion) to these products. Therefore, the fundamental health protection issues are:

• Issue #1: How long does the compound stay in the human and deliver radiation dose, and to which tissues? How insoluble is it? For inhalation exposures, the primary site of dose delivery is the lung (pulmonary region).
• Issue #2: How fast is the compound eliminated via the renal system with potential chemical toxicity to the kidneys? How soluble is it?

Over the years, studies have shown that industrial uranium compounds (e.g., as used and produced in uranium fuel cycle facilities) have demonstrated a range of solubility characteristics (depending on speciation).

This paper presents an analysis of the worker protection implications of some recent studies performed to characterize uranium products from modern uranium recovery facilities. Assumptions about the solubility (related
to the molecular species being produced) of these materials in humans are critical to properly assess radiation dose from intakes, understand chemotoxic implications, and establish protective exposure standards (airborne concentrations, limits on intake, etc.). Recent studies, as well as information in the historical professional literature, were reviewed that address the issue of solubility and related characteristics. These data are important for the design of programs for assessment of both chemical and radiological aspects of worker exposure to the products of modern uranium recovery plants (conventional uranium mills and ISR plants).

Modern uranium recovery facility products often appear quite different chemically and metabolically from the products of the past. This is yet to be recognized in the literature (with a few exceptions) and is not yet recognized by the U.S. regulatory framework [e.g., regulations of the U.S. Nuclear Regulatory Commission (NRC) at 10 CFR 20] or their associated technical basis (e.g., applicable NRC Regulatory Guides). Accordingly, implications for compliance with existing NRC regulations are also discussed in this paper.

**Historical studies**

Uranium mills and ISRs that operated in the United States during the 1960s and 1970s typically used an ammonium precipitation process producing ammonium diuranate (ADU), which was then dried (calcined) at relatively high temperatures, usually $>1,000 \degree$C. Characterization studies performed on these products, including in vitro lung fluid solubility studies (methods after Moss 1976) and x-ray diffraction analysis, indicated that the products were primarily relatively insoluble U$_3$O$_8$ and UO$_2$ (Cooke and Holt 1974; Spitz and Robinson 1981; Kalkwarf 1983; Eidson and Mewhinney 1983; Eidson 1994). In these historical studies, descriptions of the clearance of radioactive materials from the lungs used ICRP 30 models (ICRP 1979). In these models, materials were classified into three solubility Classes as D (days), W (weeks), and Y (years), referring to retention time in the pulmonary region. The retention half times for this classification system were: Class D—less than 10 d; Class W—between 10 to 100 d; and Class Y—greater than 100 d.

Most products were reported to exhibit multi-phase solubility since they included a combination of several oxides; e.g., ICRP 30 Class Y and Class W components in the same product. In some cases, all three (ICRP 30 Class D, W, and Y) were reported to be present, including more soluble UO$_3$ (Blauer and Brown 1980; Blauer et al. 1982; Eidson and Griffith 1984). Differences between individual mill products were attributed to differences in details of precipitation chemistry and thermal exposure; i.e., feed rate and temperature of the calciner (Merrit 1971; Brown/Wyoming Mineral Corporation 1980; Blauer and Brown 1980; Eidson 1994).

**Comparison of the ICRP 30 Based Solubility Classifications to Updated ICRP Models**

In the updated classification scheme in ICRP 68 (ICRP 1994) and ICRP 71 (ICRP 1995), fast/medium/slow clearance Types (F/M/S) correspond broadly to that of the D/W/Y solubility Classes of ICRP 30, with the difference that ICRP 71 bases the solubility classes on absorption rates rather than retention times. Where more specific information was not available, those compounds in Class D were assigned to Type F, Class W to Type M, and Class Y to Type S (ICRP 1995).

Annex D of ICRP 71 provides instructions on how to assign material to absorption types based on experimental data (e.g., lung fluid simulation studies) using absorption rates at different times rather than overall retention or clearance rates. Specifically, for an in vitro dissolution experiment, classification depends on the amount of undissolved material or percent retained in the sample at specified time intervals. Excluding particle transport, which is small for uranium, the classification criteria for solubility types F, M, and, S are shown in Table 1.

**More recent studies on yellowcake solubility and speciation—yellowcake produced by peroxide precipitation and low temperature vacuum dryers**

**Irigaray in situ recovery (ISR) plant (Metzger et al. 1997):** This study included the analysis of products from in situ uranium recovery at the Irigaray plant in Wyoming. At that time, the Irigaray plant leached uranium in situ via a carbonate/bicarbonate leach solution precipitated with hydrogen peroxide, and that was dried to produce the final yellowcake at ~540°C (a much lower temperature than used in earlier mills). Product composition was determined via x-ray diffraction techniques and indicated the final product’s uranium species content to contain approximately 80% UO$_4$ • 2H$_2$O and 15% UO$_3$. Air samplers were located throughout the plant to represent the majority of the locations for potential inhalation exposure throughout the process. Solubility studies using lung fluid simulants were conducted in Gambles Solution (Moss 1976) following methods of Eidson and Mewhinney (1983). The dissolution rate was determined over a period of 28 d. Airborne uranium collected from all worker areas was highly soluble, with 97% dissolving with a 0.25–0.30 d half time and the remaining 3% dissolving with a half time of 15–20 d.

Accordingly, using the ICRP 30 classification system [since this was in use at that time and is still used by their

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licensing agency (USNRC 1992; see 10CFR20, Appendix B), the authors suggested that this material should be assigned 97% solubility Class D and 3% Class W. Fig. 1 presents the dissolution rates of these products over the 28-d study period.

Cameco studies 2009–10: Yellowcake products from two ISR plants. Cameco Corporation conducted a yellowcake characterization project in 2009–2010 to assess the solubility and related characteristics of uranium concentrate from both the Crow Butte (Nebraska) and Smith Ranch-Highland (Wyoming) ISR plants. The Cameco Innovation and Technology Development Research Centre in Port Hope, Ontario, Canada, performed this work for purposes of determining dissolution rates in lung fluid simulants and chemical speciation. In addition to dissolution rates, uranium content (%) and molecular speciation via x-ray diffraction were determined. These products are produced by peroxide precipitation processes and dewatered in vacuum dryers at temperatures < 300 °C. The results of these studies are reported in Tairova et al. (2010), Tairova (2011), and Cameco (2010, 2011).

The experimental results are interpreted here in the context of both the ICRP 30 solubility classifications using retention half times in days (Class D/W/Y) and ICRP 68/71 absorption classifications of fast, medium, and slow (Type F/M/S). Both of these facilities are licensed by the NRC and therefore must comply with the ICRP 30-based models reflected in 10 CFR 20, Appendix B.

Samples used for the solubility studies were collected from several different drying batches (campaigns) as well as multiple locations within a single drum from each ISR. Additionally, Cameco analyzed the uranium content of these samples and performed x-ray diffraction on selected samples to investigate the molecular species of these products.

Solubility study results. All samples were classified primarily as ICRP 30 Class D with smaller components of Class W material. Using the F/M/S classification (ICRP 68/71), all samples were assigned Type F. To estimate the rapid and slow dissolution times and the fraction of material assigned to each category, a two-term exponential (“di-phasic”) model was used§. A di-phasic interpretation of dissolution has been reported by others (e.g., Eidson 1994; Stradling et al., 2002), and earlier studies during the 1980s involving material produced via ADU precipitation and dryer temperatures > 1,000 °C suggested tri–phasic dissolution patterns (suggesting three distinct dissolution fractions; f₁, f₂, f₃) over dissolution periods as long as 120 d (Blauer and Brown 1980; Blauer et al. 1982).

For simplicity, the di-phasic model is depicted below:

$$\frac{M}{M_0} = f_1 \exp\left(-0.693 \frac{t}{T_1}\right) + f_2 \exp\left(-0.693 \frac{t}{T_2}\right),$$

where:

$M$ = mass of undissolved uranium at time $t$;

$M_0$ = initial mass of uranium;

$t$ = elapsed time;

$f_1$ = fraction of total U with corresponding dissolution half-time $T_1$;

$f_2$ = fraction of total U with corresponding dissolution half-time $T_2$; and

$f_1 + f_2 = 100\%$.

The application of the di-phasic model to the Cameco data is presented in Table 2, which summarizes the solubility study results for both the Smith Ranch and Crow Butte sample sets (arithmetic means are used here for ease of presentation). Figs. 2 and 3 present the dissolution curves (% undissolved as a function of time) for the Smith Ranch and Crow Butte samples, respectively, aligned with the F/M/S classification system (ICRP 71, Appendix D).

Uranium content of samples and implications for molecular composition. Cameco also analyzed samples for their uranium content (%). This data is instructive in that the percent uranium contained in the oxide molecule is related to the molecular form and can be used in a predictive way, since it is related to speciation and therefore solubility characteristics. For the 10 Smith Ranch

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samples, the uranium content ranged from 77.4% to 79.5%, and for the 15 Crow Butte samples from 73.1% to 76.8%. As a comparison, Table 3 depicts the calculated uranium content based on molecular weight of various uranium compounds of interest.

A relationship between the temperature of drying (calcining in the past) and the oxidation state of the uranium in the product has been recognized for many years and is well reported in the literature (e.g. see Cook et al. 1974; Merritt 1971). In general, it has been reported that lower solubility is associated with lower oxidation states; e.g., UO₂ at +IV is less soluble than UO₃ at +VI, with U₃O₈ in between. However, historically, both UO₂ and U₃O₈ have been assigned ICRP 30 Class Y and UO₃ Class W (Rich et al., 1988; Leggett et al., 2012).

Comparison of the Cameco uranium composition data to Table 3 would suggest that the molecular forms produced by these two uranium recovery facilities are primarily uranyl peroxide (UO₄) with perhaps some uranium trioxide (UO₃) and/or their hydrates, since the uranium content was reported to be in the general range of 73–79%. This assumption is confirmed by the x-ray diffraction analysis results discussed below.

Results of x-ray diffraction analysis (XRD). The molecular composition of selected samples (three from each facility) were analyzed via x-ray diffraction (XRD) analysis. The results indicated that these yellowcake samples were all combinations of uranyl peroxide (UO₄), uranium trioxide (UO₃), and their hydrates (e.g., of the form UO₄·XH₂O where X = 1, 2, 3 etc.). This is expected given the precipitation chemistry involving peroxide and low temperature drying (less than about 300 °C) and is consistent with the % uranium analysis discussed above. At these relatively low temperatures, the amount of chemical reduction of the uranium ion is small (i.e., incomplete change in oxidation state), and by and large, just the excess water is being driven off by the low temperature vacuum dryers used.

All samples exhibited solubility characteristics that meet the definition of absorption Type F as defined in ICRP 71 that considers Type F “generally equivalent” to solubility Class D from ICRP 30; i.e., the most “soluble” category. However, some individual samples appear to exhibit smaller components typical of what was defined by ICRP 30 as Class W (moderately soluble; dissolution half-time > 10 d but < 100 d). However, in consideration of the relatively small percentage of Class W components in these products and their associated dissolution half times, the data nonetheless clearly puts them in the ICRP 71 Type F category. That is, no more than 13% of an intake remains in the lungs beyond 30 d. Accordingly, virtually all material would be translocated or systematically absorbed from the lung in time periods ≤ 1–2 mo.

Considerations of chemotoxicity versus radiotoxicity

The chemical toxicity of uranium as a heavy metal has been considered generally a greater concern for human health than its radiological toxicity (for natural or low enriched uranium). Given that natural uranium is a weakly radioactive element, its potential chemical toxicity is often of greater concern than its radiotoxicity. [low
specific activity of approximately $2.5 \times 10^4$ Bq g$^{-1}$ (see U.S. NRC 10 CFR 20, Appendix B). The chemical toxicity of uranium is associated primarily with potential damage to the kidney. There is no conclusive evidence that uranium produces cancer in humans (ATSDR 2011). Uranium (and other heavy metals such as lead, mercury, and cadmium) can damage the kidneys by chemical action in the renal proximal tubules. Although there are no unique biomarkers for uranium exposure, urinary levels of glucose, lactate dehydrogenase (LDH), and protein albumen are common indicators of exposure (often by ratio to creatinine).

However, there is no documented evidence in the literature of permanent renal injury among uranium mine and mill workers exposed to soluble and insoluble uranium compounds (Johnson et al., 2009), and there have been no reports of death in humans following an acute intake of uranium by any route of entry (Kathren and Burklin 2008).

**Implication for compliance to NRC regulations and for bioassay**

NRC regulations (10 CFR 20, Appendix B) present Annual Limits on Intake (ALI) and Derived Air Concentrations (DAC) based on ICRP 30 solubility classifications (D, W, Y). The ALI in 10 CFR 20 is defined as the intake (in μCi) of the radionuclide of interest that would result in 5 Rem (50 mSv y$^{-1}$) Total Effective Dose Equivalent (TEDE) in a year. Similarly, the DAC represents the average concentration (in μCi mL$^{-1}$) that would result in an intake of one ALI if the worker were exposed 2,000 h in a year. Table 4 presents a comparison of ALI and DAC values for natural uranium as a function of ICRP 30 solubility class (D, W, Y) from 10 CFR 20, Appendix B, Table 1. As can be seen, the “assignment” of solubility class for these various industrial uranium oxides can result in compliance values and implied worker protection perspectives that can vary by a factor of up to 20.

The yellowcake products being produced at uranium recovery facilities in the U.S. today using peroxide precipitation and low temperature vacuum dryers appear to be quite soluble. The more recent data summarized above indicate that they are ICRP 71 Type F materials (most soluble category) and therefore should be assigned ICRP 30 Class D for purposes of alignment with the NRC 10 CFR 20, Appendix B, Annual Limit of Intake for natural uranium (USNRC 1992). These products meet the definition of “low fired yellowcake” as used in NRC Regulatory Guide 8.22 (USNRC 1988), for which the technical basis was provided in NRC’s NUREG 0874 (USNRC 1986). The recommended protocol in Regulatory Guide 8.22 for bioassay for yellowcake workers potentially exposed to “low fired” (soluble) yellowcake is monthly urinalysis, with in vivo lung counting as a follow-up to urinalysis results confirmed to be above specified action levels. Subsequently, the NRC issued Draft Regulatory Guide DG—8051, Bioassay at Uranium Mills, for comment (comment period ended in May 2012). The authors provided comments to the NRC, including pointing out that this recent draft does not yet recognize the current production of these modern peroxide-precipitated low temperature products with their apparent high degree of solubility nor the associated metabolic implications. As of the time of this writing, a revision of the draft guide has not yet been issued.

However, modern products are exhibiting dissolution half times of a few days or fractions of days for the vast majority of the material. This suggests that a monthly urinalysis program may be inadequate to detect low-level chronic intakes and/or an acute intake that could have occurred as recently as a few weeks prior to voiding. Under the assumption that chemotoxicity should be the driver of worker protection for internal exposure to soluble natural uranium compounds, current bioassay programs should be reassessed given this data. Uranium recovery plants should consider their process and product specifics and in this context evaluate the accuracy and adequacy of current bioassay programs. This has been recommended previously due to the potential variability of speciation and associated characteristics of yellowcake products (Blauer and Brown 1980; Eidson and Mewhinney 1983). It is further recommended that workers potentially exposed to these very soluble yellowcake concentrates have urine samples submitted for analysis on approximately a weekly basis consistent with appropriate specimen collection protocols and work shift schedules.

**Table 3.** Percent uranium content based on molecular weight of uranium compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>U wt %</th>
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<tbody>
<tr>
<td>UO₂</td>
<td>88.1</td>
</tr>
<tr>
<td>U₂O₇</td>
<td>84.8</td>
</tr>
<tr>
<td>UO₃</td>
<td>83.0</td>
</tr>
<tr>
<td>UO₄</td>
<td>78.8</td>
</tr>
<tr>
<td>UO₂·H₂O</td>
<td>74</td>
</tr>
<tr>
<td>UO₂·2H₂O</td>
<td>70</td>
</tr>
</tbody>
</table>

**Table 4.** ALI and DAC values for natural uranium from 10 CFR 20, Appendix B per ICRP 30 Solubility Class.

<table>
<thead>
<tr>
<th>Natural uranium</th>
<th>Inhalation: Annual limit of intake$^a$ (ALI in μCi)</th>
<th>Inhalation: Derived air concentration$^b$ (DAC in μCi mL$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>1.0</td>
<td>5×10$^{-10}$</td>
</tr>
<tr>
<td>W</td>
<td>0.8</td>
<td>3×10$^{-10}$</td>
</tr>
<tr>
<td>Y</td>
<td>0.05</td>
<td>2×10$^{-11}$</td>
</tr>
</tbody>
</table>

$^a$Intake that would result in TEDE of 5 Rem (0.5 Sv) in a year.

$^b$Annual average over 2,000 working hours that would result in intake of one ALI.
CONCLUSION

In consideration of the extensive body of historical information on factors that appear directly related to the solubility and human metabolism of uranium recovery plant products (yellowcake) and more recent data on the molecular speciation and associated solubility of modern peroxide-precipitated, low temperature products, the following are suggested:

• Modern yellowcake products often appear quite different chemically and metabolically than the products of the past.

• The dosimetric impacts of these products to the pulmonary system (except perhaps in case of an extreme acute insult) would be small, and any residual pulmonary retention beyond a month or two would most likely be too small to measure by traditional urinalysis sampling or the current state-of-the-art natural uranium in vivo lung counting techniques (for discussion on applicability of in vivo lung counting, see Stradling et al., 2002).

• Modern peroxide-precipitated products dried in low temperature vacuum dryers appear to be quite soluble and meet the ICRP 71 criteria for the Type F (fast) absorption category.

• For these products, chemical toxicity clearly drives worker risk from intake - not radiation dose.

• More than 30 y of in vitro lung fluid solubility and XRF studies have demonstrated qualitative relationships between molecular species, uranium content, color, and solubility characteristics.

• The oxide form produced (and therefore, solubility) is related to precipitation chemistry and thermal exposure (dryer temperature).

• Uranium recovery plants should revisit the adequacy of current bioassay programs in the context of their process and product specifics. Workers in yellowcake areas potentially exposed to these very soluble concentrates should have urine specimens submitted for uranium analysis on approximately a weekly basis with monthly samples to also include analysis for the biomarkers associated with potential renal injury [e.g., glucose, lactate dehydrogenase (LDH), and/or protein albumen].

• Given the apparent high degree of solubility of the products being produced in modern uranium recovery facilities, operators should be paying particular attention to the “intake of soluble uranium limitation” at 10 CFR 20.1201(e), which limits intake of such materials to 10 mg wk

• NRC should revise 10 CFR 20, Appendix B, which is currently based on 40+ y-old data, with updated ICRP metabolic and dosimetric models.

• NRC, the applicable Agreement State agencies, and licensees need to recognize the importance of the uranium chemotoxicity versus dose relationship in the interest of worker protection.

REFERENCES


