# Uranium Solubility and Implications for Modern Uranium Recovery Facilities

**NMA/NRC**
Uranium Recovery Workshop 2012
Denver, Colorado
2-3 May 2012

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# Themes

- Current health physics issues
- Radiotoxicity  and chemotoxicity
- Solubility, biokinetics and dose
- Historical perspectives
- Characteristics of modern products
- Implications for worker protection and bioassay

# Uranium

- **Naturally occurring and ubiquitous**
- **Three naturally occurring isotopes**
  - U-238 and U-234 from the U-238 decay chain
  - U-235 forms its own decay chain
- **U-238 accounts for most of the mass (~ 97.275%) but U-238 and U-234 each have > 49% of activity**
- **Uranium isotopes have common chemical characteristics but very different radiological characteristics (half-lives)**

# Exposure to Uranium

- The main sources of exposure to uranium are ingestion, inhalation and skin contact
- In occupational settings, inhalation pathway dominates
- The behaviour of uranium is determined by biokinetic models, e.g. fraction inhaled deposited in lungs, fraction deposited in lungs transferred to blood, fraction distributed in body to various tissues and organs (esp. kidney), etc.
- Dosimetric models are used to calculate dose to tissue and equivalent (whole body) dose

# Biomarkers

- **Measurements of exposure**
  - Uranium in urine or faeces
  - Lung burden via external lung counting
- **Biomarkers of effect**
  - At present no biomarkers of effect unique to uranium
  - Urinary levels of glucose, lactate dehydrogenase (LDH) and protein albumen are common indicators (often by ratio to creatinine)

# Current Health Physics Issues

- **Issue #1: – how long does the compound stay in human delivering radiation dose and to what tissue?**
  - how insoluble is it ?
  - for inhalation exposures, primary site of dose delivery is lung (pulmonary region)
- **Issue # 2 – how fast is the compound eliminated via the renal system with potential chemical toxicity to kidneys ?**
  - how soluble is it ?
- **Over the years, studies have shown industrial uranium compounds have demonstrated a range of solubility characteristics (depending on speciation)**

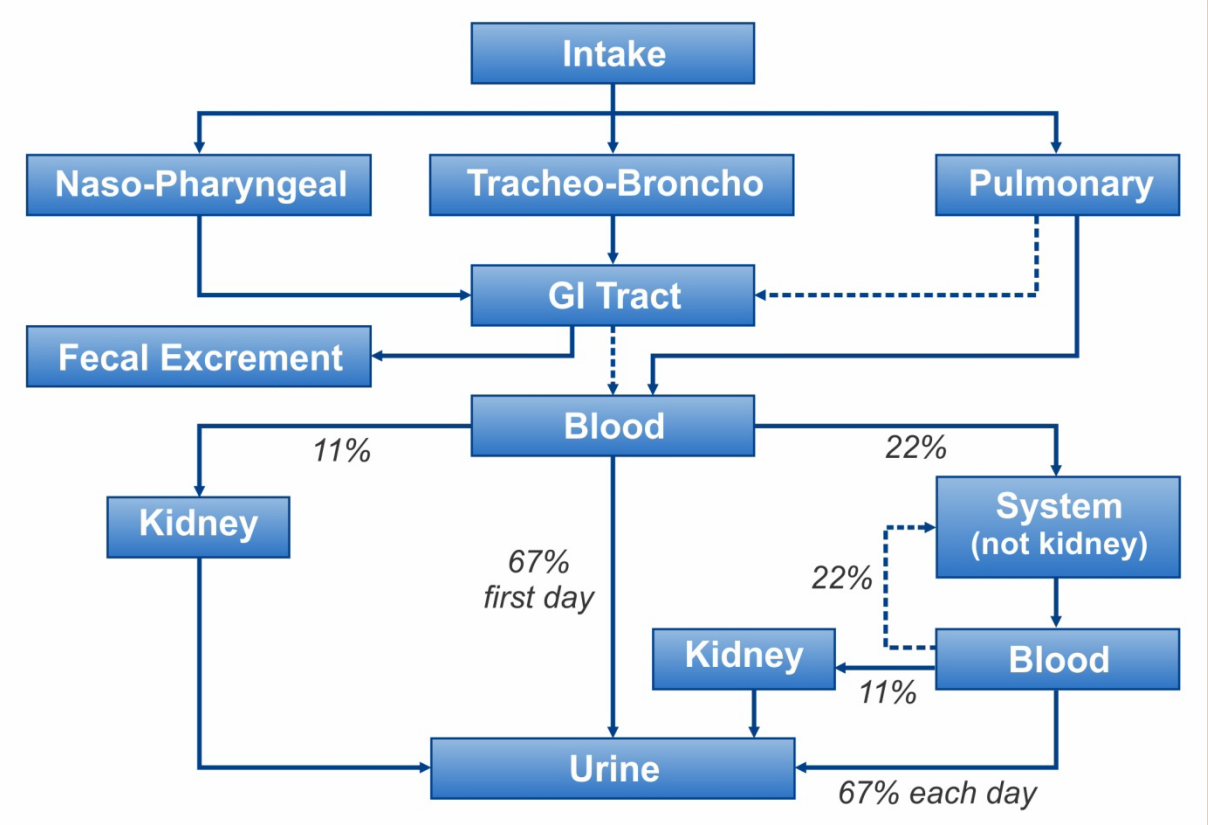
# Radiotoxicity vs Chemotoxicity

- **ATSDR 1999 [1]:**
  - Chemical toxicity primarily associated with damage to the kidney
  - There is no conclusive proof that uranium produces cancer in humans
- **The kidney is the main target for uranium toxicity**
- **However, there is no documented evidence or human data in the literature of renal injury among uranium mine and mill workers exposed to soluble and insoluble uranium compounds[2]**

[1] U.S Department of Health & Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry. *Toxicological Profile for Uranium. 1999 (revised 2011)*

[2] Health Physics Society, *NORM & TENORM*, Chapter 4: *Uranium Recovery Operations*. Johnson TJ, Johnson JA and Brown SH; Proceedings of the 2009 Professional Development School, Karem PA and Vetter BJ Editors. Minneapolis

# Simplified Uranium Metabolic Model




From NUREG 0874, Internal Dosimetry Model for Uranium (USNRC 1986) - Replaced WASH 1251, Applications of Bioassay for Uranium (USAEC 1974) –

Note that specific retention and clearance parameters depend on speciation (solubility). Many have been updated – e.g., ICRP 54 (1988), ICRP 66 ( 1994)

# Uranium Biokinetics and Solubility Classification

## ICRP 30*

- **ICRP 30 divides the respiratory tract into three regions (Task Group on Lung Dynamics, ICRP 19) - Nasopharynx, Tracheo-brochial and Pulmonary**
- **Clearance of radioactive materials from the lungs is classified as D (day), W (week), and Y (year), referring to retention time in the pulmonary region.**
- **Retention Half Time in Days:**

**Class D < 10 [i.e. soluble]**

**Class W 10 – 100**

**Class Y > 100 [i.e., insoluble]**

* Note that US NRC regulations @ 10 CFR 20 are still based on ICRP26/30 dosimetric models (1977 -1980).

# Uranium Biokinetics and Solubility Classification

## ICRP 68 (workers) and and 71 (Public)

- ICRP 66 Human respiratory tract model divides the respiratory tract into five regions
- The classification scheme in ICRP 68 and ICRP 71, “fast/medium/slow” (F/M/S), corresponds broadly to previous classifications of D/W/Y
- ICRP 68/71 bases the solubility classes on absorption rates rather than retention times
- Where more specific information was not available, compounds in Class D were assigned to Type F, Class W to Type M, and Class Y to Type S:

Absorption Rates:

Type F < 13% remains @ 30 days

Type M > 13% @ 30 days and < 87% at 180 days

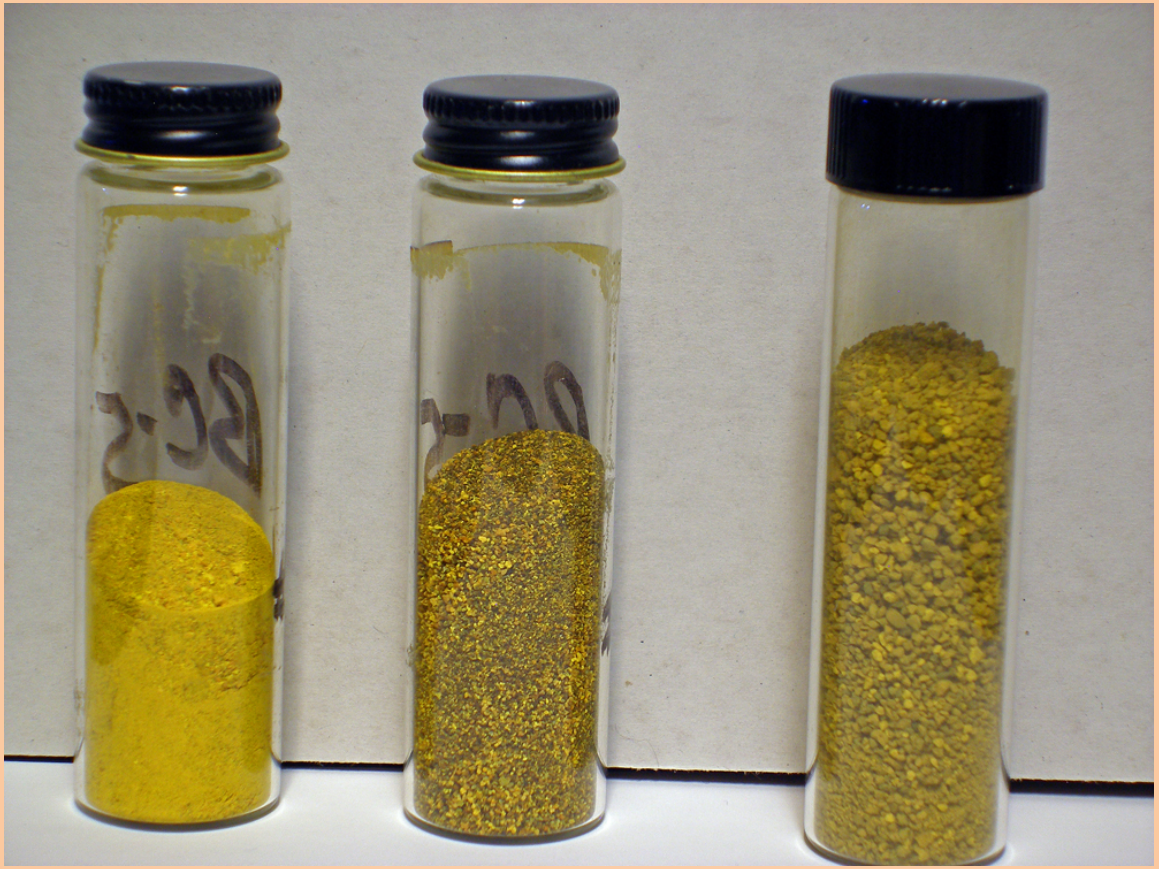
Type S > 87% remains @ 180 days

# Historical Perspectives*

- Uranium recovery facilities that operated in the 1960s and 70s used an ammonia precipitation process producing ammonium diuranate (ADU) dried (calcined) at high temperatures ( typically 1000 -1500 $^{o}$F)
- Characterization by X Ray Diffraction (XRF) and in vitro lung fluid solubility studies performed on those products indicated they were primarily relatively insoluble $U_30_8$ and $UO_2$
- Some products exhibited multi phase solubility since they included a combination of several oxides, e.g. Class Y and Class W components in same product – some had all three (D,W and Y) including more soluble $U0_3$
- Differences between individual mill products were attributed to differences in details of precipitation chemistry and thermal exposure - feed rate and temperature of calciners

*As reported in literature by Battelle, Inhalation Toxicology Research Institute, Univ. of Pittsburgh, Westinghouse, e.g.; Authors can provide bibliography including many of these published studies

# Yellowcake is Not Always Yellow



# Westinghouse Solubility Studies From Six Uranium Recovery Facilities (1979 - 80)*

- Facilities included 3 ISRs using ammonia (ADU precipitate) and high temperature calciners ( some > 1200°C)
- Dissolution > 120 days in agitated simulated liung fluids**
- X ray diffraction indicated products generally were > 80 % $U_3O_8$ with some ADU/$U0_3$ in the more soluble and some $U0_2$ in the most insoluble
- "Tri-Phasic" dissolution patterns observed

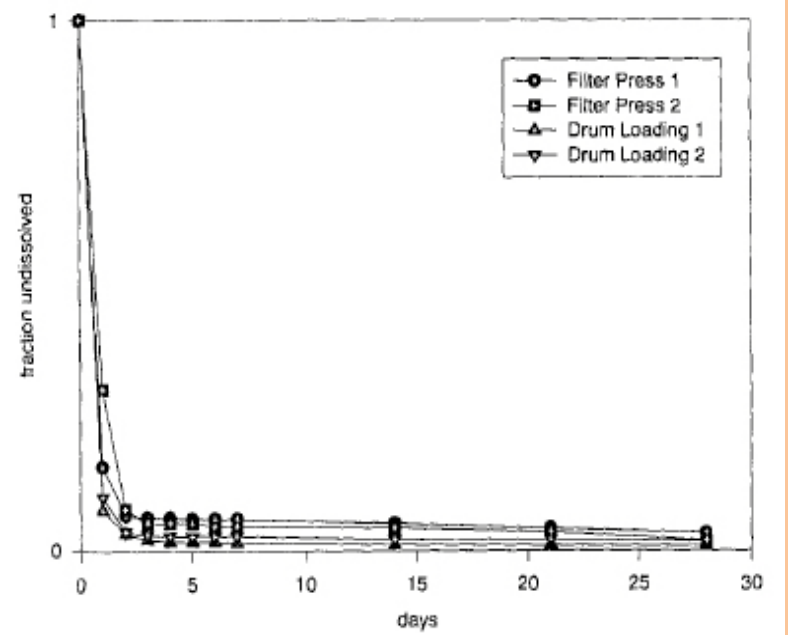
| Facility | F1 (Hours) | F2 (Days) | F3 (Weeks or months) |
|---|---|---|---|
| 1 | 17 % D | 17 % D | 66 % Y |
| 2 | 31 % D | 15 % D | 55 % W |
| 3 | 14 % D | 11 % D | 75 % Y |
| 4 | 6 % D | 3 % D | 92 % Y |
| 5 | 4 % D | 2 % D | 94 % Y |
| 6 | 13 % D | 11 % D | 76 % W |

* Wyoming Mineral Corporation, Brown S to distribution. *Yellowcake Solubility Studies 1979 -1980*. Sept 10, 1980; Blauer M and Brown S. 1980, *Physical and Chemical Parameters Affecting the Dissolution of Yellowcake in Simulated Lung Fluids.* Abstracts of the 25th Annual Meeting of Health Physics Society, Seattle, Paper # 177, Pergamon Press

** R.O.Moss, "Simulants of Lung Interstitial Fluid", Health Physics, Vol. 36, 1976, 447-448.

# Irigaray Solubility Study – 1995*

- Dissolution of both wet process material and drum load out area dusts in simulated lung fluids
- $UO_4$ precipitation process; dried @ 540° C
- Samples showed 97 % dissolution with $T_{1/2}$ < 0.3 days ; remainder $T_{1/2}$ with dissolution of 15 -20 days
- "conservatively" assigned by NRC as 85% D and 15% W




*Metzger R, Wichers D. et al 1997. Solubility *Characteristics of Airborne Uranium From an In Situ Uranium Processing Plant. Health Physics 72.3, p 418.*

# Today – Modern Yellowcake Products

- **Today's ISR facilities in the US use hydrogen peroxide precipitation and low temperature vacuum dryers ( < 400°F)**
- **XRF Studies recently conducted by 2 Uranium recovery licensees indicate products are combination of $UO_4$, $UO_3$ and their hydrates (e.g., $UO_4$* X $H_20$ where X= 1,2,3 ..)***
- **Uranium content varied from 76 – 79%**

**The Chemistry:**

**% Uranium Content**

**Based on Molecular Weight**

**of Uranium Compounds:**

| FORM | U wt % |
|---|---|
| $UO_2$ | 88.1 |
| $U_3O_8$ | 84.8 |
| $UO_3$ | 83.0 |
| $UO_4$ | 78.8 |
| $UO_4*H_2O$ | 74.0 |
| $UO_4*2H_2O$ | 70.0 |

*Cameco Corporation, Solubility of Radionuclides in Simulated Lung Fluid. G. Tairova, M. Boucher ,K. Toews, et al. Proceedings of the 3rd International Conference on Uranium. Saskatoon 2010

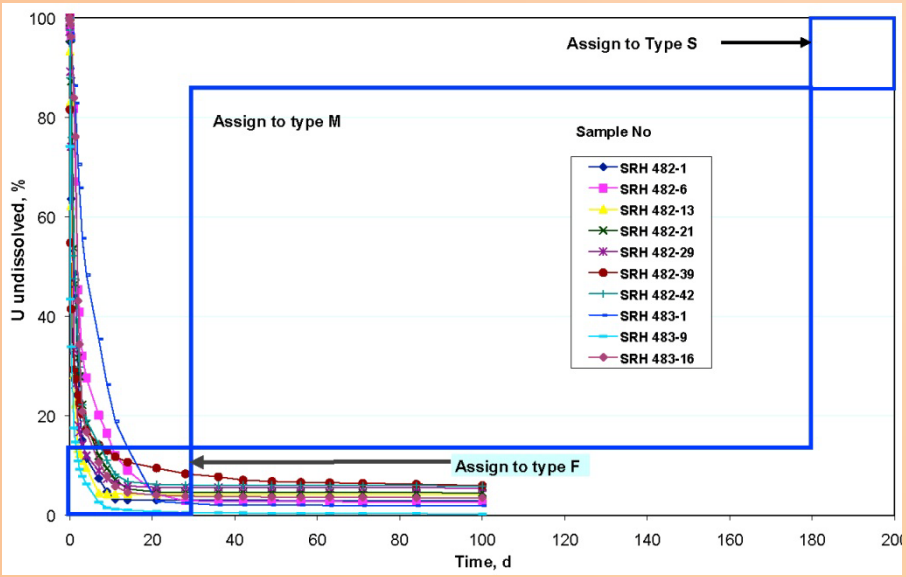
# Published U Compound Solubility*

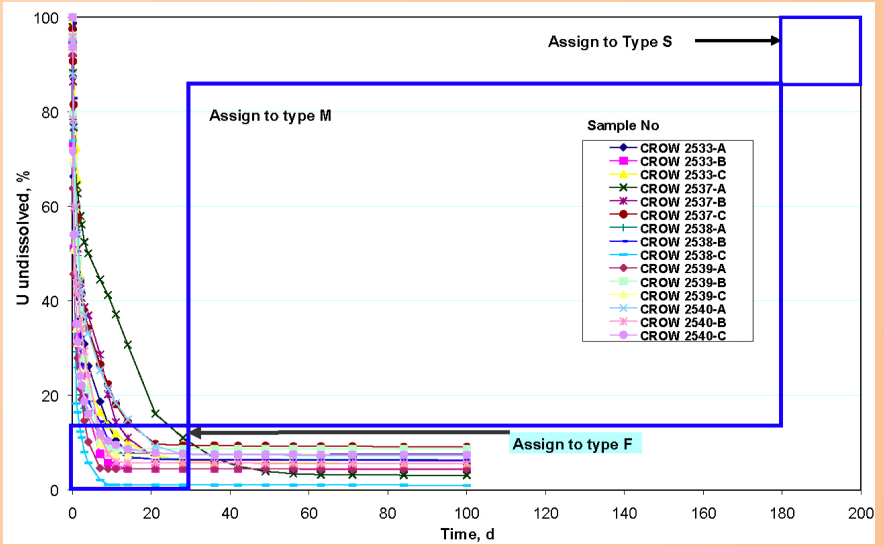
| Chemical Form | Inhalation Class |
|---|---|
| $UF_6$, $UO_2F_2$, and $U_2O_2(NO_3)_2$ | D |
| $UO_3$, $UF_4$, and $UCl_4$ | W |
| $UO_2$ and $U_3O_8$ | Y |

* For Example: Oak Ridge National Laboratory Environmental Sciences Division. *Controlling Intake Of Uranium In The Workplace: Applications Of Biokinetic Modeling and Occupational Monitoring Data.* January 2012; USNRC Draft Regulatory Guide DG 8051, *Bioassay at Uranium Mills.* March 2012 (for comment); USDOE. EG&G – 2530 UC-41, B.L. Rich et al. *Health Physics Manual of Good Practices For Uranium Facilities,* 1988

# Recent Solubility Study Results – Simulated Lung Fluid*

| Site | # of samples | $F_1$ Avg. (%) | $T_1$ Avg. (days) | $F_2$ Avg. (%) | $T_2$ Avg. (days) | ICRP 30 % D | ICRP 30 % W | ICRP 30 % Y | ICRP 71 |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 10 | 86.7 | 1.1 | 13.3 | 47.8 | 95.7 | 4 | 0.3 | All F |
| 2 | 15 | 68.6 | 0.6 | 31.4 | 34.5 | 89.5 | 9.5 | 0.5 | All F |




* US NRC ADAMS Ascension # ML110760153, J Schmuck, Cameco to R Burrows, USNRC. 15 March 2011 and M102640195, T. Young, Cameco to R. Burrows, USNRC, 17 Sept. 2010, License SUA - 1534

# Regulatory and Dosimetric Significance of Assigned Solubility Class*

**From 10 CFR 20, Appendix B, Table 1:**

| Natural Uranium | Inhalation: Annual Limit of Intake[1] (ALI in uCi) | Inhalation: Derived Air Concentration[2] (DAC in uCi/ml) |
|---|---|---|
| D | 1.0 | 5E-10 |
| W | 0.8 | 3E-10 |
| Y | 0.05 | 2E-11 |

[1] Intake that would result in TEDE of 5 Rem in a year

[2] Annual average over 2000 working hours that would result in intake of one ALI

* Based on ICRP 19 & 30 Solubility Class Definitions

# Summary and Conclusions:

## SO - What are Implications of All This ?

- **Modern yellowcake products appear quite different chemically and metabolically than 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 US regulatory framework ( e.g., 10 CFR 20) or its associated technical basis (e.g., applicable Regulatory Guides)**
- **Modern peroxide precipitated products dried in low temperature vacuum dryers appear to be quite soluble – ICRP 68/71 Type F ( > 87% eliminated in < 30 days)**
- **Low drying temperatures result in incomplete reduction of the peroxide – still retain water of hydration – considerable solubility expected**
- **For these products – Chemotoxity drives worker risk from intake – not radiation dose**

# Summary and Conclusions …cont'd

- **Over 30 years of in-vitro lung fluid solubility and XRF studies have demonstrated qualitative relationships between chemical species, uranium content, color and solubility characteristics**
- **Modern operators should be able to assign general solubility class or type based on molecular composition**
- **If chemistry and thermal history are similar, product metabolic characteristics should be very similar from plant to plant – It's just the Chemistry and the Physics !**
- **Product specific characterization data can be submitted for NRC approval (10 CFR 20.1204(c)(2)) to request use of more realistic and representative ALIs and DACs**
- **This is estimated to increase ALI and DAC values by more than a factor of 2**

# Looking Forward

- ICRP is updating it's biokinetic and dosimetric models – including those for uranium (a series of 3 reports) intended to replace ICRP 30 AND ICRP 68
- Revised dose coefficients have been calculated using ICRP 100 (Human Alimentary Tract Model) and ICRP 66 (Human Respiratory Tract Model)
- Emphasis on speciation (i.e., solubility)
- A technical paper for publication, expanded from this presentation, is under preparation by authors

# Recommendations

- **NRC should revise 10 CFR 20, Appendix B which is currently based on 30 - 40 year old data, with updated ICRP metabolic and dosimetric models**

- **Industry needs to provide NRC comments on Draft Regulatory Guide DG – 8051 , *Bioassay at Uranium Mills* to recognize and incorporate considerations for modern UR products (Comment period ends May 11, 2012)**

- **NRC and licensees both need to recognize the importance of the uranium chemotoxity vs dose relationship in the interest of worker protection**

# Recommendations …cont'd

- **Operators should be paying particular attention to the "intake of soluble uranium limitation" @ 10 CFR 20.1201(e) = 10 mg / week**

- **Operators should revisit specimen collection frequencies, protocols and related action levels of their bioassay (urinalysis) programs – Typical 30 day intervals may be missing intakes from these potentially highly soluble products**

# Disclaimer

***The opinions and recommendations presented herein are exclusively those of the authors and do not necessarily reflect the official position of the USNRC Uranium Recovery Branch nor the views of current source material licensees or applicants***

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# *QUESTIONS ?*