Some Health Physics Issues at U.S. Uranium In Situ Recovery Facilities

NMA/NRC Uranium Recovery Workshop
May 26 -27, 2010
Denver, Co. USA

Steve Brown, CHP
Douglas Chambers, PhD
SENES Consultants Ltd
1. Radiological Environment of ISRs – What we’ve measured and process knowledge gained - suggest its reasonable to assume principles of physics and chemistry hasn’t changed much in 30 + yrs

2. Nonetheless, will discuss why we may need to revisit process related assumptions and mature standards of HP practice at this time

3. Apply # 1 & 2 to a few “Open HP Issues” – describe technical basis, what we think we know and path forward to verify / validate
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.
Examples of the “HP Issues”

1. Air Sampling for Long Lived Alpha Emitters – do we have a “mixture” or just U?

2. Solubility (metabolic) of uranium ISR products – what is the correct airborne concentration limit (Derived Air Concentration – “DAC”) and appropriate “solubility class” (time for clearance from lung)

3. Bioassay programs for ISR products – product specific chemistry and behavior in humans defines methods, frequency, action levels
Examples of the “HP Issues” - continued

4. Contamination limits for release of material and equipment to unrestricted (public) areas - are historical limits adequately protective?
Radiological Environment of ISRs - Radionuclide Mobilization*

- Relatively small % of U daughter products in ore body observed to be mobilized by lixiviant
- Thorium appeared to equilibrate in circulating lixiviant and little removed
- Lead carbonate complexes relatively insoluble, little mobilized
- Small % of calculated radium in host formation mobilized
- IX selective for uranium – Ra follows Ca chemistry
- Radon gas evolution is the primary radionuclide effluent

Radionuclide Mobilization: Implications for HP Programs

- Other than U and small amounts of Ra, should be “little” other progeny (except radon) moving forward beyond IX

- First few uranium daughters growing in (Pa 234, Th 234) take approx. 4 months to reach equilibrium – just a few hrs or days from ore in situ being packaged in steel drum

- Radon gas may be released at IX/elution interface depending on design; progeny ingrowth controlled via local exhaust / HVAC (much less with modern closed systems)
Accordingly, fresh product in precipitation, drying and packaging areas should have “little” other long lived alpha emitters

But must understand U product chemistry to ensure ALARA

Radium will typically follow calcium chemistry and be associated with 11.e.2 byproducts (sock / sand and similar filtrates, tank / pipe scale, etc)
SO: Some Current Health Physics Issues – Why?

- Low level of activity in US U Industry during past 25 yrs

- Standards of HP practice accepted as “protective and compliant” and therefore essentially remained unchanged

- Several of the key NRC regulatory Guides that defined “acceptable” HP standards of practice and for environmental assessment have therefore remained unchanged over much of this time

- As many new license applications are being prepared and reviewed by NRC staff, some fundamental radiological characteristics of ISRs, U Mills and associated HP practices being questioned – That is “Healthy”
However, revisions of practice should be based on:

- good science
- well articulated technical basis
- Analysis demonstrates current practices are not adequately protective and/or do not ensure ALARA
## Example “Open HP Issues” Identified by NRC Staff to ISR Licensees / Applicants

<table>
<thead>
<tr>
<th>Issue</th>
<th>Questions</th>
<th>Compliance Drivers</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Air Sampling for Long Lived Alpha Emitters</td>
<td>Just total U OK ? Need to consider mixture (e.g. Th 230, Ra 226) ?</td>
<td>10 CFR 20.1204(f) and (g) 10 CFR 20, App B</td>
</tr>
<tr>
<td>2. Solubility (metabolic) of uranium ISR products</td>
<td>What is correct DAC in air ? What is correct solubility class for modern ISR peroxide products ?</td>
<td>10 CFR 20, App B 10 CFR 20.1204 10 CFR 20.1201(e)</td>
</tr>
<tr>
<td>4. Contamination limits for release of material and equipment to unrestricted (public) areas</td>
<td>Are current limits adequately protective ?</td>
<td>Regulatory Guide 8.30, <em>HP Surveys @ U Recovery Facilities</em> and references therein (FC 83-23; RG 1.86)</td>
</tr>
</tbody>
</table>
Health Physics Issue # 1: Air Sampling For Long Lived Alpha Emitters Recognizing ISR Process Is Selective For Uranium

Is analysis for just natural U in air adequate or need to consider “mixture” - Unat + Th 230 + Ra 226 ? (10 CFR 20,1204(f)*; Appendix B, Table 2)

* If any nuclide in mixture unknown, must use most restrictive DAC
Need to establish appropriate concentration limit (Derived Air Conc. - DAC in uCi/ml)

DAC = conc. @ which continuous exposure for 2000 hrs per yr = worker dose limit (5000 mrem / yr)

Currently assume all is Unat; Th 230 and Ra 226 DACs lower

As indicated, process knowledge suggests essentially all U nat

May need to consider a mixture – use “sum of fractions” rule

Operators may need to characterize product or representative air samples to validate – does some data already exist?
Health Physics Issue # 1: DACs from 10 CFR 20, App B, Table 1 (uCi/ml)

<table>
<thead>
<tr>
<th></th>
<th>D(F)*</th>
<th>W(M)*</th>
<th>Y(S)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>U natural</td>
<td>5E-10**</td>
<td>3E-10</td>
<td>2E-11</td>
</tr>
<tr>
<td>Th 230</td>
<td>N/A</td>
<td>3E-12</td>
<td>6E-12</td>
</tr>
<tr>
<td>Ra 226</td>
<td>N/A</td>
<td>3E-10</td>
<td>N/A</td>
</tr>
</tbody>
</table>

*Solubility Class Terminology from ICRP 19 & 30 / ICRP 66 – more next slide*

<table>
<thead>
<tr>
<th>D(F)</th>
<th>W(M)</th>
<th>Y(S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FAST</td>
<td>MODERATE</td>
<td>SLOW</td>
</tr>
</tbody>
</table>

** Typically assumed to be the correct DAC for modern U recovery products dried at low temperature (vacuum dryers typically < 400°F)**
Solubility Classes (ICRP 30/66)

F/D  –  dissolution in “days”  (≤ 10)

M/W  –  in “weeks”  (10-100 days)

S/Y  –  in months or years or never  
       ( > 100 days)
Health Physics Issue # 1 – Exclusion per 10 CFR 20.1204(g)

- Can ignore contribution in mixture in air if:
  - Total activity determined
  - For any nuclide $< 10\%$ of DAC
  - Sum of activities ignored $< 30\%$ of total activity

Isotopic analysis of product or high volume air samples can easily determine if these conditions are met
Current Health Physics Issue # 2:
Solubility (metabolic) of uranium ISR products

- Critical for establishing worker airborne exposure limits (DAC, e.g.), to assess internal dose and define appropriate bioassay programs

- What is solubility (metabolic – in human lung) of yellowcake precipitated with peroxide and dried at lower temperatures?

- Critical to assess dose and chemical risk
Why Yellowcake Solubility Characteristics are Important – Inhalation Scenario
Simplified Uranium Metabolic Model

From NUREG 0874, Internal Dosimetry Model for Uranium (USNRC 1986) - Replaced WASH 1251, Applications of Bioassay for Uranium (USAEC 1974)
## Health Physics Issue # 2 & 3 – Inhalation (Solubility)

**Class of U Compounds – It's in the Chemistry!!**

<table>
<thead>
<tr>
<th>Compound Name</th>
<th>Formula</th>
<th>Class (ICRP 19/30)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uranium Trioxide</td>
<td>UO$_3$</td>
<td>D</td>
</tr>
<tr>
<td>Uranium Oxide</td>
<td>U$_3$O$_8$</td>
<td>W</td>
</tr>
<tr>
<td>Uranium Dioxide</td>
<td>UO$_2$</td>
<td>W or Y$^3$</td>
</tr>
<tr>
<td>Ammonium Diuranate</td>
<td>(NH$_4$)$_2$ + U$_2$O$_7$</td>
<td>D and W$^4$</td>
</tr>
<tr>
<td>Uranyl Peroxide$^2$</td>
<td>UO$_4$</td>
<td>? Assumed D</td>
</tr>
</tbody>
</table>

2. Known to coexist as hydrates of form *XH$_2$O*
3. Class Y if “high fired”
4. ADU known to contain UO$_3$ and is assigned both since “di-phasic” dissolution
Doesn’t Have to be all “D” to be “Low Fired Yellowcake” and Soluble

<table>
<thead>
<tr>
<th>Fractional Composition and Lung Half Life Values for Yellowcake (in vitro studies) *</th>
<th>Fractional Composition</th>
<th>Dissolution T (1/2) (days)</th>
<th>Inhalation (Solubility) Class</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>High Temperature Drying</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Short Lived</td>
<td>0.17</td>
<td>0.125</td>
<td>D</td>
</tr>
<tr>
<td>Medium Lived</td>
<td>0.19</td>
<td>5.0</td>
<td>D</td>
</tr>
<tr>
<td>Long Lived</td>
<td>0.64</td>
<td>200.0</td>
<td>Y</td>
</tr>
<tr>
<td><strong>Low Temperature Drying</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Short Lived</td>
<td>0.61</td>
<td>0.8</td>
<td>D</td>
</tr>
<tr>
<td>Medium Lived</td>
<td>0.39</td>
<td>39.0</td>
<td>W</td>
</tr>
</tbody>
</table>

* From NUREG 0874, Internal Dosimetry Model for Uranium (USNRC 1986)
Irigaray Solubility Study

- Dissolution of both wet process material and drum load out area dusts in simulated lung fluids (Gamble’s Solution)
- $\text{UO}_4$ precipitation process; dried @ 540$^\circ$ C
- X Ray diffraction indicated 79 % $\text{UO}_4+2 \text{H}_2\text{O}$, 15% $\text{UO}_3$ and 3% $\text{CaCO}_3$
- Both exhibited 97 % dissolution with $T_{1/2} < 0.3$ days; remainder $T_{1/2} @ 15 - 20$ days - Clearly a “SUPER D”

Westinghouse Solubility Studies From 6 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 Gamble’s solution maintained @ 98.6°F.
- X-ray diffraction indicated products generally were > 80% U₃O₈ with some ADU/UO₃ in the more soluble and some UO₂ in the most insoluble.
- “Tri-Phasic” dissolution patterns observed.

<table>
<thead>
<tr>
<th>Facility</th>
<th>F1 (Hours)</th>
<th>F2 (Days)</th>
<th>F3 (Weeks or months)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>17 % D</td>
<td>17 % D</td>
<td>66 % Y</td>
</tr>
<tr>
<td>2</td>
<td>31 % D</td>
<td>15 % D</td>
<td>55 % W</td>
</tr>
<tr>
<td>3</td>
<td>14 % D</td>
<td>11 % D</td>
<td>75 % Y</td>
</tr>
<tr>
<td>4</td>
<td>6 % D</td>
<td>3 % D</td>
<td>92 % Y</td>
</tr>
<tr>
<td>5</td>
<td>4 % D</td>
<td>2 % D</td>
<td>94 % Y</td>
</tr>
<tr>
<td>6</td>
<td>13 % D</td>
<td>11 % D</td>
<td>76 % W</td>
</tr>
</tbody>
</table>

Presents data from both UK and French studies on numerous industrial U compounds including $\text{UO}_4$. For peroxide, provides the following recommendations:

- No lung monitoring measurement should be used after an acute (or chronic) inhalation.
- 30 day urine monitoring interval should be used after chronic inhalation.
- 1 to 90 day urine monitoring period should be used after an acute inhalation.

* NRPB-W22: *Industrial Uranium Compounds: Exposure Limits, Assessment of Intake and Toxicity after Inhalation*, October
Yellowcake is Not Yellowcake
is Not Yellowcake
Health Physics Issue # 3 - Bioassay – Conclusions

- Need to validate that ISR U products are “low fired” as defined in NUREG 0874 (i.e., “soluble” in lung)

- 30 + years of accumulated process knowledge, basic chemistry and the data in literature strongly supports this

- Clearance and elimination functions for these U products are measured in fractions of a day up to a few weeks, not months

- Routine monthly frequency (or more often based on shift schedules) via urinalysis using action levels from Table 1 of RG 8.22 is appropriate
Are higher limits for “uranium and daughters” adequately protective or are lower limits necessary for radium 226 in 11.e.2 byproduct wastes?

From NRC RG 8.30, and historical NRC documents referenced therein

<table>
<thead>
<tr>
<th>In DPM / 100 cm² from NRC RG 8.30, 1.86 and FC 83-23</th>
<th>Removable</th>
<th>Fixed + Removable (max)</th>
</tr>
</thead>
<tbody>
<tr>
<td>“U and Daughters”</td>
<td>1000</td>
<td>15,000</td>
</tr>
<tr>
<td>“Transuranics (Pu), Ra 226, Ra 228, etc”</td>
<td>20</td>
<td>300</td>
</tr>
</tbody>
</table>
# Health Physics Issue # 4 – Technical Basis

From USNRC NMSS Handbook For Decommissioning Fuel Cycle and Material Licenses (No longer available but data reproduced in (1))

<table>
<thead>
<tr>
<th>Nuclide Categories from RG 1.86 (1974), FC 83-23 (1987), RG 8.30 (2002)</th>
<th>Dose to Member of Public $^{2,3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>U-nat, U-235, and U-238 and daughters</td>
<td>13 mrem/yr</td>
</tr>
<tr>
<td>Ra-226, Ra-228, Transuranics</td>
<td>0.2 mrem/yr $^4$</td>
</tr>
<tr>
<td>Th-nat, Th-232, Sr-90</td>
<td>28 mrem/yr</td>
</tr>
<tr>
<td>Beta-gamma emitters</td>
<td>28 mrem/yr</td>
</tr>
</tbody>
</table>


$^2$ Exposure scenarios and assumptions used by NRC are unknown

$^3$ Note exposure levels consistent with NRC’s risk/dose based approach of 25 mrem/yr in License Termination Rule of 10 CFR 20 Subpart E and NUREG 1757

$^4$ Note that Ra 226 dose @ 20/300 dpm per 100 cm$^2$ < 1% of this limit
Health Physics Issue # 4: Release of Equipment and Materials - Conclusions

- These nuclide categories and numerical guidelines have been applied consistently throughout the nuclear fuel cycle for > 30 yrs

- Can’t find any definition of “uranium and daughters” in NRC documents – historically assumed as any mix of U nat series radionuclides, (a few specific exceptions)

- Need for use of the lower (“Transuranic”) limits not supported by NRC’s dose estimates

- Practical measurement issues in U recovery plants at lower limits – they are not “total containment” (e.g. fissile material) facilities
Much process knowledge and empirical data from measurements exist that define the radiological environments of ISRs.

It's reasonable to assume principles of physics and chemistry haven't changed much in 30+ yrs.

Nonetheless, given the current "renaissance in the domestic U recovery industry", it is "healthy" to revisit process related assumptions and our mature standards of HP practice at this time.
Most of these “historical assumptions” are easily validated by:

- Attention to basic principals of chemistry and physics
- Attention to volume of data in the literature including empirical measurements made at ISRs and on ISR products
- Some additional relatively simple and strait forward measurements in operating plants and of their products
THE BOTTOM LINE

However, revisions of practice should be based on:

- good science

- well articulated technical basis

- Analysis demonstrates current practices are not adequately protective and/or do not ensure ALARA
QUESTIONS?

Steve Brown, CHP
SENES Consultants Ltd
Englewood, CO. USA
303 524 1519
303 941 1506 (mobile)
sbrown@senes.ca