Radiological and Chemical Properties of Uranium

Module Objectives

- Recognize the basic chemical, physical, radiological properties of uranium and other radioactive materials present at uranium recovery facilities.
- Describe the properties of decay products of uranium.
- Describe the processes and health physics concerns at conventional mills and in-situ recovery facilities.

General

Natural Uranium

- There are three naturally occurring isotopes of uranium:

  U-234

  U-235

  U-238

- All three are long lived alpha-emitters.
- U-238 is the head of the uranium decay series of which U-234 is a member.
- U-235 is the head of the actinium decay series.
- These decay series include alpha, beta and gamma emitters.

Natural Uranium

- Uranium is relatively abundant in nature. Typical concentrations of uranium in soil:
  U-238 1 pCi/g of soil
  U-234 1 pCi/g of soil
  U-235 0.05 pCi/g of soil
- Uranium bearing ore is ranked by the amount of U present.
- In the U.S., most mined ore contains from 0.1% to 1% of U.
- Since 1 pCi/g U-238 ≅ 3 ppm of uranium:
  1 pCi/g U-238 ≅ 0.0003% of uranium
  100 pCi/g U-238 ≅ 0.03% of uranium
  1000 pCi/g U-238 ≅ 0.3% of uranium

Isotopes of Natural Uranium

Isotope	% by weight	Half-life
U-234	0.0055	2.47×10^5 years
U-235	0.72	7.10×10^8 years
U-238	99.28	4.51×10^9 years

Enriched uranium would have more U-234 and U-235 and less U-238

Depleted uranium would have less U-234 and U-235 and more U-238

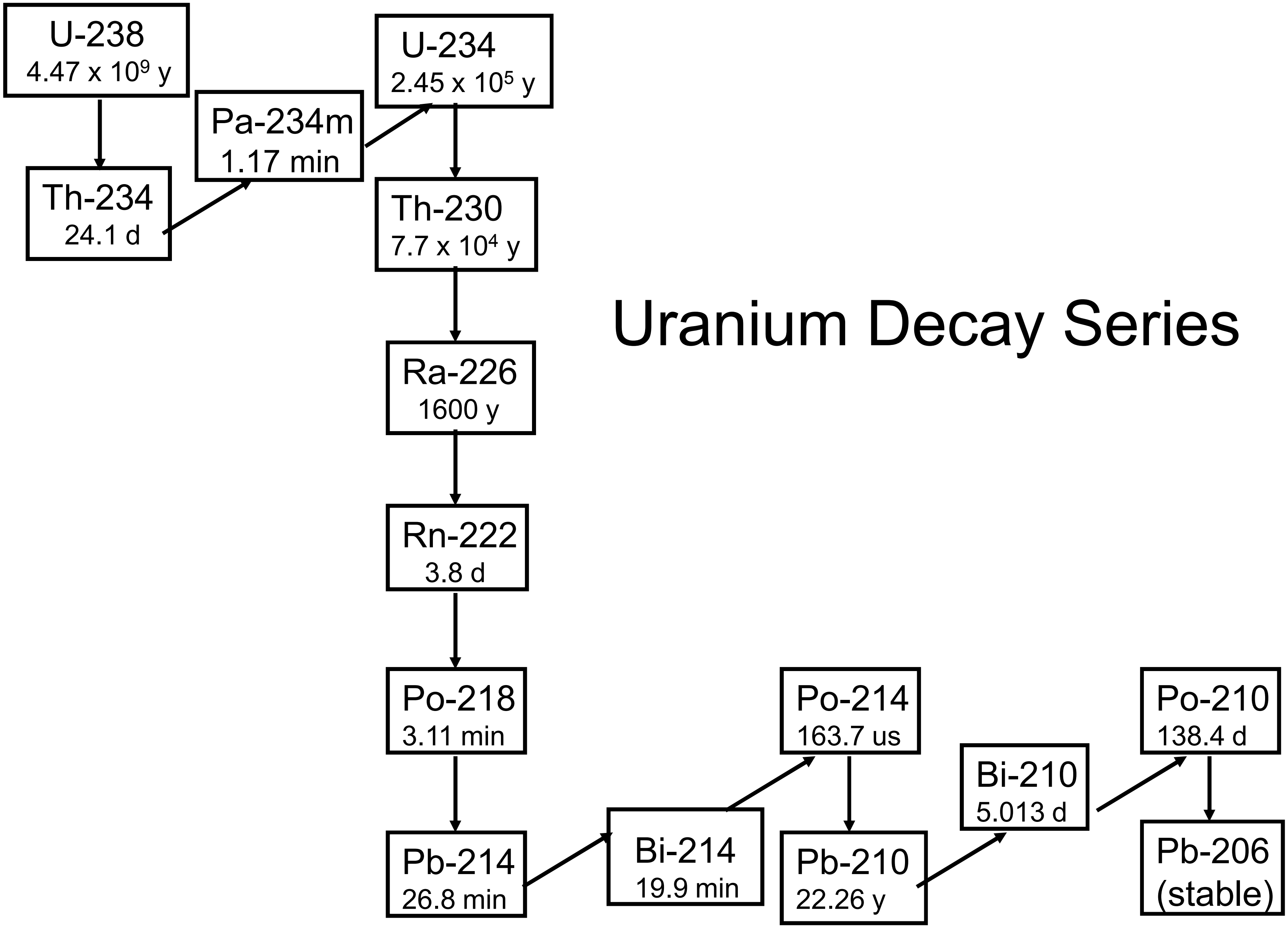
Radiological Properties (Daughter Products & Equilibrium)

- All of the uranium isotopes decay to shorter-lived decay products often referred to as “daughters.”
- U-238 and U-235 together with their decay products form a “decay chain” or “series” the final decay product of which is a stable isotope of lead.
- Natural uranium has two decay chains:

Actinium series (U-235)

Uranium series (U-238)

Uranium Decay Series



U-238
4.47 x 10^9 y

Th-234
24.1 d

Pa-234m
1.17 min

U-234
2.45 x 10^5 y

Th-230
7.7 x 10^4 y

Ra-226
1600 y

Rn-222
3.8 d

Po-218
3.11 min

Pb-214
26.8 min

Bi-214
19.9 min

Po-214
163.7 us

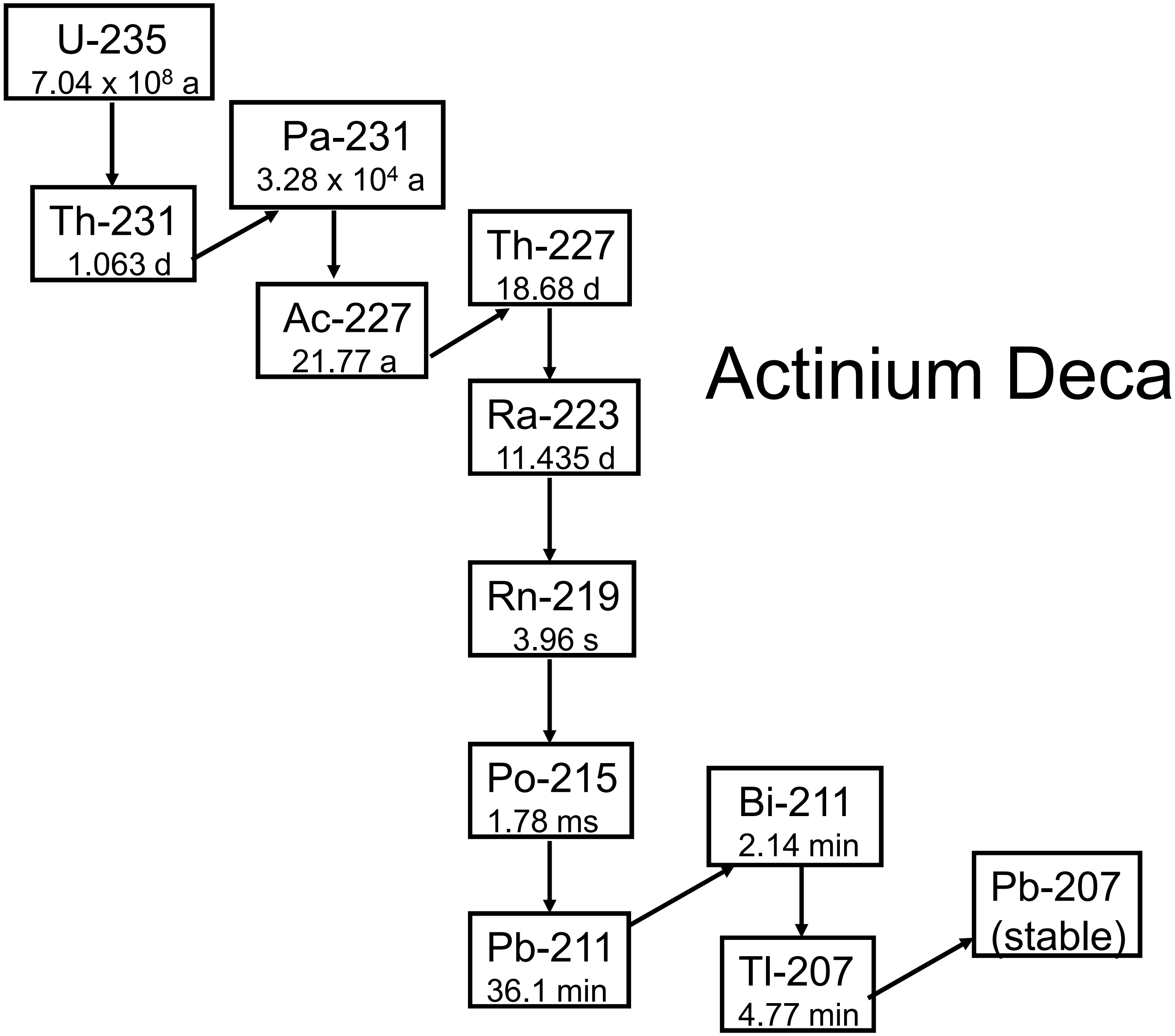
Pb-210
22.26 y

Bi-210
5.013 d

Po-210
138.4 d

Pb-206
(stable)

Actinium Decay Series



U-235
7.04×10^8 a

Th-231
1.063 d

Pa-231
3.28×10^4 a

Ac-227
21.77 a

Th-227
18.68 d

Ra-223
11.435 d

Rn-219
3.96 s

Po-215
1.78 ms

Pb-211
36.1 min

Bi-211
2.14 min

Tl-207
4.77 min

Pb-207
(stable)

Equilibrium

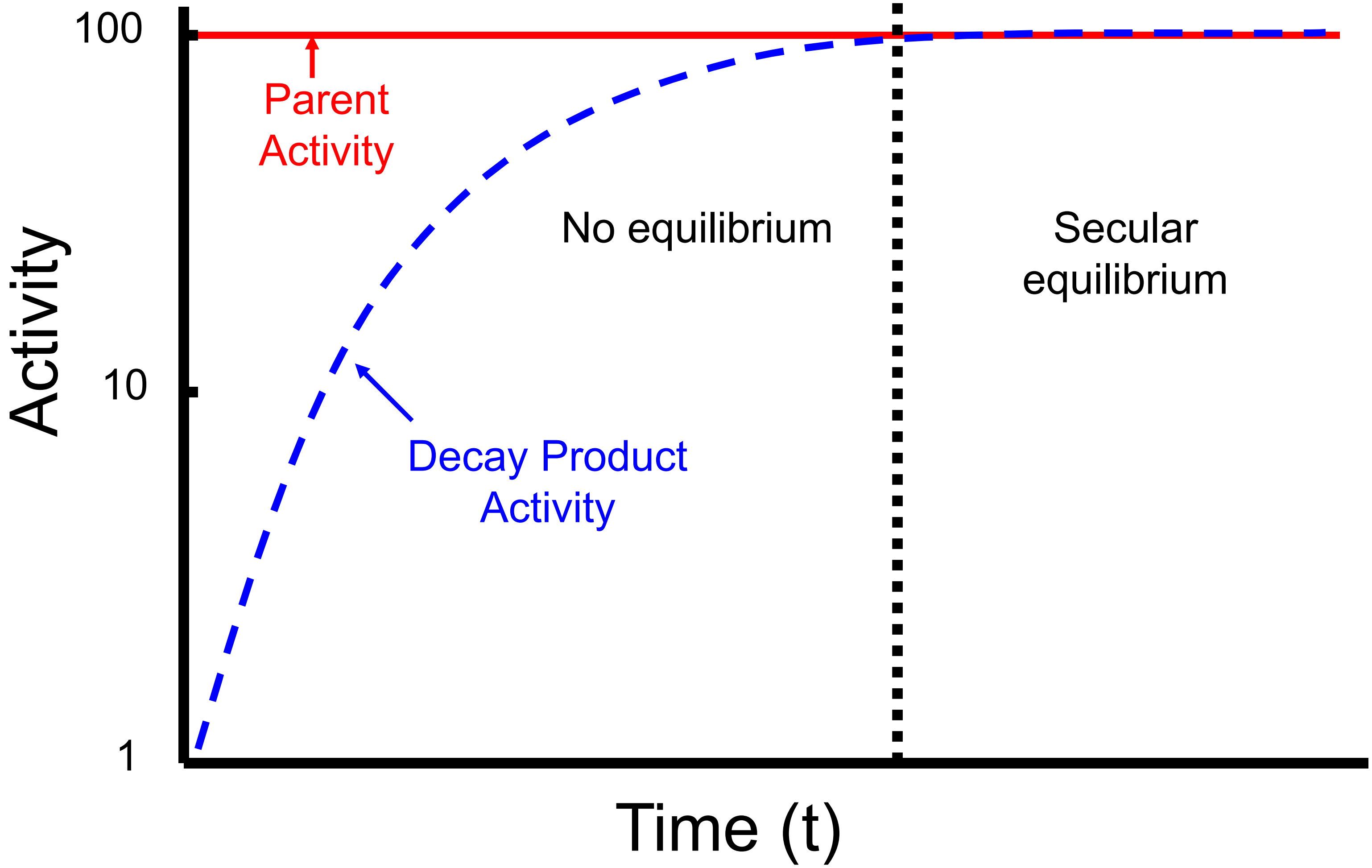
- Equilibrium occurs when a fixed ratio exists between the activity of a parent radionuclide and that of its radioactive decay product(s).
- When equilibrium exists, the activity of the decay product(s) is decreasing according to the half-life of the parent.
- There are two types of equilibrium: secular equilibrium

  transient equilibrium
- In the case of the uranium and actinium decay series, secular equilibrium is the thing of interest. Nevertheless, we will also consider transient equilibrium and the situation where no equilibrium is possible.

Secular Equilibrium

- Secular equilibrium is possible if the parent's half-life is much greater than that of the decay product.
- When secular equilibrium is achieved, the activity of the decay product equals that of the parent.
- Starting with nothing but the parent, the time to reach secular equilibrium is roughly five to ten half-lives of the daughter.
- Example: if one curie of pure radium 226 is placed in a sealed container, the activity of radon 222 will increase until it also reached one curie. This would take 20 to 30 days given the 3.8 day half life of Rn-222.

Secular Equilibrium



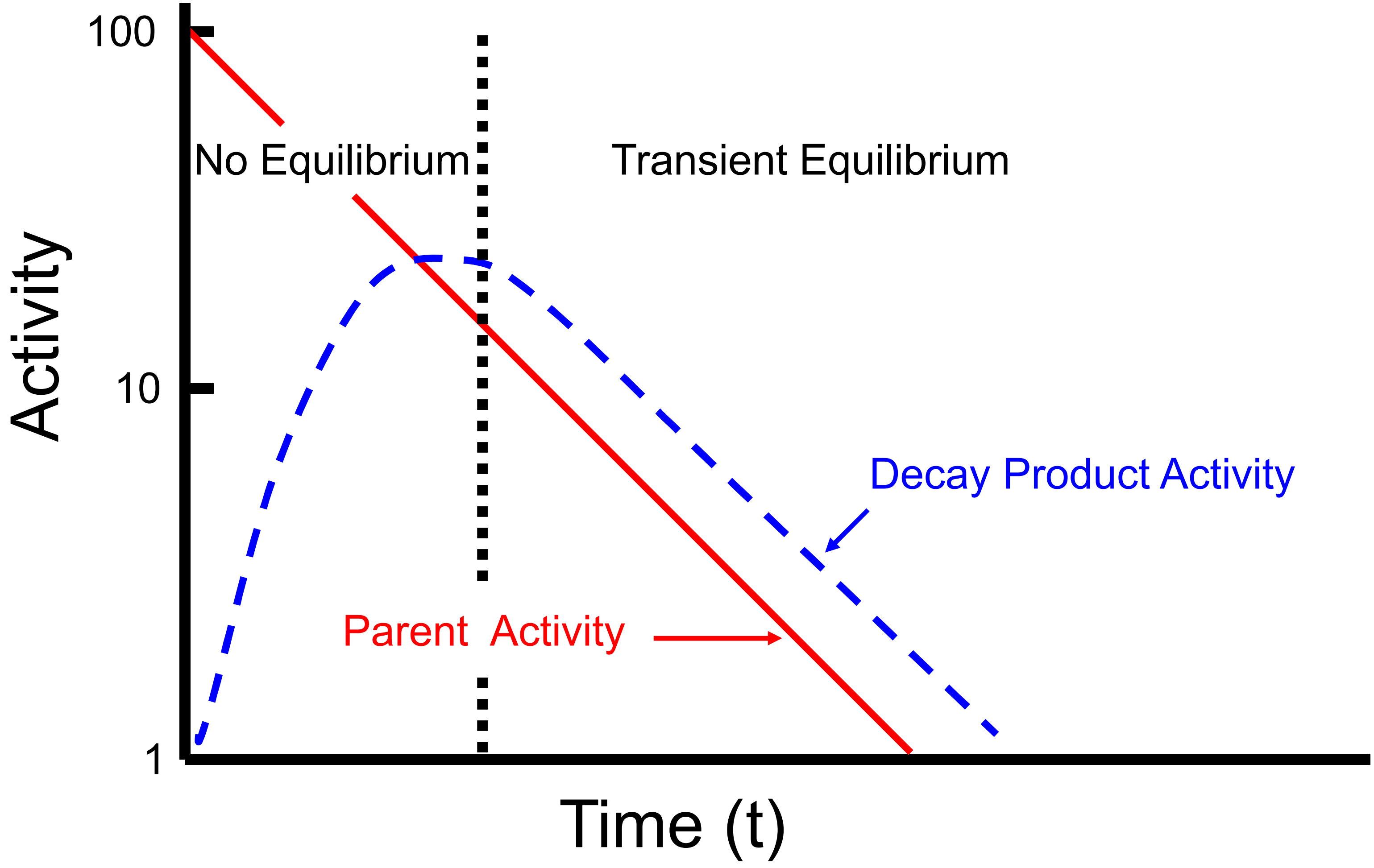
Transient Equilibrium

- If the parent nuclide’s half life is greater, but not “much” greater, than that of the daughter, a condition known as transient equilibrium can be established.
- The time to reach transient equilibrium is roughly five to ten half-lives of the daughter.
- When transient equilibrium is achieved:

  The daughter activity exceeds that of the parent.

  The daughter activity decreases according to the half-life of the parent.

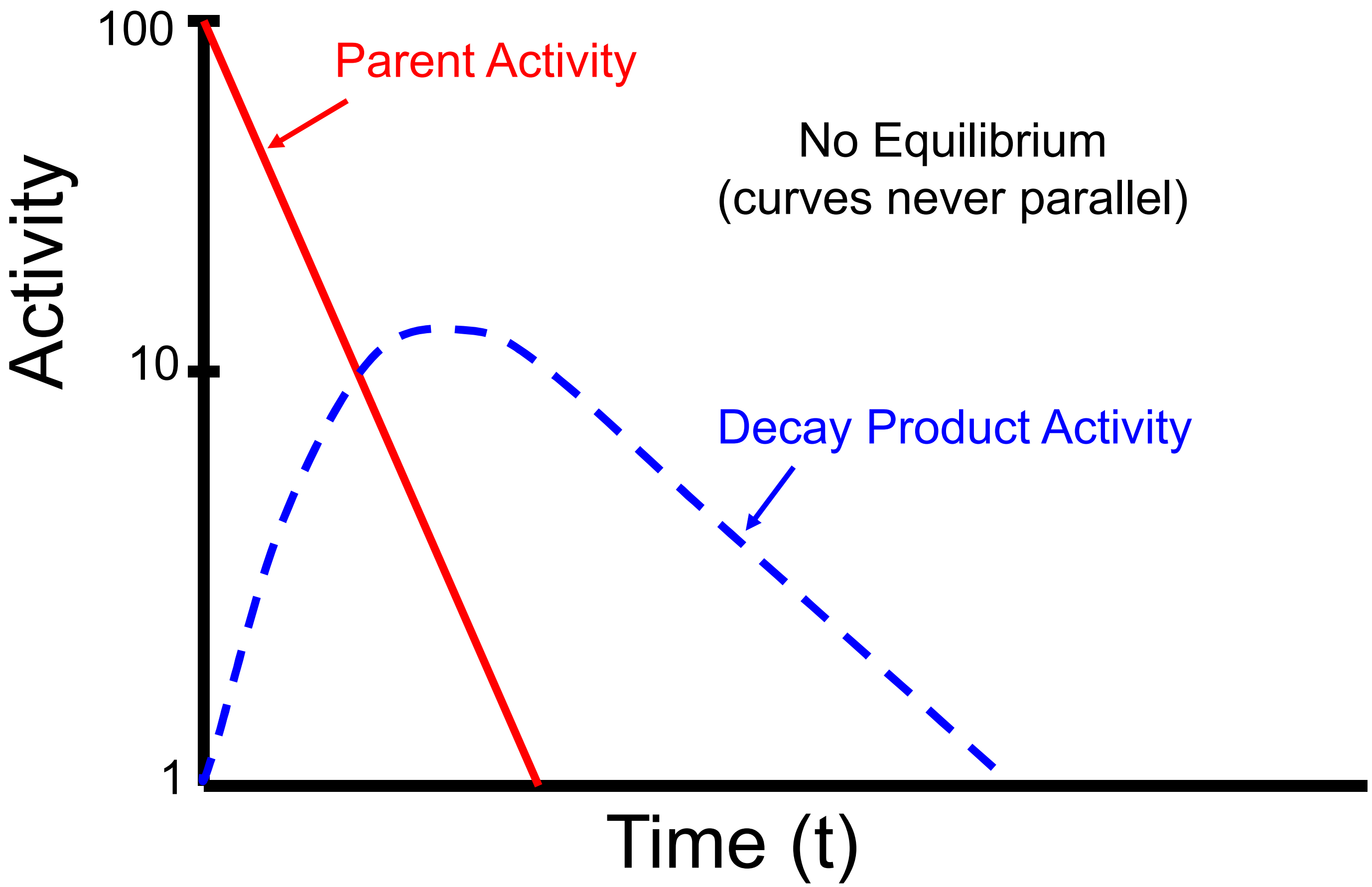
Transient Equilibrium



No Equilibrium

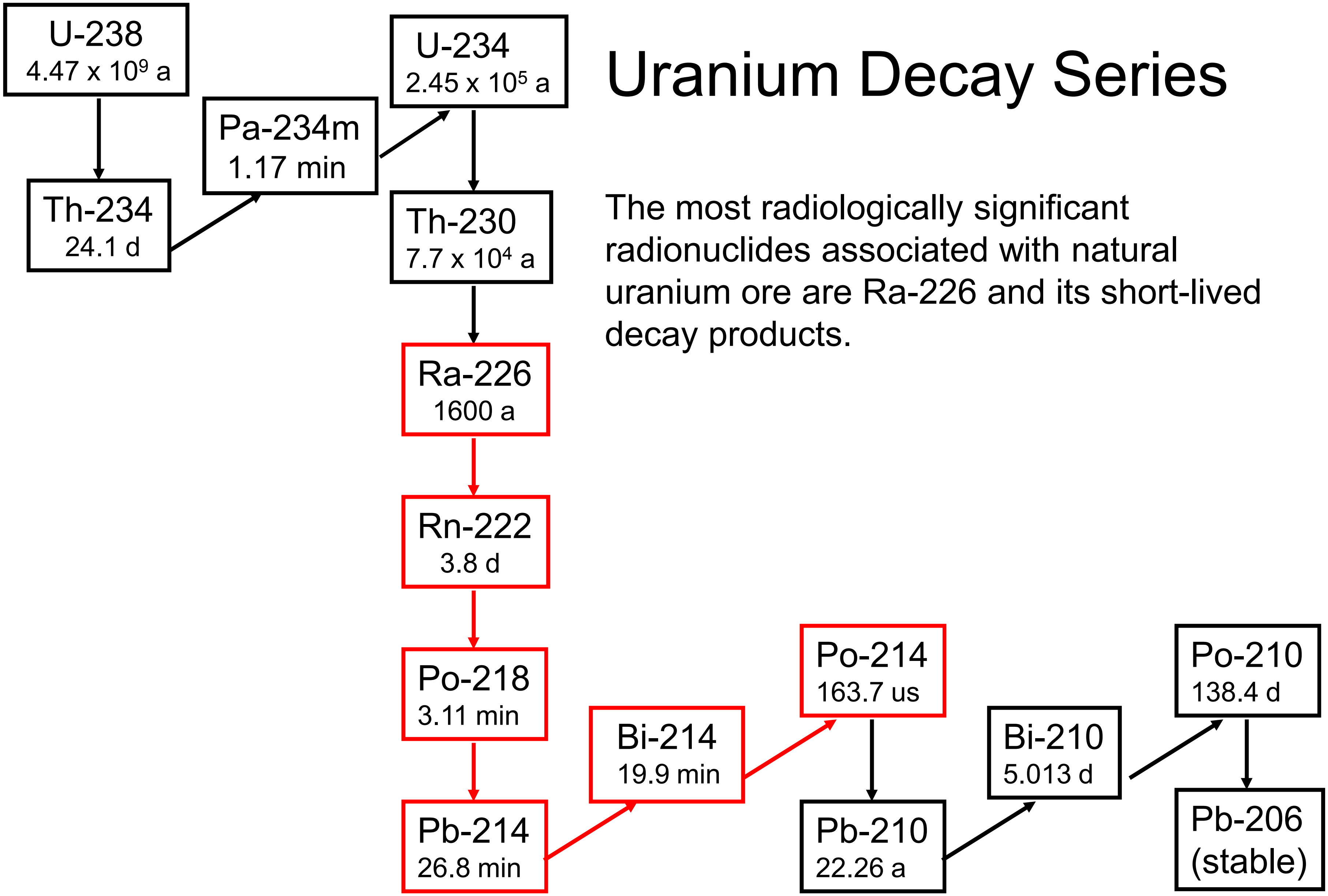
- If the parent's half life is shorter than that of the daughter, equilibrium cannot be achieved.
- The daughter activity increases from zero, reaches a maximum, and decreases at a rate primarily determined by its own half life.
- There is no increase in the total activity with time, the activity will only decrease.

No Equilibrium



Radiological Properties of Uranium

Uranium Decay Series



U-238
4.47×10^{9} a

Th-234
24.1 d

Pa-234m
1.17 min

U-234
2.45×10^{5} a

Th-230
7.7×10^{4} a

Ra-226
1600 a

Rn-222
3.8 d

Po-218
3.11 min

Pb-214
26.8 min

Bi-214
19.9 min

Po-214
163.7 us

Pb-210
22.26 a

Bi-210
5.013 d

Po-210
138.4 d

Pb-206
(stable)

The most radiologically significant radionuclides associated with natural uranium ore are Ra-226 and its short-lived decay products.

Uranium Ore - Daughter Products

Ra-226 and its short-lived decay products are the most radiologically significant radionuclides associated with uranium ore because:

- **The external gamma hazard is primarily due to Pb-214 and Bi-214. Some of their gamma rays are of high energy.**
- **Ra-226 is readily assimilated by the body ($f_1 = 0.2$)**
- **Rn-222 is a noble gas. Its decay products become attached to airborne particulates which can be inhaled.**

Uranium Ore - Daughter Products

In some situations the long lived decay products of Rn-222 (Pb-210, Bi-210 and Po-210) might be an internal radiological concern because:

- **Over time, they can accumulate on surfaces in areas with high radon levels**
- **Pb-210 is readily assimilated by the body (f_1 = 0.2)**

Purified Uranium - Daughter Products

- When natural uranium has been chemically purified, or otherwise separated from the ore, it consists of three nuclides: U-238, U-234 and U-235.
- By mass, it is almost all U-238.
- By activity, it is roughly 50% U-238 and 50% U-234.
- Over time, the activity of their decay products (initially zero) will increase.

Purified Uranium - Daughter Products

U-234 → Th-230 (75,400 a)

Although U-234 represents almost half the activity of pure uranium, the ingrowth of the U-234 daughters is relatively unimportant because:

- The decay product of U-234, the pure alpha emitter Th-230, has such a long half-life that any measureable increase in its activity will take tens of thousands of years.

Purified Uranium - Daughter Products

U-235 → Th-231 (1 d) → Pa-231 (32,800 a)

Th-231, the immediate decay product of U-235 has a one day half life. As such, it will be in secular equilibrium with U-235 within a week. Nevertheless, the ingrowth of the U-235 daughters is relatively unimportant because:

- **There is much less U-235 than U-238.**
- **Th-231 only emits low energy betas and gamma rays.**
- **The Th-231 gamma rays are of very low intensity.**
- **Any measureable increase in the Pa-231 activity will take tens of thousands of years.**

Purified Uranium - Daughter Products

U-238 → Th-234 (24.1 d) → Pa-234m (1.17m)

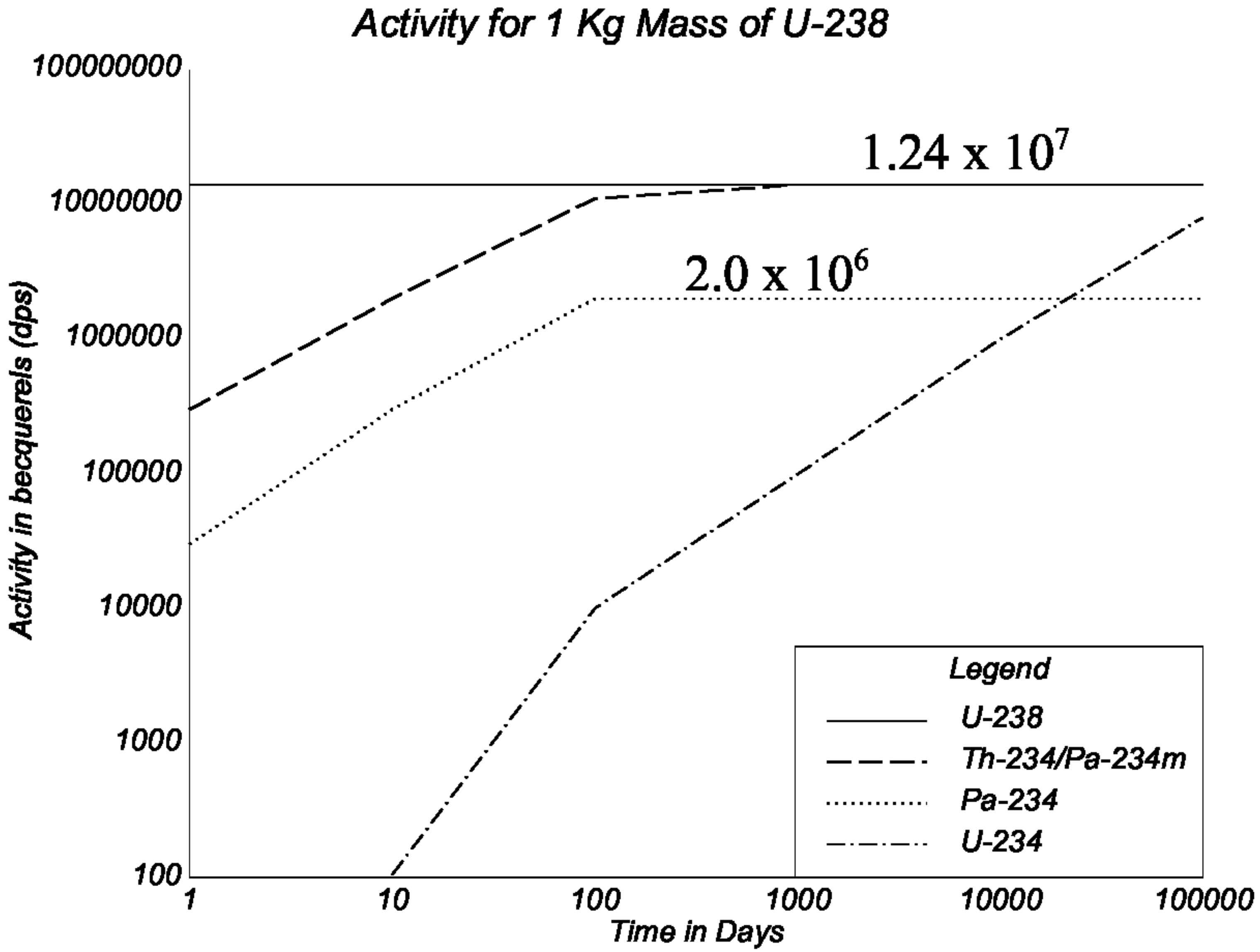
When considering ingrowth of the daughters of purified natural uranium, Th-234 and Pa-234m are the most significant.

- They achieve secular equilibrium with U-238 in approximately six months.
- They are beta-gamma emitters
- Initially purified uranium emits only alpha particles, but after six months there are two betas for every alpha.

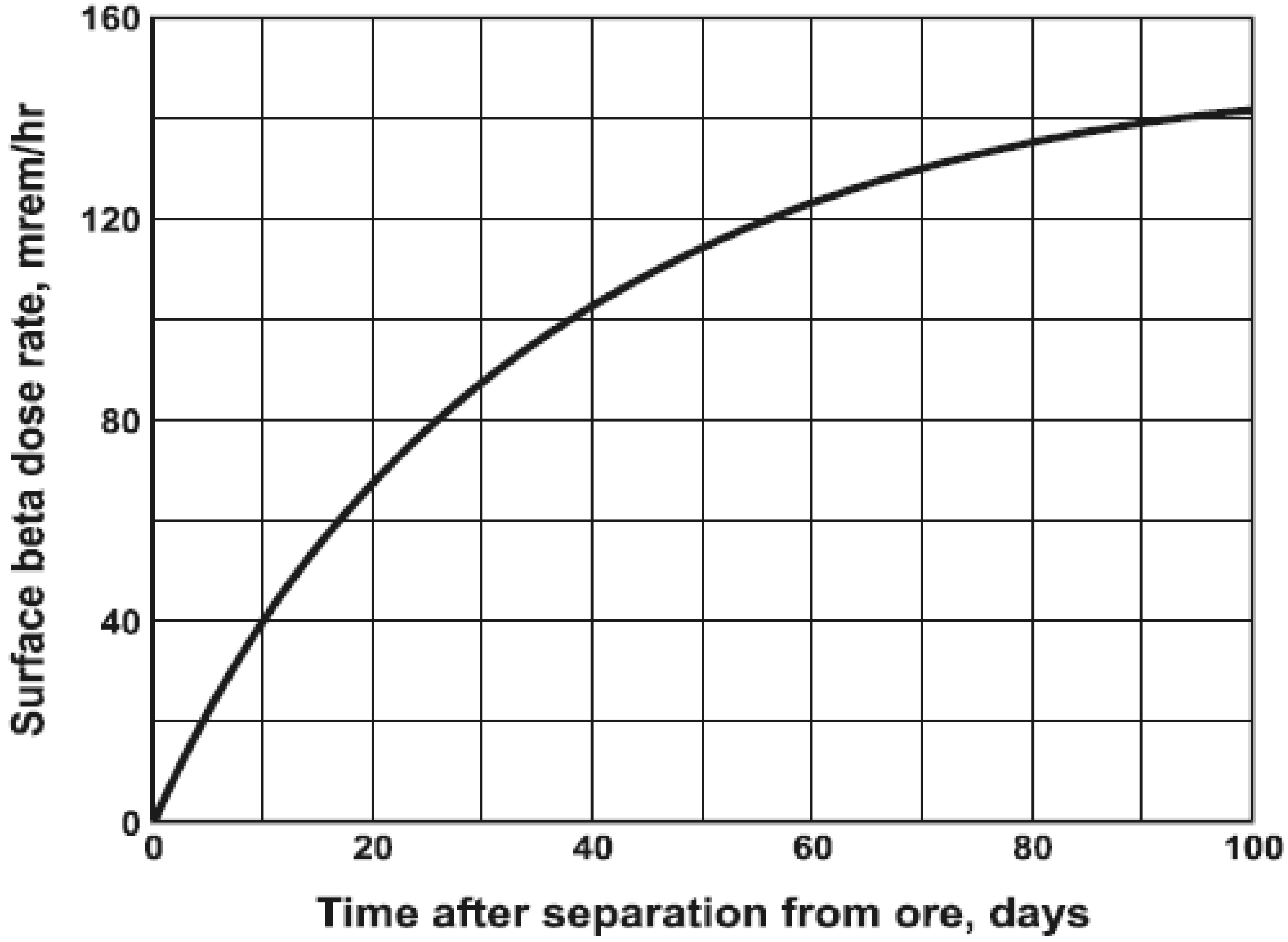
Purified Uranium - Daughter Products

U-238 → Th-234 (24.1 d) → Pa-234m (1.17m)

Th-234	Beta:	106 keV	6%
		107 keV	14%
		199 keV	78%
	Gamma:	63 keV	4%
		92 keV	4%
Pa-234m	Beta:	2270 keV	98%
	Gamma:	766 keV	0.3%
		1001 keV	0.8%


Activity for 1 Kg Mass of U-238
Activity in becquerels (dps)
100000000
10000000
1000000
100000
10000
1000
100
1
10
100
1000
10000
100000
Time in Days
1.24 x 10^7
2.0 x 10^6
Legend
U-238
Th-234/Pa-234m
Pa-234
U-234

Purified Uranium - Daughter Products



Regulatory Guide 8.30

Figure 1. Beta Dose Rate on the Surface of Yellowcake

Specific Activity

- Specific Activity (SA) is the activity per unit mass of a pure radionuclide. The units of specific activity might be Ci/g, Bq/g, etc.
- It provides an indication of the concentration of radioactivity, or the relationship between the mass of radioactive material and the activity.

Calculation of SA

Equation for specific activity (Bq/g):

$$SA = N\,\lambda$$

N = number of atoms/gram

= 6.022×10^{23} (atoms/mole) / atomic mass (g/mole)

λ = $\ln 2 / T_{1/2}$ (seconds)

For convenience, the equation can be rewritten to use the $T_{1/2}$ in years by converting from years to seconds

λ = $\ln 2 / (T_{1/2}\,y \times 3.156 \times 10^{7}\ s/y)$

= $2.1965 \times 10^{-8} / T_{1/2}\,y$

Calculation of SA (continued)

SA = N λ (in Bq/g)

= (6.022 x 10^{23}/atomic mass) x (2.1965 x 10^{-8} / $T_{1/2}$ years)

= 1.3227 x 10^{16}/ ($T_{1/2}$ years x atomic mass)

To calculate the SA in curies per gram:

SA (Ci/g) = 3.575 x 10^{5}/ ($T_{1/2}$ years x atomic mass)

Calculating the Specific Activity of U-234, U-235 and U-238

SA of U-234 $= 3.575 \times 10^5 / (T_{1/2} \text{ years} \times \text{atomic mass})$

$= 3.575 \times 10^5 / (2.455 \times 10^5 \times 234.04)$

$= 6.22 \times 10^{-3}$ Ci/g

SA of U-235 $= 3.575 \times 10^5 / (7.038 \times 10^8 \times 235.04)$

$= 2.16 \times 10^{-6}$ Ci/g

SA of U-238 $= 3.575 \times 10^5 / (4.468 \times 10^9 \times 238.05)$

$= 3.36 \times 10^{-7}$ Ci/g

Total Specific Activity of Natural Uranium

Isotope	% by weight	Weight (g)	SA (Ci/g)	Activity per gram of uranium (Ci)
U-234	0.0055	0.000055	6.22×10^{-3}	3.42×10^{-7}
U-235	0.72	0.0072	2.16×10^{-6}	1.56×10^{-8}
U-238	99.28	0.9928	3.36×10^{-7}	3.34×10^{-7}
Total	100	1	6.91×10^{-7}	6.91×10^{-7}

Weight vs. Activity of Natural Uranium

Isotope	% by weight	SA (Ci/g)	Activity per gram of uranium (Ci)	% Activity
U-234	0.0055	6.22×10^{-3}	3.42×10^{-7}	49.5
U-235	0.72	2.16×10^{-6}	1.56×10^{-8}	2.3
U-238	99.28	3.36×10^{-7}	3.34×10^{-7}	48.3

Chemical Properties of Uranium

General

- The chemical properties of uranium are important because they can affect the hazard of the material.
- The main concern is an internal intake of uranium rather than an external exposure.
- The dose and physiological consequences of such an intake are dependent on the several factors of which the chemical form is one.

UO_2 Uranium Dioxide

- Known as brown oxide or uraninite.
- The uranium in the ore body is primarily in a tetravalent state (U^{4+}) and can be considered to consist of UO_2
- One of the oxides that make up yellowcake
- Widely used to form nuclear fuel pellets.
- Low solubility in water.
- Clearance class Y (S)

UO_3 Uranium Trioxide

- Known as orange oxide.
- When heated in air will decompose to U_3O_8, when heated to high temperature (greater than 700 degree C) in the presence of H_2 will convert to UO_2.
- During the leaching process, uranium dioxide in the ore body is oxidized to uranium trioxide.
- One of the oxides that make up yellowcake.
- Moderate solubility in water.
- Clearance class W (M)

$UO_2(CO_3)$ Uranium Carbonate

- Generic form of several uranium carbonates .
- Carbonates are usually formed as charged complexes that react with other ions to form minerals.
- The charged complexes are very soluble and mobile with low affinity for soil.
- After the uranium in the ore body has been oxidized it is converted to a uranium carbonate complex. It is in this form that the uranium is extracted from the ground at an ISL facility.
- There is no “official” ICRP or NRC clearance class. Little to no data available.

UO_4-nH_2O Uranium Peroxide

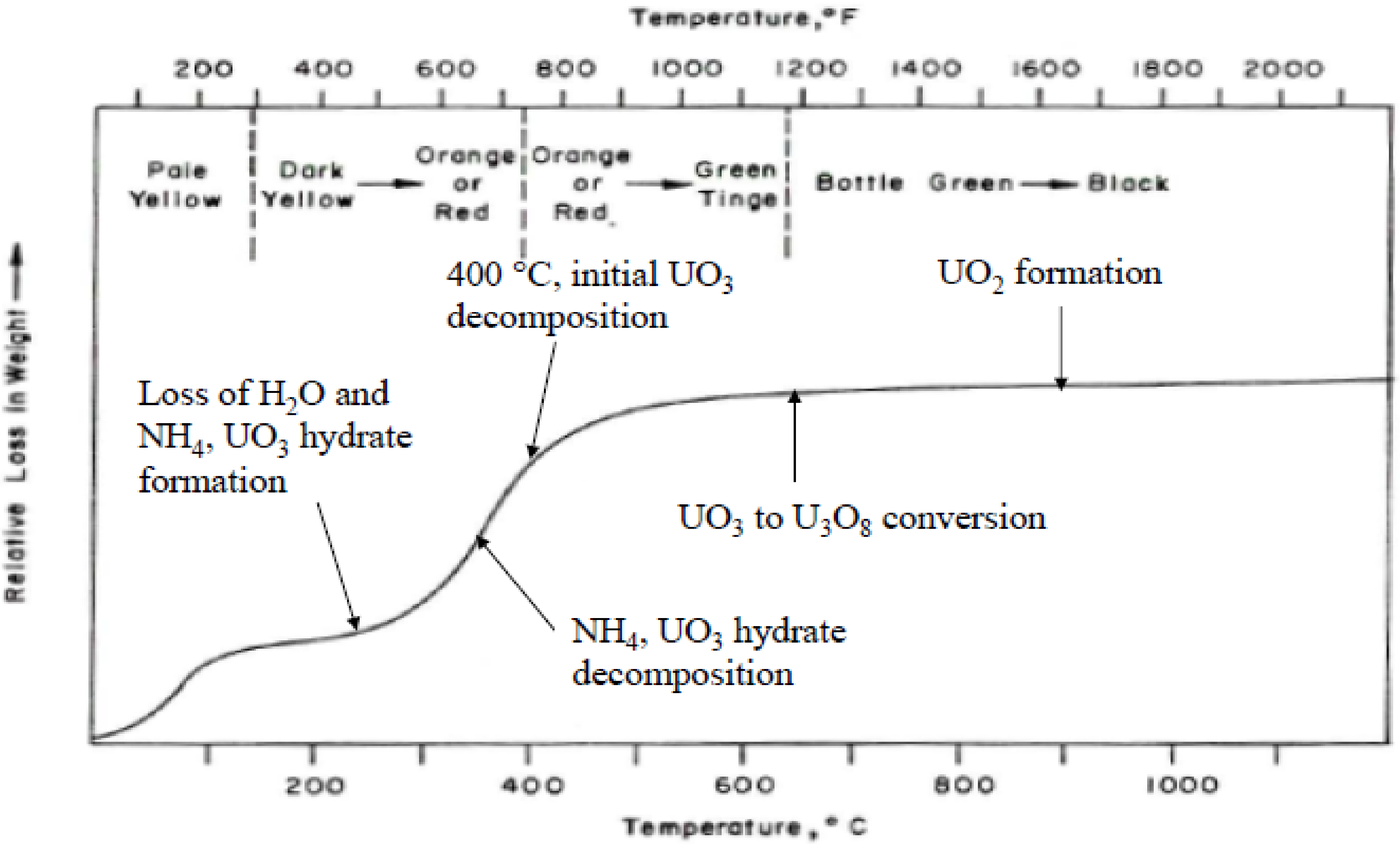
- Pale yellowish compound.
- Commonly found at ISL mills as part of the process of precipitating uranium from the pregnant eluant.
- Moderately soluble in water.
- No “official” ICRP or NRC clearance class. Some studies indicate that Class W might be appropriate (*Biokinetics and Analysis of Uranium in Man*. United States Uranium Registry, USUR-05 HEHF-47, 1984)

($(NH_4)_2U_2O_7$) Ammonium Diuranate

- One of the intermediate chemical forms of uranium produced during yellowcake production.
- The name 'yellowcake' was originally given to this bright yellow substance, now applies to mixtures of uranium oxides which are actually hardly ever yellow.
- It is precipitated during production by adding aqueous ammonium hydroxide.
- No “official” ICRP or NRC clearance class. Some studies indicate that Class D and W might be appropriate (*Biokinetics and Analysis of Uranium in Man*. United States Uranium Registry, USUR-05 HEHF-47, 1984)

Effect of Calcining Temperature on Ammonium Diuranate Decomposition

Radiological Issues at ISR Facilities (Burrows, 2009)



400 °C, initial UO_3 decomposition

UO_2 formation

Loss of H_2O and NH_4, UO_3 hydrate formation

UO_3 to U_3O_8 conversion

NH_4, UO_3 hydrate decomposition

U_30_8 Triuranium Octoxide

- Pure U_30_8 is greenish black in color.
- This is the most stable form of uranium and used for storage and disposal.
- Primary component (ca. 70 – 90%) of yellowcake.
- Low solubility in water.
- Clearance class Y (S)

Yellowcake

- Uranium concentrate. The end product of uranium recovery operations.
- Originally, the term referred to ammonium diurinate, but now it refers to the final product of purification.
- A mixture of uranium oxides: UO_2, UO_3, and U_3O_8
- The main component is $U_3O_{8.}$ But it is the other oxides that are responsible for the yellow to orange color.

Yellowcake

NRC Online Glossary:

- “The solid form of mixed uranium oxide, which is produced from uranium ore in the uranium recovery (milling) process.
- The material is a mixture of uranium oxides, which can vary in proportion and color from yellow to orange to dark green (blackish) depending on the temperature at which the material is dried (which affects the level of hydration and impurities), with higher drying temperatures producing a darker and less soluble material.”


U_3O_8
UO_3
UO_3 LOW IN NO_3
$UO_2(NO_3)_2 \cdot 6H_2O$
UF_4

Effect of Chemical Form on Hazard

- The chemical form of uranium does not affect the external dose hazard.
- It does affect the internal hazards when uranium is inhaled or ingested.
- Different chemical forms of uranium are classified by their clearance class (aka solubility class).
- This describes how quickly the chemical form of uranium is removed from the deepest portion of the respiratory system (the pulmonary region).

Class D Material

- Clearance Class D (or F) material is usually referred to as soluble uranium this includes UF_6, UO_2F_2, and UNH
- Class D material clear rapidly from the body.
- Due to rapid removal from the body uranium in this form may be more hazardous from a chemical toxicity standpoint than a radiological one.

Class W Material

- Clearance class W (or M) material is moderately soluble and includes UO_3, UF_4, and uranium peroxide.
- Class W material will clear more slowly from the body.
- Class W material is considered insoluble for internal dosimetry and toxicity purposes.

Class Y Material

- Class Y (or S) material is also known as insoluble uranium and includes U_3O_8, and UO_2.
- Class Y material is slowly cleared from the body.
- Class Y material is usually a radiological hazard with lower chemical toxicity hazards.
- Under normal environmental conditions, class D material might be chemically converted to class W, but class W material would not be converted to class Y.

Effect of Chemical Form on Hazard

- The Annual Limit on Intake (ALI) and the Derived Air Concentration (DAC) depend on the clearance class.
- If there is a mixture of chemical forms, it might be necessary to determine the percent makeup of the mixture in order to calculate the dose.

Effect of Chemical Form on Hazard

10 CFR 20 Appendix B

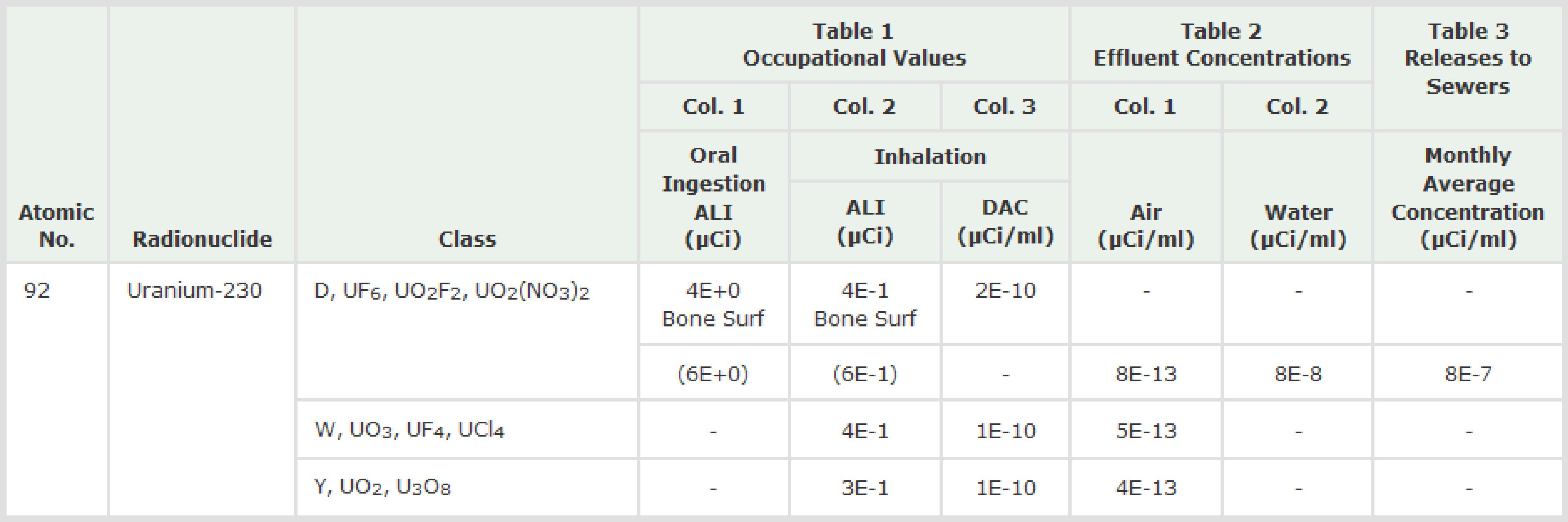
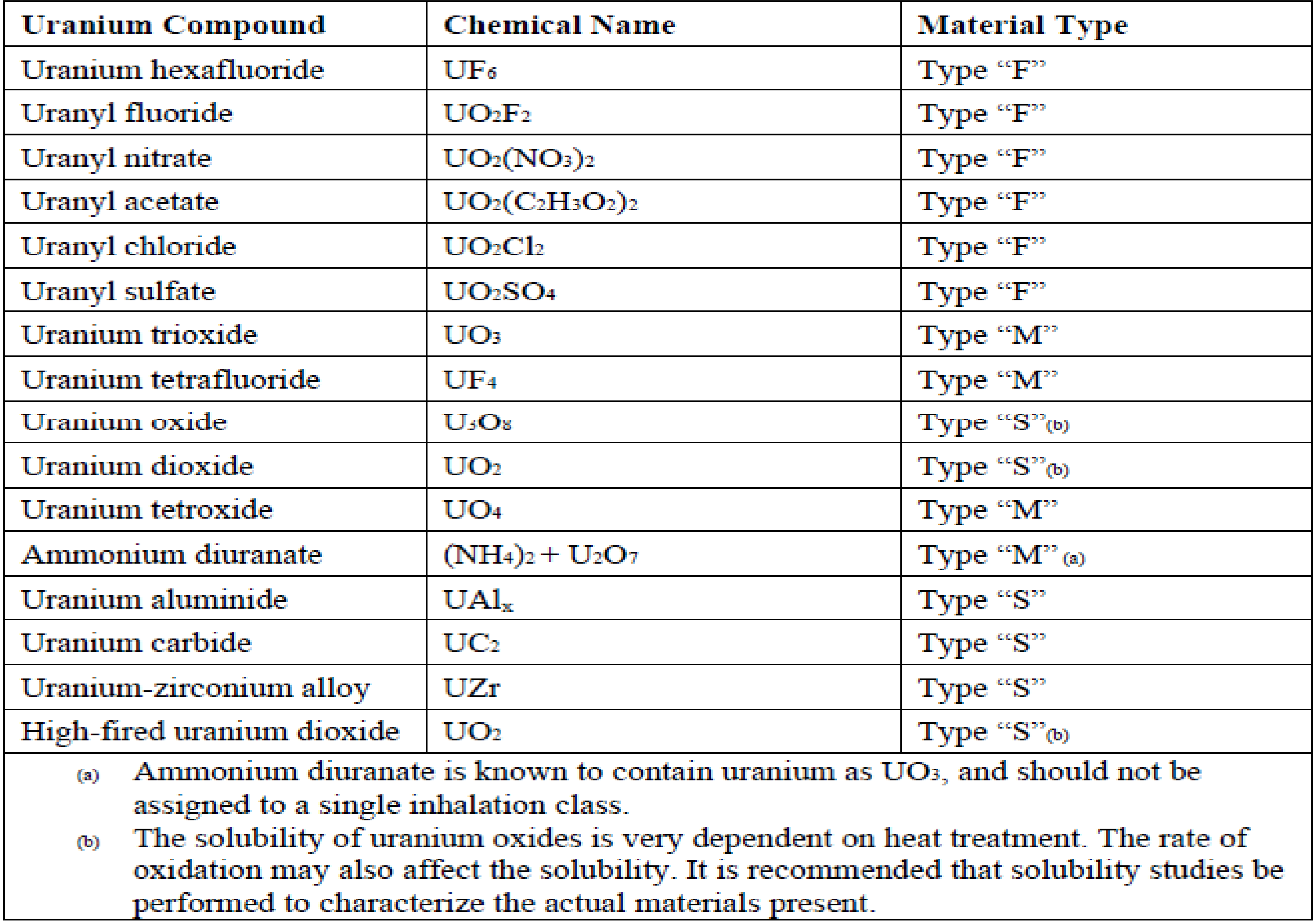


			Table 1 Occupational Values			Table 2 Effluent Concentrations		Table 3 Releases to Sewers
			Col. 1	Col. 2	Col. 3	Col. 1	Col. 2	
			Oral Ingestion	Inhalation				
Atomic No.	Radionuclide	Class	ALI (μCi)	ALI (μCi)	DAC (μCi/ml)	Air (μCi/ml)	Water (μCi/ml)	Monthly Average Concentration (μCi/ml)
92	Uranium-230	D, UF_6, UO_2F_2, $UO_2(NO_3)_2$	4E+0 Bone Surf	4E-1 Bone Surf	2E-10	-	-	-
			(6E+0)	(6E-1)	-	8E-13	8E-8	8E-7
		W, UO_3, UF_4, UCl_4	-	4E-1	1E-10	5E-13	-	-
		Y, UO_2, U_3O_8	-	3E-1	1E-10	4E-13	-	-

Guide of Good Practices for Occupational Radiological Protection in Uranium Facilities (DOE-STD-1136-2009)



Uranium Compound	**Chemical Name**	**Material Type**
Uranium hexafluoride	UF_6	Type "F"
Uranyl fluoride	UO_2F_2	Type "F"
Uranyl nitrate	$UO_2(NO_3)_2$	Type "F"
Uranyl acetate	$UO_2(C_2H_3O_2)_2$	Type "F"
Uranyl chloride	UO_2Cl_2	Type "F"
Uranyl sulfate	UO_2SO_4	Type "F"
Uranium trioxide	UO_3	Type "M"
Uranium tetrafluoride	UF_4	Type "M"
Uranium oxide	U_3O_8	Type "S"(b)
Uranium dioxide	UO_2	Type "S"(b)
Uranium tetroxide	UO_4	Type "M"
Ammonium diuranate	$(NH_4)_2 + U_2O_7$	Type "M" (a)
Uranium aluminide	UAl_x	Type "S"
Uranium carbide	UC_2	Type "S"
Uranium-zirconium alloy	UZr	Type "S"
High-fired uranium dioxide	UO_2	Type "S"(b)

(a) Ammonium diuranate is known to contain uranium as UO_3, and should not be assigned to a single inhalation class.

(b) The solubility of uranium oxides is very dependent on heat treatment. The rate of oxidation may also affect the solubility. It is recommended that solubility studies be performed to characterize the actual materials present.

Effect of Chemical Form on Hazard

Regulatory Guide 8.30

- "Yellowcake dried at low temperature, which is predominantly composed of ammonium diuranate, or in the new processes uranyl peroxide, both are more soluble in body fluids than yellowcake dried at higher temperature; and a relatively large fraction is rapidly transferred to kidney tissues . . . For purposes of compliance with 10 CFR Part 20, yellowcake undried or dried at low temperature should be classified as soluble."

Effect of Chemical Form on Hazard

Regulatory Guide 8.30

- "Yellowcake dried at high temperature is a mixture of compounds that contains a major portion of more insoluble uranium oxides. Radiation dose to the lung and other organs is the limiting consideration rather than chemical toxicity; this is primarily due to the large insoluble component. For compliance purposes, yellowcake dried at 400°C (752F) and above should be classified as insoluble

Effect of Chemical Form on Hazard

***Radiological Issues at ISR Facilities* (Burrows, 2009)**

“NRC Staff DAC Recommendations:

- **400°C remains a valid transition temperature between inhalation classes (based on UO3 decomposition).**
- **Lacking site specific data, hydrogen peroxide precipitated yellowcake, dried at < 400°C, should be considered a Class W compound for radiation protection purposes.**
- **Lacking site specific data, hydrogen peroxide precipitated yellowcake, dried at 400°C and higher, should be considered a Class Y compound for radiation protection purposes.”**

Physical Form

- The external hazard of uranium is not affected by its physical form.
- Nondispersible solids (e.g., metals or ceramics of uranium) have minimal hazard from inhalation.
- Dispersible forms can be easily made airborne and represent a potential internal hazard (e.g., powders, and liquids).

Human Response Indicators to Uranium Exposure

- Uranium has been recognized as a chemical hazard since the 1800s.
- The main chemical hazard as with most heavy metals is toxicity to the kidney.
- This was first observed in the 1800s when UNH was used to treat diabetes.
- Excessive intake of UNH resulted in kidney damage.
- This is the primary concern from a chemical toxicity standpoint.

Uranium Toxicity Limit

- Due to the potential for kidney toxicity the NRC has promulgated a limit to uranium based on U toxicity.
- 10CFR20 1201(e) states that “ In addition to the annual dose limits, the licensee shall limit the soluble uranium intake by an individual to 10 milligrams in a week in consideration of chemical toxicity.”
- 10CFR20 Appendix B footnote 3 also addresses this issue more in depth.