

*Draft*

**An Alternative Assessment of Radon Releases from K-65 Silos**

**An SC&A White Paper**

**Contract No. 200-2004-03805**

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November 2008

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## 1.0 STATEMENT OF PURPOSE

Under Task Order 5, the Advisory Board on Radiation and Worker Health (the Board) directed S. Cohen and Associates (SC&A) to perform a full review of the Feed Materials Production Center (FMPC) Special Exposure Cohort (SEC) Petition-00046 and the NIOSH SEC Petition Evaluation Report (ER). In compliance with the Board's directive, SC&A submitted its review in a draft report on May 31, 2007.

Among issues identified by SC&A was Finding 4.2-3, which stated that NIOSH may have adopted “. . . **incorrect** model assumptions pertaining to radon releases from K-65 Silos” [Emphasis added].

On October 28, 2008, the Board's Work Group on SEC Petition-00046 (Chaired by Mr. Bradley Clawson) conducted a teleconference that focused on several unresolved findings that included Finding 4.2.-3. The Work Group issued an action item, which directed SC&A to provide the following additional data/information in support of Finding 4.2-3:

- (1) Provide a quantitative calculation that supports SC&A's claim of potential Rn-222 releases between 64,500 Ci/yr to 92,000 Ci/yr from Silo 1; and
- (2) Discuss the necessary assumptions and circumstantial evidence, which support these release estimates.

## 2.0 RELEVANT BACKGROUND INFORMATION

### 2.1 RAFFINATES STORED IN SILOS 1 AND 2

The primary mission at the Feed Materials Production Center was the processing of uranium ores (and other feed materials) to high quality, finished uranium metal products. Between 1953 and 1955, FMPC processed pitchblende ores from the Belgian Congo, which contained unusually high activity levels of Ra-226. The liquid extraction of uranium from pitchblende ores in Plant 2/3 produced waste streams (or raffinates) that must reasonably be assumed to have retained nearly all of the Ra-226, as well as other radiocontaminants that had been present in the ore. Raffinates generated in Plant 2/3 were disposed directly to the storage Silos 1 and 2. In addition to raffinates generated at FMPC, a total of 13,000 55-gallon drums of African pitchblende raffinates generated at the Mallinckrodt Chemical Works (MCS) facility were also disposed in Silos 1 and 2 between July 1953 and September 1958. In total, the extraction of uranium from pitchblende ores at FMPC and MCW produced an estimated 10,000 metric tons of radium-containing raffinates that were stored in Silos 1 and 2.

Silo 3, the Metal Oxide Silo, contains the metal oxide waste raffinate from the extraction of uranium ores and concentrates. Unlike the K-65 raffinates, the metal oxide was transferred from Plant 2/3 by high-pressure air through pipes to Silo 3. All of the metal oxide material stored in Silo 3 was derived from onsite processing of ores/concentrates that had Ra-226 levels that were about 40-fold lower than the K-65 material.

Each of the three silos is 80 feet in diameter with an overall height of 36 feet, of which about 26 feet 8 inches is the height of the exterior wall with the center of the dome at 36 feet. The vertical walls are 8-inch thick concrete and the domes are a nominal 4-inch thickness of concrete. The total volume of each silo is about 160,000 feet<sup>3</sup>. While both K-65 Silos (i.e., Silos 1 and 2) are about two-thirds filled, the Metal Oxide Silo (i.e., Silo 3) is filled to near capacity at 150,000 feet<sup>3</sup> of waste. Figure 1 provides a schematic cross-section of the silos and identifies several key features that affected the release of radon, as discussed below.

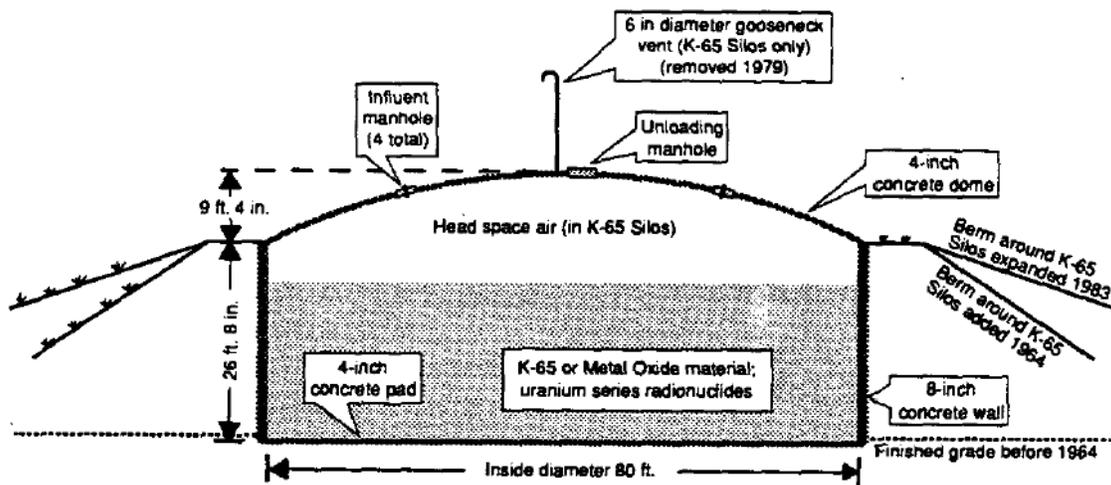


Figure 1. General Cross Section of the K-65 and Metal Oxide Silos

## 2.2 K-65 SILO DESIGN FLAWS AND MODIFICATIONS AIMED TO MITIGATE RADON RELEASES

Over the years, the rate of radon releases from K-65 silos was likely affected by design flaws, as well as the many modifications to the silos that attempted to reduce radon emissions. A brief review of these flaws/modifications is provided in a 1995 report issued by the Radiological Assessment Corporation (RAC Report CDC-5, 1995), which stated the following:

From pages 28–29 (of RAC 1995):

*The K-65 Silos have had problems of deterioration, almost since the time of construction. Significant cracking in the walls and seepage of the contents was noted from the 1950s. Because of these problems, repairs and improvements to the Silos occurred from the 1960s through the 1980s. Not all of the changes to the Silos would have had a significant effect on the releases of radon. The most important change, for radon emissions, was the sealing of penetrations of the Silo domes in 1979. This action would have significantly **reduced the ventilation** of the silo air spaces, and thus also reduced the radon releases from the Silos. The addition of an exterior foam layer on the silo domes in 1987 may have further reduced the emissions of radon. Earthen berms were built around the Silos in 1964. However, at the time the radon releases occurred primarily through*

*openings in the silo domes, so the addition of the berms would not have altered the releases. [Emphasis added.]*

From page J-22 (of Appendix J, RAC 1995)

*Since the Silos were **open to the atmosphere** [until 1979] with the **gooseneck vent**, and **other unsealed penetrations** in the domes, it seems probable that the overwhelming majority of Rn releases would have been through the dome penetrations . . .*

*. . . We also assume that a significant change may have occurred at the end of 1987, when the foam layer was added to the silo domes. [Emphasis added.]*

Table J-3 in Appendix J of the 1995 RAC Report provides additional summary descriptions, dates, and reference documents pertaining to these modifications. For convenience, Table J-3 is reproduced herein as Table 1.

**Table 1. Summary of Historical Changes to the K-65 Storage Silos**  
(Source: RAC 1995, Appendix J)

<b>Date</b>	<b>Repairs or Improvements</b>
May 1964	Cracks in silo walls were patched, waterproofing sealant applied, and earthen berm constructed to counterbalance material inside silos
End of June 1979	Openings in silo domes, including the <b>gooseneck pipe</b> and other penetrations, were sealed, with gaskets installed, to prevent Rn emissions
June 1983	The earthen berms were enlarged to correct erosion problems
Early 1986	Dome covers added to protect the center sections of the silo domes; neoprene membrane layer applied to part of Silo 2
November 1987	<b>Radon Treatment System*</b> installed to treat displaced Rn during work on Silos (not continuously operated)
December 1987	Rigid, polyurethane foam layer and urethane coating applied to exterior of silo dome surfaces to weatherproof the Silos
November 1991	Addition of layer of bentonite on top of K-65 material in Silos

\* The Radon Treatment System (RTS) is a system that pumps air in the headspace of the silos through a series of calcium sulfate and charcoal beds, which adsorb Rn-222.

### **2.3 RADIONUCLIDE CONCENTRATIONS AND DISTRIBUTIONS IN SILOS 1, 2, AND 3**

While a very limited amount of K-65 waste sampling data was collected prior to 1989, only sampling data first obtained in 1991 provide a reasonable assessment of the distribution of nuclide-specific activities in Silos 1, 2, and 3 (ASI/IT 1992). Sample locations from this program are defined by the zone and the four silo manholes from which the sample was obtained. Each zone refers to roughly one-third of the K-65 material in the Silo with Zone A the top third, Zone B the middle third, and Zone C the bottom third.

A similar set of waste samples were obtained through 3 out of 4 influent manholes of Silo 3 in a 1989 survey that was part of a Remedial Investigation (RI) Report (DOE 1990). However, the RI does not identify the locations in behalf of the individual samples. For convenience, summary results of sampling data for Silos 1 and 2, and Silo 3 are presented herein in Tables 2 and 3. Most relevant to this report are sampling data that identify the absolute, as well as relative, activity concentrations for Ra-226 and its long-lived radioactive daughter Pb-210 ( $t_{1/2}$  of 22 years) for a given silo, as well as differences between the K-65 Silos and the Metal Oxide Silo 3, as summarized in Table 4 below. An important distinction between the K-65 Silos and the Metal Oxide Silo is the extent to which Pb-210 is in disequilibrium with its parent Ra-226.

It must also be noted that NIOSH elected to cite core sampling data in Table 5-16 of ORAUT-TKBS-0017-5 that were taken in 1993 and reported by Tomes 2001. In behalf of the 1993 sample set, the mean activity values cited in Table 5 below were reported.

**Table 2. Results of Radionuclide Analyses on K-65 Material Obtained by ASI/TT from 1991 Sampling**

Sample identification <sup>b</sup>			Radionuclide concentrations in K-65 material (pCi g <sup>-1</sup> )									
number	zone	location	<sup>227</sup> Ac	<sup>210</sup> Pb	<sup>210</sup> Po	<sup>226</sup> Ra	<sup>228</sup> Th	<sup>230</sup> Th	<sup>232</sup> Th	<sup>234</sup> U	<sup>235,5</sup> U	<sup>238</sup> U
						Silo 1						
099728	C	SE	6870	235,200	267,000	601,600	nd <sup>c</sup>	105,372	981	1548	57.4	861
099743	A	NE	5623	117,700	144,000	394,900	nd	59,274	1106	750	105	677
099870	A	SE	8486	126,800	296,000	367,600	nd	54,050	nd	1466	43.7	650
099886	A	NW	4320	77,860	154,000	306,800	nd	33,100	735	489	19.1	387
099909	B	NE	17,390	144,300	269,000	397,900	nd	64,400	661	875	39.4	719
099930	B	NW	10,700	191,300	237,000	680,900	2280	52,300	nd	1089	42.1	673
099939	C	NW	8118	235,900	273,000	510,400	nd	83,627	nd	936	31.5	564
099948	C	NW	6064	r <sup>d</sup>	232,000	r	835	r	835	508	nd	486
099966	B	SE	11,130	381,400	434,000	890,700	nd	75,370	982	721	29.2	680
099975	B	SE	7016	248,100	276,000	503,300	nd	50,917	702	608	22.0	649
100004	B	NE	9931	200,900	174,000	671,700	nd	54,521	nd	758	29.2	631
100025	C	NE	9012	183,600	230,000	520,600	nd	97,353	nd	696	90.0	717
100039	C	NE	5194	182,300	166,000	550,600	nd	99,494	nd	746	39.9	687
Mean for Silo 1 <sup>e</sup>			8450	194,000	242,000	525,000	1560	69,100	857	861	45.7	645
Standard deviation <sup>e</sup>			3420	78,700	77,100	158,000	1020	22,900	169	330	26.5	116
						Silo 2						
099355	B	SE	5448	125,000	168,000	404,800	nd	93,399	nd	1945	48	943
099356	B	SE	3407	161,000	164,000	414,000	nd	95,892	1785	na <sup>f</sup>	na	na
099359	B	SE	7517	194,700	188,000	481,000	nd	90,495	nd	na	na	1925
099710	C	SE	8258	129,700	104,000	285,400	nd	43,600	nd	841	93.3	810
099721	C	SE	6722	76,210	692,000	219,700	nd,r	37,300	nd,r	1792	74.8	2299
099774 <sup>g</sup>	C	NW	7357	179,500	93,400	252,100	nd	25,200	nd	783	35.6	606
099788 <sup>g</sup>	C	NW	6210	121,700	57,900	191,600	nd	160,000	2140	852	98.5	857
099802	C	NW	5641	125,900	90,600	176,900	622	37,000	985	586	92.0	595
099811	A	NE	4474	58,160	55,300	134,900	798	20,500	nd	671	73.8	688
099831	B	NE	5649	74,650	132,000	179,500	nd	35,500	nd	1408	80.9	818
099846	C	NE	10,450	127,900	209,000	368,200	nd	74,200	983	1429	130	1265
099861	C	NE	9668	133,000	241,000	405,500	7360	99100	nd	1465	172	1356
Mean for Silo 2 <sup>e</sup>			6730	123,000	193,000	299,000	2930	65,400	1470	1220	92.4	1140
Standard deviation <sup>e</sup>			2130	40,300	175,000	119,000	3840	30,500	583	500	37.3	572
Silos 1 and 2 considered together												
Mean for Silos 1 and 2 <sup>e</sup>			7660	160,000	220,000	417,000	2380	67,400	1080	1010	65.7	861
Standard deviation <sup>e</sup>			2980	71,600	131,000	179,000	2860	26,200	464	435	38.8	452

<sup>a</sup> Ref: ASI/TT 1992. Analyses were also performed for <sup>231</sup>Pa, <sup>224</sup>Ra, and <sup>228</sup>Ra. Since these radionuclides were not detected in any samples, we do not include them in this table.

<sup>b</sup> Zone A refers to the top one-third of a complete core (thus in the top one-third of the K-65 material), zone B to the middle one-third, and zone C to the bottom one-third. The locations are the manholes, by direction, through which the sample was obtained.

<sup>c</sup> "nd" means not detected. The ASI/TT table reported a less-than value, which we do not give here.

<sup>d</sup> "r" means the data validation code, in the ASI/TT data table, indicates the analysis result was rejected (though a value was given by ASI/TT, we do not present it or use it here).

<sup>e</sup> For our calculations of the mean and standard deviation, we ignored samples with "not detected" results.

<sup>f</sup> "na" means no analysis result was reported by ASI/TT.

<sup>g</sup> Samples 099774 and 099788 were field duplicates. We averaged the results before calculating means and standard deviations.

**Table 3. Radionuclide Analyses on Metal Oxide Material from 1989 Sampling of Silo 3**

Radionuclide concentrations in metal oxide material (pCi g-1)												
number	<sup>227</sup> Ac	<sup>231</sup> Pa	<sup>228</sup> Th	<sup>230</sup> Th	<sup>232</sup> Th	<sup>224</sup> Ra	<sup>226</sup> Ra	<sup>228</sup> Ra	<sup>210</sup> Pb	<sup>234</sup> U	<sup>235,6</sup> U	<sup>238</sup> U
21	523	521	907	41,911	1451	453	2589	525	2437	1934	152	2043
22	416	401	nd <sup>b</sup>	33,881	nd	451	2192	559	2221	1618	117	1649
23	234	266	554	21,010	815	64	467	82	454	348	nd	320
24	1363	na <sup>b</sup>	nd	71,650	911	213	6435	nd	6427	1524	127	1600
25	534	556	459	40,968	411	295	3073	392	2493	1467	54	1392
26	706	889	859	41,555	nd	335	1862	441	1910	1910	76	1860
27	421	458	nd	53,227	nd	370	1518	325	1084	1317	80	1243
28	412	na	996	63,649	755	106	3702	nd	2589	1052	42	994
29	443	564	537	61,190	672	137	4169	117	3553	1843	158	1951
30	773	931	nd	68,759	581	449	2240	360	1942	1643	75	1574
33	566	431	949	65,488	672	313	4451	415	3674	1600	118	1878
mean <sup>c</sup>	581	557	752	51,200	784	290	2970	357	2620	1480	99.9	1500
stdev <sup>c</sup>	298	220	226	16,400	309	142	1650	164	1570	456	40.1	503

<sup>a</sup> Ref: DOE 1990.

<sup>b</sup> "nd" means not detected. "na" means not analyzed for this radionuclide.

<sup>c</sup> For our calculations of the mean and standard deviation (stdev), we ignored samples with "not detected" results.

**Table 4. Average Activity Levels for 1991 Data Set as Given in Tables 2 and 3 Above**

K-65 Silos	Mean Activity (pCi/g)		
	Ra-226	Pb-210	Ratio Pb-210/Ra-226
Silo 1	525,000	194,000	0.37
Silo 2	417,000	160,000	0.38
Metal Oxide (Silo 3)	2970	2620	0.88

**Table 5. Average Activity Levels fro 1993 Data Set as Cited in ORAUT-TKBS-0017-5**

K-65 Silos	Mean Activity (pCi/g)		
	Ra-226	Pb-210	Ratio Pb-210/Ra-226
Silo 1	477	202	0.42
Silo 2	263	190	0.72
Metal Oxide (Silo 3)	3.87	3.48	0.90

## 2.4 ASSUMED RADON RELEASES BY NIOSH

Section 5.2.4 of ORAUT-TKBS-0017-5 provides the following:

*As previously stated, the contents of the silos have not been disturbed during storage to any large degree. However, it has been calculated that during the 1953 to 1978 period 5,000 to 6,000 Ci/year of <sup>222</sup>Rn were released from the silos (RAC 1995). Considering the expected large differences in release rates due to*

*barometric pressure changes, the release rates would average up to 15 to 20 Ci/day after addition to the Silos were complete. [Emphasis added.]*

## **2.5 SALIENT FEATURES OF THE 1995 RAC CALCULATIONAL METHODS AND CONCLUSIONS**

The credibility of the release quantities cited in the 1995 RAC Report must be viewed with considerable caution for the following reasons:

- (1) Release values of 5,000 to 6,000 Ci/yr from Silos 1 and 2 represent **median** values; and
- (2) Release estimates were based purely on complex models that are largely defined by diffusion kinetics of radon through the waste package and head-space ventilation rates.

The authors of the 1995 RAC Report acknowledge the following limitations and uncertainties regarding these estimates:

### From Page 29:

*For some other releases at the FMPC, extensive data sets of **direct** measurements of release quantities are available. However, for radon and radon decay product releases there are **no** direct measurements of release quantities. In addition, until the 1980s there were few measurements of **parameters** that can be used **indirectly** to calculate radon releases . . .*

*The traditional model used to estimate radon releases from radium-226-bearing materials, such as uranium mill tailings, involves calculations of the quantity of radon formed in the material, and the subsequent **diffusion** of the radon through the material to the outside air. For the K-65 materials, measurements have **not** been made of the **diffusion coefficient** and **radon emanation fraction**, which are two key parameters in this traditional calculation. Literature values can be obtained for these parameters, but without site specific values, the uncertainty ranges are **extremely large**. [Emphasis added.]*

### From Pages J-71 and J-72 of Appendix J:

*. . . releases from the K-65 Silos through the diffusion pathway are relatively small, but not insignificant, compared to releases through **air exchange** . . .*  
[Emphasis added.]

*. . . even with the large associated uncertainties, it is clear that the release rate of Rn-222 from the K-65 Silos was much greater in 1959–1979 period than in the 1980–1987 period . . .*

From Page J-27 of Appendix J:

*During the period from 1980 through 1987 the **major penetrations** through the silo domes, like the six-inch gooseneck pipe, had already been sealed. However, exchange of air between the silos and the atmosphere continued, through numerous cracks in the concrete of the domes. Radon releases for this time period are based on **measured concentrations of Rn-222 in silo air and on a silo ventilation rate calculated from the daily temperature changes in air.***  
[Emphasis added.]

From Page J-28 of Appendix J:

*. . . The silo interior air was sampled on November 4, 1987, prior to the operation of the **Radon Treatment System (RTS)** and prior to the application of the exterior foam layer to the silo domes . . . The RTS is a system that pumps air from the silos through a series of calcium, sulfate and charcoal beds, which . . . removes Rn-222, and thus potential daughter products of Rn-222, from the air space of the silos, and reduces the direct radiation exposure rates **on the silo domes.** The system is used to reduce radiation exposures to personnel involved in work **on the silos.*** [Emphasis added.]

From Pages J-41 through J-44:

*If measurements of the exposure [dose] rate are obtained for a consistent geometry, for a time period when the <sup>222</sup>Rn concentration is also known, an exposure rate factor ( $mR h^{-1}$  per  $pCi L^{-1}$ , or similar) can be developed. Then, the <sup>222</sup>Rn concentration can be estimated for other time periods when **only** exposure rate data exist . . .*

*Searches through historical records of the FMPC have located some results of radiation exposure rate measurements **on** [top of] the K-65 silo domes which are summarized in Table J-19 . . . [Note: Table J-19 is reproduced herein as Exhibit 1 and Exhibit 2].*

*The data for the period **prior** to the sealing the openings, 1959 to 1979, do not indicate a significant variation in exposure rate. These measurements ranged from 65 to 90  $mR h^{-1}$  . . .*

*For the period **after** sealing openings, 1980 to 1987, the data show considerable variations (Figure J-4), but no clear trend is evident. . . [Note: Figure J-4 is reproduced herein as Exhibit 2].*

*The RTS was operated . . . on one silo at a time, with a flow rate of about 1000  $ft^3 min^{-1}$ , and was operated until radiation levels on [top of] the silo dome **surface** [i.e., contact] stopped decreasing . . . With these flow rate and operating times,*

*and an assumed removal efficiency close to 100%, the <sup>222</sup>Rn concentrations in the silo air space should have been reduced to less than 3% of the initial concentrations. . .*

*Thus, for this analysis, the exposure rate measurements made **after operation of the RTS** are considered to represent the “**background**” exposure rate, in the absence of <sup>222</sup>Rn daughters in the silo air. [Emphasis added.]*

From these statements contained in RAC 1995, the following conclusions may be drawn:

- (1) The release rates of Rn-222 (and its short-lived daughters) varied greatly over time and reflect incremental modifications to the K-65 silos aimed to mitigate the releases of Rn-222.
- (2) Undoubtedly the single most important modification for reducing radon releases was the sealing of multiple penetrations that included manhole covers, a six-inch diameter gooseneck pipe, and large numbers of cracks in June of 1979.
- (3) Contact dose rate readings on top of the silos prior to 1979 are essentially identical to the 1987 contact dose rate readings taken after the operation of the RTS (see Exhibit 1).
- (4) Based on the relationship of the 1987 contact dose rate readings on top of the silo domes and reduced activity levels in silo headspace, the derived headspace ventilation rate prior to 1980 can be assumed at 1.2/hour. Implicit in this assumption is that for years prior to 1980, there was little or **no buildup** of radon/radon daughters in the headspace of the K-65 silos as a result of unfettered releases to the environment.
- (5) The release rate of Rn-222 from the contained waste into the silo headspace, however, is key to an understanding of the radon release rate to the environment. The release of Rn-222 from the waste into the silo headspace and/or the environment precludes further decay and the formation of Pb-210 within the waste. The resultant disequilibrium between Ra-226 and Pb-210 in the raffinate may serve as the basis for estimating the environmental releases of radon, as discussed in Section 3.0 below.

## EXHIBIT #1

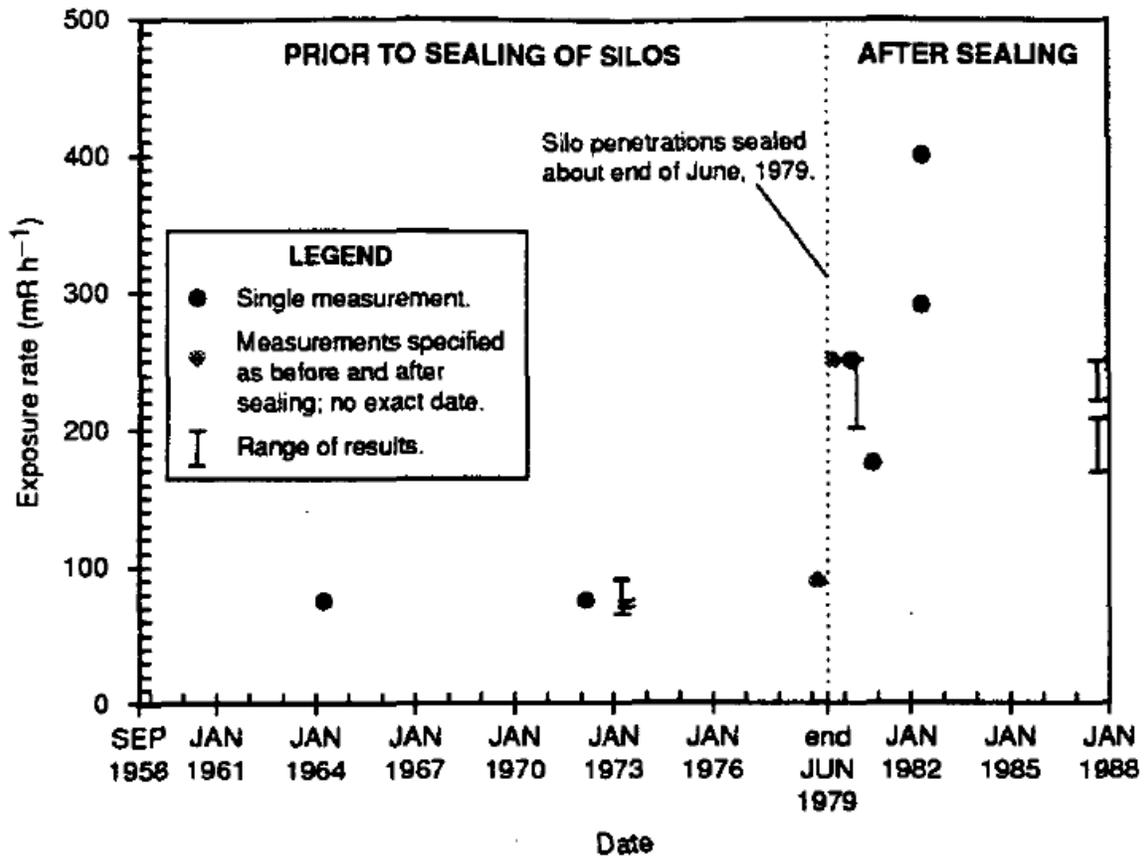
**Table J-19. Measurements of Exposure Rate (mR h<sup>-1</sup>) on Domes of K-65 Silos:  
Before and After Sealing of Dome Penetrations**

Date of Measurement	Silo	Height of Measurement	Exposure rate	Comments (reference)
Prior to Sealing Silo Openings				
→ April 1964	1	contact	75	Average value, probably silo 1. (Starkey 1964)
March 1972	ns <sup>a</sup>	ns	30	(Levy 1972)
→ March 1972	ns	contact	75	Maximum reading, assumed to be on contact. (Nelson 1972a)
→ May 1973	1	contact	65–90	Assumed on contact since other locations were. (Boback 1973)
→ May 1973	2	contact	70–75	(Boback 1973)
→ July 1973	2	ns	35	Near center of dome. (Levy 1973)
ns	ns	contact	90	Specified as before sealing of openings in 1979. (Boback 1980a)
After Sealing Silo Openings				
April 1980	1	contact	250	(Green 1980a)
April 1980	1	4 ft	150	(Green 1980a)
April 1980	2	contact	200–250	(Green 1980a)
April 1980	2	4 ft	150	(Green 1980a)
ns	ns	contact	250	Specified as after sealing of openings in 1979. (Boback 1980a)
November 1980	1	contact	175	(Green 1980b)
November 1980	1	4 ft	140	(Green 1980b)
November 1980	2	contact	85–175	The low value was near edge, rather than center. (Green 1980b)
November 1980	2	4 ft	45–100	The low value was near edge, rather than center. (Green 1980b)
May 1982	1	contact	290	(Grant and Stevens 1982)
May 1982	1	3 ft	18–250	Low value was near edge. (Grant and Stevens 1982)
May 1982	2	contact	400	(Grant and Stevens 1982)
May 1982	2	3 ft	35–280	Low value was near edge. (Grant and Stevens 1982)
April 1986	2	contact	850	Measured at crack in dome; other results not legible. (Fleming 1986)
November 1987	1	contact	168–208	Baseline, average 193. (Grumski and Shanks 1988)
→ November 1987	1	contact	35.5–68	<u>After operation of RTS<sup>b</sup>, average 55.</u> (Grumski and Shanks 1988)
November 1987	2	contact	221–250	Baseline, average 232. (Grumski and Shanks 1988)
→ November 1987	2	contact	60–76	<u>After RTS, average 68.</u> (Grumski and Shanks 1988)

<sup>a</sup> "ns" indicates that the parameter was not specified in the reference document.

<sup>b</sup> RTS is the acronym for the Radon Treatment System.

EXHIBIT 2



### 3.0 AN ALTERNATE APPROACH TO ESTIMATING RADON-222 RELEASES FROM K-65 SILOS

#### 3.1 STATES OF EQUILIBRIUM/DISEQUILIBRIUM AMONG RADIONUCLIDES OF THE U-238 DECAY CHAIN IN URANIUM ORES/RAFFINATES

In general, uranium ores are mined from deep-lying strata. The extracted ore exists in relatively large pieces that may be stockpiled for variable time periods before being transported to a uranium processing facility. The initial steps in processing raw ores involve mechanical crushing and grinding in order to produce uniformly sized smaller particles. The ground ore is subsequently placed in a slurry, which is subject to either an acid- or alkaline-based leaching process that separates the solubilized uranium from the residual and insoluble solids that become waste streams.

A condition placed on the ores from the Belgian Congo by African Metals was that the Ra-226, Ra-226 daughters, and the lead and precious metals be further extracted, stored, and returned to African Metals. Steps to extract these materials as a separate residue from the bulk ore residue resulted in the radium- and lead-bearing K-65 wastes that were subsequently stored in Silos 1 and 2.

In behalf of this assessment, SC&A attempted to identify documents from FMPC and MCW that might provide quantitative data regarding the activity levels of select radionuclides in pitchblende ores **at time of receipt** and in K-65 raffinates **at time of emplacement** in the K-65 silos. Specifically, our focus was to identify absolute and/or relative activity levels of Ra-226 and Pb-210 in pitchblende and raffinates. At this time, however, our effort has not yielded any useful information.

#### Data in the Scientific Literature

In a 1977 study (Sill 1977), uranium ores, uranium dust, and uranium mill tailings were analyzed for U-238, U-234, Th-230, Ra-226, and Pb-210 activity levels. For convenience, this study is enclosed herein as **Attachment #1**.

Table 2 of Attachment #1 identifies the results of several uranium ores from three different mills (i.e., Uravan Co., Mill A, Mill B, and Mill C) and three special samples from USGS. The second column of Table 2 gives the activity of the U-238 parent. Please note, the remaining columns give the **ratios of each daughter to that of U-238 parent**.

Inspection of Table 2 shows that, with the exception of USGS ores, values for Pb-210 are generally only a few percentage points lower than those of Ra-226, which suggests that Pb-210 exists in near equilibrium with Ra-226.

In addition to ore samples, this study analyzed **mill tailings** from two different sources: A large sample was obtained from a single mill representative of those on the Colorado plateau; and the other sample was a composite, prepared from 16 different mills (see page 403 of Attachment #1).

The tailings used in the composite were about 13 years old and the sample from the single mill was a few years younger. The analysis yielded the following results:

<u>Source</u>	<u>Ra-226 (dpm/g)</u>	<u>Pb-210 (dpm/g)</u>	<u>Pb-210/Ra-223</u>
Single mill	743	665	90%
Composite (16 mills)	1100	962	87%

The author, Claude W. Sill, concluded that:

*Lead-210 is slightly lower than its Ra-226 precursor in both samples, similar to the results obtained with the ores studied . . . analyses on the individual tailings when they were collected **initially** from active piles showed that the Pb-210 activity was nearly equal to or only slightly less than that of Ra-226 . . . . . Because of the 1602-yr half-life of its Ra-226 parent, the Pb-210 will obviously not decay significantly with age, **except for that resulting from loss of Rn-222.** [Emphasis added.]*

From information presented above, it can be concluded that the degree of disequilibrium between Ra-226 and Pb-210 is quantitatively linked to the loss of Rn-222 from ores/tailings. The **observed** disequilibrium values among core samples taken from Silos 1 and 2 in the early 1990s (see Tables 2 and 3) in themselves, however, are incomplete for estimating radon releases from Silos 1 and 2. Essential to estimating radon releases is an understanding of the state of disequilibrium that existed at the time(s) of raffinate disposal.

In the absence of empirical measurements involving pitchblende ores, the degree of disequilibrium between Ra-226 and Pb-210 at time of raffinate disposal in Silos 1 and 2 is unknown. That a significant disequilibrium from the loss of Rn-222 existed, however, must be assumed due to substantial time periods and processes that separated the initial mining of the ores and the emplacement of K-65 material in Silos 1 and 2. The following excerpt from Section 4.6 of ORAUT-TKBS-0005 identifies approximate time periods, processes, and conditions that may have led to radon releases and disequilibrium between Ra-226 and Pb-210 **before** emplacement:

*Most of the high-grade pitchblende ore processed by Mallinckrodt was obtained by AEC as a concentrate from the Belgian Congo in **1944** (AEC 1967) the so-called African ore. There is some disagreement as to how it came to St. Louis. DOE (1997) states that from **1943** on, the receiving and storage facility operated at Middlesex, New Jersey (DOE 1997) **assayed, crushed, riffled, and redrummed the ore as it came into the United States**, then sent it to the various refineries, including Mallinckrodt (AEC 1949b, Eisenbud 1975). MED (1945n) states that the African ore came through the Eldorado (Port Huron, Canada) area for processing before being sent on to the US refineries. AEC (1967) states that the concentrate was shipped from the Belgian Congo to St. Louis in **55-gallon drums** (but this could mean that it came by way of Middlesex). Whatever the case, it was*

*not likely that significant milling of this ore (as opposed to simply grinding to somewhat smaller size) was done at Mallinckrodt. . . .*

*. . . The **radon** in the Belgian Congo ore was also significant because it built up over time in containers and enclosed spaces. When drums, enclosed storage areas, the thaw house, etc., were opened, a worker could be enveloped in the escaping radon. [Emphasis added.]*

A lower-bound (and, therefore, claimant **unfavorable**) value of a disequilibrium activity ratio between Pb-210 and Ra-226 of 0.5 at time of emplacement may be estimated based on the following assumptions related to radon releases:

- (1) At time of mining, Ra-226 and Pb-210 is assumed to have existed in **secular equilibrium** (i.e., there had been no in situ loss of Rn-222)
- (2) A maximum time interval of about 22 years elapsed between mining of pitchblende and disposal of K-65 material (Note: This 22-year time interval is equal to the half-life of Pb-210.)
- (3) A 100 percent loss of Rn-222 gas from ore/raffinates throughout the 22-year time period is assumed.

In addition to the release of Rn-222, the above-cited disequilibrium ratio value of 0.5 could potentially be further reduced (or increased) due to chemical processes. For example, the extraction of uranium from pitchblende and/or the extraction of raffinates from bulk tailings may have differentially impacted the distribution of Ra-226 and Pb-210 on the basis of their solubility.

In the absence of empirical data, a further reduction of disequilibrium will be assumed (that again will lead to reduced estimates of Rn-222 releases) at time of emplacement.

For estimating Rn-222 releases from Silos 1 and 2, the state of disequilibrium empirically observed in the 1990s will, therefore, be assumed to have existed at time of the emplacement of K-65 material.

### 3.2 RADON RELEASE CALCULATIONS

The following steps may be used to calculate annual Radon-222 releases from Silos 1 and 2:

- (1) Determine amount of radon produced per year from 1 curie Ra-226.
- (2) Determine specific activity of Ra-226:

$$SpA = \lambda N = \frac{(\ln 2)(N)}{t_{1/2}}$$

where N = Number of radioactive atoms per unit mass

$$\begin{aligned}
&= 6.0225 \times 10^{23} \text{ atoms/atomic mass} \\
&= 2.6648 \times 10^{21} \text{ atoms /g of Ra-226}
\end{aligned}$$

$$\begin{aligned}
t_{1/2} &= \text{physical half-life of Ra-226} \\
&= 1602 \text{ years} \\
&= 8.4201 \times 10^8 \text{ min.}
\end{aligned}$$

$$\begin{aligned}
SpA_{Ra-226} &= \frac{0.693(2.6648 \times 10^{21})}{8.4291 \times 10^8 \text{ min}} \\
&= 2.1932 \times 10^{12} \text{ dpm/g of Ra-226} \\
&= 0.99669 \text{ Ci/gram of Ra-226}
\end{aligned}$$

- (3) Determine the number of Ra-226 atoms that decay in 1 curie per year that are transformed into Rn-222:

$$\begin{aligned}
1 \text{ Ci}_{Ra-226} &= 1.012 \text{ g of Ra-226} \\
&= (6.0225 \times 10^{23} \text{ atoms/226 g})(1.012 \text{ g}) \\
&= 2.6928 \times 10^{21} \text{ atoms of Ra-226}
\end{aligned}$$

No. of Rn-222 atoms formed/yr from the decay of 1 Ci of Ra-226:

$$\begin{aligned}
\text{Rn-222 atoms/yr} &= A_0 - A_{1 \text{ yr}} \\
&= 1.16600 \times 10^{18} \text{ atoms of Rn-222} \\
&= 4.298 \times 10^{-4} \text{ g of Rn-222}
\end{aligned}$$

- (4) Calculate the specific activity of Rn-222:

$$SpA_{Rn-222} = 153,881 \text{ Ci/g}$$

Thus, the  $4.298 \times 10^{-4}$  g of Rn-222 generated per year from 1 Ci of Ra-226 correspond to the production of 66.15 Ci of Rn-222 per year.

- (5) Calculate annual Rn-222 production in Silo 1 and Silo 2 based on data presented in Table 5-16 of ORAUT-TKBS-0017-5:

Silo 1:

$$\begin{aligned}
\text{Total Ra-226 Activity} &= (477 \text{ nCi/g})(5000 \text{ MT}) \\
&= (477 \text{ nCi/g})(5 \times 10^9 \text{ g}) \\
&= 2385 \text{ Ci}
\end{aligned}$$

$$\text{Rn-222 per year} = 2385 \text{ Ci}_{Ra-226} \times 66.15 \text{ Ci/yr/Ci}_{Ra-226}$$

$$\boxed{\text{Rn-222}_{\text{Silo 1}} = 157,767 \text{ Ci/yr}}$$

Silo 2:

$$\begin{aligned}\text{Total Ra-226 Activity} &= (263 \text{ nCi/g})(5 \times 10^9 \text{ g}) \\ &= 1315 \text{ Ci}\end{aligned}$$

$$\text{Rn-222 per year} = 1315 \text{ Ci}_{\text{Ra-226}} \times 66.15 \text{ Ci/yr/Ci}_{\text{Ra-226}}$$

$$\boxed{\text{Rn-222}_{\text{Silo 2}} = 86,987 \text{ Ci/yr}}$$

(6) Estimate annual release of Rn-222 into headspace of Silos 1 and 2

As stated in Section 3.1 above, the state of disequilibrium observed in 1993 between Ra-226 and Pb-210 is assumed to have existed unchanged from the beginning of K-65 material emplacement in silos. Under a steady-state of disequilibrium, it is assumed that the fraction of radon released from the waste package is proportional to the degree of disequilibrium.

$$\begin{aligned}\text{Rn-222}_{\text{Silo 1}} (\text{Ci / yr}) &= (157,767 \text{ Ci / yr}) \left( 1 - \frac{202 \text{ nCi / g Pb-210}}{477 \text{ nCi / g Ra-226}} \right) \\ &= 157,767 \text{ Ci/yr} (1 - 0.4235) \\ &= 90,955 \text{ Ci/yr}\end{aligned}$$

$$\begin{aligned}\text{Rn-222}_{\text{Silo 2}} (\text{Ci / yr}) &= (86,987 \text{ Ci / yr}) \left( 1 - \frac{190 \text{ nCi / g Pb-210}}{263 \text{ nCi / g Ra-226}} \right) \\ &= 24,144 \text{ Ci/yr}\end{aligned}$$

(7) Estimate Rn annual release rates into environment for all years prior to 1980:

In Section 2.0 of this report, the transient use of the RTS was estimated to reduce the Rn-222 (and daughter products) to 3% of its equilibrium value in the silo headspace. Under RTS operation, the contact dose rate on top of the dome was essentially identical to the dose rate prior to the sealants applied to dome in 1979.

On the basis of this relationship, it may be concluded that prior to 1980, 97% of radon entering the headspace was released to the environment:

Annual Environmental Releases prior to 1980:

$$\begin{aligned}\text{Rn-222 (Silo 1)} &= (0.97)(90,955 \text{ Ci/yr}) \\ &= 88,226 \text{ Ci/yr}\end{aligned}$$

$$\begin{aligned}\text{Rn-222 (Silo 2)} &= (0.97)(24,144 \text{ Ci/yr}) \\ &= 23,419 \text{ Ci/yr}\end{aligned}$$

## 4.0 SUMMARY CONCLUSIONS

NIOSH's adopted model for radon releases, as given in Section 5.2.4 of ORAUT-TKBS-0017-5, assumes “. . . that during the 1953–1978 period 5,000 to 6,000 Ci/year of Rn-222 were released from the silos (RAC 1995).”

This estimate (as openly admitted by the authors of RAC 1995) was based purely on a model for which the most basic model parameters (e.g., diffusion coefficient and radon emanation fraction) were unknown. Central to the RAC 1995 release rate(s) were estimates of air exchanges between the silo headspace and outside air that were driven by diurnal changes in temperature and barometric pressure.

A serious deficiency of the RAC model is its failure to properly account for the **Venturi effect** that is likely to have dominated the release of Rn-222 from the silo headspace prior to June of 1979, when the silos were subjected to major sealing modifications. The Venturi effect would have the following impact: during periods of low to moderate winds, a steady flow of air over the curved smooth surface of the silo dome creates a partial vacuum (much like that of an airplane wing that creates the necessary lift).

Support for high ventilation rates prior to June of 1979 and the role of the Venturi effect comes from the near-equal contact dose rate measurements taken before 1979 and after 1989 with the operation of the Radon Treatment System. Based on these data and the persistent disequilibrium between Pb-210 and Ra-226, SC&A estimates combined Rn-222 releases prior to 1980 in excess of 100,000 Ci/yr from Silos 1 and 2.

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## ATTACHMENT 1: 1977 STUDY BY CLAUDE W. SILL

*Health Physics* Pergamon Press 1977. Vol. 33 (November), pp. 393–404. Printed in Great Britain

### SIMULTANEOUS DETERMINATION OF $^{238}\text{U}$ , $^{234}\text{U}$ , $^{230}\text{Th}$ , $^{226}\text{Ra}$ , AND $^{210}\text{Pb}$ IN URANIUM ORES, DUSTS, AND MILL TAILINGS

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(Received 12 November 1976; accepted 11 May 1977)

**Abstract**—A procedure is described for determination of the five most important radionuclides of the  $^{238}\text{U}$  series in the same sample. This procedure helps to eliminate apparent changes in the isotopic composition caused by sample inhomogeneity and to maximize sensitivity and precision on air dusts when only small samples are available. The sample is decomposed with hydrofluoric acid and pyrosulfate fusion to guarantee complete conversion of refractory compounds to the ionic state before chemical separations are attempted. Thorium and radium are separated from the hydrochloric acid solution of the pyrosulfate cake by precipitation on barium sulfate. Thorium is then extracted into bis(2-ethylhexy)phosphoric acid, electrodeposited, and analyzed by alpha spectrometry. Radium is determined by the emanation procedure. Lead and bismuth are extracted into diethyldithiocarbamate from the filtrate of the barium sulfate separation, and  $^{210}\text{Pb}$  is determined by beta counting its  $^{210}\text{Bi}$  daughter. Uranium is extracted into Aliquat-336, after prior concentration on barium sulfate when the quantity of uranium present is small, electrodeposited, and analyzed by alpha spectrometry. Isotopic tracers for thorium and uranium are used and chemical yields for all four elements are higher than 85%.

On the ores and dusts analyzed, the uranium was generally depleted in  $^{234}\text{U}$  by as much as 15–20% compared to the  $^{238}\text{U}$  parent, although one sample was depleted by 56%. Thorium-230 varied from slight depletion to substantial enrichment up to 75%. Radium-226 varied from much lower to much higher than its  $^{230}\text{Th}$  precursor, depending on the particular ore. Lead-210 was depleted significantly compared to its  $^{226}\text{Ra}$  precursor in every case except a single pitchblende standard known to be in equilibrium. No great differences in the isotopic composition were observed either among ores and dusts from the same mill or as a function of particle size.

of each of the daughters, which causes apparent differences in the equilibrium if the sample is not completely homogeneous.

The present analytical scheme has been designed specifically to permit determination of the five most important radionuclides in the  $^{238}\text{U}$  chain in the same sample to eliminate any possible effects of sample inhomogeneity. It also permits the entire sample to be used for all determinations to obtain maximum sensitivity and precision on air dusts where only one sample of a kind is available and where the activities being measured might be particularly low. Because platinum dishes cannot be used when lead is being determined (Si77a), a procedure was developed by which virtually complete dissolution of the most refractory forms of elements sought could be obtained without use of more powerful fusions in platinum containers. The procedure is also designed to accommodate the small quantity of barium that is present invariably in most ores and tailings. Isotopic tracers are available for only uranium and thorium, but chemical yields are higher than 85% and quite reproducible for all four elements being determined. The same analytical scheme can be used with slight modifications on other types of samples, such as water, urine, feces, soft tissue, etc. on which similar isotopic distribution data are desired.

#### EXPERIMENTAL

##### *Sample dissolution*

Add lead-bismuth carrier to decrease sorption of lead on the glass separatory funnel during subsequent dithizone extraction (Si65) and  $^{234}\text{Th}$  tracer (Si74b) to ore or air dust, wet ash the filter in glass and/or Teflon FEP beakers, transfer to a 250-ml Erlenmeyer flask, and fuse with pyrosulfate as described for the determination of  $^{210}\text{Pb}$  (Si77a). However, replace the 5 g of sodium sulfate called for in the pyrosulfate fusion with 4.5 g of potassium sulfate to provide a high concentration of potassium ions necessary for efficient carrying of large multivalent ions on barium sulfate (Si64; Si69). After evaporating the solution to a pyrosulfate fusion, add 2 g

of anhydrous sodium sulfate and continue heating until the salt has dissolved in the fusion to increase subsequent solubility of iron, aluminum, chromium, etc. in the presence of potassium salts (Si74c). Dissolve the potassium pyrosulfate cake by boiling with 25 ml of 3M hydrochloric acid. The acid must be premixed to prevent occlusion of significant lead and/or bismuth in any barium sulfate that might form before complexation with chloride ion could occur if water and concentrated acid were added separately. Add an additional 15 ml of water and 1 ml of 25% potassium metabisulfite and boil the solution for 2 or 3 min to hydrolyze any condensed phosphates that might have formed during the fusion from orthophosphates present in the sample.

If  $^{210}\text{Pb}$  is not to be determined, sample decomposition can be shortened and made somewhat more reliable by igniting the air dust filters gently in a small platinum dish, treating the residual dust or ore with nitric and hydrofluoric acids, and fusing the residue with 3 g of anhydrous potassium fluoride. After transposing the cake with 3.5 ml of concentrated sulfuric acid and 2 g of sodium sulfate as described previously (Si77b), the pyrosulfate cake can be removed by flexing the sides of the platinum dish, dissolved in 25 ml of 3 M hydrochloric acid, and the procedure completed from that point as described above. However, a small quantity of platinum is introduced which will have to be filtered off later after reduction by titanium trichloride in the determination of uranium.

##### *Determination of $^{230}\text{Th}$ and $^{226}\text{Ra}$*

Precipitate barium sulfate by the slow dropwise addition of four successive 1-ml portions of a 0.45% solution of barium chloride dihydrate, added at a rate not faster than 1 drop every 2 or 3 sec to the boiling solution with rapid swirling and 1-min boiling periods after each 1-ml addition, as described previously (Si69). Transfer the hot solution to a 40-ml conical centrifuge tube and rinse the flask with 2 or 3 small portions of 0.5% sulfuric acid. Centrifuge at 2000 rev/min for 5 min and decant the supernate into a 250-ml separatory funnel. Suspend the precipitate in

10 ml of 0.5% sulfuric acid and recentrifuge, decanting the wash into the separatory funnel. Analyze the barium sulfate precipitate for  $^{230}\text{Th}$  and  $^{226}\text{Ra}$  as described previously (Pe74). A procedure employing Aliquat-336 (Si74c) can be used equally well for the determination of  $^{230}\text{Th}$  but has not been investigated for the simultaneous determination of  $^{226}\text{Ra}$ .

Prepare a standard from an identical aliquot of the  $^{234}\text{Th}$  tracer and correct the activity on the electrodeposited thorium plates for chemical recovery by gamma counting both standard and samples under identical conditions. If the tracer standard is prepared by electrodeposition, losses on electrode-position must be corrected by comparing the activity recovered from the electrolyte, cell, seals, etc. with an aqueous standard containing another aliquot of the tracer, again under identical counting conditions. A much simpler method of preparing the standard by direct evaporation of the tracer on a stainless steel plate, without need for corrections, has been described recently (Si77b).

Use about  $10^5$  dis/min of  $^{234}\text{Th}$  tracer to minimize the effect of  $^{234}\text{Th}$  present in the sample on the yield determination, particularly with ores and fresh tailings less than a few months old. Because 0.27% uranium ore contains 2000 dis/min/g of  $^{234}\text{Th}$ , the error will be less than 2% for samples up to 1 g. With larger samples or higher-grade ore, corrections will have to be made. The corrections can be made from the results of the uranium determination and a counting efficiency for  $^{234}\text{Th}$  determined for the conditions being used.

When analyzing samples containing high concentrations of uranium and low concentrations of  $^{230}\text{Th}$ , such as yellow cake or other uranium concentrates, the barium sulfate must be reprecipitated to remove the approx 1% of uranium that will have carried in the barium sulfate from the hexavalent state (Si69). Because the energy of alpha particles from  $^{234}\text{U}$  is only 86 keV different from that of  $^{230}\text{Th}$ , and occurs at a higher value, causing the  $^{234}\text{U}$  tail to spread down into the  $^{230}\text{Th}$  region, substantial interference from uranium will otherwise result in the determination of

small quantities of  $^{230}\text{Th}$ . Also, the chemical yield determined from the  $^{234}\text{Th}$  tracer added will have to be corrected for the relatively large and variable quantity of  $^{234}\text{Th}$  that will have ingrown into the uranium fraction since the uranium was separated chemically from its ore. If the samples are sufficiently old and equilibrium between  $^{238}\text{U}$  and  $^{234}\text{Th}$  is known to have been achieved, the correction can be obtained from the  $^{238}\text{U}$  analysis. Thorium-227 can also be used as tracer in these cases but requires a similar, although smaller, correction for the  $^{227}\text{Th}$  present from  $^{235}\text{U}$  in the sample. Because of the high and reliable recoveries resulting from the chemistry employed, an average yield determined from analysis of spiked samples can also be used satisfactorily in some cases.

*Reprecipitation of barium sulfate.* Add 1 ml of concentrated sulfuric acid to the centrifuge tube containing the barium sulfate and heat the tube gently (to avoid bumping) until the barium sulfate has dissolved completely. Add 1 drop of 72% perchloric acid to ensure complete oxidation of organic matter which otherwise will reduce uranium to the quadrivalent state in hot concentrated sulfuric acid, causing the uranium to reprecipitate with the barium sulfate. Heat just enough to decompose the perchloric acid and cool the solution to at least  $40^\circ\text{C}$ . Add 25 ml of solution containing 3 g of potassium sulfate and 3 ml of concentrated hydrochloric acid. Transfer the solution, without rinsing, to a 100-ml beaker and heat to boiling. Add 1 ml of 0.45% barium chloride dihydrate solution by slow dropwise addition, as before, to precipitate small quantities of thorium and radium that are not precipitated as completely by the inverted order of addition of barium (Si69). Boil the solution for 1 min, transfer back to the same centrifuge tube, and rinse the beaker with 2 or 3 small portions of 0.5% sulfuric acid. Centrifuge for 5 min at 2000 rev/min and discard the supernate. Analyze the barium sulfate for  $^{230}\text{Th}$  and  $^{226}\text{Ra}$  as described (Pe74).

#### *Determination of $^{210}\text{Pb}$*

Add about 30 ml of water to the solution in the 250-ml separatory funnel from separation

of barium sulfate to give a total volume of about 80 ml of 0.9 M hydrochloric acid. Add ascorbic acid, extract with three successive 10-ml portions of 1% diethylammonium diethyldithiocarbamate (DDTC) in chloroform, and finish as described previously (Si77a). Due to the lack of suitable isotopic tracers when either  $^{210}\text{Pb}$  or  $^{210}\text{Bi}$  are to be determined by gross beta counting, an average chemical yield for the procedure should be determined by separate analyses of standard samples or, preferably, by analysis of samples spiked with known quantities of  $^{212}\text{Pb}$  tracer. In this laboratory, the overall chemical yield is generally about  $98 \pm 1\%$ .

#### *Determination of $^{234}\text{U}$ and $^{238}\text{U}$*

To keep the yield on electrodeposition and the resolution of the resultant alpha spectra high and reproducible, the aliquot taken for the uranium determination should not contain more than about 100  $\mu\text{g}$  of uranium electrodeposited over an area  $3/4$  in. in diameter. If it is known that the entire sample contains less than this quantity of uranium, such as in small samples of air dusts, and if maximum sensitivity and precision are desired, transfer the entire solution from the DDTC extraction of lead to a 250-ml Erlenmeyer flask and evaporate to a pyrosulfate fusion. Add a few drops of nitric acid and/or perchloric acids, as necessary, to oxidize all ascorbic acid and other organic material. When the entire sample is to be analyzed, the  $^{232}\text{U}$  tracer should be added at the beginning of sample decomposition along with the  $^{234}\text{Th}$  tracer. The self-cleaning tracer (Si74b) should be used to avoid contaminating the  $^{230}\text{Th}$  fraction with relatively high activities of  $^{228}\text{Th}$  ingrown into the  $^{232}\text{U}$  since its last purification. The tracer added should be about equal to that of  $^{238}\text{U}$  expected in the sample but need not be less than about 25 dis/min, even for samples containing little or no uranium.

Add 35 ml of water, 6 ml of concentrated hydrochloric acid, 1 ml of 25% potassium metabisulfite, and 2 or 3 silicon carbide boiling stones to the flask containing the pyrosulfate cake and boil the solution for 2 or 3 min to hydrolyze condensed phosphates. Without interrupting the smooth evolution of water

vapor and allowing air to enter the flask, add 1 drop of 1% aqueous Safranin O indicator, 3 drops of 20% titanium trichloride, and then 3 M chromous chloride (Wi74) dropwise until all color of both the ferric chloride complex and indicator has been removed plus 5 drops excess. Keep the end of the delivery tube well into a blanket of water vapor to minimize oxidation of chromous iron by air (Wi74). Repeat the slow dropwise addition of four consecutive 1-ml portions of barium chloride as above, centrifuge the barium sulfate containing the quadrivalent uranium, and discard the supernate.

Add 1 ml of 72% perchloric acid to the centrifuge tube containing the barium sulfate and heat gently until the barium sulfate has dissolved completely and fumes of perchloric acid are evolved. Tervalent titanium tends to carry in barium sulfate to a significant extent and forms a sulfate complex that is very soluble in water but insoluble in 72% perchloric acid. Consequently, if the solution becomes turbid after the barium sulfate has dissolved, proceed to the addition of aluminum nitrate in the next step immediately. Continued heating only makes the precipitation of the titanium sulfate complex more complete. Add 10 ml of 2.2 M acidic aluminum nitrate (Si74c), cool and transfer the solution to a 60-ml separatory funnel. Rinse the beaker with another 5 ml of aluminum nitrate and add to the funnel. Add 10 ml of 30% Aliquat-336 in xylene (Si74c) and extract, wash, strip and electrodeposit as described previously (Si74c) with a few exceptions. Use 2 ml of 8 M nitric acid in each of the three nitric acid scrubs, 10 ml of 10 M hydrochloric acid in each of the three hydrochloric acid scrubs, and strip the uranium from the organic phase with 10 ml of the perchloric-oxalic acid solution (Si74c) and then with 5 ml of water as described previously (Si77b). Heat the electrodeposited plate on an uncovered hot plate for 5 min and count in an alpha spectrometer for at least  $10^3$  min. Propagate all statistical uncertainties to the final result (Si74c; Si75).

If the uranium content of the sample is unknown, or is known to contain more than 100  $\mu\text{g}$ , transfer the solution from the DDTC

extraction of lead to a 250-ml Erlenmeyer flask, rinse the separatory funnel and heat the combined solutions just until visible droplets of residual chloroform disappear. Longer heating might cause reoxidation and possible deposition of elemental sulfur. Cool the solution to room temperature, transfer quantitatively to a 100-ml volumetric flask, and dilute to volume. Estimate uranium concentration on an aliquot of a few milliliters or less by any suitably sensitive procedure, such as direct fluorometric measurement on a small pellet of fused sodium fluoride. Take an aliquot of  $X$  ml for analysis that will contain 75–100  $\mu\text{g}$  of uranium, equivalent to 55–74 dis/min of  $^{238}\text{U}$  in natural uranium. If  $X$  is 10 ml or less, place the aliquot into a 50-ml beaker, add (600–60 $X$ ) mg of sodium sulfate, 0.25 ml of concentrated sulfuric acid, 50–75 dis/min of  $^{232}\text{U}$  tracer, and evaporate the solution back to a pyrosulfate fusion to ensure complete exchange of the uranium tracer with the uranium isotopes in the sample and to eliminate the water and hydrochloric acid. Dissolve the cake in 10 ml of 2.2 M acidic aluminium nitrate, extract into aliquat-336, and finish as described above from that point.

If  $X$  is greater than 10 ml, place the aliquot into a 250-ml Erlenmeyer flask, add (4.5–0.045 $X$ ) g of potassium sulfate, 2 ml of concentrated sulfuric acid, 50–75 dis/min of  $^{232}\text{U}$  tracer, and reevaporate the solution back to a pyrosulfate fusion. If the entire sample is used and the uranium content is less than about 40  $\mu\text{g}$ , reduce the  $^{232}\text{U}$  tracer to 25 dis/min. Dissolve the cake in 35 ml of water and 6 ml of hydrochloric acid, reduce the uranium with titanium trichloride and chromous chloride, precipitate barium sulfate, and finish as described above from that point. If the  $^{232}\text{U}$  tracer was not added until after the barium sulfate separation to remove  $^{230}\text{Th}$  and  $^{226}\text{Ra}$ , the final activity should be increased by about 1% to correct for the small loss of uranium occurring in the barium sulfate separation.

The spectrum of  $^{235}\text{U}$  overlaps those of both  $^{238}\text{U}$  and  $^{234}\text{U}$ , but the corrections are small with natural uranium except when  $^{235}\text{U}$  is being determined. If a well-resolved spectrum of natural uranium is integrated from

the low points on both sides of the visible  $^{235}\text{U}$  peak, only 84.4% of the total alpha branches from  $^{235}\text{U}$  will be included, and activity in the visible resolved peak should be increased by 18.5%. Similarly, activity under the  $^{238}\text{U}$  and  $^{234}\text{U}$  peaks should be decreased by 7.3 and 11.2%, respectively, of the activity in the visible  $^{235}\text{U}$  peak. Without the correction, the ratio of  $^{235}\text{U}$  to  $^{238}\text{U}$  will not agree with the theoretical value of 0.0467 for natural uranium. Protactinium-231 normally extracts and carries through the procedure with uranium, giving another peak in the alpha spectrum between those of  $^{234}\text{U}$  and  $^{232}\text{U}$ , but is removed in the present procedure in the barium sulfate separation.

Because  $^{210}\text{Po}$  emits alpha particles having energies only 20 keV lower than those of the  $^{232}\text{U}$  used to trace the chemical recovery of uranium, special attention must be given to its complete removal. Otherwise,  $^{210}\text{Po}$  adds to the  $^{232}\text{U}$  peak and makes recovery of tracer appear to be higher than it really is. The results for uranium will be low, without any visible evidence of interference other than the abnormally high yields. In the present procedure,  $^{210}\text{Po}$  is removed quantitatively with lead and bismuth in the DDTC extraction, eliminating the interference. However, a few cases of contamination with  $^{210}\text{Po}$  after the DDTC extraction have occurred from unknown causes that resulted in apparent recoveries of uranium as high as 400%, compared to the normal value expected of about 85%. The contaminant was identified and its interference eliminated by treating another aliquot of the aqueous solution from the DDTC extraction with tellurous acid and stannous chloride in sulfuric acid, as described elsewhere (Si77b). The precipitate of elemental tellurium contained only  $^{210}\text{Po}$ , clearly identifiable by direct alpha spectrometry on the precipitate, and determination of uranium in the filtrate then gave the expected yield and correct result for uranium. Precipitation of tellurium with stannous chloride provides additional protection against contamination by  $^{210}\text{Po}$  through a later stage in the determination than the DDTC extraction but also requires an extra separation that is generally not necessary.

However, the additional separation provides a method for removing the contamination when it does occur.

If  $^{210}\text{Pb}$  is not being determined and the DDTC extraction is therefore omitted, the tellurium separation must be made to eliminate the interference from  $^{200}\text{Po}$  whether or not uranium is also being separated on barium sulfate. Also, if  $^{210}\text{Pb}$  is not being determined, sample decomposition is made more rapidly and reliably by fusion with potassium fluoride in a platinum dish, as mentioned above. However, in this event, 1 or 2 mg of platinum is dissolved from the dish and is subsequently precipitated by the powerful reducing agents required to reduce uranium to the quadrivalent state prior to its precipitation on barium sulfate. Because platinum must be filtered off before precipitation of the barium sulfate, the same operation might just as well be used to separate  $^{210}\text{Po}$  on elemental tellurium at the same time and eliminate the need for DDTC extraction. However, because the separation of polonium is not as complete with titanous and chromous chlorides from hydrochloric acid, use of stannous chloride from a sulfuric acid solution is recommended (Si77b).

#### RESULTS AND DISCUSSIONS

Accuracy of the combined procedure for simultaneous determination of all five radionuclides was checked by analysis of a standard pitchblende sample. This material was prepared from ore known to contain primary unaltered pitchblende in secular equilibrium and was standardized by determining the concentration of natural uranium by an accepted volumetric procedure. Activities calculated for both the  $^{238}\text{U}$  and  $^{235}\text{U}$  series from accepted values of the half-lives and isotopic abundances have been confirmed repeatedly by extensive determinations of each of the main radionuclides by several different investigators over a period of 12 yr (Pe74; Si65; Si74a; Si74c). Ratios of the activity of each radionuclide obtained in the present investigation to the calculated value are shown in Table 1. The uncertainty given is the standard deviation resulting from propagation of all random uncertainties incurred

Table 1. Ratio of activity obtained on standard pitchblende to known value\*

$^{238}\text{U}$	$^{234}\text{U}$	$^{230}\text{Th}$	$^{226}\text{Ra}$	$^{210}\text{Pb}$
$0.989 \pm 0.017$	$0.981 \pm 0.017$	$1.016 \pm 0.011$	$0.997 \pm 0.014$	$0.994 \pm 0.014$
$0.990 \pm 0.017$	$0.987 \pm 0.017$	$1.008 \pm 0.011$	$1.004 \pm 0.014$	$1.004 \pm 0.014$
$1.003 \pm 0.017$	$1.003 \pm 0.017$	$1.010 \pm 0.011$	$0.990 \pm 0.014$	$0.997 \pm 0.014$

\* $^{238}\text{U}$  series,  $6.06 \pm 0.04 \times 10^3$  dis/min/g.

in the entire measurement process. Every analytical result obtained obviously agrees with the known value within the statistical uncertainties of the measurement at the 95% confidence level. Apparently, there are no significant systematic uncertainties remaining in the procedure under our conditions of application, indicating the care with which sample decomposition is carried out and the efficiency of separations employed. This is particularly gratifying in view of the fact that there are no suitable isotopic tracers for the determination of either  $^{210}\text{Pb}$  or  $^{226}\text{Ra}$ , and in most cases, even the uranium determination is untraced through the sample decomposition and separations of thorium, radium, and lead. A schematic diagram of the combined procedure is shown in Fig. 1.

Table 2 shows some duplicate results obtained on several ores from three different mills, a couple of special samples, and some stagnant dusts that had collected on window ledges, beams and other horizontal surfaces inside the mill. The dusts are of unknown age and are not necessarily contemporary with the current ore samples. The second column gives the activity of the  $^{238}\text{U}$  parent obtained. The remaining columns give ratios of each daughter activity to that of the  $^{238}\text{U}$  parent and total number of alpha particles emitted per disintegration of the parent.

The Uravan sample, a yellow vanadium-containing mineral of carnotite and/or tyuyamunite, is virtually in secular equilibrium, only the  $^{210}\text{Pb}$  being low. Although carnotite is known to be a secondary mineral, the most recent alteration other than loss of radon must have occurred at least several thousand years ago.

The USGS sample, a yellowish mineral of tyuyamunite, carnotite and/or uranophane studied by Rosholt (Ro65a; Ro65b), is from a non-typical deposit in the Powder River basin of Wyoming that is remarkably deficient in  $^{234}\text{U}$ . Consequently, the concentrations of

URANIUM ORES, DUSTS AND MILL TAILINGS

WET ASH FILTER PAPER, AND DISSOLVE RESIDUE OR ORE IN HF AND PYROSULFATE FUSION USING 4.5 GRAMS OF K<sub>2</sub>SO<sub>4</sub> AND 2 GRAMS OF Na<sub>2</sub>SO<sub>4</sub>. DISSOLVE FUSION CAKE IN 40 ml OF WATER AND 6 ml HCl.

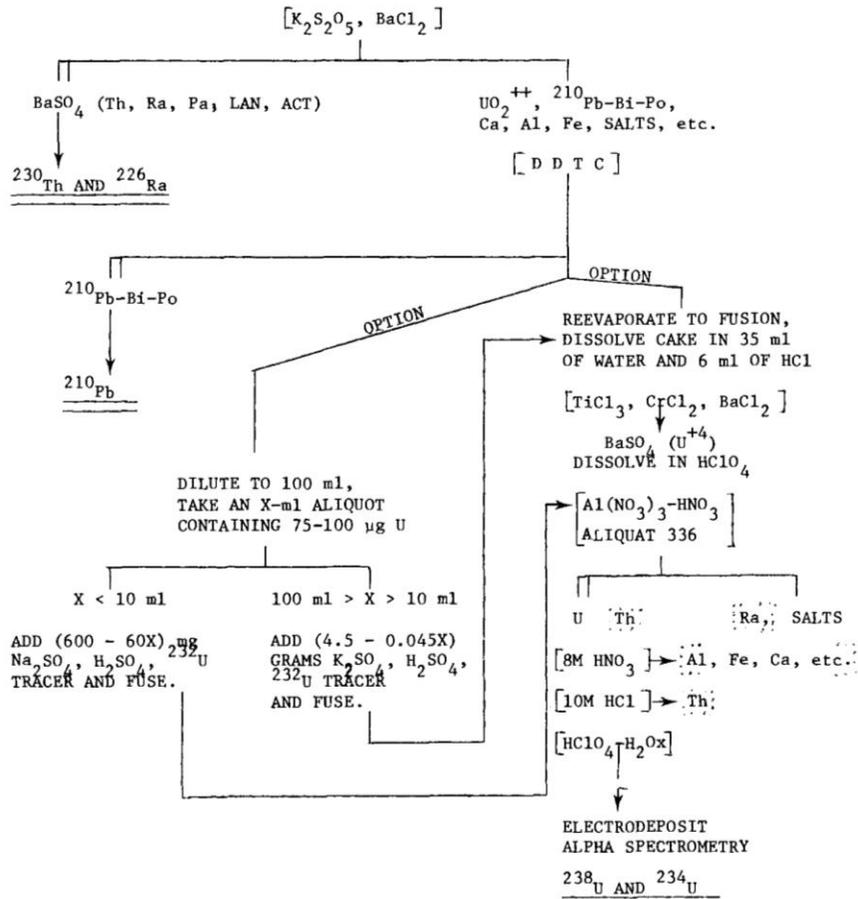


FIG. 1. Sequential separation of thorium, radium, lead and uranium. Double vertical lines indicate precipitates or organic extracts; single vertical lines indicate aqueous solutions. Square brackets indicate reagents added. Parentheses indicate elements carried in barium sulfate. Dotted brackets indicate traces of certain elements requiring special attention.

subsequent daughters in this material are of particular interest. This particular sample is 56% depleted in <sup>234</sup>U and contains about 18% more <sup>230</sup>Th and <sup>226</sup>Ra than can be supported by the <sup>234</sup>U present. Lead-210 is only 56% of its <sup>226</sup>Ra precursor, a far larger depletion than has been observed on any of the other sam-

ples. Due to the 22-yr half-life of <sup>210</sup>Pb, the original depletion must have been considerably larger than that found because of the ingrowth that has occurred during the 12 yr since the ore was removed from the ground. This suggests that substantial alterations other than loss of <sup>222</sup>Rn have oc-

Table 2. Ratio of daughter activity to  $^{238}\text{U}$  parent

Sample	$^{238}\text{U}$ , dis/min/g	$^{234}\text{U}$	$^{230}\text{Th}$	$^{226}\text{Ra}$	$^{210}\text{Pb}$	Total α/dis.	
Uravan, CO.	5561 ± 83	0.982 ± 0.007	1.008 ± 0.020	0.999 ± 0.021	0.848 ± 0.017	7.83	
			1.008 ± 0.017	1.007 ± 0.022	0.857 ± 0.016	7.88	
			0.984 ± 0.016	1.011 ± 0.019	0.898 ± 0.017	7.91	
USGS, BMK-8 No. 301711 (Ro65a) Powder River Basin, WY.	4080 ± 51	0.437 ± 0.006	0.549 ± 0.009	0.517 ± 0.010	0.291 ± 0.006	4.35	
			0.440 ± 0.005	0.502 ± 0.009	0.522 ± 0.010	0.289 ± 0.005	4.32
			0.458 ± 0.006	0.529 ± 0.010	0.518 ± 0.011	0.288 ± 0.006	4.36
Mill A Shirley Basin, WY.							
Ore No. 1	1418 ± 28	0.900 ± 0.015	1.54 ± 0.03	1.71 ± 0.04	1.13 ± 0.03	11.41	
	1373 ± 24	0.947 ± 0.014	1.57 ± 0.03	1.77 ± 0.04	1.33 ± 0.03	11.93	
Ore No. 2	1446 ± 47	0.99 ± 0.03	1.62 ± 0.06	1.86 ± 0.07	1.52 ± 0.05	12.57	
	1534 ± 27	0.932 ± 0.014	1.62 ± 0.03	1.70 ± 0.04	1.44 ± 0.03	11.79	
Ore No. 3	1368 ± 24	0.932 ± 0.014	1.56 ± 0.03	1.59 ± 0.03	1.27 ± 0.03	11.12	
	1345 ± 24	0.905 ± 0.014	1.66 ± 0.03	1.64 ± 0.04	1.44 ± 0.03	11.57	
Dust, sampling room	882 ± 17	0.912 ± 0.018	1.67 ± 0.04	2.94 ± 0.07	2.43 ± 0.06	17.77	
	846 ± 16	0.920 ± 0.017	1.74 ± 0.04	3.11 ± 0.08	2.62 ± 0.06	18.72	
Mill B Gas Hills, WY.							
Ore No. 1	1519 ± 26	0.966 ± 0.014	1.04 ± 0.02	0.93 ± 0.02	0.87 ± 0.02	7.60	
	1544 ± 16	0.959 ± 0.007	1.03 ± 0.02	0.920 ± 0.015	0.838 ± 0.015	7.51	
Ore No. 2	953 ± 21	0.83 ± 0.02	1.06 ± 0.03	0.98 ± 0.03	0.84 ± 0.02	7.65	
	984 ± 11	0.828 ± 0.008	1.02 ± 0.02	0.93 ± 0.02	0.803 ± 0.014	7.37	
Ore No. 3	1148 ± 21	0.859 ± 0.015	0.97 ± 0.02	0.90 ± 0.02	0.82 ± 0.02	7.25	
	1128 ± 20	0.871 ± 0.015	0.98 ± 0.02	0.87 ± 0.02	0.83 ± 0.02	7.16	
Dust, conveyer room	1963 ± 36	0.854 ± 0.012	0.99 ± 0.02	0.66 ± 0.02	0.611 ± 0.014	6.10	
	1821 ± 29	0.868 ± 0.011	1.03 ± 0.02	0.700 ± 0.015	0.658 ± 0.013	6.36	
Dust, drying room	1350 ± 25	0.922 ± 0.015	1.02 ± 0.02	0.79 ± 0.02	0.691 ± 0.015	6.79	
	1372 ± 14	0.918 ± 0.007	0.938 ± 0.015	0.791 ± 0.015	0.711 ± 0.012	6.73	
Dust, crushing room, upper	1873 ± 32	0.924 ± 0.012	1.05 ± 0.02	0.84 ± 0.02	0.80 ± 0.02	7.13	
	1848 ± 34	0.965 ± 0.014	1.10 ± 0.02	0.87 ± 0.02	0.84 ± 0.02	7.39	
Dust, crushing room, lower	1765 ± 30	0.930 ± 0.012	1.01 ± 0.02	0.83 ± 0.02	0.77 ± 0.02	7.03	
	1783 ± 31	0.919 ± 0.013	1.05 ± 0.02	0.85 ± 0.02	0.83 ± 0.02	7.20	
Mill C Gas Hills, WY.							
Ore No. 1	809 ± 10	0.912 ± 0.008	1.01 ± 0.02	0.92 ± 0.02	0.90 ± 0.02	7.50	
	816 ± 10	0.915 ± 0.009	0.97 ± 0.02	0.94 ± 0.02	0.886 ± 0.015	7.53	
	808 ± 11	0.908 ± 0.010	0.90 ± 0.02	0.93 ± 0.02	0.892 ± 0.017	7.42	
Ore No. 2	650 ± 8	0.928 ± 0.010	1.01 ± 0.02	0.676 ± 0.014	0.688 ± 0.016	6.33	
	611 ± 8	0.907 ± 0.010	1.00 ± 0.02	0.707 ± 0.015	0.717 ± 0.014	6.45	

curred within the last few tens of years. The present analytical results are in rather remarkable agreement with those obtained by Rosholt over 12 yr previously. Activities of  $^{238}\text{U}$  shown in the table are equivalent to  $0.551 \pm 0.007$ ,  $0.565 \pm 0.007$  and  $0.550 \pm 0.008\%$   $^{238}\text{U}$  compared to his value of 0.57% (Ro65b). In terms of the percentage of  $^{238}\text{U}$  required to support the activity of daughter present, as defined by Rosholt, the  $^{234}\text{U}$  activities are equivalent to  $0.241 \pm 0.004$ ,  $0.249 \pm 0.004$  and  $0.252 \pm 0.004$  compared to his 0.24, and the  $^{230}\text{Th}$  activities are equivalent to  $0.303 \pm 0.003$ ,  $0.284 \pm 0.003$  and  $0.291 \pm 0.003$  compared to his 0.32 (Ro65b). Unfortunately, no data were given for  $^{226}\text{Ra}$  and  $^{210}\text{Pb}$ . However, the excellent agreement is gratifying support for the accuracy of the present results.

Except for the pitchblende shown in Table 1,  $^{210}\text{Pb}$  is also lower than its  $^{226}\text{Ra}$  precursor in every sample analyzed. This result cannot

be due to a deficiency in the analytical procedure because of the accurate results obtained on the pitchblende standard which is known to be in secular equilibrium. The most obvious and likely explanation is the partial loss of its gaseous  $^{222}\text{Rn}$  precursor, either while still in the ground or during storage after mining.

Other than in the Uravan and pitchblende samples, uranium is generally depleted in  $^{234}\text{U}$ , the ores and dusts from Gas Hills being somewhat more so than those from Shirley basin. These data are consistent with the 7–22% deficiencies found by Rosholt *et al.* (Ro64) in ore sands from Shirley basin. In the present authors' opinion, the most likely explanation is that relatively more of the  $^{234}\text{U}$  produced *in situ* by radioactive decay of the  $^{238}\text{U}$  is in the hexavalent oxidation state compared to the  $^{238}\text{U}$ . In marked contrast to the quadrivalent state, hexavalent uranium is known to form very stable and water-soluble

complexes with carbonates which are generally present in ground waters in high concentrations and will be selectively leached at a much faster rate. This explanation is supported by the fact that uranium present in ground water is known to be enriched in <sup>234</sup>U sometimes by as much as 1300% relative to the <sup>238</sup>U (Kr69). Rosholt *et al.* (Ro64; Ro65a; Ro65b) give explanations of this and other possibilities in considerable detail. The fractionation must have occurred within the last few hundred thousand years or the <sup>234</sup>U would have had time to grow back to equilibrium with its long-lived parent.

The <sup>230</sup>Th is virtually in equilibrium with <sup>238</sup>U present in the Gas Hills material from either mill, while <sup>226</sup>Ra is substantially less, particularly in some of the dusts. In contrast, with the Shirley basin material, <sup>230</sup>Th is enriched to the extent of 55–65% with respect to <sup>238</sup>U and <sup>226</sup>Ra is even higher. It should be noted specifically that the single dust sample from Shirley basin contained three times as much <sup>226</sup>Ra and two and a half times as much <sup>210</sup>Pb as <sup>238</sup>U and over half again more <sup>226</sup>Ra

and <sup>210</sup>Pb than <sup>230</sup>Th despite the high enrichment of the latter. The most likely explanation is that this long-term accumulation of stagnant dust inside the mill contains substantial quantities of tailings from a pile known to have been just outside this particular mill. As will be shown below, most tailings contain somewhat more <sup>226</sup>Ra than <sup>210</sup>Pb, and substantially more of both than of <sup>230</sup>Th.

Table 3 shows some results obtained on actual individual air dusts from the same three mills from which the ores and stagnant dusts shown in Table 2 were obtained. Three main conclusions can be derived from these data. First, the yellow cake product from all three mills is relatively free of radioactive daughters, not exceeding a few activity percent of <sup>230</sup>Th or a few tenths activity percent of <sup>226</sup>Ra and <sup>210</sup>Pb. However, there are significant differences, either in the product itself or in the contamination of the air dust sample of the yellow cake with ore dust. The latter is a tempting explanation, at least for Mill A, which is known to have the ore-

Table 3. Percentage of daughter activity relative to the <sup>238</sup>U parent in some air dusts

	<sup>234</sup> U	<sup>230</sup> Th	<sup>226</sup> Ra	<sup>210</sup> Pb
<b>Ore concentrates</b>				
Mill A*	94.1 ± 2.1	3.4 ± 0.2	0.084 ± 0.003	0.39 ± 0.02
	91.8 ± 1.4	3.29 ± 0.08	0.084 ± 0.003	0.40 ± 0.02
Mill B†	89.4 ± 1.1	0.56 ± 0.03	0.066 ± 0.004	0.06 ± 0.03
	91.5 ± 1.3	0.68 ± 0.04	0.19 ± 0.01	0.18 ± 0.07
Mill C†	86.2 ± 2.1	1.16 ± 0.06	0.136 ± 0.006	0.16 ± 0.01
	89.5 ± 1.5	2.25 ± 0.07	0.382 ± 0.011	0.50 ± 0.03
<b>Crusher area</b>				
Mill A	90.4 ± 1.4	12.6 ± 0.8	6.5 ± 0.2	5.4 ± 0.3
	96.1 ± 1.5	11.9 ± 0.3	1.9 ± 0.1	3.3 ± 0.3
Probe tower	94 ± 2	105 ± 3	93 ± 3	72 ± 13
Mill B	94.5 ± 1.3	100 ± 3	89 ± 2	95 ± 2
	97.7 ± 1.5	103 ± 2	92 ± 2	106 ± 2
	94 ± 2	100 ± 2	87 ± 2	76 ± 9
	95 ± 2	104 ± 2	91 ± 3	100 ± 11
Mill C	88 ± 2	70 ± 2	65 ± 2	59 ± 2
	90 ± 2	85 ± 3	77 ± 2	71 ± 2
<b>Impactor measurements</b>				
<b>Mill A, Probe tower</b>				
Stage 0	93 ± 2	48 ± 2	48 ± 2	44 ± 5
Stage 2	99 ± 6	86 ± 8	100 ± 6	400 ± 40
Stage 4	98 ± 4	95 ± 4	71 ± 4	53 ± 13
Stage 0	97 ± 4	87 ± 4	84 ± 4	100 ± 20
Stage 2	95 ± 4	60 ± 3	53 ± 2	60 ± 20
Stage 4	99 ± 5	94 ± 5	83 ± 5	100 ± 30
<b>Mill B, Ground level crusher</b>				
Stage 0	100 ± 2	105 ± 5	97 ± 3	103 ± 6
Stage 2	94 ± 6	112 ± 10	102 ± 7	130 ± 20
Stage 4	98 ± 6	100 ± 8	100 ± 6	90 ± 30
<b>Upper level crusher</b>				
Stage 0	90 ± 3	94 ± 3	79 ± 3	380 ± 20
Stage 2	93 ± 5	98 ± 8	88 ± 6	480 ± 30
Stage 4	103 ± 6	100 ± 8	84 ± 5	60 ± 20

\*Shirley Basin.  
†Gas Hills.

crushing and product-handling areas in the same small building. However, the erratic ratios of  $^{230}\text{Th}$  to  $^{226}\text{Ra}$  to  $^{210}\text{Pb}$  do not fit the ratios present in the ore and are much more indicative of differences resulting from chemical separations. Second, the crusher area of Mill A is obviously heavily contaminated with yellow cake because of the proximity of the two operations mentioned above. The sample from the probe tower shows no significant contamination with yellow cake, but its distribution is markedly different from that found in the ores. The remaining samples show distributions of all radionuclides including  $^{234}\text{U}$  that are consistent with those shown in Table 2 for the ores and stagnant dusts. Third, although a couple of anomalies are present in the  $^{210}\text{Pb}$  results from impactor measurements, there does not appear to be any significant change in isotopic composition as a function of particle size. However, the data are too imprecise to permit really meaningful conclusions to be drawn. It is notable that uranium daughters in the impactor measurements on the probe tower sample from Mill A are deficient relative to the uranium parent. This result agrees with that obtained on the gross sample from the probe tower but does not agree with the ores in which the daughters were found to be in excess.

The same data on impactor samples shown in Table 3 are also presented in Table 4, with the quantity of each nuclide collected on each stage being given as a percentage of the total collected on the first three stages.

Table 4. Percentage distribution of radionuclides on first three impactor stages

	$^{234}\text{U}$	$^{230}\text{Th}$	$^{226}\text{Ra}$	$^{210}\text{Pb}$
Mill A,* Probe tower				
Stage 0	62.5 ± 0.9	48.0 ± 1.2	50.9 ± 0.9	30.5 ± 3.0
Stage 2	13.7 ± 0.7	17.3 ± 1.0	21.5 ± 0.6	56.2 ± 3.2
Stage 4	23.8 ± 0.7	34.7 ± 1.1	27.6 ± 1.0	13.3 ± 2.9
Stage 0	37.2 ± 1.0	40.7 ± 1.1	42.8 ± 1.1	42 ± 7
Stage 2	34.8 ± 1.0	26.7 ± 0.9	25.8 ± 0.8	23 ± 7
Stage 4	28.1 ± 1.0	32.6 ± 0.9	31.3 ± 1.0	35 ± 7
Mill B,† Ground level crusher				
Stage 0	69.2 ± 1.1	67.7 ± 1.5	67.3 ± 0.8	65.3 ± 3.1
Stage 2	17.7 ± 1.0	19.7 ± 1.3	19.2 ± 0.7	23.0 ± 2.6
Stage 4	13.2 ± 0.7	12.6 ± 0.8	13.5 ± 0.4	11.7 ± 2.8
Upper level crusher				
Stage 0	50.6 ± 1.1	51.0 ± 1.2	50.0 ± 1.0	58.1 ± 1.4
Stage 2	26.5 ± 1.0	27.4 ± 1.3	28.8 ± 1.1	38.2 ± 1.3
Stage 4	22.9 ± 1.1	21.6 ± 1.0	21.2 ± 0.7	3.7 ± 1.3

\*Shirley Basin.  
†Gas Hills.

There was very little activity of any kind on any of the later stages or on the final filter. The data show very similar distributions on a given stage except for  $^{210}\text{Pb}$  on the first and last sets. It is not clear why  $^{210}\text{Pb}$  should have a preference for the larger particle sizes. However, it does not appear that there are any substantial differences in the particle size distributions of one radionuclide over another. The distribution probably reflects the crushing and grinding of the ore more than any particle size differences peculiar to the daughters themselves.

Considerable caution should be exercised in making unverified assumptions about equilibrium in uranium ores and dusts. Unaltered minerals like pitchblende, used to obtain the data of Table 1, give the theoretical eight alpha particles per disintegration of the  $^{238}\text{U}$  parent to be expected of a system in secular equilibrium. The single carnotite sample shown in Table 2 gave an average of  $7.87 \pm 0.04$  ( $\pm 0.02$ ), also very near the theoretical value. The uncertainties given are standard deviations, the first being that of an individual about the mean, the one in parentheses being that of the mean itself. On the other hand, assuming equilibrium of  $^{222}\text{Rn}$ ,  $^{218}\text{Po}$  and  $^{214}\text{Po}$  with the  $^{226}\text{Ra}$ , and of  $^{210}\text{Po}$  with  $^{210}\text{Pb}$ , the uraninite samples shown in Table 2 averaged from  $7.3 \pm 0.4$  ( $\pm 0.2$ ) alphas per disintegration for the five Gas Hills ores to  $11.7 \pm 0.5$  ( $\pm 0.2$ ) for the three Shirley basin ores, and from  $6.8 \pm 0.4$  ( $\pm 0.15$ ) for the four Gas Hills dusts to  $18.3 \pm 0.7$  ( $\pm 0.5$ ) for the single Shirley basin dust. After chemical processing has begun, the isotopic composition will be very difficult if not impossible to predict because of the many variations possible, from two alphas per disintegration for pure yellow cake to whatever is obtained from straight ore, the actual composition depending on the point in the process at which the sample is taken.

The agreement among ores from the same source is surprisingly good. Even associated stagnant dusts, which are not necessarily contemporary with the particular ore analyzed and which probably reflect a much longer time integration of the ore processed at each particular mill, are in good agreement

with each other and with the ores analyzed. As shown by the data in Table 2 and by the experimental standard deviations of the mean given above, the agreement between samples of either ore or dusts is as good as that between aliquots of the same ore or dust. Certainly, there does not seem to be any substantial difference between ores and dusts, excluding the single Shirley basin dust, which is clearly anomalous. Probably, a particular type of ore could be characterized adequately for purposes of dose evaluation by occasional analyses for all five radionuclides. Once the isotopic ratios are known for the particular ore being processed and demonstrated to remain reasonably constant, subsequent measurements of natural uranium could be made by simple fluorometric procedure, and the alpha activity of each individual radionuclide in a given air dust sample calculated with a considerable saving in expense and effort. Possible contamination from tailings or final product would also have to be anticipated and taken into account.

Two different samples of mill tailings were prepared for subsequent use as analyzed standards for this kind of material. A large sample was obtained from a single mill representative of those on the Colorado plateau. The other sample was a composite, prepared from essentially equal weights of tailings from 16 different mills. The samples were ground to pass a 200-mesh screen and blended thoroughly in a Patterson-Kelly twin-shell blender for 48 hr to ensure homogeneity. Both samples were then analyzed about 10 times each as described except that individual aliquots were analyzed for  $^{230}\text{Th}$  by two different procedures, both involving alpha spectrometry (Pe74; Si74c), and by two different analysts to improve confidence in the results. Because of their low concentration in tailings, the uranium isotopes were not determined. Samples were also analyzed for  $^{226}\text{Ra}$  by direct gamma ray spectrometry using a Ge(Li) detector to help confirm the accuracy of the results obtained by the emanation procedure. Results obtained on the tailings from the single mill were  $590 \pm 7 (\pm 3)$  and  $577 \pm 16 (\pm 6)$  dis/min/g of  $^{230}\text{Th}$  by the two different alpha procedures, res-

pectively;  $763 \pm 32 (\pm 12)$  and  $724 \pm 16 (\pm 5)$  dis/min/g of  $^{226}\text{Ra}$  by the emanation and gamma spectrometric procedures, respectively; and  $665 \pm 8 (\pm 3)$  dis/min/g for  $^{210}\text{Pb}$ . The corresponding results for the 16-mill composite were  $691 \pm 8 (\pm 3)$  and  $688 \pm 17 (\pm 7)$  dis/min/g for  $^{230}\text{Th}$ ,  $1113 \pm 40 (\pm 15)$  and  $1087 \pm 28 (\pm 8)$  dis/min/g for  $^{226}\text{Ra}$ , and  $962 \pm 13 (\pm 4)$  dis/min/g for  $^{210}\text{Pb}$ .

Results obtained by different procedures for a given nuclide are in good statistical agreement except that the values for  $^{226}\text{Ra}$  by direct gamma spectrometry appear to be slightly low, particularly on the sample from the single mill. Lead-210 is slightly lower than its  $^{226}\text{Ra}$  precursor in both samples, similar to the results obtained with the ores studied. Thorium-230 is also lower than its  $^{226}\text{Ra}$  daughter, similar to the Shirley basin ores but unlike those from Gas Hills. However, the relationship among the daughters should not necessarily be expected to be the same from one tailing to another or the same as that in the ores from which the tailings were derived. The solubilities and reaction rates of thorium, radium, and lead compounds are markedly different, and the quantities of each that is dissolved during the extensive chemical leaching of the ore for removal of uranium will be highly dependent on the exact conditions employed. However, in the strong sulfuric acid-sulfate system widely used for beneficiation of uranium ores, it is reasonable to expect more thorium to be solubilized than either radium or lead, both of which form very insoluble sulfates, particularly if barium is present in the ore or is added during processing. This expectation is supported by the fact that  $^{230}\text{Th}$  is generally present in liquid mill effluents at a higher concentration than  $^{226}\text{Ra}$ .

The tailings used in the present composite are about 13 yr old and the sample from the single mill only a few years less, so that significant growth or decay of the 22-yr  $^{210}\text{Pb}$  could have occurred by the time the present work was carried out. However, analyses on the individual tailings when they were collected initially from active piles showed that even then the  $^{210}\text{Pb}$  activity was nearly equal to or only slightly less than that of  $^{226}\text{Ra}$ .

Apparently,  $^{210}\text{Pb}$  will frequently be nearly in equilibrium with its  $^{226}\text{Ra}$  parent even in fresh tailings because of the nearly quantitative insolubility of both in a strong sulfate system. Because of the 1620-yr half-life of its  $^{226}\text{Ra}$  parent, the  $^{210}\text{Pb}$  will obviously not decay significantly with age, except for that resulting from loss of  $^{222}\text{Rn}$ .

*Acknowledgement*—The author wishes to acknowledge the assistance of his associates, particularly; C. P. Willis for dissolution of the samples and determinations of  $^{210}\text{Pb}$ ; D. B. Martin for determinations of  $^{230}\text{Th}$  and  $^{226}\text{Ra}$ ; F. D. Hindman and D. G. Pope for determination of  $^{234}\text{U}$  and  $^{238}\text{U}$ ; R. P. Bernabee for the fluorometric determinations of uranium; N. L. Bihl for the electrodepositions; R. L. Williams and C. L. Rohwedder for the alpha spectrometry. Special thanks are also extended to S. A. McGuire of the U.S. Nuclear Regulatory Commission, who initiated the work, to A. J. Breslin and his staff of the Health and Safety Laboratory, U.S. Energy Research and Development Administration, for obtaining the samples, and to J. N. Rosholt of the U.S. Geological Survey for the special sample of uranium ore highly depleted in  $^{234}\text{U}$ .

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