

SOLUBILITY CHARACTERIZATION OF AIRBORNE URANIUM FROM AN *IN SITU* URANIUM PROCESSING PLANT

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Abstract—Solubility profiles of uranium dusts in the Irigaray uranium processing plant were determined by performing *in vitro* solubility tests on breathing zone air samples conducted in all process areas of the processing plant. The dissolution rate of the uranium on the air samples was then determined over the next 28 d in a simulant solution of the extracellular airway lining fluid (Gamble's solution). Airborne uranium in the wet process areas of the processing plant was highly soluble, with 97% dissolving in a 0.3 d half-time and 3% with a half-time of 15.6 d. The airborne uranium dusts in the drum load out area were also soluble, with 97% dissolving with a $T_{1/2}$ of 0.25 d and the remainder with a $T_{1/2}$ of 20 d. Exhaust from the drier stack and areas of the processing plant that had only this airborne uranium was slightly more insoluble, with 46% dissolving with a $T_{1/2}$ of 0.4 d and 53% with an 18 d half-time. These results compare well with x-ray diffraction analysis of the uranium samples and the bioassay program for the processing plant workers.

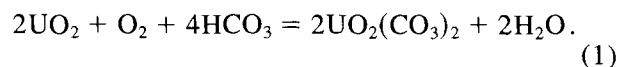
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Key words: uranium; air sampling; bioassay; radioactivity

INTRODUCTION

A STUDY was conducted to determine the solubility profiles of airborne uranium in each section of the Irigaray uranium processing plant in an effort to improve the internal dosimetry estimates for exposed employees.

In the Irigaray *in situ* leach process for uranium, a carbonate/bicarbonate leach solution and an oxidant are injected into the ore bearing sandstone through a series of wells. The oxidant (O_2) oxidizes the uraninite ore (UO_2) into a soluble form and it dissolves into the leach solution. The oxidized uranium then complexes with the bicarbonate anions present in the leach solution to form uranyl dicarbonate. The uranium-laden leach solution is drawn to a recovery well, where it is pumped to the surface and the processing plant. The underground leaching reaction is as follows:



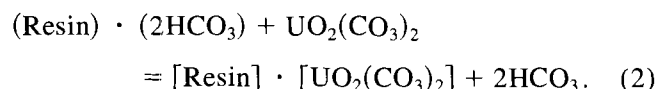
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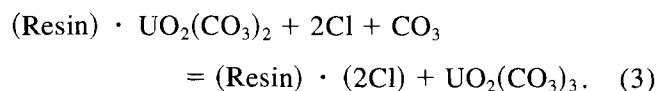
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The processing plant is organized into three sequential circuits: the ion exchange circuit with resin loading and elution; the precipitation circuit; and the yellowcake drying and packaging circuit. In the ion exchange section of the plant, the uranium laden leach solution is passed over a strong base anion exchange resin in bicarbonate form (Dowex 21K[‡] resin), which loads the uranium. The uranyl dicarbonate anions adsorb on the resin by desorbing bicarbonate anions from the resin as follows:



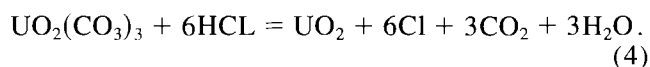
Once the resin is fully loaded with uranium, it is transferred to a second vessel, where it is eluted, or stripped from the resin. The eluant used to desorb the uranyl dicarbonate from the resin contains approximately 50 g L⁻¹ chloride and 20 g L⁻¹ carbonate at a pH of 10. This forms a rich eluate containing uranyl tricarbonate anions:



The next step of the processing is the precipitation circuit. Several chemical precipitation methods are available for uranium oxides. In the past, most conventional processing plants precipitated uranium with ammonia, caustic soda, or magnesium oxide. For the majority of these processes, it is necessary to dry the yellowcake at very high temperatures (up to 800°C) in order to decompose and remove impurities in the yellowcake, such as ammonia, sulfates and chlorides. In the Irigaray process, a precipitation method using hydrogen peroxide is used because a very clean cake is formed, with no associated impurities that require high temperature drying for removal.

The hydrogen peroxide precipitation process involves three steps. First, hydrochloric acid is added to the eluate to reduce the pH from 10 to 2.5 to break down uranyl tricarbonate into uranyl dioxide and carbon dioxide, which bubbles out of the solution. The removal of the carbonate complex reduces the solubility of uranium in preparation for precipitation:

[‡] Dowex, Dow Chemical Company, P.O. Box 92178, Chicago, IL 60675.



In the second step, hydrogen peroxide is added to precipitate the uranium to $\text{UO}_4 \cdot 2\text{H}_2\text{O}$, known as metastudite:



The above reaction produces hydrogen cations which reduce the pH to 1. Therefore, the last step in the precipitation process is the addition of caustic soda (sodium hydroxide) to increase the pH back to 4 where conditions are more favorable for metastudite crystal growth.

After precipitation, the yellowcake is washed through a filter press to remove residual chlorides and other soluble contaminants and is then de-watered to a thick slurry that is allowed to settle. Finally, the thickened slurry is fed into a multi-hearth drier, where it is dried at a relatively low temperature of 540°C. The final dried product is yellowish-orange in color.

X-ray diffraction analysis of the final dried product[§] has shown that the dried yellowcake is composed of 79% $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ (metastudite), 15% UO_3 , and 3% calcite (CaCO_3). Due to the low drying temperatures, no U_3O_8 is formed in this process.

Analysis of uranium found in the dryer scrubber emissions showed that the scrubber uranium was composed of 65% UO_3 , 0.3% U_3O_7 , 31% calcite, and 3% halite.

The $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ that is the final slurry product prior to drying, and that makes up the vast majority of the dried product, is normally a soluble form of uranium.

THE SOLUBILITY TEST METHOD

Air samples were taken in the filter press area, drum packaging room, the control room, the furnace area, and finally the scrubber stack. Two samples were taken in each area at different times over the course of 1 wk. A breathing zone pump, operated at 3 L of air per minute, was used for all areas except the filter press and control rooms, where low airborne activities required the use of a medium volume air sampler operating at 30 L of air per minute. The samples were collected using a standard 37-mm breathing zone cassette and 0.8 micron pore size Gelman^{||} GN4 filter media. Total uranium activity on the filters ranged from 0.4 Bq to 21.8 Bq. Each of the filters was covered with a clean filter of the same type to form a filter-uranium-filter sandwich, which was held together using the center sections of two breathing zone cassettes. These filters were immersed in a beaker holding 90 mL of a serum lung ultrafiltrate (SUF) (Eidson and Mewhinney 1983), which was maintained at a pH of 7.2 by keeping a layer of CO_2 over the solution. The filter sandwich was moved to a fresh beaker of solution every

day for 1 wk, and then weekly until the end of the 28-d test period. The SUF was then wet ashed with concentrated nitric acid and hydrogen peroxide to destroy the organic components in the SUF. The pH of the solution was adjusted to 2–3 with 6 M NaOH, and it was transferred to a teflon separatory funnel. One and one-half mL of the extractive scintillator Alphaex[¶] was added to the funnel and the uranium was directly phase transferred to the organic scintillator. Extractive scintillators contain an organophilic metal ion extractant that allows the phase transfer of a nuclide(s) into the scintillator from an aqueous solution. Alphaex contains bis(2-ethylhexyl) hydrogen phosphate, which has a high affinity for actinides (McDowell and McDowell 1994). Only isotopes of uranium were present on the air samples, so there was no interference from transuranic radionuclides.

After the phases had been allowed to separate, 1.0 mL of the organic scintillator was withdrawn and counted on a Photon-Electron Rejecting Alpha Liquid Scintillation (PERALS[#]) spectrometer. The PERALS spectrometer uses pulse shape discrimination to isolate the longer pulses resulting from alpha interactions in the scintillator from those resulting from β - γ emissions. A timing circuit and gate are then used to reject the β - γ pulses and the alpha pulses are sent to a multichannel analyzer for display of the alpha energy spectrum. The counter typically has a background of 0.03 counts per minute under an alpha peak and an alpha counting efficiency of >99%. Energy resolution is about 220 keV at an alpha energy of 5 MeV. The lower limit of detection for a 1-h count ranged from 0.002 to 0.003 Bq depending on the specific spectrometer used. This sensitivity makes it possible to develop solubility profiles from breathing zone air samples which contain trace quantities of radionuclides (Metzger, et al. 1995).

After the leach test period was complete, the filter sandwich containing undissolved uranium was placed in a beaker with concentrated nitric acid. The Gelman GN4 filter media readily dissolved in nitric acid. The beaker was placed on a hotplate and additions of nitric acid and hydrogen peroxide were made until the organics had all been driven off and a clear solution remained. After a pH adjustment, the uranium was extracted into the Alphaex extractive scintillator, which was counted on the PERALS spectrometer.

After the experiment was complete, the total activity and the fraction undissolved at each time period were determined and fitted to a three exponential model (eqn 6) using a standard Marquardt fitting algorithm (Kuester and Mize 1973). This fitted model was then used to find the fraction of the uranium with clearance half-times less than 10 d (ICRP Class D) (ICRP 1979), between 10 and 100 d (Class W), and beyond 100 d (Class Y):

$$\% \text{ undissolved} = A_1 e^{-\lambda_1 t} + A_2 e^{-\lambda_2 t} + A_3 e^{-\lambda_3 t}. \quad (6)$$

[¶] 4ETRAC, Inc., 1009 Alvin Weinberg Drive, Oak Ridge, TN 37830.

[#] ORDELA, Inc., 1009 Alvin Weinberg Drive, Oak Ridge, TN 37830.

[§] Hazen Research, Inc., 4601 Indiana Street, Golden, CO 80403.

^{||} Gelman Sciences, Inc., 600 S. Wagner Road, Ann Arbor, MI 48106.

RESULTS

Solubility profiles of the uranium in the filter press section of the processing plant indicate that the airborne uranium is very soluble, with 97% of the uranium dissolving with a 0.3 d half-time. The remaining 3% dissolved with a half-time of 15.6 d. The solubility test results are shown in Table 1 and Figs. 1–3 below. The correlation of the test results between the two air samples is quite good. The uranium in this area of the processing plant should be quite soluble as it has just been precipitated from the pregnant strip solution of the ion exchange circuit.

The solubility profiles for the drum loading and packaging area were also quite soluble, with 97% of the uranium dissolving with a half-time of 0.25 d and the remainder with a 20 d half-time. These results are consistent with the x-ray diffraction analysis of the product, which found it to be 79% $\text{UO}_4 \cdot 2\text{H}_2\text{O}$, a soluble compound of uranium. The correlation between the two air samples was again quite good.

The uranium air samples collected in the drier stack were more insoluble, with 46% dissolving with a 0.4 d half-time and 53% with a $T_{1/2}$ of 18 d. These results are also consistent with the x-ray diffraction analysis, which showed the drier exhaust to contain more insoluble forms of uranium.

The control room is located on the second floor of the drier building and is actually an open bay. Air in the area is drawn into the drier, which is kept under strong negative pressure. Consequently, air is drawn into the control area from outside of the building in the vicinity of the drier stack, and from other areas of the plant. The airborne uranium air concentration in the area is quite low, typically 2×10^{-3} to 1×10^{-2} Bq m^{-3} . The total activity on the air samples analyzed for solubility was only 0.23 and 0.8 Bq for samples C1 and C2, respectively. Nonetheless, the solubility tests for the samples were remarkably consistent, with 77% of the uranium dissolving with a half-time of 0.31 d and the remaining

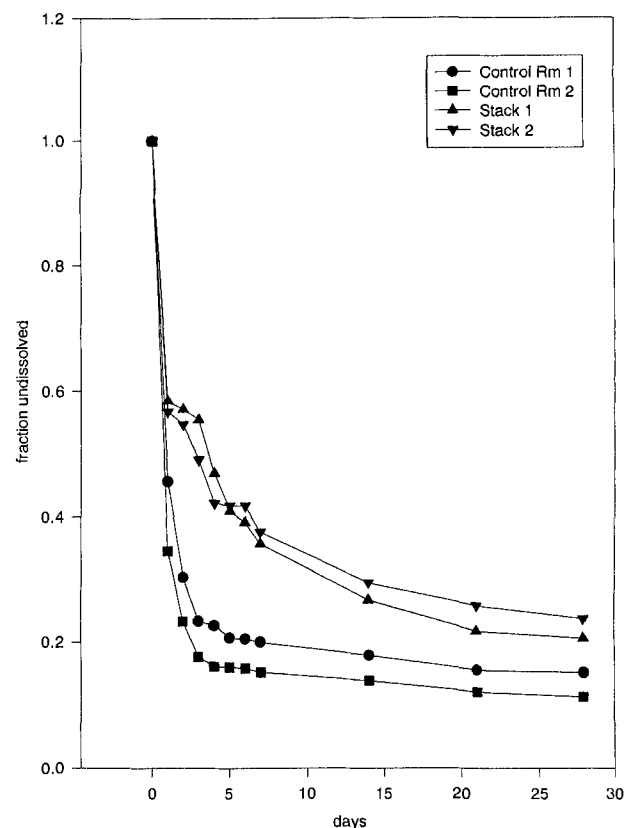


Fig. 1. Solubility profiles of airborne uranium in serum lung ultrafiltrate maintained at a pH of 7.2. Air samples were taken in the Irigaray Uranium Processing Plant control room and drier exhaust stack.

23% with a 30 d half-time. This profile is less soluble than the final uranium product and reflects the contribution from ambient air near the drier stack.

The solubility profiles from the two air samples taken in the furnace room were not consistent (Fig. 3).

Table 1. The results of solubility testing at the Irigaray Uranium Processing Plant.

Sample identification	Uranium activity (Bq)	Sample volume (L)	Airborne concentration (Bq m^{-3})	Class D	Fraction in ICRP	
					Class W	Class Y
Stack 1	5.19	393	13.21	44	56	0
Stack 2	6.19	405	15.29	50	50	0
Average stack	5.69	399	14.25	47	53	0
Control room 1	0.227	88,020	0.0026	77	23	0
Control room 2	0.806	78,930	0.010	76	24	0
Average control	0.517	83,475	0.0064	77	23	0
Drum-pack	12.35	1,269	9.73	98	2	0
Room 1						
Drum-pack	1.47	6,675	0.220	97	3	0
Room 2						
Average drum	6.91	3,972	4.98	97	3	0
Furnace room 1	6.11	3,900	1.57	72	28	0
Furnace room 2	21.83	1,284	17.00	91	9	0
Filter press 1	0.669	7,170	0.0933	94	6	0
Filter press 2	0.410	3,000	0.137	100	0	0
Average filter	0.540	5,085	0.115	97	3	0

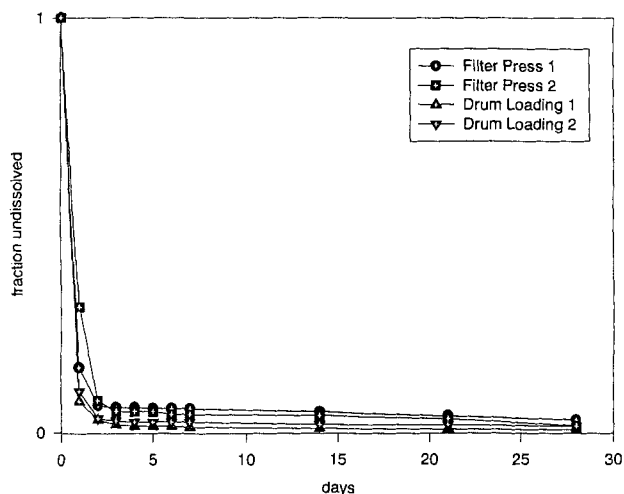


Fig. 2. Solubility profiles of airborne uranium in serum lung ultrafiltrate maintained at a pH of 7.2. Air samples were taken in the Irigaray Uranium Processing Plant drum loading and packaging room and the filter press area.

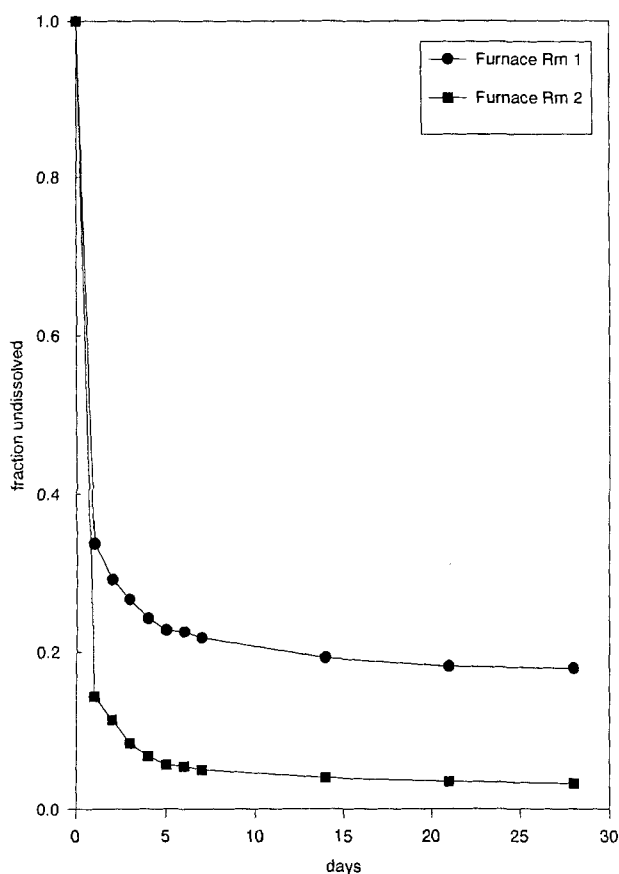


Fig. 3. Solubility profiles of airborne uranium in serum lung ultrafiltrate maintained at a pH of 7.2. Air samples were taken in the Irigaray Uranium Processing Plant furnace room.

One sample, F2, was heavily loaded with uranium resulting from an airborne release during the sampling

period. The other sample was conducted over a 3-d period with much lower airborne concentrations. The uranium on the heavily loaded sample was much more soluble than the 3-d sample. This is consistent with a release of the more soluble product into the air. The other sample had a solubility profile similar to that found in the control area. Since the two samples have significantly different profiles, only a rough estimate of solubility in this area can be made.

Dosimetry estimates

The 50-y committed dose equivalent for a theoretical exposure to 370 Bq of ^{238}U and an equivalent activity of ^{234}U with an activity median aerodynamic diameter of 1 micron was calculated for each set of solubility profiles presented in Table 1, using the internal dosimetry code CINDY (Streng et al. 1990). For comparison, the current estimate of 100% Class Y solubility for this product is also shown. Results, which are shown in Table 2, indicate that the currently assigned solubility class overestimates the actual internal dose delivered from this product by more than a factor of 20. Since soluble forms of uranium are also nephrotoxic, the current solubility profile underestimates the potential for kidney damage from acute exposures.

Comparison with bioassay data

Routine urine bioassays are collected bimonthly from processing plant workers in the drier load-out area and in other locations where there are airborne concentrations of uranium. Bioassay procedures require that a spot sample be taken at the start of the work shift. A review of the bioassay records for 1994 and 1995 indicated that, with one exception, few results exceeded the $5 \mu\text{g L}^{-1}$ lower limit of detection for the method used to analyze the samples, and these were not correlated with any particular event. On 1 August 1994, at 9:30 a.m., a yellowcake thickener tank collapsed in the filter press area of the plant and dumped a significant quantity of yellowcake slurry on the floor. Cleanup of the spill began around 11 a.m. and continued for the next 4–5 d. Both breathing zone and area air sampling were used to monitor the intake of the workers performing the cleanup work, and these indicated that the day-shift worker, whom we will call employee A, inhaled about $641 \mu\text{g}$ of yellowcake with the majority of that occurring on 1 August and 4 August. The total inhalation estimate for

Table 2. Estimates of 50-y effective dose equivalent from a theoretical acute exposure to 370 Bq of ^{234}U and 370 Bq of ^{238}U with the solubility profiles shown in Table 1. The assumed activity median aerodynamic diameter is 1 micron for all samples.

Mill area	Estimated dose equivalent (mSv)
Stack	1.1
Control	0.8
Drum pack	0.6
Filter press	0.6
100% class Y	25

the night shift worker involved in the cleanup (employee B) was estimated to be 463 μg , with the majority of this intake occurring on the 2 August night shift.

Bioassay results for employee A were 87 $\mu\text{g L}^{-1}$ for the spot urine sample collected on 6 August at 6 a.m., and 45.9 $\mu\text{g L}^{-1}$ for the 5 August sample collected at the same time. No further bioassay samples were collected until 13 August, when the uranium in urine concentration was below 5 $\mu\text{g L}^{-1}$. Employee B had 16.9 $\mu\text{g L}^{-1}$ uranium in his bioassay sample collected at 1900 hours on 4 August and 7.6 $\mu\text{g L}^{-1}$ in the sample collected on 6 August at the same time. No further samples were collected until 11 August when the uranium concentration had dropped below 5 $\mu\text{g L}^{-1}$.

Analysis of the bioassay results is complicated by the lack of knowledge regarding the exact time of the exposure(s) and the sparse bioassay data. For employee B, the air sampling data indicates that virtually all of the intake occurred on the night shift spanning 2 August to 3 August, so this intake was modeled as an acute exposure at midnight on 2 August. The *in vitro* solubility tests conducted in this area of the plant indicated that the freshly precipitated yellowcake in this area of the plant is 97% Class D and 3% Class W. Using this assumption, CINDY predicts a total intake of 476 $\mu\text{g U}$, which is quite close to the air sampling estimate of 463 μg .

The time course of the exposure for employee A was more complex, so this intake was modeled as a continuous exposure over the period 1 August to 4 August. Again using the solubility profile based on the *in vitro* tests, the CINDY code predicted an intake of 1,110 μg , which is somewhat above the 463 μg estimate derived from the air sampling. We consider this adequate agreement considering the complex exposure pattern and sparse bioassay data.

By contrast, if the same models are used with the solubility assumption changed to 100% Class Y (the current value used throughout the plant), the intake assessments are the rather absurd values of 107,000 and 65,000 μg for employees A and B, respectively. These values are completely inconsistent with the airborne concentrations in the work area at the time of the spill cleanup.

This analysis of the available bioassay data supports the findings of the solubility testing in this area of the plant.

CONCLUSION

This uranium process produces a soluble uranium product that principally consists of a $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ compound. The airborne concentrations of the uranium in the wet process and drum loading and packaging sections of the plant should be considered to be 97% Class D and 3% Class W. The emissions from the drier stack and areas of the plant that have this source as the primary contributor to the airborne uranium concentration should be considered to have a solubility profile of 46% Class D and 53% Class W. These results compare well with available bioassay data.

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