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MEASUREMENTS TO DETERMINE THE SOLUBILITY OF URANIUM YELLOWCAKE MATERIALS IN THE LUNGS OF MILLWORKERS FOLLOWING ACUTE EXPOSURE

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REPOSITORY PNL
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ABSTRACT

Measurements to determine the solubility of yellowcake in the human lung have been performed with workers who have incurred unintentional acute exposure to yellowcake at uranium mills and volunteer for examination at Battelle. Evaluation of their exposure includes sequential measurements of uranium in excreta and in the respiratory system to identify the translocation and metabolic properties of the inhaled substance and, in turn, to determine its solubility.

Our experience indicates that, although most acute inhalation exposure to yellowcake is followed by rapid excretion of uranium, we have observed examples which demonstrate that some yellowcake is significantly less soluble in the lung than expected. These cases of yellowcake exposure support findings from other solubility studies conducted *in vitro* which demonstrate that yellowcake does not exhibit a generically unique solubility classification.

This presentation will illustrate the methodology employed in this program and will establish a range of solubility for yellowcake based upon occupational exposure experience.

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INTRODUCTION

An ongoing investigation of yellowcake solubility is being performed by examination of uranium millworkers who have become unintentionally exposed in an acute manner to yellowcake resulting from an accident at work. Recent data has led to speculation that specific chemical forms of yellowcake may have a greater solubility than that of class Y in the lung, shifting the mode of toxicity and the critical organ of concern from radiotoxicity in the lung to chemical toxicity in the kidney (Ei80; Ka79).

Heretofore, yellowcake has been assumed to be primarily an insoluble class Y compound. However, other studies *in vitro* have indicated that yellowcake does not exhibit a generically unique solubility (Ei80). Supporting evidence from measurements of uranium *in vivo* and with excreta obtained from exposed workers examined in this study will be cited to demonstrate that yellowcake should be considered a mixture of uranium compounds, each with varying solubility characteristics.

Although this is an ongoing project, three typical cases will be described to support the conclusion regarding the need to classify yellowcake solubility as a mixture of several components. The results should also be useful for the regulatory agencies to consider for insuring radiological health and safety wherever yellowcake is produced.

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METHODOLOGY

Several uranium mills in Wyoming, Washington, and Utah have chosen to voluntarily participate in this program so that we may evaluate the acute uranium intake with millworkers who may, unintentionally, become exposed at the mill. An acute intake deemed of interest to this study includes any unusual incident where a yellowcake worker is exposed to uranium concentrations exceeding the MPC (viz, 0.2 mg/M^3 or 1×10^{-10} µCi/ml.) (Co80). Urinary excretion exceeding 60 µgm/day of uranium may also signify an earlier intake of yellowcake (IAEA76).

Following notification, we arrange to transport the exposed worker to our laboratory to eliminate any potential for further exposure to uranium which would complicate evaluation of the acute intake. All urine and feces excreted by the exposed worker are collected for the duration of our evaluation and analyzed for uranium content by standard fluorometric techniques following chemical dissolution of the sample. We also attempt to obtain samples of excreta collected at the mill site immediately following intake acknowledging the high probability for extraneous contamination from uranium not excreted by the worker.

Analysis of excreta samples from millworkers frequently indicates the presence of microgram quantities of uranium which, presumably, originate from low level, chronic exposure at the mill. Any acute intake of uranium that is soluble in the respiratory system or gut will become evident as an increase in the urinary concentration of uranium. Insoluble compounds of uranium deposited in the nasopharyngeal or tracheobronchial region of the respiratory system will be cleared by the muco-

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ciliary action and translocated to the gut where it will eventually be excreted in feces (Ra79).

The ICRP lung model (ICRP78) predicts the fate of inhaled particles after they deposit in the respiratory system. Used as a general guide, the relative solubility of an inhaled material (i.e., uranium yellowcake) can be determined by examining the relative temporal appearance of uranium in urine and fecal samples collected following acute intake. The ratio of activity appearing in urine and feces at various times following acute intake is also useful in determining solubility as predicted by the ICRP lung model.

The workers are also examined for the presence of yellowcake in the lung by measurement in vivo for uranium using two special dual-crystal [NaI(Tℓ)/CsI(Tℓ)] scintillation detectors positioned on the anterior thorax. Measurements in vivo are performed daily for the duration of the evaluation as a means to observe translocation of uranium from the lung. Yellowcake is determined indirectly by measurement of photons from ^{234}Th at 63 keV and 93 keV (≈4% abundance) and ^{235}U at 186 keV (54% abundance). We consider yellowcake to be similar in form to that conventionally assumed for natural uranium, i.e., 0.7% ^{235}U.

The dual-crystal "Laurer" detectors are employed in a unique manner to simultaneously measure ^{234}Th, ^{235}U, and the L-Xrays (≈16 keV) (La68; Co77; Co78a; Sh74). The L-Xrays from uranium, protactinium, and thorium are present in the measured energy spectrum whenever surface contamination from uranium is suspect on the worker being examined. In this manner, surface contamination can be distinguished from that uranium

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activity actually deposited in lung tissue.

Calibration measurements are performed with a thorax phantom structure which has natural uranium deposited uniformly in simulated lung tissue (Wa70; Pa76). The ratio of counts in the L-Xray region of the spectrum to the counts in the ^{234}Th region is calculated and results represent internally deposited uranium activity. This ratio is then compared to the ratio calculated from an actual measurement in vivo of an exposed worker. In this manner, the presence of surface uranium contamination can be quantified so that the actual internal deposition can be calculated (Co78b).

CASE A

Worker A briefly entered a yellowcake packaging room which was filled with black yellowcake dust. Immediately recognizing the hazard, the worker exited the area, donned a respirator, and re-entered the room to cap the drum which was being overfilled with yellowcake. Analysis of the worker's breathing zone air sampler indicated a concentration of 1.3×10^{-9} μCi/ml. of natural uranium which is significantly greater than the maximum permissible amount. Although the duration of this worker's exposure to yellowcake dust without respiratory protection was determined to be brief, it was apparently sufficient to produce an acute intake of yellowcake material.

Although the potential for a significant uranium intake was known immediately following analysis of the air sampler filter at the end of the work shift, no excreta samples could be obtained from Worker A since he had already departed and was on a planned vacation. Immediately

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upon returning to work, a spot urine sample was collected from Worker A and analyzed at the mill. The uranium concentration was 32 μgm/l. which is significantly greater than normal for workers at the mill who have been off work for several days.

Worker A was examined at Battelle on days 7 through 10 post intake; however, no analysis of the rapidly soluble component of this material in the body could be performed under controlled laboratory conditions because of the worker's vacation immediately following the intake. The results of uranium analysis with urine and fecal samples collected from Worker A are given on Table 1.

The total amount of uranium eliminated in feces decreased daily. The source of uranium in the body was probably a small deposit in the lung which was being cleared by mechanical means (i.e., ciliary action). However, the uranium concentration in urine, representing the soluble fraction, remained relatively constant (≈12 μgm/day) demonstrating that a slightly soluble source of uranium was present somewhere in the body, presumably the lung. The uranium being eliminated via urine must be from a source which has a solubility faster than that of class Y in the lung (i.e., 500 days).

The yellowcake produced at this mill is a fine, very black powder and is dried at approximately 800°C. These characteristics usually indicate an insoluble compound according to informal industry criteria. However, the continuous excretion of approximately 12 μgm of uranium per day during the week following intake supports the presence of some slightly soluble (i.e., class W) component in this uranium yellowcake

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material produced at this mill. A diminishing excretion of uranium in feces during the observation period represents clearance of particles from the upper respiratory system where cilia and mucosal transport can remove particles so that they can be swallowed. However, measurements *in vivo* to detect uranium in the lung were below the detection level (i.e., 2 mg) which implies that the source of uranium is small.

CASE B

Worker B was hit by a large lump of yellowcake which fell from the drier above his head and completely dislodged his respirator while B was performing maintenance in the yellowcake drier. He was completely covered with dark black yellowcake including inside his mouth and nose. Immediately following decontamination, urine samples were collected and analyzed by the mill. Analysis continued at Battelle on day 6 post intake. Aliquots of these urine samples collected at the mill were re-analyzed for uranium at Battelle as well as all new urine and fecal samples collected from Worker B during his visit to PNL. The results of all the analyses for uranium in excreta are given on Table 2.

Measurements *in vivo* for uranium with Worker B detected externally deposited surface contamination on his skin and especially in his hair. However, no internally deposited uranium above the detection level (≈2 mg) was found in the thorax or kidney region of Worker B.

Worker B apparently ingested a large quantity of yellowcake following the occurrence and probably had a quantity of the large particles of yellowcake deposited in the nasopharyngeal (NP) and tracheobronchial (TB) region of the respiratory system. The uranium detected in the first

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urine sample could be due to contamination or rapidly soluble (class D) material from the lung or gut. The rapid decrease in the urinary excretion of uranium following this occurrence suggests that the material was probably very soluble.

The concentration of uranium in feces was approximately a factor of ten greater than the concentration in urine on days 5 and 7 post intake. This fecal excretion is probably due to translocation of large or insoluble particles of yellowcake from the tracheobronchial region of the respiratory system to the gut. Although this yellowcake has the characteristic appearance of an insoluble compound, it is apparently very soluble in the body (i.e., class D).

CASE C

A sample of urine collected from Worker C indicated that he had been exposed to uranium sometime following his last routine sample collected ten days earlier. No unique source of exposure could be identified by this worker since, as a new employee, he was unfamiliar with most routine procedures at the mill. Urine samples collected from other men working with C were all within normal range for uranium. Evidently, Worker C was involved in an isolated exposure event since he was the only yellowcake worker at the mill to have significantly positive amounts of uranium in urine. Routine surveillance of the mill with high volume air samplers and calculation of the time-weighted air concentration of uranium existing at various locations visited by Worker C did not identify any unusual airborne uranium contamination source.

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Had Worker C not been required to provide urine samples bimonthly, his intake would have probably been undetected.

Table 3 lists the results of analyses for uranium in excreta collected from Worker C. All urine samples, except those obtained during his visit to Battelle on days 34 - 36, represent single voids. During sampling, Worker C was restricted to areas of the mill where additional uranium intake was unlikely. From day 20 to day 35, average uranium excretion was 8.0 ± 1.7 μgm/l. which probably represents elimination of slightly soluble (class W) uranium remaining in the lung. Assuming that the ICRP lung model can be applied to this intake, the uranium present in feces on day 35 arises from that material mechanically cleared from the ciliated region of the tracheobronchial region of the respiratory system and subsequently swallowed. Uranium excreted in urine arises from the slightly soluble (class W) fraction deposited in lung.

Approximately 19 μgm of uranium was excreted in feces on day 35, whereas less than half that amount (viz, 7.1 μgm) was excreted in urine. Uranium solubility in the gut would not make an appreciable contribution to urinary excretion since, according to ICRP 30, the absorption fraction is only 0.05 for water-soluble compounds of uranium. Therefore, after other deposition sites (gut, bone) and entry routes (wound, ingestion) were eliminated, it was determined that the uranium detected in excreta arises from a deposition in the respiratory system. Although no analysis of the rapidly soluble (class D) uranium material was possible, it is apparent that there is a measurable class W component for this uranium material in the lung.

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All measurements *in vivo* performed with Worker C were negative. No uranium above the detection limit (viz, ≈2 mg) was found in the anterior thorax (lung). Likewise, measurements *in vivo* to determine whether any uranium could be detected in the head (skull) or kidney were also negative. Although uranium measurements *in vivo* were negative, the excretion of uranium in urine and feces two weeks post intake supports the presence of a small burden of uranium in the respiratory system.

CONCLUSIONS

These three (and other) exposure cases demonstrate that yellowcake exhibits various solubility classifications in body fluids. Early, rapid clearance of uranium in urine can originate from a soluble yellowcake component in the lung or gut. However, delayed excretion of uranium in urine following acute intake predominantly arises from soluble components in the lung since rapid clearance and a small soluble fraction (0.05) of uranium in the gut cannot adequately support observed results. A small uranium store in bone may be available following translocation of the initial soluble fraction in lung and gut. However, the magnitude of the delayed uranium excretion cannot be credited solely to skeleton. Delayed uranium excretion in feces supports existence of a continuing lung burden, some of which may be soluble and acting as the source of the uranium in urine. Therefore, yellowcake should be considered as a combination of class D, class W, and class Y soluble components.

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TABLE 1

CASE A

URANIUM IN EXCRETA FROM EXPOSED MILL WORKER LK[1]

	Days Post Intake	Total Uranium Excretion
Urine:	7	14 μg
	8	11 μg
	9[2]	7 μg
	10	14 μg
Feces:	7	98 μg
	9	25 μg
	10	10 μg

1. Worker off-shift and on vacation for seven days prior to sampling.
2. Total collection of excreta incomplete for this day.

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TABLE 2

CASE B

URANIUM IN EXCRETA FROM EXPOSED MILL WORKER SS[1]

	Days Post Intake	Result
Urine:	(-1)[2]	2.5 μgm/l.[3]
	0	220.0 μgm/l.
	1	26.4 μgm/l.
	2	7.2 μgm/l.
	3	≤0.4 μgm/l.
	4	4.9 μgm/l.
	5	3.4 μgm/l.
	6	≤0.4 μgm/l.
	7*	2.4 μgm/l.
	8*	1.2 μgm/l.
Feces:	5*	49.4 μgm/day
	7*	16.0 μgm/day

1. All samples (except *) represent a single (i.e., spot) sample of excreta. The * results were determined from analysis of a total collection of excreta for 24 hours.
2. This sample was a routine spot sample obtained at the mill one day prior to the occurrence.
3. The systematic error associated with the analytical procedure to determine uranium in urine is less than ± 20% as determined with standard and blank samples.

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TABLE 3

CASE C

URANIUM IN EXCRETA FROM EXPOSED MILLWORKER TS

	Days Post Intake[1]	Uranium Concentration[2]
Urine:	(-10)	0.1 μgm/l.
	1	64.0 μgm/l.
	7	37.9 μgm/l.
	13	60.7 μgm/l.
	14	14.4 μgm/l.
	15	14.8 μgm/l.
	20[3]	7.0 μgm/l.
	21	7.5 μgm/l.
	22	8.9 μgm/l.
	23	6.8 μgm/l.
	24	7.9 μgm/l.
	25	5.1 μgm/l.
	26	10.5 μgm/l.
	27	9.8 μgm/l.
	28	10.6 μgm/l.
	29	5.5 μgm/l.
	34[4]	8.3 μgm/l.
	35[4,5]	8.8 μgm/l.
	36[4]	1.5 μgm/l.
	46[6]	12.1 μgm/l.
Feces:	35[4,5]	18 μgm/day

1. Exact occurrence date unknown.
2. Overall systematic error is ± 20%.
3. Worker on vacation five days and restricted thereafter to avoid additional intake of uranium.
4. Samples collected at PNL.
5. Analysis of 24-hour excreta sample.
6. Worker returned to job at mill.

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