

**Cameco Resources In-Situ Recovery Process-Specific
Yellowcake Solubility Characteristics
March 14, 2011**

1.0 INTRODUCTION

Cameco conducted an experiment to assess the dissolution properties of uranium concentrate from both the Crow Butte and Smith Ranch-Highland operations in simulated lung fluid. This report provides a summary and dosimetry interpretation of the experiment performed by the Cameco Innovation and Technology Development Research Centre (I&TDRC)¹ to determine the process-specific solubility characteristics.

The experimental results were interpreted in the context of both the ICRP 30² solubility classifications of days, weeks, and years (D/W/Y) and ICRP 71³ classifications of fast, medium, and slow (F/M/S). In addition, annual limit on intake (ALI) and derived air concentrations (DAC) were determined for each sample individually using software based on ICRP 66 Human Respiratory Tract Model for Radiological Protection⁴. Where possible, it is recommended by the ICRP to use process-specific cc solubility parameters, rather than default parameters.

In terms of the D/W/Y classification, the majority of the samples were classified as type D with a very small component of type Y material. Using the F/M/S classification, all samples were type W. In addition, the experimental results showed that use of the default Type D ALI and DAC values is conservative when compared to the results calculated using the actual solubility parameters and Human Respiratory Tract Model.

2.0 EXPERIMENT

The experimental circuit used in this experiment was designed specifically to study the kinetics of uranium dissolution in simulated lung fluids. Details of the experiment design and set up are found in the report Solubility of Radionuclides in Simulated Lung Fluid¹. In brief, each site submitted several samples of their uranium concentrate for analysis. The samples were passed through a 20 µm filter and the filtered uranium powder placed between two glass fiber filters in 47-mm polypropylene filter holders that were used as extraction cells. The simulated lung fluid was then passed over the sample at a predetermined flow rate. After passing over the product samples, the simulated lung fluid was collected and analyzed in a lab for uranium content. This uranium dissolution experiment was continued for 100 days.

3.0 SOLUBILITY CLASSIFICATION – BACKGROUND INFORMATION

Two methods were used to assess solubility classifications for the uranium concentrate samples, ICRP 30 and ICRP 71. Current United States regulations in relation to internal dosimetry and solubility classifications are based on ICRP 30. More recently, updates have been made to the human respiratory tract model, ICRP 66, and to solubility classifications, ICRP 71, derived from this new model. Both methods were used so as to compare the results to existing practices and to interpret the results based on the most recent recommendations of the ICRP.

The primary difference between the models is that ICRP 30 is based on retention time of the material in the pulmonary region of the lungs, while the newer respiratory tract model in ICRP 66 and solubility classes are based on the time dependent clearance rates for both

particle transport and absorption to body fluids. ICRP 66 also recommends that whenever possible that the process-specific absorption rates be used rather than the default parameters.

ICRP 30 divides the respiratory tract into three regions and within each region are a number of compartments, each associated with a clearance pathway (absorption or particle transport). To describe the clearance of radioactive materials from the lungs, the materials are classified as D (day), W (week), and Y (year), referring to retention time in the pulmonary region. The retention times for the classifications are as follows:

	Retention Time (d)
Type D	up to 10
Type W	10 – 100
Type Y	greater than 100

The human respiratory tract model, ICRP 66, divides the respiratory tract into five regions. For all but the first region, the anterior nasal, inhaled material can be cleared through absorption to the blood and through transport to the GI tract, as with ICRP 30. The anterior nasal region is cleared through physical means such as nose blowing.

The classification scheme in ICRP 68⁵ (workers) and ICRP 71 (public), fast/medium/slow clearing (F/M/S), corresponds broadly to that of D/M/Y with the difference that ICRP 71 bases the solubility classes on absorption rates rather than retention times. Where more specific information was not available, those compounds in class D were assigned to type F, class W to type M, and class Y to type S.

Research on the new respiratory tract model has shown that the rate of particle transport and absorption of material to the blood changes with time. Using the ICRP 66 model, materials are described by the fraction of material that dissolves rapidly, the dissolution time for that rapid fraction and the dissolution time of the fraction of material that dissolves more slowly.

Annex D of ICRP 71 provides instruction on how to assign material to absorption types based on experimental data using absorption rates at different times rather than overall retention or clearance rates. Specifically, for an in vitro dissolution experiment, classification depends on the amount of undissolved material, or percent retained, at specified time intervals. Excluding particle transport, which is small for uranium, the classification criteria for solubility types F, M, and S are as follows:

	Retention Rate
Type F	less than 13% at 30 days
Type M	between 13% at 30 days and 87% at 180 days
Type S	greater than 87% at 180 days

That being said, if the process-specific solubility parameters are available, it is not necessary to classify the product into F/M/S or D/W/Y or use the default values for ALI. Rather the best practice, according to ICRP would be to use the parameters specific to that product not the defaults.

4.0 FORMULA FOR CALCULATING PARAMETERS

The dissolution half-times for samples were calculated using the two-exponential model⁶, where the percentage of undissolved uranium [M/M₀] is expressed in equation (1) as:

$$\frac{M}{M_0} = f_1 \exp(-0.693 \frac{t}{T_1}) + f_2 \exp(-0.693 \frac{t}{T_2}) \quad (1)$$

Where:

M - mass of undissolved uranium at time t

M₀ - initial mass of uranium

t - elapsed time

f₁ - fraction of total U with corresponding dissolution half-time T₁

f₂ - fraction of total U with corresponding dissolution half-time T₂

f₁ + f₂ = 100%

A software program⁷, developed at the RC [formerly Cameco technology development (CTD)], was employed for the determination of dissolution parameters. The program employed a Simplex algorithm to minimize the functional F calculated as the sum of squared differences between the experimental and theoretical values characterizing the uranium content (fraction of dissolved or undissolved uranium). To ensure that the global minimum was found, the minimization calculations were repeated several hundred times using the Monte Carlo technique to vary the initial conditions. It was assumed that the global minimum was the set of optimized parameters corresponding to the smallest functional found in the series of these 200 to 500 minimizations.

The procedure was tested several times and it was confirmed that 200 repetitions were sufficient to locate the global minimum.

After the global minimum was found, the Hessian matrix consisting of the second derivatives of F with respect to all the free parameters involved in the model was calculated. The calculations were performed using analytical expressions for the second derivatives (as opposed to numerical differentiation in most of the programs such as MathCAD or Mathematica). The standard deviations of the parameters were calculated from the inverse Hessian matrix using the mean square error (MSE) calculated as the square root of f/(N-v), where N is the number of data points and v is the number of parameters used in the model. (N - v is the number of degrees of freedom).

The program automatically tested several kinetics models applied to the same set of experimental data. For each model, the minimization was repeated 200 to 500 times and the program then selected the model that had the smallest MSE, which was considered to be the best approximation to the experimental data. Some models with a large number of adjustable parameters that showed lower F were not the best description for the experiment because they had higher MSEs (lower denominator).

The absolute values of standard errors for parameters are given in parenthesis in Tables 1 and 2.

The value of the mean square deviation (MSD) characterizes an average error for the curve fitting, i.e., the difference between the experimental values of uranium extraction, (1 - M/M₀)*100%, and the theoretical value.

Dissolution half-times for uranium-bearing samples were calculated using two-exponential model and equation (1) shown above.

When $f_1=100\%$, the two-exponential equation (2) was reduced into a single-exponential form:

$$\frac{M}{M_0} = f_1 \exp\left(-0.693 \frac{t}{T_1}\right) \quad (2)$$

In some cases, when $T_2 \rightarrow \infty$, equation (3)

$$\frac{M}{M_0} = f_1 \exp\left(-0.693 \frac{t}{T_1}\right) + f_2 \quad (3)$$

was employed to obtain a better fit for the experimental data.

The value of the mean square deviation (MSD) characterizes an average error for the curve fitting, i.e., the difference between the theoretical value and the experimental values of uranium extraction, $(1-M/M_0)*100\%$. Generally, the MSD is higher for samples with lower uranium loading ($<400\mu\text{g}$).

In all tables of dissolution parameters, MSD is expressed in %. Absolute values of standard errors for dissolution half-times are expressed in days, absolute values of standard errors for fractions of total U are expressed in %. All dissolution half-times higher than 100 days, were considered as ∞ .

In earlier publications⁸, a three-term equation was applied for determination of dissolution parameters:

$$\frac{M}{M_0} = f_1 \exp\left(-0.693 \frac{t}{T_1}\right) + f_2 \exp\left(-0.693 \frac{t}{T_2}\right) + f_3 \exp\left(-0.693 \frac{t}{T_3}\right) \quad (4)$$

The addition of more terms, i.e., three exponents, instead of two, in equation used for calculation of parameters, may improve the fit. However, the error in determining the parameters for data fitting increases and in many cases such additional parameters may become statistically insignificant. The software developed at I&TD-RC for the SLF data analysis calculates the errors for the fitting parameters and pt also determines whether the addition of more parameters is statistically justified.

Unfortunately, the paper⁸, which used also the 3rd term for calculation of dissolution parameters, has not addressed the issue of statistical significance for the data fitting parameters and did not calculate the errors in the data they presented.

During the development and testing the kinetic model for SLF Cameco determined that the third (or higher) terms (exponents) were statistically insignificant and their addition led to a significant increase in the error (uncertainty) for parameters f_1 , T_1 and f_2 , T_2 . It could be the main reason why in all recent related publications in the literature (as well as in The ICRP Publication 71) primarily two-exponential equations were considered for determination of parameters.

5.0 RESULTS

Using the experiment and calculation methods described above and detailed in the I&TDR report¹, process-specific solubility parameters were determined for both the Crow Butte and Smith Ranch-Highland product samples. Each site provided multiple samples for analysis to better characterize the material on average and to limit the potential impact of any outliers in the final results. Table 1 shows the average solubility parameters (from equation (1)), mean square deviation (MSD is the difference between experimental and theoretical uranium extraction values), and ICRP 71 solubility type classification determined for the Crow Butte and Smith Ranch-Highland samples, respectively.

Table 1: Crow Butte and Smith Ranch-Highland Solubility Parameters

	f_1 (%)	T_1 (d)	f_2 (%)	T_2 (d)	MSD ^a (%)	Type
Crow Butte	68.6	0.6	31.4	34.5	3.4	F
Smith Ranch-Highland	87.7	1.1	13.3	47.8	3.0	F

^aThe two-exponential model was applied for calculations

The ICRP 71 Type F classification roughly matches Type D. Figures 1 and 2 illustrate this classification. The areas outlined in blue show each of the type F, M, and S regions based on retention rates at specific times after intake. Measured retention rates can be used to assign materials to each type.

The equation $S = \ln(2)/T$ allows the dissolution half times to be converted into the dissolution rate constants used by ICRP.

Figure 1: Classification of Crow Butte Samples into Type F, M, and S

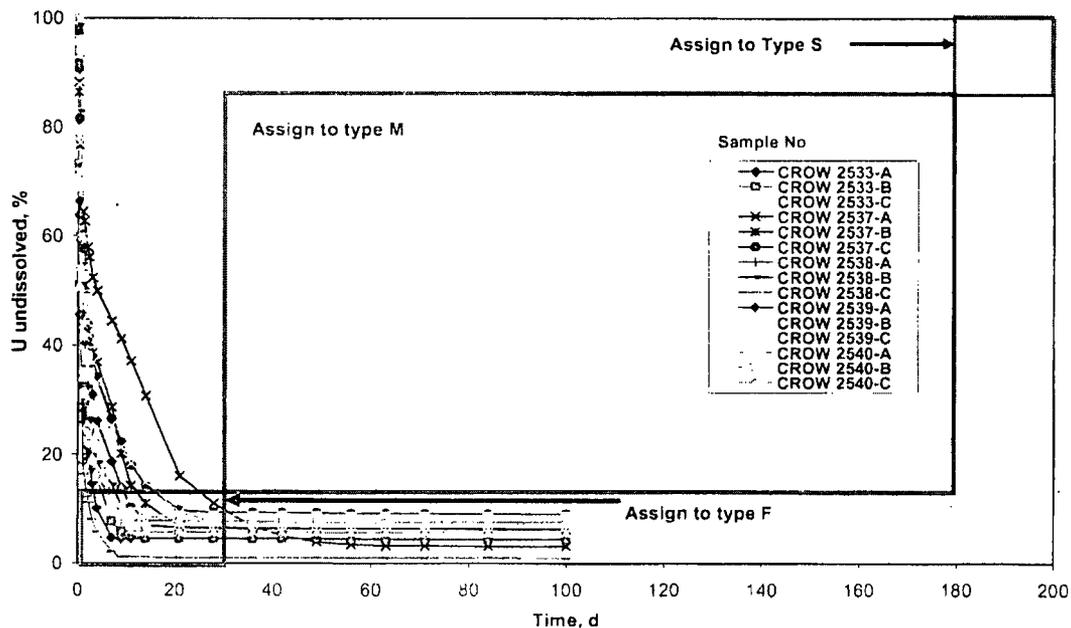
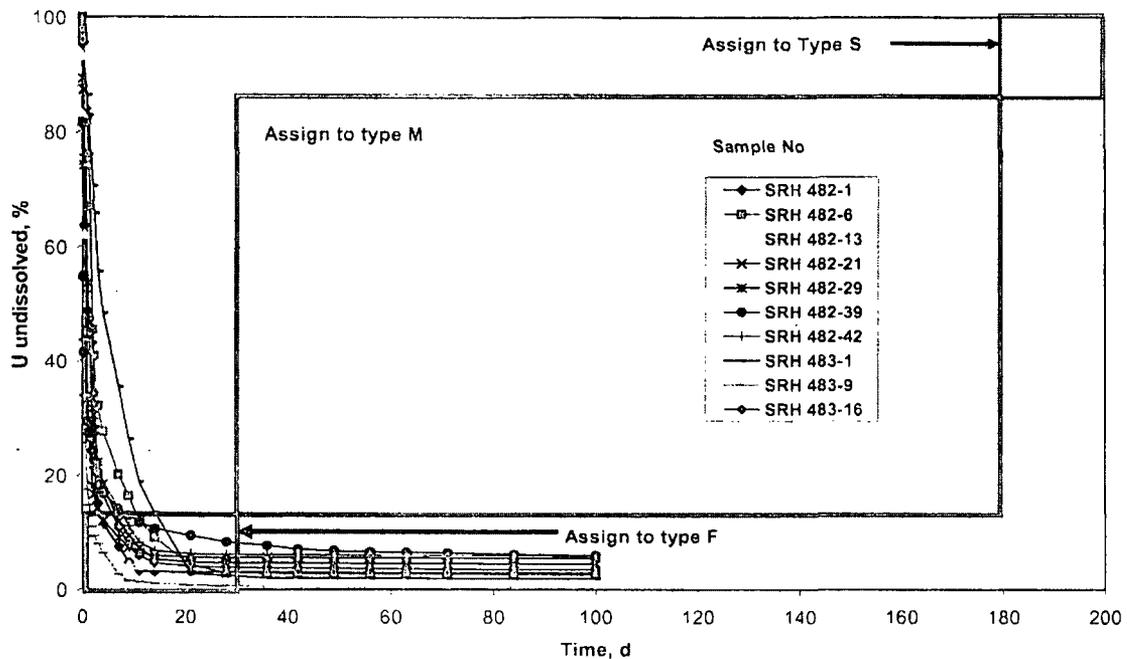


Figure 2: Classification of Smith Ranch-Highland Samples into Type F, M, and S



Though the material has been shown to fit within the bounds of a Type F material, process-specific values will be used to determine the risk from each product, not default values. Once the solubility parameters are calculated, the associated dosimetric quantities (i.e. annual limit on intake and derived air concentration) can be determined using IMBA (Integrated Modules for Bioassay Analysis) software developed by the National Radiological Protection Board⁹. The version of the software used for these calculations is IMBA-URAN v 3.0.13, which was developed for Cameco Corporation specifically for calculations related to uranium compounds. It uses the calculations and methodologies of ICRP 66 respiratory tract and uranium biokinetic models to determine dose based on an intake of uranium.

The inputs required by this software are the isotopic composition of the material (U234, U235, and U238 in naturally occurring proportions), the intake method (inhalation), the calculated absorption parameters, and the aerosol characteristics (5 μm AMAD with a 2.5 GSD – ICRP 66 defaults). The software also requires an intake amount to calculate the dose received as a result of that intake. For each of the samples a unit intake of 1 pCi entered. The resulting dose is presented in the unit of mSv/pCi. Once this dose conversion factor is known, the ALI and DAC values can be calculated using equations (5) and (6), respectively. Tables 3 and 4 contain the dose conversion factor (in mSv/pCi and rem/ μCi) for each sample, the ALI, and the DAC for the samples from each site along with an average ALI and DAC values for all samples.

$$\text{ALI } (\mu\text{Ci}) = \frac{5 \text{ rem}}{\text{DCF (rem}/\mu\text{Ci})} \quad (5)$$

$$\text{DAC } (\mu\text{Ci/ml}) = \frac{\text{ALI}(\mu\text{Ci})}{2400000000 \text{ ml}} \quad (6)$$

Table 3: ICRP 66 Average Dosimetric Quantities for Crow Butte and Smith Ranch-Highland Operation

	DCF (mSv/pCi)	DCF (rem/ μ Ci)	ALI (μ Ci)	DAC (μ Ci/ml)
Crow Butte	1.51E-05	1.51	3.49	1.46E-09
Smith Ranch-Highland	1.49E-05	1.49	3.43	1.43E-09

Using the method documented in NUREG/CR-1428, which is similar to that already described and further elaborated on in an addendum provided by I&TDRC, the samples were also classified based on the ICRP 30 classification (D/W/Y). Table 5 provides the results for Crow Butte and Smith Ranch-Highland. These tables also include the dosimetric implications, ALI and DAC, for each sample and as a plant average. The final ALI and DAC values were calculated by taking a weighted sum of the percent contribution of each solubility class within a sample multiplied by the default ALI and DAC for that solubility class, from 10 CFR 20.

Table 5: ICRP 30 Average Classification and Dosimetric Quantities for Crow Butte and Smith Ranch-Highland

	Type D (%)	Type W (%)	Type Y (%)	ALI (μ Ci)	DAC (μ Ci/ml)
Crow Butte	89	11	0	0.98	4.8E-10
Smith Ranch-Highland	92	8	0	0.98	4.8E-10

6.0 CONCLUSION

A simulated lung fluid experiment was performed to determine the solubility characteristics and dosimetric implications of the uranium products produced at both the Crow Butte and Smith Ranch – Highland Operations. The experimental data was assessed using methodologies described in ICRP 30 and in ICRP 66 / 71. The results show that using the earlier classifications (ICRP 30) that the material produced are primarily type D with a very small portion being a type W. Using the most recent classification methods (ICRP 71), all materials can be considered type F. More importantly, the experiment provided the solubility parameters that can be used to represent that actual dose and toxicity risk of our materials.

The dosimetry implications are that using the ICRP 30 classification, and weighting by the percentage of each class of material present, the ALI and DAC drop slightly from the default value of 5.0E-10 for Natural Uranium.

7.0 REFERENCE LIST

- ¹Cameco Innovation and Technology Development Research Centre, Solubility of Radionuclides in Simulated Lung Fluid, Report Number 200183, Report Number RC-09-05, 2009
- ²ICRP, Limits for Intakes of Radionuclides by Workers, ICRP Publication 30 Part 1, Ann ICRP 2(3-4), 1979.
- ³ICRP, Age-dependent Doses to Members of the Public from Intakes of Radionuclides: Part 4 Inhalation Dose Coefficients, ICRP Publication 71, Ann. ICRP 25(3-4), 1995.
- ⁴ICRP, Human Respiratory Tract Model for Radiological Protection, ICRP Publication 66. 1994, Ann. ICRP 24 (103), 1994.
- ⁵ICRP, Dose Coefficients for Intakes of Radionuclides by Workers, ICRP Publication 68, Ann ICRP 24(4), 1994.
- ⁶T.T. Mercer, "On the Role of Particle Size in the Dissolution of Lung Fluid", Health Physics, Pergamon Press, 1967, Vol. 13, 1211-1221.
- ⁷G. Tairova and M. Ioffe, "U Solubility in Simulated Lung Fluid", Project PHR•P7665, September 2002.
- ⁸D.R. Kalkwarf, Solubility Classification of Airborne Uranium Products from LWR-Fuel Plants, Report No. NUREG/CR-1428, PNL-3411, Pacific Northwest Laboratory, Prepared for Nuclear Regulatory Commission.
- ⁹ACJ and Associates, IMBA Professional Plus Technical Basis, August 2005.