

## **Appendix L**

### **Crow Butte Solubility Characteristics of Crow Butte Yellowcake Kinetics of Uranium Dissolution in Simulated Lung Fluids**

#### **1.0 SUMMARY**

Based on discussions with the NRC and internal discussions within Cameco, an analysis of the solubility characteristics of Crow Butte yellowcake was performed and the material was classified according to the days, weeks, and years (D/W/Y) classification scheme of 10CFR20. This report provides a summary and dosimetry interpretation of the experiment performed by the Cameco Technology and Innovation Research Centre (CTI-RC)[1] to determine these solubility characteristics. This submission supersedes any previous reports submitted on this topic as it incorporates the most recent comments from the NRC and internal discussions.

The experimental results were interpreted in the context of the ICRP 30[2] solubility classifications of days, weeks, and years (D/W/Y) used by 10 CFR20. In addition, the annual limit on intake (ALI) and derived air concentrations (DAC) were calculated for each sample. The individual results were then averaged to establish the typical solubility characteristics, ALI and DAC for Crow Butte material. In terms of the D/W/Y classification, the majority of the samples were classified as type D with a small component of type W material. The resulting ALI and DAC values are the same as the default type D material at 1  $\mu\text{Ci}$  and  $5\text{E-}10$   $\mu\text{Ci/ml}$ , respectively.

#### **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 experimental design and set up are found in the report Solubility of Radionuclides in Simulated Lung Fluid [1]. In brief, each site submitted several samples of their uranium concentrate for analysis. The samples were passed through a 20  $\mu\text{m}$  filter and the filtered uranium powder placed between two glass fiber filters in 47-mm polypropylene filter holders that were used as extraction cells. A 20  $\mu\text{m}$  filter was used to ensure that only particles of a size range, which may reach lungs and react with lung fluid, were included in the analysis; a more detailed analysis of the particulate size analysis conducted as part of this experiment is presented a CTI-RC Memo[3]. 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. At the end of the experiment the residual uranium on a filter was analyzed using an X-Ray fluorescence method.

### 3.0 SOLUBILITY CLASSIFICATION

Current United States regulations in relation to internal dosimetry and solubility classifications are based on ICRP 30. 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 (corresponding to dissolution half-time of the material) in the pulmonary region. The retention times for the classifications are as follows:

	Retention Time (Corresponds to Dissolution Half-Time)
Type D	up to 10
Type W	10 – 100
Type Y	greater than 100

### 4.0 RESULTS

The simulated lung fluid study conducted on the Crow Butte uranium product by the Cameco Technology and Innovation Research Centre followed published methods in performing this experiment [Ansoborlo et al. 1999][4]. The study was run for 100 days and was followed up with an X-ray fluorescence (XRF) measurement of the residual material left on the glass fiber filter.

Table 1 shows the fraction of uranium remaining on the filter (retention fraction) at each sampling time based on ICP Mass Spectrometry analysis. Standard errors on these results vary from 5% to 10%, with the higher errors occurring later in the testing, near the 100 day mark. Table 2 shows the summary of the XRF results taken at the end of the experiment. It is important to note that though the ICP-MS indicated that between approximately 1% and 8% ( $\pm 10\%$ ) of the uranium remained undissolved at 100 days (Table 1), it was later shown through the XRF analysis that the majority of that material was dissolved uranium that had been reabsorbed by the filter. To determine if there had been reabsorption of uranium on the filter, first the filter was inspected visually. There were no visual traces of undissolved uranium remaining on the filter. It is relatively easy to see undissolved material (if any is present) on the filter. Following the visual inspection, the filter was dissolved and analyzed. The amount of uranium found was lower than or close to the detection limit of the method. This means that within experimental error there is essentially no material remaining undissolved at 100 days.

**Table 1: Crow Butte Material Dissolution Kinetics**

Sample No	CROW 2533-A	CROW 2533-B	CROW 2533-C	CROW 2537-A	CROW 2537-B	C ROW 2537-C	CROW 2538-A	CROW 2538-B	CROW 2538-C	CROW 2539-A	CROW 2539-B	CROW 2539-C	CROW 2540-A	CROW 2540-B	CROW 2540-C
<b>U Total in 50 mg Sample (%)</b>	74.12	74.04	74.24	73.51	73.44	73.26	76.7	76.78	76.81	74.44	74.45	74.42	73.12	73.18	73.1
<b>U Total (mg)</b>	37.06	37.02	37.12	36.76	36.72	36.63	38.35	38.39	38.41	37.22	37.23	37.21	36.56	36.59	36.55
<b>Elapsed Time (d)</b>	<b>Retention (%)</b>														
0	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
0.02	94.40	94.90	99.00	97.90	92.40	97.50	95.60	98.80	95.10	92.00	96.00	93.50	94.80	95.80	93.60
0.13	72.90	73.30	97.00	88.20	86.40	90.70	78.40	92.80	73.80	63.80	79.30	70.10	87.80	78.40	71.70
0.31	66.30	51.00	94.40	76.70	77.10	81.50	59.10	82.90	50.60	45.60	69.10	50.80	77.10	59.80	54.00
1	45.50	34.90	72.30	64.40	54.30	60.20	29.20	54.60	18.30	30.70	52.50	34.20	59.90	43.80	35.10
1.31	40.80	32.30	65.60	62.70	51.00	57.60	25.90	49.40	16.40	27.90	48.60	31.10	54.30	41.40	31.30
2	36.10	26.30	45.30	57.90	42.50	44.00	20.10	32.30	12.30	21.40	38.10	25.40	44.10	36.10	24.10
2.31	34.50	24.20	37.40	56.10	40.60	41.50	19.00	26.60	11.10	19.20	34.70	23.20	41.80	34.10	22.10
3	30.90	20.10	27.60	52.40	38.60	37.80	17.30	20.70	8.00	14.60	27.90	19.20	36.90	29.30	18.70
4	26.20	15.90	21.80	50.00	36.90	34.10	15.50	18.60	5.70	10.10	21.20	16.00	33.20	24.30	16.10
7	18.70	7.60	16.40	44.50	28.60	26.50	11.70	14.50	2.10	4.60	10.40	9.70	25.30	11.50	11.90
9	13.90	5.70	13.70	41.20	20.20	22.30	9.90	10.60	1.10	4.40	8.80	7.70	21.40	7.60	10.40
11	10.50	5.10	11.90	37.10	14.30	18.10	8.40	8.30	1.10	4.40	8.70	7.50	18.40	5.90	9.50
14	7.80	4.50	9.90	30.70	11.00	14.30	7.00	6.80	1.10	4.40	8.70	7.50	14.90	5.70	8.60
21	7.60	4.50	7.40	16.10	6.70	9.70	6.50	6.50	1.00	4.40	8.70	7.50	9.30	5.70	7.80
28	7.60	4.50	5.90	11.00	6.30	9.40	6.50	6.40	1.00	4.40	8.70	7.50	7.50	5.70	7.60
36	7.60	4.50	5.80	6.70	6.30	9.40	6.40	6.40	1.00	4.40	8.70	7.50	7.40	5.70	7.50
42	7.50	4.50	5.70	5.00	6.30	9.30	6.40	6.40	1.00	4.40	8.70	7.50	7.40	5.70	7.50
49	7.50	4.50	5.70	3.90	6.30	9.30	6.40	6.40	1.00	4.40	8.70	7.50	7.40	5.60	7.50
56	7.50	4.40	5.70	3.40	6.30	9.20	6.40	6.30	1.00	4.40	8.60	7.50	7.30	5.60	7.50
63	7.50	4.40	5.70	3.20	6.30	9.20	6.40	6.30	1.00	4.30	8.60	7.50	7.30	5.60	7.40
71	7.50	4.40	5.60	3.20	6.30	9.20	6.40	6.30	1.00	4.30	8.60	7.40	7.30	5.60	7.40
84	7.50	4.40	5.60	3.10	6.20	9.10	6.40	6.30	1.00	4.30	8.60	7.40	7.30	5.60	7.40
100	7.50	4.40	5.60	3.10	6.20	9.10	6.30	6.30	0.90	4.30	8.60	7.40	7.30	5.60	7.40

**Table 2: X-Ray Fluorescence Results**

Sample No	CROW 2533-A	CROW 2533-B	CROW 2533-C	CROW 2537-A	CROW 2537-B	CROW 2537-C	CROW 2538-A	CROW 2538-B	CROW 2538-C	CROW 2539-A	CROW 2539-B	CROW 2539-C	CROW 2540-A	CROW 2540-B	CROW 2540-C
U Total in 50 mg Sample, (%)	74.12	74.04	74.24	73.51	73.44	73.26	76.7	76.78	76.81	74.44	74.45	74.42	73.12	73.18	73.1
U in a Sample Initial (mg)	37.06	37.02	37.12	36.76	36.72	36.63	38.35	38.39	38.41	37.22	37.23	37.21	36.56	36.59	36.55
U in a Sample Calculated from Extracted U (mg)	34.3	35.4	35.04	35.62	34.43	33.3	35.9	36	38	35.6	34	34.5	33.9	34.5	33.8
U Residual on a Filter After the Completion Calculated (mg)	2.76	1.62	2.08	1.14	2.29	3.33	2.45	2.39	0.41	1.62	3.23	2.71	2.66	2.09	2.75
U Residual on a Filter XRF Analyses After the Completion (mg)	0.6	0.7	0.7	0.8	0.8	0.8	0.4	0.4	1.8	0.5	0.6	0.3	0.3	0.5	0.4
Difference	2.16	0.92	1.38	0.34	1.49	2.53	2.05	1.99	-1.39	1.12	2.63	2.41	2.36	1.59	2.35
Standard Error (%)	6	2	4	1	4	7	5	5	-4	3	7	6	6	4	6

#### 4.1 Absorption parameters and Dosimetric Quantities

This equation and the methods used to determine the parameters are described in detail in the CTI-RC report [1].

The method that was used to determine the DWY classification is to fit a curve to the dissolution data in Table 1 and use the fit parameters from that curve to classify the material into DWY. To estimate the dissolution times and the fraction of material assigned to each category, an exponential model was used. The number of terms used in the model was based on statistical tests; the decision as to how many terms to use was based on the amount of error associated with each fit. For this experiment, the equation with the lowest error was chosen for each sample. In all but one case, for Crow Butte samples, the equation with the lowest error was three-term equation; in the one exception a two-term equation had the lower error. The three term equation used was:

$$\frac{M}{M_0} = f_1 \exp(-0.693 \frac{t}{T_1}) + f_2 \exp(-0.693 \frac{t}{T_2}) + f_3 \exp(-0.693 \frac{t}{T_3}) \quad (1)$$

Where:

M - mass of undissolved uranium at time t

M<sub>0</sub> – initial mass of uranium

t – elapsed time

f<sub>1</sub> - fraction of total U with corresponding dissolution half-time T<sub>1</sub>

f<sub>2</sub> - fraction of total U with corresponding dissolution half-time T<sub>2</sub>

f<sub>3</sub> - fraction of total U with corresponding dissolution half-time T<sub>3</sub>

f<sub>1</sub> + f<sub>2</sub> + f<sub>3</sub> = 100%

Note: the two term equation was of the same format, with the term involving f<sub>3</sub> and T<sub>3</sub> removed.

The results of the X-Ray diffraction analysis indicated that the Crow Butte concentrate samples were composed mainly of two well-defined crystal phases, namely, metaschoepite, UO<sub>3</sub>·2H<sub>2</sub>O, and metastudtite, UO<sub>4</sub>·2H<sub>2</sub>O [3]. Very small quantities of unidentified amorphous material might also be present in almost all samples.

A program was developed at Cameco research centre for calculation of dissolution parameters using non-linear regression analysis. The standard deviations of parameters were calculated from the inverse Hessian matrix using the MSE (Mean Square Error) 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 tests several kinetics models applied to the same set of experimental data. For each model, the minimization is repeated 200 to 500 times (this number is specified by the user). Then, the program selects the model that has the smallest MSE, which is considered to be the best approximation to the experimental data. Some models with a large number of adjustable parameters that show lower F are not the best description for the experiment because they have higher MSE (lower denominator).

Absolute values of standard errors for parameters are given in parenthesis. In some cases, when calculated values of uncertainties are high, an additional sampling during first day and (or) after last day of extraction is required in order to obtain lower uncertainties.

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,  $(1 - M/M_0) * 100\%$ , and the theoretical value.

## 4.2 Dosimetric Quantities

The current ALI and DAC used at Crow Butte are based on the type D Uranium Natural parameters in 10CFR20. The purpose of this experiment was to determine the site specific solubility for material at Crow Butte. Part of this assessment was to determine the breakdown of Crow Butte uranium product into the DWY solubility types defined by ICRP 30 and 10CFR20. In addition, we needed to consider whether any mixture of isotopes existed. Isotopic analysis of the uranium product showed that only isotopes of uranium were present in fresh yellowcake. To assess the main plant, outside of drying an packaging areas, smears from surfaces throughout the main plant were collected and analyzed for the presence of alpha (natural uranium) and beta/gamma ( $\text{Th}^{234}$  and  $\text{Pa}^{234\text{m}}$ ) emitters. A dual channel alpha and beta/gamma counter was used to measure the emissions from the smears. These smears characterize the material that has the potential to be made airborne throughout the plant and inhaled by workers. The smears indicated that natural uranium and the short-lived decay products are in approximate equilibrium. To account for the presence of these short-lived decay products at the time of inhalation, a mixed ALI and DAC was calculated and presented Table 3; the calculation used was  $(C_{\text{U}_{\text{nat}}}/\text{ALI}_{\text{U}_{\text{nat}}} + C_{\text{Th}^{234}}/\text{ALI}_{\text{Th}^{234}} + C_{\text{Pa}^{234\text{m}}}/\text{ALI}_{\text{Pa}^{234\text{m}}})^{-1}$  and similarly for the DAC, where C represents the concentration ratio of each material assuming equilibrium. As shown, the ALI and DAC for each solubility class are unchanged from the Uranium Natural values. Note, as per standard protocol, all final results are shown to one significant digit as this is the number of significant digits shown in 10CFR20 and therefore the maximum that can be used in the final output of the equations.

**Table 3: Mixed ALI and DAC Values**

Isotope	Solubility	ALI ( $\mu\text{Ci}$ )	DAC ( $\mu\text{Ci/ml}$ )
Uranium Natural	D	1	5E-10
	W	0.8	3E-10
	Y	0.05	2E-11
<sup>234</sup> Th	W*	200	8E-8
	Y	200	6E-8
<sup>234</sup> Pa	W*	8000	3E-6
	Y	7000	3E-6
Final Default Mixture	D	1	5E-10
	W	0.8	3E-10
	Y	0.05	2E-11

\* The solubility class for <sup>234</sup>Th and <sup>234</sup>Pa was assumed to be W, because the isotopes are not expected to be in oxide or hydroxide forms.

As part of the proposed sampling plan to the NRC, additional sampling for isotopes such as Ra226 is ongoing. Should any subsequent analysis indicate the detectable presence of additional radionuclides, the mixed ALI and DAC will be adjusted accordingly.

Table 4 shows the solubility parameter fit results following the method outlined in the report Solubility of Radionuclides in Simulated Lung Fluid [1]. The F values represent the fraction of material with the given dissolution half-time (the T value). It is again important to note that this fit was performed based on the results of Table 1 and the fraction assigned to retention times (T values) greater than 100 days should be reassigned to the time from of 10-100 days as subsequent analysis showed no measureable material remaining after 100 days, within error. This is a conservative assignment because some of that material absorbed onto the filter could have been dissolved before day 10, however we are assuming all of the absorbed material was dissolved after day 10.

Along with the solubility parameters, Table 4 also shows the subsequent DWY classification. Each sample is assigned to DWY based on the dissolution half time values, T values, and the fraction assigned to each classification is based on the F values. For example, using sample CROW 2533-C, T<sub>1</sub> is less than 10 days, so 90.0% (the F<sub>1</sub> value) is assigned to class D and 10.0% (F<sub>2</sub>) is assigned to class W because T<sub>2</sub> is between 10 and 100. In cases where both T<sub>1</sub> and T<sub>2</sub> are below 10 days, the fraction considered Class D is the sum of F<sub>1</sub> and F<sub>2</sub>. As stated, where a T<sub>3</sub> exists, its associated F value is included in the Type W fraction based on XRF results.

For all samples, except CROW 2537-A, the fraction of material classed as Type D is greater than 90%. For that one sample, the kinetics data in Table 1 shows that in reality nearly 60% of the material had been dissolved by day 9 and within experimental error, the T<sub>2</sub> value of 11.16 days could actually be less than 10 days. This means that within experimental error, this sample could also have a Type D fraction of greater than 90%.

Finally, Table 4 includes the ALI and DAC for each sample and an overall 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 appropriate mixed ALI and DAC for that solubility class, from Table 3. One additional note is that the default ALI and DAC from 10CFR20 are based on a particle size of 1  $\mu\text{m}$ . The particulate size analysis for Crow Butte product shows that particle sizes are significantly larger than the default assumption. This means that use of default values based on a 1  $\mu\text{m}$  assumption are conservative for our product; a larger particle size would be associated with a lower dose. However, the more conservative defaults have been used in determining the site specific ALI and DAC for Crow Butte. Again, the final result is to one significant digit as this is the number of digits available in 10CFR20, with two significant digits have been carried through the intermediate calculations as per standard protocol.



**Table 3: Crow Butte Solubility Parameters and Dosimetric Quantities**

<b>Sample No. <sup>a</sup></b>	<b>F<sub>1</sub> (%)</b>	<b>T<sub>1</sub> (d)</b>	<b>F<sub>2</sub> (%)</b>	<b>T<sub>2</sub> (d)</b>	<b>F<sub>3</sub> (%)</b>	<b>T<sub>3</sub> (d)</b>	<b>MSD (%)</b>	<b>Type D (%)</b>	<b>Type W (%)</b>	<b>ALI (μCi)</b>	<b>DAC (μCi/ml)</b>
CROW 2533-A	45.4	0.14	47.2	2.98	7.4	3.93E+08	1.7	92.6	7.4	0.99	4.9E-10
CROW 2533-B	53.5	0.13	42.2	2.1	4.3	7.02E+09	0.7	95.7	4.3	0.99	4.9E-10
CROW 2533-C	90.0	1.5	10.0	76			2.9	90.0	10.0	0.98	4.8E-10
CROW 2537-A	34.1	0.22	64.4	11.16	1.6	2.42E+08	1.8	34.1	65.9 <sup>a</sup>	0.87	3.7E-10
CROW 2537-B	43.6	0.3	50.6	4.89	5.9	6.89E+08	2	94.1	5.9	0.99	4.9E-10
CROW 2537-C	48.0	0.55	43.1	4.98	9.0	1.56E+09	1.2	91.0	9.0	0.98	4.8E-10
CROW 2538-A	72.5	0.27	21.1	3.29	6.4	1.15E+08	0.4	93.6	6.4	0.99	4.9E-10
CROW 2538-B	81.4	0.9	12.4	5.36	6.2	8.22E+08	1.4	93.8	6.2	0.99	4.9E-10
CROW 2538-C	76.8	0.23	22.3	1.86	0.9	19317409	0.5	99.1	0.9	1.00	5.0E-10
CROW 2539-A	52.6	0.09	43.2	1.46	4.2	7.84E+09	0.4	95.8	4.2	0.99	4.9E-10
CROW 2539-B	23.4	0.07	68.2	1.65	8.4	2.84E+10	0.6	91.6	8.4	0.98	4.8E-10
CROW 2539-C	52.9	0.12	39.8	1.74	7.4	2.23E+10	0.3	92.6	7.4	0.99	4.9E-10
CROW 2540-A	45.7	0.42	47.1	5.03	7.2	94634910	1.6	92.8	7.2	0.99	4.9E-10
CROW 2540-B	42.8	0.13	52.0	2.54	5.3	1.69E+09	1.1	94.7	5.3	0.99	4.9E-10
CROW 2540-C	50.0	0.13	40.8	1.46	9.2	213.001	0.7	90.8	9.2	0.98	4.8E-10
									<b>Average</b>	<b>1</b>	<b>5E-10</b>

Note: <sup>a</sup> Within experimental errors this fraction could be assigned to class D or W.

## 5.0 CONCLUSION

Cameco has completed a solubility study to analyze the solubility characteristics of the Crow Butte yellowcake product. This study showed that the yellowcake produced at Crow Butte was primarily of solubility type D with a relatively low type W component. The resulting ALI and DAC values are the same as the default type D material at 1  $\mu\text{Ci}$  and  $5\text{E}-10 \mu\text{Ci/ml}$ . As stated in the introduction, this analysis of the data incorporates the most recent comments from the NRC and Cameco and supersedes all previous submissions in this area.

## 6.0 REFERENCE LIST

- Cameco Innovation and Technology Development Research Centre, Solubility of Radionuclides in Simulated Lung Fluid, Report Number 200183, Report Number RC-09-05, 2009
- ICRP, Limits for Intakes of Radionuclides by Workers, ICRP Publication 30 Part 1, Ann ICRP 2(3-4), 1979.
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- Ansoborlo, E.; Hengé-Napoli, M.H.; Chazel, V.; Gibert, R.; Guilmette, L.A. *Review and Critical Analysis of Available In Vitro Dissolution Tests*, Health Physics, **77**(6): 638-645; 1999.