SOLUBILITY CLASSIFICATION OF YELLOWCAKE PRODUCED BY A BRAZILIAN URANIUM MILL

E.S. Mansur and S.M. Carvalho
Instituto de Radioproteção e Dosimetria
Cx. Postal 37025, CEP 22602, Rio de Janeiro, RJ, Brazil

INTRODUCTION

The end product of uranium milling yellowcake, can vary in composition. Variations from ammonium diuranate to mixtures of uranium oxides, sulfates, nitrates and sodium compounds occur among different mills. Ore body characteristics, chemical extraction techniques as well as drying temperature vary and the uranium coupounds produced are expected to be process or site specific. Variations among batches are also expected (Eidscn and Mewhinney, 1978, 1980; Kalkwarf, 1989; Eidson and Griffith Jr., 1984) and so the dissolution characteristics of yellowcake in lung fluid. All this variability in solubility complicates the interpretation of bioassay results obtained during occupational monitoring of uranium mill workers.

This study was performed to classify the dissolution rate of yellowcake samples produced at the Poços de Caldas uranium mill according to the ICRP categories (ICRP, 1979), that is, class D, dissolution half-time less than 10 days, class W, from 10 to 100 days and class Y, greater than 100 days.

MATERIALS AND METHODS

Samples were automatically taken from 6 different yellowcake batches produced under routine operation of the mill. Two 6 mg samples of each batch were sieved and grounded and placed in tubes with 6 ml simulated lung fluid, SLF, prepared according to Moss (1979). The physical and chemical process was based on the work of Thein et al. (1982). After 3 minutes in a sonic bath to disperse aglomerates and/or avoid wall losses, the tubes were transferred to a shaker water bath and kept agitating and at 37ºC, to maximize dissolution rates. Samples were taken after 11 time intervals, equal to 0, 2, 4, 6, 12, 24, 72, 120, 336, 504 and 720 hours. Once removed from the water bath the samples were centrifuged. The supernate was pipetted off the tube using a plastic seringe and filtered through a 22 μm, 13 mm Millipore filter. Fresh SLF was replaced every 2 to 3 days. The pH was maintained at 7.3 - 7.4 by addition of dilute HCl acid. After a 30 day period, the residual uranium was dissolved with 6 ml concentrated nitric acid and analysed by neutron activation. A thermal neutron flux (2×10^{12} n/cm^2.s) was used to irradiate the samples. They were counted with a germa-

nium detector (ORTEC GMx-10180) and analysed using a Nuclear Data ND65-system. The software used for espectral analysis is detailed elsewhere (Vasconcellos, 1972 and Delgado, 1984).

RESULTS AND DISCUSSION

The results of the dissolution studies are summarized in Table 1. The dissolution behaviour of uranium in simulated lung fluid follows an exponential relation with time and can be described by the following equation (Mercer, 1967).

$$F = f_1 \cdot \exp\left[\frac{-0{,}693}{T_{1/2}(1)}\right]t + f_2 \cdot \exp\left[\frac{-0{,}693}{T_{1/2}(2)}\,t\right]$$

where F is the fraction of uranium remaining undissolved in the sample at time t and f represents the fraction of the sample dissolving with dissolution half-time $T_{1/2}$.

Table 1: Dissolution Parameters of Yellowcake in S.L.F.

Sample Number	More Soluble Percentage $f_1 \pm \sigma$(%)	More Soluble Dissolution Half-Time $T_{1/2} \pm \sigma$(hours)	Less Soluble Dissolution Half-Time $T_{1/2} \pm \sigma$ (days)
1	86 ± 2.1	14 ± 0.78	14 ± 0.99
2	83 ± 2.8	7.7 ± 0.028	12 ± 2.3
3	69 ± 1.0	8.2 ± 0.049	33 ± 1.8
4	76 ± 1.0	9.5 ± 0.014	30 ± 1.2
5	66 ± 2.0	9.4 ± 0.13	31 ± 0.50
6	72 ± 1.0	8.0 ± 0.34	30 ± 0.35

The generated non linear regression fit for all the 132 fractions presented correlation coefficient greater than 0.996. The pairwise comparisons among the fractions f_1 and f_2 and dissolution half-times were performed by the Newman-Keuls (N-K) test provided the variances were homogeneous (Bartlett's test). According to the N-K test on f_1, f_2 and $T_{1/2}(2)$, samples 1 and 2 were not statistically different at $\alpha = 0.01$ as well as samples 3, 4, 5 and 6. The test on $T_{1/2}(1)$ showed statistical difference only for sample number 1 with no significant difference ($\alpha = 0.01$) for all the others.

The differences encountered when $T_{1/2}(1)$ was tested seem too small (hours) when one looks at the solubility classification (days) presented by ICRP (ICRP, 1979). When compared to Kalkwarf (1979) results, the short half-time component behaves as ammonium diuranate, a form of UO_3. A range varying from zero to 24 hours can be used as the criteria to interpret the results obtained (Eidson and Griffith Jr., 1984). Based on the above discussion one can present the results of the short dissolution half-times as a single group and the long dissolution half-times and dissolution fraction as two distinct groups as indicated in Table 2.

Table 2: Results of the In Vitro Dissolution Experiment

Batch Number	f_1 (%)	σ(%)	$T_{1/2}$ (1) hours	$T_{1/2}$ (2) days
1 and 2	84	2.8	9.4	13
3, 4, 5 and 6	71	2.7	9.4	31

CONCLUSIONS

The yellowcake samples present a fast dissolution component, class D, and a slow component, class W. The fast component indicates that the yellowcake sampled contains ammonium diuranate, ADU, dissolving with half-times varying around 9.4 hours. The slow dissolution component (greater than 10 days) may characterize big ADU particles or small U_3O_8 ones dissolving in the lung fluid. The results indicate the presence of two specific chemical forms in the batches sampled but variable relative quantity of dissolved uranium among batches.

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