

CABOT

September 12, 1996

ADD TO
ADAMS

Judith M. Greenwald
Division of Waste Management
Office of Nuclear Material Safety and Safeguards
U.S. Nuclear Regulatory Commission
One White Flint North
11555 Rockville Pike
Rockville, MD 20852-2738

**RE: CHARACTERIZATION OF READING SLAG PILE -- LEACH RATE
METHODOLOGY**

Dear Ms. Greenwald:

By letter dated July 11, Cabot submitted a methodology for calculating the leach rate for the Reading slag pile which was prepared by our consultant, Environmental Resources Management, Inc. ("ERM"). Since that time, ERM personnel have discussed the methodology and related issues with NRC technical staff. It is our understanding that NRC staff considers the approach developed by ERM to be appropriate, subject to clarification regarding the relative solubility of thorium. ERM has researched that issue and addressed it in the enclosed revised Leaching Analysis document.

Please note the following with respect to the enclosed Leaching Analysis:

1. The leach rate methodology for uranium is the same as appears in the July 11 version of this document.
2. In response to a question raised by NRC technical staff, further research on the relative solubility of thorium has been undertaken. That research confirms that thorium is less soluble than uranium. Based upon literature values, ERM has been able to derive a leach rate and a partitioning coefficient for the slag at Reading. The results of this additional work are incorporated and explained in the enclosed document.

Cabot Performance Materials
P.O. Box 1608
County Line Road
Boyertown, Pennsylvania 19512-1608
Phone: 610-367-2181



3. *The Leaching Analysis has been expanded to include a calculation of the partitioning coefficients for uranium and thorium as these elements exist in the slag/soil/sand matrix at Reading. These coefficients account for the fact that the slag is mixed with other solid material rather than being concentrated in a homogeneous mass.*

We believe that the Leaching Analysis addresses the outstanding issues in an appropriate manner and, if NRC staff concurs, we will revise the characterization report consistent with this methodology.

Finally, as you are aware, the NRC staff has raised similar questions regarding the leach rate methodology applicable to the Revere facility. Once we have received confirmation that the methodology developed by ERM is acceptable, we will direct our consultant to revise the Revere Risk Assessment by applying this methodology to the site-specific data available for Revere. Cabot is hopeful that this can be accomplished soon so that the decommissioning of the Revere facility can proceed.

Should you have any questions, please call me.

Sincerely,
CABOT PERFORMANCE MATERIALS



Anthony T. Campitelli
Manager, Environmental Affairs

Enclosure

cc: JBradbury/NRC (w/enclosure)

/cas
nrc-0910.atc

LEACHING ANALYSIS FOR URANIUM AND THORIUM FROM THE READING SLAG PILE

INTRODUCTION

Environmental Resources Management, Inc. (ERM) has been retained by Cabot Corporation to assess the potential rate of leaching of radionuclides from slag produced by the Kawecki Chemical Company and placed on a slag pile at a Reading, Pennsylvania industrial facility. It is necessary to determine the rate at which the in-place slag may leach the radionuclides uranium and thorium, for input into a fate and transport model which will support a decision on decommissioning the pile in keeping with the requirements of the U.S. Nuclear Regulatory Commission (NRC). The NRC has requested that this determination be made, on the basis of modeling, for a period of 1000 years. In support of this type of determination, the NRC has published guidance document NUREG/CR 6232 PNL 9750 ("Assessing the Environmental Availability of Uranium in Soil and Sediments"), which discusses the behavior of uranium in the natural environment.

Cabot has submitted to the NRC a Characterization Report for the Reading Slag Pile, which was prepared by NES, Inc. As a part of that work, NES sent a slag sample to an independent laboratory for leach testing. As described in NUREG/CR - 6232, the results were reported in terms of totally available uranium (TAU), readily available uranium (RAU) and slowly available uranium (SAU).

In order to develop a leach rate using the NRC guidance, it is necessary to understand the implications of the TAU, RAU, and SAU determinations. This is briefly described as follows:

- The TAU is determined by a 5% hydrochloric acid extraction of all potentially available uranium, which goes far beyond geochemical conditions actually encountered in the natural environment.
- The RAU is determined by a modified Toxicity Characteristic Leaching Procedure (TCLP) leach in water adjusted to pH 2.9 using acetic acid, and performed four times sequentially on the same sample aliquot. The guidance considers this procedure to extract essentially all exchangeable and surface-bound uranium, and hydrous uranyl oxide minerals, and some uranyl silicates, under the assumption that these would be available to dissolve most readily under natural environmental conditions. This is a very conservative assumption, as

the pH of natural rain water is closer to the range of 5 to 5.5. Furthermore, the sample aliquot is ground before the procedure, vastly increasing the surface area of the material which is available for contact with the leaching waters.

- The SAU is extracted under basic conditions, using a pH 8.3 NaHCO_3 solution, and adding hydrogen peroxide to oxidize uranium into soluble form. Such conditions are not encountered in the natural environment.

Of these three analytical procedures, the RAU procedure best approximates what might be available under natural environmental conditions in eastern Pennsylvania, although this procedure is extremely conservative. In Pennsylvania, acid rain can create ground water recharge below pH 5, at times; however, the pH of rainfall in Pennsylvania is not continuously 2.9.

In addition to geochemical conditions associated with leaching, the NRC is concerned about changes in the physical state of the slag as it weathers over a 1000 year period. If such weathering occurs and some "soil" is formed out of the slag, there would be increased slag surface area available for contact with infiltrating waters. The grinding of the sample aliquot prior to the leaching can reasonably be assumed to simulate this. However, literature reviews of studies of the weathering rate of obsidian (which can be considered a reasonable analog to slag), show that soil formation by weathering would be limited. The literature reviews indicate that the degree of weathering would likely be in the range of 0.002 mm to 0.015 mm of surface thickness over 1000 years, which is essentially inconsequential. Therefore, performance of the leaching test on a ground slag sample results in a much higher slag surface area in contact with the leaching water than will actually occur at the pile. This provides a very conservative result which overestimates the rate of radionuclide leaching.

Given these factors, ERM has used the TAU and RAU results to estimate the leaching rates for uranium and thorium from the Reading slag pile. Again, it should be recognized that the leaching analysis is very conservative, as:

- the pH 2.9 water used in the leach test is between 10 and 100 times more acidic than in the natural environment; and
- the surface area of slag available in the pile to contact infiltrating waters will be much lower than that in the leaching procedure, due to the thorough grinding of the sample into small particles before leaching analysis.

DEVELOPMENT OF LEACHING MODEL

The leaching model presented herein was developed by ERM based on the nature of the TAU and RAU leaching tests and on the characteristics of the slag, after conversations with NRC staff responsible for development of the leaching model for the Shieldalloy site in Ohio. It should be noted that the approved Shieldalloy model approach is similar to ERM's; however, the Shieldalloy method is less conservative, as it is based on the ASTM Synthetic Precipitation Leaching Procedure (SPLP) test, which is conducted at a pH more comparable to that of recharge in the natural environment.

The TAU should represent a practical upper bound on potentially environmentally available uranium, while the RAU represents that most easily leached. Although they are not determined by exactly the same analytical method, the TAU and RAU are both acid extractions, and respectively provide conservative upper bound estimates of what might leach from the pile, and at what rate. Therefore, ERM has modeled the rate of leaching from the Reading slag using the following assumptions:

- All water which infiltrates into the pile comes in contact with radionuclide-bearing slag material. This assumption is very conservative, as such slag constitutes only a portion of the total material contained in the pile.
- The leaching will be a linear partitioning process, which will occur as a first order reduction of radionuclide mass in the pile.
- The TAU, determined by NES to be 0.824 ug of uranium per/gram of slag (or ppm), represents all environmentally available uranium.
- The RAU can be used to determine the rate at which the TAU will leach out of the pile. This is very conservative, as after the RAU (determined by NES to be 0.128 ug/gram (or ppm)) has all leached, the remainder of the TAU will leach much more slowly.
- The slag is uniformly mixed with the soil and sand in the pile.

Partitioning Coefficient

The partitioning coefficient (K_d) describes the equilibrium ratio between the concentration of available uranium in the slag (C_{slag}) and the concentration of uranium dissolved in the water which is in contact with the slag (C_l). K_d is determined from the relationship TAU/C_l , where C_l is the concentration of uranium in the leachate. The C_l is determined from the RAU analysis results. For the RAU analysis, the laboratory combined

four aliquots of leachate into one sample and analyzed that sample for dissolved uranium. Thus the RAU represents the concentration of uranium leachable from one gram of slag in 80 ml of pH 2.9 water (the four 20 ml sequential leaches). Therefore, the concentration in the leachate, C_l , was $(1.81 \mu\text{g}/80 \text{ ml}) \times (1000 \text{ ml}/\text{L}) = 22.6 \mu\text{g}/\text{L}$, or 0.0226 ppm. From this, the partitioning coefficient for the uranium in the slag can be determined:

$$K_{d\text{slag}} = C_{\text{slag}} / C_l = 85.8 \text{ ppm} / 0.0226 \text{ ppm} = 3796$$

This K_d is for the slag itself. However, the material in the pile is a mixture of slag, soil, and sand. For modeling purposes, it is necessary to determine a K_d for the mixture of the slag with the soil and sand (which do not contain uranium) in the pile. The K_d for the pile is smaller than the K_d for the slag due to the additional volume of solid material.

The NES report identified 600 tons of slag, 1,080 tons of soil, and 1,040 tons of sand. The average concentration of TAU in the pile is:

$$\begin{aligned} C_{\text{pile}} &= C_{\text{slag}} \times 600 / (600 + 1080 + 1040) \\ &= 85.8 \text{ ppm} \times 600 / 2720 \\ &= 18.9 \text{ ppm} \end{aligned}$$

The K_d for the pile material is the average concentration of available uranium in the pile divided by the leachate concentration, C_l :

$$K_{d\text{pile}} = 18.9 \text{ ppm} / 0.0226 \text{ ppm} = 836$$

Leaching Rate Model

The rate of leaching by a first order reduction of mass is described by the equation:

$$dM/dV = -kM, \text{ where:} \quad (1)$$

M = mass remaining in the slag after a volume V has been leached; and

$-k$ = mass reduction rate.

This can be integrated to:

$$M = M_0 e^{-kV}, \text{ where:} \quad (2)$$

M_0 = mass of uranium in soil at time $T=0$; and

V = total volume of leaching solution added since time = 0.

It is assumed that the partitioning of uranium into the leaching waters occurs instantaneously.

The mass reduction rate k in equation 2 can be readily determined by rearranging the equation:

$$k = (1/V) * \ln(M/M_0) \quad (3)$$

From equation 2, the rate of leaching can then be determined:

$$dM/dV = -k M_0 e^{-kV} \quad (4)$$

Using equations 2 and 4, the concentration of uranium in the leachate and the mass remaining in the slag can be determined after any volume of leaching water passes through the slag.

ANALYSIS OF URANIUM LEACHING

The leaching rate model determines the uranium concentration in leachate as volumes of water continuously infiltrate through the pile. Thus, Figures 1 and 1A depict the results of the model with cumulative leachate volume (in ft^3) passing through the pile shown on the X axis, and a modeled leachate concentration shown on the Y axis.

The modeled leachate concentration as a function of time is shown on Figure 2 [2A]. This is determined using the rate at which infiltrating water will be added to the slag pile. At the Reading Site, the volume of water infiltrating the pile is determined by the rate of precipitation recharge into the pile, which is the area ground water recharge rate. In eastern Pennsylvania, an average recharge rate of $1 \text{ ft}^3/\text{yr}$ per square foot of land surface is commonly used.

NES has determined that the pile has a surface area of 162 ft by 15 ft, or $2,430 \text{ ft}^2$. At a recharge rate of $1.0 \text{ ft}^3/\text{yr}$ per foot of surface area, $2,430 \text{ ft}^3$ of water will recharge the pile annually. This amount of infiltration is assumed to enter the pile every year; thus the cumulative volume through the pile, as shown on the X axis of Figure 1, is:

$$V_c = 2,430 \text{ ft}^3 \times T$$

where

V_C = cumulative volume in ft^3 , and

T = time, in years

To convert the Figure 1 X-axis to time, the equation is rearranged to be:

$$T = V_C / 2,430 \text{ ft}^3/\text{yr}$$

On Figures 2 and 2A, the X axis has been divided into 100-year increments:

$$T = V_C / (2,430 \text{ ft}^3] \times 100 \text{ yr})$$

For example, the 100-year line on the X axis of Figure 2 represents 243,000 ft^3 of cumulative leachate volume on the X axis of Figure 1 [1A].

The concentration of uranium in the leachate at any given year can be taken from Figure 2 or 2A, and used in a fate and transport model to simulate environmental effects beginning in that year. Again, because the TAU and RAU leach conditions are much more rigorous than the actual conditions at the site, the fate and transport model results will significantly overestimate the effects of the slag on environmental systems and/or receptors modeled.

The rate of leaching from the slag can also be represented as a percentage of mass removed per year. For the first year:

$$R_l = M_y / \text{TAU}$$

Where:

M_y = mass leached per year; and

R_l = the leach rate in % of available mass/year.

This rate will remain constant over time, with the uranium available in the slag decreasing every year as leaching occurs, and the M_y also decreasing by the same factor.

The total slag at the site has been estimated by NES as 600 tons, or 1,200,000 pounds. The TAU (85.8 $\mu\text{g}/\text{g}$) is equivalent to 85.8 ppm. Therefore, the environmentally available uranium in the entire pile is $(1,200,000 / 1,000,000) \times 85.8 = 102.96 \text{ lb}$. The beginning concentration as

derived from the RAU is 0.0226 ppm. Therefore, the mass of uranium leached (My) during year 1 is $((2,430 \text{ ft}^3 \times 62.4 \text{ lb/ft}^3)/(1,000,000)) \times 0.0226 \text{ ppm} = 0.0034 \text{ lb}$ (where 62.4 lb is the weight of 1 cubic foot of water). Thus, the leaching rate, expressed in percent of remaining mass, is $0.0034 \text{ lb}/102.96 \text{ lb} = 0.000033$, or 0.0033 percent.

ANALYSIS OF THORIUM LEACHING

The NRC Guidance used for the above analysis addresses only uranium. However, thorium is known to be present in the Reading slag and may also leach from the pile. To complete a leaching analysis for thorium consistent with the analysis for uranium presented above, two critical factors needed to be determined: the K_d for thorium, and the mass concentration (in ppm) of the available thorium in the pile.

Several references were identified which concluded that thorium will leach less than uranium, i.e. the thorium K_d will be greater; however these references did not include sufficient data to derive a K_d value for thorium. The results of a study conducted by Sheppard and Thibault (Journal of Environmental Quality, 20:101-114, 1991), however, did provide the necessary information to determine the ratio of the K_d for uranium to the K_d for thorium.

Sheppard and Thibault performed controlled leaching tests for uranium and thorium on natural soil columns, and obtained K_d values for both elements. To achieve this, they introduced uranium and thorium into soil columns by adding a liquid solution containing dissolved uranium and thorium. The uranium and thorium partitioned from liquid onto the soils in the column. The cores were placed in lysimeter sleeves and left in an outdoor area to leach under natural conditions. One half of the cores were collected and analyzed after one year, the other half were collected and analyzed after four years. The results after four years were used for the analysis described herein because the K_d data were more complete from the 4-year analysis. Interestingly, Sheppard and Thibault described the leaching of both uranium and thorium as "negligible" and observed that there was no significant migration of thorium over the four year study time.

Given the method by which uranium and thorium were introduced to the soil column, it is reasonable to expect that those elements would be more easily leached from the test soil columns than from the Reading slag material. First, the uranium and thorium in the soil were introduced only

to the surface of the soil, and thus adsorption was the only operative attenuation mechanism. The uranium and thorium in the Reading Site slag are components of the crystalline rock matrix itself, and as such should be far less available for leaching. Second, the soil in the field study exposes much greater surface area to infiltrating water than does the Reading slag. Thus, the K_d values from the Shepard and Thibault study should be lower than the K_d values from the slag.

After four years, K_d was evaluated at four soil horizons in the column: Litter (surface to approximately 1 inch deep), Ae (approximately 1 inch to 5 inches deep), Upper B (approximately 5 to 10 inches deep), and Lower B (approximately 10 to 20 inches deep). The table below described the K_d values determined after four years of leaching:

Soil Horizon	K_d Thorium	K_d Uranium	K_d Ratio
Litter	1,600	58	27.6
Ae	1,900	295	6.44
Upper B	1,150	160	7.19
Lower B	207	45.4	4.56

The surficial soil, the litter, contained a high concentration of organic material and is considered inappropriate for comparison with the slag pile. The three lower samples exhibited similar ratios of the thorium to uranium K_d , with an average value of 6.06. For purposes of the Reading slag analysis, it is reasonable to assume that the ratio of the K_d for uranium versus the K_d for thorium reported from the study would be comparable to the ratio for the Reading slag. From this, the partitioning coefficients for thorium are calculated as:

$$\begin{aligned}
 K_{d\text{slag}} &= 6 \times 3,796 = 22,776, \text{ and} \\
 K_{d\text{pile}} &= 6 \times 836 = 5,022.
 \end{aligned}$$

The mass concentration of thorium in the pile is calculated based on the thorium activity concentrations reported by NES. The ^{232}Th activity is 316 pCi/g of slag. As with uranium, only a portion of the total thorium (which is what the activity represents) is available for leaching. Unlike uranium, no laboratory leaching analyses are available for thorium. However, an estimate of total available thorium (TAT) equivalent to the TAU concentration can be made by assuming that the ratio of total thorium (or ^{232}Th) to the TAT is equal to the ratio of total uranium to the TAU. From the NES data, that ratio is (676 ppm)/(85.8 ppm) or 7.88.

Thus, the activity of the total available ^{232}Th is converted to a mass concentration of ^{232}Th by the following units conversion formula:

$$C \text{ (g/g)} = \frac{(\text{activity} \times (t_{1/2}/0.693) \times 2.2 \times \text{atomic mass})}{6.023 \times 10^{23} / 7.88}$$

where: activity is in pCi/g
 $t_{1/2}$ is the isotope half life in minutes
 $(t_{1/2}/0.693)$ is average number of minutes between decay events in minutes/decay
2.2 is the number of decays per minute per pCi
atomic mass in g/mole
 6.023×10^{23} is Avogadro's Number, the number of atoms per mole

The half life of ^{232}Th is 1.41×10^{10} years, or 7.42×10^{15} minutes, the atomic mass is 232.038; then, the concentration of available ^{232}Th in the slag is:

$$\begin{aligned} C_{\text{slag}} \text{ (}\mu\text{g/g)} &= (316 * (7.42 \times 10^{15} / 0.693) * 2.2 * 232.038 / \\ &\quad 6.023 \times 10^{23}) / 7.88 \\ &= 0.000364 \text{ g/g} \\ &= 364 \mu\text{g/g or } 364 \text{ ppm} \end{aligned}$$

Although thorium has numerous isotopes, ^{232}Th is essentially 100% of the thorium mass in the slag. As a result, the thorium mass concentration is essentially the same as the concentration of ^{232}Th .

As presented for uranium, the average concentration of total available thorium in the pile is then:

$$\begin{aligned} C_{\text{pile}} &= C_{\text{slag}} \times 600 / (600 + 1080 + 1040) \\ &= 364 \text{ ppm} \times 600 / (600 + 1080 + 1040) \\ &= 80.3 \text{ ppm} \end{aligned}$$

A leaching rate can be determined from the total mass of available thorium in the slag and the mass leached out in one year. The total mass of available thorium in the pile is: $(1,200,000 \text{ lb slag}) \times 364 \text{ ppm} \times (1/1,000,000 \text{ ppm}) = 437 \text{ lb}$. The concentration of thorium in the leachate is given by:

$$\begin{aligned} C_l &= C_{\text{pile}} / K_d \text{pile} \\ &= 80.3 \text{ ppm} / 5,022 \\ &= 0.0160 \text{ ppm} \end{aligned}$$

The mass of thorium removed in one year is: $(2,430 \text{ ft}^3 \text{ water/yr} \times 62.4 \text{ lb/ft}^3 \text{ water}) \times 0.0160 \text{ ppm} \times (1/1,000,000 \text{ ppm}) = 0.0024 \text{ lb/yr}$ of thorium leached. Figure 3 shows the 1000-year leaching curve for the thorium. The leaching rate is $0.0024 \text{ lb/yr} / 437 \text{ lb} = 0.0000055$, or 0.00055 % per year. It should be noted that this leaching rate is exactly 6 times less than the

leaching rate for uranium, as would be expected from the 6 times greater K_d for thorium versus uranium.

CONCLUSIONS

ERM has drawn the following conclusions regarding the rate of leaching of radionuclides from the Reading Slag Pile:

- Of the available data, the TAU represents a very conservative upper bound on what might ever leach from the pile.
- The RAU represents a conservative upper bound on what might leach most readily from the pile under natural environmental conditions.
- Using the available data, the best model for predicting leaching is a first order reduction of available mass from the slag, with the rate of leaching dependent on the volume of water entering the slag on an annualized basis.
- The partitioning coefficient between the slag and water for uranium is 3796 and the rate of leaching is 0.0033% of remaining uranium mass in the slag per year.
- Based on the work of Sheppard and Thibault, 1991, the partitioning coefficient for thorium is estimated to be 6 times greater than that for uranium. Because K_d is increased by a factor of 6, the leaching rate of thorium is 6 times less than the leaching rate for uranium. The thorium leaching rate is thus 0.00055 % per year.
- Because the RAU leach is more rigorous than the actual conditions at the site, fate and transport model results will overestimate the effects of the uranium and thorium in the slag on environmental systems and/or receptors modeled.
- ERM's model results can be used to determine the theoretical concentrations of uranium and thorium in leachate within the slag, for any year between 1 and 1000, for input to a fate and transport model.