Thermodynamic Data Base Needs for Modeling Studies of the Yucca Mountain Project

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The document, "Thermodynamic Data Base Needs for Modeling Studies of the Yucca Mountain Project" was written some time prior to 1991 by Robert Silva (LLNL, Task Leader-Thermodynamic Data Determination) and sub-contractor Jerome Bucher (LBL). The document was used by LLNL and the Solubility Working Group (SolWoG) to evaluate and prioritize thermodynamic data needs for the Yucca Mountain Project from the time it was written through FY95. During that time period the document was referred to by its LLNL record segment identification number: LLYMP9112144.

As part of the FY96 YMSCP effort to document work that had not been previously recorded I chose to complete the review process of this document. Because this document has been used so extensively no changes were made to the content of the document during the review process (other than editorial corrections). It is my intent that this document remain as it was written and as it has been referred to during the intervening years. This document is one of two that provides the rational for the Project's thermodynamic data needs.

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Thermodynamic Data Base Needs for Modeling Studies of the Yucca Mountain Project

Introduction

This document is the first in a series of documents outlining the thermodynamic data needs for performing geochemical modeling calculations in support of various waste package performance assessment activities for the Yucca Mountain Project. The documents are intended to identify and justify the critical thermodynamic data needs for the data base to be used with the models. They are to outline the minimum data base and thus to bound the amount of information that is critically needed. They will, also, provide the framework for the experimental program in support of the data base, i.e., the Thermodynamic Data Determinations task of the EQ3/6 Geochemical Modeling effort J-20-8. Liberal use of the Yucca Mountain Site Characterization Plan [1] was made during the preparation of this report.

The Thermodynamic Data Determinations task supplies data needed to resolve performance or design issues and the development of the data base will remain an iterative process as needs change or data improve. For example, data are needed to predict: (1) major ion groundwater chemistry and its evolution, (2) mineral stabilities and evolution, (3) engineered barrier near-field transport and retardation properties, (4) changes in geochemical conditions and processes, (5) solubilities, speciation and transport of waste radionuclides and (6) the dissolution or corrosion of construction and canister materials and the effect on groundwater chemistry and radionuclide solubilities and transport. The system is complex and interactive, and data need to be supplied in order to model the changes and their effect on other components of the system, e.g., temperature, pH and redox conditions (Eh) [2]. Through sensitivity and uncertainty analyses, the critical data and system parameters will be identified and the acceptable variations in them documented.

Groundwater Chemistry

At present, only water from saturated-zone wells on and near Yucca Mountain have been available for chemical analysis. Groundwater from all pumped wells in and near the site have been analyzed. The results have been reported and discussed in the YMP Site Characterization Plan [3]. The major and minor inorganic constituents of these groundwaters are given in Tables 1 and 2 taken from the SCP [4]. Trace elements found in these waters are barium (<.001-.011 mg/l), bromine (<.2-14.5 mg/l), lithium (.04-.95 mg/l), phosphorous (<1.2 mg/l), strontium d(<.001-.07 mg/l), titanium (<.012-.03 mg/l) and vanadium (<.004-.03 mg/l) [5].

The chemical analyses indicate that the groundwaters are primarily sodium bicarbonate waters with low total dissolved solids. Sodium is the dominant cation. Other major cations in the groundwaters are calcium, potassium and magnesium. The major anion is bicarbonate; sulphate, chloride, nitrate and fluoride are present at about a factor of 10 less on a molar scale. The dissolved silica (reported as Si) is in the form $Si(OH)_4$ or $SiO(OH)_3^-$ at a pH around 7 [6] and could be an important inorganic anion for the formation of solid phases and complexes. Of the trace anions, phosphorous could be important for multivalent cations even at these low concentrations.

The presence of dissolved oxygen in most of the waters indicates oxidizing conditions as confirmed by the Eh measurements. The pH values are in the range 7.0 to 7.5 for the most part. Temperature in the repository horizon is expected to be 25 to 35°C and the pressure close to atmospheric for the altitude before implacement of the waste [7]. The water from the J-13 well is thought to be representative of interstial and fracture waters in the Yucca Mountain tuff and it has been recommended as the reference water until more direct data can be obtained [8]. It is the components of the J-13 work that will be used in our analyses to identify the important solid phases and solution complexes.

In order to determine the effect of temperature on the composition of water in contact with tuff, a number of rock-water interaction studies have been conducted [9-14]. In these studies, J-13 water was placed in contact with tuff samples at temperatures up to 150°C. The results of these measurements demonstrate that the composition of the water undergoes very little change and remains benign. The major changes involved an increase in silica and a loss of calcium, magnesium, and carbonate from the water. The pH increased slightly but remained near neutral. The anion concentration were basically unchanged. Glassley [15] has suggested maximum cation and anion concentrations in solution during high temperature rock-water interactions. These maximum concentrations are included in Tables 1 and 2.

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Well	Field pH	Ca	Mg	Na	K	Li	Fe	Mn	Al	Si
USW VH-1	7.5	10	1.5	80	1.9	0.090	—	—	—	23
USW H-6	7.4	5.5	0.22	74	2.1	0.10	0.12	0.04	0.12	20.0
USW H-3	9.4	0.8	0.01	124	1.5	0.22	0.13	0.01	0.51	16.9
USW H-5	7.1	1.1	0.03	54	2.3	0.04	0.01	—	0.17	17.4
USW G-4	7.1	9.2	0.15	56	2.5	0.08	0.04	0.02	0.02	19.6
USW H-1	7.5	6.2	<0.1	51	1.6	0.04	—	—	—	19
USW H-4	7.4	10.8	0.19	84	2.6	0.16	0.03	0.005	0.04	25.9
UE-25b#1	7.7	19.7	0.68	56	3.3	0.28	0.04	0.004	0.03	31.5
UE-25b#1	7.2	18.4	0.68	46	2.5	0.30	0.69	0.36	0.04	28.7
UE-25b#1	7.3	17.9	0.66	37	3.0	0.17	0.08	0.07	0.06	28.8
J-13	6.9	11.5	1.76	45	5.3	0.06	0.04	0.001	0.03	30.0
UE-29b#2	7.0	11.1	0.34	51	1.2	0.10	0.05	0.03	0.04	25.8
J-12	7.1	14	2.1	38	5.1	-	-	-	-	25
UE-25p#1	6.7	87.8	31.9	171	13.4	0.32	<0.1	<0.01	0.1	30
High Temp.	6.9-7.6	<15	<5	<65	<15	-	-	-	<5	<160

Table 1. Cation Concentrations in Groundwater from the
Vicinity of Yucca Mountain

Well	F$^-$	Cl$^-$	SO$_4^{2-}$	HCO$_3^-$	NO$_2^-$	NO$_3^-$	O$_2$	Detergent	Eh (mv)
USW VH-1	2.7	11	44	167	—	—	—	—	—
USW H-6	4.1	7.7	27.5	—	—	5.3	5.6	—	395
USW H-3	5.4	8.3	31.2	245	<0.10	0.2	<0.1	<0.02	-123
USW H-5	1.3	5.7	14.6	—	—	8.6	6.3	<0.005	353
USW G-4	2.4	5.5	15.7	—	—	5.5	6.4	—	402
USW H-1	1.0	5.8	19	122	—	—	—	—	—
USW H-4	4.5	6.2	23.9	—	—	4.7	5.8	>2	216
UE-25b#1	1.2	7.1	20.6	—	—	0.6	1.8	—	220
UE-25b#1	1.5	9.8	21.0	—	0.5	2.2	<0.1	2.7	-18
UE-25b#1	1.2	6.6	20.3	—	—	4.5	1.8	0.02	160
J-13	2.1	6.4	18.1	143	—	10.1	5.7	—	—
UE-29a#2	0.56	8.3	22.7	—	-	18.7	5.7	—	305
J-12	2.1	7.3	22	119	—	—	—	—	—
UE-25p#1	3.5	37	129	698	—	<0.1	—	<0.2	360
High Temp.	<5	<10	<25	<140	-	<15	-	-	-

Table 2. Anion Concentrations and Other Measurements for Groundwater
from the Vicinity of Yucca Mountain

Effects of Temperature on Reaction Constants

In situ temperatures at the proposed Yucca Mountain repository site, before the waste implacement at a depth of about 300 m beneath the surface, are expected to be in the range 22-30°C [16]. Three hundred years after implacement, the minimum life time required of the canister, a typical modeled thermal history of a vertically emplaced spent fuel waste package and surrounding host rock show temperatures at the surface of the canister and nearby host rock of about 150°C [17]. At the elevation of the repository horizon, the boiling point of pure water is ~95°C [18]. The boiling point elevation is <1°C [19] for a solution that is as much as 100 times more concentrated than J-13 water in ionic salt components. Thermodynamic data for modeling reactions over the temperature range 20-100°C are a minimum requirement.

Virtually all of the published thermodynamic data in aqueous solutions come from experiments conducted at or near 25°C, i.e., room temperature. Chemical equilibria are affected by changes in temperature, and reaction constants are in general a function of temperature. Therefore, solubilities or other chemical reactions measured or calculated for one temperature could not be expected to apply to other temperatures. Extrapolation of 25°C data to 125°C strains present theory severely and must assume that there is no change in the heat capacity over that temperature range.

The relationship for describing the change of equilibrium constants (K) with temperature (T) at a constant pressure is given by the van't Hoff equation [20],

$$\frac{d \ln K}{dT} = \frac{\Delta H^\circ}{RT^2}$$

Where ΔH° is the standard heat (enthalpy) change of the reaction, R is the gas constant and T is the absolute temperature (°K). Thus, the equilibrium constant may increase or decrease depending on the sign and magnitude of the change in enthalpy of the reaction as a function of temperature. In addition, ΔH° is in general a function of temperature and the change in ΔH° with T is related to the standard heat capacity change, ΔC_p°, through the equation:

$$\frac{d \Delta H^\circ}{dT} = \Delta C_p^\circ$$

The heat capacity change, ΔC_p, is also in general a function of temperature.

To provide a thermodynamic data base which can be used with confidence over the temperature range 20-125°C, either stability constants, solubilities, etc. must be measured

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at frequent intervals over the temperature range or the enthalpy of reaction (heat of solution) can be measured at a few temperatures. In the latter case, if ΔC_p is zero or a constant, the van't Hoff equation allows extrapolation to other temperatures. If ΔC_p varies with temperature, more detailed experiments will be necessary to evaluate quantitatively the variation.

The standard method for the determinations of enthalpies is via calorimetric measurements. The advantage of the calorimetric approach, compared to direct measurement of stability constants and solubilities, is that fewer experiments are required.

In many systems, both the stability constants and the enthalpies of complexation reactions can be obtained from the calorimetric data. Thus, in principle, a broader thermodynamic data base, i.e. including ΔG, ΔH, and ΔS, can be developed in a fewer number of experiments.

It should be sufficient to obtain data at ca. 70°C and ca. 125°C, in addition to 25°C, to ascertain whether ΔH or ΔC_p are constant. If the enthalpy were found to vary slightly, data at these three temperatures should be adequate to obtain a satisfactory ΔC_p value for calculating thermodynamic constants at temperatures between 25°C and 125°C. If the enthalpies change appreciably with temperature, a larger number of measurements can be made over the 25°C to 125°C range to evaluate the temperature dependence of ΔC_p.

The types of calorimeters required at 70°C and at 125°C are quite different so separate instruments would be required for these two temperature regions. In addition, it is desirable that these calorimeters be variable temperature instruments over a 30 to 40°C region about 70 and 125°C. This is not a normal requirement for calorimeters and some development is necessary. These instruments would be adequate, along with the existing room temperature calorimeters, to study reactions at temperatures between 20°C and 125°C. Thus, if a strong nonlinear dependence of enthalpy is observed, calorimetry could be performed at whatever series of temperatures in this range that is needed. A 70°C variable temperature calorimeter had been designed, constructed, and is undergoing final testing at Florida State University for use on this program; a 125°C variable temperature calorimeter is in a similar state of development at Lawrence Livermore National Laboratory.

Waste Radionuclides

A large number of long-lived actinides, actinide decay products, fission products and fuel cladding activation products are present in spent reactor fuel in sufficient quantities even

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1000 years after implacement in a repository that they will remain a radiological hazard to man and will need to be controlled. The most frequently used method for estimating the quantities of various radionuclides in spent fuel is through the use of the advanced computer code ORIGEN developed at the Oak Ridge National Laboratory [21,22]. It is now possible to obtain a spent fuel repository characteristics data base on PC diskette from the Systems Integration Program at ORNL [23]. The program is intended to provide technical data for DOE and its supporting contractors and is outlined in a recent Office of Civilian Nuclear Waste Management document [24].

In the absence of the reprocessing of commercial spent fuel, light water reactor (LWR) spent (low enrichment uranium) fuel would be the predominant source of radioactivity for geological repositories [25]. The quantities of various waste radionuclides in pressurized water reactor (PWR) and boiling water reactor (BWR) fuels as a function of burnup and decay time are accessible through the data base. Decay times cover the period 1 to 10^6 years while the burnup amounts run from 5,000 to 60,000 megawatt-days (MWd) per metric ton of initial heavy metal (MTIHM) for PWRs and 5,000 to 40,000 MWd/MTIHM for BWRs. Examples of the results that can be obtained from the data base are given in Appendix B. These results include complete lists of radionuclides calculated by the ORIGEN code for a standard and high burnup of 30,000 and 60,000 MWD/MTIHM for a typical PWR fuel and a low and standard burnup of 5,000 and 30,000 MWD/MTIHM for a typical BWR fuel for decay periods ranging from 100 to 1,000,000 years. The inventory data are presented in three ways for comparisons. The first is ordered by atomic number (as presented by the Oak Ridge data base), the second by increasing amount in the inventory, and the third by decreasing percentage of the inventory.

Both the Nuclear Regulatory Commission (NRC) and the Environmental Protection Agency (EPA) have issued rules governing release rate requirements for the disposal of high-level radioactive waste in geologic repositories. The EPA final rule (40 CFR Part 191 subpart 191.13a) [26] sates that "disposal systems for spent nuclear fuel or high-level or transuranic wastes shall be designed to provide a reasonable expectation, based upon performance assessments, that the cumulative releases of waste to the accessible environment for 10,000 years after disposal from all significant processes and events that may affect the disposal system shall: (1) have a likelihood of less than one chance in 10 of exceeding the quantities calculated according to Table 1 (Appendix A of 40CFR 191), and (2) have a likelihood of less than one chance in 1,000 of exceeding ten times the quantities calculated according to Table 1". It is further stipulated that " in cases where a

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mixture of radionuclides is projected to be released to the accessible environment, the limiting values shall be determined as follows: For each radionuclide in the mixture, determine the ratio between the cumulative release quantity projected over 10,000 years and the limit for that radionuclide as determined from Table 1. The sum of such ratios for all the radionuclides in the mixture may not exceed one" for the 1 chance in 10 case "and may not exceed 10" for the 1 chance in 1000 case. The EPA made it clear, however, in the comments section under "Time Period for Containment Requirements" that "there was not intention to indicate that times beyond 10,000 years were unimportant" and that public and environment protection was expected well beyond 10,000 years. Release rate performance out to 100,000 years was suggested for the comparison of different sites.

The EPA included in the rule, additional protection requirements on groundwaters. Subpart 191.15 reads: "disposal systems for spent nuclear fuel or high-level or transuranic radioactive wastes shall be designed to provide a reasonable expectation that, for 1,000 years after disposal, undisturbed performance of the disposal system shall not increase the average annual radioactive concentrations in any major source of groundwater or any sole source aquifer (outside of any controlled area, which is assumed to exist for no more than 100 years after disposal) by more than: a) picocuries per liter of radium-226 and radium-228; b) 15 picocuries per liter of alpha-emitting radionuclides (including radium-226 and radium-228); or c) the combined concentrations of radionuclides that emit either beta or gamma radiation that would produce an annual dose equivalent to the total body or any internal organ greater than 4 millirem per year if an individual continuously consumed 2 liters per day of drinking water from such a source of groundwater."

In 10 CFR Part 60 (subpart 60.113B) [27], the NRC specifies that "the release rate of any radionuclide from the engineered barrier system following the containment period shall not exceed one part in 100,000 per year of the inventory of that radionuclide calculated to be present at 1,000 years after permanent closure, or such other fraction of the inventory as may be approved or specified by the Commission; provided, that this requirement does not apply to any radionuclide which is released at a rate less than 0.1% of the calculated total release rate limit. The calculated total release rate limit shall be taken to the one part in 100,000 per year of the inventory of radioactive waste, originally emplaced in the underground facility, that remains after 1,000 years of radioactive decay." The required containment period of the high-level waste by the waste package "shall not be less than 300

years nor more than 1,000 years after permanent closure of the geologic repository."

For our analysis to delineate the waste radionuclides most important to control, the data for a PWR fuel with a burnup of 30,000 MWd/MTIHM presented in Appendix B of this report was used because it is the average value used for calculating release limits in 40CFR191. BWR fuels have very similar compositions to the PWR fuels, as can be seen by comparing the compositions for these two types of reactors at 30,000 MWd/MTIHM presented in Appendix B. However, BWR fuels tend to have slightly lower average burnup times, i.e., 27,000 MWd/MTIHM [28]. The figures of Appendix A show graphically the curies per metric ton of heavy metal (MTHM) for a PWR fuel with burnup of 30,000 MWd/MTIHM as a function of time after discharge from reactor over the range 100 to 1,000,000 years for each of the radionuclides calculated by the ORIGEN code to have a total activity greater than 0.1% of the total amount of radioactivity in the waste/MTHM after 1000 years of radioactive decay. This cutoff limit was selected because the NRC release rate limit requirement does not apply to a radionuclide that is released at a rate less than 0.1 percent of the calculated total release rate limit at 1000 years. Daughter radionuclides with half-lives less than about 25 years were included with and taken to be in secular equilibrium with the parent in the decay chain with a half-life of 1000 years or more. Dashed lines have been included on the graphs to indicate the total NRC release limits per year and 0.1% of those limits. Also included in the figures are dashed lines indicating the EPA release limits for cumulative releases to the accessible environment for 10,000 years after disposal. As noted on the graphs, C-14, Tc-99 and Th-230 have been given individual values. Figures 1 and 2 are composites of the curves shown in the figures of Appendix A for beta and alpha emitting radionuclides, respectively. The curves represent the combined radioactivity for an element due to all isotopes. The nuclides included in this analysis, their half-lives[1], modes of decay, inventory at 1000 years following discharge from reactor and the individual EPA and NRC release limits are given in Table 3. The NRC release limits are either 1 part in 10,000 of the inventory of a given radionuclide or 0.1% of 1 part in 10,000 of the total inventory of radionuclides, whichever is larger. It should be remembered that these limits are for the individual radionuclides and that the release of multiple radionuclides must conform to the summation limits. The limits given in Table 3 are thus upper limits and the allowable release amounts could be less depending on the exact radionuclides that are released. For

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[1]The half-lives were taken from the Table of Radioactive Isotopes [29]. The values agree well with those used by the ORIGIN code [30] for all isotopes except Ce-142. The half-life quoted in ref [30] is about 100,000 times shorter than given in the Table of Isotopes.
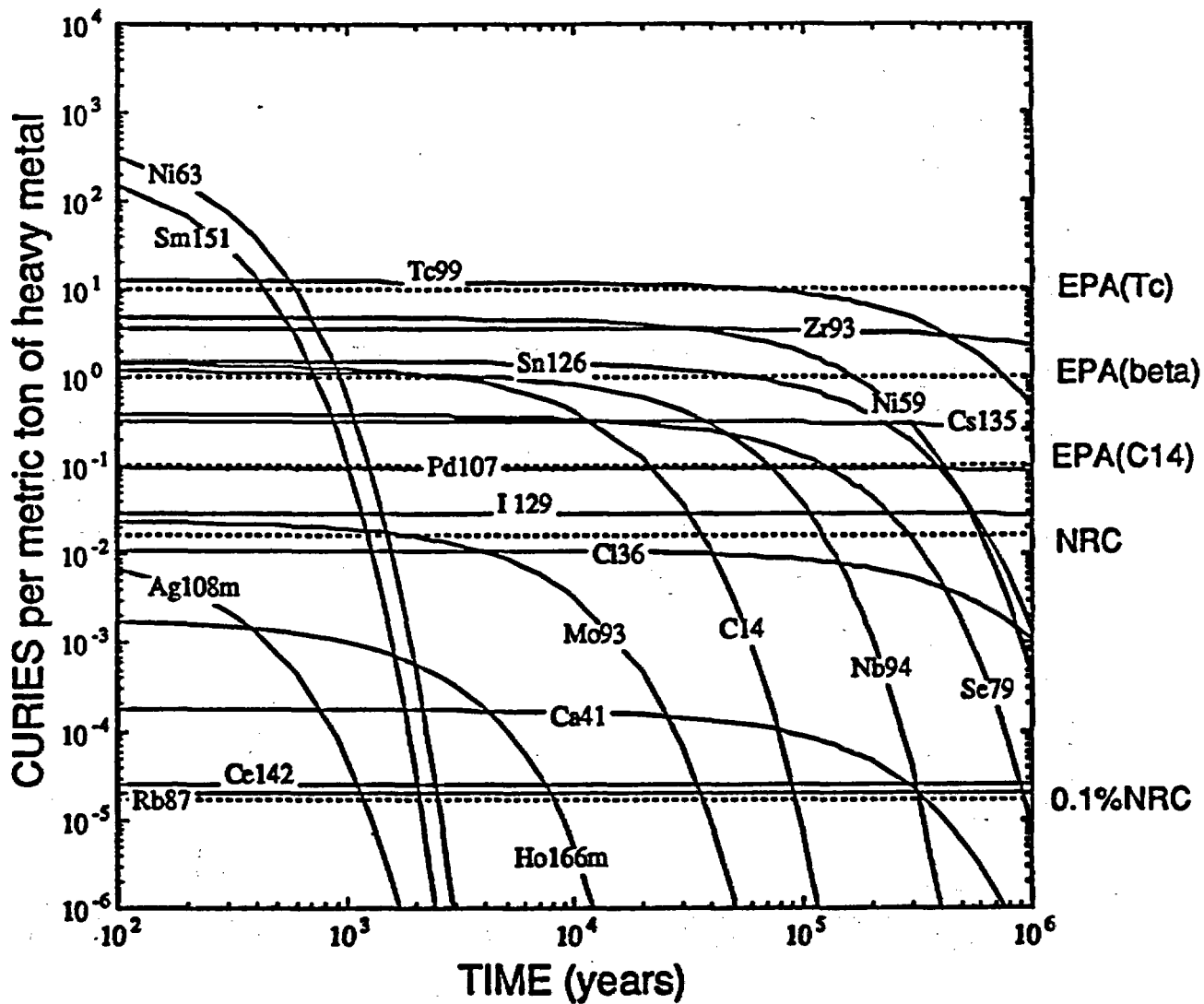
Figure 1. Log-log plot of Curies per metric ton of heavy metal for beta emitting radionuclides vs. Time, in years. The curves shown are composite curves for the same element as shown in Appendix A figures for each individual radionuclide.
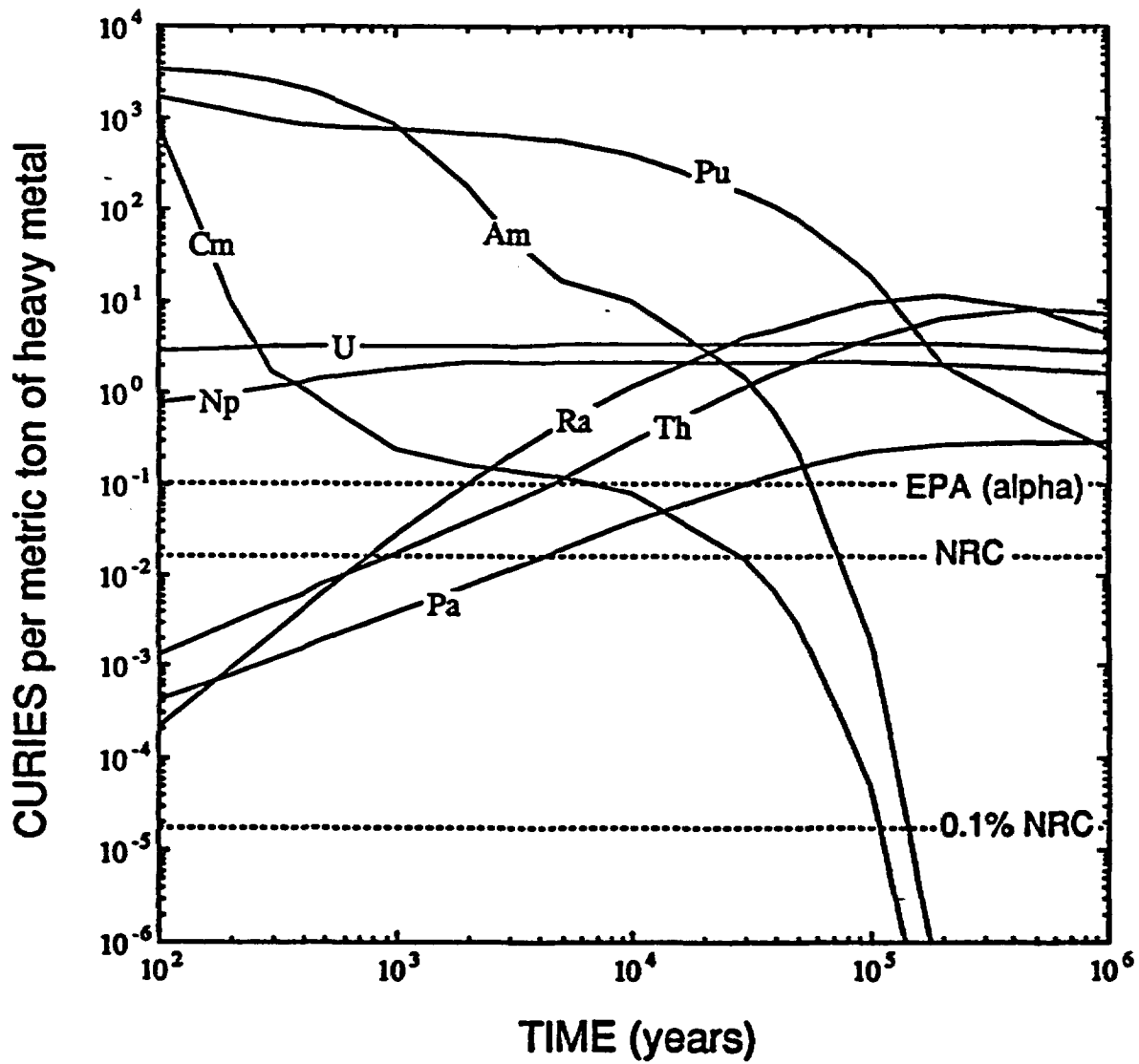
Figure 2. Log-log plot of Curies per metric ton of heavy metal for alpha emitting radionuclides vs. Time, in years. The curves shown are composite curves for the same element as shown in Appendix A figures for each individual radionuclide.

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Table 3. Radionuclides in Reactor Fuel Whose Release From a Repository Waste Form Needs Controlling

Radionuclides	Mode of Decay	Half-Life	Inventory at 1000 yrs (Ci/MTHM)	NRC Release Limit (Ci/MTHM/Yr)	EPA Release Limit (Ci/MTHM/ 10,000 Yr)
C-14	beta, β^-	5.73E+03 y	1.23E+00	1.60E-05	0.10
Cl-36	98.1%β^-, 1.9%EC	3.01E+05 y	1.09E-02	1.60E-05	1.00
Ca-41	EC,	1.03E+05 y	1.71E-04	1.60E-05	1.00
Ni-59	EC	7.50E+04 y	4.64E+00	1.60E-05	1.00
Ni-63	beta, β^-	1.00E+02 y	3.37E-01	1.60E-05	1.00
Se-79	beta, β^-	6.50E+04 y	3.70E-01	1.60E-05	1.00
Rb-87	beta, β^-	4.80E+10 y	1.98E-05	1.60E-05	1.00
Zr-93*	beta, β^-	1.53E+06 y	1.78E+00	1.60E-05	1.00
(Nb-93m)	IT	1.36E+01 y	1.69E+00	1.60E-05	1.00
Mo-93	EC	3.50E+03 y	1.90E-02	1.60E-05	1.00
Nb-94	beta, β^-	2.03E+04 y	1.11E+00	1.60E-05	1.00
Tc-99	beta, β^-	2.13E+05 y	1.20E+01	1.60E-05	10.00
Pd-107	beta, β^-	6.50E+06 y	9.63E-02	1.60E-05	1.00
Ag-108m	91.3%EC, 8.7%β^-	1.27E+02 y	5.06E-05	1.60E-05	1.00
Sn-126*	beta, β^-	1.00E+05 y	6.89E-01	1.60E-05	1.00
(Sb-126)	beta, β^-	3.39E-02 y	9.64E-02	1.60E-05	1.00
(Sb-126m)	86%β^-, 14%IT	3.61E-06 y	6.89E-01	1.60E-05	1.00
I-129	beta, β^-	1.57E+07 y	2.85E-02	1.60E-05	1.00
Cs-135	beta, β^-	2.95E+06 y	3.13E-01	1.60E-05	1.00
Ce-142	alpha, α	>5E+16 y	2.47E-05	1.60E-05	1.00
Sm-151	beta, β^-	9.00E+01 y	1.55E-01	1.60E-05	1.00
Ho-166m	beta, β^-	1.20E+03 y	1.03E-03	1.60E-05	1.00
Ra-226*	alpha, α	1.60E+03 y	2.97E-03	1.60E-05	0.10
(Rn-222)	alpha, α	1.05E-02 y	2.97E-03	1.60E-05	0.10
(Po-218)	alpha, α	5.91E-07 y	2.97E-03	1.60E-05	0.10
(Pb-214)	beta, β^-	5.10E-07 y	2.97E-03	1.60E-05	1.00
(Bi-214)	beta, β^-	3.78E-07 y	2.97E-03	1.60E-05	1.00
(Po-214)	alpha, α	5.20E-12 y	2.97E-03	1.60E-05	0.10
(Pb-210)	beta, β^-	2.23E+01 y	2.97E-03	1.60E-05	1.00
(Bi-210)	beta, β^-	1.37E-02 y	2.97E-03	1.60E-05	1.00
(Po-210)	alpha, α	3.79E-01 y	2.97E-03	1.60E-05	0.10
Th-229*	alpha, α	7.34E+03 y	1.12E-04	1.60E-05	0.10
(Ra-225)	beta, β^-	4.05E-02 y	1.12E-04	1.60E-05	1.00
(Ac-225)	alpha, α	2.74E-02 y	1.12E-04	1.60E-05	0.10
(Fr-221)	alpha, α	9.32E-07 y	1.12E-04	1.60E-05	0.10
(At-217)	alpha, α	1.02E-09 y	1.12E-04	1.60E-05	0.10
(Bi-213)	97.8%β^-, 2.2% α	8.69E-06 y	1.12E-04	1.60E-05	1.00
(Po-213)	alpha, α	1.33E-13 y	1.10E-04	1.60E-05	0.10
(Pb-209)	beta, β^-	3.71E-05 y	1.12E-04	1.60E-05	1.00
Th-230	alpha, α	7.54E+04 y	1.63E-02	1.60E-05	0.10

EC - electron capture
IT - internal transition
* - parent nuclide
( ) - daughter nuclide

Table 3. Radionuclides in Reactor Fuel Whose Release From a
Repository Waste Form Needs Controlling (Continued)

Radionuclides	Mode of Decay	Half-Life	Inventory at 1000 yrs (Ci/MTHM)	NRC Release Limit (Ci/MTHM/Yr)	EPA Release Limit (Ci/MTHM/ 10,000 Yr)
Pa-231*	alpha, α	3.28E+04 y	4.36E-04	1.60E-05	0.10
(Ac-227)	98.6%β^-, 1.4% α	2.18E+01 y	4.36E-04	1.60E-05	1.00
(Th-227)	alpha, α	5.12E-02 y	4.30E-04	1.60E-05	0.10
(Ra-223)	alpha, α	3.12E-02 y	4.36E-04	1.60E-05	0.10
(Rn-219)	alpha, α	1.25E-07 y	4.36E-04	1.60E-05	0.10
(Po-215)	alpha, α	5.64E-11 y	4.36E-04	1.60E-05	0.10
(Pb-211)	beta, β^-	6.86E-07 y	4.36E-04	1.60E-05	1.00
(Bi-211)	alpha, α	4.07E-07 y	4.36E-04	1.60E-05	0.10
(Tl-207)	beta, β^-	9.07E-07 y	4.35E-04	1.60E-05	1.00
U-233	alpha, α	1.59E+05 y	2.87E-03	1.60E-05	0.10
U-234	alpha, α	2.45E+05 y	1.90E+00	1.60E-05	0.10
U-235*	alpha, α	7.04E+08 y	2.03E-02	1.60E-05	0.10
(Th-231)	beta, β^-	2.90E-03 y	2.03E-02	1.60E-05	1.00
U-236	alpha, α	2.34E+07 y	2.60E-01	1.60E-05	0.10
U-238*	alpha, α	4.47E+09 y	3.18E-01	1.60E-05	0.10
(Th-234)	beta, β^-	6.60E-02 y	3.18E-01	1.60E-05	1.00
(Pa-234)	beta, β^-	7.70E-05 y	3.18E-01	1.60E-05	1.00
Np-237*	alpha, α	2.14E+06 y	8.95E-01	1.60E-05	0.10
(Pa-233)	beta, β^-	7.39E-02 y	8.95E-01	1.60E-05	1.00
Pu-238	alpha, α	8.77E+01 y	8.78E-01	1.60E-05	0.10
Pu-239	alpha, α	2.41E+04 y	3.01E+02	1.60E-05	0.10
Pu-240	alpha, α	6.56E+03 y	4.40E+02	1.60E-05	0.10
Pu-242	alpha, α	3.76E+05 y	1.39E+00	1.60E-05	0.10
Am-241	alpha, α	4.33E+02 y	8.07E+02	1.60E-05	0.10
Am-242m*	IT	1.41E+02 y	7.09E-02	1.60E-05	0.10
(Am-242)	82.7%β^-, 17.3%EC	1.83E-04 y	7.05E-02	1.60E-05	1.00
(Cm-242)	alpha, α	4.46E-01 y	5.83E-02	1.60E-05	0.10
Am-243*	alpha, α	7.38E+03 y	1.12E+01	1.60E-05	0.10
(Np-239)	beta, β^-	6.46E-03 y	1.12E+01	1.60E-05	1.00
Cm-245*	alpha, α	8.50E+03 y	7.89E-02	1.60E-05	0.10
(Pu-241)	beta, β^-	1.44E+01 y	7.90E-02	1.60E-05	1.00
Cm-246	alpha, α	4.73E+03 y	1.37E-02	1.60E-05	0.10

example, if all the radionuclides were released at their limit, the release rate of 1.69×10^{-2} Ci/MTHM would exceed the allowable NRC release rate of 1.60×10^{-2} Ci/MTHM. Radionuclides that represent large percentages of the total radioactivity obviously have the greatest influence.

In order to compare the relative contributions to the waste, the waste radionuclides are placed in order of the ratio of their inventory at 1000 years to the total allowed NRC release rate in Table 4, i.e., 1 part in 100,000 of the total inventory at 1000 years. Clearly, elements like Am and Pu will need isolation for well over 10,000 years because their inventories exceed even the total NRC release limit by 10's of thousands. Also shown in Table 4 are the radionuclides in order of the ratio of their inventory at 1000 years to the total allowed EPA release over 10,000 years. Again, the inventories of Am and Pu far exceed the EPA limit for 10,000 years. Other alpha particle emitting nuclides appear higher on this list than the previous one because the EPA allowable limits for alpha particle emitters is ten times less than for nuclides that decay by other modes, with the exception of C-14, Tc-99, and Th-230 which have been given individual limits. This table is a little misleading for a few of the waste radionuclides that appear high on the list but have relatively short half-lives. For example, the inventories of Ni-63, Sm-151 and Pu-238 fall below the NRC limit for control in 2 to 3 thousand years. After 100,000 years of decay, Am and Pu no longer dominate the radioactivity of the waste but the actinide decay products Ra, Th, and Pa have grown in to the extent that they become major contributors. However, the total inventory has decreased by several orders of magnitude by that time.

Also shown in Table 4 are the nuclides ordered by the ratio of their inventories to their NRC release rate limits. Analyses [31] indicate that the long term dissolution rate of all species in the waste form will likely be controlled at the same rate as the dissolution of the spent fuel matrix, with possible exception of an initial rapid release of small percentages of Cs, C, I and Tc. If the waste form were to dissolve at a rate of 0.1% per year, a relatively high value [32], no further control would be necessary for radionuclides below Th-230 in the list (below the dashed line). For radionuclides between Sm-151 and Th-230 (between solid and dashed lines), a factor of ten lower dissolution rate, a value considered conservative by Kerrish [33], or some other mechanism for the reduction of the radionuclide solution concentration by a factor of ten (limited solubility or sorption) would be needed of the waste package in order to meet the NRC release rate limit. With the exception of I-129, which may be released at a rate higher than matrix dissolution [34], these radionuclides are

Table 4. Comparison of Radionuclide Inventory with NRC and EPA Release Limits

Radionuclides	Inventory at 1000 yrs/NRC Total Release Limit	Radionuclides	Inventory at 1000 yrs/EPA Total Release Limit	Radionuclides	Inventory at 1000 yrs/NRC Individual Release Limit
Am-241	5.04E+04	Am-241	8.07E+03	Am-243*	1.00E+05
Pu-240	2.75E+04	Pu-240	4.40E+03	(Np-239)	1.00E+05
Pu-239	1.88E+04	Pu-239	3.01E+03	Am-241	1.00E+05
Tc-99	7.50E+02	Am-243*	1.12E+02	Pu-240	1.00E+05
Am-243*	7.00E+02	U-234	1.90E+01	Pu-239	1.00E+05
(Np-239)	7.00E+02	Pu-242	1.39E+01	U-234	1.00E+05
Ni-59	2.90E+02	C-14	1.23E+01	Tc-99	1.00E+05
U-234	1.19E+02	(Np-239)	1.12E+01	Zr-93*	1.00E+05
Zr-93*	1.11E+02	Np-237	8.95E+00	(Nb-93m)	1.00E+05
(Nb-93m)	1.06E+02	Pu-238	8.78E+00	Ni-59	1.00E+05
Pu-242	8.69E+01	Ni-59	4.64E+00	Pu-242	8.69E+04
C-14	7.69E+01	U-238*	3.18E+00	C-14	7.69E+04
Nb-94	6.94E+01	U-236	2.60E+00	Nb-94	6.94E+04
Np-237*	5.59E+01	Zr-93*	1.78E+00	Pu-238**	5.49E+04
(Pa-233)	5.59E+01	(Nb-93m)	1.69E+00	Np-237	5.00E+04
Pu-238	5.49E+01	Tc-99	1.20E+00	(Pa-233)	5.00E+04
Sn-126*	4.31E+01	Nb-94	1.11E+00	Sn-126*	4.31E+04
(Sb-126m)	4.31E+01	(Pa-233)	8.95E-01	(Sb-126m)	4.31E+04
Se-79	2.31E+01	Cm-245*	7.89E-01	(Sb-126)	6.02E+03
Ni-63	2.11E+01	Am-242m*	7.09E-01	Se-79	2.31E+04
U-238*	1.99E+01	(Sb-126m)	6.89E-01	Ni-63**	2.11E+04
(Th-234)	1.99E+01	Sn-126*	6.89E-01	U-238*	1.99E+04
(Pa-234)	1.99E+01	(Cm-242)	5.83E-01	(Th-234)	1.99E+04
U-236	1.63E+01	Se-79	3.70E-01	(Pa-234m)	1.99E+04
Sm-151	9.69E+00	Ni-63	3.37E-01	U-236	1.63E+04
(Sb-126)	6.03E+00	(Th-234)	3.18E-01	Sm-151**	9.69E+03
Pd-107	6.02E+00	Cs-135	3.13E-01	Pd-107	6.02E+03
Cm-245*	4.93E+00	(Pa-234m)	3.18E-01	Cm-245*	4.93E+03
(Pu-241)	4.94E+00	U-235*	2.03E-01	(Pu-241)	4.94E+03
Am-242m*	4.43E+00	Th-230	1.63E-01	Am-242m	4.43E+03
(Am-242)	4.41E+00	Sm-151	1.55E-01	(Am-242)	4.41E+03
(Cm-242)	3.64E+00	Cm-246	1.37E-01	(Cm-242)	3.64E+03
I-129	1.78E+00	(Sb-126)	9.64E-02	I-129	1.78E+03
U-235*	1.27E+00	Pd-107	9.63E-02	U-235*	1.27E+03
(Th-231)	1.27E+00	(Pu-241)	7.90E-02	(Th-231)	1.27E+03
Mo-93	1.19E+00	(Am-242)	7.05E-02	Mo-93	1.19E+03
Th-230	1.02E+00	(Po-214)	2.97E-02	Th-230	1.02E+03
Cm-246	8.56E-01	(Rn-222)	2.97E-02	Cm-246	8.56E+02
Cl-36	6.81E-01	(Po-210)	2.97E-02	Cl-36	6.81E+02
Cs-135	3.13E-01	(Po-218)	2.97E-02	Cs-135	3.13E+02
Ra-226*	1.86E-01	Ra-226*	2.97E-02	Ra-226*	1.86E+02
(Rn-222)	1.86E-01	U-233	2.87E-02	(Rn-222)	1.86E+02

* - parent nuclide
** - Relatively short half-life
( ) - daughter nuclide

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Table 4. Comparison of Radionuclide Inventory with NRC and EPA Release Limits (Continued)

Radionuclides	Inventory at 1000 yrs/NRC Total Release Limit	Radionuclides	Inventory at 1000 yrs/EPA Total Release Limit	Radionuclides	Inventory at 1000 yrs/NRC Individual Release Limit
(Po-218)	1.86E-01	I-129	2.85E-02	(Po-218)	1.86E+02
(Pb-214)	1.86E-01	(Th-231)	2.03E-02	(Pb-214)	1.86E+02
(Bi-214)	1.86E-01	Mo-93	1.90E-02	(Bi-214)	1.86E+02
(Po-214)	1.86E-01	Cl-36	1.09E-02	(Po-214)	1.86E+02
(Pb-210)	1.86E-01	(Po-215)	4.36E-03	(Pb-210)	1.86E+02
(Bi-210)	1.86E-01	(Ra-223)	4.36E-03	(Bi-210)	1.86E+02
(Po-210)	1.86E-01	(Rn-219)	4.36E-03	(Po-210)	1.86E+02
U-233	1.79E-01	Pa-231*	4.36E-03	U-233	1.79E+02
Ho-166m	6.44E-02	(Bi-211)	4.36E-03	Ho-166m	6.44E+01
Pa-231*	2.73E-02	(Th-227)	4.30E-03	Pa-231*	2.73E+01
(Ac-227)	2.73E-02	(Bi-210)	2.97E-03	(Th-227)	2.73E+01
(Th-227)	2.69E-02	(Pb-210)	2.97E-03	(Ac-227)	2.73E+01
(Ra-223)	2.73E-02	(Bi-214)	2.97E-03	(Ra-223)	2.73E+01
(Rn-219)	2.73E-02	(Pb-214)	2.97E-03	Rn-219	2.73E+01
(Po-215)	2.73E-02	(Fr-221)	1.12E-03	Po-215	2.73E+01
(Pb-211)	2.73E-02	(Ac-225)	1.12E-03	Pb-211	2.73E+01
(Bi-211)	2.73E-02	(At-217)	1.12E-03	Bi-211	2.73E+01
(Tl-207)	2.72E-02	Th-229*	1.12E-03	Tl-207	2.73E+01
Ca-41	1.07E-02	(Po-213)	1.10E-03	Ca-41	1.07E+01
Th-229*	7.00E-03	Ho-166m	1.03E-03	Th-229*	7.00E+00
(Ra-225)	7.00E-03	(Pb-211)	4.36E-04	(Ra-225)	7.00E+00
(Ac-225)	7.00E-03	(Ac-227)	4.36E-04	(Ac-225)	7.00E+00
(Fr-221)	7.00E-03	(Tl-207)	4.35E-04	(Fr-221)	7.00E+00
(At-217)	7.00E-03	Ca-41	1.71E-04	(At-217)	7.00E+00
(Bi-213)	7.00E-03	(Bi-213)	1.12E-04	(Bi-213)	7.00E+00
(Po-213)	6.88E-03	(Pb-209)	1.12E-04	(Po-213)	6.88E+00
(Pb-209)	7.00E-03	(Ra-225)	1.12E-04	(Pb-209)	7.00E+00
Ag-108m	3.16E-03	Ag-108m	5.06E-05	Ag-108m**	3.16E+00
Ce-142	1.54E-03	Ce-142	2.47E-05	Ce-142	1.54E+00
Rb-87	1.24E-03	Rb-87	1.98E-05	Rb-87	1.24E+00

likely to be easily controlled. For the radionuclides from U-236 through Pu-242, waste form dissolution rates (or other mechanisms for concentration limitations by the waste packages) of between 0.01 and 0.001% per year would be required to meet the NRC requirements. Controls other than dissolution rate may be necessary for these waste nuclides. For the radionuclides above Pu-242 in the list, a dissolution rate of 0.001% or greater would be needed. This control would be required for a period in excess of 10,000 years for these nuclides and controls other than dissolution rate should be considered. Controls based on natural processes, e.g. solubility limitations or sorption, rather than man-made physical barriers would be the most reliable approach. Therefore, experimental data necessary for the prediction of solubilities and speciation of the radionuclides above Sm-151 in Table 4 column 6 are needed, with special emphasis on Am and Pu because they represent such a large fraction of the total inventory. A priority list is given in Table 5.

Priority	Element
1	Americium
1	Plutonium
1	Neptunium
1	Uranium
1	Technetium
1	Zirconium
1	Nickel
2	Carbon
2	Niobium
2	Tin
2	Antimony
2	Selenium
3	Palladium
3	Curium
3	Iodine
3	Molybdenum
3	Thorium

Table 5. Priority List for the Determination of Thermodynamic Data
for Waste Elements

1. Top priority. Will need thermodynamic data.
2. Second priority. Will probably need some thermodynamic data.
3. Third priority. Probably will not need further thermodynamic data.

Waste Package Container Materials

Six candidate materials are being evaluated for the waste package container; they are austenitic stainless steel alloys and copper based alloys [35]. The copper based materials are oxygen-free copper (CDA 102), 8% aluminum-bronze (CDA 613) and 70-30 copper-nickel (CDA 715). The austentitic materials are AISI 304L, AISI 316L and alloy 825. The nominal compositions of these alloys are given in Tables 6 and 7 taken from Reference [36].

Various forms of corrosion and oxidation attack by the repository environment constitute the most likely degradation modes of the metal canisters [37]. Therefore, for modeling purposes, the thermodynamic data that describe the reactions of the canister metals with the groundwater and the solution species formed by the dissolved canister materials as a function of temperature need to be known. In addition, evaporation and other salt concentrating mechanisms may increase the ionic content of the water near the canisters and favor increased corrosion; this is particularly true for chloride. Thus, thermodynamic data at high ionic strengths may be necessary for modeling this system. The elements that need to be considered for interaction with the groundwater components are C, Cr, Si, Fe, Cu, Ni, Zn, Al, Pb, Sn and Mn.

Common Alloy Designation	Chemical Composition (wt %)							
	C	Mn	P	S	Si	Cr	Ni	Other Element
304L	0.03	2.00	0.045	0.03	1.0	18.0-20.0	8.0-12.0	N: 0.10 max
316L	0.03	2.00	0.045	0.03	1.0	16.0-18.0	10.0-14.0	Mo: 2.0-3.0 N: 0.10 max
825	0.05	1.0	Not specified	0.03	0.5	19.5-23.5	38.0-46.0	Mo: 2.5-3.5 Ti:0.6-1.2 Cu:1.5-3.0 Al:0.2 max

Table 6. Iron Alloy Compositions for Candidate Container
Materials in Reference Alloy Systems

Alloy Designation	Chemical Composition (wt %)							
	Cu	Fe	Pb	Sn	Al	Mn	Ni	Zn
CDA 102 (Oxygen-free Copper)	99.95 (min)	–	–	–	–	–	–	–
CDA 613 (Aluminum Bronze)	92.7 (nom)	3.5 (max)	–	0.2-0.5	6.0-8.0	0.5 (max)	0.5	–
CDA 715 (70-30 Copper-Nickel)	69.5 (nom)	0.4-0.7	0.5 (max)	–	–	1.0 (max)	29.0-33.0	1.0 (max)

Table 7. Copper Alloy Compositions for Candidate Container Materials

Mineral Phases

Understanding the mineral stability and evolution at Yucca Mountain will depend on the quality of the thermodynamic data base available [38]; therefore, the gathering of thermodynamic data is fundamental to this understanding. Data will be especially important in verifying the relationship between silica activity and mineral stability, particularly that of the framework silicates such as the zeolites. Clinoptilolite, heulandite, albite and analcime, along with silica polymorphs, are principal components of important mineral reactions observed to have taken place in Yucca Mountain. Both thermodynamic data for the end-members of these minerals and a description of solid-solution and order-disorder phenomena are needed [39].

Zeolites

The principal zeolites occurring at Yucca Mountain are clinoptilolite-group minerals (clinoptilolite and heulandite), mordenite, and analcime [40, 41]. The chemical and physical processes relating to zeolites that need to be modeled in order to predict repository performance are: dissolution-precipitation, ion-exchange, dehydration, and thermal contraction. Equilibrium thermodynamic data and validated solid-solution models will be required in order to model the first three of the above processes. Data for the reaction kinetics of dissolution-precipitation of these phases will also be needed. Of the above, clinoptilolite is probably the most important mineral for which thermodynamic and kinetic data is needed. It is the most abundant zeolite, has a large cation exchange capacity, contains a significant quantity of water of hydration ("zeolitic water"), and is distributed near enough to the proposed repository to be affected by a thermal pulse. Analcime is the least important because of its depth (furthest from the repository), its lack of significant ion-exchange, its relatively small quantity of water of hydration, and its relatively high thermal stability.

Recently, new and revised data for the thermodynamic stability of the zeolite types found at Yucca Mountain have been published [42-46]. These data, which are based on calorimetric methods, together with thermochemical data from other sources, have been incorporated into the EQ3/6 database. The aforementioned studies utilized natural zeolites which (with the exception of analcime) contained a mixture of alkali and alkaline earth cations on the exchange sites. Apparently, there are no published data for zeolites with end-member compositions (i.e., exchange site occupied by a single cation). The database also contains data for zeolites and zeolite solid-solutions that have been estimated using oxide

summation algorithms [47]. The zeolite data set presently in the database (especially the set of estimated values) has not been critically analyzed to insure either internal consistency or consistency with the set of data for rock-forming minerals (i.e., SUPCRT data).

Thermodynamic data are available for ion-exchange of selected alkali and alkaline earth cations on some of these zeolites. Using the available ion-exchange data together with the thermochemical stability data of Johnson et al. [46] and methods for estimating heat capacities and entropies, a modified ideal site-mixing solid-solution model for clinoptilolite (mixing on exchange sites only) has been generated [48]. Additional ion exchange data is required to describe the observed variation in exchange-site occupancy at Yucca Mountain. In addition, data is required for exchange reactions involving radionuclides. The model was developed from data obtained from binary ion-exchange isotherms by assuming ideal exchange (i.e., ion-exchange between any two ions is not influenced by the presence of any other ion on the exchange site). To test this assumption and validate the model ternary and quaternary exchange experiments will need to be undertaken. In order to confidently extend the model to higher temperatures, experimental measurements of ion-exchange equilibria at elevated temperatures will also be necessary. The solid-solution model will also need to be extended to describe mixing of silicon and aluminum on the tetrahedral site. Until more data is available, solid-solution models for zeolites will necessarily be restricted to those describing mixing on the exchange site. Finally, solid-solution models need to be validated using experimental and/or field data.

The data reported by Johnson et al, refer to zeolites with zeolitic water contents defined by equilibrium with an atmosphere at 50% relative humidity at room temperature. Clearly, this does not correspond to the water content associated with these minerals in a water-saturated environment. The significance of this difference (and any difference in water contents or zeolitic water properties between end-member compositions) on predicted mineral equilibria has not been elucidated. It is clear, however, that in order to model the dehydration of these minerals in an unsaturated environment (e.g., a possible scenario in the repository) the properties of the zeolitic water need to be known. Van Reeuwijk [49] has studied the thermodynamic properties of water in zeolites and their equilibrium dehydration reactions. Based on Van Reeuwijk's [49] results we believe, that for clinoptilolite, the significance of the zeolitic water on reaction equilibria in saturated systems to be small. However, a more thorough analysis of this problem is necessary.

Data suitable for extracting rates of dissolution for the zeolites of interest are limited

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to a single study of heulandite [50]. Similar dissolution experiments using clinoptilolite and mordenite will also be needed. At the present time there are no available data for rates of precipitation of these phases. This lack of information will have to be addressed in any planned experimental program.

At this point it appears there exists a critical mass of relevant thermodynamic data which should be tabulated and carefully analyzed before proceeding with additional experiments on zeolites. This analysis should: 1) reconcile differences between published values for thermodynamic parameters and attempt to develop a zeolite data set that is both internally consistent and consistent with the data for the rock-forming minerals in the current database; 2) insofar as data is available, validate solid-solution models with field occurrences and/or results of hydrothermal experiments; 3) determine what level of information is needed for modeling the zeolite dehydration process and develop an appropriate model; 4) critically evaluate ion-exchange data and models for zeolites of interest; and 5) use geochemical modeling to help evaluate the degree to which model predictions are controlled by the kinetics of dissolution/precipitation. Following this analysis an appropriate experimental program could be designed to acquire equilibrium thermodynamic data, to measure dissolution and/or precipitation rates, and to validate solid-solution models.

Clay Minerals

Existing thermodynamic data for clays are sparse [51,52]. The data base currently used with the EQ3/6 geochemical modeling code does not contain experimentally measured data for clays. The data base contains thermochemical approximations for idealized clays based on the summation of oxide components obtained by analysis of thermochemical data for macroscopic layer silicate analogues of clay minerals [53,54]. While the agreement between experimental values and the approximations are reasonable, this approach does not allow a realistic prediction of mineral fluid interaction for solid solutions such as clays. These short comings are related to the lack of quality experimental data, which in turn is directly related to the experimental and theoretical complexities of thermochemical analysis of clay minerals. Effective geochemical modeling of water-solid interactions at the temperatures and pressures expected in nuclear waste repositories will require a significant increase in the quantity and quality of the data for clay minerals. Smectite and illite clays are likely to play important roles in modeling the geochemical behavior of the site, however little data are available and existing data are often of questionable quality. Smectite is probably the most

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important clay mineral with respect to the performance modeling. It is the most surface active of the clay minerals, e.g., it has the largest specific surface and the largest specific cation exchange capacity of common clays [55]. It has a large stability field within the pressure, temperature and solution composition regimes expected for the repository [56], hence it is a likely clay mineral to form as a result of alteration of repository rocks. Smectites are widespread throughout the units underlying the Topopah Spring Member [57] and occur along possible water flow paths. Abundances as high as 50 percent occur in some units. Data on smectites are important for modeling the sorptive properties of the site as well.

Illite is also an important phase because it is ubiquitous, relatively abundant and can, under some conditions of temperature, pressure, solution composition and saturation, form from smectite [56,58]. Because the surface chemical and swelling properties of illite are appreciably different from smectite [55], such a transformation could significantly degrade the performance of engineered barriers based on smectite. Kaolinite and chlorite are not nearly as surface active as smectite and illite, do not have as large a stability field under projected repository conditions and, in the case of kaolinite have relatively well defined thermodynamic properties [59].

A critical evaluation of the clay data are needed in order to develop an experimental program to develop the necessary thermodynamic data base. Thermodynamic data for naturally occurring smectites is restricted to free energies of formation determined from room temperature solubility measurements. Studies have included montmorillonites and beidellite. Montmorillonites of the Wyoming-type have been reasonably well studied [60, 61, 62], but the rest of the smectite field is not well represented in the literature. There are no experimental data for any iron-rich species, e.g. nontronite, a necessity for modeling the full range of geochemical conditions.

There is a need to develop a geochemical data base for clays through a combination of experiment and critical evaluation of existing data. While the scope will depend on analysis of existing data and the findings of site-specific tests, the following elements should comprise the major portion of the work.

1. Develop a thermodynamic data base for a set of clay mineral specimens (primarily smectites and illites) whose mineralogical and compositional range is inclusive for the clays of importance in the proposed site.

2. Synthesize and measure thermodynamic properties for smectites and illites with com-

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positions that follow octahedral site binary exchange isotherms and develop solid-solution models for them.

3. Develop a set of interlayer cation exchange constants and mixing models for selected alkali and alkaline earth cartions on smectites over the temperature range of interest and for an appropriate range of surface charge densities.

Cements

The cohesive properties of cements are activated by mixing water with a largely anhydrous, finely-ground and reactive solid. The anhydrous solid is produced by calcining limestone with controlled amounts of aluminosilicates; gypsum is added after calcining to form cement. Portland cements are a family of such solids, with ranges of both major and minor phases and chemistry. The ranges depend both upon ultimate application of the cement and upon manufacture and raw materials. Additives are frequently used to tailor cement to a given application. Cements are thus calcium based phases. Solid solutions predominate both in the starting material and the grout that is formed by hydration. Hydration and consequent reactions occur over a period of seconds through years. Therefore, for temperatures up to at least 100°C, both the kinetics of hydration and metastability of phases formed need to be known. Furthermore, the sequence of phases formed and consumed, as well as the rates of reactions, will change as a function of temperature. The thermodynamics of cement is thus exceptionally complex and must draw upon experimentally determined kinetics as well as observations of the solid solutions and their coupled reactions.

The major phases of the anhydrous cement, excluding glassy material, and significant phases of the hydrous grout are listed in Table 8. This listing does not include the multitude of minor phases that are found in every cement and grout and does not include alkali metals, and possibly other ions, that can affect kinetics of hydration and transformation. However, a small percentage of alkalis is extremely important in buffering or "conditioning" large quantities of groundwater. The release of alkalis is thought to be responsible for maintaining pH values of groundwater in contact with cements at approximately 10.5 rather than predicted values of greater than 13 [63]. This important effect must be incorporated into new solid solutions models.

By volume, alite and belite are the most important materials in cement, and both hy-

drate to form C-S-H and CH[1]. The solutions produced are thus highly alkaline. Adequacy of thermochemistry and thermochemical models of highly alkaline, Ca-rich solutions thus need to be evaluated. Both alite and belite are solid solutions, even though the thermochemistry of the pure phases corresponding to alite and belite are well measured, no thermochemical measurements have been made on the solid solutions.

The hydration rate for alite is much more rapid than for belite. The control on hydration probably depends much more on the kinetics of hydration than on solid solution thermodynamics, although no data in the literature have been located that explore this question. Kinetic hydration experiments [64, 65, 66] in which incubation periods for hydration are investigated are in agreement but interpretations differ.

Calcium aluminate and "ferrite" are lesser reactant phases. The end members and their solid solution thermochemistry at 25°C has been investigated, but higher temperature thermochemistry of the solid solution has not.

Gypsum and portlandite are the only relatively pure phases in Table I and the thermochemistry of these two phases is well known.

The primary cementing agent in grout, up to at least 100°C, is C-S-H. The composition is variable, although it is approximately $C_3S_2H_3$. C-S-H (so written to imply no stoichiometry) has undergone extensive experimental investigation but as yet the varieties of C-S-H and transformation from one to another (if any) and transformations of C-S-H to well-defined phases are still unclear. A sophisticated chemical model for C-S-H has recently been proposed [67, 68] and can be tested in a thermochemical code. C-S-H increases its degree of polymerization as a function of time, at least through several years' duration, so a thermochemical code that attempts to model the behavior of C-S-H may need to include arbitrary kinetic functions to mimic this aging effect.

Ettringite is the other cementing agent in grouts, taking into its structure much of the S, A, and F of the system. Little thermochemistry has been done on ettringite, whether of an end member or the solid solution; the Russian data is of uncertain origin. No high temperature data on ettringite exist. Since ettringite contains the bulk of sulphate, knowledge of its thermochemistry is important in modeling the attack of sulphate-bearing waters on cement.

Almost no experimental thermodynamic data exist for two other significant phases that form around room temperature and above—C_4AH_{13} and the monosulphate solid solution.

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[1]Standard cement nomenclature, explained in the footnote to Table 8, is used.

At temperatures above 100°C, neither C-S-H nor ettringite is significant, but instead, the phases listed as "high temperature products" in Table I are generated. The only thermochemical data on these phases, whether at 298K or above, are from the Russian literature [69] and their source is uncertain; even whether the data are experimental or calculated is uncertain. Considering the importance of >100°C performance in the waste program, the thermochemistry of these compounds should be determined. At the elevated temperatures there is more of a tendency towards equilibrium, hence the thermochemical data for "high temperature products" would likely involve fewer kinetic models. True equilibration as calculated by a model such as EQ6, however, tends to yield a number of anhydrous phases not noted either in cemenets set at elevated temperaures or in "ancient" cements. No kinetic experiments have been found on transformation of hydrous "cement" phases to anhydrous products. Such kinetic experiments would be necessary to predict the performance of cement over a time span of thousands of years.

The data on "high temperature products" of cement setting come from the limited number of experiments in which the cement was set under hydrothermal conditions to mimic conditions in oil well or geothermal well cementing. Little literature has been found that explores the phase chemistry of cements that have initially set near room temperature but have been subjected to elevated temperatures for an extended period of time such as might occur in a repository. Ambient-temperature setting of cement with later heating may be the conditions in a repository, hence this lack of data needs to be remedied. Experiments should be performed on setting cement at room temperature and then subjecting them to hydrothermal conditions for extended time. Such experiments would yield data both on kinetic mechanisms of hydration and temperature ranges over which individual phases are important. Such data would also aid in testing and developing kinetic and thermodynamic models on the aging of cements that always remain at ambient temperature.

Table 8. Significant Cement Phases*

	Phase name	Cement Nomenclature**
ANHYDROUS PHASES		
SOLID SOLUTIONS		
(reactant)	alite	C_3S
(reactant)	belite	C_2S
(reactant)	aluminate	C_3A
(reactant)	ferrite	$C_6A_2F\text{-}C_6AF_2$
HYROUS PHASES		
PURE PHASES		
(reactant)	gypsum	$C\bar{S}H_2$
(product)	portlandite	CH
SOLID SOLUTIONS		
(product)	calcium silicate hydrate get	$C\text{-}S\text{-}H$
(product)	ettringite	$C_6A\bar{S}_3H_{32} - C_6A_{0.5}\ F_{0.5}\bar{S}_3H_{32}$
(product)		C_4AH_{13}
(product)	monosulfate	$C_3A.C\bar{S}.H_{12}$
HIGH TEMPERATURE PRODUCTS		
(>100 <200 C)	hillebrandite?	alpha-C_2SH
(>200 C)		$C_6S_2H_3$
(>100 <150 C)	tobermorite	$C_5S_6H_5$
(>150 C with added SiO_2)	xonotlite	C_6S_6H
(>150 C with added SiO_2)	gyrolite	$C_2S_3H_2$

*Largely after Bensted (1983)

**Nomenclature: $A = Al_2O_3$ $F = Fe_2O_3$ $C = CaO$ $S = SiO_2$

$\bar{S} = SO_4$ $H = H_2O$

Acknowledgements

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APPENDIX A

Plots of the Inventory of Waste Radionuclides in Spent
PWR Reactor Fuel with a Burnup of 30,000 MWd/MTIHM
as a Function of Time After Discharge from Reactor
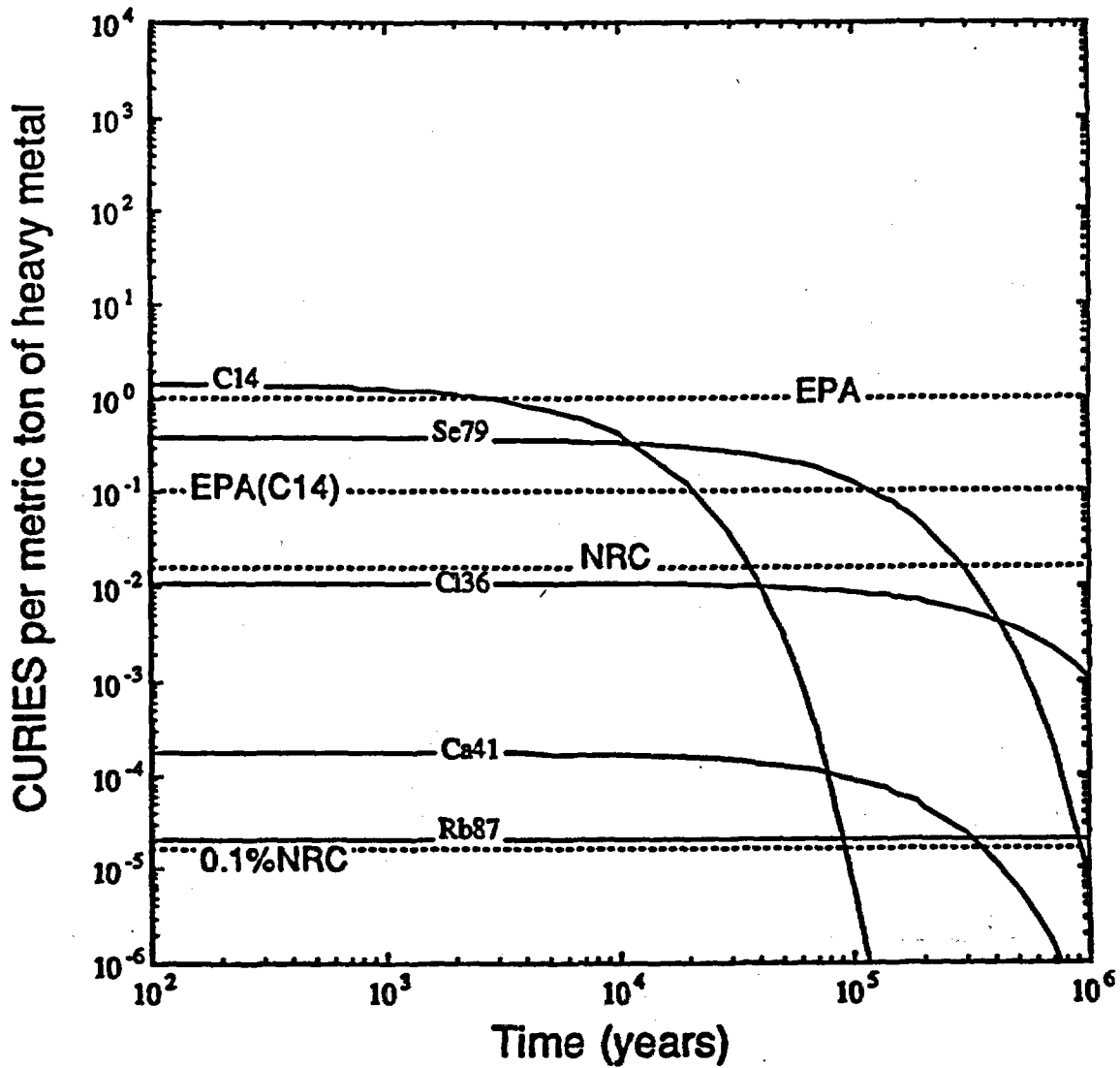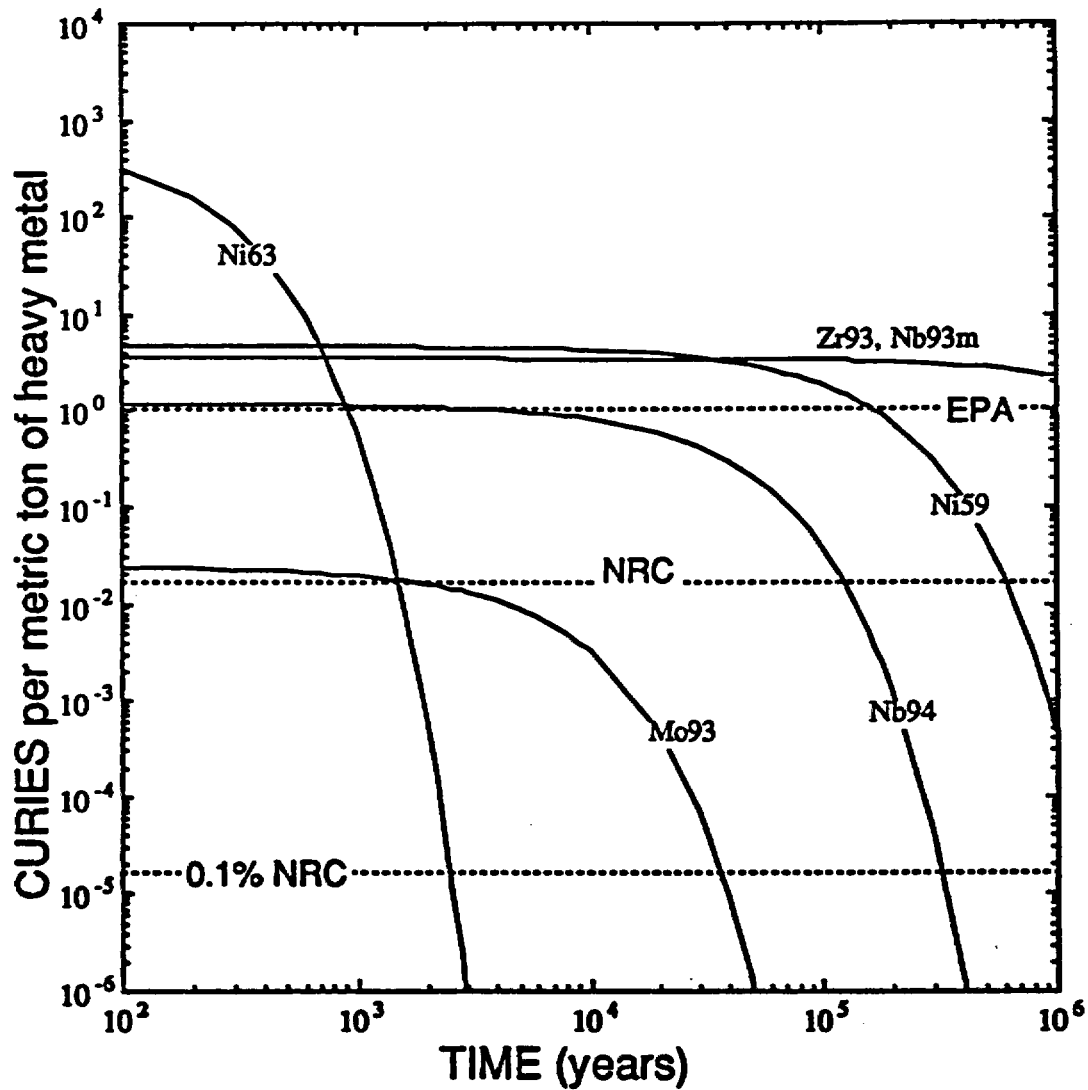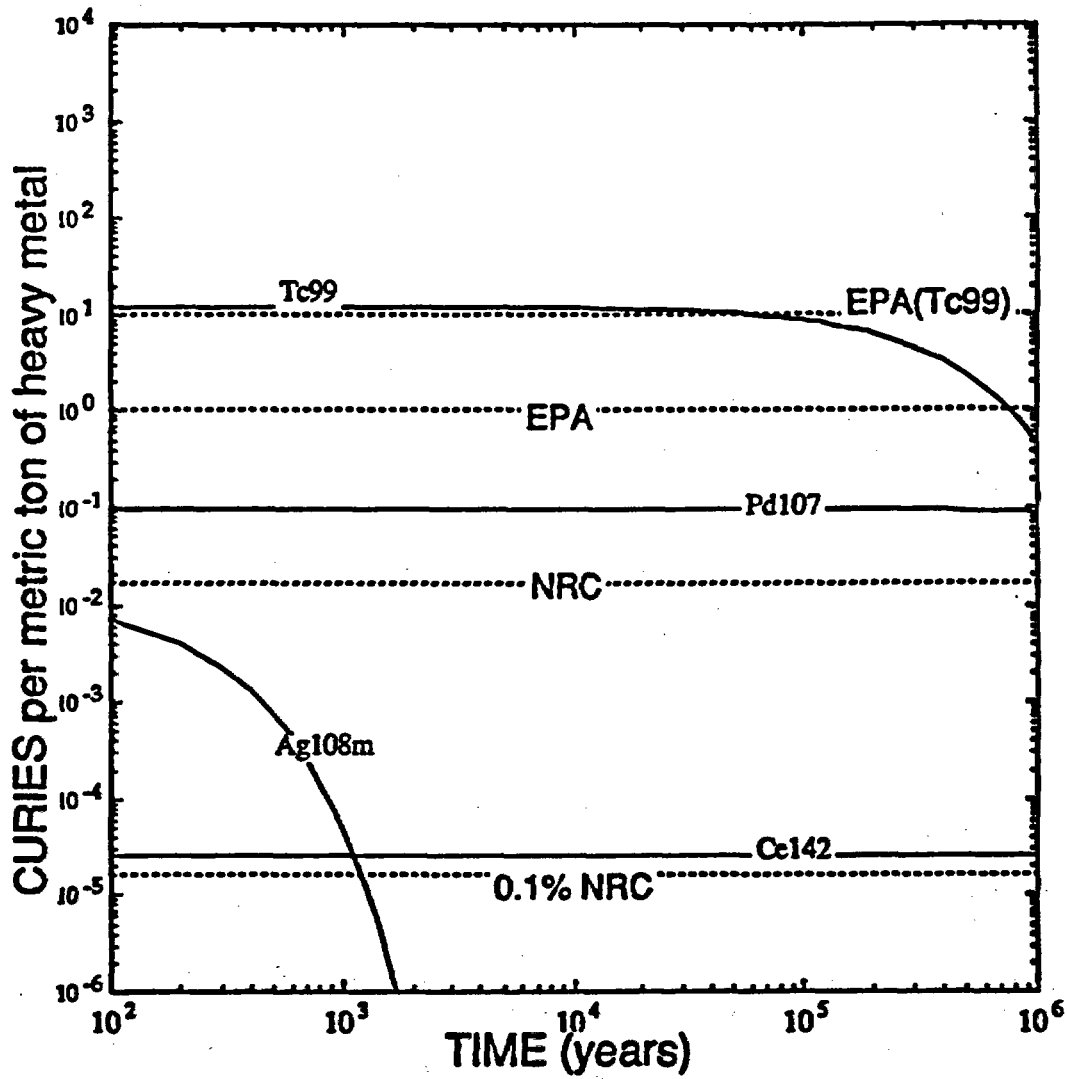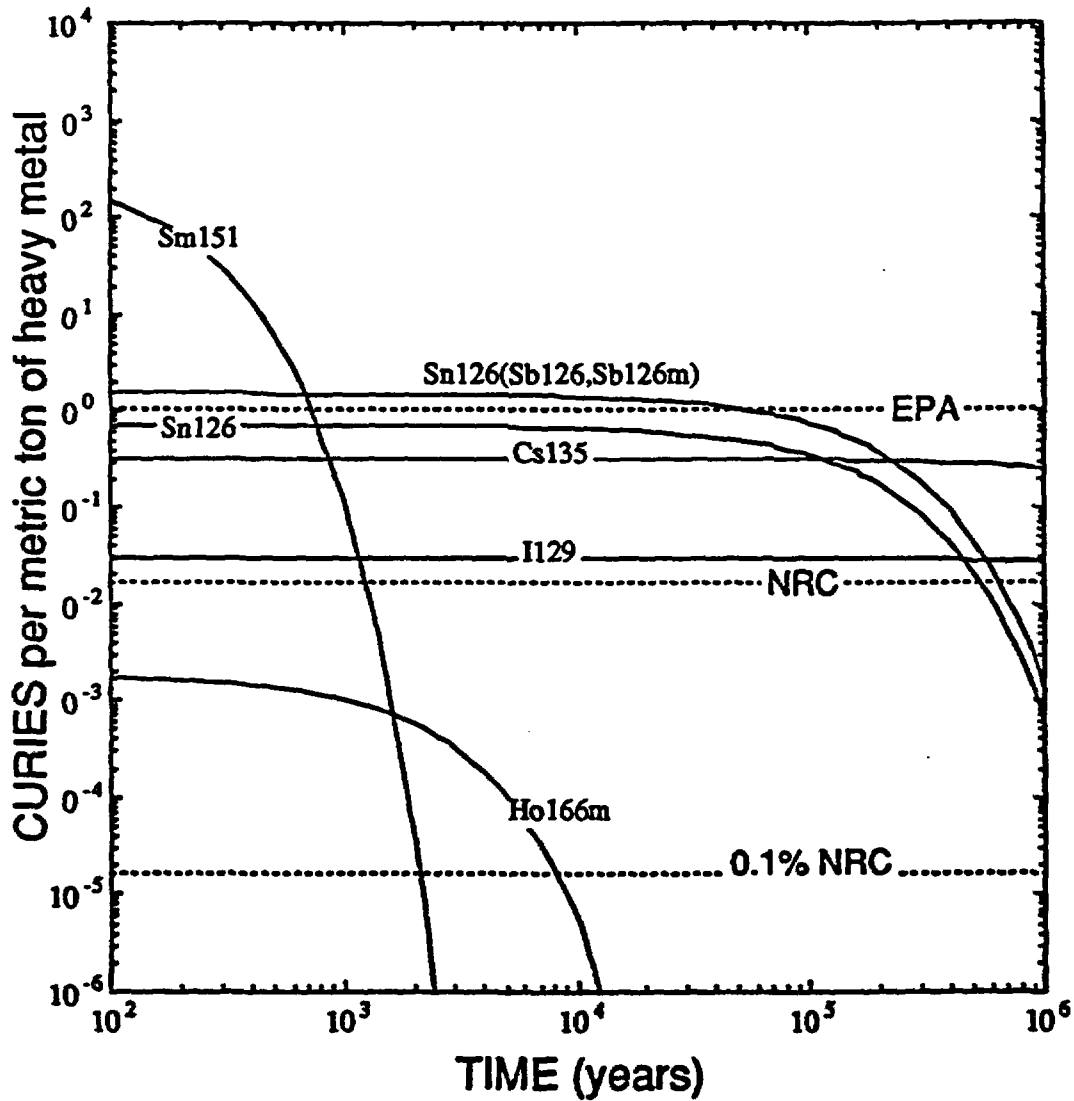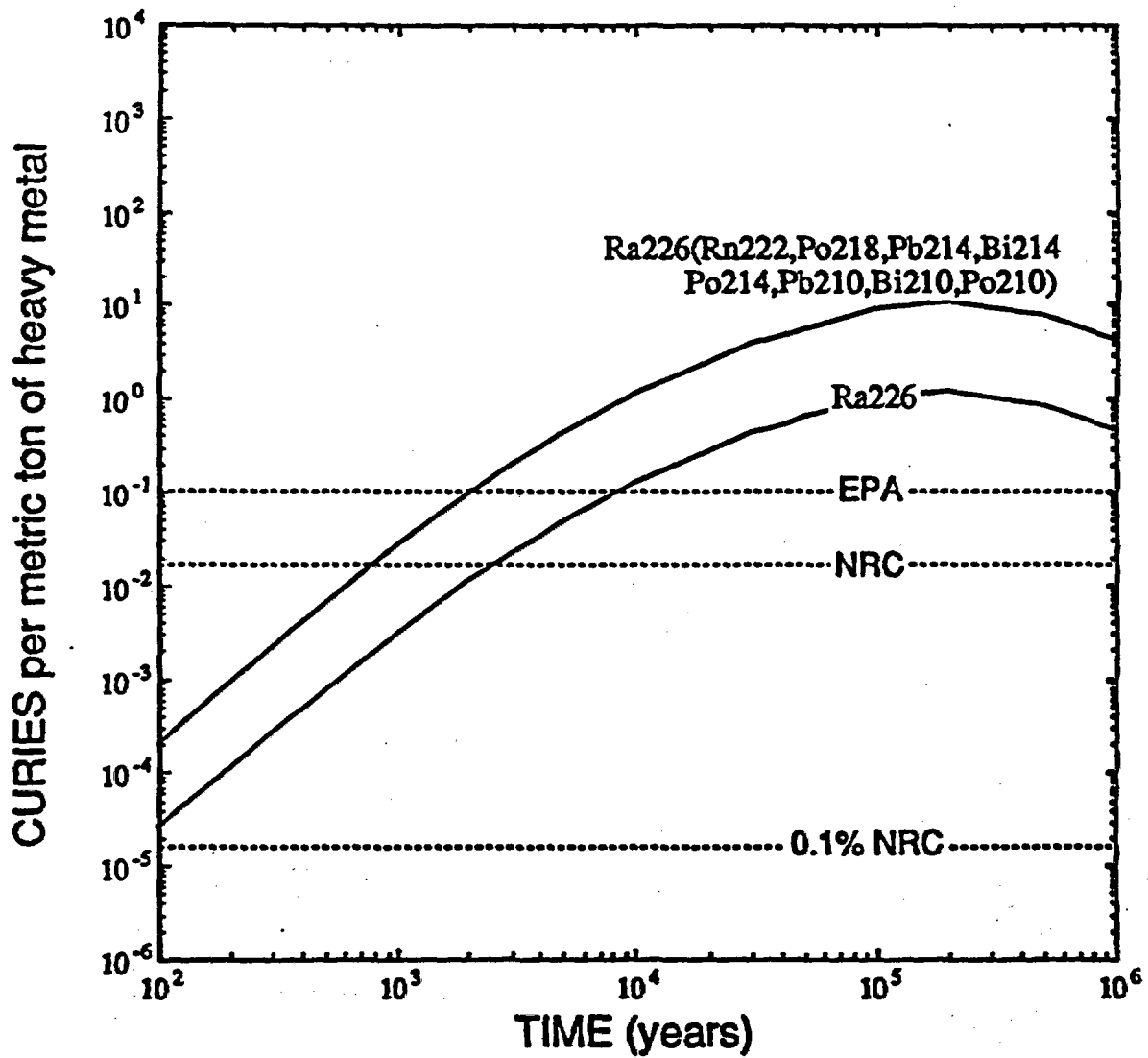
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Appendix A

Figure A-1. Log-log plot of the quantity of beta (β^-) emitting radionuclides in a 30,000 megawatt-day (MWd)/MTIHM reactor fuel burnup in units of Curies per metric ton of initial heavy metal (MTIHM) for ^{14}C, ^{36}Cl, ^{41}Ca, ^{79}Se, and ^{87}Rb vs. Time. See the text for a discussion of the several NRC and EPA release limits indicated by the dashed lines.

Figure A-2. Log-log plot of the quantity of beta (β^-) emitting radionuclides in a 30,000 megawatt-day (MWd)/MTIHM reactor fuel burnup in units of Curies per metric ton of initial heavy metal (MTIHM) for ^{59,63}Ni, ^{93}Zr, ^{93}Mo, and ^{93}m, ^{94}Nb vs. Time. See the text for a discussion of the several NRC and EPA release limits indicated by the dashed lines.
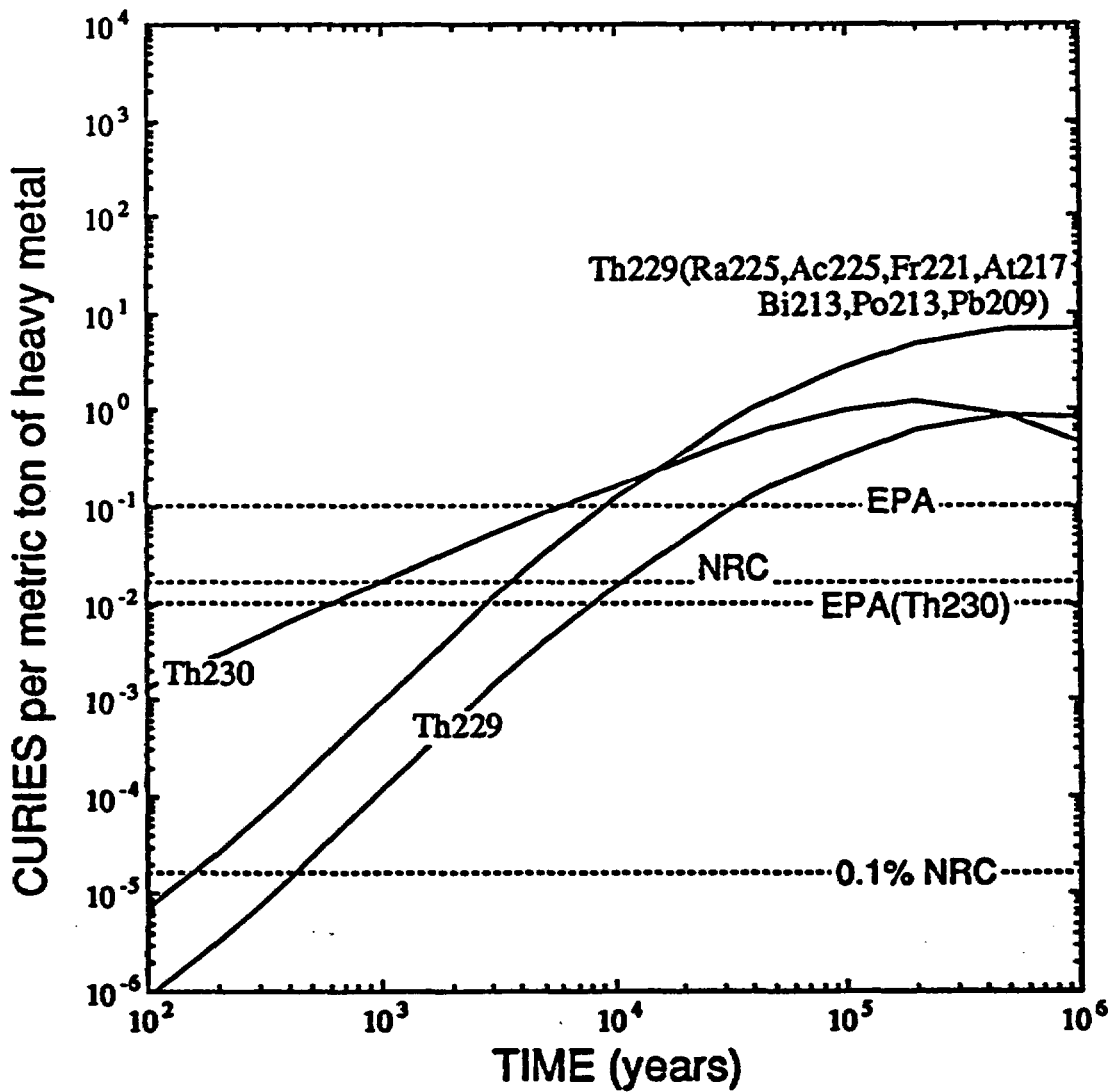
Figure A-3. Log-log plot of the quantity of beta (β^-) emitting radionuclides in a 30,000 megawatt-day (MWd)/MTIHM reactor fuel burnup in units of Curies per metric ton of initial heavy metal (MTIHM) for ^{99}Tc, ^{107}Pd, ^{108m}Ag, and ^{142}Ce vs. Time. See the text for a discussion of the several NRC and EPA release limits indicated by the dashed lines.
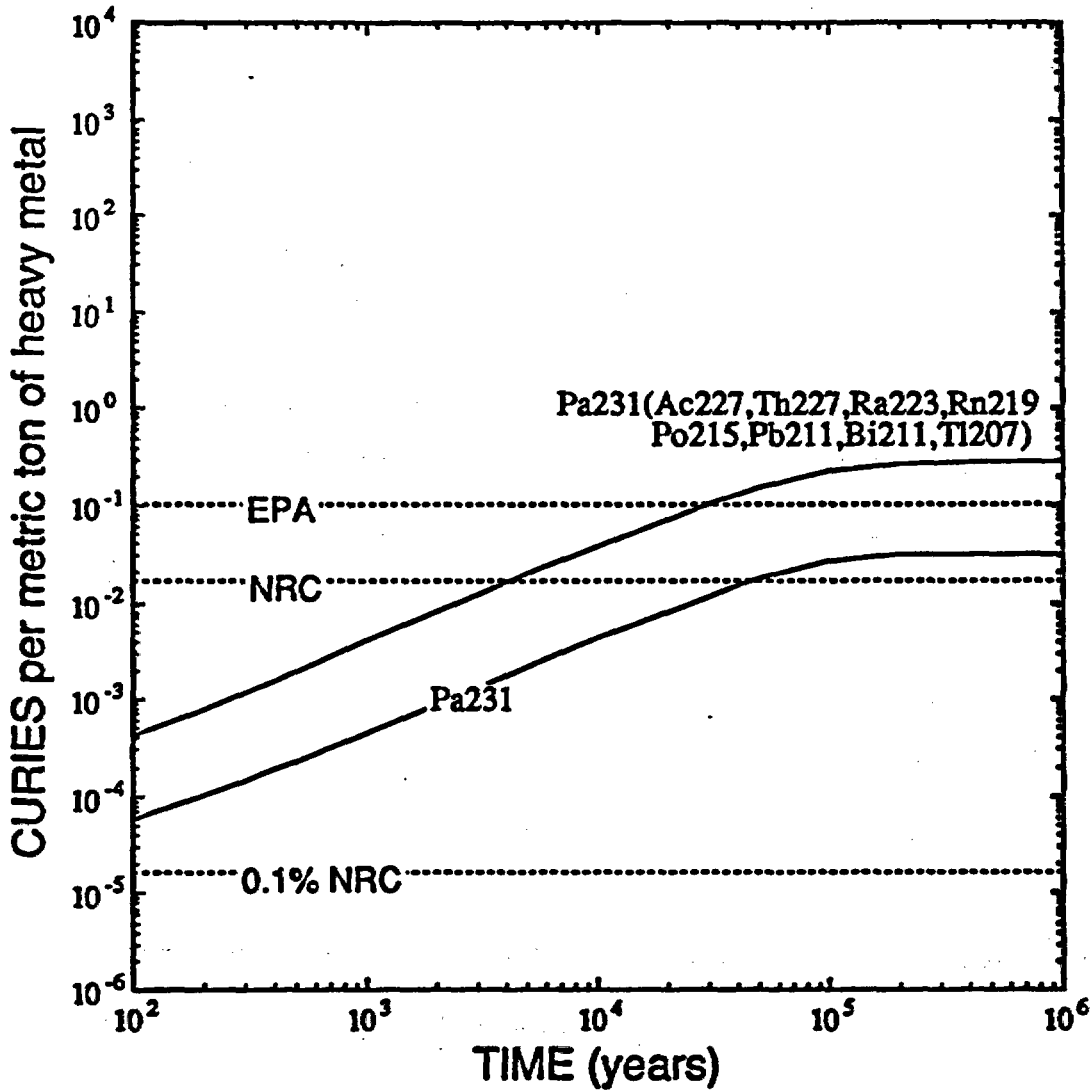
Figure A-4. Log-log plot of the quantity of beta (β^-) emitting radionuclides in a 30,000 megawatt-day (MWd)/MTIHM reactor fuel burnup in units of Curies per metric ton of initial heavy metal (MTIHM) for ^{126,126m}Sb, ^{126}Sn, ^{129}I, ^{135}Cs, and ^{166m}Ho vs. Time. See the text for a discussion of the several NRC and EPA release limits indicated by the dashed lines.

Figure A-5. Log-log plot of the quantity of alpha (α) emitting radionuclides in a 30,000 megawatt-day (MWd)/MTIHM reactor fuel burnup in units of Curies per metric ton of initial heavy metal (MTIHM) for ^{226}Ra and the associated relatively short lived daughters (< 25 years) vs. Time. See the text for a discussion of the several NRC and EPA release limits indicated by the dashed lines.
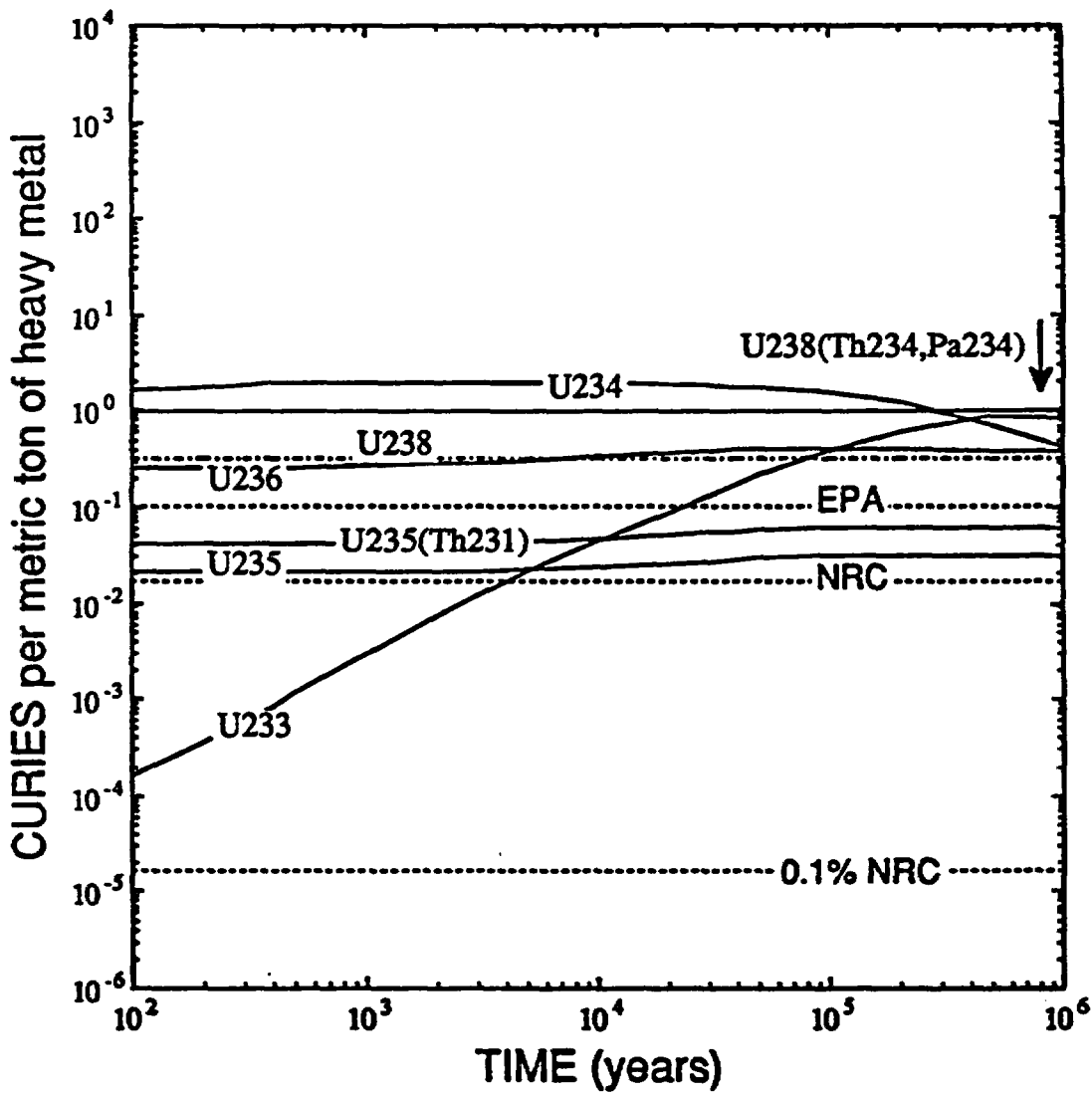
Figure A-6. Log-log plot of the quantity of alpha (α) emitting radionuclides in a 30,000 megawatt-day (MWd)/MTIHM reactor fuel burnup in units of Curies per metric ton of initial heavy metal (MTIHM) for ^{229}Th and the associated relatively short lived daughters (< 25 years) and ^{230}Th vs. Time. See the text for a discussion of the several NRC and EPA release limits indicated by the dashed lines.

Figure A-7. Log-log plot of the quantity of alpha (α) emitting radionuclides in a 30,000 megawatt-day (MWd)/MTIHM reactor fuel burnup in units of Curies per metric ton of initial heavy metal (MTIHM) for [231]Pa and the associated relatively short lived daughters (< 25 years) vs. Time. See the text for a discussion of the several NRC and EPA release limits indicated by the dashed lines.
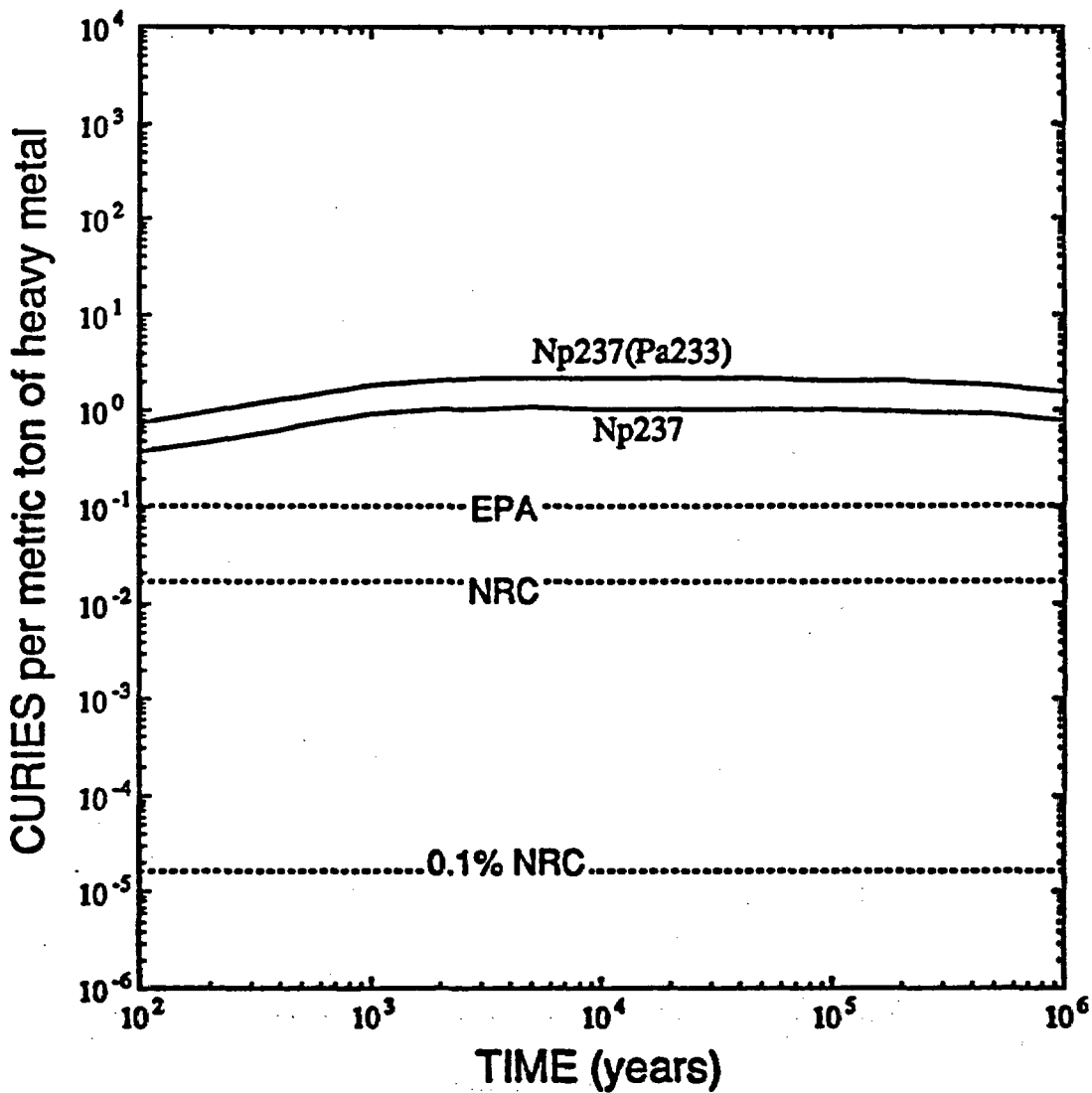
Figure A-8. Log-log plot of the quantity of alpha (α) emitting radionuclides in a 30,000 megawatt-day (MWd)/MTIHM reactor fuel burnup in units of Curies per metric ton of initial heavy metal (MTIHM) for ^{233,234,235,236,238}U and the associated relatively short lived daughters (< 25 years) vs. Time. See the text for a discussion of the several NRC and EPA release limits indicated by the dashed lines.
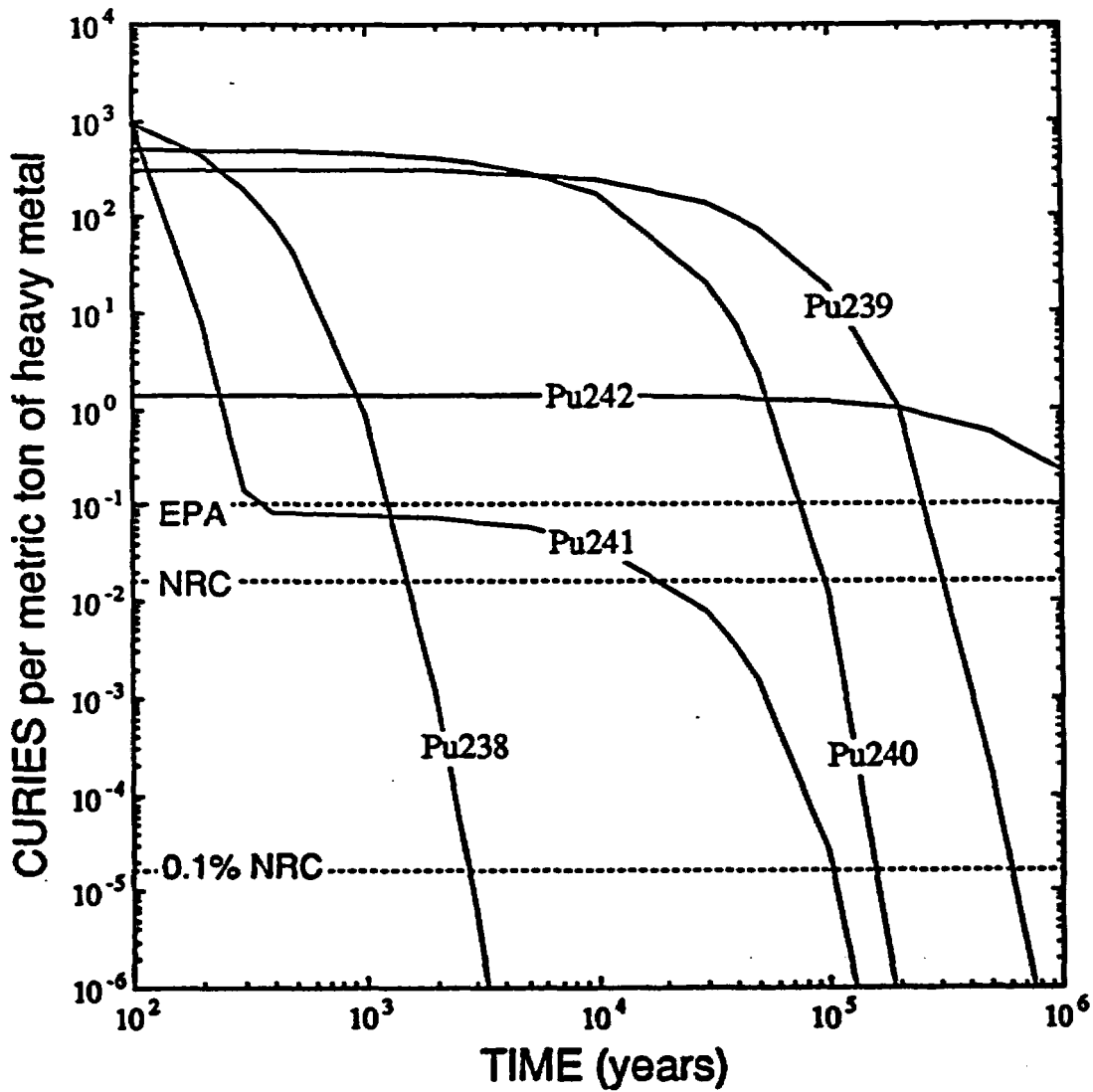
Figure A-9. Log-log plot of the quantity of alpha (α) emitting radionuclides in a 30,000 megawatt-day (MWd)/MTIHM reactor fuel burnup in units of Curies per metric ton of initial heavy metal (MTIHM) for ^{237}Np and the associated relatively short lived daughter (< 25 years) vs. Time. See the text for a discussion of the several NRC and EPA release limits indicated by the dashed lines.
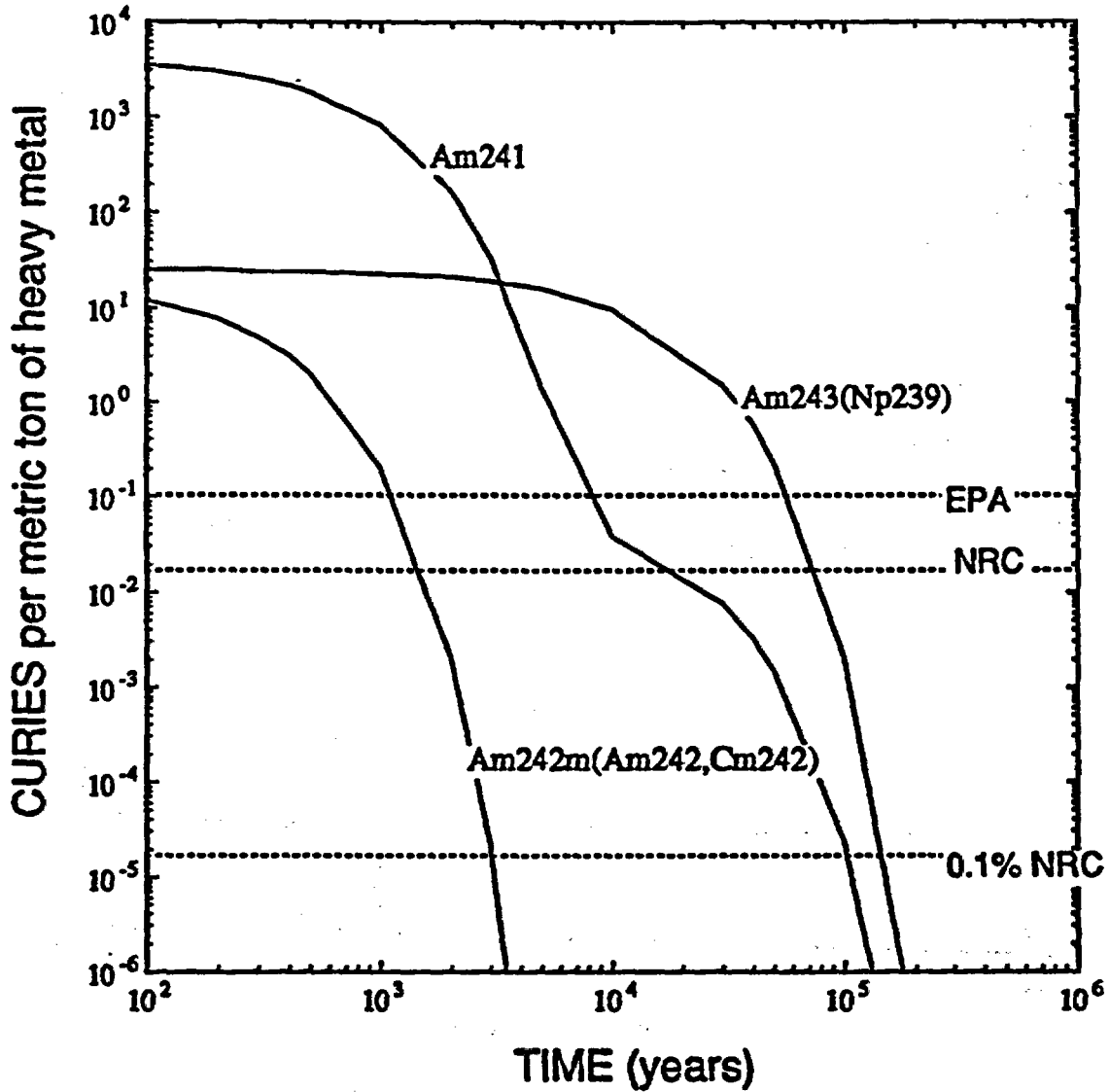
Figure A-10. Log-log plot of the quantity of alpha (α) emitting radionuclides in a 30,000 megawatt-day (MWd)/MTIHM reactor fuel burnup in units of Curies per metric ton of initial heavy metal (MTIHM) for ^{238,239,240,241,242}Pu vs. Time. See the text for a discussion of the several NRC and EPA release limits indicated by the dashed lines.

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Figure A-11. Log-log plot of the quantity of alpha (α) emitting radionuclides in a 30,000 megawatt-day (MWd)/MTIHM reactor fuel burnup in units of Curies per metric ton of initial heavy metal (MTIHM) for ^{241,242,242m,243}Am and the associated relatively short lived daughters (< 25 years) vs. Time. See the text for a discussion of the several NRC and EPA release limits indicated by the dashed lines.
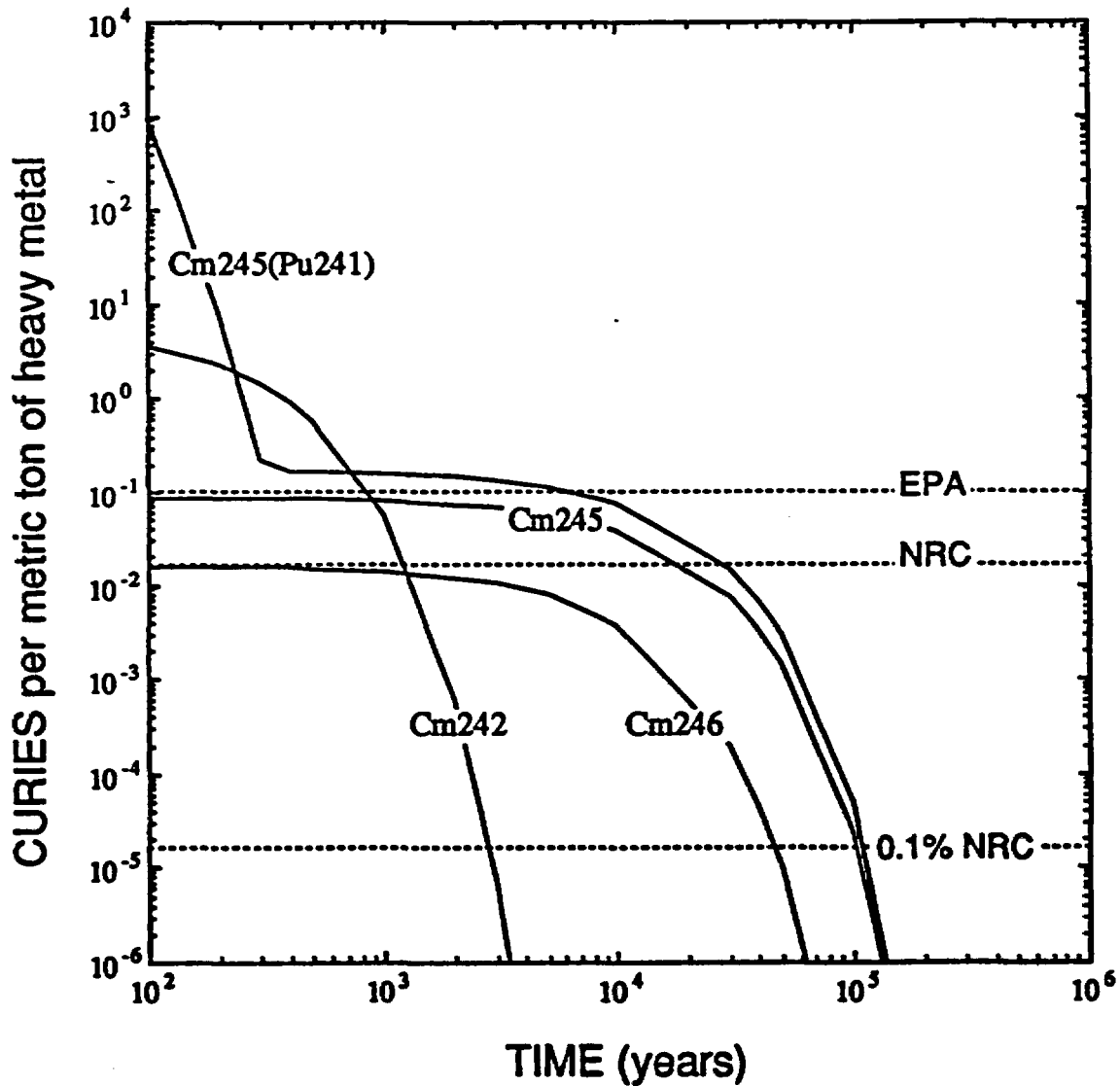
Figure A-12. Log-log plot of the quantity of alpha (α) emitting radionuclides in a 30,000 megawatt-day (MWd)/MTIHM reactor fuel burnup in units of Curies per metric ton of initial heavy metal (MTIHM) for ^{242,245,246}Cm and the associated relatively short lived daughter (< 25 years) vs. Time. See the text for a discussion of the several NRC and EPA release limits indicated by the dashed lines.

APPENDIX B

Inventory of Waste Radionuclides in Spent PWR and BWR Reactor Fuel
for Various Burnup Periods andTimes After Discharge from Reactor

Inventory of Waste Radionuclides in a
Boiling Water Reactor (BWR) for a 5,000 Megawatt-Day
Burnup Period and for Various Times
After Discharge from the Reactor

Inventory of Waste Radionuclides in a
Boiling Water Reactor (BWR) for a 30,000 Megawatt-Day
Burnup Period and for Various Times
After Discharge from the Reactor

	Elapsed Decay Time	Pages
1.	100 years	B-69,72
2.	200 years	B-73,76
3.	300 years	B-77,80
4.	400 years	B-81,84
5.	500 years	B-85,88
6.	1,000 years	B-89,92
7.	2,000 years	B-93,96
8.	3,000 years	B-97,100
9.	5,000 years	B-101,104
10.	10,000 years	B-105,108
11.	30,000 years	B-109,112
12.	40,000 years	B-113,116
13.	50,000 years	B-117,120
14.	100,000 years	B-121,124
15.	200,000 years	B-125,128
16.	500,000 years	B-129,132
17.	1,000,000 years	B-133,136

Inventory of Waste Radionuclides in a
Pressurized Water Reactor (PWR) for a 30,000 Megawatt-Day
Burnup Period and for Various Times
After Discharge from the Reactor

Inventory of Waste Radionuclides in a
Pressurized Water Reactor (PWR) for a 60,000 Megawatt-Day
Burnup Period and for Various Times
After Discharge from the Reactor

	Elapsed Decay Time	Pages
1.	100 years	B-205,208
2.	200 years	B-209,212
3.	300 years	B-213,216
4.	400 years	B-217,220
5.	500 years	B-221,224
6.	1,000 years	B-225,228
7.	2,000 years	B-229,232
8.	3,000 years	B-233,236
9.	5,000 years	B-237,240
10.	10,000 years	B-241,244
11.	60,000 years	B-245,248
12.	40,000 years	B-249,252
13.	50,000 years	B-253,256
14.	100,000 years	B-257,260
15.	200,000 years	B-261,264
16.	500,000 years	B-265,268
17.	1,000,000 years	B-269,272