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Waste Inventory And Preliminary Source Term Model For The Greater Confinement Disposal Site At The Nevada Test Site

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WASTE INVENTORY AND PRELIMINARY SOURCE TERM MODEL
FOR THE GREATER CONFINEMENT DISPOSAL SITE
AT THE NEVADA TEST SITE

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ABSTRACT

Currently, there are several Greater Confinement Disposal (GCD) boreholes at the Radioactive Waste Management Site (RWMS) of the Nevada Test Site. These are intermediate-depth boreholes used for the disposal of special case wastes, that is, radioactive wastes within the Department of Energy complex that do not meet the criteria established for disposal of high-level waste, transuranic waste, or low-level waste. A performance assessment is needed to evaluate the safety of the GCD site, and to examine the feasibility of the GCD disposal concept as a disposal solution for special case wastes in general. This report documents the effort in defining all the waste inventory presently disposed of at the GCD site, and the inventory and release model to be used in a performance assessment for compliance with the Environmental Protection Agency's 40 CFR 191.

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MASTER

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1.0 INTRODUCTION

Since the authorization of the Waste Isolation Pilot Plant deep geologic repository in 1980 [Public Law 96-164], permanent disposal of transuranic (TRU) radioactive wastes resulting from defense activities has become a primary focus of the U.S. defense waste management program. In compliance with the Energy National Security and Military Applications of the Nuclear Energy Act of 1982, the U.S. Department of Energy (DOE) issued a reference plan in June 1983 for permanent disposal of these wastes and outlined the long-term strategy for disposal of newly generated wastes, as well as for wastes that have been in retrievable storage at several sites in the U.S.

Although comprehensive, this reference plan did not address a permanent disposal strategy for wastes that do not meet the certification and acceptance criteria for the Waste Isolation Pilot Plant. In response to recommendations from the U.S. General Accounting Office in 1985 [GAO, 1985], the DOE issued a supplemental reference plan in June 1987 and analyzed comparative methods for management of these difficult-to-certify transuranic wastes. The supplemental reference plan indicates that only approximately two percent of the volume of all difficult-to-certify transuranic waste will not be practicably certifiable by further processing and that an alternative disposal method for these special case TRU wastes will be needed.

In 1985, the U.S. Environmental Protection Agency (EPA) promulgated environmental protection standards for land disposal of high-level and transuranic radioactive wastes (40 CFR 191)[EPA, 1985]. Although directed primarily at disposal in deep geologic repositories, these standards apply to land disposal by any method and apply to any alternative disposal method for transuranic special case wastes proposed by the DOE.

The Low-Level Radioactive Waste Policy Act in 1985 [Public Law 99-240] identified the DOE as the federal agency responsible for disposal of low-level waste (LLW) that exceeds the Class C limits defined by the U.S. Nuclear Regulatory Commission [NRC, 1982]. It is generally agreed that greater-than-Class-C waste is not suitable for conventional shallow land burial and that an alternative disposal method will be needed [DOE, 1988a].

A group of wastes that does not fit into typical management plans developed for the major waste types has thus emerged that is called "special case wastes," or "orphan wastes." These wastes require special management and disposal schemes yet to be specified.

In 1981, the Defense Low-Level Waste Management Program sponsored by the DOE approved funding at the Nevada Operations Office to demonstrate the Greater Confinement Disposal (GCD) technology primarily for low-level radioactive waste not suitable for conventional shallow land burial. At the U.S. DOE Nevada Test Site (NTS), GCD utilizes intermediate-depth, vertical-borehole technology in desert alluvium and has demonstrated the technical feasibility of intermediate-depth disposal of a variety of low-level wastes. Because of the location and design, the NTS GCD site is also potentially

suited for the disposal of special case transuranic (TRU) wastes. As a result, this technology may be a candidate solution for the DOE's alternate disposal methods for special case wastes in general.

Adaptation of existing GCD technology for disposal of large quantities of special case wastes requires the design, permitting, construction, and operation of a radioactive waste disposal facility. Critical to planning such a facility is an early assessment of the potential for success in meeting the various disposal requirements. Because a small inventory of transuranic waste has been disposed of at the site, there is an excellent opportunity for conducting a preliminary performance assessment for 40 CFR 191. The objectives of a preliminary performance assessment of the existing transuranic waste inventory are twofold. First, the results of the preliminary assessment will indicate the likelihood of meeting the 40 CFR 191 requirements. Second and more important, the results of these analyses can be used to identify the important parameters and components driving the overall performance of the disposal system.

The first step in a performance assessment analysis is to characterize the various components of the system and develop a conceptual model. There are three components of the disposal system: waste inventory, facility, and site geology and hydrology. For the waste inventory, not only do the initial amounts need to be defined, but also potential releases of radionuclides from the GCD boreholes need to be specified in the performance assessment calculations. A preliminary performance assessment of the GCD site is being conducted using the information from this report [Price, et al., 1991].

Three subtasks were performed to define the initial inventory and the potential releases to be used for a performance assessment:

1. Identification and definition of all presently disposed of GCD wastes.
2. Determination of which of these wastes are ruled by 40 CFR 191, and
3. Definition of potential radionuclide releases from GCD boreholes.

This report documents the results of the above subtasks. The waste inventory in each GCD borehole is described in Chapter 2. Chapter 3 explains how and why certain waste inventory was included for the 40 CFR 191 compliance assessment. Finally, the preliminary release model used in the performance assessment is described in Chapter 4.

2.0 PRESENTLY BURIED GCD WASTES

The GCD site is located at the Radioactive Waste Management Site (RWMS) in Area 5 of the NTS on an alluvial fan in the Frenchman Flat area (Figure 2.1). Figure 2.2 shows the design of a GCD borehole. The disposal facility consists of an unlined 10-ft-diameter, 120-ft-deep borehole. Wastes are placed in the borehole to 70 ft below the land surface, and the borehole is then backfilled with the original soil to the top. Appendix A describes in detail the operations for the receipt and disposal of GCD wastes.

Currently there are 13 GCD boreholes at the RWMS (Figure 2.3). Of the 13 boreholes, 9 contain wastes, and 4 are empty. Of the 9 boreholes that contain wastes, 7 have been filled and backfilled, and 5 contain classified wastes. The classified boreholes are located within the classified area of RWMS. The status of each GCD borehole is summarized in Table 2.1.

Table 2.1
GCD Boreholes at the Area 5 RWMS

<u>Borehole</u>	<u>Area</u>	<u>Status</u>
1	Classified	Closed
2	Classified	Closed
3	Classified	Closed
4	Classified	Closed
5	Unclassified	Closed
6	Unclassified	Open
7	Classified	Open
8	Classified	Empty
9	Unclassified	Empty
10	Unclassified	Closed
11	Unclassified	Empty
12	Unclassified	Empty
GCDT	Unclassified	Closed

A "brute force" approach was used in defining the contents of the 9 GCD boreholes that contain wastes. First, all documents relevant to the buried GCD inventory were examined, including reports documenting wastes destined for GCD, waste shipping records sent to the DOE/NV, and waste receipt records at Reynolds Electrical & Engineering Company (REECo), which manages the RWMS site. These documents were compared with each other and also with the computer data base maintained at the RWMS.

Figure 2.1. Location Map for the GCD Site (Dickman, 1989)

Figure 2.2. GCD Borehole Design

Figure 2.3. GCD Borehole Locations at the RWMS

Whenever discrepancies or inadequate information were identified, further information was requested by telephone. If this did not lead to a satisfactory resolution, the facility that generated the original wastes was visited. At the waste-generating facility, site personnel were consulted, and sometimes shipping records were examined. Table 2.2 summarizes the trips taken for this task. With this approach, satisfactory resolutions could usually be obtained. When discrepancies could not be resolved, all reported values were assumed to be equally reliable, and a range was used to represent the uncertainty of the inventory.

With the approach described above, the contents in each GCD borehole were identified with reasonable confidence.

A transuranic (TRU) waste is defined in 40 CFR 191 as a waste that contains alpha-emitting transuranic elements (i.e., elements with atomic numbers greater than 92) with half-lives greater than 20 years and in concentrations greater than 100 nCi per gram of waste. Otherwise, the transuranic radionuclide is categorized as low-level waste (LLW). Therefore, whenever an alpha-emitting transuranic radionuclide is present in a GCD waste, the concentration of that radionuclide in the waste needs to be determined to decide whether the waste is TRU waste or LLW. Unfortunately, many of the GCD records show only the gross weight of a waste-containing package, so it is not possible to determine the exact weight of the waste. Instead, the activity of a transuranic radionuclide is divided by the gross weight of the whole package; if the result is an order-of-magnitude less than 100 nCi/g, the waste is categorized as LLW in this report. On the other hand, if the result is greater than or close to 100 nCi/g, the waste is considered to be TRU waste.

The following is a detailed description of the wastes in each borehole. The reported amount of radioactivity corresponds to the inventory as of January 1991.

2.1 Contents of Boreholes 1, 2, and 3—Nuclear Weapon Accident Residues (NWAR) Wastes

The NWAR wastes were generated from various nuclear weapon accidents. Because these wastes usually contain shapes that are classified in nature, they have been categorized as classified wastes.

2.1.1 Waste Quantity

The NWAR wastes were disposed of at the GCD site in March 1984 in two shipments. They are contained in 15 packages in 3 GCD boreholes (Boreholes 1, 2, and 3). These wastes are packaged in plywood and metal boxes, and in metal barrels. The plywood boxes are coated with fiberglass. Table 2.3 [Mason & Hanger, 1983] provides information on the NWAR packages. Figure 2.4 [REECo, 1984] shows the arrangement of NWAR packages in the GCD boreholes. Probertite, which has a high boron content, was used to backfill around the packages in the boreholes, as indicated by the hashmarked areas in Figure 2.4.

Table 2.2
Trips Taken for Defining GCD Inventory

Date	Trip #	Facility & Location	Contact	Activity
12/14-15/89	1	REEC Las Vegas, NV	Art Vollmer	Examine unclassified GCD files
12/15/89		DOE/NV Las Vegas, NV	Darrell Warren	Discuss GCD waste acceptance criteria Examine classified NWAR document
12/21/89	2	Rocky Flats Plant Golden, CO	Rick Bauma	Review general operations Examine waste generation streams Examine packaging procedures
02/06/90	3	Rockwell Int'l Canoga Park, CA	Bob Frazier	Review general operations Examine waste generation streams Examine waste shipment records
02/07/90		REEC Las Vegas, NV	Art Vollmer Dick Roberts	Review and critique draft inventory document Address questions and discrepancies
02/08/90		EG&G-Idaho Idaho Falls, ID	Eric Williams Don Kudera Charles Wickland	Discuss Defense Low Level Waste Management Program (DLLWMP) survey Resolve some inventory discrepancies Review Rocky Flats Plant information
02/20/90	4	DOE/AL Albuquerque, NM	Tom Jones	Discuss NWAR wastes

Table 2.2
Trips Taken for Defining GCD Inventory (concluded)

Date	Trip	Facility & Location	Contact	Activity
02/26/90	5	DOE/NV Las Vegas, NV	Bob Ramstead Darrell Warren	Examine classified files Review classified NWAR document
02/28/90	6	DOE/AL Albuquerque, NM	Dave Foster	Discuss NWAR wastes
03/26/90	7	DOE/NV Las Vegas, NV	Bob Ramstead	Review DOE Form 741s
12/13/90	8	DOE/NV REECo Las Vegas, NV	Bob Ramstead Dick Roberts	Examine DOE Form 741s Examine REECO records

Table 2.3
Information on NWAR Waste Packages

Item No.	Overpack Description				Container Within Overpack	
	Gross Weight (lb)	Cubic Feet	Size	Type	Size	Type
1	9,500	400.0	8.8 x 6.5 x 7.0 ft.	Metal Pan w/ply cover	8.5 x 6.2 x 7.0 ft.	CONEX
2	7,000	400.0	8.8 x 6.5 x 7.0 ft.	Metal Pan w/ply cover	8.5 x 6.2 x 7.0 ft.	CONEX
3	7,000	400.0	8.8 x 6.5 x 7.0 ft.	Metal Pan w/ply cover	8.5 x 6.2 x 7.0 ft.	CONEX
4	14,000	400.0	8.8 x 6.5 x 7.0 ft.	Metal Pan w/ply cover	8.5 x 6.2 x 7.0 ft.	CONEX
5	4,200	400.0	8.8 x 6.5 x 7.0 ft.	Metal Pan w/ply cover	8.5 x 6.2 x 7.0 ft.	CONEX
6	3,500	120.0	7.0 x 4.0 x 4.3 ft.	744-7A Plywood	Transferred from dumpster container	
7	3,300	130.0	5.2 x 5.0 x 5.0 ft.	Metal	As received; heavy metal	
8	320	8.0	35 x 24 D. in.	55 gal	26 x 18 D. in.	AN CAN
9	380	13.0	2.4 x 2.4 x 2.3 ft.	Plywood	18 x 25 D. in.	AN CAN
10	340	13.0	2.4 x 2.4 x 2.3 ft.	Plywood	18 x 25 D. in.	AN CAN

Table 2.3
Information on NWAR Waste Packages (Concluded)

Item No.	Overpack Description				Container Within Overpack	
	Gross Weight (lb)	Cubic Feet	Size	Type	Size	Type
11	1,200	64.0	4 x 5 x 3.2 ft.	Plywood	21 x 17 D. in. 22 x 22 D. in. 18 x 29 D. in. 22 x 24 D. in.	AN CAN AN CAN AN CAN AN CAN
12	380	14.0	39 x 28 D. in.	83 gal	35 x 24 D. in.	55 gal
13	400	14.0	39 x 28 D. in.	83 gal	34 x 24 D. in.	55 gal
14	1,500	73.0	4.6 x 4.4 x 3.6 ft.	Plywood	4-1/4 x 3-3/4 x 2-3/4 ft.	Wood
15	1,750	90.0	5.4 x 4.75 x 3.5 ft.	Plywood	5 x 4-1/2 x 2-3/4 ft.	Wood

Shaft #3 - 10' dia.
No Scale

Shaft #2 - 12' dia.
No Scale

Shaft #1 - 12' dia.
No Scale

Figure 2.4. NWAR Wastes in GCD Boreholes [Caldwell and Bieri, 1983]

The waste inventory information for these 15 packages is documented in six sources: REEC's Form 167 (waste receipt form), a classified NWAR document, two classified Los Alamos reports, classified DOE Form 741, and a criticality study report by the Los Alamos National Laboratory. In the Los Alamos reports, the fissile and fertile isotope contents for each package were estimated using high-resolution gamma-ray spectrometry, passive neutron output, and both gamma-ray and neutron scans. In addition, extensive radiography was performed on these waste containers. The REEC and DOE forms contain shipment records that include isotope weights for each container. Table 2.4 summarizes the inventory amount reported by REEC, and Table 2.5 shows the inventory documented in DOE Form 741s. Table 2.6 shows the inventory reported by the various Los Alamos reports and the NWAR report.

A careful comparison between the various sources of information leads to the following observations:

1. The first set of inventory reports came from the Los Alamos measurements, and the reported quantities are generally order-of-magnitude numbers (e.g., kg).
2. The data in Table 2.6 are generally quite consistent among reports.
3. Records from DOE Form 741s and receipt records at REEC are identical for most packages. However, for some packages, some uranium quantities reported by REEC are exactly one order larger than the DOE numbers (e.g., packages 1 and 2).
4. There are significant discrepancies reported between DOE/REEC and Table 2.6, especially for depleted uranium. Also, the numbers reported by DOE/REEC are generally more precise than those in Table 2.6.
5. DOE Form 741 is the only source that reports the large quantity of lithium and deuterium in Borehole 1. It is not clear what forms lithium and deuterium are in, but a reasonable guess is that lithium is in the form of lithium hydride.

Because it is not possible to reconcile the differences among the reported values, it is assumed that the reported inventory values are all equally valid. Therefore, a range is used to represent the inventory. The smallest and the largest numbers reported are used as the lower and the upper bound of the possible inventory range. It should be emphasized that the largest uncertainty is for depleted uranium, and the impact on the performance assessment of the GCD site should be minimal because of the low activity levels of U238 (the main radionuclide of depleted uranium). In addition, in these references, U235, U238, and Pu239 are often used interchangeably with enriched uranium, depleted uranium, and weapon-grade plutonium, respectively. In this report, it is assumed that the reported U235 amount represents enriched uranium, U238 represents depleted uranium, and Pu239

Table 2.4
NWAR Inventory Reported by REECo (Grams)

Borehole Number	Item No.	U235	U238	Pu239
1	1	6,755	134,000	20
	2			
	5			
	14			
	15			
2	3	3,360	68,000	44
	4			
	6			
	11			
3	7	1,624	5,000	1,270
	8			
	9			
	10			
	12			
	13			

Table 2.5
NWAR Inventory Reported by DOE Form 741s (Grams)

Borehole Number	Item No.	U235	Depleted Uranium	Pu239	Lithium	Deuterium
1	1	4,505	622,000	895	34,000	11,000
	2					
	5					
	14					
	15					
2	3	1,100	68,630	44		
	4					
	6					
	11					
3	7	1,624	10,100	1,270		
	8					
	9					
	10					
	12					
	13					

Table 2.6
NWAR Inventory Reported by Other Sources (Kilograms)

Borehole Number	Item No.	Enriched Uranium	Depleted Uranium	Weapon-Grade Plutonium	Am241	Cs137	Ref
1	1	16.6-26.6	423.4-591.4	1.0	0.0002-0.01		1,2,3,4,5
	2						
	5						
	14						
	15						
2	3	3.44-23.44	2.63-11.63	0.044	2x10 ⁻⁴	0.01151	1,2,3
	4						
	6						
	11						

Table 2.6
NWAR Inventory Reported by Other Sources (Kilograms) (Concluded)

Borehole Number	Item No.	Enriched Uranium	Depleted Uranium	Weapon-Grade Plutonium	Am241	Cs137	Ref
3	7	5.52-11.2	6.1	0	0.003	0	1,2,3,4
	8						
	9						
	10						
	12						
	13						

References

- 1. Bieri and Caldwell, 1982
- 2. McMenamin, 1983.
- 3. Caldwell and Bieri, 1983
- 4. Caldwell, Bieri, and Hsu, 1983.
- 5. Private Communication, A. Manthei, 1990

represents weapon-grade plutonium. Table 2.7 summarizes the final NWAR inventory based on this procedure.

For those packages that contain Pu239, the concentrations of Pu239 per gram of gross weight of packaged waste far exceed the 100 nCi/g limit. These packages should be considered as TRU wastes.

2.1.2 Waste Forms

NWAR wastes consist of various remains of weapons parts recovered from the scene of four different accidents. In each of these accidents, the weapons have been involved in either a fire or a nonnuclear (i.e., high explosive) detonation.

The residues recovered from fire accidents can be described as highly charred, irregular lumps of material. In the opinion of those who investigated the accidents, the fire was intense enough to melt the metallic parts of the weapons. These parts, in their molten state, mixed in undetermined fractions to form a melt that then resolidified after the fire. Final shapes depended on the flow of the melt and its environs when it resolidified. No detailed data were found on final shapes, but they are probably relatively flat with many jagged, perhaps crusted, edges. The final mixture of the resolidified metal was not determined. Some evaluations indicate that other than uranium and plutonium, the principal constituent is aluminum.

Uranium and plutonium recovered from detonation accidents were in the form of heavy surface contamination on parts of the weapon found intact after the accidents. Apparently, some of the particulates, upon accelerating outward, impacted and became embedded in the surviving parts as the surviving parts themselves were being driven off by the resulting blast wave. These uranium and plutonium contaminants essentially became a coating on the solid surface of the surviving parts.

2.2 Contents of Borehole 4 - Classified Waste from Rocky Flats Plant and Lawrence Livermore National Laboratory

Classified wastes disposed of in Borehole 4 were generated by the Rocky Flats Plant (RFP) and Lawrence Livermore National Laboratory (LLNL). They are described below.

RFP Wastes

GCD wastes from the RFP were generated from either the manufacturing of new weapons or from the disassembly of retired weapons. These wastes were destined for GCD because they are classified wastes. Fifty-five gallon barrels were typically used as containers for RFP wastes. Usually, wastes were packed first in cylindrical fiberboard containers; then two of these containers were bagged in heavy plastic and placed in the barrels (Figure 2.5).

Table 2.7
Summary of NWAR Inventory (Kilograms)

Borehole Number	Item No.	Enriched Uranium	Depleted Uranium	Weapon-Grade Plutonium	Am241	Cs137	Li	D
1	1	18.105-31.5	423.4-722.4	0.895-2.03	2.8x10 ⁻⁴ -0.01		34.0	11.0
	2							
	5							
	14							
	15							
2	3	1.11 - 23.44	2.63-68.6	0.044	2x10 ⁻⁴	0.01151		
	4							
	6							
	11							

Table 2.7
Summary of NWAR Inventory (Kilograms) (Concluded)

Borehole Number	Item No.	Enriched Uranium	Depleted Uranium	Weapon-Grade Plutonium	Am241	Cs137	Li	D
3	7	1.40-11.2	6.1-10.1	1.27-1.43	0.003			
	8							
	9							
	10							
	12							
	13

Figure 2.5. Typical Container for RFP TRU Wastes

Information on the RFP wastes at the GCD site are reported in the classified DOE Form 741s and REEC Co Form 167s. According to these records, 258 drums of RFP wastes were disposed of in GCD Borehole 4 between July 1985 and October 1987 in five shipments. RFP wastes consist of only transuranic elements. The concentration of transuranic elements in these wastes ranges from 2,000 to more than 14,000 nCi/g, according to the DOE Form 741s. Therefore, these wastes are considered TRU wastes.

The inventory contents reported for the RFP wastes in Borehole 4 are consistent between DOE Form 741 and the REEC Co Form 167 and summarized in Table 2.8.

Depending on the sources of waste generation, five specific waste forms have been identified for the RFP wastes [Bauman, 1989]:

1. Graphite shapes - used for casting certain parts at RFP.
2. Tooling - bits used in machining castings.
3. Plastic shapes - used to secure parts during shipment to RFP.
4. Studs from uranium parts - lugs on plastic shapes to facilitate handling.
5. Metal shapes - parts removed from retired nuclear weapons.

In all five cases, these wastes have been, in one way or another, in intimate contact with either uranium or plutonium. In the process, their surfaces have become contaminated with TRU waste. The amount of contamination is small, a fraction of a gram of either uranium or plutonium, on each part.

LLNL Wastes

Eight boxes of wastes generated by LLNL were disposed of in Borehole 4 in January 1987. According to the REEC Co shipment records, these wastes contain H3, U238, Th232, and Li6. Four boxes contain classified metal parts contaminated with U238, one box contains classified metal parts contaminated with U238 and Th232, two boxes contain classified metal parts contaminated with U238 and H3, and one box contains LiH in classified assemblies. According to DOE Form 741, these wastes also contain 252 g of U235, so U235 is included in addition to these radionuclides reported by REEC Co. Although Li6 is not radioactive, it is included in the inventory because of the high reactivity of LiH. The resulting inventory from this shipment is shown in Table 2.8. The activity of H3 reported in January 1987 was 16.2 curies. This activity was reduced to account for the decay up to the present and then converted to grams.

Table 2.8
Contents of Borehole 4 (Curies/Grams)

Generator	Number of Packages	U235	Pu239	Am241	U238	Th232	H3	Li6
RFP	258 Drums	1.0E-4/45.0	136.8/2230	3.43/1.0				
LLNL	8 Boxes	5.6E-4/252.0			0.43/1.28E6	0.02/1.8E5	12.6/0.0013	0.0/6.05E4

2.3 Contents of Borehole 5 - Wastes from Lawrence Livermore National Laboratory and Mound Plant

Borehole 5 contains unclassified low-level wastes. There were three shipments from LLNL and five shipments from the Mound Plant.

LLNL Wastes

Two shipments of wastes from LLNL were sent to the NTS to be disposed of during 1986 and 1987. The first shipment included 17 drums that contained H3, Co60, Fe55, Fe59, and U238. The second shipment included 5 drums of waste that contained only H3. Records from REEC Co and DOE Form 741 are consistent for the second shipment; however, Form 741 for the first shipment could not be located, so only the REEC Co information was used. Table 2.9 shows the inventory as of January 1991.

Mound Wastes

Five shipments of low-level wastes were sent to the GCD site between September 1985 and February 1987. Although DOE Form 741 for one of the five shipments could not be located, the records between REEC Co and the Form 741s for the other four shipments were found to be consistent. According to these records, the wastes contain only tritium. For this report, the activities of tritium reported by REEC Co have been reduced to account for decay since shipment, and the resulting activities are then converted to grams as shown in Table 2.9.

Table 2.9
Contents of Borehole 5 (Curies/Grams)

Generator	Number of Packages	H3	Co60	Fe55	U238
LLNL	22 Drums	2.13E5/22	0.168/1.E-3	1.0E-2/4.0E-7	3.29E-5/98
Mound	99 Drums 2 Boxes	1.292E6/133.65			

These wastes were generated by liquid wastes from laboratory and process operations contaminated with high levels of tritium. The liquid wastes were then solidified in cement and packaged in 30-gal steel drums with polyethylene drum liners, which were emplaced in bituminous asphalt inside 55-gal 17 H steel drum overpacks. The final waste form is a solid.

2.4 Contents of Borehole 6 - Wastes from Rockwell, Canoga Park (RCP)

The Canoga Park wastes were generated during the reprocessing of DOE's Experimental Breeder Reactor (EBR) fuel elements. The wastes consist mainly of pieces of cladding materials (0.043-in. steel) disassembled from the fuel elements. These outer claddings were removed from the fuel assemblies by a laser cutting operation [Frazier, 1990]. The claddings are contaminated with fission products that migrated into the cladding while in the reactor and during its subsequent storage before disassembly. Many pieces of cladding were packaged in one aluminium cylindrical canister. Figure 2.6 shows the dimensions of these canisters. Between 1986 and 1987, 164 canisters were disposed of at GCD Borehole 6.

Shipping records from the RCP and REEC_o were examined carefully to determine the inventory contents of these wastes. The reported activities of the isotopes were then reduced to account for decay since shipment. Table 2.10 summarizes the total inventory of RCP wastes at the GCD site. Due to the high initial surface radiation level of these canisters, these wastes were disposed of in the boreholes by remote handling.

Table 2.10
Contents of Borehole 6

Generator	Number of Packages	Isotope	Inventory (Curies/Grams)
Rockwell, Canoga Park	164 Canisters	Co60	3,096/2.73
		Cs137	243/2.79
		Sr90	242/1.71

2.5 Contents of Borehole 7 - Wastes from Rocky Flats Plant

According to DOE Form 741, 38 drums of classified wastes were disposed of in GCD Borehole 7 in June 1986. The reported isotopic contents include less than 1 gram each of Pu and U238 in a gross weight of over 10,000 lbs of wastes. These wastes are reported as metals or plastics that contain classified shapes.

According to REEC_o's records, 48 drums of wastes were disposed of in Borehole 7. The reported inventory includes 1.885 curies of U238. Since it is felt that generally REEC_o's records are more reliable than DOE Form 741s, data from REEC_o are used in Table 2.11.

Figure 2.6. RCP Waste Container

Table 2.11
Contents of Borehole 7 (Curies/Grams)

Generator	Number of Drums	U238
RFP	48	1.885/5.6E6

2.6 Contents of Borehole 10 - Wastes from Lawrence Livermore National Laboratory, Mound Plant, and Sandia National Laboratories, Livermore

According to REEC's records, there was one shipment of low-level wastes from LLNL, three shipments from the Mound Plant, and two shipments from Sandia, Livermore, to GCD Borehole 10 between May 1987 and October 1989.

Records between REEC and DOE Form 741 for the LLNL and Mound waste were found to be consistent. The number of packages of Sandia waste reported by the two sources are different; 19 packages are reported in Form 741 and 8 drums are reported by REEC. Wastes from the Mound plant consist of tritium that was solidified into cement and packaged in drums and boxes. Wastes from LLNL and Sandia, Livermore, contain tritium similarly packaged in drums. Table 2.12 summarizes the inventory in Borehole 10. Again, the inventory shown in Table 2.12 has been reduced from the original reported values to account for decay since the times of shipments. Also, the number of packages for Sandia shown in the table is from REEC's record, since it is generally felt that REEC's record is more reliable than DOE Form 741s.

Table 2.12
Contents of Borehole 10

Generator	Radionuclide	Number of Packages	Curies/Grams
LLNL	H3	10 Drums	3.5E4/3.62
Mound	H3	67 Drums 7 Boxes	7.477E5/77.32
Sandia, Livermore	H3 U238	8 Drums	4.24E4/4.385 0.00171/5.085E3

2.7 Wastes from the Greater Confinement Disposal Test (GCDT)

The GCDT project was initiated in 1984. The main objectives of the project were to demonstrate the effective isolation of radioactive waste considered unsuitable for shallow land disposal using the GCD concept, and quantitatively to assess, predict, and verify the performance of the wastes. Various wastes, including some heat-generating wastes, were buried in this borehole.

The GCDT facility consists of a central borehole and nine monitoring shafts. The central borehole was 36 m deep and 3 m in diameter. Wastes were emplaced in five layers (Figure 2.7). Level A consists of sifted alluvium. The heat source drum contained several encapsulated sources of Sr90, Cs137, and Co60. Level C contained Sr90 in radioactive thermoelectric generators, and Ra226 and Ac227 in 55-gal and 30-gal drums, respectively. Levels D through F contained H3 in 55-gal drums. The activity and thermal output for each level of waste, as of May 1, 1984, are given by Dickman [1989]. The reported values from Dickman have been reduced to account for decay since then, and the present inventory and thermal output are shown in Table 2.13.

Table 2.13
Activity and Thermal Output of GCDT Wastes

Level	Radionuclide	Number of Drums	Curies/Grams	Watts
G	--	--	--	--
F	H3	35	121,653/12.6	4.09
E	H3	28	184,743/19.1	6.25
D	H3	13	105,557/10.9	3.54
C	Sr90 Ra226 Ac227		34,075/240.9 100/100 8.1/0.11	232.8
B	Sr90 Cs137 Co60		388,512/2746.8 17,642/202.7 169.6/0.15	2676.5
A	Alluvial Backfill

DEPTH MEASUREMENTS ARE FROM SURFACE
ALL DIMENSIONS ARE IN METERS

Figure 2.7. Waste Emplacement in GCDT (Dickman, 1989)

2.8 Hazardous Waste Components in the GCD Boreholes

According to DOE Order 5820.2A, radioactive wastes that contain hazardous components as defined by the Resource Conservation and Recovery Act (RCRA) are also subject to the requirements of the RCRA for the management of the wastes. RCRA regulates all aspects of hazardous waste for generators and transporters as well as for treatment, storage, and disposal facilities. To decide whether RCRA is applicable to the disposal of the GCD wastes, it is necessary to determine whether there are GCD wastes that meet the definition of "hazardous" under RCRA. The approach in this determination process consisted of two steps. First, the definition of hazardous waste as defined in 40 CFR 261 of the RCRA was reviewed [Wagner, 1991]. Second, records of GCD inventory were examined carefully, and processes used to generate the wastes were evaluated for any information that may suggest the presence of hazardous components.

2.8.1 Definition of Hazardous Waste

Three categories of hazardous wastes are defined in the RCRA: listed, characteristic, and other (Table 2.14). In determining if a waste is RCRA hazardous, the protocol is first to determine whether it is a listed hazardous waste. If it is not listed, a determination must be made if the waste exhibits any characteristics of hazardous waste: ignitability, corrosivity, reactivity, and/or toxicity. In addition, there are other hazardous wastes, such as mixtures, waste derived from processing wastes, and wastes contained in nonwastes, that meet the definition of hazardous. The definition for each of the three categories of hazardous wastes is summarized below.

Listed Hazardous Waste

There are hundreds of RCRA-listed hazardous wastes, and they are listed in 40 CFR 261.30 through 261.33. The listed hazardous wastes include material-specific and process-specific wastes. They are separated into three categories:

- Wastes from nonspecific sources
- Wastes from specific sources
- Commercial chemical products

Wastes from nonspecific sources are generally material specific and generated by a variety of processes. This category of wastes includes solvent wastes, electroplating wastes, and dioxin-containing wastes. The second category of listed hazardous wastes includes those generated from specific sources. These wastes are listed according to the specific industrial process that generates the waste rather than what is generated. Examples of the processes include wood preservation, inorganic pigments, petroleum refining, and coking. The third category of listed hazardous wastes include commercial chemical products. The hazardous waste in this last category must be a commercial product in an "unused" form.

Table 2.14
Categories of RCRA Hazardous Waste

Listed Hazardous Wastes	Characteristic Hazardous Wastes	Other Hazardous Wastes
<ul style="list-style-type: none"> • Nonspecific sources (F codes) • Specific sources (K codes) • Commercial chemical products - Acutely hazardous (U codes) 	<ul style="list-style-type: none"> • Ignitable • Corrosive • Reactive • Toxic 	<ul style="list-style-type: none"> • Mixtures (hazardous and nonhazardous) • Derived-from wastes (treatment residues) • Materials containing listed hazardous wastes

Characteristic Hazardous Wastes

The characteristic hazardous wastes defined in RCRA are those wastes that exhibit characteristics of ignitability, corrosivity, reactivity, and toxicity. The responsibility of determining whether a waste exhibits a characteristic rests with the generator.

Ignitability: A waste is an ignitable waste if it meets any of the following condition:

1. It is a liquid with a flash point of less than 140° F as determined either by a Pensky-Martens or a Setaflash Closed-Cup Test.
2. It is a solid that can spontaneously combust through friction, absorption, or loss of moisture.
3. It is an ignitable compressed gas as defined by the Department of Transportation in 49 CFR 173.300.
4. It is an oxidizer as defined by the Department of Transportation in 49 CFR 173.151. An oxidizer is a substance that yields oxygen readily when involved in a fire. Examples are chlorate, permanganate, inorganic peroxide, or nitrates.

Corrosivity: A waste is a corrosive waste if it meets any of the following criteria:

1. Aqueous with pH below 2 or above 12.5; or
2. Liquid and corrosive to steel at a rate of 6.35 mm or more per year as determined by the National Association of Corrosion Engineers (NACE).

It is important to note that when a waste is in a solid form, it is not considered a corrosive waste.

Reactivity: A waste is a reactive waste if it can explode or undergo violent chemical changes in a variety of situations. The following criteria are used by RCRA for reactivity:

1. Instability and readiness to undergo violent change.
2. Violent reactions when mixed with water.
3. Formation of potentially explosive mixtures when mixed with water.
4. Generation of toxic fumes in quantities sufficient to pose a danger to human health or the environment when mixed with water.
5. Cyanide or sulfide-bearing material that generates toxic fumes when exposed to acidic conditions.
6. Ease of detonation or explosion when exposed to pressure or heat.
7. Ease of detonation or explosive decomposition or reaction at standard temperature and pressure.
8. Defined as a forbidden explosive or a Class A or Class B explosive by the Department of Transportation.

For the most part, the reactivity characteristic requires a determination based more on judgement than a standardized quantitative test.

Toxicity: The toxicity characteristic is designed to identify wastes likely to leach hazardous constituents from a disposal facility. A toxicity characteristic leaching procedure test (TCLP) is prescribed by the EPA to determine whether a waste exhibits toxicity characteristics. For example, for a solid waste, the solid material is placed in a rotary agitation device with an acidic solution and rotated at 30 rpm for 18 hours. After extraction (rotation), solids are filtered from the liquid extract and discarded. If any contaminants in the TCLP extract meet or exceed any maximum

levels listed in Table 2.15, the waste is classified as a Toxicity Characteristic hazardous waste.

Other Hazardous Waste

A mixture of hazardous waste and a nonhazardous waste is considered a hazardous waste by RCRA. There is no minimum amount that qualifies for an exclusion. However, if the mixture contains a hazardous component because of a characteristic, and the resultant mixture no longer retains that characteristic, it is not considered a hazardous waste. For example, a mixture of a reactive waste and a nonhazardous waste will become nonhazardous if the mixture no longer exhibits the reactivity characteristic.

Any waste generated from the treatment, storage, or disposal of a hazardous waste will remain a hazardous waste unless the waste no longer exhibits the characteristic of a hazardous waste. This rule can have serious implications during the treatment of hazardous wastes during corrective actions in that the hazardous wastes after the treatment are still considered hazardous in spite of the much lower toxicity.

2.8.2 Identification of Hazardous Waste in the GCD Inventory

The first step in determining whether hazardous components are present in the GCD inventory was to determine whether there is any listed hazardous waste. Since GCD wastes were not generated commercially, the only possible category in the listed hazardous waste is the nonspecific sources wastes. For this category, there are four types of wastes: solvent wastes, electroplating wastes, metal heat-treating wastes, and dioxin wastes. Electroplating wastes are derived from anodizing, chemical etching, and milling. Wastes from metal heat treatment include quenching bath residues from oil baths, salt bath pot cleaning, and quenching wastewater treatment sludges. There is no evidence that electroplating or metal heat treatment processes were used in the generation of the GCD wastes; therefore, only solvent waste is a potential listed hazardous waste. In addition to the listed wastes, a determination must be made whether any component in the GCD inventory exhibits one or more of the characteristics of hazardous waste: ignitability, corrosivity, reactivity, and/or toxicity.

Records that document the GCD wastes were examined carefully for any information that may suggest the presence of solvent wastes and characteristic wastes. Attention was especially given to the NWAR wastes because these wastes were generated from weapons accidents and may include ignitable or reactive components. In addition, processes used in the generation of the GCD wastes were analyzed to determine if any hazardous wastes may be introduced. There are six generators for the GCD wastes: NWAR, Rocky Flats Plant (RFP), Mound Plant, Canoga Park (Rockwell), Lawrence Livermore Laboratory (LLNL), and Sandia National Laboratories, Livermore (SNLL). Wastes from each of the generator are discussed below for the possible presence of hazardous constituents.

Table 2.15
RCRA Toxicity Characteristic Levels

Containment	Limit (mg/1)
Arsenic	5.000
Barium	100.0
Benzene	0.5
Cadmium	1.0
Carbon Tetrachloride	0.5
Chlordane	0.03
Chlorobenzene	100.0
Chloroform	6.0
Chromium	5.0
<i>o</i> -Cresol	200.0
<i>m</i> -Cresol	200.0
<i>p</i> -Cresol	200.0
Cresol	200.0
2,4-D	10.0
1,4-Dichlorobenzene	7.5
1,2-Dichloroethane	0.5
1,1-Dichloroethylene	0.7
2,4-Dinitrotoluene	0.13
Endrin	0.02
Heptachlor	0.008
Hexachlorobenzene	0.13
Hexachlorobutadiene	0.5
Hexachloroethane	3.0
Lead	5.0
Lindane	0.4
Mercury	0.2
Methoxychlor	10.0
Methyl Ethyl Ketone	200.0
Nitrobenzene	2.0
Pentachlorophenol	100.0
Pyridine	5.0
Selenium	1.0
Silver	5.0
Tetrachloroethylene	0.7
Toxaphene	0.5
Trichloroethylene	0.5
2,4,5-Trichlorophenol	400.0
2,4,6-Trichlorophenol	2.0
2,4,5-TP Silvex	1.0
Vinyl Chloride	0.2

The GCD wastes from the RFP were generated during the manufacturing of new weapons or the disassembly of retired weapons. Personnel at the RFP were consulted about the processes used in these operations. The leaching process during disassembly appears to be the only operation in which a hazardous component might have been introduced. However, for this process, a thorough cleansing operation is used following the leaching to remove any residual acid [Bauman, 1989]. RFP has recently taken a general position that none of its GCD waste contains any hazardous constituents [RFAO, 1989]. However, this position only applies to the waste generated after 1987 when RCRA was determined to apply to the GCD waste. The pre-1987 workers at the RFP are no longer available for questioning concerning their waste management procedures. Therefore, it is not possible to establish that the pre-1987 GCD waste from the RFP is non-hazardous [Henrie, 1991].

The GCD wastes from the Mound Plant consist exclusively of solidified tritium. The waste stream consists of liquid wastes from laboratory and process operations contaminated with high levels of tritium. The liquid waste was solidified in cement, so the final waste form is a solid. The Mound Plant has declared that "this waste stream is not suspected to be hazardous under RCRA definitions, based on process knowledge and administrative controls" [EG&G, 1990]. For this report, it is therefore assumed that no RCRA wastes are present in the GCD wastes from the Mound Laboratory. The wastes from SNLL are very similar to those from the Mound plant, and so are also assumed to contain no RCRA wastes.

The GCD wastes from Canoga Park consist of pieces of cladding materials disassembled from the fuel elements of the Experimental Breeder Reactor. The only operation involved in the disassembly process was a laser cutting operation. Therefore, it is reasonable to assume that there is no RCRA hazardous constituent in the GCD wastes from the Canoga Park.

In Borehole 4, 60.5 kg of lithium hydride in one container from LLNL is documented in REEC's shipping record. This information was also confirmed with the manager of the RWMS at NTS. The RWMS site manager claimed that he personally lowered this box into Borehole 4, and it was the last container that emplaced before the boreholes was backfilled [Roberts, 1990]. Lithium hydride is the hydride of an alkali metal, so it is potentially reactive.

For the NWAR wastes, a total of 45.0 kg of lithium deuteride in two containers in Borehole 1 is documented in the DOE Form 741. A classified document from Los Alamos National Laboratory describing the origin of the NWAR wastes also reported the presence of lithium deuteride in these containers. This document also mentions the potential chemical hazard posed by lithium deuteride.

Borehole 3 contains NWAR wastes resulting from a fire accident of some weapons. A classified document from the Los Alamos National Laboratory reported that these NWAR

wastes included some melted high explosives. It is not clear what state these high explosives are in and whether there is a potential for explosion.

To determine whether lithium hydride and lithium deuteride exhibit any of the characteristics of hazardous wastes, the Material Safety Data Sheet (MSDS) from Sigma-Aldrich Corporation was used for the characteristics of LiH and LiD. It is reported in the MSDS that LiH and LiD react violently with water (See Appendix B for the MSDS). According to the definition of reactivity in RCRA, violent reactions with water would qualify the material as hazardous. It is therefore concluded that the GCD inventory does contain RCRA hazardous wastes and that the hazardous components are lithium hydride and lithium deuteride.

3.0 INVENTORY RULED BY 40 CFR 191

The EPA promulgated generally applicable environmental standards for the management and disposal of spent nuclear fuel and high-level and transuranic radioactive wastes. The standard, 40 CFR 191, establishes several different types of requirements for disposal of these materials [EPA, 1985]. The primary standards of disposal are long-term containment requirements that limit projected releases of radioactivity to the accessible environment for 10,000 years after disposal. Another set of requirements limits the exposures to individual members of the public for 1,000 years after disposal. Finally, a set of groundwater protection requirements limits radionuclide concentrations for 1,000 years after disposal in water withdrawn from most Class I groundwaters to the concentrations allowed by EPA's drinking water standards.

40 CFR 191 applies to three types of radioactive wastes as defined in Section 191.02:

1. Spent nuclear fuel - fuel that has been withdrawn from a nuclear reactor following irradiation, the constituent elements of which have not been separated by reprocessing.
2. High-level radioactive waste - such wastes as defined in the Nuclear Waste Policy Act of 1982.
3. Transuranic radioactive waste - waste containing more than 100 nanocuries of alpha-emitting transuranic isotopes, with half-lives greater than 20 years, per gram of waste.

The Nuclear Waste Policy Act defines high-level waste as including (1) the highly radioactive material resulting from the reprocessing of spent nuclear fuel, including liquid waste produced directly in reprocessing and any solid material derived from such liquid waste that contains fission products in sufficient concentrations and (2) other highly radioactive material that the Commission, consistent with existing law, determines by rule requires permanent isolation. This definition allows for inclusion of highly radioactive material not related to reprocessing of spent nuclear fuel to be regulated under 40 CFR 191.

Defining the GCD inventory regulated by 40 CFR 191 therefore involves sorting through all existing wastes currently disposed of at the GCD site and establishing which ones fall under the definition described above.

From Chapter 2, it is apparent that the wastes currently disposed of at the GCD site do not contain any spent nuclear fuel. The remaining two categories that need to be considered are high-level waste and transuranic (TRU) waste.

Since the NWAR waste inventory in Table 2.7 is presented in terms of enriched uranium, depleted uranium, and weapon-grade plutonium, the following assumptions were used to present the NWAR inventory in terms of specific radionuclides:

1. Enriched uranium is assumed to be all U235.
2. Depleted uranium is assumed to be all U238.
3. Weapon-grade plutonium is assumed to be composed of (by weight) 94% Pu239, 5.9% Pu240, and 0.014% Pu238. Am241 and Pu241 (which has a short half-life and decays to Am241) are not included because the inventory of Am241 is being measured and reported separately.

According to DOE Order 5820.2A, the lower concentration limit for transuranic waste (>100 nCi/g of waste) should apply to the contents of *any single package*. Many of the NWAR packages in Boreholes 1, 2, and 3 contain Pu239 with concentrations exceeding 100 nCi/g, so these packages are considered to be TRU wastes according to DOE Order 5820.2A. These TRU packages include:

- Items 1, 2, 15, and 14 in Borehole 1;
- Items 3 and 11 in Borehole 2; and
- Items 12 and 13 in Borehole 3.

The remaining NWAR packages contain only U235 and U238, so they should not be categorized as TRU wastes. However, since these packages are physically located within the same boreholes as the TRU packages, they are included in the TRU inventory for the performance assessment analysis. It should be emphasized that because of the low activities of U235 and U238, the inclusion of these questionable packages in the TRU inventory probably would not significantly impact the conclusions of the performance assessment.

Classified wastes from RFP in Borehole 4 contain Pu239 with concentrations much greater than 100 nCi per gram of wastes. These RFP wastes are therefore considered as TRU wastes.

The total TRU inventory at the GCD site is shown in Table 3.1. These are TRU wastes that are regulated by 40 CFR 191 and should therefore be considered in a performance assessment for 40 CFR 191.

Table 3.1
TRU Waste Inventory Ruled by 40 CFR 191 (Curies/Grams)

Borehole Number	U235	U238	Pu239	Pu238	Pu240	Am241
1	3.88E-2 - 6.75E-2 /18,100 - 31,500	1.41E-1 - 2.41E-1 /423,400 - 722,400	51.6 - 117.0 /841.3 - 1908.2	2.22 - 4.79 /0.13 - 0.28	12.2 - 27.7 /52.8 - 119.8	0.96 - 34.3 /0.28 - 10
2	2.66E-3 - 5.63E-2 /1,110 - 23,440	8.78E-4 - 2.29E-2 /2,630 - 68,600	2.54/41.4	0.10/0.006	0.6/2.6	0.686/0.2
3	3.36E-3 - 2.69E-2 /1,400 - 11,200	2.03E-3 - 3.37E-3 /6,100 - 10,100	73.2 - 82.4 /1,194 - 1,344	3.1 - 3.4 /0.18 - 0.20	17.3 - 19.5 /74.9 - 84.4	10.28/3.0
4	1.08E-4/45	0.43/1.28E6	128.6/2,096	5.31/0.31	30.4/131.6	3.43/1.0

Because of the broad definition of high-level waste in the Nuclear Waste Policy Act, it is not clear which of the non-TRU wastes at the GCD site fall under the definition. The containment requirements section of 40 CFR 191 has a table that specifies the release limits allowed for individual radionuclides. This table includes TRU radionuclides as well as some non-TRU radionuclides such as Sr90 and Cs137. A possible approach to determining which non-TRU radionuclides are regulated by 40 CFR 191 is to use those radionuclides that appear in the table in the containment requirements of 40 CFR 191. If this method is used, those wastes that contain the following radionuclides may be regulated by 40 CFR 191: Sr90, Cs137, Ra226, Th232, U235, U238, and Ac227.

Table 3.2 summarizes the non-TRU wastes at the GCD site that appear in the containment requirements of 40 CFR 191. These non-TRU radionuclides may not be defined as high-level wastes and may therefore not be regulated by 40 CFR 191. One way to resolve this issue is to analyze the impact of inclusion of this group of non-TRU wastes on compliance with 40 CFR 191 by doing performance assessment calculations with and without the non-TRU wastes.

Table 3.2
Non-TRU Waste Inventory Possibly Ruled by 40 CFR 191 (Curies/Grams)

Borehole Number	Sr90	Cs137	Ra226	Ac227	U235	Th232	U238
2		998./ 11.51					
4					5.6E-4/ 252	0.02/ 1.8ES	
6	242/ 1.7	243/ 2.8					1.885/ 56E6
GCDT	4.23E5/ 2987.7	17,642/ 202.7	100/ 100	8.1/ 0.11			

4.0 PRELIMINARY SOURCE-TERM MODEL

Source term is defined here as the time-dependent rate of radionuclide release from the boundary of the GCD borehole. This definition means that a source-term model should account for the quantity of disposed radionuclides, physical and chemical forms of the radionuclides, breach rate and degradation of containers, leach rates of radionuclides from the containers, and transport and mixing of radionuclides with water in the disposal borehole.

4.1 Container Degradation

For the GCD system, there are a variety of containers. The NWAR wastes are packaged in either metal or plywood containers. Fifty-five gallon metal barrels are typically used as containers for the RFP wastes. For the RCP wastes, aluminum cylindrical containers are used. It is reasonable to expect that the different types of containers would degrade at different rates.

Many corrosion models are available that describe the degradation of metal containers. However, there are usually large uncertainties associated with these corrosion models from two main sources. First, many corrosion phenomena are poorly understood, in particular the rate of pit growth and the areal pit density. More important, corrosion rate usually depends strongly on the geochemical environment. Knowledge of geochemical environment is often lacking in the disposal unit.

Because of the uncertainties in data needed to implement container degradation models, a simplified approach to modeling the failure of containers is recommended for a performance assessment calculation. This simplified approach is to treat the container failure time as a delay time to the onset of radionuclide releases. The containers are assumed to fail instantly and completely at a specified time. This failure time is assumed in a performance assessment analysis and can be varied in a sensitivity analysis.

4.2 Radionuclide Leach Rates

Radionuclide-containing wastes can dissolve when in contact with water. The process of dissolution, or preferential solute mass transfer from solid to liquid phase, is known as leaching [Treybal, 1980]. There are three leaching mechanisms typically being modeled for the release of radionuclides from waste forms. The most conservative leach model is to assume that the contaminants reside on the solid surface and are instantly washed off by passing water. The second model assumes that the waste form itself is degraded, thus freeing the radionuclides from the bulk waste form. This is usually called the congruent dissolution model. The third model assumes that radionuclides have to diffuse through the pore space of the waste form before they are released. For this mechanism, the release rate is limited by the diffusion rate in the waste form.

For a performance assessment analysis, the most conservative leach mechanism is used; that is the contaminants are assumed to reside on the surface of the waste form and are instantly washed off upon contact with water. Because the GCD site is extremely arid, the amount of available water contacting the wastes is expected to be very small. Therefore, it is reasonable to assume that the amount of radionuclides transported by water is determined by the solubility of the radionuclides multiplied by the flux of water. With this release model, the release rate of a radionuclide (R_i) can be expressed by the following equation:

$$R_i = S_i \times F \times A \quad (4-1)$$

where

S_i = Solubility of radionuclide i in water (g/g)

F = Flux of water through borehole (cm/yr), and

A = Cross-sectional area of the GCD borehole (cm²).

With this source-term model, it is assumed that all the dissolved radionuclides in a borehole are available for transport and that travel time within the borehole is neglected. This release rate is assumed until the inventory is depleted.

As the report neared completion, it was found that there is RCRA hazardous wastes in the GCD boreholes. Due to the time constraint, the impact of the hazardous wastes on the releases of radionuclides are not addressed in this report. The impact will be investigated in another task.

4.3 Solubility Data Used for Performance Assessment Analysis

Since chemical elements in water can exist as various chemical species, the solubility of an element is affected by the tendency of the element to form complexes and by the concentrations of species with which it can complex [DOE, 1988b]. In general, solubility increases as the variety and concentration of complexes of the element increase. Speciation and solubility therefore depend on the chemical properties of the chemical element and the state of the water (chemical composition, pH, Eh, and temperature). Concentrations of aqueous species are usually calculated using the formation constants of possible aqueous species with the equilibrium thermodynamic methods. These calculations usually require extensive thermodynamic data. It is important to note that solubility and speciation are in terms of the total concentration of an element in the solution; the concentration of the radionuclide depends on the isotopic composition of the element.

Because the water composition at the GCD borehole location is not available, water compositions believed to be similar to that at the GCD location are used to estimate the solubility of radionuclides. Two water compositions can be used for performance assessment analyses. The first is the J-13 water from Yucca Mountain. The second is the Well 5-B water at the NTS. For all the available water composition information near the GCD site, water composition from Well 5-B is thought to be most similar to the water in the GCD borehole horizon because Well 5-B is the shallowest well near the GCD site. J-13 water is also chosen because the water composition is similar to that of Well 5-B and because vast amounts of solubility data are available. Table 4.1 gives the water composition of the two wells.

Appendix C describes in detail the solubility data reported in the literature for J-13 water, and Table 4.2 summarizes the solubility of elements to be used for a performance assessment calculation.

Table 4.1
Well 5-B and J-13 Water Chemistry

Element	Concentration (Mg/L)	
	Well 5-B	Well J-13
Ca ⁺⁺	1.0 - 2.2	11.5
Cl ⁻	20 - 27	6.4
F ⁻	0.8 - 1.2	2.1
K ⁺	11 - 14	5.3
Li ⁺	0.02 - 0.03	0.06
Mg ⁺⁺	0.5 - 2.3	1.76
NO ₂ ⁻ + NO ₃ ⁻	1.1 - 3.3	10.1
Na ⁺	92 - 180	45.0
PO ₄ ⁼	0.001 - 0.009	---
SO ₄ ⁼	51 - 64	18.1
Si ⁺⁴	45 - 72	30.0
Alkalinity	140 - 170	
pH	7.5 - 8.3	7.0
T(°C)	24.0 - 26.0	25.0

Table 4.2
Solubility Based on J-13 Water

Element	Moles/L	g/g	Distribution
Americium	9.0E-7 - 1.3E-6	2.2E-7 - 3.1E-7	Uniform
Plutonium	1.4E-6 - 5.0E-5	3.4E-7 - 1.2E-5	Loguniform
Uranium	4.0E-3	9.4E-4	
Neptunium	6.5E-4 - 2.2E-3	1.5E-4 - 5.2E-4	Uniform
Radium	3.0E-7	6.8E-8	
Strontium	8.0E-4	7.2E-5	
Cesium	High	5.0	
Actinium	High	5.0	
Protactinium	High	5.0	
Thorium	1.0E-9	2.3E-10	
Lead	6.0E-6	1.3E-6	

Because no solubility data of radionuclides in Well 5-B water are available, a set of solubility calculations was performed by LLNL using the Well 5-B water composition. Computer code EQ3 was used to calculate the radionuclide concentrations in equilibrium with a variety of solid phases. Computer code EQ6 was used to calculate the effect of pH on radionuclide concentrations and on the identity of the solubility-limiting solids. Bruton [Appendix D] reports the details of this set of calculations. For a performance assessment analysis, the most important solid(s) are identified for each radioelement, and then a range of solubility is chosen based on the solubility between a pH of 6 and 10. This pH range is used to reflect the uncertainty of the geochemical environment in the borehole. The solid phases assumed for radionuclides in defining the solubilities are listed below:

- Thorium - $\text{Th}(\text{OH})_4$ is assumed to be the most important solid phase (Fig. 3 of Appendix D).
- Uranium - Haiweeite and soddyite are assumed to be the important solid phases (Fig. 9 of Appendix D).
- Neptunium - $\text{NpO}_2\text{OH}(\text{Am})$ is assumed to be the solubility-controlling solid phase (Fig. 13 of Appendix D).

- Plutonium - $\text{Pu}(\text{OH})_4$ is assumed to be the solubility-controlling solid phase (Figure 18 of Appendix D).
- Americium - $\text{Am}(\text{OH})(\text{CO}_3)$ is assumed to be the solubility-controlling phase (Figure 22 of Appendix D).
- Strontium - Strontianite is the solubility-controlling solid in the calculations of solubilities (Figure 26 of Appendix D). Since the dependence of solubility on pH is very large, a lognormal distribution is used for the range of solubilities between a pH of 6 and 10 so that the solubilities between a pH of 7 and 8 are emphasized.
- Radium - RaSO_4 is the solid phase that controls the solubility (Figure 28 of Appendix D).
- Lead - Cerussite, plattnerite, and alamosite are assumed to be the solubility-controlling solid phases, and phosphate-bearing solids are not considered (Figure 32 of Appendix D).

Table 4.3 summarizes the solubility ranges recommended for the preliminary source term model based on this approach.

Table 4.3
Solubility Based on Well 5-B Water

Element	Solubility (g/g)	Distribution
Thorium	1.0E-7 - 3.0E-7	Uniform
Uranium	1.0E-11 - 1.0E-6	Log Uniform
Neptunium	2.0E-5 - 3.0E-4	Uniform
Plutonium	2.0E-5 - 6.0E-5	Uniform
Americium	1.0E-9 - 5.0E-7	Log Uniform
Strontium	9.0E-9 - 9.0E-5	Log Normal
Radium	2.5E-8 - 3.0E-8	Uniform
Lead	3.0E-9 - 5.0E-7	Log Uniform

5.0 SUMMARY AND CONCLUSIONS

Currently, there are a few intermediate-depth boreholes at the Radioactive Waste Management Site of the Nevada Test Site. These GCD boreholes were used for the disposal of radioactive wastes that were not suitable for conventional shallow land disposal methods. Because of site location and design, the GCD technology is a candidate solution for the DOE's alternative disposal methods for special case wastes in general. Critical to accepting the GCD concept as a potential solution to DOE's special case waste disposal is the early assessment of the potential of success in meeting the requirements of various disposal regulations. Presently, a small inventory of transuranic waste is disposed of at the site, and it provides an ideal basis for performing a preliminary performance assessment for compliance with EPA 40 CFR 191.

The first step in a performance assessment analysis is to define the waste inventory and potential releases of the wastes. The purpose of this report is to define the waste inventory and potential releases for the performance assessment for 40 CFR 191. Three subtasks were performed to achieve this objective:

1. Identification and definition of all wastes presently being disposed of at GCD.
2. Determination of which of these wastes are governed by 40 CFR 191.
3. Definition of potential radionuclide releases from GCD boreholes.

There are nine GCD boreholes that contain wastes. The contents of each borehole are summarized below.

Boreholes 1, 2, and 3

The wastes are from the NWARs. Because these wastes contain classified shapes, they have been categorized as classified wastes. Various reports and documents were used in defining the inventory in these three boreholes. The data contained in these sources are sometimes inconsistent. Since there is no way to determine which source is more reliable, all data are assumed to be equally reliable, and a range of values is used to define the inventory quantity. Fortunately, the largest uncertainty is for depleted uranium, which has very low activity levels. There are 15 boxes in the three boreholes, and they contain kg quantities Pu239, tens of kg of U235, hundreds of kg of U238, and a very small quantity of Am241. Because of the long half-lives of U235 and U238, their activity levels are very low. Only Pu239 poses significant radioactivity (about 200 curies).

Borehole 4

This borehole contains 258 drums and 8 boxes of TRU wastes. These wastes are classified metal parts contaminated with various radionuclides. The major radionuclide is Pu239 (kg quantity), and there are large quantities (1,000 kg) of U238 and Th232. There are a total of over 100 curies, mostly from Pu239.

Borehole 5

Borehole 5 contains unclassified low-level wastes that consist almost exclusively of tritium. There are about 100 grams of tritium, which corresponds to about a million curies of activity.

Borehole 6

Borehole 6 contains 164 canisters that contain pieces of cladding materials generated from the disassembly of fuel elements. These unclassified wastes consist of fission products Co60, Cs137, and Sr90. There are a total of a few thousand curies.

Borehole 7

Borehole 7 contains 48 drums of classified TRU wastes. There is a large weight quantity (a few thousand kilograms) of U238 in the wastes; however, because of its long half-life, the activity is very low.

Borehole 10

Borehole 10 contains unclassified low-level wastes that consist almost entirely of tritium. The activity level is presently estimated to be close to a million curies. The wastes were solidified into cement and packaged in drums.

GCDT Borehole

This borehole was established in 1984 for testing the GCD concept. Various unclassified low-level wastes were emplaced in the borehole for the testing. Some heat-producing wastes as well as tritium were used. The major thermal waste is Sr90, which produces about 3000 Watts of thermal output. There are about 400,000 curies each of tritium and Sr90, and some Cs137, Ra226, Ac227, and Co60.

The NWAR wastes in Boreholes 1, 2, and 3, and the wastes in Boreholes 4, are TRU wastes; therefore, they are regulated by 40 CFR 191. The total amount of TRU waste inventory in these boreholes consists of a few hundred kilograms of U238, tens of kilograms of U235, and a few kilograms of Pu239.

Because of the broad definition of high-level waste as defined in the Nuclear Waste Policy Act, it is possible that some of the non-TRU wastes at the GCD site may be regulated by 40 CFR 191. The following non-TRU radionuclides have been identified as potential wastes to be regulated by 40 CFR 191: Sr90, Cs137, Ra226, U235, U238, Th232, and Ac227. They are chosen because they appear in the release limit table of the containment requirements in 40 CFR 191. Boreholes 2, 4, 6, 7, and the GCDT borehole contain these radionuclides, with Sr90 being the most abundant (a few kilograms).

A total of 45.0 kg of lithium deuteride in two containers in Borehole 1 is documented. Also, there is 60.5 kg of lithium hydride in Borehole 4. Since LiH and LiD react violently with water, they qualify as characteristic hazardous waste according to the RCRA. It is therefore concluded that the GCD inventory contains RCRA hazardous waste.

For a performance assessment calculation for 40 CFR 191, a conservative source-term model is recommended in predicting the releases of radionuclides from GCD boreholes. In this model, contaminants are assumed to reside on the surface of the waste form and are instantly washed off upon contact with infiltrating recharge water. It is further assumed that the amount of radionuclide transported by water is limited by the solubility of the radionuclide. With this release model, the release rate of a radionuclide from the borehole is thus equal to the solubility multiplied by the flux of water. This release rate persists until the inventory is depleted. For this report, the impact of hazardous wastes on the releases of radionuclides is not addressed.

The solubility of a chemical element depends on the chemical properties of the element and the state of the water (chemical composition, pH, Eh, and temperature). Since the water composition at the GCD borehole location is not available, two water compositions believed to be similar to that at the GCD location were used to estimate the solubility of radionuclides. The first is the J-13 water from Yucca Mountain, and the second is the Well 5-B water, both from NTS. Because vast amounts of solubility data for J-13 water are available in the literature, no solubility calculations were performed for J-13 water, and the existing data were used. For Well 5-B water, a set of solubility calculations was performed using the computer code EQ3/6 to estimate the solubilities of radionuclides.

6.0 REFERENCES

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APPENDIX A
Operations at the GCD Site

On March 26 and 27, 1990, E. A. Bernard, M. S. Y. Chu, and J. D. Johnson of Sandia National Laboratories (SNL) visited the Radioactive Waste Management Site (RWMS) to meet with Dick Roberts of Reynolds Electrical and Engineering Company (REECo). Dick Roberts is the Maintenance and Operations Section Chief of the RWMS. The main purpose of the meeting was to acquire detailed information about the operational procedures relating to the receipt and disposal of Greater Confinement Disposal (GCD) wastes for the System Configuration Task.

A.1 OPERATIONAL PROCEDURES

A detailed description of the handling of GCD wastes from their arrival at the main gate of the Nevada Test Site (NTS) to the final disposal into the boreholes was given orally by Dick Roberts.

A.1.1 Unclassified Waste Procedures

1. For every shipment of wastes into the NTS, advance notice from the generator of the wastes is sent to the DOE at the NTS and relayed to the RWMS. When a truck arrives at the NTS, it first stops at the receiving station outside the main gate. At the receiving station, Wackenhut security personnel, REECo traffic personnel, and radiation control personnel perform the initial inspections.
 - a. The truck driver presents the appropriate paperwork to the above-mentioned people.
 - b. The compliance of 40 CFR 173 is checked on the truck to see if the 200 mrem/h dose rate is satisfied. Also the security seals on the truck are inspected to make sure that they agree with those described in the paperwork and that they are intact.
 - c. After this inspection, REECo Form 837 is then issued to indicate the satisfactory receipt and inspection of the truck. If there are any minor discrepancies, they are noted on this form.
2. The truck proceeds to the main gate, passes through after routine checks by the guard, and then drives to Area 5.
3. When the truck arrives at the RWMS, the driver shows the paperwork to the clerk at the receiving desk in the RWMS building. The clerk examines the paperwork, signs on the security pass, enters the arrival information into the computer file, and collects his copies of the paperwork from the driver.
4. The radiation personnel of Area 5 then survey the truck, check the security seals, and measure the surface dose rate of the truck. If everything proves acceptable, the driver

moves his truck through the control entry gate to the unloading point inside the unclassified disposal area.

5. At the disposal location, the truck backs up to the loading ramp.
 - a. Here, a monitor again checks the seals on the truck.
 - b. Then an ironworker breaks the seals and opens the door slightly.
 - c. The monitor checks the radiation level at the door. (For mixed wastes, the presence of organic gases and tritium is also monitored.)
 - d. If everything is in order, the door of the truck is then fully opened.
 - e. The drums are unloaded from the truck with a barrel picker, and the boxes are unloaded with a fork lift.
 - f. While the truck is being unloaded, the monitor checks off the inventory list for every package and also inspects the integrity of each package. In addition, swipes are taken on about 10% of the waste containers.
 - g. When unloading is complete, the monitor surveys the inside of the cargo compartment of the truck. The monitor also takes paper swipes of the floor and the tires of the truck. The truck is then released to the entry control gate.
6. The truck is held at the entry control gate until all release procedures are completed:
 - a. All the swipes taken are counted at the gate house for α and β radiations using a Tennelec 5100 monitor.
 - b. The truck driver is also monitored.
 - c. After it is determined that everything is free of contamination, the driver is sent back to the clerk.
7. The clerk enters the radiation survey results on the paperwork and releases the truck to leave Area 5. (The driver needs this paperwork to exit the NTS gate.) The clerk enters the departure information into the computer file and also notifies the REECO traffic personnel.
8. As for the actual disposal of the wastes, a cargo net that carries about 10 containers is used to lower the wastes into the borehole. As the waste is lowered, sounding lines are used to locate the top of the waste.

9. After the borehole is filled to about 70 feet below the surface, the borehole is backfilled with the original dirt to within 10 feet from the surface. The Corrugated Metal Pipe (CMP) at the top of the borehole is now pulled out and the borehole is then backfilled all the way to the top.

A.1.2 Classified Waste Procedures

1. The DOE/NV Safeguard and Security personnel notify traffic, security, and radiation control personnel about the impending classified shipment.
2. When the truck arrives at the NTS gate, the Safeguard and the Security people escort the truck to Area 5. The DOE Safeguard representative has Form 741 in hand.
3. When the truck arrives at the RWMS, the truck is surveyed for compliance with 40 CFR 173 (200 mrem/h radiation). The Safeguard people then escort the truck to the classified disposal site.
4. The truck is then opened the same way as for unclassified wastes. REECo Form 167 (which contains the waste inventory information) is inside the truck, and now the security person takes the form and counts each package as it is unloaded. The security person then signs on the form to indicate that the number of packages unloaded checks with the number recorded on the Form 167.
5. If it is not late in the day, the wastes are disposed of right away in the same manner as unclassified wastes are disposed of. Otherwise, the classified wastes are put into the International Cargo Container (ICC) for storage overnight and disposed of the following day. The ICCs are locked with security locks.
6. After unloading of the wastes, the truck goes through the same monitoring and exit procedures as for unclassified wastes.

A.2 SUPPORT FACILITIES AND EQUIPMENT

RWMS support facilities include building 5-7 for administrative assistance and building 5-6 to accommodate warehousing.

DWMD (Defense Waste Management Department) equipment available consists of one crane with remote controls, three forklifts, a 40-foot flatbed trailer, a tractor, and one stake-bed truck. Additional equipment is available as needed.

A Waste Examination Building is in the planning stage at the RWMS. The building will be about 40 feet by 25 feet and will serve the following two functions:

- A 420-keV machine will be used to look through 55-gallon drums and wooden or steel boxes (up to 4'x4'x7' in size) for waste content. At most, 10% of the incoming wastes will be checked this way.
- The building will also be used to open up containers when unacceptable items are found. These items (e.g., pressurized vessels) will be removed from the waste containers.

The Waste Examination Building is estimated to cost about \$1.2 M, \$450 K of which will be for equipment and hardware.

A.3 EXCAVATION OF GCD BOREHOLES

According to Dick Roberts, it costs about \$20 K to drill a GCD borehole. Also, the existing NTS rigs can drill only to 120 feet.

APPENDIX B

Material Safety Data Sheet (MSDS) Information for LiH and LiD

B-2

Sigma-Aldrich Corporation
1001 West Saint Paul Ave. Milwaukee, WI 53233 USA

	Sigma	Aldrich
For Emergency Contact USA/Canada	800-325-5832	800-231-8327
Outside USA/Canada	314-771-5765	414-273-3850

LiH

----- IDENTIFICATION -----

PRODUCT #: 20104-9 NAME: LITHIUM HYDRIDE
CAS #: 7580-67-8
MF: HLI

SYNONYMS

HYDRURE DE LITHIUM (FRENCH) * LITHIUM HYDRIDE (ACGIH, DOT, OSHA) * UN
1414 (DOT) * UN 2805 (DOT) *

----- TOXICITY HAZARDS -----

RTECS NO: OJ6300000

LITHIUM HYDRIDE

IRRITATION DATA

EYE-RBT 5 MG/M3

AMIHAB 14,468,56

EYE-GPG 5 MG/M3

AMIHAB 14,468,56

REVIEWS, STANDARDS, AND REGULATIONS

ACGIH TLV-TWA 0.025 MG/M3 85INA8 5,349,86

MSHA STANDARD-AIR:TWA 0.025 MG/M3 DTLVS* 3,147,71

OSHA PEL:8H TWA 0.025 MG/M3 FEREAC 54,2923,89

OSHA PEL FINAL:8H TWA 0.025 MG/M3 FEREAC 54,2923,89

NOHS 1974: HZD 43115; NIS 1; TNF 11; NOS 1; TNE 11

EPA TSCA CHEMICAL INVENTORY, JUNE 1990

DATA IS PRESENTED HERE. SEE ACTUAL ENTRY IN RTECS FOR COMPLETE INFORMATION.

----- HEALTH HAZARD DATA -----

ACUTE EFFECTS

HARMFUL IF SWALLOWED, INHALED, OR ABSORBED THROUGH SKIN.
MATERIAL IS EXTREMELY DESTRUCTIVE TO TISSUE OF THE MUCOUS MEMBRANES
AND UPPER RESPIRATORY TRACT, EYES AND SKIN.
INHALATION MAY BE FATAL AS A RESULT OF SPASM, INFLAMMATION AND EDEMA
OF THE LARYNX AND BRONCHI, CHEMICAL PNEUMONITIS AND PULMONARY EDEMA.
SYMPTOMS OF EXPOSURE MAY INCLUDE BURNING SENSATION, COUGHING,
WHEEZING, LARYNGITIS, SHORTNESS OF BREATH, HEADACHE, NAUSEA AND
VOMITING.
TO THE BEST OF OUR KNOWLEDGE, THE CHEMICAL, PHYSICAL, AND
TOXICOLOGICAL PROPERTIES HAVE NOT BEEN THOROUGHLY INVESTIGATED.

FIRST AID

IN CASE OF CONTACT, IMMEDIATELY FLUSH EYES WITH COPIOUS AMOUNTS OF
WATER FOR AT LEAST 15 MINUTES.
IN CASE OF CONTACT, IMMEDIATELY WASH SKIN WITH SOAP AND COPIOUS
AMOUNTS OF WATER.
IF INHALED, REMOVE TO FRESH AIR. IF NOT BREATHING GIVE ARTIFICIAL
RESPIRATION. IF BREATHING IS DIFFICULT, GIVE OXYGEN.
IF SWALLOWED, WASH OUT MOUTH WITH WATER PROVIDED PERSON IS CONSCIOUS.
CALL A PHYSICIAN.
WASH CONTAMINATED CLOTHING BEFORE REUSE.

----- PHYSICAL DATA -----

MELTING PT: 680 C
SPECIFIC GRAVITY: 0.820

APPEARANCE AND ODOR

WHITE TO LIGHT-GREY OR

----- FIRE AND EXPLOSION HAZARD DATA -----

EXTINGUISHING MEDIA

CLASS D FIRE-EXTINGUISHING MATERIAL ONLY.
DO NOT USE WATER.
DO NOT USE CARBON DIOXIDE EXTINGUISHER ON THIS MATERIAL.
DO NOT USE DRY CHEMICAL POWDER EXTINGUISHER ON THIS MATERIAL.

SPECIAL FIREFIGHTING PROCEDURES

WEAR SELF-CONTAINED BREATHING APPARATUS AND PROTECTIVE CLOTHING TO
PREVENT CONTACT WITH SKIN AND EYES.
FLAMMABLE SOLID.

UNUSUAL FIRE AND EXPLOSIONS HAZARDS

THIS MATERIAL, LIKE MOST MATERIALS IN POWDER FORM, IS CAPABLE OF
CREATING A DUST EXPLOSION.
EMITS TOXIC FUMES UNDER FIRE CONDITIONS.
MATERIAL READILY REACTS WITH WATER GENERATING FLAMMABLE AND/OR
EXPLOSIVE HYDROGEN GAS.
CATCHES FIRE IF EXPOSED TO AIR.

----- REACTIVITY DATA -----

INCOMPATIBILITIES

STRONG OXIDIZING AGENTS
ACIDS
ALCOHOLS
REACTS VIOLENTLY WITH WATER.

HAZARDOUS COMBUSTION OR DECOMPOSITION PRODUCTS

LIBERATES FLAMMABLE/EXPLOSIVE HYDROGEN GAS.

----- SPILL OR LEAK PROCEDURES -----

STEPS TO BE TAKEN IF MATERIAL IS RELEASED OR SPILLED

SHUT OFF ALL SOURCES OF IGNITION.

WEAR SELF-CONTAINED BREATHING APPARATUS, RUBBER BOOTS AND HEAVY RUBBER GLOVES.

COVER WITH DRY-LIME, SAND, OR SODA ASH. PLACE IN COVERED CONTAINERS USING NON-SPARKING TOOLS AND TRANSPORT OUTDOORS.

VENTILATE AREA AND WASH SPILL SITE AFTER MATERIAL PICKUP IS COMPLETE.

WASTE DISPOSAL METHOD

UNDER AN INERT ATMOSPHERE, CAUTIOUSLY ADD THE MATERIAL TO DRY BUTANOL IN AN APPROPRIATE SOLVENT. THE CHEMICAL REACTION MAY BE VIGOROUS AND/OR EXOTHERMIC. PROVISIONS MUST BE MADE FOR THE VENTING OF LARGE VOLUMES OF HIGHLY FLAMMABLE HYDROGEN AND/OR HYDROCARBON GASES.

NEUTRALIZE THE SOLUTION WITH AQUEOUS ACID. FILTER OFF ANY SOLID RESIDUES FOR DISPOSAL AS HAZARDOUS WASTE. BURN THE LIQUID PORTION IN A CHEMICAL INCINERATOR EQUIPPED WITH AN AFTER BURNER AND SCRUBBER. OBSERVE ALL FEDERAL, STATE, AND LOCAL LAWS.

--- PRECAUTIONS TO BE TAKEN IN HANDLING AND STORAGE ---

CHEMICAL SAFETY GOGGLES.

COMPATIBLE CHEMICAL-RESISTANT GLOVES.

NIOSH/MSHA-APPROVED RESPIRATOR.

SAFETY SHOWER AND EYE BATH.

USE ONLY IN A CHEMICAL FUME HOOD.

AVOID BREATHING DUST.

AVOID CONTACT WITH EYES, SKIN AND CLOTHING.

AVOID PROLONGED OR REPEATED EXPOSURE.

WASH THOROUGHLY AFTER HANDLING.

CORROSIVE.

KEEP TIGHTLY CLOSED.

DO NOT ALLOW CONTACT WITH WATER.

KEEP AWAY FROM HEAT, SPARKS, AND OPEN FLAME.

HANDLE AND STORE UNDER NITROGEN.

STORE IN A COOL DRY PLACE.

----- ADDITIONAL PRECAUTIONS AND COMMENTS -----

ADDITIONAL INFORMATION

THE POWDERED MATERIAL BURNS READILY ON EXPOSURE TO AIR OR NITROUS OXIDE (DINITROGEN OXIDE). MIXTURES OF THE POWDERED HYDRIDE AND LIQUID OXYGEN ARE DETONATABLE EXPLOSIVES.

THE ABOVE INFORMATION IS BELIEVED TO BE CORRECT BUT DOES NOT PURPORT TO BE ALL INCLUSIVE AND SHALL BE USED ONLY AS A GUIDE. SIGMA ALDRICH SHALL NOT BE HELD LIABLE FOR ANY DAMAGE RESULTING FROM HANDLING OR FROM CONTACT WITH THE ABOVE PRODUCT. SEE REVERSE SIDE OF INVOICE OR PACKING SLIP FOR ADDITIONAL TERMS

Sigma-Aldrich Corporation
1001 West Saint Paul Ave. Milwaukee, WI 53233 USA

	Sigma	Aldrich
For Emergency Contact USA/Canada	800-325-5832	800-231-8327
Outside USA/Canada	314-771-5765	414-273-3850

LID

----- IDENTIFICATION -----
PRODUCT #: 22163-5 NAME: LITHIUM DEUTERIDE, 98+ ATOM % D
CAS #: 13587-16-1
MF: DLI

----- TOXICITY HAZARDS -----
DATA NOT AVAILABLE

----- HEALTH HAZARD DATA -----

ACUTE EFFECTS

HARMFUL IF SWALLOWED, INHALED, OR ABSORBED THROUGH SKIN.
MATERIAL IS EXTREMELY DESTRUCTIVE TO TISSUE OF THE MUCOUS MEMBRANES
AND UPPER RESPIRATORY TRACT, EYES AND SKIN.
INHALATION MAY BE FATAL AS A RESULT OF SPASM, INFLAMMATION AND EDEMA
OF THE LARYNX AND BRONCHI, CHEMICAL PNEUMONITIS AND PULMONARY EDEMA.
SYMPTOMS OF EXPOSURE MAY INCLUDE BURNING SENSATION, COUGHING,
WHEEZING, LARYNGITIS, SHORTNESS OF BREATH, HEADACHE, NAUSEA AND
VOMITING.

TO THE BEST OF OUR KNOWLEDGE, THE CHEMICAL, PHYSICAL, AND
TOXICOLOGICAL PROPERTIES HAVE NOT BEEN THOROUGHLY INVESTIGATED.

FIRST AID

IN CASE OF CONTACT, IMMEDIATELY FLUSH EYES WITH COPIOUS AMOUNTS OF

IN CASE OF CONTACT, IMMEDIATELY WASH SKIN WITH SOAP AND COPIOUS AMOUNTS OF WATER.
IF INHALED, REMOVE TO FRESH AIR. IF NOT BREATHING GIVE ARTIFICIAL RESPIRATION. IF BREATHING IS DIFFICULT, GIVE OXYGEN.
IF SWALLOWED, WASH OUT MOUTH WITH WATER PROVIDED PERSON IS CONSCIOUS. CALL A PHYSICIAN.
WASH CONTAMINATED CLOTHING BEFORE REUSE.

ADDITIONAL INFORMATION

LARGE DOSES OF LITHIUM ION HAVE CAUSED DIZZINESS AND PROSTRATION, AND CAN CAUSE KIDNEY DAMAGE IF SODIUM INTAKE IS LIMITED. DEHYDRATION, WEIGHT LOSS, DERMATOLOGICAL EFFECTS AND THYROID DISTURBANCES HAVE BEEN REPORTED. CENTRAL NERVOUS SYSTEM EFFECTS THAT INCLUDE SLURRED SPEECH, BLURRED VISION, SENSORY LOSS, ATAXIA AND CONVULSIONS MAY OCCUR. DIARRHEA, VOMITING AND NEUROMUSCULAR EFFECTS SUCH AS TREMOR, CLONUS AND HYPERACTIVE REFLEXES MAY OCCUR AS A RESULT OF REPEATED EXPOSURE TO LITHIUM ION.

----- PHYSICAL DATA -----

MELTING PT: 680 C
SPECIFIC GRAVITY: 0.820

APPEARANCE AND ODOR
GREY SOLID

----- FIRE AND EXPLOSION HAZARD DATA -----

EXTINGUISHING MEDIA

CLASS D FIRE-EXTINGUISHING MATERIAL ONLY.
DO NOT USE WATER.
DO NOT USE DRY CHEMICAL POWDER EXTINGUISHER ON THIS MATERIAL.
DO NOT USE CARBON DIOXIDE EXTINGUISHER ON THIS MATERIAL.

SPECIAL FIREFIGHTING PROCEDURES

WEAR SELF-CONTAINED BREATHING APPARATUS AND PROTECTIVE CLOTHING TO PREVENT CONTACT WITH SKIN AND EYES.
FLAMMABLE SOLID.

UNUSUAL FIRE AND EXPLOSIONS HAZARDS

THIS MATERIAL, LIKE MOST MATERIALS IN POWDER FORM, IS CAPABLE OF CREATING A DUST EXPLOSION.
EMITS TOXIC FUMES UNDER FIRE CONDITIONS.
MATERIAL READILY REACTS WITH WATER GENERATING FLAMMABLE AND/OR EXPLOSIVE HYDROGEN GAS.
CATCHES FIRE IF EXPOSED TO AIR.

----- REACTIVITY DATA -----

INCOMPATIBILITIES

STRONG OXIDIZING AGENTS
ACIDS
ALCOHOLS
REACTS VIOLENTLY WITH WATER.

HAZARDOUS COMBUSTION OR DECOMPOSITION PRODUCTS

LIBERATES FLAMMABLE/EXPLOSIVE HYDROGEN GAS.

----- SPILL OR LEAK PROCEDURES -----

STEPS TO BE TAKEN IF MATERIAL IS RELEASED OR SPILLED

EVACUATE AREA.
SHUT OFF ALL SOURCES OF IGNITION.
WEAR SELF-CONTAINED BREATHING APPARATUS, RUBBER BOOTS AND HEAVY RUBBER GLOVES.
COVER WITH DRY-LIME, SAND, OR SODA ASH. PLACE IN COVERED CONTAINERS USING NON-SPARKING TOOLS AND TRANSPORT OUTDOORS.
VENTILATE AREA AND WASH SPILL SITE AFTER MATERIAL PICKUP IS COMPLETE.

UNDER AN INERT ATMOSPHERE, CAUTIOUSLY ADD THE MATERIAL TO DRY BUTANOL IN AN APPROPRIATE SOLVENT. THE CHEMICAL REACTION MAY BE VIGOROUS AND/OR EXOTHERMIC. PROVISIONS MUST BE MADE FOR THE VENTING OF LARGE VOLUMES OF HIGHLY FLAMMABLE HYDROGEN AND/OR HYDROCARBON GASES. NEUTRALIZE THE SOLUTION WITH AQUEOUS ACID. FILTER OFF ANY SOLID RESIDUES FOR DISPOSAL AS HAZARDOUS WASTE. BURN THE LIQUID PORTION IN A CHEMICAL INCINERATOR EQUIPPED WITH AN AFTER BURNER AND SCRUBBER. OBSERVE ALL FEDERAL, STATE, AND LOCAL LAWS.

--- PRECAUTIONS TO BE TAKEN IN HANDLING AND STORAGE ---
CHEMICAL SAFETY GOGGLES.
COMPATIBLE CHEMICAL-RESISTANT GLOVES.
NIOSH/MSHA-APPROVED RESPIRATOR.
SAFETY SHOWER AND EYE BATH.
USE ONLY IN A CHEMICAL FUME HOOD.
AVOID BREATHING DUST.
AVOID CONTACT WITH EYES, SKIN AND CLOTHING.
AVOID PROLONGED OR REPEATED EXPOSURE.
WASH THOROUGHLY AFTER HANDLING.
CORROSIVE.
KEEP TIGHTLY CLOSED.
DO NOT ALLOW CONTACT WITH WATER.
KEEP AWAY FROM HEAT, SPARKS, AND OPEN FLAME.
HANDLE AND STORE UNDER NITROGEN.
STORE IN A COOL DRY PLACE.

----- ADDITIONAL PRECAUTIONS AND COMMENTS -----

ADDITIONAL INFORMATION

THE POWDERED MATERIAL BURNS READILY ON EXPOSURE TO AIR OR NITROUS OXIDE (DINITROGEN OXIDE). MIXTURES OF THE POWDERED HYDRIDE AND LIQUID OXYGEN ARE DETONATABLE EXPLOSIVES.

THE ABOVE INFORMATION IS BELIEVED TO BE CORRECT BUT DOES NOT PURPORT TO BE ALL INCLUSIVE

APPENDIX C

Solubility Data Using J-13 Water
at the Nevada Test Site

C.1 INTRODUCTION

This appendix presents the solubility data for radioelements based on J-13 water composition that will be used in the Preliminary Performance Assessment (PPA) analysis of the Greater Confinement Disposal (GCD) site located in Area 5 of the Nevada Test Site (NTS).

It is important to note that solubility limits are used only for the source-term calculations. In other words, solubility limits of radionuclides are taken into consideration in the estimate of the amount of radionuclides released from the boundary of the GCD boreholes. Solubilities are not considered in the subsequent transport in the geosphere once the radionuclides are outside the borehole.

Much of the material presented below is based on the following two sources: Site Characterization Plan for Yucca Mountain [DOE, 1988] and Repository Site Data Report for Tuff: Yucca Mountain, Nevada [Guzowski et al., 1983].

C.2 SOLUBILITY PARAMETERS USED IN THE PERFORMANCE ASSESSMENT

C.2.1 Processes Affecting Radionuclide Concentrations in Solution

C.2.1.1 Speciation

Since chemical elements in water can exist as various chemical species, the solubility of an element is affected by the tendency of the element to form complexes and by the concentrations of species with which it can complex [DOE, 1988]. In general, solubility increases as the variety and concentration of complexes of the element increase. Speciation and solubility, therefore, depend on the chemical properties of the chemical element and the state of the water (chemical composition, pH, Eh, and temperature). Concentrations of aqueous species are usually calculated using the formation constants of possible aqueous species with the equilibrium thermodynamic methods. These calculations usually require extensive thermodynamic data. It is important to note that solubility and speciation are in terms of the total concentration of an element in the solution; the concentration of the radionuclide depends on the isotopic composition of the element.

C.2.1.2 Precipitation

Precipitation is usually not an equilibrium phenomenon. If the process kinetics is very slow, the equilibrium thermodynamic conditions may never be reached. In this case, kinetic data are required to estimate the aqueous concentrations. On the other hand, if dissolution and precipitation kinetics are fast on the time scale of interest, equilibrium can be assumed. The solubility limit can then be estimated from equilibrium speciation calculations.

C.2.1.3 Colloid Formation

It has been shown that some actinides can form natural colloids under certain conditions [Olofsson et al., 1981]. These colloids are particulates suspended in the solution. Therefore, the formation of colloids can be viewed as an increase of the solubility. There is some indication that plutonium and americium are two elements that have the tendency to form colloids [DOE, 1988]. However, currently there is no available method to predict the formation of colloids under known solution conditions.

C.2.1.4 Radiolysis

Radiation can affect the solubility of chemical elements by changing the composition of the water [DOE, 1988]. Alpha and gamma radiation can reduce the pH and increase the Eh of the water. In addition, solids composed of alpha emitters tend to show self-irradiation damage to the crystal structure and tend to be more soluble.

C.2.2 Water Composition Used for Estimation of Solubilities

Because solubilities are used in the estimation of releases of radionuclides from the boreholes, the water composition used for estimating solubilities should reflect the conditions within the waste-bearing boreholes. This is the water that infiltrates into the boreholes from recharge and may also contain degradation products of waste containers and waste forms. However, at present, the only water available for chemical analysis in Area 5 of NTS is from three ground-water sampling wells from the saturated zone [Black, 1990]. Well UE-5C is located about 1 mile southwest of the Radioactive Waste Management Site (RWMS) and goes into the alluvial aquifer to a depth of about 1,100 feet. Well 5-C is located about 4 miles South of the RWMS and is about 1,200 feet deep into the alluvial aquifer. Well 5-B is about 3 miles south of the RWMS, and water was pumped from the alluvial aquifer at 700 to 900 feet. Because the water from Well 5-B is the shallowest of the three, the water composition from this well is probably most similar to that in the unsaturated zone. This water composition is therefore used as the reference water for the solubility estimates for PPA.

Since solubility depends on the composition, pH, Eh, and temperature of the water, it is important to use solubility data in water that is similar to that in Area 5 of the NTS. Solubility data for selected elements from three Yucca Mountain wells are available: Well J-13, Well UE-25p-1, and Well H-3. Data from Well H-3 water are eliminated first because the water is reducing. Out of the remaining two wells, the ground water chemistry of J-13 is most similar to that of Well 5-B at the NTS because the water is strongly oxidizing and is less saline than the water of UE-25p-1 [Bruton, 1990]. Therefore, solubility data for Well J-13 water are chosen to be used in the PPA. Table C.1 compares the water compositions of Well J-13 and Well 5-B.

C.2.3 Solubility and Speciation Data

In general, the prediction of solubility and speciation of radionuclides is made by two approaches. The first uses geochemical models with input based solely on equilibrium thermodynamic solution data. In the second, solubilities of chemical elements are determined in laboratory experiments using the water of interest.

The radionuclide chains whose transport will be analyzed explicitly in the PPA are shown below [Price, 1990]. Therefore, solubilities of 11 elements are needed: Ac, Am, Cs, Np, Pa, Pb, Pu, Ra, Sr, Th, and U. However, Pa is a daughter product that exists in only minute quantities, and its release would have very little effect on the performance assessment results. The solubility limits of Pa are therefore assumed to be very large. Also, from personal communication with Carol Bruton of Lawrence Livermore Laboratory [Bruton, 1990], it seems that there are practically no thermodynamic data available for Ac, so the solubility of Ac is conservatively assumed to be large.

1. Pu239 → U235 → Pa231 → Ac227.
2. Pu240 → U236 → Th232.
3. Pu241 → Am241 → Np237 → U233 → Th229.
4.

Pu238
↓

U234 → Th230 → Ra226 → Pb210.

↑
Pu242 → U238
5. Sr90.
6. Cs137.

For the rest of the radionuclides, that is, Am, Pu, U, Ra, Pb, Cs, Sr, Np, and Th, the available solubility data are described below. These data are based either on calculations from chemical-equilibrium models or experimental measurements.

Americium. Americium(III) is the only stable oxidation state observed in neutral waters. Experimental data indicate that in a neutral electrolyte at 25°C and pH 7, americium has a solubility of about 10^{-6} to 10^{-4} moles/L [DOE, 1988]. In well J-13 water, the solubility has been measured to be 9×10^{-7} to 1.3×10^{-6} moles/L [Nitche and Edelstein, 1985]. Solubility has also been calculated using EQ3/6 by Ogard and Kerrisk [1984]. The calculated solubility was about 100 times smaller than the measured solubility. The EQ3/6 thermodynamic data base for americium has since been revised.

Plutonium. Under oxidizing conditions, plutonium(V) and plutonium(VI) are the primary aqueous species. In a neutral electrolyte in contact with air, plutonium solubility

Table C.1
Well 5-B and J-13 Water Chemistry

Element	Concentration (mg/L)	
	Well 5-B	Well J-13
Ca	1.0 - 2.2	11.5
Cl	20 - 27	6.4
F	0.8 - 1.2	2.1
K	11 - 14	5.3
Li	0.02 - 0.03	0.06
Mg	0.5 - 2.3	1.76
NO ₂ +NO ₃	1.1 - 3.3	10.1
Na	92 - 180	45.
PO ₄	0.001 - 0.009	---
SO ₄	51 - 64	18.1
Si	45 - 72	30.0
Alkalinity	140 - 170	
pH	7.5 - 8.3	7.0
T(°C)	24.0 - 26.0	25.0

solubility has been measured to be in the range of 10^{-8} to 10^{-6} moles/L [DOE, 1988]. Solubility in Well J-13 water has been measured to be in the range of 1.4×10^{-6} to 5×10^{-5} moles/L, depending on the initial species [Nitche and Edelstein, 1985]. Ogard and Kerrisk [1984] calculated the solubility of plutonium in J-13 water using EQ3/6, and the result was about five times lower than the average of the measured values.

Uranium. In a neutral electrolyte under oxidizing conditions, uranium is the dominant aqueous species, and schoepite ($\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$) is the most stable solid phase at 25°C . At higher temperatures, beta-uranium dioxide may be more stable [Robins, 1966]. So far there are no direct measurements of uranium solubility in J-13 water. Experiments were performed on spent fuel dissolution in Well J-13 water, and they showed maximum uranium concentrations of 2×10^{-5} moles/L. Although the samples in these experiments were exposed to air, uranium(IV) is the primary species in spent fuel; the applicability of these data are questionable. Ogard and Kerrisk [1984] calculated the solubility of uranium in J-13 water using EQ3/6 and found it to be about 4×10^{-3} moles/L. Calculations performed under similar conditions by PHREEQUE found the solubility to be 2.5×10^{-5} moles/L [Guzowski et al., 1983].

Neptunium. Nitche and Edelstein [1985] measured the solubility of neptunium in well J-13 water to be in the range of 6.5×10^{-4} to 2.2×10^{-3} moles/L and in the range of 3.4×10^{-4} to 4.5×10^{-4} moles/L in a neutral electrolyte. In both solutions, neptunium(V) was the only oxidation state observed. No calculation has been performed for neptunium solubility.

Strontium. Ogard and Kerrisk [1984] reported the calculated solubility of strontium in J-13 water to be 8×10^{-4} . No measured value of solubility has been reported, and there is no plan for any measurement for the Yucca Mountain Project.

Radium. The solubility of radium was calculated by Ogard and Kerrisk [1984], using EQ3/6 in J-13 water at pH 7, to be 3×10^{-7} moles/L. The solubility under the same conditions was calculated by PHREEQUE to be 1×10^{-6} moles/L [Guzowski et al., 1983]. Solubility measurements are planned for radium for the Yucca Mountain Project.

Cesium. The solubility of cesium is expected to high [Rai and Serne, 1978]. No numerical limit was found in the literature.

Thorium. The solubility of thorium is expected to be low [Apps et al., 1983]. A solubility limit of 4×10^{-15} moles/L was reported from calculations using PHREEQUE in J-13 water [Guzowski et al., 1983]. A value of 1×10^{-9} moles/L was reported by Kerrisk [1985]; however, it is not clear how the value was obtained. Solubility measurements are planned for the Yucca Mountain Project.

Lead. The solubility of lead in J-13 water was calculated by PHREEQUE to be 6.3×10^{-6} moles/L [Guzowski et al., 1983]. These appear to be the only relevant data available.

Because the calculations performed using PHREEQUE used thermodynamic data that are older than those used by Ogard and Kerrisk using EQ3/6, the calculated solubilities by Ogard and Kerrisk, therefore, are used for PPA when they are available. The calculations by PHREEQUE are used only when there are no other data available. When both experimental and theoretical data are available, the higher number is used for PPA. Since the solubility of cesium has only been reported as "high" in J-13 water, solubilities of several cesium compounds in water were used as the basis for selecting a numerical value used for PPA. The solubilities of CsCl, Cs₂CO₃, and CsF are 162, 261, and 367 grams per 100 cc of cold water, respectively [Weast, 1982]. For the PPA, a value of 500 g/100 cc, or 5 g/g, is chosen as the solubility of cesium. The solubilities of Ac and Pa were also chosen to be 5 g/g. Table C.2 summarizes the solubility of elements used in the PPA. Since the distributions for the ranges of solubilities are not known, uniform distributions are used.

Table C.2
Solubility Based on J-13 Water

Element	Moles/L	g/g	Distribution
Americium	9.0E-7 - 1.3E-6	2.2E-7 - 3.1E-7	Uniform
Plutonium	1.4E-6 - 5.0E-5	3.4E-7 - 1.2E-5	Uniform
Uranium	4.0E-3	9.4E-4	
Neptunium	6.5E-4 - 2.2E-3	1.5E-4 - 5.2E-4	Uniform
Radium	3.0E-7	6.8E-8	
Strontium	8.0E-4	7.2E-5	
Cesium	High	5.0	
Actinium	High	5.0	
Protactinium	High	5.0	
Thorium	1.0E-9	2.3E-10	
Lead	6.0E-6	1.3E-6	

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APPENDIX D

Solubility Calculations Based on Well 5-B Water at the Nevada Test Site

Date: November 8, 1990

Work Performed by Lawrence Livermore National Laboratory
Under Sandia Contract No. 27-0853

**Equilibrium Controls of
Radionuclide Concentrations in
Nevada Test Site Waters:
Preliminary Results for Th, U, Np, Pu, Am,
Sr, Ra and Pb**

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Summary

Solubility limits imposed by solid phases on concentrations of Th, U, Np, Pu, Am, Sr, Ra and Pb in Nevada Test Site (NTS) waters at 25°C were calculated using the EQ3/6 geochemical modeling code package. The chemistry of water from well 5B was chosen to represent water chemistries across the NTS. The impact of changes in solution Eh and pH on predicted radionuclide concentrations was also determined.

The calculations do not provide for redox disequilibrium, kinetics, elevated temperature, and the presence of organic species and/or colloids.

Ranges of predicted radionuclide concentrations in solution corresponding to changes in the identity of the solid phase, Eh and pH can be used to formulate reasonable input constraints to performance assessment calculations.

Introduction

Ranges of potential concentrations of radionuclides in solution are required to make performance assessment calculations for waste disposal at the Nevada Test Site. Many variables can affect estimates of radionuclide concentrations in solution – groundwater chemistry, Eh, pH, temperature, solid precipitation, colloid formation, surface reactions, and so on. Calculations in this paper focus on solubility constraints imposed by solid phases on radionuclide concentrations in solution, and on the impact of changes in Eh and pH on radionuclide concentrations in solution. As a first approximation, it was assumed that the major element chemistries of NTS waters do not vary significantly.

Results presented for each radionuclide include: 1) radionuclide concentrations calculated to be in equilibrium with various solid phases; 2) effect of changes in Eh and pH on radionuclide concentrations in equilibrium with selected solid phases; and 3) effect of changes in pH on both radionuclide concentrations in solution and the identity of the solid precipitate. Preceding presentation of the results are discussions of: 1) the calculational tools used to obtain the results; 2) the assumptions inherent in the calculations; and 3) the calculational techniques employed to obtain estimates of radionuclide concentrations in solution.

Description of Calculational Tools and Thermodynamic Data Bases

Computer code EQ3 (Wolery, 1983) was used to calculate the radionuclide concentrations in equilibrium with a variety of solid phases. Computer code EQ6 (Wolery and Daveler, 1990) was used to calculate the effect of pH on radionuclide concentrations and on the identity of the solubility-limiting solid. The software quality assurance documents for these codes were previously sent to Dr. Margaret Chu at Sandia National Laboratory, Albuquerque, NM. EQ3 and EQ6 are commonly referred to jointly as "EQ3/6". EQ3/6 does not differentiate among isotopes of a given element. In all calculations, the isotopes of an element are assumed to act in an identical fashion, and only the total molality of the element is considered.

The Eh-pH diagrams showing the impact of Eh and pH on radionuclide concentrations and the identity of the solubility-limiting phase were constructed using the computer code SOLUPLOT. SOLUPLOT was written in 1978 by Craig Bethke, and the code is now readily available in the public domain.

EQ3 and EQ6 both operate on basic thermodynamic principles, and require a thermodynamic data base for their operation. The thermodynamic data base compiled and evaluated by Lawrence Livermore National Laboratory to support EQ3/6 and used in this study is version number DATA0.com.R3. Thermodynamic data required by SOLUPLOT was also obtained from DATA0.com.R3 to ensure consistency among the calculations.

A magnetic tape containing the source codes for EQ3 and EQ6, associated libraries and files, and data base DATA0.com.R3 are being sent to Dr. Chu at Sandia under separate cover.

Assumptions

The following calculations were made assuming the maintenance of thermodynamic equilibrium. No kinetic constraints to the precipitation or dissolution of solid phases were considered. The potential influence of kinetics is discussed in the text, and reference is made to studies that have explicitly recorded the importance of kinetic factors.

No kinetic inhibitions to the formation and destruction of redox-sensitive aqueous species were considered. All reactions have been assumed to occur instantaneously, although redox-sensitive reactions in the aqueous phase may take days to weeks to come to equilibrium, if at all. The calculations in this paper represent an ideal equilibrium "base-line" towards which systems approach with time.

Purely inorganic systems were considered; no organics were provided for in the calculations. Aqueous organic species have been found to be effective complexing agents, and may significantly impact solution pH. If organic species may be incorporated into the waters of interest through interactions with waste, the calculations in this paper may not be relevant.

No provision has been made for the presence of colloids. Colloid formation can sequester radionuclides and may impact the transport of radionuclides.

The reported chemistries of waters from the Nevada Test Site were used in the calculations. Interactions with corroding metals, organics or other foreign materials in the subsurface may substantially alter the chemical characteristics of water. The following calculations do not provide explicitly for any such material interactions. The potential impacts of changes in Eh and pH can, however, be estimated from the calculations.

All calculations have been made at 25°C. The thermodynamic data base for radionuclide-bearing aqueous species and solids is incomplete at higher temperature. There is growing worldwide recognition of the need to acquire high-temperature data. However, we can not expect such data in the near future.

Calculational Approach

The following three sections review briefly how the results presented in this report were obtained.

Radionuclide Concentrations in Equilibrium with Solid Precipitates

Series of EQ3 runs were made to calculate the concentrations of radionuclides in equilibrium with selected solids. The solids were chosen to represent potential ranges of radionuclide concentrations in solution. Concentrations can be lower if equilibrium with respect to a given phase has not been achieved, or can be higher if kinetic inhibitions to solid precipitation exist.

The solution composition was assumed to equal that of sample 73-01 from well 5B with a pH of 7.9. Sample 73-01 was considered to be representative of the series of samples taken from well 5B. The oxidation potential was assumed to be fixed at 0.2 bars by equilibrium with the atmosphere. Measured concentrations of Pu, Ra and U in well 5B waters were deleted from the water analyses to better represent the composition of groundwaters before contamination. The reported analysis for sample 76-01 appears to be in error. The concentration of Mg is given as 210 mg/L, whereas a value two orders of magnitude less is consistent with the remainder of the Mg analyses and with the maintenance of charge balance.

Results for each radionuclide are discussed individually. However, similarities exist among all results. If the solid under consideration was composed of an element in an oxidation state that was not favored in well 5B water, the solid could not be brought to equilibrium with the fluid phase, no matter how high the radionuclide concentration in solution. For example, none of the sulfide solids considered (such as ThS_2 , SrS) could be equilibrated with Well 5B water because SO_4^{-2} is the stable redox state of sulfur in the water, rather than S^{-2} . In general, solids containing fluoride, nitrate, phosphate (except for Pb) or chloride as major components were not considered because sample calculations suggested that equilibrium with respect to these phases could not be achieved in NTS waters. However, all solids were considered explicitly when calculating Eh-pH diagrams and making the EQ6 simulations described below. Thus, all solids of importance are likely to be considered in the calculations.

Effects of Eh and pH on Radionuclide Concentrations In Equilibrium with Solid Precipitates

Eh-pH diagrams, sometimes called Pourbaix diagrams, depict the stability of aqueous species and solids as a function of Eh (redox potential) and pH. An excellent description of the construction and interpretation of Eh-pH diagrams can be found in Garrels and Christ (1965). The diagrams are drawn for a fixed activity of a metal (a radionuclide, in this study) at a given temperature. The activity of a species is related to its concentration in solution, expressed in molality (m), where m = moles of solute/kilogram of water, by $a = \gamma m$. The dominant aqueous species containing the metal in any given region of Eh-pH space is assigned this fixed activity.

The upper and lower stability limits of water comprise the upper and lower sloping boundaries of the diagrams. The upper boundary is defined by the reaction:

when the partial pressure of $\text{O}_{2(g)}$ equals 1.

The lower boundary is defined by the reaction:

when the partial pressure of $\text{H}_{2(g)}$ equals 1.

In this study, an Eh-pH diagram illustrating the dominant radionuclide-bearing aqueous species at 25°C was constructed for each element. These diagrams are useful for determining the dominant oxidation state of the radionuclide at the Eh and pH of interest. In addition, the existence of the radionuclide-bearing aqueous species as a cation, anion or neutral species is important in predicting its potential behavior in solution. A cation, for example, can participate in surface reactions with clays and oxides in tuffs. It is possible that some cationic radionuclide species could be removed from the fluid and sequestered via surface complexation reactions.

To supplement the Eh-pH diagram showing aqueous speciation, Eh-pH diagrams considering both solid and aqueous species were constructed. The location and movement of the boundaries between solid and aqueous species in response to variations in the activity of the radionuclide illustrate the ability of solids to sequester radionuclides under varying Eh and pH conditions. The diagrams also show how the identities and compositions of solubility-limiting solids vary with Eh and pH.

The conversion of the activity of the dominant radionuclide to its concentration may be of importance in applying the Eh-pH diagrams to field situations. The conversion is dependent on knowing the activity coefficient of the dominant aqueous species. The extended Debye-Huckel equation was used in EQ3/6 to calculate activity coefficients. Activity coefficients vary with solution concentration, and with the charge of the aqueous species. Neutral species have an activity coefficient of 1. Generally, as the charge of the aqueous species increases, so does the activity coefficient. For reference, in well 5B water, the activity coefficient of most tri-, di- and mono-valent species range from 1 to 0.5. Quadra-valent species have even smaller activity coefficients—0.29 for $\text{UO}_2(\text{CO}_3)_3^{(-4)}$, for example. More information can be supplied regarding activity coefficients if needed.

The extended Debye-Huckel equation can be generally applied to solutions whose ionic strengths do not greatly exceed 0.1. For reference, well 5B has an ionic strength of about 0.007 or less. Sample 76-01 has a higher ionic strength, but the reported concentration of Mg appears to be in error, as mentioned earlier.

Warning: Even though some of the Eh-pH diagrams are constructed from pH values of 0 to 14, their reliability and validity below a pH of about 3 and above 11 should be seriously questioned. It may not be appropriate to use equilibrium calculations with available data in these regions. Little is known about the equilibrium response of most natural systems under conditions that extreme.

Effect of pH on Radionuclide Concentrations and the Identity of the Solid Precipitate

In the Eh-pH diagrams discussed previously, the composition of the water was held constant while only Eh and pH varied. In a natural system, Eh and pH will change only when there is a driving force for change. The next set of calculations was designed to better illustrate a system's response to a driving force which changes the system pH. EQ3 was first used to saturate well 5B water with the most insoluble solid bearing the radionuclide of interest. Using EQ6, NaOH(aq) was then added to the equilibrated water to increase the pH. The accompanying change in water chemistry, including the change in radionuclide concentration and the change in the identity of the radionuclide-bearing precipitate, was calculated by EQ6 as a function of pH. The process was repeated to simulate reaction in an acidic system by adding HCl(aq) to well 5B water. Results from the alkaline and acidic regions were then combined to obtain the figures shown later in this report.

Warning: The rapid increase in radionuclide concentrations at high and low pH in these diagrams should only be used as a guide to concentration trends with pH. By the time tens and hundreds of mg/kg radionuclides have been added to solution, original solution chemistries have been drastically altered. Dissolution of solids that were stable in well 5B water but later become unstable may also significantly alter water chemistry. Therefore, the diagrams should be used as a general guide to system response at high and low pH values. If the system response to a given scenario is being considered, it would be more appropriate to simulate the specific scenario using EQ6. This would yield results directly applicable to the specific problem.

Results

Thorium (Th)

Figure 1 shows the dominant aqueous species of Th in well 5B water as a function of Eh and pH at 25°C. $\text{Th}(\text{OH})_4(\text{aq})$ dominates at pH values greater than about 5.5, whereas ThF_3^+ dominates below pH of 5.5. The Eh-pH diagram shown in Figure 2 outlines the stability field of thorianite (ThO_2) as a function of Eh and pH for Th concentrations of 10^{-10} and 10^{-12} m (about 2×10^{-5} and 2×10^{-7} mg/kg, respectively). Thorianite is the stable Th-bearing solid over a wide Eh-pH range. Its precipitation maintains Th concentrations below the parts per trillion level above pH values of about 5.

Table 1 shows the predicted concentrations of Th in well 5B water in equilibrium with selected Th solids. The solid species Th, $\text{Th}(\text{OH})_4$, thorianite (ThO_2), ThS_2 , $\text{Th}(\text{SO}_4)_2$ and $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ were considered in the calculations. Other Th-sulfide species, and ThCl_4 and ThF_4 were omitted from consideration. Of the species considered, only the oxide thorianite and the hydroxide $\text{Th}(\text{OH})_4$ could come into equilibrium with well 5B water.

$\text{Th}(\text{OH})_4$ and thorianite (ThO_2) equilibria illustrate ranges in Th concentration that can result from a change in the stability and form of the precipitate. Thorianite is the crystalline ordered phase with the lowest solubility. $\text{Th}(\text{OH})_4$ may better represent the first phase to precipitate from solution— an amorphous hydroxide that, with time, would be expected to age into a more crystalline form such as thorianite, ThO_2 .

Table 1.

Solid	Th	
	Concentration	
	mg/l	molality (moles/kg)
Thorianite (ThO_2)	0.2130E-8	0.9180E-14
$\text{Th}(\text{OH})_4$	0.14	0.5904E-6

Figure 3 shows the dependence of Th concentration on pH while also providing for the control of pH on the identity of the Th precipitate. At pH values greater than 6.5, thorianite is the most stable phase and controls Th concentration at about 10^{-14} m (2×10^{-9} mg/kg). However, Th concentrations increase as pH decreases and the dominant Th aqueous species changes from $\text{Th}(\text{OH})_4(\text{aq})$ to $\text{Th}(\text{SO}_4)_2$, $\text{Th}(\text{HPO}_4)$ and other species. Figure 4 shows the changing aqueous speciation as a function of pH over this critical range. As more aqueous species containing Th form, more Th is able to be held in solution. These results are consistent with those of Langmuir and Herman (1980). Their compilation and critical evaluation of data for Th species are the source of thermodynamic data for many of the Th aqueous species under consideration.

As pH decreases to 3.9, the solid phase $\text{Th}(\text{SO}_4)_2$ co-precipitates with thorianite. Further decrease in the pH to 2.9 results in the addition of $\text{ThF}_4 \cdot 2.5\text{H}_2\text{O}$ to the phase assemblage as a co-precipitate. Predictions of Th concentrations in solution become questionable below pH values of at least 3. Nonetheless, it can be seen that Th concentrations begin to increase dramatically with decreasing pH.

To emphasize the potential ranges in Th concentration that could result from the precipitation of an initial amorphous and/or hydrous phase rather than a well-crystallized form, Th concentrations in equilibrium with $\text{Th}(\text{OH})_4$ were calculated as a function of pH (Figure 5). In contrast to Figure 3 in which all Th-bearing solids were considered as potential precipitates, only $\text{Th}(\text{OH})_4$ was allowed to precipitate over the entire pH range in Figure 5. Above a pH of 6, Th concentration is maintained at a constant value of 0.14 mg/kg. The dominant aqueous species of Th over this pH range is $\text{Th}(\text{OH})_4(\text{aq})$ (Figure 4), and the reaction between $\text{Th}(\text{OH})_4(\text{solid})$ and $\text{Th}(\text{OH})_4(\text{aq})$ is pH-independent.

Uranium (U)

Figure 6 shows the predominance diagram for U aqueous species as a function of Eh and pH at 25°C. Note the switch from uranyl (U^{+6}) species to U^{+4} species along the boundary between and roughly paralleling the upper and lower stability limits of water. This boundary is usually associated with a significant decrease in U concentrations in solution, because U^{+6} species are more soluble than U^{+4} species.

Figures 7a, b and c show the ranges of Eh and pH over which various U-bearing solids sequester U as the U activity increases from 10^{-10} to 10^{-6} . (For reference, Appendix A gives a list of the mineral names and formulas used in this report.) Figure 7d summarizes the results in terms of Eh-pH ranges over which solids are stable relative to aqueous species. For U, an activity of 10^{-8} corresponds to 2.38 ppb (parts per billion; 1 mg/kg = 1000 ppb). The key to maintaining low U concentrations under oxidizing conditions is the availability of silica for the precipitation of the U-silicates, soddyite and haiweeite. At very low Eh, the U-silicate coffinite precipitates to sequester U. If silica is not present in well 5B water, or is depleted by some reactions or processes in the system, potential U concentrations will increase dramatically.

Table 2 shows the predicted concentrations of U in well 5B water in equilibrium with selected solids at 25°C. The U-silicates maintain the lowest U concentrations in solution. In natural systems, uranophane is the most dominant U-silicate, although it is not dominant in these calculations. Thermodynamic data for uranophane in the EQ3/6 data base is estimated, and may not be accurate. In the siliceous tuffs of the Nevada Test Site, there is an abundant source of silica available to sequester U in a solid phase. Thus haiweeite and soddyite, in the absence of reliable data for uranophane, are reasonable candidates for phases expected to sequester U in siliceous systems. These two phases have been identified in spent fuel dissolution tests in J-13 water (Wilson and Bruton, 1989).

Table 2.

U		
Solid	Concentration	
	mg/l	molality (moles/kg)
Haiweeite Ca(UO₂)₂Si₆O₁₅•5H₂O	0.3633E-4	0.1526E-9
Soddyite (UO₂)₂SiO₄•2H₂O	0.017	0.7303E-7
CaUO₄	1.87	0.7842E-5
Schoepite UO₃•2H₂O	27.17	0.1141E-3
Uranophane Ca(UO₂)₂(SiO₃)₂(OH)₂	31.28	0.1314E-3
UO₂(OH)₂(beta)	33.14	0.1392E-3

The dependence of the U-bearing solid on pH is shown in Figure 8. Haiweeite is the most insoluble phase in well 5B water, given its measured pH which averages about 8. As pH increases, the U in solution increases until CaUO₄ and then soddyite precipitate to help sequester U. By the time pH increases to 11, 0.46 mg/kg U exists in solution, as compared to less than 0.000037 at a pH of 7.9. When pH decreases to 5.2, soddyite co-precipitates with haiweeite, although U concentrations continue to increase in solution.

The shape of the solubility curve in Figure 8 is typical for solids. Many solids exhibit minimum solubility at near-neutral values of pH. Their solubility tends to increase at both higher and lower pH, which results in the characteristic shape of the curve in Figure 8. In contrast, the solubility curve for Th previously shown (Figure 3) did not exhibit the increase in concentration at high pH. At high pH, the only major aqueous species of Th in solution was Th(OH)₄(aq). The reaction between thorianite and Th(OH)₄(aq) is independent of pH, which translates into a lack of dependence of Th concentrations in solution on pH. For other nuclides, changes in pH correspond to the potential for the formation of a wider variety of aqueous species that are available to hold additional nuclide masses in solution.

The dependence of U concentrations on pH assuming equilibrium with haiweeite, soddyite and schoepite are shown in Figure 9. In contrast to figure 8, the identity of the U-bearing phase was assumed to be invariant with pH. Three different EQ6 runs were made to construct Figure 9. Each run specified that equilibrium be maintained with a specific U-bearing phase as pH changed. In a real system, the identity of the solid phase would be expected to change with pH, as shown in Figure 8. Figure 9 may be useful in determining potential ranges of U concentrations in solution.

As mentioned previously, haiweeite and soddyite are potential U-bearing precipitates in Si-rich systems, such as NTS tuffs. The hydrated U-oxide schoepite (UO₃•2H₂O) will tend to precipitate

in a Si-poor system. A system can be initially Si-poor or can become Si-deficient if Si is depleted by the precipitation of silicates. Schoepite commonly precipitates in laboratory experiments with spent fuel and UO_2 in systems lacking Si and in systems depleted in aqueous Si by precipitation.

Neptunium (Np)

Figure 10 shows the aqueous speciation for Np at 25°C. Note the transition from Np^{+5} species to Np^{+4} species at the top of the NpF_2^{++} , $\text{Np}(\text{OH})_4(\text{aq})$ and $\text{Np}(\text{OH})_5^-$ fields of predominance. Under oxidizing conditions in contact with the atmosphere, as expected at the Nevada Test Site, Np^{+5} is the expected oxidation state of Np. Consideration of Np-phosphate aqueous species adds a predominance field for $\text{Np}(\text{HPO}_4)_5^{(-6)}$ between the $\text{Np}(\text{OH})_4(\text{aq})$ and $\text{Np}(\text{OH})_5^-$ fields. Table 3 shows the predicted concentrations of Np in solution in equilibrium with selected solids. NpO_2 is by far the most insoluble precipitate of Np in well 5B water. Much greater concentrations of Np are required before other Np-bearing solids can precipitate. It is unlikely that $\text{NpO}_2(\text{OH})_2$ will ever precipitate unless it is favored by extreme kinetic constraints.

Table 3.

Solid	Np	
	Concentration	
	mg/l	molality (moles/kg)
NpO_2	0.36	0.1512E-5
$\text{NaNpO}_2\text{CO}_3 \cdot 3.5\text{H}_2\text{O}$	30.17	0.1273E-3
$\text{NpO}_2(\text{OH})(\text{am})$	78.23	0.3300E-3
Np_2O_5	254.93	0.1075E-2
$\text{NpO}_2(\text{OH})_2$	7419.	0.3130E-1

Initially, it might be reasonable to choose the equilibrium concentrations NpO_2 and $\text{NpO}_2(\text{OH})(\text{am})$ as lower and upper bounds on expected Np concentrations in solution. NpO_2 represents the most insoluble phase; $\text{NpO}_2(\text{OH})(\text{am})$ represents the precipitation of a less crystalline, hydroxide-bearing phase which may be more likely to precipitate owing to kinetic constraints. (See the more extended discussion of the impact of kinetics on the nature of the precipitate in the following section "Plutonium (Pu)").

$\text{NaNpO}_2\text{CO}_3 \cdot 3.5\text{H}_2\text{O}$ was not chosen as the upper limit on Np concentration because its precipitation is dependent on Na and CO_3 concentrations in solution, as well as Np. The choice of $\text{NpO}_2(\text{OH})(\text{am})$ avoids these complications.

The dependence of Np concentration on Eh and pH, assuming precipitation of NpO_2 , is shown in Figure 11. If the Eh is reducing, Np is maintained at very low concentrations over a wide range in pH. Even at a Np concentration of 10^{-12} molal, which corresponds to a vanishingly small concentration of 2.37×10^{-7} mg/kg, NpO_2 is stable up to a pH of 10.

If the environment is oxidizing, the situation is considerably different. The Eh of well 5B water in equilibrium with the atmosphere is about 0.75 volts at a pH of 7.9. This point of the Eh-pH diagram falls very near the upper stability limit of water. In this region, reductions of just a few tenths of volts produce orders of magnitude changes in Np concentrations in solution. The dependence of Np concentrations on Eh is a well-recognized phenomenon. The concentration of Np in equilibrium with NpO_2 in well 5B water was calculated to equal about 10^{-6} molal assuming atmospheric conditions (Table 3). If some process acts in the subsurface at NTS to reduce the effective Eh for Np, the concentration of Np in solution would be expected to decrease. Interactions with buried metals or organics, for instance, could reduce the Eh.

Figures 12 and 13 show how Np concentrations vary with pH assuming equilibrium with NpO_2 and $\text{NpO}_2\text{OH(am)}$, respectively. NpO_2 was the stable Np-bearing solid over the entire range of pH in Figure 12. Note that as pH decreases, Np concentrations rapidly increase. The calculation was carried out assuming that well 5B water was in equilibrium with the atmosphere. Figure 12 is, in effect, a transverse across Figure 11 very close to and parallel to the upper stability limit of water. Because pH is decreasing while Eh remains strongly oxidizing, Np concentrations increase rapidly, as they do in Figure 11. The importance of providing for the anticipated redox conditions, and any spatial and/or temporal variations in the redox conditions in the waste site, cannot be over-emphasized.

Np concentrations in equilibrium with $\text{NpO}_2(\text{OH})(\text{am})$ are shown in Figure 13 as a function of pH. Neither NpO_2 nor any other Np-bearing phase other than $\text{NpO}_2(\text{OH})(\text{am})$ was allowed to precipitate in order to simulate kinetic inhibitions to the precipitation of more stable phases. Np concentrations have a strong dependence on pH near the pH of well 5B waters.

Plutonium (Pu)

The aqueous speciation of Pu at 25°C in well 5B water is shown in Figure 14. The species $\text{Pu}(\text{OH})_5^+$, with Pu in the $+5$ state, dominates at pH values greater than about 7. Below a pH of 7, a variety of Pu species complexed by sulfate, fluoride, carbonate, oxygen and hydroxide dominate. The abrupt bend in the $\text{PuSO}_4^+/\text{Pu}^{+++}$ boundary is caused by the changing speciation of the sulfur species. Below a pH of about 2, HSO_4^- with S in the $+6$ state dominates instead of SO_4^{--} . This conversion accounts for the vertical portion of the $\text{PuSO}_4^+/\text{Pu}^{+++}$ boundary. Under reducing conditions, both SO_4^{--} and HSO_4^- yield to $\text{H}_2\text{S(aq)}$ with S in the $+2$ state as the dominant species in solution. This conversion accounts for the sloping portion of the $\text{PuSO}_4^+/\text{Pu}^{+++}$ boundary. Pu exists in the $+6$ state only under very oxidizing conditions; Pu dominates in the $+3$, $+4$ and $+5$ state over the most Eh-pH ranges.

The concentrations of Pu in equilibrium with Pu solids in well 5B water is given in Table 4. Crystalline PuO_2 controls Pu at the lowest levels in solution, whereas the amorphous hydroxide $\text{Pu}(\text{OH})_4$ requires almost eight orders of magnitude more Pu in solution before it will precipitate. The oxy-hydroxide $\text{PuO}_2(\text{OH})_2$ falls between these two end-members.

Table 4.

Pu		
Solid	Concentration	
	mg/l	molality (moles/kg)
PuO₂	0.2620E-6	0.1074E-11
PuO₂(OH)₂	0.9881E-2	0.4050E-7
Pu(OH)₄	29.40	0.1205E-3

Rai and Ryan (1982) have shown that the initial Pu precipitate to form from solution is often not a pure crystalline PuO₂, but rather an amorphous hydroxide. There are various kinetic (that is, rate-limiting) constraints to the precipitation of crystalline phases from solution, especially at low temperatures. Precipitation of amorphous phases prior to the crystalline form is common in nature at low temperatures. Increased temperatures favor the precipitation of the thermodynamically more stable phase.

The initial amorphous precipitate will tend to age to the crystalline form with time. How long the aging process takes is not known, however. (See Wilson and Bruton, 1989 for further discussion.) In addition, the effects of radiation will tend to slow the ageing process (Rai and Ryan, 1982). For the purposes of making performance assessment calculations, I suggest that Pu concentrations ranging from PuO₂ to Pu(OH)₄ be used to represent the best-case scenario (PuO₂) to the worst-case scenario (Pu(OH)₄).

Both the best-case and worst-case scenarios are used to calculate the effects of Eh and pH on Pu concentrations shown in Figures 15 and 16 for PuO₂ and Pu(OH)₄, respectively. It can be seen from Figure 15 that Pu concentrations are maintained at very low levels by the precipitation of PuO₂ over wide ranges of pH and Eh. Under strongly oxidizing conditions, Pu concentrations will not exceed 10⁻⁶ molal (0.24 mg/kg) until the pH decreases to less than 4. At pH values greater than 6, Pu concentrations are maintained at less than 2.4x10⁻⁵ at all values of Eh, that is, under all redox conditions.

Pu concentrations in solution increase dramatically if kinetic constraints do not allow PuO₂ to precipitate. Figure 16 was constructed by not allowing PuO₂ to form. PuO₂(OH)₂ is the stable phase under highly oxidizing conditions, whereas Pu(OH)₄ precipitates at slightly lower values of Eh. Pu concentrations routinely exceed 10⁻⁸ molal (0.0024 mg/kg) over a wide range of Eh and pH when PuO₂ is not allowed to precipitate from solution owing to kinetic considerations.

The dependence of Pu concentrations on pH is shown in Figures 17 and 18. PuO₂ is the solubility-limiting phase over the entire pH range in Figure 17. The impact of kinetic inhibitions to PuO₂ precipitation were not considered in constructing this figure. The classic minimum in concentration is encountered from about pH 8 to 10. Unless the pH of the system at NTS is expected to generate pH values of less than 6 or greater than 11 under oxidizing (atmospheric) conditions, PuO₂ can be expected to maintain Pu concentrations in solution well below the parts per billion level.

Concentrations of Pu in equilibrium with Pu(OH)₄ as a function of pH are shown in Figure 18. Figure 18 was constructed by suppressing the precipitation of all solids except Pu(OH)₄. Pu con-

centrations in Figures 17 and 18 can be used to obtain upper and lower bounds on Pu concentrations in equilibrium with Pu-bearing solids.

Americium (Am)

Am is complexed primarily by carbonate over the pH range of about 6 to 10 (Figure 19). As the pH increases to 10.7, and the OH⁻ content of the water increases, the hydroxide Am(OH)₃(aq) dominates. At pH values less than about 6, the sulfate and fluoride complexes of Am become important.

The tendency of Am to be associated with carbonate is reflected by the stability of Am-bearing solids as a function of Eh and pH (Figure 20). The solid AmOHCO₃ is stable from a pH of less than 6 to 10.7. The solid Am(OH)₃ is stable at pH values greater than 10.7.

Figure 21 shows the contours of Am concentration in equilibrium with AmOHCO₃. To the lower pH side of the contours, only various Am aqueous species exist. Am concentrations are not high enough to support precipitation of an Am-bearing solid. As the concentration of Am increases, the stability field of Am extends to lower pH. At a pH of about 8, Am concentrations will be limited to about 10⁻⁸ molal (0.0024 mg/kg) by the precipitation of AmOHCO₃. The solid Am(OH)₃ will precipitate above a pH of 10.7 when the concentration of Am(OH)₃(aq), the main aqueous species above pH 10.7, exceeds 10^{-8.4} molal (0.00097 mg/kg).

My previous studies have shown that the precipitation of Am-carbonates is sensitive to the carbonate concentration in solution. More Am is held in solution rather than precipitating as a solid Am-carbonate when carbonate concentrations in solution increase. This behavior results from the predominance of the Am-carbonate aqueous species shown in Figure 19. Precipitation of carbonates such as calcite with increasing temperature or interactions with waste components could potentially change the carbonate concentrations in well 5B water. The impact of such variations should be more fully explored in a future study.

Table 5 lists the Am concentrations in equilibrium with selected solids in well 5B water. At the pH of about 8 and oxidizing conditions of well 5B waters, AmOHCO₃ is the least soluble phase, resulting in the lowest Am concentrations in solution. Under these conditions of Eh and pH, Am(OH)₃ is more soluble and requires greater Am concentrations in solution to precipitate. There also exists an amorphous form of Am(OH)₃ which requires about 30 times more Am in solution than required for its crystalline counterpart before it can precipitate. However, as discussed previously, the first Am-bearing phase to precipitate from solution may be less-than-perfectly crystalline.

Table 5.

Solid	Am	
	Concentration	
	mg/l	molality (moles/kg)
AmOHCO ₃	0.0030	0.1225E-7
Am(OH) ₃	3.98	0.1637E-4
Am(OH) ₃ (am)	90.05	0.3706E-3

Previous experimental tests of spent fuel dissolution in J-13 water (Wilson and Bruton, 1989) have suggested that Am concentrations in solution do not reach concentrations as high as those in Table 5. Predicted Am concentrations in equilibrium with AmOHCO_3 were higher than those measured in the tests. It was hypothesized that co-precipitation or sorption could have accounted for the lower Am in solution. In either case, the trend is for thermodynamic predictions to overestimate Am concentrations in solution. Predictive values would thus represent conservative estimates for input to performance assessment codes.

Figure 22 shows the dependence of Am concentrations in solution on pH and the Am-bearing solid. AmOHCO_3 is the solubility-limiting phase up to a pH of 10.5, at which point $\text{Am}(\text{OH})_3$ begins to co-precipitate with it to limit Am concentrations in solution. Although the solids are effective at controlling Am concentrations from pH values from about 8 to 10.5, higher and lower pH values result in rapidly increasing Am concentrations in solution. Am concentrations are still maintained at less than 0.1 mg/kg over the pH range of 6 to 11 under oxidizing, atmospheric conditions.

Strontium (Sr)

The aqueous speciation of Sr in well 5B water at 25°C is quite simple, as shown in the Eh-pH diagram in Figure 23. The divalent cation Sr^{++} dominates until the pH exceeds 10, at which point $\text{SrCO}_3(\text{aq})$ and then SrOH^+ gain dominance. There are likewise few solids bearing Sr as their primary component which can precipitate in well 5B water. Figure 24 shows the primary Sr-bearing solids as a function of Eh and pH at a Sr concentration of 10^{-6} molal (0.088 mg/kg Sr). From a pH of about 8 to 13 at this Sr concentration, the carbonate strontianite (SrCO_3) will precipitate, followed by the silicate SrSiO_3 at pH greater than about 13. Sr exists in one oxidation state ($+2$) only, so its concentration in solution is not dependent on Eh or the redox potential unless it is sequestered by a ligand which is Eh-sensitive. The stability of strontianite and SrSiO_3 are not dependent on Eh.

Table 6 lists the Sr concentrations in equilibrium with strontianite in well 5B water.

Table 6.

Solid	Sr	
	Concentration	
	mg/l	molality (moles/kg)
Strontianite (SrCO_3)	0.39	0.4459E-5

Figure 25 shows that Sr concentrations can reach as high as 10^{-4} molal (8.8 mg/kg) at a pH of about 6.3 before strontianite precipitates to sequester further additions of Sr to solution. For simplicity in this diagram, the fields of strontianite and SrSiO_3 are grouped together as "solid" and the aqueous species field as "aqueous". As the pH of the system increases, less Sr can be held in solution.

In addition to precipitating as an individual phase, Sr can also be removed from solution as a component of a carbonate solid solution. In fact, this is a more likely scenario than precipitating as a separate phase. Calcite (CaCO_3) can precipitate with varying amounts of Sr replacing the Ca in its structure. Carbonates become less soluble with increasing temperature, and thus if well 5B water is heated, it may be expected to precipitate a calcite solid solution. The Sr content of the solid solution depends on the temperature and the Ca and Sr content of the waters at the time of precipitation.

Our geochemical models which predict the dynamic interactions among solids and fluids contain the solid solution models needed to model Sr sequestration in a calcite solid solution. Given scenarios as to the rates of temperature increase relative to the rates of Sr addition of water, we could calculate the mass of Sr that could precipitate as part of a calcite solid solution. This phenomenon could be investigated more fully in the future.

Neglecting solid solutions for the time being, strontianite (SrCO_3) is the only potential Sr-bearing precipitate from well 5B water at 25°C . As shown in Table 6, its precipitation will maintain Sr concentrations at about 0.39 mg/kg, given current carbonate concentrations in well 5B water. However, if carbonate concentrations decrease owing to precipitation of solid carbonates, Sr concentrations in equilibrium with strontianite will increase to adjust for the loss of carbonate.

Figure 26 shows the relation between Sr concentration in solution and pH. Only one solid, strontianite, is stable over the entire pH range. Sr concentrations are maintained at less than 1 mg/kg as long as the pH is greater than about 7.5. As pH decreases, the concentration of Sr increases as needed to balance the increased H^+ in solution according to the equation:

However, as mentioned previously, the possibility that Sr will be sequestered as part of a carbonate solid solution must be considered. This would tend to decrease the Sr in solution, which would make the calculated value of 0.39 mg/kg in Table 6 a conservative estimate of Sr in solution.

Radium (Ra)

There is only one aqueous species of Ra in the EQ3/6 thermodynamic data base at the present time— Ra^{++} . Thus Ra^{++} is calculated to be stable over the entire stability range of water. Only three solid phases containing Ra are in the data base— $\text{Ra}(\text{NO}_3)_2$, $\text{RaCl}_2 \cdot 2\text{H}_2\text{O}$ and RaSO_4 . Table 7 shows that of these three solids, only RaSO_4 can come into equilibrium with well 5B water. In fact, only 0.023 mg/kg Ra in solution will cause RaSO_4 to precipitate given the Eh and pH of well 5B water. Even as Eh and pH vary, RaSO_4 still effectively sequesters Ra (Figure 27). RaSO_4 is only unstable at extremely low pH and Eh. Its stability limits are defined by the outer limits of the predominance field of $\text{SO}_4^{=}$, as previously discussed in the section on Pu.

According to the reaction

one can calculate the activity of Ra in solution for a given amount of $\text{SO}_4^{=}$. For the quantity of $\text{SO}_4^{=}$ in well 5B water, Table 7 shows that no Ra precipitate is predicted to form if the Ra concentration is less than 0.023 mg/kg. RaSO_4 precipitation will maintain Ra concentrations at 0.023 mg/kg if sufficient $\text{SO}_4^{=}$ remains in solution and is not depleted by precipitation or other effects. If $\text{SO}_4^{=}$ is depleted, Ra concentrations in solution will increase to try to maintain equilibrium with RaSO_4 .

Table 7.

Ra		
Solid	Concentration	
	mg/l	molality (moles/kg)
RaSO₄	0.023	0.1036E-6

Figure 28 shows the effect of pH on Ra concentrations in equilibrium with RaSO₄ at 25°C. These calculations suggest that Ra concentrations will be maintained at less than 0.1 mg/kg over the pH range of 2 to 12, providing the sulfate content of well 5B water does not change significantly.

The paucity of thermodynamic data for Ra-bearing aqueous species and solids in the EQ3/6 data base suggests that it would be useful to conduct a literature survey for such data in the future.

Lead (Pb)

The aqueous speciation of Pb in well 5B water at 25°C is shown in Figure 29. Pb exists in the +2 valence state over the entire Eh-pH range, so the speciation of Pb is a function of pH only. Pb^{++} is the dominant aqueous species only at pH values of less than about 8.

The Pb system was unique in this study because the calculations suggested that Pb-phosphate-bearing solids can effectively limit Pb concentrations in solution. For example, Table 8 shows that pyromorphite ($Pb_5(PO_4)_3Cl$) is the least soluble phase in well 5B water at 25°C, followed by the carbonate cerussite. It has been suggested by Nriagu (1974) that Pb-phosphates control the migration and fixation of Pb in the environment. The impact of phosphate-bearing solids and the reliability of their thermodynamic data should be the subject of further study. Table 8 shows that a variety of Pb-bearing solids can act to limit Pb concentrations in solution to below 0.1 mg/kg.

Table 8.

Pb		
Solid	Concentration	
	mg/l	molality (moles/kg)
Pyromorphite $Pb_5(PO_4)_3Cl$	0.3458E-3	0.1669E-8
Cerussite ($PbCO_3$)	0.2659E-2	0.1283E-7
Plattnerite (PbO_2)	0.012	0.5720E-7
Plumbogummite $PbAl_3(PO_4)_2(OH)_5 \cdot H_2O$	0.017	0.8410E-7
Hydrocerussite $Pb_3(CO_3)_2(OH)_2$	0.018	0.8643E-7
$PbSiO_3$	0.026	0.1270E-6
$(Pb(OH)_2)_3 \cdot PbCl_2$	0.86	0.4167E-5
$PbCO_3 \cdot PbO$	1.59	0.7663E-5
Pb_2SiO_4	2.75	0.1328E-4
Minium $Pb_2^{+2}Pb^{+4}O_4$	6.33	0.3057E-4
Anglesite ($PbSO_4$)	22.56	0.1089E-3
Litharge (PbO)	569.19	0.2747E-2
Massicot (PbO)	868.93	0.4194E-2

Figures 30 and 31 show the stability of Pb-bearing solids as a function of Eh and pH. Figure 30 was constructed by taking explicit account of the phosphate content of well 5B water, but neglecting the carbonate content. Figure 31 was constructed by accounting for the carbonate, but neglecting the phosphate. Carbonate and phosphate could not be considered in the same diagram because the speciation of both elements are pH-dependent. Only one pH-dependent ligand species can be provided for in a given Eh-pH diagram.

The stability of Pb-bearing solids in the phosphate system is shown in Figure 30 as function of Eh, pH and the activity of Pb. Pyromorphite and plumbogummite, both containing phosphate, dominate except at very low Eh values, at which point galena (PbS) stability is favored. Galena stability is related to the destabilization of SO_4^{2-} relative to S^{+2} with decreasing Eh, as discussed earlier. Contours of Pb activity show that the stability fields of pyromorphite and galena move to higher pH with decreasing Pb concentrations. Even at 10^{-6} molal Pb (0.21 mg/kg), Pb solids will tend to precipitate when the pH decreases to 5.

The stability of Pb-bearing solids when carbonate is selected as the pH-dependent ligand is shown in Figure 31. The phosphate-bearing species are not considered in this diagram. The phosphate-bearing pyromorphite and plumbogummite are replaced by cerussite, alamosite and plattnerite. Comparison of Figures 30 and 31 shows that for a given Pb concentration, Pb-bearing solids containing phosphate extend to lower values of pH. This reflects the fact that the Pb-phosphate-bearing solids are more stable than the Pb-carbonate (cerussite) and Pb-silicate (alamosite) solids. For example, at a pH of 6, the Pb-carbonate cerussite limits Pb concentrations to 10^{-6} molal (0.21 mg/kg). This is approximately an order-of-magnitude less effective than the phosphate-bearing solids under the same conditions.

The boundaries of the galena field vary between Figures 30 and 31. Galena is stable at very low Eh over the entire range of pH in the carbonate system, but terminates at pH of about 9.8 in the phosphate system. The galena/alamosite stability boundary is a function of pH, whereas the galena/plumbogummite boundary is not.

The tendency of Pb-phosphates to buffer Pb at lower concentrations than Pb-carbonates is emphasized in Figures 32 and 33, which show the dependence of the Pb-bearing solid and Pb concentration on pH. Figure 32 was constructed neglecting the phosphate content of well 5B water; Figure 33 was constructed taking explicit account of both carbonate and phosphate species. Pb-phosphate solids precipitate preferentially to Pb-carbonate (cerussite) and silicate (alamosite) over the entire pH range. In addition, Pb-phosphates control the Pb content of the water an order-of-magnitude lower than the Pb-carbonate. The Pb-oxide plattnerite is stable in both systems when the pH becomes alkaline.

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APPENDIX A. MINERAL NAMES AND FORMULAS

NAME	FORMULA
Alamosite	PbSiO_3
Anglesite	PbSO_4
Cerussite	PbCO_3
Coffinite	USiO_4
Haiweeite	$\text{Ca}(\text{UO}_2)_2(\text{Si}_2\text{O}_5)_3 \cdot 5\text{H}_2\text{O}$
Hydrocerussite	$\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$
Litharge	PbO
Massicot	PbO
Minium	Pb_3O_4
Plattnerite	PbO_2
Plumbogummite	$\text{PbAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$
Pyromorphite	$\text{Pb}_5(\text{PO}_4)_3\text{Cl}$
Pyromorphite-OH	$\text{Pb}_5(\text{OH})(\text{PO}_4)_3$
Schoepite	$\text{UO}_3 \cdot 2\text{H}_2\text{O}$
Soddyite	$(\text{UO}_2)_2(\text{SiO}_4) \cdot 2\text{H}_2\text{O}$
Strontianite	SrCO_3
Thorianite	ThO_2
Uranophane	$\text{Ca}(\text{UO}_2)_2(\text{SiO}_3)_2(\text{OH})_2$

Figure 1. Aqueous speciation of Th as a function of Eh and pH at 25°C.

Figure 2. Stability of Th-bearing solids as a function of Eh and pH assuming an activity of Th-bearing aqueous species of 10^{-10} and 10^{-12} at 25°C.

Figure 3. Dependence of Th concentration on pH and the stable Th-bearing solid(s) at 25°C.

Figure 4. Aqueous speciation of Th as a function of pH at 25°C.

Figure 5. Th concentration as a function of pH assuming equilibrium with Th(OH)_4 at 25°C.

Figure 6. Aqueous speciation of U as a function of Eh and pH at 25°C.

Figure 7a. Stability of U-bearing solids as a function of Eh and pH assuming an activity of U-bearing aqueous species of 10^{-10} at 25°C .

Figure 7b. Stability of U-bearing solids as a function of Eh and pH assuming an activity of U-bearing aqueous species of 10^{-8} at 25°C .

Figure 7c. Stability of U-bearing solids as a function of Eh and pH assuming an activity of U-bearing aqueous species of 10^{-6} at 25°C .

Figure 7d. Summary of stability of U-bearing solids as a function of Eh and pH shown in Figures 7a through 7c.

Figure 8. Dependence of U concentration on pH and the stable U-bearing solid(s) at 25°C.

Figure 9. Dependence of U concentration on pH assuming the presence of various U-bearing solids at 25°C.

Figure 10. Aqueous speciation of Np as a function of Eh and pH at 25°C.

Figure 11. Contours of Np activity in equilibrium with NpO_2 at 25°C. Area outside contours represents stability fields of various aqueous species of Np.

Figure 12. Np concentration as a function of pH assuming equilibrium with NpO_2 at 25°C.

Figure 13. Np concentration as a function of pH assuming equilibrium with $\text{NpO}_2\text{OH}(\text{am})$ at 25°C.

Figure 14. Aqueous speciation of Pu as a function of Eh and pH at 25°C.

Figure 15. Contours of Pu activity in equilibrium with PuO_2 at 25°C. Area outside of contours represents stability fields of various aqueous species of Pu.

Figure 16. Contours of Pu activity in equilibrium with $\text{Pu}(\text{OH})_4$ at 25°C . Area outside of contours represents stability fields of various aqueous species of Pu. Note appearance of solid $\text{PuO}_2(\text{OH})_2$ at high Eh.

Figure 17. Dependence of Pu concentration on pH and the stable Pu-bearing solid(s) at 25°C .

Figure 18. Pu concentration as a function of pH assuming equilibrium with Pu(OH)_4 at 25°C.

Figure 19. Aqueous speciation of Am as a function of Eh and pH at 25°C.

Figure 20. Stability of Am-bearing solids as a function of Eh and pH assuming an activity of Am-bearing aqueous species of 10^{-6} at 25°C .

Figure 21. Stability of Am-bearing solids as a function of Eh, pH and activities of Am-bearing aqueous species of 10^{-4} , 10^{-6} and 10^{-8} at 25°C .

Figure 22. Dependence of Am concentration on pH and the stable Am-bearing solid(s) at 25°C.

Figure 23. Aqueous speciation of Sr as a function of Eh and pH at 25°C.

Figure 24. Stability of Sr-bearing solids as a function of Eh and pH assuming an activity of Sr-bearing aqueous species of 10^{-6} at 25°C .

Figure 25. Stability of Sr-bearing solids as a function of Eh, pH and activities of Sr-bearing aqueous species of 10^{-4} , 10^{-6} and 10^{-8} at 25°C .

Figure 26. Dependence of Sr concentration on pH and the stable Sr-bearing solid(s) at 25°C.

Figure 27. Stability of Ra-bearing solids as a function of Eh and pH assuming an activity of Ra-bearing aqueous species of 10^{-6} at 25°C.

Figure 28. Dependence of Ra concentration on pH and the stable Ra-bearing solid(s) at 25°C.

Figure 29. Aqueous speciation of Pb as a function of Eh and pH at 25°C.

Figure 30. Stability of Pb-bearing solids as a function of Eh, pH and activities of Pb-bearing aqueous species of 10^{-5} and 10^{-6} at $25^{\circ}C$. Phosphate was assumed to serve as the pH-dependent ligand; no carbonate species were considered.

Figure 31. Stability of Pb-bearing solids as a function of Eh, pH and activities of Pb-bearing aqueous species of 10^{-5} and 10^{-6} at $25^{\circ}C$. Carbonate was assumed to serve as the pH-dependent ligand; no phosphate species were considered.

Figure 32. Dependence of Pb concentration on pH and the stable Pb-bearing solid(s) at 25°C. Phosphate-bearing solids were not considered.

Figure 33. Dependence of Pb concentration on pH and the stable Pb-bearing solid(s) at 25°C. Both phosphate- and carbonate-bearing solids were considered.