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# **Tank Farm Zeolite Historical Review and Current Inventory Assessment**

B. A. Hamm

June 10, 2005

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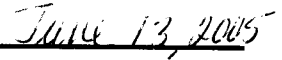
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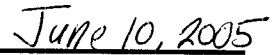




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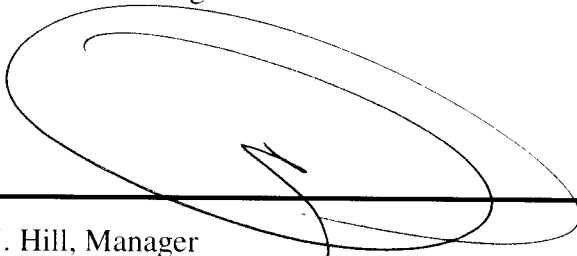
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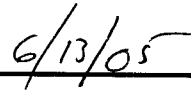




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## TABLE OF CONTENTS

<b>1. Introduction.....</b>	<b>3</b>
<b>2. Background.....</b>	<b>3</b>
2.1 Tank Farm Operations .....	3
2.2 Cesium Removal Columns Historical Overview .....	4
<b>3. Ion Exchange Resin Information.....</b>	<b>5</b>
3.1 Fundamentals of Ion Exchange Using Zeolites .....	5
3.2 Tank Farm Ion Exchange Resins .....	6
3.3 Zeolite Bulk Density .....	7
3.4 Zeolite Radionuclide Loading.....	7
3.5 Initial Radionuclide Loading .....	8
3.6 Radiation Stability .....	9
<b>4. Historical Information on Zeolite in Individual Tanks.....</b>	<b>9</b>
4.1 Tank 19F .....	9
4.1.1 Tank 19F Zeolite Discharges (1964 to 1984) .....	10
4.1.2 Tank 19F Salt Removal (1980 to 1981) .....	10
4.1.3 Tank 19F Heel Removal (2000 to 2001) .....	11
4.2 Tank 18F .....	11
4.3 Tank 7F .....	11
4.4 Tank 24H .....	12
4.4.1 Initial Use (1965 to 1983) .....	12
4.4.2 Waste Removal (1983) .....	13
4.4.3 Continued Tank 24H Zeolite Disposal (End of 1983 through 1984) .....	13
4.4.4 Tank 24H Chemical Treatment (1984) .....	13
4.4.5 Tank 24H Current Inventory.....	14
4.5 Tank 38H .....	14
4.6 Tank 25F .....	14
4.7 Tank 27F .....	14
4.8 Tank 42H .....	15
4.9 Tank 32H .....	16
4.10 Tank 40H .....	16
4.11 Tank 51H .....	17
4.12 Defense Waste Processing Facility .....	17
<b>5. Inventory Summary For Year 2005 .....</b>	<b>17</b>
5.1 Curie Counting.....	18
<b>6. Uncertainty of Data.....</b>	<b>18</b>
<b>7. References .....</b>	<b>19</b>

## LIST OF TABLES

<b>Table 1.</b> Zeolite Discharged to SRS High Level Waste Tanks (1963 to 1989) .....	5
<b>Table 2.</b> Zeolite Bulk Density Measurements .....	7
<b>Table 3.</b> Zeolite Cs-137 Analytical Data.....	8
<b>Table 4.</b> Tank 19F Zeolite Cs-137 Loading Basis Sample Data (2005 Basis).....	8
<b>Table 5.</b> Tank 19F Cs-137 Curies per Gallon In Year Deposited Estimate .....	9
<b>Table 6.</b> Tank 19F Historical Zeolite Inventory and Equivalent 2005 Cs-137 Curies.....	10
<b>Table 7.</b> Tank 18F, 19F, 7F Zeolite Transfer Summary .....	11
<b>Table 8.</b> Tank 24H Historical Zeolite Inventory Up To Waste Removal in 1983 .....	12
<b>Table 9.</b> Tank 24H First Waste Removal (1983) .....	13
<b>Table 10.</b> Tank 24H Additional Zeolite Batches (1983 – 1984).....	13
<b>Table 11.</b> Tank 24H Second Waste Removal (Chemical Treatment, 1984).....	13
<b>Table 12.</b> Tank 38H Zeolite Transfer Summary .....	14
<b>Table 13.</b> Tank 25F Historical Zeolite Inventory and Equivalent 2005 Cs-137 Curies.....	14
<b>Table 14.</b> Tank 27F Historical Zeolite Inventory and Equivalent 2005 Cs-137 Curies.....	15
<b>Table 15.</b> Tank 42H Historical Zeolite Inventory and Equivalent 2005 Cs-137 Curies .....	15
<b>Table 16.</b> Tank 42H Zeolite Transfer Summary .....	16
<b>Table 17.</b> Tank 32H Historical Zeolite Inventory and Equivalent 2005 Cs-137 Curies.....	16
<b>Table 18.</b> Tank 40H Zeolite Transfer Summary .....	17
<b>Table 19.</b> Tank 51H Zeolite Transfer Summary .....	17
<b>Table 20.</b> DWPF Zeolite Transfer Summary .....	17
<b>Table 21.</b> Tank Farm and DWPF Overall Zeolite Inventory .....	18

# 1. INTRODUCTION

Zeolite is the general term used to describe a material with a structure of pores and chambers that allow some molecules to pass through and others to be excluded. Zeolites occur naturally as a mineral but synthetic forms are also available. Zeolites have many useful purposes such as ion exchange, filtering, odor removal, gas adsorption and chemical separation.

The Savannah River Site uses evaporators to concentrate liquid waste by driving off excess water. Radioactive cesium tended to carry over into this water during the evaporation process. Columns loaded with zeolite removed cesium from these streams. Once loaded with cesium, the columns discharged the zeolite to one of six waste tanks (19F, 24H, 25F, 27F, 32H, and 42H).

This report provides a summary of the historical information on zeolite discharges to tanks, an estimate of the current volume of zeolite, and an estimate of the amount of cesium on the zeolite.

## 2. BACKGROUND

### 2.1 Tank Farm Operations

The first waste tank was put into service in November 1954. It quickly became filled, which prompted further investigation into ways to reduce the waste volume. It was decided to reduce the volume of waste by evaporating the supernatant liquid. Salts from the evaporator concentrate would form and remain in the tank as solids until future waste removal efforts retrieved them for long term disposal. Removing excess water also made storing the waste safer because it would be less mobile as a solid salt than it would be as a liquid. This reduced the chance of a waste leak from a tank.

Two evaporators were built in the 1960s, one in each tank farm. They were designated the 242-F and the 242-H evaporators.

In an effort to reduce the activity level of the water stream released to the seepage basins, a polishing step using zeolite was developed to remove the incidental radioactive cesium. This was done by adding a zeolite packed column, known as the *cesium removal column* or CRC, to the overheads treatment system.

Two additional evaporators were constructed in the late 1970s and early 1980s. Each of these was also equipped with a CRC for the treatment of evaporator overheads. (A third evaporator constructed in the 1990s was not fitted with a cesium removal column since the overheads stream no longer went to seepage basins.)

The practice of discharging evaporator overheads to seepage basins was discontinued in 1990 after the construction of the Effluent Treatment Facility (ETF). The ETF provides enhanced decontamination of the overheads stream prior to release to the environment. Although the

cesium removal columns remained available, they were found to be unnecessary and eventually removed from service.

## **2.2 Cesium Removal Columns Historical Overview**

Radioactive cesium makes up about 95% of the gamma activity in the evaporator overheads. Ion exchange using inorganic resin was started in 1962 to remove this activity.

Typical ion exchange applications are designed with multiple columns and equipment for resin regeneration. Rather than regenerate the resin, SRS decided to use the resin until the activity level of the treated stream became too high and then discharge the resin to the waste tanks.

The first column was installed in Tank 19F in November 1963 to treat the overheads from Evaporator 242-F. It was packed with Decalso™ ion exchange resin. Decalso™ is a man-made zeolite used experimentally at other DOE sites with good results. Although the laboratory studies had shown the resin to be satisfactory, actual field performance was unacceptable because of the high solubility of the clay binder material in the hot evaporator overheads. SRS attempted to improve resin life by lowering overheads temperature and using better quality zeolite, but these efforts were unsuccessful. In the meantime, excellent experimental results were being demonstrated with a resin manufactured by Union Carbide called Linde AW-500. This is a natural (mined) zeolite made up of refine chabazite and erionite. Linde AW-500 proved effective in removing cesium from the overheads.

A CRC using the Linde AW-500 resin was installed in Tank 24H to treat two streams: evaporator 242-H overheads and reactor fuel pool water. The fuel pool water came from the Receiving Basin for Offsite Fuels and Resin Regeneration Facility (RBOF/RRF), which produced high volumes of liquid with low levels of radioactivity. Rather than evaporate this waste stream, it was processed through a CRC, when possible, and then released.

When new evaporators were constructed in the late 1970s and early 1980s, additional columns were installed. Tank 27F was equipped with a CRC to treat Evaporator 242-16F overheads. Tank 42H was outfitted with a CRC for the Evaporator 242-16H.

In the mid-1980s, the original columns were decommissioned and replaced. Tank 25F housed the CRC used for the Evaporator 242-F and Tank 32H housed the CRC used to treat Evaporator 242-H overheads.

Over the history of CRC operation (1963 to 1989), there were varying grades of documentation of CRC performance and zeolite usage. Monthly reports recorded the number of CRC changes, sometimes individually and sometimes totaled at the end of each month. Starting in the 1980s, the monthly report recorded total resin volume in the waste tanks.

As expected, operating history records were better in some years than in others. To account for the resin discharged to the tanks, the available information sources were used to reconstruct annual volumes of zeolite. The values were reconciled where possible to match as many known

pieces of information as possible. The final volume of zeolite reported was matched as closely as possible. Overall, about 74,000 gallons were discharged to the tanks.

**Table 1.** Zeolite Discharged to SRS High Level Waste Tanks (1963 to 1989)

<b>Tank</b>	<b>Operation Years</b>	<b>Evaporator System</b>	<b>Zeolite Discharged (gallons)</b>
19F	1963 – 1984	242-F	12,440
25F	1985 –1988	242-F	1,050
24H	1965 – 1983	242-H plus RBOF/RRF	42,150
24H	After salt removal in 1983 through 1984	242-H plus RBOF/RRF	1,500
32H	1985 -1988	242-H plus RBOF/RRF	6,700
27F	1982 – 1989	242-16F	4,990
42H	1982 – 1989	242-16H	5,100
<b>TOTAL</b>			<b>73,930</b>

The Decalso™ resin and the Linde AW-500 resin were the only resins used on an operational scale. Over the years, the resin name was changed to IE-95. However, the IE-95 material was essentially the same as the Linde AW-500 resin.

Six batches of Decalso™ were used between November 1963 and June 1965. At 325 pounds per batch, roughly 1,950 pounds of this zeolite was discharged to Tank 19F. During this time, two batches of Linde AW-500 were run to determine resin viability. When the switchover to Linde AW-500 occurred in June 1965, the column was loaded with 275 pounds of resin (50 pounds less than earlier). The lighter charge helped alleviate problems with over packing.

### 3. ION EXCHANGE RESIN INFORMATION

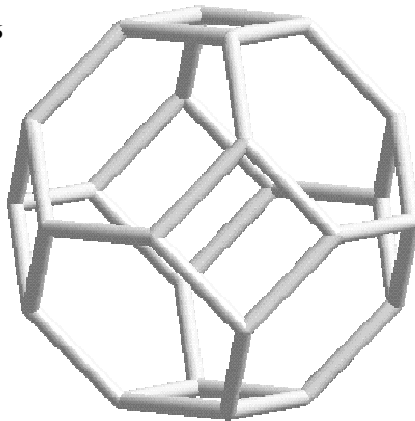
#### 3.1 Fundamentals of Ion Exchange Using Zeolites

Ion exchange is a reversible chemical reaction where an ion from a solution is exchanged for a similarly charged ion attached to an immobile solid particle. Ion exchange resins provide the immobile solid material. They can be natural substances mined from the earth or man-made structures specifically designed for ion exchange use. At present, over 150 synthetic zeolites and 40 natural zeolites are known.

Several ion exchange resins have been examined for their usefulness in treating radioactive solutions. The resin with the best combination of cesium removal, radiation stability and chemical stability are of the type known as zeolites. Zeolites are crystalline hydrated aluminosilicates. They have three-dimensional framework of silicate (SiO<sub>4</sub>) tetrahedra in which the four corner oxygen molecules of each tetrahedra are shared with adjacent tetrahedra.

The simplest form of this is shown below. In this compound, there is a silicon atom at each intersection of the structure. An oxygen atom exits between each pair of silicon atoms.





In nature, the silicon atom is sometimes replaced with the triply charged aluminum atom ( $\text{Al}^{3+}$ ). This causes a deficiency in the positive charge that can be balanced by the incorporation of positively charged atoms such as sodium ( $\text{Na}^+$ ), potassium ( $\text{K}^+$ ), and cesium ( $\text{Cs}^+$ ) as well as calcium ( $\text{Ca}^{++}$ ) and magnesium ( $\text{Mg}^{3+}$ ).

Aluminum can only replace some of the silicon. To obey Lowenstein's Rule, there can not be an Al-O-Al linkage. Therefore, the largest number of possible aluminum atoms would be 12. This would be  $\text{Si}_{12}\text{Al}_{12}\text{O}_{36}$ , (a Si:Al ratio of 1:1). The lower the Si:Al ratio, the better the compound is for ion removal.

### 3.2 Tank Farm Ion Exchange Resins

Approximately 74,000 gallons of zeolite reside in the waste tanks at SRS. Of this, about 73,600 gallons are Linde AW-500 (later renamed IE-95) and about 400 gallons of Decalso™. Other DOE sites used these types of resins to remove cesium from aqueous solutions.

The first resin used on Tank 19F was Decalso™ (also known as Ionac C-103), an aluminosilicate. This was a synthetic zeolite manufactured by the Ionic Chemical Corporation of the Permutit Co. Only six batches of Decalso™ were used because of problems with the resin durability.

The tank farm switched to Linde AW-500 zeolite and it became the primary resin for both tank farms. This zeolite, prepared by the Linde Division of the Union Carbide Company, is manufactured from the minerals chabazite and erionite, which is fired, sized and mixed with a clay binder for commercial sale. The mineral analysis of chabazite is  $0.15\text{Na}_2\text{O} \cdot 0.83\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 4.98\text{SiO}_2 \cdot 6.78\text{H}_2\text{O}$  (or  $\text{Na}_{0.09}\text{Ca}_{1.72}\text{Al}_{3.47}\text{Si}_{9.51}\text{O}_{24}$ ). A detailed discussion of the structure and properties of various zeolites is beyond the scope of this document. A comprehensive discussion of the compositions of the zeolites used at SRS (and their degradation products) can be found in Jantzen, 2003.

Long term exposure to the caustic solutions in the waste tank gradually converts the zeolites to cancrinites and sodalites (Jantzen, 2003). The essential conclusion of these reports is that the various compounds identified (such as chabazite, erionite, davyne, natrodavyne and sodalite) are in the same mineral subgroup (tectosilicates), and these compounds still preferentially hold onto cesium compared to the other ions in the waste.

### 3.3 Zeolite Bulk Density

The bulk density of hydrated zeolite has been measured and the results vary from 5.2 to about 8 pounds per gallon. The conversions from weight to volume performed in this document were based on 8 pounds of zeolite per gallon of wet zeolite material, which conservatively overestimates the mass of zeolite in the given volume.

**Table 2.** Zeolite Bulk Density Measurements

<b>Density (lbs/gal)</b>	<b>Basis</b>	<b>Source Document</b>
5.2	Monthly Report (325 lbs in 63 gal)	Monthly Reports (6/65, 4/67)
6.2	Manufacturer	SRS, 1980, p. 5.66
6.6	IE-95 zeolite	Jantzen, 2003, p. 28
6.7	TMI Study	Bibler, 1981
7.1	Fresh IE-95	Swingle, Sept. 2002, p. 8
7.6	TNX measurement	SRS, 1980, p. 5.66
8.0	Packed, settled solids from Tank 19F	Swingle, Sept. 2002, p. 2

### 3.4 Zeolite Radionuclide Loading

The design basis for the first CRC was to treat a dilute liquid waste stream containing up to  $2 \times 10^4$  dpm/ml in about 10,000 column volumes (Prout, 1964). Converting this to curies per gallon of zeolite, the loading expected on the column was 0.34 Ci of Cs-137 per gallon zeolite. In practice, the beds rarely treated this many column volumes of solution.

There are a limited number of sample results of radionuclides on zeolite. Since the resin is heavy and settles rapidly, samples are taken by scooping up solids from the tank floor. This is a difficult process because of the large size of the tanks and limited accessibility to the settled zeolite.

Sample data considered for the basis of the radionuclide loading estimate is summarized in the following table.

**Table 3.** Zeolite Cs-137 Analytical Data

Location	Result Cs-137 mCi /g	Cs-137 Ci/gal (at 8 lb/gal)	Year	Source Document	Cs-137 (2005 Ci) Ci/gal
Tank 18F	0.721	2.6	2003 Average (5 samples)	Thomas, April 2005a	2.5
Tank 19F	0.825	3.0	2001 Average (3 samples)	Thomas, April 2005b	2.7
Tank 19F	0.908	3.3	1996 (1 sample)	Hay, 1997	2.7
Tank 19F	1.3	4.7	1981 (1 sample)	Goslen, 1986	2.7

mCi/g is millicurie per gram; Ci/gal is curies per gallon

The concentration of Cs-137 in the discarded resin ranges from 2.5 to 2.7 Ci per gallon (as of 2005) and is much higher than can be explained from the evaporator and RBOF operations. Therefore, most of the activity was absorbed after the resin was discharged to the waste tank.

### 3.5 Initial Radionuclide Loading

A value of 10 Ci Cs-137 per gallon initial loading has been used in this report.

This value is based on the Tank 19F data since it was the tank with the highest concentration of Cs-137.

**Table 4.** Tank 19F Zeolite Cs-137 Loading Basis Sample Data (2005 Basis)

Source Document	Sample Year	Cs-137 ( $\mu$ Ci/g)	Years of Decay	Cs-137 ( $\mu$ Ci/g) 2005 value
Goslen, 1986	1983	1300	22	782
Hay, 1997	1996	908	9	738
Swingle, March 2002	2001	791	4	721
Swingle, March 2002	2001	821	4	749
Swingle, March 2002	2001	862	4	786

For the purposes of this report, all of the cesium is assumed to be in the zeolite. Taking the average of these five values (748  $\mu$ Ci per gram solids) and converting to Ci per gallon results in 2.7 Ci Cs-137 per gallon solids in 2005. This value is based on the solids in Tank 19F. Since this material is only 65.6% zeolite, it must be corrected to a zeolite only basis by dividing by 0.656; this results in a value of 4.1 Ci Cs-137 per gallon of zeolite solids in 2005.

**Table 5.** Tank 19F Cs-137 Curies per Gallon In Year Deposited Estimate

Category	Value	Units
Average of 5 samples	748	μCi/g solids (in 2005)
Convert to Ci/gal	2.7	Ci/gal solids (in 2005)
65.6% zeolite correction	4.1	Ci/gal zeolite solids (in 2005)
Initial concentration resulting in 4.1 Ci/gal	8.6	Ci/gal (in year deposited)
Initial concentration selected	10	Ci/gal (in year deposited)

Using the tank 19F zeolite addition history, an initial concentration of 8.6 Ci per gallon for each year zeolite was added to the tank results in a 2005 value of 4.1Ci per gallon. Rounding off, the value of 10 Ci Cs-137 per gallon of zeolite solids was used as the initial concentration of cesium-137 for the Tank 19F zeolite additions. This value was used for the tank zeolite radionuclide estimates. Note this method is conservative and will over predict the Cs-137 as compared to sample data from Tank 18F and 24H.

### 3.6 Radiation Stability

There is limited information on the effects of radiation on the zeolite material. The best information is in Bibler, 1981. Tests with Co-60 gamma radiation indicated doses up to  $3 \times 10^{10}$  rads had no effect on the crystal structure of the material or on its ability to retain Cs-137. For the use studied (cleanup of radioactively contaminated basin water at the Three Mile Island nuclear plant), the scoping calculations assumed the zeolite was contained in an 8 ft<sup>3</sup> canister and was loaded with 60,000 Ci of Cs-137. The estimated average radiation dose was  $3.5 \times 10^{10}$  rads from a concentration of 1,200 Ci Cs-137 per gallon. At SRS Cs-137 concentrations of about 10 Ci per gallon or less, we will be well under the absorbed dose range of the experiment. In summary, the zeolite material should be unaffected by radiation exposure under tank farm storage conditions.

## 4. HISTORICAL INFORMATION ON ZEOLITE IN INDIVIDUAL TANKS

### 4.1 Tank 19F

Tank 19F is a 1.3 million gallon, un-cooled, Type IV tank located in F-area. It was primarily used as an evaporator concentrate (saltcake) receiver. The first six batches of zeolite were Decalso™ and the remaining batches were Linde AW-500. The monthly reports indicate the cumulative volume of zeolite discharged to the tank was 12,440 gallons. This is approximately 197 batches at 63 gallons per batch.

#### 4.1.1 Tank 19F Zeolite Discharges (1964 to 1984)

The following table shows the total amount of zeolite discharged to the tank based on a reconstruction of the tank zeolite usage history.

**Table 6.** Tank 19F Historical Zeolite Inventory and Equivalent 2005 Cs-137 Curies

Evaporator System: 242-F  
63 gallons per batch  
Initial loading rate = 10 Ci Cs-137 per gallon

Year	Batches per Year	Cumulative Batches	Gallons per Year	Cumulative Gallons	Cumulative Gallons per Monthlies	Cs-137 Deposited Curies	Years since Deposit	Cs-137 2005 Curies
1964	6	6	378	378	N/a	3,780	41	1,473
1965	2	8	126	504	N/a	1,260	40	502
1966	2	10	126	630	N/a	1,260	39	514
1967	1	11	63	693	N/a	630	38	263
1968	13	24	819	1,512	N/a	8,190	37	3,498
1969	24	48	1,512	3,024	N/a	15,120	36	6,608
1970	20	68	1,260	4,284	N/a	12,600	35	5,635
1971	26	94	1,638	5,922	N/a	16,380	34	7,496
1972	10	104	630	6,552	N/a	6,300	33	2,950
1973	13	117	819	7,371	N/a	8,190	32	3,924
1974	29	146	1,827	9,198	N/a	18,270	31	8,957
1975	8	154	504	9,702	N/a	5,040	30	2,528
1976	9.4	163.4	592	10,294	N/a	5,922	29	3,040
1977	6	169.4	378	10,672	N/a	3,780	28	1,986
1978	7	176.4	441	11,113	N/a	4,410	27	2,370
1979	2	178.4	126	11,239	N/a	1,260	26	693
1980	2	180.4	126	11,365	N/a	1,260	25	709
1981	5	185.4	315	11,680	11,618	3,150	24	1,814
1982	2	187.4	126	11,806	11,788	1,260	23	743
1983	9	196.4	567	12,373	12,376	5,670	22	3,419
1984	1	197.4	63	12,436	12,437	630	21	389
<b>Total</b>				<b>12,436</b>				<b>59,511</b>

#### 4.1.2 Tank 19F Salt Removal (1980 to 1981)

The following information was taken primarily from the Tank 19F salt removal report (Goslen, 1986). From July 1980 to August 1981, salt removal was conducted in four batches. At the beginning of salt removal, it was estimated there were 1,054,000 gallons of salt, 30,000 gallons of supernate, 12,000 gallons of sludge and 13,000 gallons of zeolite (rounded up from 12,436).

At the end of salt removal, an estimated 33,000 gallons of solids were left in the tank (13,000 gallons of salt, 13,000 gallons of zeolite and 7,000 gallons of sludge). It is believed no zeolite was removed during salt removal.

A sample of the solids taken at the end of salt removal was determined to contain (on a per gram of solids basis) 1.3 mCi of Cs-137, 0.13 mCi of Sr-90, 0.01 mCi of Ru-106, 0.006 mCi of Ce-

144, and 0.3  $\mu\text{Ci}$  of Eu-154/155. It was believed the cesium was primarily from the zeolite and the strontium was from the sludge.

The final estimate was there were 57,300 Ci of Cs-137 and 34,800 Ci of Sr-90 left in the tank. The other nuclides together totaled less than 2 curies (in 1981).

#### **4.1.3 Tank 19F Heel Removal (2000 to 2001)**

The following information was taken primarily from the Tank 19F characterization report (Tran, March 2005). From September 2000 to June 2001, heel removal was performed. The final volume of solids in the tank is estimated to be 15,100 gallons of which 9,906 gallons are zeolite solids. Applying a ratio of the volumes and using the factor to the total curies gives an estimate of 47,383 Ci of Cs-137. The characterization report provides a value of 48,800 Ci of Cs-137. This number is slightly higher because it is based on the 95% upper confidence level on the data. Readers should consider which value is more suitable to their use. For the purposes of this report, 47,383 Ci of Cs-137 is used.

#### **4.2 Tank 18F**

Tank 18F is a 1.3 million gallon, un-cooled, Type IV tank located in F-area. Sludge and zeolite solids were transferred to this tank as a part of the Tank 19F waste removal effort. In 2003, waste removal was conducted in Tank 18 by transferring most of the solids to Tank 7F (and then from Tank 7F to Tank 51H for incorporation into sludge feed to DWPF, discussed further in the section on Tank 7). An estimated 4,320 gallons of solids remain in the tank of which 2,049 gallons are zeolite solids.

The 2005 characterization study by Tran reports a Cs-137 value in solids of 1,234 Ci. The zeolite balance in this report predicts 9,785 Ci of Cs-137. The material balance in this report is based on data from the tank with the highest activity level of Cs-137; as expected, the predicted Cs-137 value is conservative when compared to the actual tank samples. Refer to Table 7 for a summary of the material balance.

**Table 7.** Tank 18F, 19F, 7F Zeolite Transfer Summary

<b>Event</b>	<b>Gallons</b>	<b>Cs-137 2005 Curies</b>
Transfer from Tank 19F	12,440-9,906 = 2,534	59,511-47,383 = 12,128
Remaining in Tank 18	2,049	9,785
Transfer to Tank 7	2,534-2,049 = 485	12,128-9,785 = 2,343

#### **4.3 Tank 7F**

Tank 7F is a 750,000 gallon, cooled, Type I tank located in F-area. Sludge and zeolite solids were transferred to this tank as a part of the Tank 18F and 19F waste removal efforts. Subsequently, the solids were removed from Tank 7F to Tank 51H for incorporation into sludge feed to DWPF. The waste removal from Tank 7F was conducted in multiple batches (Chander, 2003); however, at the end of the program about 73% of the sludge had been removed. Applying

this same percentage to the zeolite gives an estimate of 130 gallons of zeolite. Applying a ratio of the volume fraction to the total curies gives an estimate of 623 Ci of Cs-137.

#### 4.4 Tank 24H

Tank 24H is a 1.3 million gallon, un-cooled, Type IV tank located in H-area used to receive 242-H evaporator concentrate. In 1965, a CRC was installed incorporating lessons learned from the Tank 19F installation. The column was used to treat evaporator overheads as well as to directly process relatively lightly contaminated waste streams from the RBOF/RRF facility.

The Tank 24H calculations are complicated given the history of the tank. It was used from 1965 to 1983 to receive spent zeolite and salt. In 1983, it underwent salt removal. Following salt removal it was again used to receive spent zeolite. In 1984 zeolite discharges were stopped and a chemical cleaning process using oxalic acid was performed.

Overall, 582 batches of zeolite were discharged to the tank for a total zeolite volume of 43,650 gallons.

##### 4.4.1 Initial Use (1965 to 1983)

The initial discharge of zeolite took place between 1965 and 1983.

**Table 8.** Tank 24H Historical Zeolite Inventory Up To Waste Removal in 1983

Evaporator System: 242-H  
75 gallons per batch  
Initial loading rate = 10 Ci Cs-137 per gallon

Year	Batches per Year	Cumulative Batches	Gallons per Year	Cumulative Gallons	Cumulative Gallons per Monthlies	Cs-137 Deposited Curies	Years since Deposit	Cs-137 2005 Curies
1965	4	4	300	300	N/a	3,000	40	1,196
1966	7	11	525	825	N/a	5,250	39	2,142
1967	8	19	600	1,425	N/a	6,000	38	2,504
1968	62	81	4,650	6,075	N/a	46,500	37	19,860
1969	60	141	4,500	10,575	N/a	45,000	36	19,667
1970	35	176	2,625	13,200	N/a	26,250	35	11,739
1971	52	228	3,900	17,100	N/a	39,000	34	17,847
1972	51	279	3,825	20,925	N/a	38,250	33	17,910
1973	50	329	3,750	24,675	N/a	37,500	32	17,968
1974	63	392	4,725	29,400	N/a	47,250	31	23,166
1975	56	448	4,200	33,600	N/a	42,000	30	21,071
1976	2	450	150	33,750	N/a	1,500	29	770
1977	24	474	1,800	35,550	N/a	18,000	28	9,455
1978	34	508	2,550	38,100	N/a	25,500	27	13,707
1979	15	523	1,125	39,225	N/a	11,250	26	6,188
1980	6	529	450	39,675	N/a	4,500	25	2,533
1981	6	535	450	40,125	N/a	4,500	24	2,592
1982	13	548	975	41,100	41,076	9,750	23	5,746
1983	14	562	1,050	42,150	42,147	10,500	22	6,331
<b>Total</b>				<b>42,150</b>				<b>202,390</b>

#### **4.4.2 Waste Removal (1983)**

Up until 1983, approximately 42,150 gallons of zeolite had been discharged to the tank. Approximately 80 percent of the solids were transferred to Tank 38H as a result of the waste removal effort. Applying this waste removal fraction to the estimated Cs-137 inventory, 161,912 Ci Cs-137 were transferred to Tank 38H

**Table 9.** Tank 24H First Waste Removal (1983)

<b>Event</b>	<b>Gallons</b>	<b>Cs-137 2005 Curies</b>
First Waste Removal to Tank 38H	33,720	161,912

#### **4.4.3 Continued Tank 24H Zeolite Disposal (End of 1983 through 1984)**

The tank continued to be used to receive spent zeolite through 1984. This added another 1,500 gallons of zeolite.

**Table 10.** Tank 24H Additional Zeolite Batches (1983 – 1984)

<b>Year</b>	<b>Batches per year</b>	<b>Cumulative batches</b>	<b>Gallons per year</b>	<b>Cumulative Gallons</b>	<b>Cs-137 Ci</b>	<b>Years since deposit</b>	<b>Cs-137 2005 Curies</b>
1983	3	3	225	225	2,250	22	1,357
1984	17	20	1,275	1,500	12,750	21	12,750
<b>Total</b>				<b>1,500</b>			<b>9,224</b>

#### **4.4.4 Tank 24H Chemical Treatment (1984)**

In 1984, the residual heel of about 9,930 gallons was treated with oxalic acid in an attempt to remove activity and make the solids easier to move. It was believed two slurry treatments with 4 weight% oxalic acid at 70-85°C would dissolve 50 to 70 weight% of the insoluble solids and convert the acid-insoluble residue to a finely divided solid would be easier to slurry (Thomas, 1984).

The results were less than expected and only about 45% of the solids and 20% of the Cs-137 were removed (Monthly Report, August 1985). Based on these removal fractions, the amount transferred to Tank 38H is shown in the following table.

**Table 11.** Tank 24H Second Waste Removal (Chemical Treatment, 1984)

<b>Event</b>	<b>Gallons</b>	<b>Cs-137 2005 Curies</b>
Second Waste Removal to Tank 38H	4,469	9,940



#### 4.4.5 Tank 24H Current Inventory

At present, Tank 24H is estimated to contain about 5,462 gallons of zeolite with 39,762 Curies of Cs-137.

#### 4.5 Tank 38H

Tank 38H is a 1.3 million gallon, Type III waste tank located in H area. It received 33,720 gallons of zeolite from Tank 24H during waste removal in 1983. It then received 4,469 gallons of zeolite from Tank 24H from chemical cleaning in 1984.

**Table 12.** Tank 38H Zeolite Transfer Summary

Event	Gallons	Cs-137 2005 Curies
First Transfer from 24H to 38H	33,720	161,912
Second Transfer from 24H to 38H	4,469	9,940

Therefore, Tank 38H holds 38,189 gallons of the original Tank 24H solids. The zeolite contains about 171,852 curies of Cs-137 as estimated in 2005.

#### 4.6 Tank 25F

Tank 25F is a 1.3 million gallon, Type III waste tank located in F-area. The CRC treated 242-F evaporator overheads and operated from 1985 to 1988. Overall, approximately 14 batches of zeolite were discharged to the tank. The total volume of zeolite was 1,050 gallons. It is currently used as a salt storage tank.

**Table 13.** Tank 25F Historical Zeolite Inventory and Equivalent 2005 Cs-137 Curies

Evaporator System: 242-F

75 gallons per batch

Initial loading rate = 10 Ci Cs-137 per gallon

Year	Batches per Year	Cumulative Batches	Gallons per Year	Cumulative Gallons	Cumulative Gallons per Monthlies	Cs-137 Deposited Curies	Years since Deposit	Cs-137 2005 Curies
1985	5	5	375	375	375	3,750	20	2,368
1986	7	12	525	900	900	5,250	19	3,392
1987	1	13	75	975	975	750	18	496
1988	1	14	75	1,050	1050	750	17	507
<b>Total</b>				<b>1,050</b>		<b>10,500</b>		<b>6,763</b>

#### 4.7 Tank 27F

Tank 27F is a 1.3 million gallon, Type III waste tank located in F-area. A CRC for the 242-16F evaporator overheads was installed in the early 1980s. Approximately 67 batches of zeolite (about 4,990 gallons) were discharged to the tank. The tank is currently used as a salt storage tank.

**Table 14.** Tank 27F Historical Zeolite Inventory and Equivalent 2005 Cs-137 Curies

Evaporator System: 242-16F

75 gallons per batch

Initial loading rate = 10 Ci Cs-137 per gallon

Year	Batches per Year	Cumulative Batches	Gallons per Year	Cumulative Gallons	Cumulative Gallons per Monthlies	Cs-137 Deposited Curies	Years since Deposit	Cs-137 2005 Curies
1980	4	4	300	300	N/a	3,000	25	1,688
1981	7	11	525	825	N/a	5,250	24	3,023
1982	9	20	675	1,500	1,497	6,750	23	3,978
1983	8.8	28.8	660	2,160	2,163	6,600	22	3,980
1984	3	31.8	225	2,385	2,390	2,250	21	1,388
1985	9.7	41.5	727.5	3,113	3,115	7,275	20	4,593
1986	7	48.5	525	3,638	3,640	5,250	19	3,392
1987	11	59.5	825	4,463	4,465	8,250	18	5,454
1988	3	62.5	225	4,688	4,690	2,250	17	1,522
1989	4	66.5	300	4,988	4,990	3,000	16	2,077
<b>Total</b>				<b>4,990</b>				<b>31,095</b>

#### 4.8 Tank 42H

Tank 42H is a 1.3 million gallon, Type III waste tank located in H-area. A CRC was used to treat the 242-H evaporator overheads. The CRC was in service from 1981 to 1990.

Approximately 68 batches were discharged to the tank. The total volume was 5,100 gallons.

**Table 15.** Tank 42H Historical Zeolite Inventory and Equivalent 2005 Cs-137 Curies

Evaporator System: 242-16H

75 gallons per batch

Initial loading rate = 10 Ci Cs-137 per gallon

Year	Batches per Year	Cumulative Batches	Gallons per Year	Cumulative Gallons	Cumulative Gallons per Monthlies	Cs-137 Deposited Curies	Years since Deposit	Cs-137 2005 Curies
1982	6	6	450	450	442	4,500	23	2,652
1983	11	17	825	1,275	1,260	8,250	22	4,975
1984	2	19	150	1,425	1,386	1,500	21	926
1985	7.6	26.6	570	1,995	2,000	5,700	20	3,599
1986	5.75	32.35	431	2,426	2,425	4,313	19	2,786
1987	8.6	40.95	645	3,071	3,075	6,450	18	4,264
1988	12	52.95	900	3,971	3,975	9,000	17	6,088
1989	11	63.95	825	4,796	4,800	8,250	16	5,711
1990	4	67.95	300	5,096	5,100	3,000	15	2,125
<b>Total</b>				<b>5,100</b>				<b>33,126</b>

In 1998, most of the sludge in this tank was transferred to either Tank 40 or Tank 51. The transfer fraction shown in WCS was applied to the volume of zeolite and the curies of Cs-137 to produce the values in the following table.

**Table 16.** Tank 42H Zeolite Transfer Summary

Event	Transfer Fraction	Volume of Zeolite (gallons)	Cs-137 2005 Curies
Transfer from 42H to 40H	0.054	277	1,941
Transfer from 42H to 51H	0.864	4,406	30,845

Based on the transfers in and out of the tank, Tank 42H currently has 416 gallons of zeolite with 2,914 Ci of Cs137.

#### 4.9 Tank 32H

Tank 32H is a 1.3 million gallon, Type III waste tank located in H area. It is currently used as an evaporator feed tank. The CRC installed on this tank was 150 gallons nominal capacity (the others were either 63 or 75 gallons). The CRC first started processing evaporator 242-H overheads in June of 1985. There were no zeolite additions to the tank after 1988. The total volume of zeolite discharged to the tank was 6,700 gallons. This is equal to approximately 45 batches. There have not been any sludge waste removal campaigns in this tank. The current zeolite volume and Cs-137 activity are shown in the table below.

**Table 17.** Tank 32H Historical Zeolite Inventory and Equivalent 2005 Cs-137 Curies

Evaporator System: 242-H

150 gallons per batch

Initial loading rate = 10 Ci Cs-137 per gallon

Year	Batches per year	Cumulative Batches	Gallons per year	Cumulative Gallons	Cumulative Gallons per Monthlies	Cs-137 Deposited Curies	Years since Deposit	Cs-137 2005 Curies
1985	18.6	18.6	2,790	2,790	2,800	27,900	20	17,615
1986	22	40.6	3,300	6,090	6,100	33,000	19	21,320
1987	3	43.6	450	6,540	6,550	4,500	18	2,975
1988	1	44.6	150	6,690	6,700	1,500	17	1,015
<b>Total</b>				<b>6,700</b>				<b>42,925</b>

#### 4.10 Tank 40H

Tank 40H is a 1.3 million gallon, Type III waste tank located in H area. It received zeolite from transfers of solids from both Tanks 42H and 51H. The current zeolite volume is estimated at 825 gallons and the Cs-137 activity is estimated at 5,151.

**Table 18.** Tank 40H Zeolite Transfer Summary

<b>Event</b>	<b>Gallons</b>	<b>Cs-137 2005 Curies</b>
Transfer from 42H to 40H	1,941	277
Transfer from 51H to 40H	608	3,712
Transfer from 40H to DWPF	156	1,069

#### 4.11 Tank 51H

Tank 51H is a 1.3 million gallon, Type III waste tank located in H area. It received zeolite from transfers from Tanks 42H and 7F. It has also sent zeolite to the DWPF. Currently, the tank contains 41 gallons of zeolite with 250 curies of Cs-137.

**Table 19.** Tank 51H Zeolite Transfer Summary

<b>Event</b>	<b>Gallons</b>	<b>Cs-137 2005 Curies</b>
Transfer from 42H to 51H	4,406	30,845
Transfer from 51H to DWPF	(3,884)	(27,185)
Transfer from 7F to 51H	358	1,720
Transfer from 51H to 40H	(840)	(5,130)

#### 4.12 Defense Waste Processing Facility

The Defense Waste Processing Facility is used to process high level waste sludge for permanent storage by incorporating it into a glass waste form. The amount of zeolite fed to this facility to date is about 4,176 gallons and 29,105 Curies Cs-137 (2005 basis).

**Table 20.** DWPF Zeolite Transfer Summary

<b>Event</b>	<b>Gallons</b>	<b>Cs-137 2005 Curies</b>
Transfers from 51H to DWPF	3,884	27,185
Transfers from 40H to DWPF	293	1,920

## 5. INVENTORY SUMMARY FOR YEAR 2005

Information on zeolite usage was put on an annual basis for each tank so accounting of radionuclide activity over time could be performed. It is important to account for decay because the half life of the isotope (30 years) and the period of interest (approximately 100 years) are on the same time scale. The concentration of cesium is reduced 50% for each 30 years. For

example, 1.0 curie of Cs-137 placed in a tank in 1963 will be 0.5 curies in 1993 and 0.25 curies in 2023.

The reconstructed tank histories were used to determine the volume of zeolite discharged to each tank. Information on waste transfers was used to account for the movement of zeolite between tanks. The Cs-137 concentration was conservatively estimated based on the tank with the highest Cs-137 measured values to date.

The following table summarizes the results in this report.

**Table 21.** Tank Farm and DWPF Overall Zeolite Inventory

<b>Current Zeolite Location</b>	<b>Current Zeolite Volume (gallons)</b>	<b>Cs-137 2005 Curies</b>
7F	130	623
19F	9,906	47,383
18F	2,049	9,785
24H	5,462	39,762
38H	38,189	171,852
25F	1,050	6,763
27F	4,990	31,095
32H	6,700	42,925
40H	825	5,151
42H	416	2,914
51H	41	250
DWPF	4,176	29,105
<b>Total</b>	<b>73,933</b>	<b>387,608</b>

## 5.1 Curie Counting

The radionuclide of interest in this report is Cs-137. It is understood the Cs-137 decays to Ba-137m and then to stable Ba-137. The inventories in this document have not separately accounted for the Ba-137m. For the purposes of curie counting and in order to be consistent with current methodology, the Cs-137 curies should be counted at 100% for Cs-137 and an additional 94.6% for Ba-137m.

## 6. UNCERTAINTY OF DATA

There are several areas that introduce uncertainty in the estimates discussed in this report. First, there is some confusion about the volume of zeolite in a *batch*. According to some sources, the 75-gallon volume of the column is the full volume. The zeolite was only loaded to the extent of 63 gallons, thereby allowing some extra space.

The monthly report inventories were sometimes estimated using 63 gallons per batch and sometimes 75 gallons per batch. In addition, not all batches were full batches. Some were intentionally loaded to a smaller volume to alleviate operational problems such as plugging. In some cases, the full charge of zeolite could not be discharged, and the fresh charge consisted of only the amount of fresh zeolite put into the tank.

The information about the number of batches has been re-created from entries in the monthly reports and data records. There are gaps and inaccuracies (typos, etc) in the information reported. When in doubt, a conservative estimate of the dates and volumes of zeolite discharged to the tanks was developed based on this information.

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1981 through 1984	Waste Management Monthly Reports	DPSP-81-21-1 through DPSP-84-21-1
1985 through 1988	WMT Monthly Data Record	No document numbers
1989 through 1992	HLWE Monthly Data Report	WSRC-RP-89-78-1 through WSRC-RP-93-78-XX.
1984 through 1985	High Level Waste Engineering Monthly Data Report	WSRC-RP-94-841-1 through WSRC-RP-95-841-XX

There were a few instances of numbering inconsistencies not noted here.