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Ferrocyanide Tank Safety Program:

Cesium Uptake Capacity of Simulated Ferrocyanide Tank Waste: Final Report

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Summary

The objective of this project is to determine the capacity for ^{137}Cs uptake by mixed metal ferrocyanides present in Hanford Site waste tanks, and to assess the potential for aggregation of these ^{137}Cs-exchanged materials to form "hot-spots" in the tanks. This research, performed at Pacific Northwest Laboratory (PNL) for Westinghouse Hanford Company, stems from concerns regarding possible localized radiolytic heating within the tanks. After ferrocyanide was added to 18 high-level waste tanks in the 1950s, some of the ferrocyanide tanks received considerable quantities of saltcake waste that was rich in ^{137}Cs. If radioactive cesium was exchanged and concentrated by the nickel ferrocyanide present in the tanks, the associated heating could cause tank temperatures to rise above the safety limits specified for the ferrocyanide-containing tanks, especially if the supernate in the tanks is pumped out and the waste becomes drier.

For this study, two simulants, In-Farm-2 and U-Plant-2, were chosen to represent the waste generated by the cesium scavenging process. These simulants were formulated using protocols from the original cesium scavenging campaign. The effects from later additions of cesium-rich waste from various processes were also considered. The simulants were prepared and centrifuged to obtain a moist ferrocyanide sludge. This moist sludge was then used in three different sets of experiments: 1) batch equilibrium testing, 2) layering tests, and 3) intercalation of excess dissolved cesium into the settled sludge.

The batch equilibrium testing was performed at room temperature to examine the effects of cesium and the cesium-to-nickel ferrocyanide ratio on the distribution coefficients (K_d). The maximum capacities of U-Plant-2 and In-Farm-2 simulants were also determined from these experiments. The maximum capacity of U-Plant-2 simulant was 0.50 mole of cesium per mole of nickel ferrocyanide and the maximum capacity of In-Farm-2 simulant was 0.80 mole of cesium per mole of nickel ferrocyanide. An evaluation of the effects of the sodium concentration and the sodium-to-cesium ratio indicated a slight but noticeable decrease in the distribution coefficients as the concentration of sodium was increased.

Potential concentration mechanisms were also evaluated. A concentrated region of ^{137}Cs nickel ferrocyanide could form in several ways, depending upon the settling and intercalation characteristics of the materials: 1) after exchange of cesium from solution, the cesium form of the nickel ferrocyanide could settle at a different rate than the sodium form of nickel ferrocyanide; 2) after exchange of cesium from solution, the cesium nickel ferrocyanide could settle at a different rate than the remaining solids present in the bulk of the waste (sodium salts). This concentration mechanism assumes a large portion of the nickel ferrocyanide exists as cesium nickel ferrocyanide. A concentration region of ^{137}Cs-enriched nickel ferrocyanide could also form if, at a later time, cesium-rich supernate was added to the solid nickel ferrocyanide and the cesium did not diffuse through the waste solids.

These three potential concentration mechanisms were examined by 1) treating the U-Plant-2 and In-Farm-2 simulants with a cesium nitrate spike containing ^{137}Cs and measuring the concentration of ^{137}Cs as the radionuclide settles within a column; or 2) adding a spike containing cesium nitrate and

^{137}Cs to a previously settled column of U-Plant-2 or In-Farm-2 simulants. None of the experiments performed to examine the potential concentration mechanisms yielded evidence that a significantly concentrated region of ^{137}Cs had formed. The layering experiments yielded a settled solid that was essentially homogeneous with respect to the concentration of ^{137}Cs. The intercalation experiments indicated the cesium will diffuse through the settled bed of simulant and disperse.

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1.0 Introduction

The research performed for this activity is part of an effort that started in the mid-1980s to characterize the materials stored in the single-shell waste storage tanks (SSTs) at the U.S. Department of Energy (DOE) Hanford Site. Various radioactive waste from defense operations have accumulated at the Hanford Site in underground waste tanks since the early 1940s.

During the 1950s, additional tank storage space was required to support the defense mission. Hanford Site scientists developed two procedures to obtain this additional storage volume within a short time period without constructing additional storage tanks. One procedure involved the use of evaporators to concentrate the waste by removing water. The second procedure involved developing precipitation processes for scavenging radiocesium and other soluble radionuclides from tank waste liquids. The scavenging processes used sodium and potassium ferrocyanide and nickel sulfate to precipitate radioactive cesium from solutions containing nitrates and nitrites. Radioactive strontium and cobalt were scavenged from some of the solutions using calcium or strontium nitrate and sodium sulfide, respectively. After allowing the radioactive precipitates to settle, the decontaminated solutions were pumped to disposal cribs, thereby providing additional tank storage volume. Later, some of the tanks were found to be leaking; pumpable liquids were removed from these tanks, leaving behind a wet solid (sludge) residue containing the ferrocyanide precipitates (Burger et al. 1991). In implementing this process, approximately 140 metric tons of ferrocyanide [calculated as $Fe(CN)_6^{4-}$] were added to waste that was later routed to 18 large (500,000 - 750,000 gallon) underground SSTs.

The explosive nature of ferrocyanides in the presence of oxidizers has been known for decades, but the conditions under which impure mixtures containing nitrates and nitrites can undergo propagating reactions had not been thoroughly studied. At the Hanford Site, the potential reactivity of mixtures of ferrocyanides, nitrates, and nitrites was first recognized when the radiocesium scavenging process using ferrocyanide was investigated for application to radioactive waste produced by the next generation processing technology. The investigation found that cesium zinc ferrocyanide and nitrate exploded when heated (Hepworth et al. 1957). In the laboratory, mixtures of ferrocyanide and oxidizing materials, such as nitrates and nitrites, have been shown to undergo energetic reactions when heated to high temperatures (exceeding 250°C) or exposed to an electrical spark of sufficient energy to heat the mixture (Scheele et al. 1991, Cady 1993). Because the scavenging process precipitated ferrocyanide from solutions containing nitrate and nitrite, an intimate mixture of ferrocyanides and nitrates and/or nitrites is likely to exist in some regions of the ferrocyanide tanks.

Efforts have been underway since the mid-1980s to evaluate the potential for ferrocyanide reactions in Hanford Site SSTs (Burger 1984, Burger and Scheele 1988, Meacham et al. 1995). The 1987 Environmental Impact Statement (EIS), *Final Environmental Impact Statement, Disposal of Hanford Defense High-Level Transuranic and Tank Waste, Hanford Site, Richland, Washington* (DOE 1987), included an environmental impact analysis of potential explosions involving ferrocyanide-nitrate mixtures. The EIS postulated that an explosion could occur during mechanical retrieval of saltcake or sludge from a ferrocyanide waste tank. The EIS concluded that this worst-case accident could create enough energy to release radioactive material to the atmosphere through ventilation openings, exposing persons offsite to a short-term radiation dose of approximately 200 mrem. A General Accounting Office (GAO) study (Peach 1990) postulated a greater worst-case accident, with independently

calculated doses of one to two orders of magnitude greater than postulated in the DOE EIS. Uncertainties regarding the safety envelope of the Hanford Site ferrocyanide waste tanks led to the declaration of the ferrocyanide unreviewed safety question (USQ) in October 1990.

Despite the fact that the measured temperatures in these tanks continue to drop from the continued decrease in radioactive decay (Hanlon 1995), there has been a good deal of speculation as to the possibility of "hot spots" forming in the tanks from radiolytic heating. In order to address these concerns, a number of studies have been conducted by Westinghouse Hanford Company (WHC), Pacific Northwest Laboratory (PNL),[a] and others in an effort to identify the reactions that occur, and to quantify the magnitude of the energy released during reactions (Burger 1984; Burger and Scheele 1988, 1990; Scheele et al. 1991, 1992; Scheele and Cady 1989; Hallen et al. 1991; Dickinson et al. 1993; Epstein et al. 1994; McLaren 1992).

This report focuses on the determination of cesium exchange and settling characteristics of ferrocyanide waste. Studies were conducted to examine the capability of solid nickel ferrocyanides present in tank waste simulants to exchange cesium from solution and to examine potential concentration mechanisms for the ^{137}Cs exchanged by the solids. The exchange capacity and concentration mechanisms are of interest because waste added to the tanks after the 1950s contained soluble cesium that may have contacted the ferrocyanide layers and been exchanged by the nickel ferrocyanide precipitates. This exchange process could allow the ^{137}Cs to become more concentrated, possibly leading to hotter regions within the tank.

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2.0 Experimental Work

The experimental work for the cesium uptake capacity subtask began with batch distribution measurements. Batch distribution coefficients (K_d) were determined for U-Plant-2 and In-Farm-2 waste simulants reacted with cesium to determine the capacity of the waste simulants to exchange cesium from solution. The experimental design for this work is discussed in Section 2.1. Section 2.2 describes the batch distribution measurements; Sections 2.2.3 and 2.2.4 discuss experiments designed to evaluate the feasibility of potential concentration mechanisms. All experiments were performed using ^{137}Cs tracer and gamma-counting equipment.

The batch distribution measurements discussed in Section 2.2.1 are reported in Section 3.0, and the potential concentration mechanisms discussed in Sections 2.2.2 and 2.2.3 are reported in Section 4.0. The mechanism for intercalation of excess dissolved cesium into simulated ferrocynanide waste is discussed in Section 5.0.

2.1 Experimental Design

2.1.1 Variables to be Considered for Cesium Uptake Capacity Measurements

The alkaline waste treated by the ferrocyanide scavenging campaign in the 1950s had a variable amount of sodium and cesium concentrations. Therefore, the effects of these concentrations on the batch distribution values were examined. The concentration ranges selected cover the expected tank conditions and beyond to thoroughly examine the effect of these variables. The sodium concentration was varied from 5.8 M to 3.4 E-5 M. The concentration of cesium was varied from 0.71 M to 3.6 E-6 M. Two sets of experiments were designed to examine the effect of cesium and sodium on exchange capabilities of the nickel ferrocyanide solids present in the waste simulants.

The concentration range of cesium represented cesium-to-nickel ferrocyanide ratios approximating three ranges: 1) the initial scavenging campaign conditions (approximately 0.003 to 0.006) and lower (to 0.0005), 2) to the theoretical capacity of 2 mole of cesium per mole of nickel ferrocyanide, and 3) to extreme excesses of cesium. Because there were additions of cesium-containing waste solutions to the settled nickel ferrocyanide solids, the top portion of nickel ferrocyanide solids would be exposed to the full amount of cesium in the added solutions, assuming the liquid could intercalate through the solids.

2.1.2 Preparation of Synthetic Waste

U-Plant-2 and In-Farm-2 waste simulants were chosen to represent the ferrocyanide waste (Tables 2.1 and 2.2). The simulants were prepared following the recipes developed through process knowledge (Jeppson and Wong 1993). The U-Plant-2 simulant represents the high ferrocyanide concentration for the U-Plant scavenging process. Approximately 24 L of U-Plant-2 simulant were

Table 2.1. U-Plant-2 Simulant Waste Components

Molecular Formula	Component	Concentration, M
Na_2SO_4	Sodium Sulfate	0.20
Na_3PO_4	Sodium Phosphate	0.15
$NaNO_3$	Sodium Nitrate	2.8
$NaNO_2$	Sodium Nitrite	0.86
NH_2SO_3H	Sulfamic Acid	0.0034
$Fe(NH_4)_2(SO_4)_2$	Ferrous Ammonium Sulfate	0.017
$Na_4Fe(CN)_6$	Sodium Ferrocyanide	0.005
$NiSO_4$	Nickel Sulfate	0.005

Table 2.2. In-Farm-2 Simulant Waste Components

Molecular Formula	Component	Concentration, M
Na_2SO_4	Sodium Sulfate	0.17
Na_3PO_4	Sodium Phosphate	0.16
$NaNO_3$	Sodium Nitrate	3.75
$NaNO_2$	Sodium Nitrite	1.25
$Ca(NO_3)_2$	Calcium Nitrate	0.010
$CsNO_3$	Cesium Nitrate	0.00025
$Na_4Fe(CN)_6$	Sodium Ferrocyanide	0.005
$NiSO_4$	Nickel Sulfate	0.005

prepared, resulting in the isolation of 1000 g of the U-Plant-2 solids from the supernate. The In-Farm-2 simulant represents the intermediate ferrocyanide concentration for the In-Farm scavenging process. Approximately 31 L of In-Farm-2 simulant were prepared, resulting in the isolation of 1100 g of In-Farm-2 solids from the supernate. These two simulants represent 92% of the total ferrocyanide used in the ferrocyanide scavenging campaign.

2.2 Measurements and Content Analysis

2.2.1 Batch Distribution Measurements

The batch distribution experiments were performed at room temperature using 0.50 g of centrifuged solid waste simulant and 20.00 mL of treated simulant supernate. The supernate was collected after the synthetic waste was prepared and the solids were removed. Multiple solutions were prepared by adding cesium nitrate to the supernate, then adding 100 μL of a 6-μCi/mL ^{137}Cs stock solution. An aliquot of the treated supernate was pulled and used as the time zero solution concentration (C_0). The appropriate amount of remaining supernate was then added to the solids and stirred on a magnetic stir plate for 2 days or longer to obtain equilibrium. A homogeneous mixture was transferred and centrifuged to separate the solids and liquid. The liquid portion was then filtered using 0.45-μm Nylon syringe filters to remove any suspended particles. Four milliliters of each solution were transferred to another container to be counted. The time zero supernate solutions were filtered and counted in the same manner as the reacted supernate. All batch distribution experiments were performed using 100 μL of the 6-μCi/mL ^{137}Cs stock solution. Using a 5-minute counting time, 4 mL of the time zero (C_0) solution resulted in approximately 100,000 counts. Radioactive counting was performed using a 3-in. NaI(Tl) crystal with a 3-in. well placed within a lead cave. The background activity for a 5-minute counting period was determined to be 5-20 counts.

2.2.2 Determination of $Na_2NiFe(CN)_6$ Content in Simulated Waste Using Fourier Transform Infrared Spectroscopy (FTIR)

Cyanide FTIR Standards

Appropriate amounts of $Na_4Fe(CN)_6 \cdot 10\ H_2O$ were dissolved in 25.0 g of dissolution reagent (Bryan et al. 1993). The dissolution reagent consisted of 5% EDTA and 5% ethylenediamine in deionized water. The calibration standards varied in concentration from 1000 to 5000 mg/L cyanide. Lower concentrations (100 to 500 mg/L) were prepared by diluting the 1000 mg/L standard using the dissolution reagent.

Analysis of Simulants for Cyanide Content

The solid simulant was weighed out (1.0000 g) and 10.00 g of the dissolution reagent was added. The mixture was stirred for 2 hours to ensure complete dissolution of the alkali metal nickel ferrocyanide solids. Filtration through a 0.45-μm filter did not remove the suspended particles present in the U-Plant-2 simulant; therefore, each solution was permitted to settle and the supernate was sampled for analysis. The simulant supernate and a blank were also analyzed for cyanide content.

Calculation of Nickel Ferrocyanide Content

The concentration of dissolved nickel ferrocyanide was calculated using the slope and intercept from the calibration curve. (The correlation coefficient was 0.9999.) The analysis of the simulant supernate confirmed that no residual cyanide remained in the liquid portion of the simulant. The concentration of sodium nickel ferrocyanide was calculated assuming it was the only species in

solution containing cyanide. However, the In-Farm-2 simulant is prepared using a small amount of cesium; therefore, this assumption is incorrect. The simulant should contain small amounts of either $Cs_2NiFe(CN)_6$ or $NaCsNiFe(CN)_6$. The added cesium was one-twentieth of the total ferrocyanide; therefore, depending upon the form of the cesium nickel ferrocyanide [$Cs_2NiFe(CN)_6$ or $NaCsNiFe(CN)_6$], 2.5% to 5.0% of the nickel ferrocyanide would already contain cesium and would be unlikely to exchange additional cesium from solution. Thus, the concentration of nickel ferrocyanide available for ion exchange would be less than the measured value calculated from the measured cyanide. Because the concentration of each form of the cesium-containing ferrocyanide cannot be readily determined, and because the error would be small (2.5% to 5%), the sodium nickel ferrocyanide concentration was not corrected.

Results of FTIR Determination of $Na_2NiFe(CN)_6$ Content in Simulated Waste

The analysis of the centrifuged simulant sludges for $Na_2NiFe(CN)_6$ content was used to determine the amount of cesium to be added to the solids to obtain the desired cesium-to-nickel ferrocyanide ratios. The ferrocyanide concentration in the homogenized batch of U-Plant-2 simulant was 40 mg $Na_2NiFe(CN)_6$/g centrifuged sludge. The ferrocyanide content of the homogenized batch of In-Farm-2 simulant was measured to be 37 mg $Na_2NiFe(CN)_6$/g centrifuged sludge. The solids isolation yielded a U-Plant-2 sludge with 37% solids content and an In-Farm-2 sludge with 35% solids. The In-Farm-2 simulant preparation included a small amount of cesium nitrate, indicating that either $Cs_2NiFe(CN)_6$ or $NaCsNiFe(CN)_6$ would exist in the sludge. The dissolution solution used in this experiment will dissolve both the sodium and cesium form of nickel ferrocyanide (Bryan et al. 1993). Thus, the measured concentration of $Na_2NiFe(CN)_6$ in the In-Farm-2 sludge will be approximately 2.5% to 5% high (as discussed in the previous paragraph). No additional analyses were performed on the In-Farm-2 sludge to quantify the amount of $Cs_2NiFe(CN)_6$ present; therefore, there was no basis for correcting the nickel ferrocyanide concentration.

2.2.3 Concentration of ^{137}Cs by Layering During Sedimentation

The layering experiments were performed using slurries of U-Plant-2 and In-Farm-2 solids reacted with treated supernate (see Section 2.2.1). Several mixtures of the corresponding solid waste simulant and the supernate were prepared by weighing out appropriate amounts of the solid and supernate to provide mixtures containing a total percent solids concentration of 30% to 5%. The concentration of $Na_2NiFe(CN)_6$ present in each mixture was calculated from knowledge of the mass of the U-Plant-2 or In-Farm-2 present. A stock solution of $CsNO_3$ in supernate spiked with 4 mL of the 6-μCi/mL ^{137}Cs stock was then added to each mixture to give a cesium-to-nickel ferrocyanide mole ratio of 0.50 for the U-Plant-2 solids and a cesium-to-nickel ferrocyanide mole ratio of 0.80 for the In-Farm-2 solids. The samples were stirred for 3-4 days to obtain equilibrium and then transferred to a 1.5 X 30 cm column and allowed to settle at room temperature for at least 5 days. The ^{137}Cs was measured spatially down the length of the column using a NaI gamma detector placed behind lead shielding containing a collimated slit to permit the gamma counting of a small thickness of the column.

2.2.4 Concentration of ^{137}Cs by Intercalation Following Sedimentation

The intercalation experiments were performed using slurries of both U-Plant-2 and In-Farm-2 solids reacted with treated supernate (see Section 2.2.1 and 2.2.3). Several slurries of the correspond-

ing solid waste simulant and the supernate were prepared by mixing known amounts of solid and supernate to provide mixtures containing a total percent solids concentration of approximately 20% for the U-Plant-2 columns and 26% for the In-Farm-2 columns. The columns were permitted to settle for several weeks and then were spiked with a supernate solution containing $CsNO_3$ and an aliquot of 6-μCi/mL ^{137}Cs stock solution. Four columns of each material were treated with enough cesium to give a ratio of 20, 0.50, 0.01, and 0.0030 mole of cesium per mole of nickel ferrocyanide. The concentration of ^{137}Cs was measured spatially down the length of the column using a NaI gamma detector placed behind lead shielding containing a collimated slit to permit the gamma counting of a small region of the column.

3.0 Measurements of Cesium Distribution in Simulated Ferrocyanide Waste: Batch Distribution (K_d) Measurements

The batch distribution coefficient (K_d) is a measure of the overall ability of the solid phase to remove an ion from solution (Amphlett 1964). Batch distribution results are reported as distribution coefficients in mL/g (mL of solution exchanged per mass of exchanger). The batch distribution value represents a solid-liquid equilibrium distribution for the exchange of cesium from the liquid phase into the solid phase. The K_d expression is defined as follows:

$$K_d = \frac{C_s}{[Cs]} = \frac{(C_o - C_f)V}{C_f \cdot m} = \frac{mL}{g} \quad (1)$$

where C_s = cesium concentration in solid, moles/g
[Cs] = cesium concentration in liquid, moles/mL
C_o = initial cesium concentration in solution
C_f = final cesium concentration in solution
V = volume of solution
M = mass of exchanger.

Experimentally, the K_d value is measured for specific solutions where the initial concentration of the ion of interest is known (in this case, cesium) and the concentration of competing ions of interest is also known (in this case, sodium). The K_d value is significant because this value represents the total volume of solution from which all cesium present could be removed. This value can be used only for comparison with solutions that have identical composition as the solution for which the K_d was measured. Since the K_d value is determined by difference, as more and more of the ion of interest is removed, the K_d values become quite large.

Distribution coefficients were measured for U-Plant-2 and In-Farm-2 centrifuged solid waste simulants. The cesium-to-nickel ferrocyanide ratio was varied from 200 to 0.0010 while the concentration of sodium was kept constant. This experiment allows for the measurement of K_d values at various cesium levels covering a range of conditions representative of the ferrocyanide waste. The results are reported in Tables 3.1 and 3.2.

The results listed in Tables 3.1 and 3.2 corroborate the expectation that U-Plant-2 and In-Farm-2 solids should behave similarly with respect to the exchange of cesium from solution. In these two experiments, the sodium concentration was kept constant while the cesium concentration was varied. To determine if sodium significantly affected the exchange of cesium, the experiments were repeated maintaining a constant sodium-to-cesium ratio while varying the concentration of cesium. The ratio of cesium to nickel ferrocyanide was varied from 200 to 0.0010 using serial dilutions of a stock solution. The results for U-Plant-2 and In-Farm-2 simulants are reported in Tables 3.3 and 3.4, respectively.

Figures 3.1 and 3.2 show that the maximum capacity of each exchanger can be determined from this experiment. The U-Plant-2 simulant has a maximum capacity of 0.50 mole cesium per mole nickel ferrocyanide, under the conditions of the experiment, and the In-Farm-2 simulant has a maximum capacity of 0.80 mole cesium per mole nickel ferrocyanide. The simple theoretical cesium capacity of a ferrocyanide solid is 2 mole cesium per mole ferrocyanide. This capacity is an upper limit for ion exchange and is rarely realized in practice (Haas 1993). The reported maximum exchange capacity of cesium by nickel ferrocyanide ranges from 0.35 to 1.9 mole cesium per mole nickel ferrocyanide (Loos-Neskovich and Federoff 1989).

Table 3.1. Effect of Cesium Concentration on the Cesium Distribution Coefficients for U-Plant-2 Simulant at pH 9

Sample #	Na/Cs Ratio	Cs/NiFeCN Ratio	[Cs], moles	K_d, mL/g	Cs Removed, %
1	4.50e+02	206	1.30e-02	0.45	1%
2	9.00e+02	100	6.47e-03	1.7	4%
3	1.80e+03	51	3.22e-03	1.3	3%
4	3.60e+03	25	1.61e-03	2.5	6%
5	9.00e+03	10	6.50e-04	2.1	5%
6	1.80e+04	5	3.24e-04	3.0	7%
7	4.50e+04	2	1.29e-04	4.6	10%
8	8.70e+04	1	6.69e-05	9.3	19%
9	1.80e+05	0.50	3.29e-05	17	30%
10	8.90e+05	0.10	6.57e-06	180	82%
11	1.70e+06	0.050	3.35e-06	620	94%
12	8.70e+06	0.010	6.66e-07	6600	99%
13	1.80e+07	0.005	3.30e-07	6400	99%
14	3.40e+07	0.0027	1.70e-07	6500	99%
15	8.90e+07	0.0010	6.56e-08	6500	99%

Table 3.2. Effect of Cesium Concentration on the Cesium Distribution Coefficients for In-Farm-2 Simulant at pH 9

Sample #	Na/Cs Ratio	Cs/NiFeCN Ratio	[Cs], moles	K_d, mL/g	Cs Removed, %
1	2.00e+02	195	1.16e-02	0.9	2%
2	4.00e+02	98	5.86e-03	1.4	3%
3	8.00e+02	49	2.92e-03	1.0	3%
4	1.60e+03	24	1.46e-03	5.7	5%
5	4.00e+03	10	5.83e-04	2.4	6%
6	8.00e+03	5	2.92e-04	3.4	8%
7	2.00e+04	2	1.17e-04	6.8	15%
8	4.10e+04	1	5.73e-05	13	26%
9	8.10e+04	0.5	2.87e-05	24	37%
10	4.00e+05	0.1	5.76e-06	230	85%
11	8.10e+05	0.05	2.87e-06	580	94%
12	4.30e+06	0.009	5.36e-07	5900	99%
13	8.10e+06	0.005	2.86e-07	6600	99%
14	1.60e+07	0.0024	1.43e-08	7600	99%
15	4.30e+07	0.0009	5.42e-08	8700	99%

Table 3.3. Effect of Cesium Concentration on the Cesium Distribution Coefficients for U-Plant-2 Simulant with Constant Na/Cs Mole Ratio of 4.8

Sample #	Cs/NiFeCN Ratio	[Cs], moles	K_d, mL/g	Cs Removed, %
1	200	1.28e-02	<DL	<DL*
2	100	6.37e-03	0.21	1%
3	49	3.18e-03	0.38	1%
4	25	1.60e-03	0.7	2%
5	10	6.51e-04	1.3	3%
6	5	3.30e-04	3.2	7%
7	2	1.31e-04	6.7	14%
8	1	6.57e-05	12	23%
9	0.50	3.30e-05	26	40%
10	0.10	6.57e-06	1600	98%
11	0.050	3.28e-06	8700	99%
12	0.010	6.61e-07	30200	99%
13	0.0050	3.28e-07	30000	99%
14	0.0025	1.63e-07	14000	99%
15	0.0010	6.61e-08	16000	99%

* Less than detection limit.

Table 3.4. Effect of Cesium Concentration on the Cesium Distribution Coefficients for In-Farm-2 Simulant with Constant Na/Cs Mole Ratio of 7.5

Sample #	Cs/NiFeCN Ratio	[Cs], moles	K_d, mL/g	Cs Removed, %
1	200	1.17e-02	3.0	7%
2	100	5.86e-03	3.0	8%
3	50	2.93e-03	0.7	2%
4	24	1.45e-03	1.7	4%
5	10	5.90e-01	3.0	7%
6	5	2.89e-04	6.7	15%
7	2	1.16e-04	17	30%
8	1	5.81e-05	41	51%
9	0.50	2.91e-05	170	81%
10	0.10	5.81e-06	31000	99%
11	0.050	2.91e-06	35000	99%
12	0.010	5.81e-07	20000	99%
13	0.005	2.91e-07	54000	99%
14	0.0025	1.46e-08	28000	99%
15	0.0010	5.82e-08	26000	99%

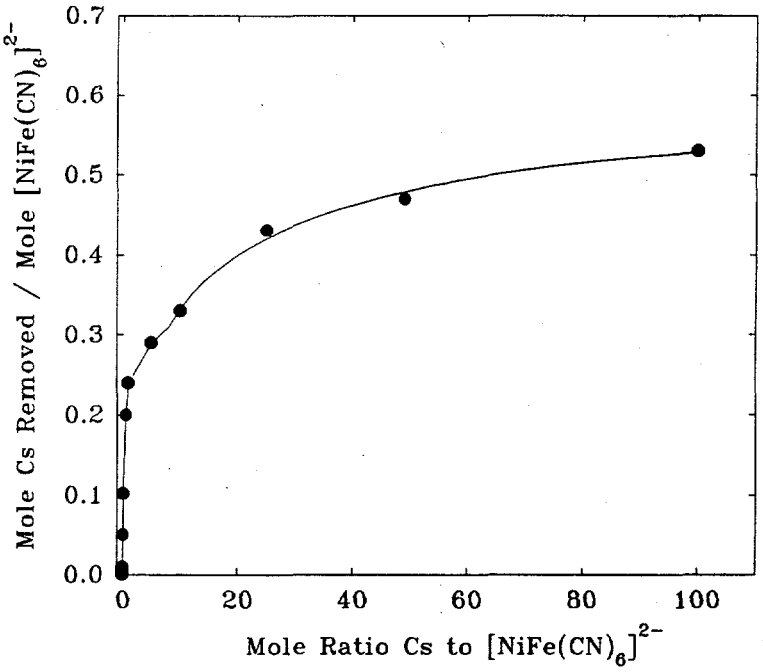

Figure 3.1. Maximum Capacity of U-Plant-2 Ferrocyanide Waste Simulant for Exchanging Cesium from Solution

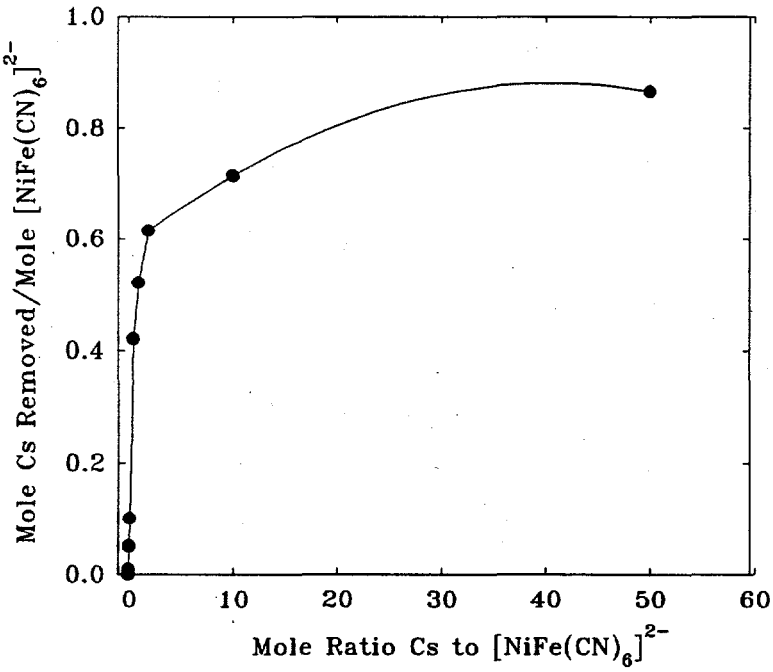

Figure 3.2. Maximum Capacity of In-Farm-2 Ferrocyanide Waste Simulant for Exchanging Cesium from Solution

The results from these four series of experiments indicate the In-Farm-2 simulant was better at exchanging cesium from solution than was the U-Plant-2 simulant. Table 3.5 compares the In-Farm-2 and U-Plant-2 distribution coefficients corrected for the amount of $Na_2NiFe(CN)_6$ present in the solids, as determined by fourier transform infrared spectroscopy (FTIR). However, the In-Farm-2 simulant was prepared using a small amount of cesium; therefore, the simulant contains small amounts of either $Cs_2NiFe(CN)_6$ or $NaCsNiFe(CN)_6$. The added mole quantity of cesium was one-twentieth of the total ferrocyanide; therefore, depending upon the form of the cesium nickel ferrocyanide [$Cs_2NiFe(CN)_6$ or $NaCsNiFe(CN)_6$], 2.5% to 5.0% of the nickel ferrocyanide would already contain cesium and would be unlikely to exchange additional cesium from solution. Thus, the concentration of nickel ferrocyanide available for ion exchange would be less than the measured value calculated from the measured cyanide. After applying this correction, the difference between the exchange capacity of the two materials is even larger (0.86 mole of cesium per mole of nickel ferrocyanide present in In-Farm-2 simulant).

The effective capacity of nickel ferrocyanide to exchange cesium depends on the molar ratio of cesium to nickel ferrocyanide, as illustrated by the K_d values (see Figure 3.1). In the initial scavenging campaign, the mole ratio of cesium to nickel ferrocyanide was quite small, approximately 0.006 to 0.003. Under these conditions and with lower ratios, the K_d values were quite large, and cesium was readily removed from solution. However, when the ratio of cesium to nickel ferrocyanide was increased to 2 and beyond, the K_d values were significantly decreased (see Tables 3.1 through 3.4).

The K_d values for the U-Plant-2 and In-Farm-2 waste simulant, based on the concentration of $Na_2NiFe(CN)_6$ present, agree quite well with the literature values for solutions with similar concentrations of ions (Table 3.6). The experimental K_d values are lower than literature values because the cesium-to-nickel ferrocyanide ratios in the experiments were higher than the cesium-to-nickel ferrocyanide ratio in the literature studies (Campbell et al. 1991). At the higher levels of cesium (thus a higher ratio of cesium to nickel ferrocyanide), the K_d values are low with respect to the results of Campbell et al. However, at the lower concentrations of cesium, the results compare well with the literature values.

Table 3.5. Distribution Coefficients for U-Plant-2 and In-Farm-2 Simulants Based on the Total Concentration of $Na_2NiFe(CN)_6$ Present in the Simulant

Sample #	Cs-to-NiFeCN Ratio	U-Plant-2 Simulant, K_d mL/g	In-Farm-2 Simulant, K_d mL/g
1	200	<DL*	<DL
2	100	5.0	<DL
3	50	9.0	17
4	25	20	43
5	10	30	72
6	5	80	170
7	2	170	420
8	1	300	1000
9	0.50	650	4200
10	0.10	39000	770000
11	0.050	220000	880000
12	0.0010	750000	500000
13	0.0050	740000	1300000
14	0.0025	340000	700000
15	0.0010	390000	650000

* Less than detection limit.

Table 3.6. Summary of Experimental and Literature K_d Values for U-Plant-2 and In-Farm-2 Simulated Ferrocyanide Waste and Pure $Na_2NiFe(CN)_6$

Material	K_d	Conditions
U-Plant-2	6.5×10^2 - 7.5×10^5	[Na]= 3.66 M [Cs]= 3.3×10^{-5} - 6.6×10^{-8} M [Cs]/[NiFeCN]= 0.50 - 0.0010 M
In-Farm-2	4.2×10^2 - 1.3×10^6	[Na]= 5.82 M [Cs]= 2.9×10^{-5} - 5.8×10^{-8} M [Cs]/[NiFeCN]= 0.50 - 0.0010 M
$Na_2NiFe(CN)_6$	6.0×10^4 - 1.0×10^6	[Na]= 4.5 M [(a)] [K] = 0.25 M [Cs]= 1.0×10^{-5} - 2.5×10^{-7} M [Cs]/[NiFeCN]= 0.30 - 7.9×10^{-4} M

(a) Campbell et al. (1991).

4.0 Concentration Mechanisms for ^{137}Cs in Ferrocyanide Waste by Sedimentation

The results of the distribution coefficient and maximum capacity experiments presented in Section 3.0 demonstrated that cesium can be exchanged from solution by previously precipitated and settled nickel ferrocyanide solids. The cesium capacity of the U-Plant-2 and In-Farm-2 waste simulants was large enough for significant amounts of ^{137}Cs to be exchanged from solution and potentially form concentrated regions of ^{137}Cs; therefore, potential concentration mechanisms were examined to address this possibility.

Waste treated for cesium removal by the addition of ferrocyanide was generally handled by mixing a soluble ferrocyanide and then nickel sulfate with tank supernate, then directly adding this mixture into the waste tank (In-Farm flowsheet) or mixing the ferrocyanide and nickel salts together in the waste streams before pumping the streams to the tank farm (U-Plant flowsheet). In either process there exists a potential for a layer of ^{137}Cs-enriched nickel ferrocyanide to form from the preferential settling of the nickel ferrocyanide from the bulk of the waste material. Section 4.1 discusses this concentration mechanism. Additionally, there is a possibility that radiocesium could be selectively adsorbed into a layer of previously settled nickel ferrocyanide waste by the addition of cesium-enriched supernate to the waste tank at a later time. A concentrated region of ^{137}Cs-enriched nickel ferrocyanide could then be formed if the cesium did not intercalate through the solid region, as discussed in Section 4.2.

4.1 Mechanisms for Concentrating ^{137}Cs by Layering During Sedimentation

Sedimentation is a process by which solid particles will settle through a fluid under the influence of gravity (Nelson 1988). Sedimentation best describes the settling of particles greater than 1 μm in diameter. In contrast, extremely small (colloidal) particles may not settle under the influence of gravity, and remain in suspension indefinitely because of thermal jostling (Brownian motion). Sedimentation rates are affected not only by particle sizes but by fluid and particle densities, fluid viscosity, and solid loadings. When the solid loading is high (>0.10), convection cells may develop where descending columns with high solids loadings are adjacent to ascending columns of clarified liquids. However, at very high solids loadings, such as exist in ferrocyanide-containing waste tanks, the slurry may be too hindered to permit convection cells. The solids will still settle under the influence of gravity, controlled by the rate at which liquids leak upwards through the pores.

To examine the possibility of ^{137}Cs-enriched nickel ferrocyanide separating from the bulk waste material through the preferential settling of the nickel ferrocyanide, the settling of ^{137}Cs-enriched nickel ferrocyanide was examined by equilibrating a solution of ^{137}Cs and cesium-spiked supernate

with the solid waste simulant and allowing the material to settle within a column. The concentration of ^{137}Cs was measured spatially down the length of the column using a gamma detector shielded with a collimated slit to permit the spatial resolution of a radiocesium-enriched layer. Figure 4.1 depicts a schematic of the system. Similar collimated detection systems have been employed for the detection of gamma emitters adsorbed on chromatography columns (Burger and Scheele 1982).

4.2 U-Plant-2 Synthetic Waste Layering Experiments

Two sets of columns of U-Plant-2 waste simulant were prepared using two cesium-to-nickel ferrocyanide ratios. The processing of the ferrocyanide tanks used a cesium-to-nickel ferrocyanide ratio of approximately 0.0033:1 mole of cesium per mole of nickel ferrocyanide. One set of columns was therefore prepared using this ratio to examine whether the cesium form of nickel ferrocyanide [$Na_{2-x}Cs_xNiFe(CN)_6$] would settle out from the sodium form [$Na_2NiFe(CN)_6$], thus providing a mechanism for the formation of concentrated regions of radioactive cesium. Another set of columns was prepared using a cesium-to-nickel ferrocyanide ratio of 0.50:1 (maximum capacity as determined in Section 3.1). This ensured that the majority of the $[NiFe(CN)_6]^{-2}$ was in the cesium form and provided the means to examine whether the cesium nickel ferrocyanide solids will settle out from the other solids (sodium salts) present in the bulk of the simulant. The results of these experiments are reported at the end of this section in Tables 4.1 through 4.7 and Figures 4.2 through 4.8.

The two sets of experiments examined different aspects of the same issue: Does the cesium form of nickel ferrocyanide concentrate after ion exchange occurs? As shown in Figure 4.2, there is no evidence of a concentrated region of ^{137}Cs activity forming within the column. Figure 4.2 shows the

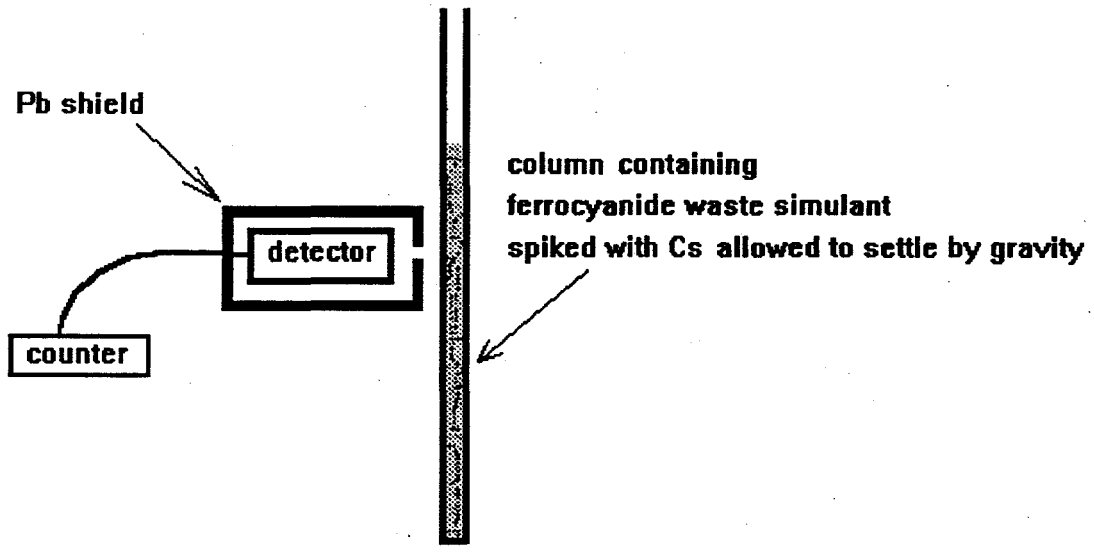

Figure 4.1. Design Schematic of Counting Equipment for Measuring ^{137}Cs Layering During Settling within a Column

results for U-Plant-2 waste simulant reacted with 0.50 mole of cesium per mole of nickel ferrocyanide prepared with a total solids composition of 30%. The measurements were taken from the bottom of the column and up through the total depth of the solids to the liquid supernate. Thus, the height represented in the x-axis of all the layering graphs always references the bottom of the column as zero centimeters in height and increases through the solid bed and into 3 to 5 cm of the supernate. In Figure 4.3, the solution above the settled solids contained a slight amount of activity and this value remained essentially constant from 14 to 10 cm. As the solid liquid interface (8.5 cm) was approached, some of the activity of the solid portion was detected and the measured activity increased through 9 to 7 cm. After passing the interface, the activity was essentially constant again, indicating there was no concentration of the ^{137}Cs during settling (6 to 0 cm).

The above description illustrates the same trend of the settled columns, shown in Figures 4.2 through 4.7, with the following exceptions. The U-Plant-2 column containing 5% solids did not behave in the same manner because of the resolution of the detection system with respect to the total height of the solids. The solid bed was 3.2 cm high, too short to provide resolution of the activity within the solids, as can be seen in Figure 4.4. The data were obtained using a collimated slit approximately 0.5 cm wide and 5.0 cm thick. To address this problem, the column was remeasured using a thinner collimated slit with the detector system (0.1 cm wide and 3.5 cm thick). With this adaptation, only slightly better results were obtained (Figure 4.8). With the better resolution, the activity increased only slightly, moving down through the solid bed to the bottom of the column. The slight decrease in measured activity at the bottom of the column was from a slight scatter in the measurements.

The resolution of the detection system was determined using a small volume of concentrated ^{137}Cs, approximately 0.1 cm high. The resolution of the 0.5-cm collimated slit was approximately 2-3 cm. The same experiment, using a 0.1-cm collimated slit, offered only slightly better resolution (1-2 cm), but greatly reduced the sensitivity of the system. Since the resolution was only slightly increased but the sensitivity was significantly decreased (requiring counting times of 30 minutes per measurement) using the smaller collimated slit, the larger collimated slit was used for the majority of the measurements.

Tables 4.1 through 4.6 show the distribution of ^{137}Cs through the settled solids. The data in the tables should be used in conjunction with the graphs (Figures 4.2 through 4.8) to obtain a complete picture of the layering. For example, Figure 4.2 illustrates a stable relative concentration of ^{137}Cs in the solid region. The activity varied by less than 1000 counts, or approximately 10% of the total activity. The distribution of cesium within the settled solids varied by less than 1%, as shown in Table 4.1. In Figure 4.6, the relative concentration of ^{137}Cs increased throughout the solid region, thus giving the appearance of the concentration of cesium at the bottom of the solid layer. However, examination of the distribution of the percent cesium throughout the settled solids reported in Table 4.6 indicates the ^{137}Cs distribution changed only 3% within the solids, which represents 85% of the total cesium. While there may be increased activity of ^{137}Cs within the settled solids, there is clearly not a significant increase in the distribution of the ^{137}Cs within the solids.

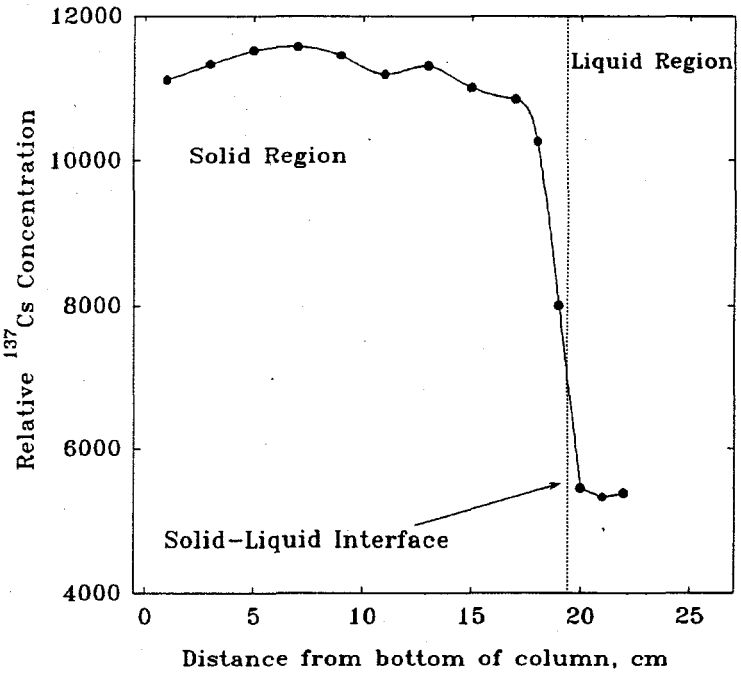

Figure 4.2. Determination of the Layering Characteristics of U-Plant-2 Simulant Treated with a 0.50:1 Mole Ratio of Cesium-to-Nickel Ferrocyanide and 30% Total Solids Content

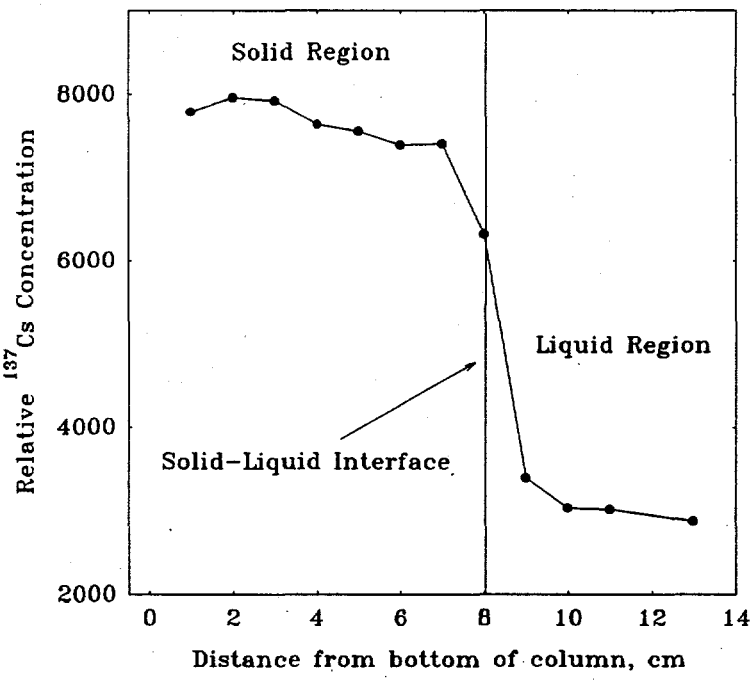

Figure 4.3. Determination of the Layering Characteristics of U-Plant-2 Simulant Treated with a 0.50:1 Mole Ratio of Cesium-to-Nickel Ferrocyanide and 15% Total Solids Content

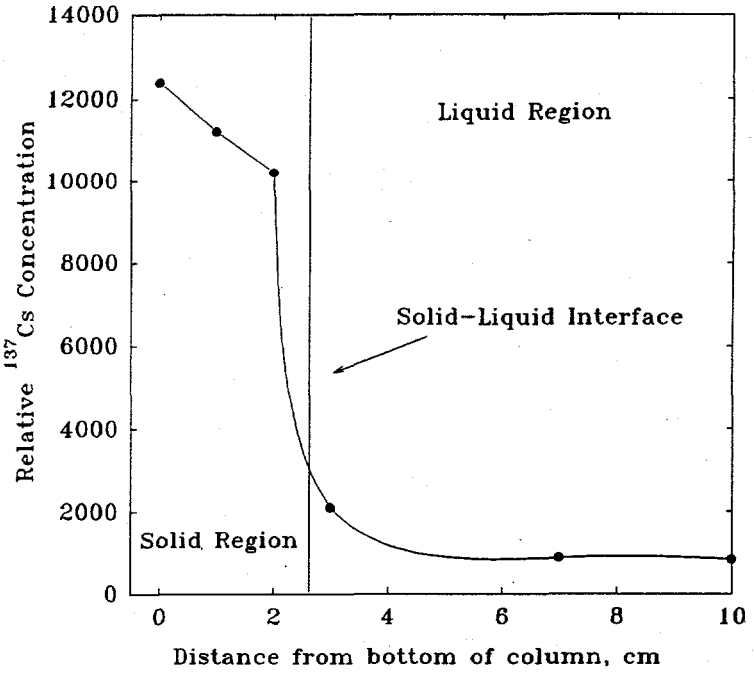

Figure 4.4. Determination of the Layering Characteristics of U-Plant-2 Simulant Treated with a 0.50:1 Mole Ratio of Cesium-to-Nickel Ferrocyanide and 5% Total Solids Content

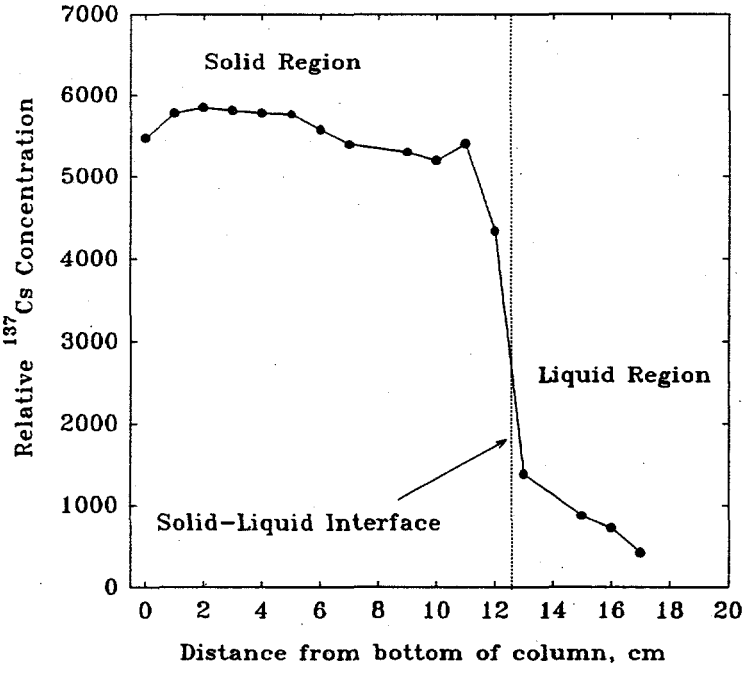

Figure 4.5. Determination of the Layering Characteristics of U-Plant-2 Simulant Treated with a 0.0033:1 Mole Ratio of Cesium-to-Nickel Ferrocyanide and 30% Total Solids Content

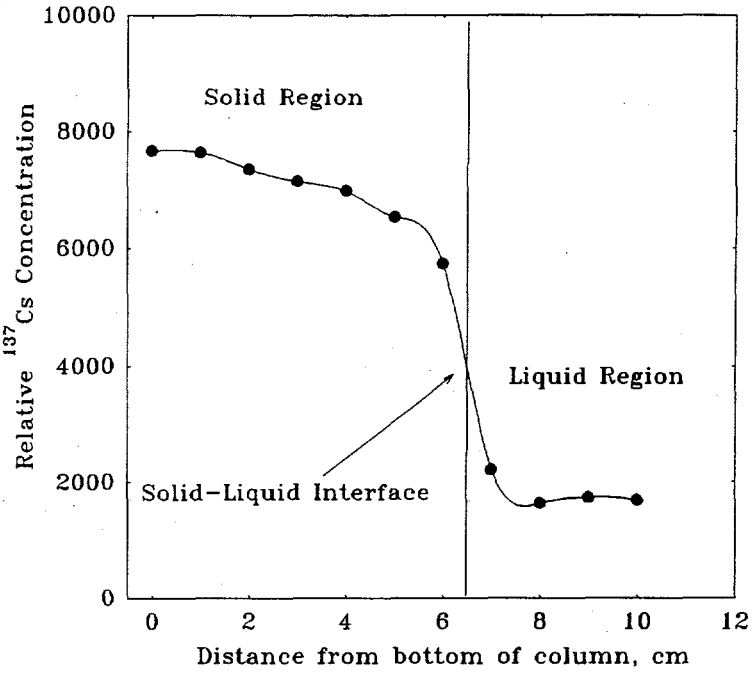

Figure 4.6. Determination of the Layering Characteristics of the U-Plant-2 Simulant Treated with a 0.0033:1 Ratio of Cesium-to-Nickel Ferrocyanide and 15% Total Solids Content

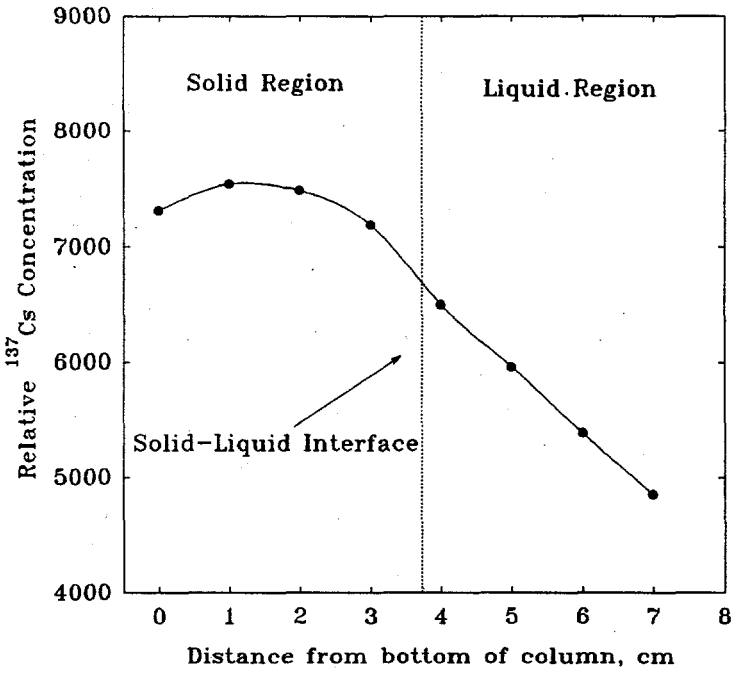

Figure 4.7. Determination of the Layering Characteristics of U-Plant-2 Simulant Treated with a 0.0033:1 Ratio of Cesium-to-Nickel Ferrocyanide and 5% Total Solids Content

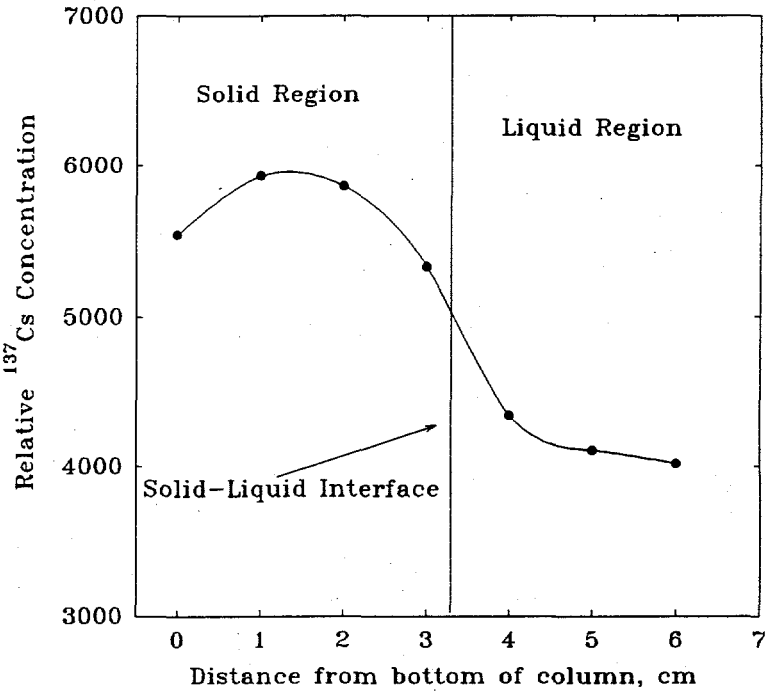

Figure 4.8. Repeat Determination of the Layering Characteristics of U-Plant-2 Simulant Treated with a 0.50:1 Ratio of Cesium-to-Nickel Ferrocyanide and 5% Total Solids Content

Table 4.1. Layering of U-Plant-2 Waste Simulant Containing 0.50:1 Ratio of Cesium to Nickel Ferrocyanide and 30% Solids

Layer	Distance from Bottom of Column, cm	Relative ^{137}Cs Concentration, Counts	Total Cesium, %
Liquid	22	5380	3.7
Liquid	21	5320	3.6
Liquid	20	5450	3.7
Solid-Liquid Interface	19	8000	5.4
Solid	18	10300	7.0
Solid	17	10800	7.4
Solid	16	11300	7.7
Solid	15	11000	7.5
Solid	13	11300	7.7
Solid	11	11200	7.6
Solid	9	11400	7.8
Solid	7	11600	7.9
Solid	5	11500	7.8
Solid	3	11300	7.7
Solid	1	11100	7.6

Table 4.2. Layering of U-Plant-2 Waste Simulant Containing 0.50:1 Ratio of Cesium to Nickel Ferrocyanide and 15% Solids

Layer	Distance from Bottom of Column, cm	Relative ^{137}Cs Concentration, Counts	Total Cesium, %
Liquid	13	2890	3.6
Liquid	11	3030	3.8
Liquid	10	3040	3.8
Liquid	9	3400	4.2
Solid-Liquid Interface	8	6320	7.8
Solid	7	7400	9.2
Solid	6	7390	9.2
Solid	5	7560	9.4
Solid	4	7650	9.5
Solid	3	7920	9.9
Solid	2	7960	9.9
Solid	1	7790	9.7
Solid	0	8240	10.2

Table 4.3. Layering of U-Plant-2 Waste Simulant Containing 0.50:1 Ratio of Cesium to Nickel Ferrocyanide and 5% Solids

Layer	Distance from Bottom of Column, cm	Relative ^{137}Cs Concentration, Counts	Total Cesium, %
Liquid	10	840	2.2
Liquid	7	880	2.3
Solid-Liquid Interface	3	2100	5.6
Solid	2	10200	27.1
Solid	1	11200	29.7
Solid	0	12400	33.0

Table 4.4. Remeasurement of Layering of U-Plant-2 Waste Simulant Containing 0.50:1 Ratio of Cesium to Nickel Ferrocyanide and 5% Solids Using the Thin Collimated Slit

Layer	Distance from Bottom of Column, cm	Relative ^{137}Cs Concentration, Counts	Total Cesium, %
Liquid	6	4020	11.4
Liquid	5	4110	11.7
Liquid	4	4340	12.4
Solid-Liquid Interface	3	5330	15.2
Solid	2	5860	16.7
Solid	1	5930	16.9
Solid	0	5540	15.8

Table 4.5. Layering of U-Plant-2 Waste Simulant Containing 0.0033:1 Ratio of Cesium to Nickel Ferrocyanide and 30% Solids

Layer	Distance from Bottom of Column, cm	Relative ^{137}Cs Concentration, Counts	Total Cesium, %
Liquid	17	420	0.6
Liquid	16	730	1.1
Liquid	15	870	1.3
Liquid	13	1380	2.0
Solid-Liquid Interface	12	4340	6.3
Solid	11	5400	7.8
Solid	10	5200	7.5
Solid	9	5300	7.7
Solid	7	5390	7.8
Solid	6	5570	8.1
Solid	5	5760	8.3
Solid	4	5770	8.4
Solid	3	5800	8.4
Solid	2	5840	8.5
Solid	1	5780	8.4
Solid	0	5490	7.9

Table 4.6. Layering of U-Plant-2 Waste Simulant Containing 0.0033:1 Ratio of Cesium to Nickel Ferrocyanide and 15% Solids

Layer	Distance from Bottom of Column, cm	Relative ^{137}Cs Concentration, Counts	Total Cesium, %
Liquid	11	1690	3.0
Liquid	9	1730	3.1
Liquid	8	1630	2.9
Liquid	7	2220	3.9
Solid-Liquid Interface	6	5730	10.2
Solid	5	6520	11.6
Solid	4	6980	12.4
Solid	3	7140	12.7
Solid	2	7350	13.1
Solid	1	7640	13.6
Solid	0	7670	13.6

Table 4.7. Layering of U-Plant-2 Waste Simulant Containing 0.0033:1 Ratio of Cesium to Nickel Ferrocyanide and 5% Solids

Layer	Distance from Bottom of Column, cm	Relative ^{137}Cs Concentration, Counts	Total Cesium, %
Liquid	7	4850	9.3
Liquid	6	5390	10.3
Liquid	5	5960	11.4
Solid-Liquid Interface	4	6500	12.4
Solid	3	7190	13.8
Solid	2	7480	14.3
Solid	1	7540	14.4
Solid	0	7310	14.0

4.3 In-Farm-2 Synthetic Waste Layering Experiments

One set of In-Farm-2 waste simulant columns was prepared using a cesium-to-nickel ferrocyanide ratio of 0.80:1 (maximum capacity as determined in Section 3.1) to compare the layering behavior of In-Farm-2 simulant with that of the U-Plant-2 simulant. Based on the results of the U-Plant-2 experiments, only one potential concentration mechanism was examined since only one comparison should be needed to prove that the two simulants have the same layering behavior. Three columns of In-Farm-2 simulant were prepared using a range of total percent solids from 30% to 5%. The results are reported at the end of this section in Tables 4.8 to 4.10 and Figures 4.9 to 4.11. This experiment was performed to confirm that the In-Farm-2 waste simulant behaved like the U-Plant-2 simulant with respect to forming layers, specifically to examine the possibility of the cesium form of nickel ferrocyanide [$Na_{2-x}Cs_xNiFe(CN)_6$] settling out from the bulk material of the solids and thus providing a mechanism for the formation of concentrated regions of radioactive cesium.

Figure 4.9 shows the results for In-Farm-2 simulant reacted with 0.80 mole of cesium per mole of nickel ferrocyanide prepared with a total solid composition of 30%. The measurements were performed from the bottom of the column and up through the total depth of the solids to the liquid supernate. Thus, the height represented in the x-axis of all the layering graphs always references the bottom of the column as zero centimeters in height and increases through the solid bed and into 3 to 5 cm of the supernate. In Figure 4.9, the solution above the settled solids contains a slight amount of activity and this value decreased slightly from 19 to 22 cm. As the solid liquid interface (16 cm) was approached, some of the activity of the solid portion was detected and the measured activity increased through 18 to 12 cm. After passing the interface, there was a slight increase in activity; however, the increase was less than 10%, indicating that there was no appreciable concentration of the ^{137}Cs during settling (12 to 0 cm).

The trend described above was observed for each of the settled In-Farm-2 columns. As shown in Figures 4.10 through 4.11, there was no evidence of a concentrated region of ^{137}Cs activity forming within the columns during layering. This result confirmed the U-Plant-2 and In-Farm-2 simulated waste behave similarly under the same conditions.

The experiments described here and in the previous section examined the potential ^{137}Cs concentration mechanisms through 1) the cesium form of nickel ferrocyanide settling at a different rate than the sodium form of nickel ferrocyanide [$Na_2NiFe(CN)_6$], and 2) the cesium nickel ferrocyanide [$Na_{2-x}Cs_xNiFe(CN)_6$] settling out from the remaining solid materials. The layering experiments performed with the U-Plant-2 and In-Farm-2 waste simulants indicated that neither of the two proposed mechanisms for the concentration of cesium occurred. The conditions of this experiment should be considered conservative since the columns of solid material were permitted to settle within a homogeneous environment (no previously settled material) without the presence of thermal convection, etc., conditions which would decrease the likelihood of layering because of mixing occurring and which most certainly are present within the storage tanks.

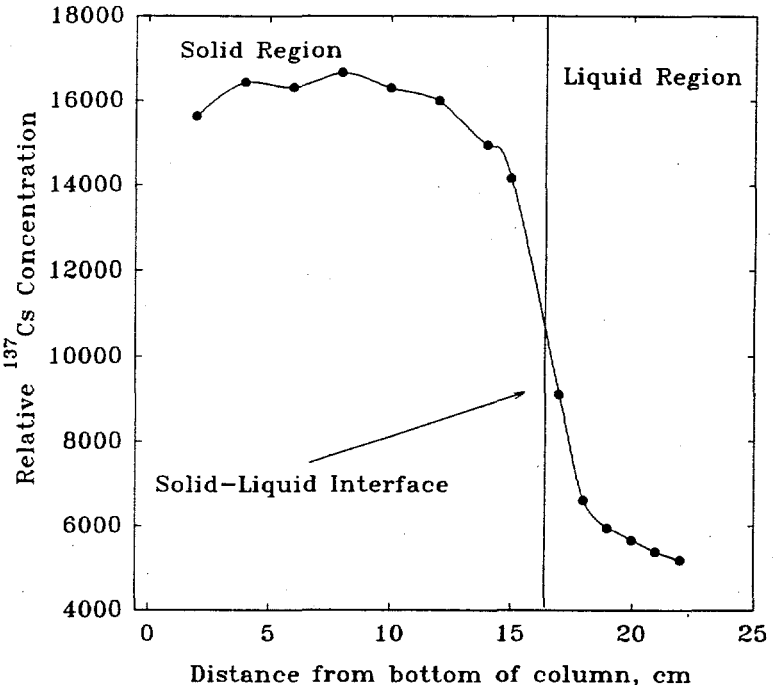

Figure 4.9. Determination of the Layering Characteristics of In-Farm-2 Simulant Treated with a 0.80:1 Ratio of Cesium-to-Nickel Ferrocyanide and 30% Total Solids Content

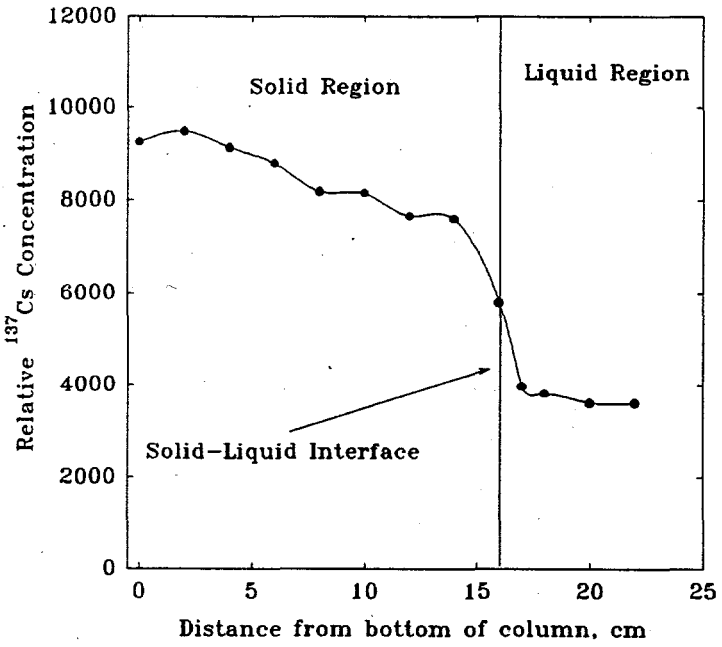

Figure 4.10. Determination of the Layering Characteristics of In-Farm-2 Simulant Treated with a 0.80:1 Ratio of Cesium-to-Nickel Ferrocyanide and 15% Total Solids Content

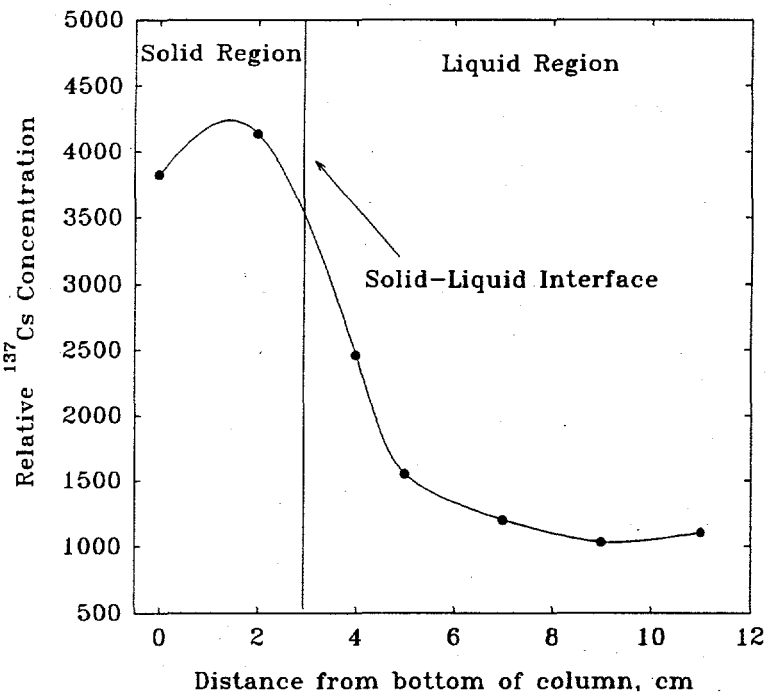

Figure 4.11. Determination of the Layering Characteristics of In-Farm-2 Simulant Treated with a 0.80:1 Ratio of Cesium-to-Nickel Ferrocyanide and 5% Total Solids Content

Table 4.8. Layering of In-Farm-2 Waste Simulant Containing 0.80:1 Ratio of Cesium to Nickel Ferrocyanide and 30% Solids

Layer	Distance from Bottom of Column, cm	Relative ^{137}Cs Concentration, Counts	Total Cesium, %
Liquid	22	5180	2.9
Liquid	21	5380	3.1
Liquid	19	5650	3.2
Liquid	18	5940	3.4
Liquid	17	6610	3.8
Solid-Liquid Interface	16	6610	3.8
Solid	15	14200	8.0
Solid	14	14900	8.5
Solid	12	16000	9.1
Solid	10	16300	9.3
Solid	8	16700	9.5
Solid	6	16300	9.3
Solid	4	16400	9.3
Solid	2	15600	8.9
Solid	0	14300	8.1

Table 4.9. Layering of In-Farm-2 Waste Simulant Containing 0.80:1 Ratio of Cesium to Nickel Ferrocyanide and 15% Solids

Layer	Distance from Bottom of Column, cm	Relative ^{137}Cs Concentration, Counts	Total Cesium, %
Liquid	22	3610	4.1
Liquid	20	3610	4.1
Liquid	18	3810	4.3
Liquid	17	3970	4.5
Solid-Liquid Interface	16	5810	6.5
Solid	14	7600	8.5
Solid	12	7660	8.6
Solid	10	8160	9.2
Solid	8	8190	9.2
Solid	6	8790	9.9
Solid	4	9140	10.3
Solid	2	9500	10.7
Solid	0	9250	10.4

Table 4.10. Layering of In-Farm-2 Waste Simulant Containing 0.80:1 Cs Ratio of Cesium to Nickel Ferrocyanide and 5% Solids

Layer	Distance from Bottom of Column, cm	Relative ^{137}Cs Concentration, Counts	Total Cesium, %
Liquid	11	1100	7.2
Liquid	9	1000	6.7
Liquid	7	1200	7.8
Solid	5	1600	10.1
Solid-Liquid Interface	4	2500	16.0
Solid	2	4100	27.0
Solid	0	3800	25.0

5.0 Mechanism for Concentrating ^{137}Cs by Intercalation of Cesium from Solution into Simulated Ferrocyanide Waste

The potential exists for a layer of radiocesium-enriched nickel ferrocyanide to form from the selective adsorption of ^{137}Cs onto a layer of previously settled nickel ferrocyanide waste as a result of the addition of cesium-enriched supernate to the waste tank at a later time. A concentrated region of ^{137}Cs-enriched nickel ferrocyanide could then be formed if the cesium did not diffuse through the solids. To examine the possibility of ^{137}Cs-enriched nickel ferrocyanides forming a layer as a result of adsorption without diffusion, the intercalation of ^{137}Cs and cesium-spiked supernate added to a previously settled column of solid simulant was examined. The concentration of ^{137}Cs was measured spatially down the length of the column using a gamma detector shielded with a collimated slit to allow for the spatial resolution of a radiocesium-enriched layer (see Figure 4.1).

A small volume of a concentrated cesium solution was carefully added to the surface of several settled columns of U-Plant-2 and In-Farm-2 waste simulant to obtain several different mole ratios of cesium to the total nickel ferrocyanide present in the column. The following ratios were used: 1) the maximum capacity of the simulant (0.50:1 for the U-Plant-2 simulant and 0.80:1 for the In-Farm-2 simulant), 2) 0.01 moles of cesium to nickel ferrocyanide, and 3) 0.0033:1 moles of cesium to nickel ferrocyanide. These were selected to examine 1) the intercalation of cesium when an excess of cesium is available, 2) the intercalation when only a slight excess of cesium is available, and 3) the intercalation when the available cesium is very limited. Immediately after adding the spiked supernate, the concentration of ^{137}Cs was measured spatially from the top to the bottom of the column. Each column was then periodically measured over several weeks to observe the ability of the solution to intercalate over time. The results for both the U-Plant-2 and In-Farm-2 simulants are reported in Tables 5.1 through 5.6 and Figures 5.1 through 5.6.

As shown in Figures 5.1 and 5.4, when the top few centimeters of the simulant is exposed to an excess of cesium, the cesium quickly intercalated through the simulants and became dispersed. The curves for each measurement are overlaid to illustrate the changes occurring over time. The 1-day curve in each figure represents the initial distribution of ^{137}Cs immediately after treating the column with cesium solution. The other curves follow the distribution of ^{137}Cs through 2 to 5 days. After this time period, the concentration of ^{137}Cs was dispersed through the first three-fourths of the column. The other columns treated with a limited amount of cesium were not expected to diffuse through an appreciable amount of the solids and indeed did not, as shown in Figures 5.2, 5.3, 5.5, and 5.6. The top graph shows the initial distribution of the ^{137}Cs spike in the liquid portion of the column. The 1-day curve in each figure shows the ^{137}Cs moved readily into the solid, thus producing the drop in the activity for the first measured region of the column and the increase in activity for the second measured region. The later curves demonstrate the static state of the ^{137}Cs, presumably because all of the available cesium was bound in the upper layers of the nickel ferrocyanide.

The experiments performed in this section examined the potential concentration mechanisms through the selective adsorption of ^{137}Cs onto a layer of previously settled nickel ferrocyanide without appreciable diffusion through the solids. The intercalation experiments performed with both U-Plant-2 and In-Farm-2 waste simulants indicated that diffusion of cesium solution occurred readily through a

bed of settled solids containing $Na_2NiFe(CN)_6$, when the concentration of cesium exceeded the experimentally determined capacity of the simulant. The conditions of this experiment were more rigorous than those expected to exist within the tanks, since convection and other forms of jostling of tank waste occurred within the tanks, especially after adding additional solution to the settled solids of the tank. With such jostling, it is expected that any layers that did form would be mixed to some degree with the contents of the tank.

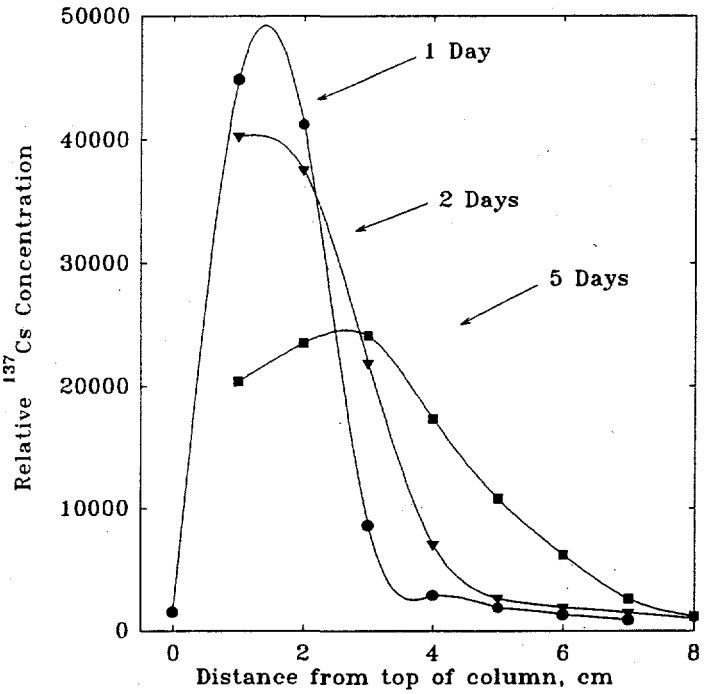

Figure 5.1. Intercalation of Cesium Solution with a 0.50:1 Cesium-to-Nickel Ferrocyanide Ratio into a Settled Column of U-Plant-2 Simulant

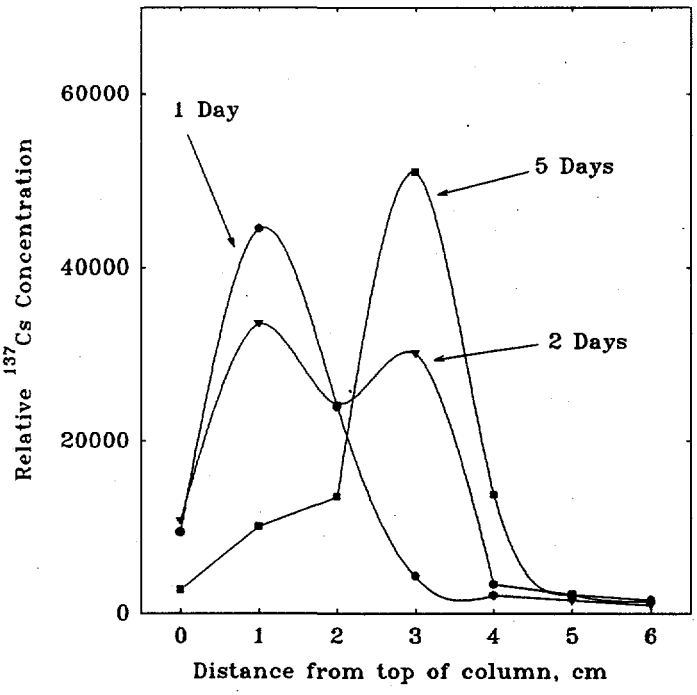

Figure 5.2. Intercalation of Cesium Solution with a 0.01:1 Cesium-to-Nickel Ferrocyanide Ratio into a Settled Column of U-Plant-2 Simulant

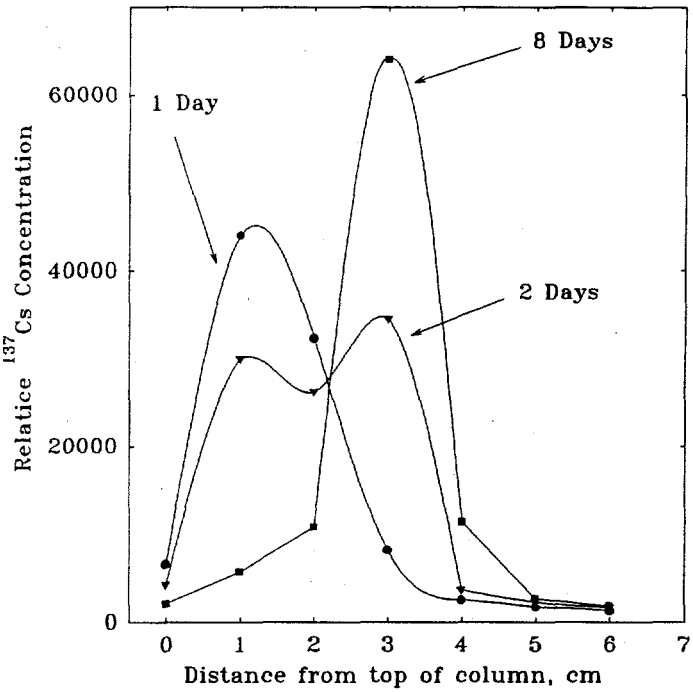

Figure 5.3. Intercalation of Cesium Solution with a 0.0033:1 Cesium-to-Nickel Ferrocyanide Ratio into a Settled Column of U-Plant-2 Simulant

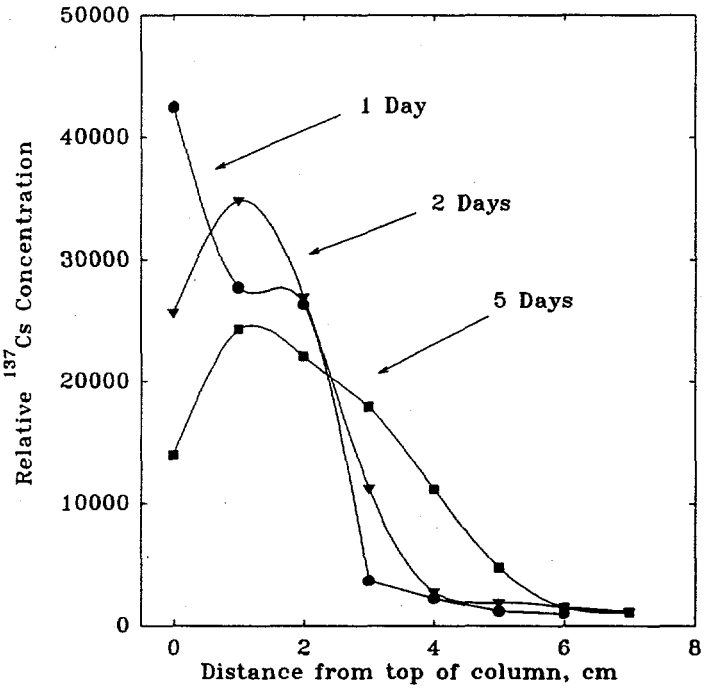

Figure 5.4. Intercalation of Cesium Solution with a 0.80:1 Cesium-to-Nickel Ferrocyanide Ratio into a Settled Column of In-Farm-2 Simulant

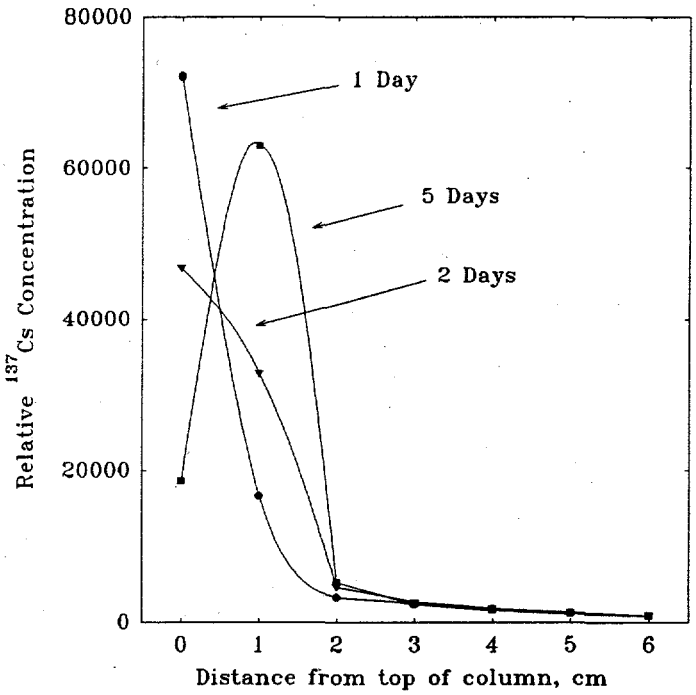

Figure 5.5. Intercalation of Cesium Solution with a 0.01:1 Cesium-to-Nickel Ferrocyanide Ratio into a Settled Column of In-Farm-2 Simulant

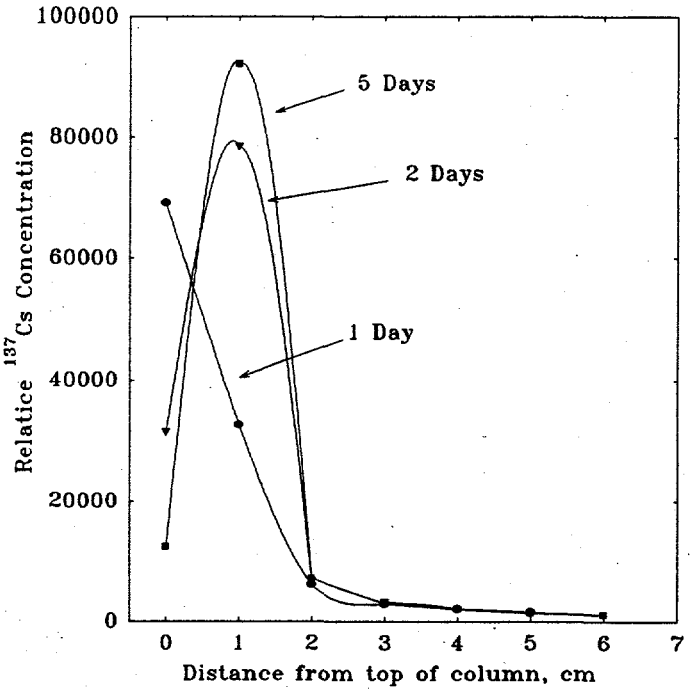

Figure 5.6. Intercalation of Cesium Solution with a 0.0033:1 Cesium-to-Nickel Ferrocyanide Ratio into a Settled Column of In-Farm-2 Simulant

Table 5.1. Intercalation of Cesium Solution with a 0.50:1 Cesium-to-Nickel Ferrocyanide Ratio into a Settled Column of U-Plant-2 Simulant [(a)]

Distance from Top of Column, cm	Layer	1 Day		2 Days		5 Days	
		Relative ^{137}Cs Concen.	Percent of Total Cesium	Relative ^{137}Cs Concen.	Percent of Total Cesium	Relative ^{137}Cs Concen.	Percent of Total Cesium
0	Liquid	1530	1.5	NA	NA	NA	NA
1	Liquid	44900	43.5	40300	35.5	20400	19.7
2	Solid	41200	40	37500	33.1	23500	22.8
3	Solid	8580	8.3	21800	19.2	24100	23.3
4	Solid	2850	2.8	7000	6.2	17300	16.8
5	Solid	1850	1.8	2620	2.3	10800	10.4
6	Solid	1330	1.3	1880	1.7	6170	6.0
7	Solid	880	0.9	1460	1.3	2570	2.5
8	Solid	NA	NA	980	0.9	1150	1.0

(a) The maximum cesium capacity of U-Plant-2 simulant is 0.50 mole of cesium per mole of NiFeCN

Table 5.2. Intercalation of Cesium Solution with a 0.01:1 Cesium-to-Nickel Ferrocyanide Ratio into a Settled Column of U-Plant-2 Simulant [(a)]

Distance from Top of Column, cm	Layer	1 Day		2 Days		5 Days	
		Relative ^{137}Cs Concen.	Percent of Total Cesium	Relative ^{137}Cs Concen.	Percent of Total Cesium	Relative ^{137}Cs Concen.	Percent of Total Cesium
0	Liquid	9400	10.8	10700	10.1	2780	2.9
1	Liquid	44500	51.2	33600	31.7	10000	10.6
2	Solid	24100	27.7	24300	22.9	13500	14.3
3	Solid	4330	5.0	30200	28.5	50900	53.7
4	Solid	2130	2.4	3400	3.2	13800	14.5
5	Solid	1530	1.8	2200	2.1	2320	2.4
6	Solid	1000	1.1	1580	1.5	1470	1.5

(a) The maximum cesium capacity of U-Plant-2 simulant is 0.50 mole of cesium per mole of NiFeCN

Table 5.3. Intercalation of Cesium Solution with a 0.0033:1 Cesium-to-Nickel Ferrocyanide Ratio into a Settled Column of U-Plant-2 Simulant [(a)]

Distance from Top of Column, cm	Layer	1 Day		2 Days		5 Days	
		Relative ^{137}Cs Concen.	Percent of Total Cesium	Relative ^{137}Cs Concen.	Percent of Total Cesium	Relative ^{137}Cs Concen.	Percent of Total Cesium
0	Liquid	6590	6.8	4220	4.1	2050	2.1
1	Liquid	44000	45.6	30000	29.3	5700	5.8
2	Solid	32400	33.6	26200	25.6	10800	11.0
3	Solid	8090	8.4	34500	33.7	64000	65.2
4	Solid	2500	2.6	3640	3.6	11300	11.5
5	Solid	1670	1.7	2260	2.2	2600	2.7
6	Solid	1320	1.4	1680	1.6	1780	1.8

(a) The maximum cesium capacity of U-Plant-2 simulant is 0.50 mole of cesium per mole of NiFeCN

Table 5.4. Intercalation of Cesium Solution with a 080:1 Cesium-to-Nickel Ferrocyanide Ratio into a Settled Column of In-Farm-2 Simulant [(a)]

Distance from Top of Column, cm	Layer	1 Day		2 Days		5 Days	
		Relative ^{137}Cs Concen.	Percent of Total Cesium	Relative ^{137}Cs Concen.	Percent of Total Cesium	Relative ^{137}Cs Concen.	Percent of Total Cesium
0	Solid	42500	42.3	25700	24.2	13900	14.4
1	Solid	27800	27.6	34800	32.9	24300	25.1
2	Solid	23100	23.0	26900	25.4	22000	22.8
3	Solid	3680	3.7	11300	10.6	17900	18.5
4	Solid	2210	2.2	2760	2.6	11200	11.6
5	Solid	1200	1.2	1890	1.8	4750	4.9
6	Solid	NA	NA	1500	1.4	1520	1.6
7	Solid	NA	NA	1140	1.1	1100	1.1

(a) The maximum cesium capacity of In-Farm-2 simulant is 0.80 mole of cesium per mole of NiFeCN

Table 5.5. Intercalation of Cesium Solution with a 0.01:1 Cesium-to-Nickel Ferrocyanide Ratio into a Settled Column of In-Farm-2 Simulant [(a)]

Distance from Top of Column, cm	Layer	1 Day		2 Days		5 Days	
		Relative ^{137}Cs Concen.	Percent of Total Cesium	Relative ^{137}Cs Concen.	Percent of Total Cesium	Relative ^{137}Cs Concen.	Percent of Total Cesium
0	Solid	72200	73.9	46800	51.3	18600	20.0
1	Solid	16700	17.1	32800	36.0	62900	67.7
2	Solid	3340	3.4	4690	5.1	5290	5.7
3	Solid	2370	2.4	2710	3.0	2370	2.6
4	Solid	1810	1.8	1880	2.1	1650	1.8
5	Solid	1300	1.3	1360	1.5	1210	1.3
6	Solid	NA	NA	900	1.0	910	1.0

(a) The maximum cesium capacity of In-Farm-2 simulant is 0.80 mole of cesium per mole of NiFeCN

Table 5.6. Intercalation of Cesium Solution with a 0.0033:1 Cesium-to-Nickel Ferrocyanide Ratio into a Settled Column of In-Farm-2 Simulant [(a)]

Distance from Top of Column, cm	Layer	1 Day		2 Days		5 Days	
		Relative ^{137}Cs Concen.	Percent of Total Cesium	Relative ^{137}Cs Concen.	Percent of Total Cesium	Relative ^{137}Cs Concen.	Percent of Total Cesium
0	Solid	69100	60.3	31500	25.4	12500	10.5
1	Solid	32700	28.5	78500	63.3	92200	77.8
2	Solid	6190	5.4	6910	5.6	7180	6.1
3	Solid	2900	2.5	3300	2.7	2940	2.5
4	Solid	2090	1.8	2160	1.7	2120	1.8
5	Solid	1590	1.4	1600	1.3	1520	1.3

(a) The maximum cesium capacity of In-Farm-2 simulant is 0.80 mole of cesium per mole of NiFeCN

6.0 Conclusions

The experimental work for this task included the measurement of batch distribution coefficients for the ion exchange of cesium from solution using the solids isolated from the preparation of ferrocyanide tank waste simulants. Two tank waste simulants were used: U-Plant-2 and In-Farm-2. The maximum capacity of each simulant was also determined. In addition, several potential concentration mechanisms were examined to assess the potential for aggregation of the ^{137}Cs exchanged material to form "hot spots" in a tank. All experiments were performed at room temperature.

The alkaline waste treated by the ferrocyanide scavenging campaign had a variable concentration of sodium and cesium. Therefore, it was necessary to examine the effects of these concentrations on the batch distribution values. Several experiments were performed to cover a wide range of concentrations of cesium and sodium. The ranges selected cover the expected tank conditions, and values several orders of magnitude above and below the expected tank conditions and beyond the expected concentrations to more thoroughly examine the effect of these variables.

Two sets of batch distribution experiments were designed to examine the effects of cesium, sodium, and the cesium-to-nickel ferrocyanide ratio on the K_d values. The evaluation of the effect of the cesium-to-nickel ferrocyanide ratio indicated the effective capacity of nickel ferrocyanide to exchange cesium depended on the molar ratio of cesium to nickel ferrocyanide present. The measured K_d values for the $Na_2NiFe(CN)_6$ within the simulated waste, after conversion to the mass of sodium nickel ferrocyanide present within the waste solids, were consistent with literature results. The effects of sodium concentration and the sodium-to-cesium ratio were evaluated and indicated there was a slight but definitely measurable decrease in ion exchange capacity of the waste simulants as the concentration of sodium was increased. The batch capacity measurements indicated the maximum capacity of the U-Plant-2 simulant was 0.50 mole of cesium per mole of nickel ferrocyanide and the capacity of the In-Farm-2 simulant was 0.80 mole of cesium per mole of nickel ferrocyanide. Although these values do not approach the theoretical capacity of 2 mole of cesium per mole of nickel ferrocyanide, they do compare well with literature results.

The cesium scavenging campaign used sodium or potassium ferrocyanide and nickel sulfate by 1) adding each compound to the tank supernate, then directly adding this mixture into the waste tank; or 2) mixing the ferrocyanide and nickel salts together in the waste stream before pumping the stream to the tank farm. In either case there exists a potential for a layer of ^{137}Cs-enriched nickel ferrocyanide to form by the preferential settling of the ^{137}Cs-containing nickel ferrocyanide solids. A concentrated region of ^{137}Cs could form in several ways, depending upon the settling characteristics of the solids: 1) after exchange of cesium from solution, the cesium form of nickel ferrocyanide $[Na_{2-x}Cs_xNiFe(CN)_6]$ could settle at a different rate than the sodium form $[Na_2NiFe(CN)_6]$; or 2) after the exchange of cesium from solution, the cesium nickel ferrocyanide solid could settle out from the remaining solids present in the bulk of the waste (sodium salts). The latter concentration mechanism assumes a large proportion of the nickel ferrocyanide simulant exists as cesium nickel ferrocyanide.

The two settling concentration mechanisms were evaluated by permitting a homogeneous mixture of cesium and sodium nickel ferrocyanide to settle within a column and then measuring the concentration of the ^{137}Cs tracer using a gamma detector shielded with a collimated slit to permit the spatial

resolution of a radiocesium-enriched layer. The settling experiments were performed using 30%, 15% and 5% total simulant solids suspended in the simulant supernate. This allowed for the settling to occur at various rates. Examination of U-Plant-2 and In-Farm-2 simulants after several weeks of settling indicated no evidence of concentration of the ^{137}Cs tracer within the column.

In addition to the layering concentration mechanisms, it is possible that radiocesium could be selectively adsorbed into a layer of previously settled nickel ferrocyanide waste with the addition of cesium-enriched supernate to the waste tank following the initial processing of the ferrocyanide tanks. A concentrated region of ^{137}Cs-enriched nickel ferrocyanide could then be formed if the cesium did not evenly diffuse through the solids. This possibility was examined by allowing several columns of U-Plant-2 and In-Farm-2 simulants to settle for several weeks, then adding simulant supernate spiked with cesium. The ^{137}Cs concentration was then monitored using a gamma detector equipped with a collimated slit to allow the spatial resolution of the radiocesium tracer.

Several concentrations of cesium were analyzed to determine the extent of intercalation into the simulants. The intercalation experiments performed with both U-Plant-2 and In-Farm-2 simulants indicated that the cesium solution diffused readily through a bed of settled solids containing $Na_2NiFe(CN)_6$. When an excess of cesium was available (Cs:NiFeCN ratio of 0.80 or 0.50) the cesium quickly intercalated through the solids and dispersed. When only a slight amount of cesium was available, the cesium did not diffuse through an appreciable amount of the solids because all of the available cesium was bound by the nickel ferrocyanide present in the first several centimeters of the simulant.

The distribution coefficients and maximum capacity measurements indicated the U-Plant-2 and In-Farm-2 simulants were capable of exchanging significant amounts of cesium from solution even in the presence of extreme excesses of sodium. However, the layering and intercalation experiments indicated there is no discernable formation of localized concentrations of radioactive cesium resulting from the exchange of cesium from solution. Additionally, the intercalation experiments showed that when excess cesium is added to the solid waste simulant, it readily diffuses through the solids, even in a static environment.

7.0 References

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