**Ferrocyanide Safety Project
Interim Report FY 1994**

**Cesium Uptake Capacity of
Simulated Ferrocyanide Tank Waste**

I. E. Burgeson
S. A. Bryan
L. E. Burger

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Pacific Northwest Laboratory
Richland, Washington 99352

MASTER

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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 waste tanks, and to assess the potential for aggregation of these ^{137}Cs -exchanged materials to form tank "hot-spots." This research, performed at the Pacific Northwest Laboratory (PNL) for the Westinghouse Hanford Company (WHC), stems from concerns of possible localized radiolytic heating within the tanks. If radioactive cesium is exchanged and concentrated by the remaining nickel ferrocyanide present in the tanks, this heating could cause temperatures to rise above the safety limits specified for the ferrocyanide tanks.

For the purposes of this study, two simulants, In-Farm-2 and U-Plant-2, were chosen to represent the wastes generated by the scavenging processes. These simulants were formulated using protocols from the original cesium scavenging campaign. Later additions of cesium-rich wastes from various processes also were considered. The simulants were prepared and centrifuged to obtain a moist ferrocyanide sludge. The centrifuged sludges were treated with the original supernate spiked with a known amount of cesium nitrate. After analysis by flame atomic absorption spectrometry, distribution coefficients (K_d) were calculated.

The capacity of solid waste simulants to exchange radioactive cesium from solution was examined. Initial results showed that the greater the molar ratio of cesium to cesium nickel ferrocyanide, the less effective the exchange of cesium from solution. The theoretical capacity of 2 mol cesium per mol of nickel ferrocyanide was not observed. The maximum capacity under experimental conditions was 0.35 mol cesium per mol nickel ferrocyanide. Future work on this project will examine the layering tendency of the cesium nickel ferrocyanide species.

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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 wastes 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 $\text{Fe}(\text{CN})_6^{4-}$], were added to waste that was later routed to 20 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 have 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 wastes 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 270°C) or exposed to an electrical spark of sufficient energy to heat the mixture (Scheele et al. 1991). 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). 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 1993), 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 in FY 1994 were conducted to examine the capability of solid nickel ferrocyanides to exchange cesium from solution. The exchange capacity is 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 would allow the ^{137}Cs to become more concentrated and possibly lead to hotter regions within the tank. Because of the high concentration of sodium present in the tank waste simulants, the experiments were designed using ^{137}Cs tracer and gamma-counting equipment to measure cesium uptake.^(b)

(a) Operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

(b) Initially, all experiments were designed to be performed using ^{137}Cs tracer and gamma-counting equipment. However, because of the suspension of 325 building radiological activities in April 1994, all experiments were redesigned to be performed with cold cesium using flame atomic absorption spectroscopy (FAA).

2.0 Experimental

The experimental work covered in FY 1994 for the cesium uptake capacity subtask includes batch distribution and batch capacity measurements. In-Farm-2 and U-Plant-2 waste simulants were selected for use (Jeppson and Wong 1993). The In-Farm-2 simulant is representative of 11 intermediate ferrocyanide batches processed during the In-Farm scavenging campaign. The U-Plant-2 simulant represents the U-Plant sludge material with the greatest expected concentration of ferrocyanide. Approximately 66% of the total ferrocyanide used for scavenging waste at the Hanford Site was used to treat the U-Plant waste and approximately 26% was used to treat In-Farm waste. The remaining ferrocyanide (8%) was used to treat T-Plant waste (Jeppson and Wong 1993). Initially, all experiments were designed to be performed using ^{137}Cs tracer and gamma-counting equipment. However, because of the suspension of the 325 building radiological activities in April 1994, several experiments were redesigned and performed with cold cesium using flame atomic absorption spectroscopy (FAA).

2.1 Experimental Design

2.1.1 Batch Distribution Measurements

The batch distribution experiments were performed using 1 g of centrifuged solid waste simulant and 20 mL of simulant supernate spiked with appropriate levels of cesium nitrate. Samples were shaken on a maxi mixer or stirred on a magnetic stir plate for 1 day or longer to obtain equilibrium. After contact with the solid, the solutions were separated from the solid by centrifuge or syringe (0.45 μm or 30,000 MWC) filtration and prepared for analysis. Tracer studies were performed using 100 μL of ^{137}Cs stock which would result in 100,000 counts, using 4 mL of solution and a 5-minute counting time. Radioactive counting was performed using a Na(I) gamma detector. Cold analyses were performed on an Analyte 16 Flame Atomic Absorption Spectrophotometer after dilution with 2% HNO_3 and addition of potassium chloride as an ionization suppressant.

2.1.2 Batch Capacity Measurements

The batch capacity measurements were performed using 0.5 g of centrifuged solid simulant. The simulant was weighed into a vial and 0.5 to 5.0 mL of cesium spiked supernate was added in increments of 0.5 mL to each vial. These volume additions represented 1.5 to 15 column volumes of supernate. The samples were shaken on a maxi mixer for one day. After contact with the solid, the solutions were separated from the solid by decanting, centrifuge filtration, or syringe filtration and prepared for analysis. Cold analyses were performed on an Analyte 16 Flame Atomic Absorption Spectrophotometer after dilution with 2% HNO_3 and addition of potassium chloride as an ionization suppressant.

2.1.3 Determination of $\text{Na}_2\text{NiFe}(\text{CN})_6$ Content in Simulated Wastes Using Fourier Transform Infrared Spectroscopy (FTIR)

Cyanide FTIR Standards

Appropriate amounts of $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10 \text{H}_2\text{O}$ were dissolved with the addition of 25.0 g of dissolution reagent. The dissolution reagent consisted of 5% (w/v) EDTA and 5% (w/v) 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 (1.0 g) and 10.0 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- μ m 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 also were 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 0.9992. 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 $\text{Cs}_2\text{NiFe}(\text{CN})_6$ or $\text{NaCsNiFe}(\text{CN})_6$. The added cesium was one-twentieth of the total ferrocyanide; therefore, depending upon the form of the cesium nickel ferrocyanide ($\text{Cs}_2\text{NiFe}(\text{CN})_6$ or $\text{NaCsNiFe}(\text{CN})_6$) 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%), no correction was made to the sodium nickel ferrocyanide concentration.

Results of FTIR Determination of $\text{Na}_2\text{NiFe}(\text{CN})_6$ Content in Simulated Wastes

The analysis of the centrifuged simulant sludges 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 U-Plant-2 and In-Farm-2 simulants was measured to be 45 mg $\text{Na}_2\text{NiFe}(\text{CN})_6/\text{g}$ centrifuged sludge for both simulants. The solids isolation yielded a U-Plant-2 sludge with 64% solid content and an In-Farm-2 sludge with 58% solids. The In-Farm-2 simulant contained a small amount of cesium nitrate, indicating that either $\text{Cs}_2\text{NiFe}(\text{CN})_6$ or $\text{NaCsNiFe}(\text{CN})_6$ would exist in the sludge. The dissolution reagent used in this experiment will dissolve both the sodium and cesium form of nickel ferrocyanide (Bryan et al. 1993). Thus, the measured concentration of $\text{Na}_2\text{NiFe}(\text{CN})_6$ 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 $\text{Cs}_2\text{NiFe}(\text{CN})_6$ present; therefore, there was no basis for correction to the nickel ferrocyanide concentration.

2.1.4 Variables to be Considered for Cesium Uptake Capacity

The alkaline waste treated by the ferrocyanide scavenging campaign had a variable amount of sodium and cesium concentrations. Therefore, the effects of these concentrations on the batch

distribution values were examined. The 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. Three sets of experiments were designed to examine the effect of cesium, sodium, and sodium-to-cesium ratio on the exchange capabilities of nickel ferrocyanide solids.

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 mol cesium per mol nickel ferrocyanide and 3) out to 200 mol cesium per mol nickel ferrocyanide. 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 the full amount of cesium contained in the added solutions, assuming the liquid could intercalate through the solids. Therefore, both the batch capacity (which mimics column activity) and batch distribution (which measures the capacity of the exchanger) should be examined.

2.2 Preparation of Synthetic Wastes

U-Plant-2 and In-Farm-2 waste simulants were chosen to represent the ferrocyanide waste (Tables 2.1 and 2.2). U-Plant-2 simulant represents the high ferrocyanide concentration for the U-Plant scavenging process. The In-Farm-2 simulant represents the intermediate ferrocyanide concentration for the In-Farm scavenging process. These two simulants represent 92 % of the total ferrocyanide used in the ferrocyanide scavenging campaign. The simulants were prepared following the recipes developed through process knowledge (Jeppson and Wong 1993).

2.3 Batch Distribution (K_d)

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

Table 2.1. U-Plant-2 Simulant Waste Components

<u>Molecular Formula</u>	<u>Component</u>	<u>Concentration, M</u>
Na ₂ SO ₄	Sodium Sulfate	0.20
Na ₃ PO ₄	Sodium Phosphate	0.15
NaNO ₃	Sodium Nitrate	2.8
NaNO ₂	Sodium Nitrite	0.86
NH ₂ SO ₃ H	Sulfamic Acid	0.0034
Fe(NH ₄) ₂ (SO ₄) ₂	Ferrous Ammonium Sulfate	0.017
Na ₄ Fe(CN) ₆	Sodium Ferrocyanide	0.005
NiSO ₄	Nickel Sulfate	0.005

Table 2.2. In-Farm-2 Simulant Waste Components

<u>Molecular Formula</u>	<u>Component</u>	<u>Concentration, M</u>
Na ₂ SO ₄	Sodium Sulfate	0.17
Na ₃ PO 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 ₄ Fe(CN) ₆	Sodium Ferrocyanide	0.005
NiSO ₄	Nickel Sulfate	0.005

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:

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

where C_o = Initial concentration of cesium in solution
 C_f = Final concentration of cesium 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.

2.4 Batch Capacity

Batch capacity measurements were utilized to examine the capacity of nickel ferrocyanide solids to exchange cesium. Typically, batch capacity measurements are performed to simulate column exchange of solution through the exchanger. The same information can be obtained during column testing. A specific mass of exchanger is treated with increasing volumes of the solution containing the ion to be exchanged. The plot of C/C_o versus the number of column volumes is then used to evaluate the capacity of the exchanger. The value of C/C_o is a normalized measure of the ion concentration remaining in

solution where C is the final ion concentration and C_0 is the initial concentration in solution. During column experiments, the number of column volumes at a C/C_0 value of 0.50 can be an estimate of the total capacity of the ion exchanger for the ion of interest, depending upon the kinetics of the exchange reaction. If the kinetics are fast enough, the number of column volumes will equal the batch distribution value.

3.0 Results and Discussion

The objective of this research is to determine the capacity for ^{137}Cs uptake by ferrocyanide present in Hanford waste, and to assess the potential for aggregation of these ^{137}Cs -exchanged materials to form "hot spots." Batch distribution measurements were discussed in Section 2.3 and are also discussed in Section 3.1. Batch capacity measurements simulating solution column exchange using the simulated ferrocyanide waste as the ion exchange material is discussed in Section 3.2. Section 3.3 discusses the mechanisms for ^{137}Cs concentration in ferrocyanide waste by sedimentation and by intercalation.

3.1 Batch Distribution (K_d)

The distribution coefficients were measured for U-Plant-2 and In-Farm-2 centrifuged solid waste simulants. An initial experiment was performed in a simple matrix containing only sodium nitrate. The results of this experiment are shown in Table 3.1 and Figure 3.1.

Additional K_d experiments were performed using the supernate from each simulant by spiking the supernate with a known amount of cesium to obtain the desired cesium-to-nickel ferrocyanide ratio. The batch distribution measurements were performed to examine the effect of cesium concentration at a constant sodium concentration. The results are shown in Tables 3.2 and 3.3. The effect of sodium on the distribution coefficient was examined by maintaining a constant cesium concentration and varying the concentration of sodium; however, because the solutions contained radioactive cesium, the data cannot be obtained until radioactive work is permitted to resume in the 325 building.

Table 3.1. Effect of Cesium Concentration on the Cesium Distribution Coefficients for U-Plant-2 Simulant and Sodium Nitrate

<u>Molar Ratio of Cs to NiFeCN</u>	<u>K_d (mL solution/ g simulant)</u>	<u>K_d (mL solution/ g NiFeCN)</u>
1.98	6.5	310
0.97	6.8	320
0.50	9.6	460
0.24	32	1,500
0.10	280	13,400
0.05	1,400	66,400

Figure 3.1. Distribution Coefficients (K_d) Measurements for U-Plant-2 Ferrocyanide Waste Simulant

Table 3.2. Effect of Cesium Concentration on the Cesium Distribution Coefficients for U-Plant-2 Simulant at pH 9 with Constant Sodium-to-Cesium Ratio

Molar Ratio of Cs to NiFeCN	K_d (mL solution/g simulant)	K_d (mL solution/g NiFeCN)	Percent Cs Removal
193	2	30	4
9.6	1	20	3
1	5	100	10
0.095	60	1400	60
0.047	390	8800	90
0.01	3100	69000	99
0.0048	3800	83000	99
0.0024	8000	178000	100
0.0009	16000	356000	100

Table 3.3. Effect of Cesium Concentration on the Cesium Distribution Coefficients for In-Farm-2 Simulant at pH 9 with Constant Sodium-to-Cesium Ratio

Molar Ratio of Cs to NiFeCN	K_d (mL solution/g simulant)	K_d (mL solution/g NiFeCN)	Percent Cs Removal
25	0.3	8	1
2	10	200	20
1	30	800	50
0.48	100	2300	70
0.05	840	18700	96
0.005	980	21600	96
0.002	780	17200	95
0.001	3200	71300	96

The K_d values for U-Plant-2 simulated waste ($6.5 - 1.4 \times 10^3$) are lower than the literature values for pure $\text{Na}_2\text{NiFe}(\text{CN})_6$ ($6 \times 10^4 - 3 \times 10^6$) (Table 3.4). When the K_d values for the U-Plant-2 waste are based on the concentration of $\text{Na}_2\text{NiFe}(\text{CN})_6$ in the waste, the calculated K_d values increase ($3.1 \times 10^2 - 6.6 \times 10^4$) and are in agreement with the literature measurements for solutions with similar concentrations of ions. That the experimental K_d values are lower than literature can be explained by the cesium ion concentration in the U-Plant-2 simulant being higher than the cesium concentration in the literature studies (Campbell et al. 1991). The cesium concentration in the literature work was based on Oak Ridge National Laboratory (ORNL) low-level liquid waste, which has lower cesium activity than the ferrocyanide tank waste, as can be seen in Table 3.4.

Table 3.4. Summary of Experimental and Literature K_d Values for U-Plant-2 Simulated Ferrocyanide Waste and for Pure $\text{Na}_2\text{NiFe}(\text{CN})_6$

Material	K_d	Conditions
U-Plant-2	$6.5 \times 10^0 - 1.4 \times 10^3$	based on mass of U-Plant-2 simulant
U-Plant-2	$3.1 \times 10^2 - 6.6 \times 10^4$	based on mass of $\text{Na}_2\text{NiFe}(\text{CN})_6$ [Na] = 0.44 M [Cs] = $3.7 \times 10^{-3} - 7.5 \times 10^{-6}$ M [Cs]/[NiFe(CN) ₆] = 2.0 - 0.50
$\text{Na}_2\text{NiFe}(\text{CN})_6$	$6 \times 10^4 - 3 \times 10^6$	[Na] = 2- 4 M, K_d independent of [Na] ^(a) [K] = 1.0 - 0.25 M [Cs] = $1.0 \times 10^{-5} - 2.5 \times 10^{-7}$ M [Cs]/[NiFe(CN) ₆] = $3.1 \times 10^{-1} - 7.9 \times 10^{-4}$

(a) DO Campbell et al. (1991).

The significance of K_d is that this value can be related to the total volume of solution for which the ion of interest can be completely removed. These data can be directly related to batch capacity measurements. The K_d value is a good predictive tool for the number of batch volumes (or column volumes in related column tests) that will pass through the ion exchange material before the equilibrium concentration of the exchanged ion remaining in solution (C) is equal to 50% of the initial concentration of that ion added to the batch test (i.e., $C/C_0 = 0.5$). The number of batch (column) volumes required to achieve breakthrough at $C/C_0 = 0.5$ is the practical measure of the total capacity of the ion exchange material.

Batch capacity tests were performed using U-Plant-2 material as the ion exchange material and the same sodium and cesium concentrations as in the K_d measurements described previously. These experiments are described in Section 3.2.

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 (Figure 3.1). In the initial scavenging campaign, the mol 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 are quite large, and cesium was readily removed from solution. However, when the ratio of cesium to nickel ferrocyanide was increased through to 2 and beyond, the K_d values were significantly decreased (see Table 3.2 and 3.3). The difference between the U-Plant-2 and In-Farm-2 results could be caused by slower exchange, thus the solutions may not have been at equilibrium. Further experiments need to be performed to confirm the magnitude of difference for cesium ion exchange using the two centrifuged waste solids.

3.2 Batch Capacity

Batch capacity measurements were utilized to examine the exchange capacity of nickel ferrocyanide solids for cesium. The batch capacity experiment was designed to have the same conditions as the second K_d value reported in Table 3.1. A plot of C/C_0 versus the number of column volumes is used to evaluate the capacity of an exchanger, in this case a nickel ferrocyanide complex. The C/C_0 ratio is a measure of the amount of cesium retained on the exchanger. When the C/C_0 ratio is 0.50, the corresponding number of column volumes should equal the batch distribution coefficient. Thus the batch capacity experiments should corroborate the batch distribution results. Figure 3.2 shows a batch capacity experiment and the expected batch distribution coefficient; the two experiments corroborate one another extremely well.

The batch capacity also provides information about the total capacity of the exchanger under the specific conditions of the experiment. The simple theoretical cesium capacity of a ferrocyanide solid is 2 mol cesium/mol ferrocyanide. This capacity is an upper limit for ion exchange and is rarely realized in practice (Haas 1993). The reported maximum capacity for cesium exchange onto nickel ferrocyanide ranges from 0.35 to 1.9 mol cesium per mol nickel ferrocyanide (Loos-Neskovich and Federoff 1989). The maximum observed capacity of nickel ferrocyanide for cesium for these experiments was 0.35 mol cesium per mol nickel ferrocyanide. This value is within the range reported in the literature.

Figure 3.2. Batch Loading Capacity Measurements for U-Plant-2 Ferrocyanide Waste Simulant

3.3 Concentration Mechanisms for ^{137}Cs in Ferrocyanide Waste

Waste treated for cesium removal by the addition of ferrocyanide was handled generally by mixing a soluble ferrocyanide and then nickel sulfate with tank supernate followed by the direct addition of this mixture into the waste tank (In-Farm flowsheet), or by mixing the ferrocyanide and nickel salts together in the waste streams prior to pumping to the tank farm (U-Plant flowsheet). In either case there exists a potential for a layer of ^{137}Cs -enriched nickel ferrocyanide to form from the preferential settling of this compound from the bulk of the waste material. 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.

The following experiments have been planned to address these concerns.^(a)

(a) These experiments were originally proposed for the FY 1994 work scope but have been delayed into FY 1995 by the administrative hold on radiological work within the 325 building.

3.3.1 Formation for Concentrating ^{137}Cs by Layering During Sedimentation

Settling experiments using ferrocyanide flowsheet simulant wastes containing cesium would enable the detection of cesium concentration by preferential layering. This experiment is designed to demonstrate whether a tendency exists for the cesium-rich layer to preferentially form by sedimentation processes.

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 $1\ \mu$ 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 solids loadings. An expression for sedimentation velocities has been given by:

$$v = (P_s - P_l) g d^2 (1 - \phi_s)^{4.5} / (18 \eta) \quad (2)$$

where P_s and P_l are the densities of the solid and liquid phases, respectively; g is the acceleration from gravity; d is the particle diameter; ϕ_s is the volume fraction; and η is the viscosity of the liquid phase. Equation (2) is applicable for solids loadings $\phi_s < 0.10$. For solids loadings $\phi_s > 0.10$, convection cells may develop where descending columns with high solids loadings are adjacent to ascending columns of clarified liquids. At very high solids loadings, such as exists in ferrocyanide 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. Although Equation (2) cannot be used quantitatively to describe settling rates in tank waste slurries, it is useful in predicting qualitative trends. Models to quantitatively describe settling rates in slurries with very high solids loadings have not been developed yet.

The settling of ^{137}Cs -enriched nickel ferrocyanides will be determined by mixing ^{137}Cs -spiked supernate with solid waste simulant within a column. The liquid and solid material will be shaken and the ^{137}Cs will be located as the material settles. The concentration of ^{137}Cs will be measured spatially down the length of the centrifuge tube by placing a gamma detector beside the container with appropriate collimated slits to allow for the spatial resolution of a radiocesium-enriched layer. A schematic of the system to be used is depicted in Figure 3.3. Simulated ferrocyanide waste is added to column after being spiked with ^{137}Cs . Similar collimated detection systems have been employed for the detection of gamma emitters adsorbed on chromatography columns (Burger and Scheele 1982).

3.3.2 Mechanism for Concentrating ^{137}Cs by Intercalation Following Ferrocyanide Sedimentation

The potential exists for a layer of radiocesium-enriched nickel ferrocyanide to form from the selective adsorption of ^{137}Cs into a layer of previously settled nickel ferrocyanide waste by the addition of cesium-enriched supernate to the waste tank at a later time. By adding a radiocesium spike to the

Figure 3.3. Design Schematic of Counting Equipment for Measuring ^{137}Cs Layering by Settling within a Column

supernate of a ferrocyanide waste simulant previously allowed to settle (and compacted by centrifugation), it will be demonstrated whether a mechanism exists for the formation of a concentrated layer of radiocesium from the preferential adsorption of ^{137}Cs at the interface of a supernate-solid boundary.

Experiments allowing radiocesium to intercalate from the supernate into a compacted solid ferrocyanide waste would reveal the difference between the cesium (a) concentrating at the interface of the layers and (b) being dispersed throughout the ferrocyanide waste by migrating throughout the solid layer. This experiment is designed to demonstrate whether or not a mechanism exists for a cesium-rich supernate layer added to a previously settled and compacted solid layer of ferrocyanide-containing waste to form a concentrated ^{137}Cs layer at the interface.

The concentration of ^{137}Cs will be measured spatially down the length of the centrifuge tube periodically by placing a gamma detector beside the container with appropriate collimated slits to allow for the detection of the formation of a radiocesium-enriched layer. A diagram depicting this system is shown in Figure 3.4. The ^{137}Cs -spiked supernate is added to top of column. The ^{137}Cs front is monitored by the movable gamma detector as it migrates into simulated ferrocyanide waste.

Figure 3.4. Schematic Diagram of Counting Equipment for Measuring ^{137}Cs Migration Through Simulated Ferrocyanide Waste by Intercalation

4.0 Status of Cesium Uptake Capacity

The experimental work covered in FY 1994 for the cesium uptake capacity subtask included batch distribution and batch capacity measurements. Initially, all experiments were designed to be performed using ^{137}Cs tracer and gamma-counting equipment. However, because of the suspension of the 325 building radiological activities in April 1994, the K_d experiments were redesigned and performed with cold cesium using FAA.

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

Three sets of experiments were designed examining the effect of cesium and sodium, and the cesium-to-nickel ferrocyanide ratio on the K_d values. The evaluation of the effect of cesium-to-nickel ferrocyanide ratio has been performed. The effective capacity of nickel ferrocyanide to exchange cesium depends on the molar ratio of cesium to nickel ferrocyanide. The measured K_d values for the simulated wastes were consistent with other researchers' results. However, further experiments need to be performed to confirm the magnitude of difference for cesium ion exchange between U-Plant-2 and In-Farm-2 waste simulants.

The effect of sodium concentration and the sodium-to-cesium ratio will be evaluated in future experiments. The experiments will be performed as follows: 1) The effect of sodium concentration on the K_d values will be examined by varying the sodium concentration while maintaining a constant cesium concentration. The sodium-to-cesium ratio will be varied as in the previous experiments, and the cesium-to-nickel ferrocyanide ratio will be 0.0025 (scavenging campaign ratio) and 1 (an upper limit based on reported maximum cesium capacity of nickel ferrocyanides). 2) The effect of cesium concentration on the K_d values will be examined while maintaining a constant sodium concentration. The cesium concentration will be varied as in the sodium experiment, and the cesium-to-nickel ferrocyanide ratio will vary as in previous experiments.

The potential concentration mechanisms for ^{137}Cs also will be evaluated. The cesium scavenging campaign utilized ferrocyanide and nickel sulfate by 1) adding each to the tank supernate followed by the direct addition of this mixture into the waste tank or 2) mixing the ferrocyanide and nickel salts together in the waste streams prior to pumping to the tank farm. In either case there exists a potential for a layer of ^{137}Cs -enriched nickel ferrocyanide to form from the preferential settling of this compound from the bulk of the waste material. Moreover, 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.

The settling of ^{137}Cs -enriched nickel ferrocyanides will be determined by mixing ^{137}Cs -spiked supernate with solid waste simulant within a column. The liquid and solid material will be shaken and

the ^{137}Cs will be located as the material settles. The concentration of ^{137}Cs will be measured spatially down the length of the centrifuge tube using a gamma detector with appropriate collimated slits to allow for the spatial resolution of a radiocesium-enriched layer.

The examination of ^{137}Cs intercalation will be performed after sedimentation by adding ^{137}Cs -spiked supernate to the top of a settled column of simulated waste. The ^{137}Cs front will be monitored using a gamma detector with collimated slits as it migrates into the simulated ferrocyanide waste. The concentration of ^{137}Cs will be measured spatially down the length of a centrifuge tube to detect any formation of a radiocesium-enriched layer. This experiment is designed to demonstrate whether a mechanism exists for a cesium-rich supernate layer added to a previously settled and compacted ferrocyanide sludge layer to form a concentrated ^{137}Cs layer at the sludge/supernate interface.

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