**Ferrocyanide Safety Project
Task 3 Ferrocyanide Aging Studies
FY 1993 Annual Report**

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Summary

The Hanford Ferrocyanide Task Team is addressing issues involving ferrocyanide precipitates in single-shell waste storage tanks (SSTs), in particular the storage of waste in a safe manner. This Task Team, composed of researchers from Westinghouse Hanford Company (WHC), Pacific Northwest Laboratory (PNL), and outside consultants, was formed in response to the need for an updated analysis of safety questions about the Hanford ferrocyanide tanks.

The Ferrocyanide Safety Project at PNL is part of the Waste Tank Safety Program led by WHC. The overall purpose of the WHC program, sponsored by the U.S. Department of Energy's Tank Farm Project Office, is to 1) maintain the ferrocyanide tanks with minimal risk of an accident, 2) select one or more strategies to assure safe storage, and 3) close out the unreviewed safety question (USQ).

This annual report gives the results of the work conducted by PNL in FY 1993 on Task 3, Ferrocyanide Aging Studies, which deals with the aging behavior of simulated ferrocyanide wastes. Aging processes include the dissolution and hydrolysis of nickel ferrocyanides in high pH aqueous solutions. Investigated were the effects of pH variation; ionic strength and sodium ion concentration; the presence of anions such as phosphate, carbonate, and nitrate; temperature; and gamma radiation on solubility of ferrocyanide materials including In-Farm-1A, Rev. 4 flowsheet-prepared $\text{Na}_2\text{NiFe}(\text{CN})_6$.

Vendor-prepared $\text{Na}_2\text{NiFe}(\text{CN})_6$ dissolves in aqueous base to give primarily insoluble $\text{Ni}(\text{OH})_2$ and soluble $\text{Na}_4\text{Fe}(\text{CN})_6$. The rate of dissolution of $\text{Na}_2\text{NiFe}(\text{CN})_6$ in aqueous base increases with increasing pH. At pH 14, 95% dissolution is observed after 0.5 h. Addition of sodium ion in the form of Na_2SO_4 or NaNO_3 suppresses dissolution at pH 13. However, 1 M Na^+ in the form of Na_2CO_3 , Na_3PO_4 , or SST simulant salts (mixed sodium salts of phosphate, carbonate, nitrate, nitrite, sulfate, and hydroxide) results in an enhancement of the rate of solubilization. At pH 14 these effects are not seen, dissolution being rapid even in the presence of 4 M sodium ion. The rate of dissolution is influenced most by base concentration.

Cesium nickel ferrocyanide is not easily dissolved. A material containing a $\text{Cs}_2\text{NiFe}(\text{CN})_6$ phase (2.3 moles Cs/moles ferrocyanide) was found to be insoluble in up to 4 M NaOH after stirring for 144 h. In-Farm-1A, Rev. 4 (IF-1A), containing 4.51×10^{-2} moles Cs/mole ferrocyanide, dissolved more slowly than the vendor material under identical conditions at both pH 13 and pH 14. The inhibition of IF-1A dissolution may be due to concentration of an insoluble (or less soluble) $\text{Cs}_2\text{NiFe}(\text{CN})_6$ phase at the particle surface as $\text{Na}_2\text{NiFe}(\text{CN})_6$ dissolves.

Studies of the hydrolysis of IF-1A in 4 M NaOH at 90°C were initiated. Experiments were conducted in the gamma pit with identical controls outside the gamma field. Gamma promotes ferrocyanide hydrolysis. Over 42% of the cyanide ions were hydrolyzed in the radiation field

compared with 4.8% in the control. Similar experiments at pH 10 and 60°C indicated IF-1A was insoluble outside of the gamma pit and only very slightly soluble when irradiated. Only a trace of hydrolysis products was detected in the irradiated pH 10 solution.

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Abbreviations

AA	atomic absorption spectroscopy
DOE	U.S. Department of Energy
EDS	energy dispersive spectroscopy
EDTA	ethylenediamine tetraacetic acid
EIS	Environmental Impact Statement
ESEM	environmental scanning electron microscopy
FECN-14	PNL-prepared cesium nickel ferrocyanide material
FTIR	Fourier transform infrared spectroscopy
GAO	General Accounting Office
IC	ion chromatography
IF-1A	In-Farm-1A, Rev. 4, WHC-prepared flowsheet ferrocyanide material
PNL	Pacific Northwest Laboratory
SST	single-shell storage tank at Hanford
TBP	tributyl phosphate
USQ	unreviewed safety question
WHC	Westinghouse Hanford Company
XRD	x-ray diffraction spectroscopy

1.0 Introduction

The research performed for this project 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 (Burger 1984; Burger and Scheele 1988, 1991; Scheele et al. 1991). The Environmental Impact Statement (EIS) for the SSTs, **Disposal of Hanford Defense High-Level, Transuranic and Tank Wastes** (DOE 1987), projected a worst case exposure scenario for an explosion in a ferrocyanide tank to be a short-term radiation dose of 200 mrem to the public. The worst case exposure scenario estimated in a later study by the General Accounting Office (GAO) (Peach 1990) was 1 to 2 orders of magnitude larger than the 1987 EIS. A special Hanford Ferrocyanide Task Team was commissioned in September 1990 to address all technical aspects involving SSTs containing ferrocyanide wastes. In October 1990, Secretary of Energy James D. Watkins announced a Supplemental EIS would be prepared that would contain an updated analysis of the safety questions for the Hanford SSTs (DOE 1990).

The Hanford Ferrocyanide Task Team is composed of technical experts from Westinghouse Hanford Company (WHC), Pacific Northwest Laboratory (PNL)^(a), and outside consultants. The Ferrocyanide Task Team reports to the DOE Richland Operations Office, Tank Farm Project Office, through the Ferrocyanide Safety Program function within WHC. WHC has primary program responsibility for work performed by PNL.

The work described in this topical report was performed in FY 1993 as part of the Ferrocyanide Tank Safety Project, Task 3 - Ferrocyanide Aging Studies, and deals with the aging behavior of simulated ferrocyanide tank wastes. The work is a continuation of FY 1992 studies reported previously (Lilga et al. 1992). This report is divided into two activities:

1. Dissolution Studies
2. Hydrolysis Studies.

The report also includes a background section, conclusions from the FY 1993 work, and a discussion of future work.

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2.0 Background

Radioactive waste resulting from the production of defense nuclear materials has been stored in underground storage tanks at the Hanford Site since the early 1940s. During this time, new technologies were developed, and waste was transferred among tanks to separate different types of waste and to reduce the need for additional tanks. For example, during the 1950s, additional storage volume was required to accommodate the accumulation of high- and low-level radioactive waste while minimizing the construction of additional storage tanks. As a result, Hanford scientists developed a technology to scavenge radiocesium from either process wastes or waste liquids already stored in the SSTs. This process involved the carrier-precipitation of cesium nickel ferrocyanide by addition of sodium ferrocyanide and nickel sulfate. The decontaminated supernate was then pumped to a crib. While providing more storage volume within the tanks, this process added large quantities of ferrocyanide (about 145 metric tons) to the SSTs.

There were three flowsheets used to scavenge the radiocesium from aqueous wastes. The first was used to treat first-cycle waste from the bismuth phosphate process (T-Plant Flowsheet). This generated about 10% of the total ferrocyanide waste. The second, the U-Plant Flowsheet, treated "metal waste" dissolved in nitric acid after the uranium had been recovered using the tributyl phosphate (TBP) process. The U-Plant Flowsheet produced about 70% of the total ferrocyanide wastes. The third process, the In-Farm Flowsheet, treated the basic "metal waste" for recovery of uranium. This process produced the remaining 20% of the total ferrocyanide waste.

T-Plant and U-Plant Flowsheet-treated waste contained substantial metal concentrations that precipitated when neutralized with sodium hydroxide. The ferrocyanide was thereby diluted, assuming that the solids-settling behaviors of the metals and ferrocyanides were approximately the same. It is anticipated that the T-Plant and U-Plant Flowsheets would have a significantly lower concentration of ferrocyanide than In-Farm Flowsheet waste.

As part of subsequent waste management operations, aluminum decladding waste or double-shell slurry from the concentration of reprocessing wastes was added to tanks containing bedded ferrocyanide (Anderson 1990). These solutions were generally quite alkaline with NaOH concentrations approximately 1 M.

Of the 177 waste storage tanks on the Site, 149 are SSTs. Records at Hanford show 18 SSTs contain at least 200 kg (1000 g-mol) of ferrocyanide precipitates. The ferrocyanide content of the individual tanks ranges from 200 kg up to possibly 16,600 kg (in Tank BY-104) calculated as the $\text{Fe}(\text{CN})_6^{4-}$ anion (Borsheim and Simpson 1991). Other wastes in these tanks probably include significant quantities of sodium nitrate, sodium nitrite, silicates, aluminates, hydroxides, phosphates, sulfates, carbonates, uranium, copper, and calcium in addition to the fission products present from the processing of irradiated fuel.

Ferrocyanide by itself is a stable complex of ferrous ion and cyanide that is considered nontoxic because it does not readily dissociate in aqueous solutions. However, in the laboratory, in the presence of oxidizing materials such as nitrates and/or nitrites, dry ferrocyanide can be made to explode by heating to temperatures above 280°C or by an electrical spark of sufficient energy (Burger and

Scheele 1991). The explosive nature of ferrocyanide in the presence of an oxidizer has been known for decades, but the conditions under which the compound can undergo an uncontrolled exothermic reaction have not been thoroughly studied. Explosion propagation properties for large quantities of the material are unknown, and the effects of moisture content and other diluents (or possible catalysts or initiators) that may be present in the tanks are currently being studied. Because the scavenging process involved the precipitation of ferrocyanide from solutions containing nitrates and nitrites, it is likely that an intimate mixture of ferrocyanides and nitrates/nitrites exists in parts of some of the SSTs.

The ultimate goal of the Aging Studies task is to understand the long-term behavior of ferrocyanide tank wastes in the SST environments. This report characterizes the dissolution and hydrolysis of ferrocyanide waste simulants in aqueous base under a variety of conditions. A possible mechanism for delivery of caustic to bedded ferrocyanide layers is the topic of a recent model prepared in a parallel task (McGrail et al. 1993). This work provides baseline data that will be useful as actual SST samples are obtained and analyzed. These results will directly assist in determining 1) which one or more strategies will assure safe storage and 2) how to close out the unreviewed safety question (USQ) and resolve the safety issue.

3.0 Work Accomplished

The work conducted in FY 1993 for Task 3, Ferrocyanide Aging Studies, is discussed below. Aging is defined as any process that may have altered the chemical nature of the ferrocyanide waste. Primary aging routes investigated are dissolution of alkali metal nickel ferrocyanides, shown in Eq. (1) for the sodium compound, and hydrolysis of ferrocyanide ion, shown in Eq. (2) (Robuck and Luthy 1989).

3.1 Dissolution Studies

Dissolution studies in FY 1993 were conducted on three ferrocyanide-containing materials. Studies of the vendor material, with approximate composition $\text{Na}_2\text{NiFe(CN)}_6 \cdot \text{Na}_2\text{SO}_4 \cdot 4.5 \text{H}_2\text{O}$, were continued from FY 1992 work. In addition, two cesium-containing ferrocyanide materials, PNL-prepared $\text{Cs}_2\text{NiFe(CN)}_6$ (FECN-14) and the Westinghouse-prepared flowsheet material In-Farm-1A, Rev. 4 (IF-1A), were investigated. Table 3.1 shows the compositions of these materials as determined by atomic absorption (AA) and Fourier transform infrared (FTIR) spectroscopy analyses of samples dissolved in ethylenediamine/ethylenediamine tetraacetic acid (EDTA).

3.1.1 Solubility of Vendor-Prepared Ferrocyanide Material

Studies of vendor material solubility, conducted in FY 1993 for Task 3, Ferrocyanide Aging Studies, are continued from FY 1992 work previously reported (Lilga et al. 1992; Babad et al. 1993). In a typical experiment, 1 g of the vendor material was stirred in 50 mL of aqueous base for 144 h.

Table 3.1. Moles of Analyte/Gram Ferrocyanide Material Used in Dissolution and Hydrolysis Experiments. Analyses of Cs, Fe, Ni, and Na by AA; Fe(CN)_6^{4-} by FTIR.

Analyte	moles/g Vendor	moles/g FECN-14	moles/g IF-1A
Cs	--	3.06×10^{-3}	2.96×10^{-5}
Fe	1.93×10^{-3}	1.33×10^{-3}	6.56×10^{-4}
Ni	2.00×10^{-3}	1.51×10^{-3}	1.00×10^{-3}
Na	7.36×10^{-3}	3.35×10^{-4}	1.02×10^{-2}
Fe(CN)_6^{4-}	1.86×10^{-3}	1.30×10^{-3}	7.13×10^{-4}

Solution samples were periodically taken and analyzed for iron (ferrocyanide anion) by AA. The reaction products were identified with use of FTIR, powder X-ray diffraction (XRD), and energy dispersive spectroscopies (EDS) combined with environmental scanning electron microscopy (ESEM).

In FY 1992 work, it was demonstrated that the vendor-prepared ferrocyanide material reacts with NaOH to form insoluble $\text{Ni}(\text{OH})_2$ and soluble $\text{Na}_4\text{Fe}(\text{CN})_6$ according to Eq. (1). The rate of dissolution of $\text{Na}_2\text{NiFe}(\text{CN})_6$ in aqueous base was found to increase with increasing pH. At pH 14, 95% dissolution was observed after 0.5 h. Addition of 1 M Na^+ ions in the form of Na_2SO_4 suppressed dissolution at pH 13. However, 1 M Na^+ in the form of a mixture of salts (NaNO_3 , 80.47 wt%; NaNO_2 , 4.37 wt%; Na_2CO_3 , 1.52 wt%; NaOH , 3.12 wt%; Na_2SO_4 , 1.48 wt%; Na_3PO_4 , 9.04 wt%), simulating the composition of a typical SST, resulted in an enhancement of the rate of dissolution. The enhancement may arise from buffering of the solution by phosphate since the pH of the solution was nearly unchanged at the end of the experiment. Even when the solution was not stirred, dissolution was relatively rapid. Approximately 40% of the $\text{Na}_2\text{NiFe}(\text{CN})_6$ dissolved in 24 h and 90% after 140 h in an unstirred pH 13 solution containing SST salts.

In FY 1993, sodium ion dependence was further investigated. At pH 13, addition of sodium nitrate suppresses dissolution; increasing sodium concentration results in decreasing rates of reaction (Figure 3.1). Although ionic strength also increases with concentration, the effect is most likely attributed to sodium ion concentration (activity). For example, at 1 M Na^+ , Na_2SO_4 results in a dissolution rate faster than NaNO_3 , even though its ionic strength is greater than that of the nitrate solution. The sodium activity is lower in the presence of doubly charged sulfate, leading to relatively higher rates.

Carbonate and phosphate anions promote dissolution at pH 13. Figure 3.2 illustrates the enhanced rates when 1 M Na^+ is present as Na_2CO_3 , Na_3PO_4 , or as SST simulant salts. Atomic absorption data indicate that the carbonate dissolution follows closely the phosphate dissolution, but analysis of the reaction products indicates otherwise. From FTIR analysis, the insoluble fraction at the end of the phosphate dissolution is not the starting material but, rather, a re-precipitated iron-cyanide of unknown composition. From AA measurements, the re-precipitated material represents about 6% of the iron introduced. However, the remaining insoluble ferrocyanide fraction in the carbonate dissolution is primarily the expected unreacted vendor ferrocyanide containing only a small quantity of the re-precipitated material. Dissolution according to Eq. (1) is apparently more rapid in phosphate than in carbonate media, but the precipitation reaction gives the appearance, in plots of soluble iron as a function of time, that the rates are similar. The insoluble material from the SST simulant salt-containing experiment also showed a small amount of re-precipitated iron-cyanides.

The accelerated rate in the SST simulant salt-containing solutions was originally thought to arise from phosphate buffering since the pH (glass electrode) dropped only 0.1 unit, from 13.0 to 12.9 (Lilga et al. 1992). However, independent experiments containing only carbonate or phosphate showed pH drops of about 0.6 units in each case, not consistent with the buffering hypothesis (Table 3.2). This pH drop is consistent with the use of two equivalents of hydroxide for each equivalent of ferrocyanide dissolved, as expected from Eq. (1) (see below). Precipitation of the highly insoluble nickel phosphate might be expected to increase the rate of dissolution; however, its presence has not yet been verified. Absorption bands possibly arising from phosphate appear in FTIR spectra

Figure 3.1. Solubility of Vendor Material at pH 13 as a Function of Sodium Ion Concentration

Figure 3.2. Solubility of Vendor Material at pH 13 and 1 M Na⁺ in the Presence of Carbonate and Phosphate

Table 3.2. Vendor Material Dissolution Data

Solution Composition	pH12	pH13	pH14	1 M Na ⁺ as Na ₂ SO ₄ *	1 M Na ⁺ as Na ₂ CO ₃	1 M Na ⁺ as NaNO ₃		
Dissolution Time	144h	144h	144h	144h	144h	73h	95h	148h
% vendor dissolved	8.99	84.44	95.46	65.7	94.25	50.48	52.90	55.31
moles vendor dissolved	1.66E-4	1.56E-3	1.77E-3	1.22E-3	1.75E-3	9.35E-4	9.80E-4	1.02E-3
measured starting pH	12	12.9	14	12.9	12.95	12.9	12.9	12.9
starting moles NaOH	5.00E-4	3.97E-3	5.00E-2	3.97E-3	4.46E-3	3.97E-3	3.97E-3	3.97E-3
measured final pH	11.6	12.4	13.4	12.4	12.33	12.48	12.47	12.21
final moles NaOH	1.99E-4	1.26E-3	1.26E-2	1.26E-3	1.07E-3	1.51E-3	1.48E-3	8.11E-4
moles OH used	3.01E-4	2.72E-3	3.74E-2	2.72E-3	3.39E-3	2.46E-3	2.50E-3	3.16E-3
moles OH/ moles FeCN	1.81	1.74	21.17	2.23	1.94	2.63	2.55	3.08

Solution Composition	4 M Na ⁺ as NaNO ₃				6 M Na ⁺ as NaNO ₃		1 M Na ⁺ as Na ₃ PO ₄			
Dissolution Time	8h	26.5h	53h	122h	120h	144h	7h	73h	95h	148h
% vendor dissolved	25.51	31.35	37.20	44.20	36.71	37.92	78.36	86.38	91.26	93.67
moles vendor dissolved	4.73E-4	5.81E-4	6.89E-4	8.19E-4	6.80E-4	7.03E-4	1.45E-3	1.60E-3	1.69E-3	1.74E-3
measured starting pH	12.8	12.8	12.8	12.8	12.7	12.7	13	13	13	13
starting moles NaOH	3.15E-3	3.15E-3	3.15E-3	3.15E-3	2.51E-3	2.51E-3	5.00E-3	5.00E-3	5.00E-3	5.00E-3
measured final pH	12.3	12.37	12.32	12.2	11.87	11.5	12.9	12.65	12.6	12.4
final moles NaOH	9.98E-4	1.17E-3	1.04E-3	7.92E-4	3.71E-4	1.58E-4	3.97E-3	2.23E-3	1.99E-3	1.26E-3
moles OH used	2.16E-3	1.98E-3	2.11E-3	2.36E-3	2.14E-3	2.35E-3	1.03E-3	2.77E-3	3.01E-3	3.74E-3
moles OH/ moles FeCN	4.56	3.41	3.06	2.88	3.14	3.34	0.71	1.73	1.78	2.16

Table 3.2. (contd)

Solution Composition	0.1g Vendor Material, 1 M Na ⁺ as NaNO ₃					0.25g Vendor Material, 1 M Na ⁺ as NaNO ₃			
Dissolution Time	7h	24h	48h	72h	144h	8h	26.5h	53h	122h
% vendor dissolved	86.96	91.79	94.69	99.52	99.52	68.79	81.93	89.47	87.54
moles vendor dissolved	1.61E-4	1.70E-4	1.75E-4	1.84E-4	1.84E-4	3.19E-4	3.79E-4	4.14E-4	4.05E-4
measured starting pH	12.9	12.9	12.9	12.9	12.9	12.9	12.9	12.9	12.9
starting moles NaOH	3.97E-3	3.97E-3	3.97E-3	3.97E-3	3.97E-3	3.97E-3	3.97E-3	3.97E-3	3.97E-3
measured final pH	12.53	12.63	12.72	12.52	12.42	12.49	12.54	12.5	12.42
final moles NaOH	1.69E-3	2.13E-3	2.62E-3	1.66E-3	1.32E-3	1.55E-3	1.73E-3	1.58E-3	1.32E-3
moles OH used	2.28E-3	1.84E-3	1.35E-3	2.32E-3	2.66E-3	2.43E-3	2.24E-3	2.39E-3	2.66E-3
moles OH/ moles FeCN	14.14	10.81	7.68	12.56	14.41	7.62	5.90	5.77	6.55

* Sufficient amount of compound added to NaOH to yield [Na⁺] shown.

of the insoluble solids, but assignment to a nickel phosphate phase has not been possible. Powder XRD spectra for independently prepared nickel phosphate show this material to be amorphous, rendering XRD detection impossible. Nickel hydroxide has been positively identified in the insoluble solids by FTIR and XRD.

The influence of sodium ion concentration and the presence of various anions is minimal in pH 14 solution. Figure 3.3 compares data from experiments at pH 14 with 1 M Na⁺, as sodium hydroxide; 4 M Na⁺, adjusted with sodium nitrate; and 2 M Na⁺, adjusted with sodium carbonate. Unlike the pH 13 results, no effect is seen. Dissolution is over 90% complete within 1 h in each solution. These results indicate that dissolution is more sensitive to hydroxide ion concentration than to sodium ion concentration.

The dependence of the rate of dissolution on initial quantity of vendor material present was investigated at pH 13. Results of experiments using 1.0 g, 0.25 g, and 0.1 g vendor material each in 50 mL of a pH 13 solution containing 1 M Na⁺ adjusted with NaNO₃ are shown in Figure 3.4. Normalized to a weight percent dissolved basis, more rapid dissolution is observed when less ferrocyanide is present or, in other words, when the hydroxide ion to ferrocyanide ion molar ratio is high. Figure 3.5 shows the same pH 13 data for the first 12 h of reaction compared with a pH 14 dissolution experiment. At a hydroxide ion to ferrocyanide ion molar ratio of 27.0, the pH 14 dissolution is observed to be much more rapid than in pH 13 solution. Although the hydroxide ion to ferrocyanide ion molar ratio determines the rate at pH 13, the overall hydroxide concentration is still the major factor influencing the rate of dissolution.

Figure 3.3. Dissolution of Vendor Material in pH 14 Solutions

Figure 3.4. Solubility of Vendor Material at pH 13, 1 M Na⁺, as a Function of Grams of Ferrocyanide Material Used

Figure 3.5. Solubility of Vendor Material as a Function of Hydroxide Ion to Ferrocyanide Ion Molar Ratio, 1 M Na⁺

Table 3.2 summarizes pH data taken during vendor material dissolution experiments conducted in FY 1992 and FY 1993. Moles of hydroxide consumed, as estimated from pH meter measurements (glass electrode), are ratioed against the moles of vendor material dissolved. Any inaccuracies in the measured pH values (0.1 units) will result in variations in the OH⁻/ferrocyanide mole ratio of about 0.5 to 1; the calculated ratio is sensitive to the accuracy of the pH measurement. In most cases this ratio is approximately 2 as predicted from the stoichiometry of the dissolution reaction (Eq. 1). Ratios greatly different from 2 are observed in pH 14 solution and in cases where only a small amount of dissolution (small change in [OH⁻]) has occurred, such as when 0.1 and 0.25 g of vendor material (as opposed to 1 g) were used. High sodium nitrate concentrations had relatively little effect on the calculated OH⁻/ferrocyanide mole ratios, indicating that measured changes in pH may be accurate even though absolute pH values from glass electrode measurements in these high sodium solutions are uncertain.

3.1.2 Solubility of a Cs₂NiFe(CN)₆-Containing Material

Dissolution tests were conducted with the PNL-prepared material FECN-14. Analyses indicate this material contains 2.3 moles Cs/mole ferrocyanide anion (Table 3.1) and has a Ni/Fe mole ratio of 1.14. Experiments show that Cs₂NiFe(CN)₆ remains completely insoluble in 0.1 M to 4.0 M NaOH solutions after stirring for 144 h at room temperature. Infrared spectra indicate that the supernate solution consists of NaNO₃ and NaOH, with no dissolved Fe(CN)₆⁻⁴. Atomic absorption analyses also indicated that iron was not present in the supernate solution. The insoluble material remaining after 144 h had the same FTIR spectrum as the starting material. These results suggest that if a Cs₂NiFe(CN)₆ phase is present in ferrocyanide waste, it would not easily dissolve when contacted with caustic. These results also suggest that NaOH is not a suitable choice for dissolving ferrocyanide tank samples for subsequent analysis. The FECN-14 material dissolved readily in the ethylenediamine/EDTA solvent used for FTIR and AA analyses.

The reason for the insolubility of Cs₂NiFe(CN)₆, in light of the solubility of the sodium analog, is unknown at this time. Possible explanations include a greater lattice energy than the sodium analog, a different crystal structure, and fewer defects or smaller channels through which base can enter the crystal lattice. The literature indicates that alkali metal nickel ferrocyanides are isomorphous regardless of composition, having cubic structures with unit cell parameters between 9.9 and 10.2 Å (Loos-Neskovic et al. 1984, 1989; Loos-Neskovic and Fedoroff 1989). In a constant-sized unit cell, replacement of sodium with the larger cesium cation could block channels within the extended ferrocyanide structure. Thus, while dissolution may be thermodynamically favorable, the process could be kinetically slow.

3.1.3 Solubility of In-Farm-1A, Rev. 4 Flowsheet Material

Dried IF-1A, a top-layer In-Farm Flowsheet simulant (Jeppson and Wong 1993), was used for dissolution and hydrolysis studies. Upon drying to constant weight at 60°C under vacuum, the material lost 46% of its weight as water. Analytical results (iron, cesium, nickel, and sodium by AA, ferrocyanide anion by FTIR) for the dried simulant dissolved in ethylenediamine/EDTA solution were summarized in Table 3.1. This material contains 4.51×10^{-2} moles Cs/mole ferrocyanide (as determined from AA data). The Cs/Na mole ratio of 2.9×10^{-3} is smaller than the expected ratio of 9×10^{-3} based on the flowsheet recipe. Most of the cesium apparently is associated with the bottom

ferrocyanide layer obtained in the flowsheet preparation. Infrared and AA data are consistent for iron and ferrocyanide anion, giving a $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}$ ratio of 1.09, showing that iron is predominantly present in the form of ferrocyanide anion. The Ni/Fe ratio of 1.52 is greater than the stoichiometric ratio of 1.0 observed in the vendor material and FECN-14. The IF-1A material either contains other nickel compounds, such as nickel phosphate, or contains ion-exchanged nickel within the ferrocyanide phase.

Two dissolution experiments, one initially containing 1 M sodium ion at pH 13 (NaNO_3 used to adjust $[\text{Na}^+]$) and the other at pH 14 (1 M Na^+ as NaOH), were conducted in which 4.29 g of IF-1A were stirred in 75 mL of caustic solution. The quantities were chosen to give about the same final ferrocyanide concentration (if all dissolved) and the same ferrocyanide/hydroxide mole ratio as in previous experiments utilizing the vendor material. Iron and cesium concentrations in periodically drawn solution samples were determined by AA.

Dissolution (solution iron concentration) as a function of time is shown in Figure 3.6, which compares the behavior of IF-1A with that of the vendor material under similar conditions. The rate of dissolution of IF-1A is generally suppressed relative to the vendor material; initial dissolution at pH 14 is rapid with a slow increase to about 85% dissolution after 144 h, while the vendor material was over 90% dissolved after 0.5 h. In pH 13 solution, the IF-1A material dissolved very slowly with only about 18% in solution after 144 h. The suppressed rates are probably not a result of higher sodium ion concentrations arising from dissolution of salts from the IF-1A material (which would increase the $[\text{Na}^+]$ about 0.5 M). The rate of dissolution of IF-1A in pH 13 solution is lower than that of the vendor material in a pH 13, 6 M Na^+ solution, which reached about 30% after 144 h (Figure 3.1).

None of the solution samples contained cesium; i.e., cesium is not solubilized even in pH 14 solution. Ferrocyanides are known to be good ion exchange materials for cesium sorption (Campbell et al. 1990; Loos-Neskovic and Fedoroff 1989), and it is likely that any cesium liberated by ferrocyanide dissolution would exchange back into the solid to form a $\text{Cs}_2\text{NiFe}(\text{CN})_6$ or $\text{NaCsNiFe}(\text{CN})_6$ phase. Accumulation of cesium at the particle surface may explain the suppressed dissolution, since FECN-14, containing $\text{Cs}_2\text{NiFe}(\text{CN})_6$, was found to be insoluble in up to 4 M NaOH .

The temperature dependence of IF-1A dissolution was investigated at 60°C and 90°C using pH 13 solutions adjusted to 1 M sodium ion with NaNO_3 . These experiments were conducted in Teflon labware. Figure 3.7 illustrates the increase in soluble iron (sodium ferrocyanide) with time. The extent of dissolution increases with increasing temperature. At 25°C, after 144 h, about 18 wt% of the ferrocyanide is dissolved. At 60°C and 90°C, the reaction apparently approaches equilibrium dissolution of about 47% and 63%, respectively. Atomic absorption analysis again shows no dissolved cesium in any of the reaction solutions.

Figure 3.6. Vendor Material and In-Farm-1A Solubility at pH 13 and pH 14 With 1 M Na⁺

Figure 3.7. Temperature Dependence of IF-1A Dissolution at pH 13, 1 M Na⁺

3.2 Hydrolysis Studies

Hydrolysis screening studies were conducted at two widely different potential tank conditions. In one experiment, hydrolysis in 4 M NaOH at 90°C was investigated to simulate conditions when highly caustic decladding waste or evaporator bottoms were added to bedded ferrocyanides. The other experiment, at pH 10 and 60°C, investigated conditions in areas of the tanks that may not have been exposed to high pH waste.

Dried IF-1A (5.725 g) was contacted with 4 M NaOH (100 mL) for 3 weeks at 90°C in a gamma field of 1.43×10^5 Rad/h. The reaction solution was sparged with argon before sealing. An identical reaction mixture was heated to 90°C outside the pit as a control. Neither solution was stirred mechanically. The final reaction solutions were analyzed for ammonia using an ammonia-selective electrode (Table 3.3). The ammonia concentration in the gamma-irradiated solution (0.0938 M) was 8.6 times that found in the control (0.0109 M). Preliminary infrared analytical results also indicate a higher ammonia concentration in the gas phase over the gamma-irradiated solution. The theoretical ammonia concentration (all cyanide ions converted to ammonia by hydrolysis and all ammonia being in solution) is 0.225 M, indicating a percent conversion of at least 42% in the gamma field and 4.8% in the control, based only on the solution concentrations. These results suggest that gamma radiation promotes hydrolysis, possibly by facilitating the dissociation of cyanide ions from the iron coordination center.

Table 3.3 summarizes other analytical results from the 4 M NaOH experiments. The formate concentration (IC) in the control solution (outside the gamma field) is in excellent agreement with the measured solution concentration of ammonia. However, the one-to-one correlation is not observed in the gamma-irradiated solution, with a formate concentration about 8 times lower than the ammonia concentration. Gamma radiation degrades formate to CO_2^- radical anion (Goldstein et al. 1988), which should form carbonate in basic solution. This is consistent with infrared spectra of the insoluble solids, which showed more carbonate in the gamma solids than in the control. Gamma solids were red, suggesting the presence of iron oxides. X-ray diffraction also suggested that a small amount of crystalline Fe_2O_3 was present, but its presence is uncertain because XRD peaks for this phase were very small and difficult to separate from ferrocyanide and nickel hydroxide peaks. Also, Robuck and Luthy reported Fe_3O_4 (Robuck and Luthy 1989). Infrared was inconclusive regarding

Table 3.3. Solution Analytical Data for Reaction Products from Hydrolysis of In-Farm-1A, Rev. 4

Analyte	4 M NaOH, 90°C		pH 10, 60°C	
	Control	Gamma	Control	Gamma
NH_3	0.0109 M	0.0938 M	2.88×10^{-4} M	1.80×10^{-3} M
HCO_2^-	0.015 M	0.015 M	0.0039 M	0.0021 M
NO_3^-	0.288 M	0.146 M	1.063 M	0.937 M
NO_2^-	0.090 M	0.252 M	0.102 M	0.216 M
Fe	1,675 ppm	890 ppm	0.57 ± 0.68 ppm	4.34 ± 0.41 ppm
Cs	5.1 ppm	8.7 ppm	8.0 ± 1.8 ppm	0.52 ± 0.56 ppm

the presence of Fe_2O_3 or other iron oxide phases. The concentration of soluble iron was found (by AA) to be 1675 and 890 ppm for the control and gamma solutions, respectively. Infrared is being used to determine what fraction of this iron is in the form of ferrocyanide. The lower iron concentration in the gamma sample is consistent with more extensive hydrolysis, which should result in the precipitation of iron oxides. A small amount of cesium was detected in solution; however, the concentrations are close to the detection limit in the high sodium ion media and should be interpreted with caution. The concentrations reported in Table 3.3 correspond to 2% to 4% cesium dissolution.

A similar experiment was conducted at pH 10 and 60°C for 4 weeks at the same dose rate. The Na^+ concentration was adjusted to 1 M with NaNO_3 . Compared with the 4 M NaOH experiment, 2 orders of magnitude less ammonia (just above the detection limit of the ammonia probe) was observed for both the control and irradiated solutions. The measured formate concentrations were also much lower, and also approach the detection limit. The control supernate was colorless and contained no soluble iron, indicating no dissolution at pH 10. The irradiated solution showed a trace of soluble iron corresponding to 0.2% dissolution. Little or no cesium dissolution occurred.

Analyses for NO_3^- and NO_2^- in 4 M NaOH and pH 10 solutions are consistent with the amounts initially added. The NO_3^- and NO_2^- concentrations in the 4 M NaOH control experiment are essentially those arising from dissolution of the IF-1A material, calculated to be 0.301 M and 0.100 M, respectively. The sum of the concentrations, 0.4 M, is maintained in the gamma solutions, although a net conversion of NO_3^- to NO_2^- is observed. Similarly, the concentrations of these anions in the pH 10 control solution are the same as those calculated to have been added, and the sum (1.165 M) remains about constant on gamma irradiation.

4.0 Conclusions

Vendor-prepared $\text{Na}_2\text{NiFe}(\text{CN})_6$ dissolves in aqueous base to give primarily insoluble $\text{Ni}(\text{OH})_2$ and soluble $\text{Na}_4\text{Fe}(\text{CN})_6$. The rate of dissolution of $\text{Na}_2\text{NiFe}(\text{CN})_6$ in aqueous base increases with increasing pH. At pH 14, 95% dissolution is observed after 0.5 h. Addition of sodium ion in the form of Na_2SO_4 or NaNO_3 suppresses dissolution at pH 13. However, 1 M Na^+ in the form of Na_2CO_3 , Na_3PO_4 , or SST simulant salts (mixed sodium salts of phosphate, carbonate, nitrate, nitrite, sulfate, and hydroxide) results in an enhancement of the rate of solubilization. At pH 14 these effects are not seen, dissolution being rapid even in the presence of 4 M sodium ion. The rate of dissolution is influenced most by base concentration.

Dissolution of IF-1A, containing 4.51×10^{-2} moles Cs/moles ferrocyanide, takes place more slowly than the vendor material under identical conditions at both pH 13 and pH 14. A material containing a $\text{Cs}_2\text{NiFe}(\text{CN})_6$ phase (2.3 moles Cs/moles ferrocyanide) was found to be insoluble in up to 4 M NaOH after stirring for 144 h. The inhibition of IF-1A dissolution may be due to concentration of an insoluble (or less soluble) $\text{Cs}_2\text{NiFe}(\text{CN})_6$ or $\text{NaCsNiFe}(\text{CN})_6$ phase at the particle surface as $\text{Na}_2\text{NiFe}(\text{CN})_6$ dissolves.

Studies of the hydrolysis of IF-1A in 4 M NaOH indicate that gamma accelerates the hydrolysis reaction. After 3 weeks at 90°C, gamma-irradiated IF-1A was at least 42% degraded to ammonia. An identical control experiment not receiving gamma radiation showed about 8.6 times less hydrolysis. Little dissolution and hydrolysis occurs in pH 10 solution at 60°C.

5.0 Future Work

The kinetics of hydrolysis of ferrocyanide materials is an area for continued research in FY 1994. A better understanding of hydrolysis rates and determination of the activation energy for hydrolysis under tank conditions is needed in order to determine the extent of ferrocyanide destruction that may have occurred during decades of storage. The effect of limiting the NaOH to below stoichiometric amounts will also be evaluated. Experiments investigating bench top and gamma pit hydrolysis in the presence of a decladding waste simulant should be conducted. Aging kinetic studies coupled with microconvective modeling studies now being conducted will indicate the plausibility of the aging mechanism.

Dissolution of the IF-1A flowsheet material should be investigated under conditions of constant pH. As conducted now, the pH decreases as the ferrocyanide dissolves, preventing determination of the rate of dissolution. Maintaining a constant pH will remove this complicating factor. Because the reaction is heterogeneous, other complicating factors will remain, such as particle size and stirring rate variations. These effects can be minimized to obtain global dissolution rates.

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