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FY 1993 FERROCYANIDE TANK SAFETY
PROJECT: EFFECTS OF AGING ON
FERROCYANIDE WASTES TEST PLAN
FOR THE REMAINDER OF FY 1993

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INTRODUCTION

Researchers in the Hanford Ferrocyanide Task Team are studying safety issues associated with ferrocyanide precipitates in single shell waste storage tanks (SST). Sodium and potassium nickel ferrocyanides were used in the 1950's for scavenging radiocesium from dissolved wastes. Ferrocyanide is a stable complex of ferrous ion and cyanide ion that is considered nontoxic because it does not dissociate readily in aqueous solutions. However, in the laboratory at temperatures in excess of 180°C and in the presence of oxidizers such as nitrates and nitrites (that can be found in the SSTs in high concentrations), dry ferrocyanide and ferrocyanide waste simulants can be made to react exothermically.

The Ferrocyanide Safety Project at the Pacific Northwest Laboratory (PNL) is part of the Waste Tank Safety Program at Westinghouse Hanford Company (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).

Tank ferrocyanide wastes were exposed to highly alkaline wastes from subsequent processing operations. Chemical reactions with caustic may have changed the ferrocyanide materials during 40 years of storage in the SSTs. Research in the "Effects of Aging on Ferrocyanide Wastes" task is targeted at studying aging, i.e., dissolution and long-term degradation (hydrolysis), of ferrocyanide tank simulants and other ferrocyanide materials to obtain a better understanding of how tank materials may have changed over the years. Verification of simulant study findings by comparison with results with actual waste will also be required.

OBJECTIVE

The objective of research on the "Effects of Aging on Ferrocyanide Wastes" task is to determine the solubility and hydrolysis characteristics of simulated ferrocyanide tank wastes in alkaline media. The results of this work will give a better understanding of the long-term behavior of ferrocyanide tank wastes and will provide the baseline needed to interpret analytical results for actual SST samples.

The behavior of ferrocyanide simulant wastes is being determined by performing chemical reactions under conditions that mimic the potential ranges in SST environments. Experiments are conducted at high pH, at high ionic strength, and in the presence of gamma radiation. Identification of reaction products (soluble and insoluble) indicates likely aging pathways.

Research on the dissolution of the vendor-prepared ferrocyanide material was completed in the first half of FY 1993. Conditions for these experiments are summarized in Table i. This test plan, which supersedes Test Plan # 93-01-01, guides dissolution and hydrolysis experiments utilizing In-Farm 1A, Rev. 4 flowsheet material. The previous test

plan was modified to include more vigorous conditions thought to be more representative of tank conditions when highly caustic wastes were added to the ferrocyanide sludges.

EXPERIMENTAL PROCEDURES

Research for the remainder of FY 1993 will focus on the solubility and hydrolysis of In-Farm-1A, Rev. 4 flowsheet ferrocyanide material (top layer) that has been dried to constant mass at 60°C under vacuum. A bottom-layer flowsheet simulant containing more ferrocyanide and cesium may also be examined in selected solubility experiments. Experiments will be run using enough of the dried material to give the same moles of ferrocyanide as 1 gram of the vendor-prepared material used in previous studies. This material will typically be contacted with 50 mL of dissolving solution. Temperature, pH, and gamma radiation effects will be investigated. Experiments to be completed in FY 1993 are outlined in Table 2 and described below. Contingency and other experiments relevant to the Ferrocyanide Safety Program are also discussed and may be considered for FY 1994 research.

Solubility studies will be conducted first and will be run at 25°C, 60°C, and 90°C with an initial pH of 13 and at 25°C with an initial pH of 14. These experiments will give information about the temperature dependence of dissolution, as well as give a point of reference to previous results for the vendor material. Dissolution in a pH 14 solution is expected to be rapid. Because In-Farm flowsheet materials contain a small amount of cesium, information about the partitioning of this ion will be obtained. Previous studies demonstrated the insolubility of a relatively pure cesium nickel ferrocyanide material in up to 4M NaOH. Studies with the In-Farm-1A material will indicate whether cesium, when initially present in low concentrations and dispersed throughout the ferrocyanide simulant, remains in the solid phase or dissolves. If cesium concentrations are too low to adequately determine partitioning, the top-layer simulant containing more cesium will be investigated this fiscal year.

Both hydrolysis and solubility data will be gathered from the other experiments listed in Table 2. Dissolution of $\text{Na}_2\text{NiFe}(\text{CN})_6$ in pH 14 and 4M NaOH solutions should be complete and rapid, especially at 90°C. Hydrolysis will occur slowly in these solutions and will be monitored by following changes in the ammonia concentration in the solution or gas phase with use of an ammonia-selective electrode or with gas chromatography. The gas phase will be monitored for CO_2 with gas chromatography, and the liquid phase will be tested for the presence of formate with ion chromatography. Results in FY 1992 indicated the possibility that gamma radiation may promote dissociation of cyanide, much like visible light is known to do. Free cyanide should hydrolyze more rapidly than iron-bound cyanide. As a result, hydrolysis in the gamma experiments may be more extensive than in the nonirradiated control experiments. Rates of reaction should be obtainable from data gathered in these experiments.

The high pH hydrolysis experiments have a high priority and will be run as soon as a reliable ammonia analysis method is demonstrated. Benchtop experiments will be conducted first, followed by experiments in the gamma pit. Subsequent experiments and

conditions of those experiments will depend on the hydrolysis rates obtained. For example, determination of the activation energy for hydrolysis under tank conditions will require easily measurable reaction rates. If rates are very slow, determination of activation energy may be postponed until next fiscal year in order to complete other scheduled experiments. Similarly, the feasibility of investigating the effect of limiting the NaOH to below stoichiometric amounts will be evaluated after results at high pH are obtained. Replicates are planned only for experiments in which significant hydrolysis is observed.

The pH 10 experiments shown in Table 2 mimic conditions within any sludge that has not been exposed to highly caustic wastes. The extent of dissolution and hydrolysis is expected to be low at this pH but could be sufficient to alter the ferrocyanide after 30 years of storage.

An experiment investigating benchtop hydrolysis in the presence of a decladding waste simulant will be conducted this fiscal year. The conditions of this experiment and the composition of the simulant will be determined after consulting with George Borsheim and Dan Reynolds of WHC. Gamma pit experiments with decladding waste simulant should also be conducted in the future.

The kinetics of hydrolysis is an area for continued research in FY 1994. A better understanding of hydrolysis rates is needed in order to determine the extent of ferrocyanide destruction that may have occurred during decades of storage. Aging kinetic studies coupled with microconvective modeling studies now being conducted will indicate the plausibility of the aging mechanism.

Dissolution of the In-Farm I flowsheet material should be investigated (in FY 1994) 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.

Thermochemical studies have shown that ferricyanides react with nitrate/nitrite more energetically than ferrocyanides. If their presence is demonstrated, aging of ferricyanides should be investigated.

ANALYTICAL PROCEDURES

Solubility studies in FY 1992 have consistently shown formation of $\text{Na}_4\text{Fe}(\text{CN})_6$ and $\text{Ni}(\text{OH})_2$ as products of the dissolution reactions, except under more vigorous conditions, such as in the gamma field. As a result, not all of the techniques used in FY 1992 will be used routinely in FY 1993 studies. Initial and final pH will be determined. Reaction progress of bench-top experiments will be monitored by following the change in soluble iron with atomic absorption spectroscopy (AA). Fourier transform infrared spectroscopy (FT-IR) will be used at the end of each reaction to monitor cyanide-containing species as

a way to determine if more complicated processes than expected are occurring. Analytical techniques that will only be used when more complex reaction mixtures are obtained include scanning electron microscopy (SEM), X-ray diffraction spectroscopy (XRD), and Mössbauer spectroscopy.

Hydrolysis experiments, which will be conducted under more vigorous conditions, will likely result in more complicated product mixtures requiring more extensive analysis. Ammonia generated in these experiments will be determined by use of an ion selective electrode or gas chromatography. The ion selective electrode will be calibrated by generating a known concentration of ammonia through addition of NaOH to ammonium chloride solutions. Determination of ammonia generated in the stainless steel reactors used in the gamma pit and sampled through the long stainless steel tubing connected to the reactors must be tested before gamma pit experiments are conducted. Formate, another product of hydrolysis, will be analyzed using ion chromatography.

Details of each analytical technique follow:

AA

The reaction mixtures will be sampled periodically during the 144-hour experiments. Aliquots (1 mL) will be filtered through a 0.45- μ m syringe filter and analyzed for iron by AA to determine rate of dissolution of the ferrocyanide materials.

FT-IR

The soluble and insoluble solids recovered from the reactions will be analyzed using FT-IR. The FT-IR analysis will primarily be used to characterize the cyanide-containing species in the reaction products. This technique will also be useful for identifying reaction products that are unique to a set of experimental conditions. Additional analytical techniques such as SEM and XRD will be used to characterize crystalline reaction species that have not been previously identified using IR spectroscopy. It will be necessary to use IR microscopy to characterize amorphous solids, such as nickel phosphate.

SEM and XRD

The chemical composition of reaction products will be determined with SEM and XRD. These data coupled with IR data should help to identify the majority of crystalline reaction species.

Mössbauer Spectroscopy

Mössbauer spectroscopy will be useful in detecting iron-containing hydrolysis products. This technique will be used when FT-IR indicates the presence of unexpected products or complex product mixtures.

Table 1. Completed Solubility Experiments Using Vendor-Prepared Material $[\text{Na}_2\text{NiFe}(\text{CN})_6 \cdot \text{Na}_2\text{SO}_4 \cdot 4.5 \text{H}_2\text{O}]$

Vendor Material Solubility	[Na ⁺], M			[Na ⁺] as NaNO ₃ , M			1 M [Na ⁺]			g/50mL	Gamma Pit
	0.01	0.1	1	1	4	6	SST Mix	PO ₄ ³⁻	CO ₃ ²⁻		
12	■		■ ^a								
pH 13		■	■ ^a	■	■	■	■	■	■	■	■
14			■		■				■		

a) [Na⁺] adjusted to 1 M with Na₂SO₄

Table 2. Planned Solubility/Hydrolysis Experiments Using Flowsheet Material

Flowsheet Material Solubility/Hydrolysis	25°C			60°C			90°C		
pH 10 ^a						□ ^c			
Bench pH 13 ^b			□			□			□
pH 14			□						□ ^c
4M NaOH									□ ^c
pH 10 ^a						□ ^c			
Gamma pH 14									□ ^c
4M NaOH									□ ^c

a) Dissolving solution contains 1 M [Na⁺], Na₂CO₃ buffer.

b) Dissolving solution contains 1 M [Na⁺], NaNO₃.

c) Test for hydrolysis products.

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