

DESTRUCTION OF FERROCYANIDE COMPOUNDS FOUND IN THE HANFORD SITE'S RADIOACTIVE WASTE

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ABSTRACT

This paper reports the test results of candidate waste treatment processes to destroy nickel-ferrocyanide compounds contained in the Hanford Site's radioactive waste storage tanks. Candidate processes, including ozone oxidation, hydrogen peroxide oxidation, and calcination, were tested in the laboratory using a nonradioactive simulated waste. Ozone oxidation and calcination successfully destroyed the nickel-ferrocyanide. However, tests indicate that nickel-ferrocyanide is not easily destroyed using hydrogen peroxide.

To determine the ozone/nickel-ferrocyanide oxidation rate, a laboratory scale prototype ozone reactor was employed. The prototype reactor provides excellent gas-liquid mass transport, which is envisioned to increase the overall nickel-ferrocyanide destruction rate. The analytical results indicate that 250 grams of ozone are required to oxidize 1 gram of nickel-ferrocyanide. At this reaction rate, the process would require excessively large quantities of ozone to process the waste at the Hanford Site. Efforts are currently underway to increase the reaction kinetics for the process.

Finally, one processing option successfully demonstrated in the laboratory that encompasses calcination not only destroys ferrocyanides, but also separates the transuranics from the bulk nonradioactive waste.

INTRODUCTION

The 540-mi² Hanford Site reservation is located in southern Washington state, near the Columbia river. Figure 1 shows the location of the Hanford Site in Washington and the separations area on the site where the waste storage tanks are located.

Spent nuclear fuel has been processed at the Hanford Site to recover nuclear material since the 1940's, and as a result, radioactive waste has been generated and stored on the site in underground tanks. Presently, 177 tanks store 41 million gal of radioactive waste that has been generated over the last 40 yr (1).

Twenty-four of the Hanford Site's tanks have been identified as containing 200,000 kg of nickel-ferrocyanide. Concern exists that at elevated temperatures, the ferrocyanide could react in the storage tanks; thus, releasing heat and gases.

CANDIDATE WASTE TREATMENT PROCESSES

No practices have been formerly used to destroy the nickel-ferrocyanide compounds in the Hanford Site's radioactive storage tanks. Several candidate waste treatment processes were evaluated in this study to destroy the nickel-ferrocyanide wastes, including the following:

- Ozone oxidation,
- Peroxide oxidation,
- Calcination.

Additional waste treatment processes that were not evaluated include acid digestion and dilution. The ferrocyanide compounds can be destroyed using various concentrated acids. Acid destruction, although an alternative process, would require dealing with large acid additions to the presently caustic waste. Water dilution would require long-term management of the tanks to ensure that the waste remains wet. Also, the water could serve as a medium to transport radioactive and hazardous constituents into the groundwater, especially in tanks that are already leaking.

WASTE SIMULANTS

The Hanford Site's wastes contain radioactive constituents, making tests with actual waste difficult. Therefore, a nonradioactive waste simulant was prepared in the laboratory to evaluate the candidate waste treatment processes. The nickel-ferrocyanide waste simulant composition is shown in Table I.

TABLE I

Ferrocyanide Waste Simulant Composition

Chemicals	Concentration (gmol/L)
NO ₃	7.79
NO ₂	1.65
CO ₃	0.29
OH	0.01
Al	2.43
Fe	0.03
Ca	0.02
Mg	0.012
Mn	0.009
Ni	0.015
PO ₄	0.037
Si	0.092
NaNiFe(CN) ₆	0.100
Sr	0.001
Cs	0.005

TESTING METHOD

The analytical method used by Pacific Northwest Laboratory (PNL) was acid distillation followed by titrimetric cyanide analysis of the off-gases produced from the distillation. The solutions were distilled twice for 2-hour intervals, which is 3 hours more than that prescribed by published methods.

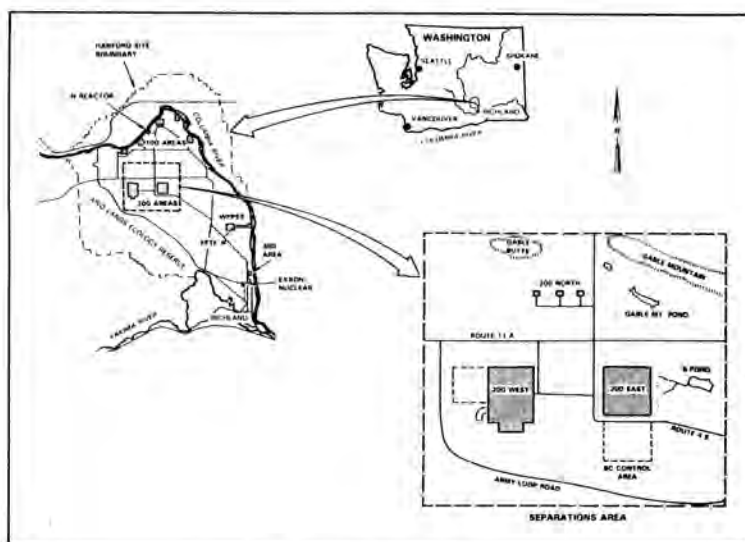
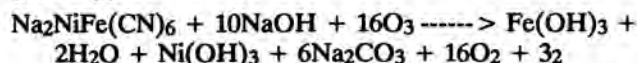


Fig. 1. The Hanford Site area map.

DESTRUCTION OF NICKEL-FERROCYANIDE COMPOUNDS USING OZONE

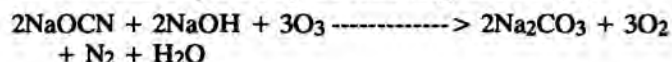
Ozone has been demonstrated in the laboratory to effectively destroy nickel-ferrocyanide compounds contained in a waste simulant. The ozone chemistry has many advantageous features. The pH required for the process is ≥ 12 , which is essentially the same pH as in the storage tanks. Also, ozone oxidation would not add reagents to the waste other than oxygen and does not increase the present volume of waste. The ozone chemistry functions at ambient temperature and pressure.

The following overall ozone reaction equation is suggested (2):



It is postulated that nickel-ferrocyanide becomes soluble above pH 12, allowing ozone to oxidize the compound in solution. Ozonation of nickel-ferrocyanide produces a precipitate of colloidal $\text{Fe}(\text{OH})_3$ and $\text{Ni}(\text{OH})_3$. Pure $\text{Ni}(\text{OH})_3$ is black/brown and $\text{Fe}(\text{OH})_3$ is burgundy, producing a dark brown solution.

Cyanate may be formed as an intermediate product. Ozone oxidizes cyanate by the following reaction (3):



Prototype Ozone Reactor

To determine the ozone reaction rate, a laboratory scale prototype ozone reactor was employed. The ozone reactor used is a three-phase, batch recycle reactor that provides excellent gas-liquid mass transport. The reactor provides the advantage of high throughput and extensive homogenization of solids and high viscosity slurries typically found in the Hanford Site's waste tanks. Figure 2 depicts the overall flow diagram used in the laboratory.

An in-line static mixer was used in conjunction with the proposed homogenizer/reactor to further increase the mass transport of ozone into solution. The static mixer is comprised of a section of pipe containing internal radial mixing blades

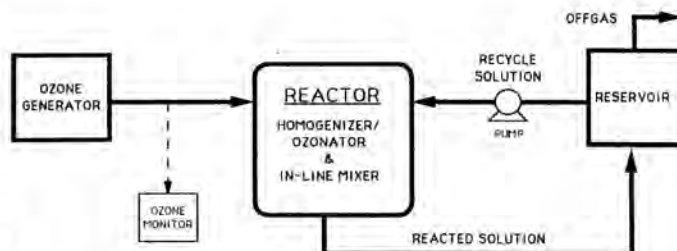


Fig. 2. Prototype Homogenizer/Ozonator flow diagram.

that create turbulent flow. Literature indicates that in-line static reactors are efficient ozone reactors (4).

The proposed homogenizer/ozonator uses extremely short residence times because of the ozone's fast decomposition rate at high pH's (10 to 14). At pH = 9, dissolved ozone decomposes into oxygen in 20 min. At pH = 10.4, 100% decomposition occurs in < 1 min. The fast ozone kinetics enable the use of small reactors with high throughput (2).

The proposed homogenizer/ozonator serves to both break up larger particles and to disperse the ozone into solution. The waste targeted for ozone oxidation varies in consistency from peanut butter to rock candy. Homogenation either before or during ozone oxidation is essential for efficient mass transport.

Analytical Results

The homogenizer/ozonator processed a simulated waste containing nickel-ferrocyanide compounds. The analytical results are shown in Fig. 3. The concentration of nickel-ferrocyanide (y axis) is plotted against the accumulative ozone added (x axis).

The line fitting the data was derived using a standard trend analysis. The slope of the line indicates that 250 grams of ozone are required to oxidize 1 gram of nickel-ferrocyanide. At this reaction rate, the process would require excessively large quantities of ozone to process the waste at the Hanford Site.

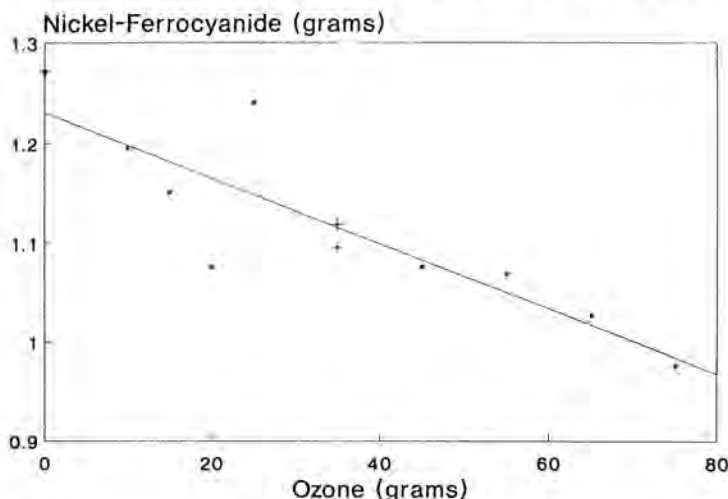


Fig. 3. Analytical results for destroying Nickel-Ferrocyanide compounds in the Prototype Ozone Reactor.

Efforts are currently underway to increase the reaction kinetics for the process. Future testing includes using hydrogen peroxide in conjunction with the ozone, which is intended to increase the effectiveness of the ozone. The hydrogen peroxide decomposes to form hydroxyl radical intermediates that aid ozone's oxidation capability. In addition, the process will be run at higher pH's and temperature to identify their effects on the overall oxidation rate.

DESTRUCTION OF NICKEL-FERROCYANIDE COMPOUNDS USING HYDROGEN PEROXIDE

Tests indicate that nickel-ferrocyanide is not easily destroyed using hydrogen peroxide. Hydrogen peroxide tests were performed at solution pH 2, 7, and 12 and solution temperatures up to 80°C with no apparent destruction of nickel-ferrocyanide compounds.

Hydrogen peroxide was evaluated because it is a good oxidizing agent that decomposes into water. Also, laboratory tests measured the destruction of free cyanide using hydrogen peroxide and therefore, further testing of nickel-ferrocyanide was pursued.

Analytical Results

Table II lists the analytical results showing the percent nickel-ferrocyanide destruction that resulted from hydrogen peroxide oxidation at pH 2, 7, and 12.

It is noteworthy to mention that hydrogen peroxide destroyed 40% of relatively pure nickel-ferrocyanide at pH 2. The elements found in the waste simulant apparently interfere with the peroxide reaction with the ferrocyanide.

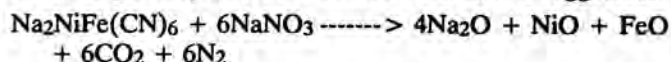
TABLE II

Hydrogen Peroxide Oxidation of a Ferrocyanide Waste Simulant

Adjusted pH of Waste Simulant	Percent Nickel-Ferrocyanide Destruction
2	0
7	1
12	-4

DESTRUCTION OF NICKEL-FERROCYANIDE COMPOUNDS USING CALCINATION

The nonradioactive waste simulant containing the nickel-ferrocyanide was heated to 800°C in the laboratory and 100% destruction of ferrocyanide was measured. The following overall high temperature calcination reaction is suggested:



The reaction is exothermic evolving 1655 kJ of heat.

Proposed Processing Concept

One processing option successfully demonstrated in the laboratory that encompasses calcination not only destroys ferrocyanides and organics, but also separates the transuranics from the bulk nonradioactive waste. The process exhibits many advantageous features that are listed below.

- The process destroys organics and nickel-ferrocyanides found in the waste, which remediates an unresolved tank safety issue.
- Calcining the waste reduces the total mass of waste by venting nitrogen, oxygen, and carbon gases.
- The long-lived radionuclides are separated into a small volume, leaving most of the waste volume suitable for near-surface disposal.
- The final form of both waste streams is amenable to a variety of further disposal/treatment alternatives.
- The waste is processed in its current form with no chemical additions.
- The chemistry is simple and able to treat a wide variety of complex wastes that contain high concentrations of sodium salts.
- The process destroys nitrates and nitrites found in the waste, which decreases the waste volume.

Analytical Results

The process's chemistry has recently been demonstrated using a nonradioactive simulated waste, representative of tank waste at the Hanford Site. Assuming that the lanthanides behave similarly to the actinides, the test indicates that actinides will be separated into a relatively small volume from the bulk of the nonradioactive material.

CONCLUSION

Destruction of nickel-ferrocyanide compounds using ozone, hydrogen peroxide, and thermal oxidation was evaluated in the laboratory. Ozone destroys the nickel-ferrocyanide compounds without altering the current waste form and can be accomplished at 25°C and 0 lb/in² gage. The analytical results indicate that 250 grams of ozone are required to oxidize 1 gram of nickel-ferrocyanide. At this reaction rate, the process would require excessively large quantities of ozone to process the waste at the Hanford Site. Efforts are currently underway to increase the reaction kinetics for the process.

No destruction was measured using a simulated waste containing nickel-ferrocyanide using hydrogen peroxide at pH 2, 7, or 12.

Finally, calcination of the waste would not only destroy the nickel-ferrocyanide but also would reduce the total volume of radioactive waste by venting nonradioactive nitrogen, oxygen, and carbon gases. One processing option successfully demonstrated encompasses calcination that destroys ferrocyanides and organics and also separates the transuranics from the bulk nonradioactive waste.

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