RMIS View/Print Document Cover Sheet

This document was retrieved from the Boeing ISEARCH System.

Accession #: D196071826

Document #: SD-WM-RPT-195

Title/Desc:

FERROCYANIDE SAFETY PROGRAM FY1995 REPORT ON
MOSSBAUER SPECTROSCOPY TASK ACTIVITIES

ENGINEERING DATA TRANSMITTAL

Page 1 of 1
1. EDT No 612317

2. To: (Receiving Organization) Distribution	3. From: (Originating Organization) TWRS Safety Engineering	4. Related EDT No.: N/A
5. Proj./Prog./Dept./Div.: TWRS Safety Basis	6. Cog. Engr.: F. R. Riedel	7. Purchase Order No.: N/A
8. Originator Remarks: This EDT is for approval of WHC-SD-WM-RPT. This report is the FY 1995 report on Mossbauer Spectroscopy Task Activities		9. Equip./Component No.: N/A
		10. System/Bldg./Facility: N/A
		12. Major Assm. Dwg. No.: N/A
11. Receiver Remarks:		13. Permit/Permit Application No.: N/A
		14. Required Response Date: N/A

15. DATA TRANSMITTED					(F)	(G)	(H)	(I)
(A) Item No.	(B) Document/Drawing No.	(C) Sheet No.	(D) Rev. No.	(E) Title or Description of Data Transmitted	Approval Designator	Reason for Transmittal	Originator Disposition	Receiver Disposition
1	WHC-SD-WM-RPT-195		0	Ferrocyanide Safety Program: FY 1995 Report on Mossbauer Spectroscopy Task Activities	N/A	1	1	

16. KEY		
Approval Designator (F)	Reason for Transmittal (G)	Disposition (H) & (I)
E, S, Q, D or N/A (see WHC-CM-3-5, Sec.12.7)	1. Approval 4. Review 2. Release 5. Post-Review 3. Information 6. Dist. (Receipt Acknow. Required)	1. Approved 4. Reviewed no/comment 2. Approved w/comment 5. Reviewed w/comment 3. Disapproved w/comment 6. Receipt acknowledged

17. SIGNATURE/DISTRIBUTION (See Approval Designator for required signatures)										(G)	(H)
Rea-son	Dis-p.	(J) Name	(K) Signature (M) MSIN	(L) Date	(J) Name	(K) Signature (M) MSIN	(L) Date	Rea-son	Dis-p.		
1	1	Cog.Eng. F. R. Riedel	<i>[Signature]</i>		47	<i>[Signature]</i>	8/23/95				
1	1	Cog. Mgr. R. J. Cash	<i>[Signature]</i>								
		QA									
		Safety									
		Env.									

18. <i>[Signature]</i> Signature of EDT Date Originator	19. _____ Authorized Representative Date for Receiving Organization	20. <i>[Signature]</i> R. J. Cash Cognizant Manager Date	21. DOE APPROVAL (if required) Ctrl. No. ☐ Approved ☐ Approved w/comments ☐ Disapproved w/comments
---	---	--	---

RELEASE AUTHORIZATION

Document Number: WHC-SD-WM-RPT-195, REV 0

Document Title: Ferrocyanide Safety Program: FY 1995 Report on Mossbauer Spectroscopy Task Activities

Release Date: 10/2/95

**This document was reviewed following the
procedures described in WHC-CM-3-4 and is:**

APPROVED FOR PUBLIC RELEASE

WHC Information Release Administration Specialist:

Kara Broz

10/2/95

TRADEMARK DISCLAIMER. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors.

This report has been reproduced from the best available copy. Available in paper copy. Printed in the United States of America. To obtain copies of this report, contact:

Westinghouse Hanford Company - Document Control Services
P.O. Box 1970, Mailstop H6-08, Richland, WA 99352
Telephone: (509) 372-2420; Fax: (509) 376-4989

SUPPORTING DOCUMENT		1. Total Pages 109
2. Title Ferrocyanide Safety Program: FY 1995 Report on Mössbauer Spectroscopy Task Activities	3. Number WHC-SD-WM-RPT-195	4. Rev No. 0
5. Key Words Characterization, Mössbauer, Spectroscopy, Iron Spectroscopy	6. Author Name: F. R. Riedel <i>E. F. Riedel</i> Signature Organization/Charge Code 74210/N211C	
7. Abstract <p>This report summarizes FY 1995 activities on the Mössbauer Spectroscopy task. The National Aeronautics and Space Administration has developed a miniaturized Mössbauer spectrometer that is small enough to perform elevation scans in the Hanford Site waste tank liquid observation wells. Mössbauer spectroscopy is a sensitive and selective method that can detect and distinguish between different iron-based compounds in many types of chemical environments. Iron is major constituent of ferrocyanide waste and information about its location and composition in the tanks supports interim safe storage of the waste and final resolution of the Ferrocyanide Safety Issue. Results obtained from studies of ferrocyanide waste simulants and those from the first test in a hot cell environment using radioactive tank waste are presented.</p>		
8. RELEASE STAMP <div style="border: 1px solid black; padding: 10px; width: fit-content; margin: 0 auto;"> <p>OFFICIAL RELEASE BY WHC DATE OCT 02 1995</p> </div>		

FERROCYANIDE SAFETY PROGRAM: FY 1995 REPORT ON MÖSSBAUER SPECTROSCOPY TASK ACTIVITIES

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

Westinghouse
Hanford Company Richland, Washington

Management and Operations Contractor for the
U.S. Department of Energy under Contract DE-AC06-87RL10930

Approved for public release

FERROCYANIDE SAFETY PROGRAM: FY 1995 REPORT ON MÖSSBAUER SPECTROSCOPY TASK ACTIVITIES

E. F. Riedel

Date Published
September 1995

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

**Westinghouse
Hanford Company** Richland, Washington

Management and Operations Contractor for the
U.S. Department of Energy under Contract DE-AC06-87RL10930

Approved for public release

**FERROCYANIDE SAFETY PROGRAM:
FY 1995 REPORT ON MÖSSBAUER SPECTROSCOPY TASK ACTIVITIES**

ABSTRACT

This report summarizes the activities that occurred during fiscal year 1995 on the Mössbauer Spectroscopy task. This is a small task activity that is part of the Ferrocyanide Safety Program in the Tank Waste Remediation System division of Westinghouse Hanford Company. This task is investigating the physical and chemical nature of iron within ferrocyanide tank waste. The National Aeronautics and Space Administration has developed a miniaturized Mössbauer spectrometer that is small enough to perform elevation scans in the Hanford Site waste tank liquid observations wells. Mössbauer spectroscopy is a sensitive and selective method that can detect and distinguish between different iron-based compounds in many types of chemical environments. Iron is a major constituent of ferrocyanide waste and information about its location and composition in the tanks supports safe interim storage and final resolution of the Ferrocyanide Safety Issue. Preliminary results with the Mössbauer spectrometer have proven very promising. Results obtained from studies of ferrocyanide waste simulants are presented as well as those from the first test in a hot cell using radioactive tank waste.

CONTENTS

1.0 INTRODUCTION	1
2.0 DESCRIPTION OF ACTIVITIES	2
2.1 ANALYSIS OF TANK WASTE SIMULANTS	2
2.2 ANALYSIS OF LOW MATERIAL	3
2.3 HOT CELL ACTIVITIES	4
3.0 FUTURE ACTIVITIES	4
4.0 REFERENCES	5

LIST OF TABLES

1. Summary of Mössbauer Spectrometer Parameters for Tank Waste Simulants.	3
---	---

1.0 INTRODUCTION

Mössbauer spectroscopy is a very sensitive and selective method that is capable of "seeing" iron in numerous different types of chemical environments. It is very sensitive to the local environment and can readily distinguish iron (II) from iron (III), and even far more subtle nuances around the iron atom. Mössbauer spectroscopy can also identify a large number of different mineralogical species if they contain iron in a different chemical environment. A recent development in this type of spectroscopy is the use of reflectance rather than transmission spectroscopy, thus allowing information to be gained in situ. Specifically this task activity is focusing on the detection of and differentiation between the ferro- and ferri-cyano complexes found within the Hanford Site tank waste.

The National Aeronautics and Space Administration (NASA) is developing a miniaturized Mössbauer spectrometer at the Johnson Space Center in Houston, Texas for use on various planets as part of the space program. Dr. Richard Morris is in charge of the NASA program and has been working with Westinghouse Hanford Company to adapt the miniature spectrometer so that it can be used to take measurements inside a waste tank liquid observation well (LOW)¹. Iron is a major constituent of ferrocyanide waste and although iron is also present as fission product, iron concentrations will be higher in tanks that received ferrocyanide waste in the 1950s. As an additional benefit this spectrometer also has the ability to perform x-ray fluorescence EDS (energy-dispersive spectroscopy). This technique is capable of doing qualitative elemental analysis.

The results of this task will also be of general use in the characterization of tank waste. For example, if iron (II) is found to be present, the presence of chromium (VI) is ruled out. The presence or absence of other specific chemical species may also be inferred. This technique will complement the ongoing Hanford Site efforts in the areas of infrared and UV-visible spectroscopy.

The physical and chemical nature of the iron within the ferrocyanide tank waste is needed to accurately assess the waste's composition. By knowing the iron concentration and species as a function of elevation, it should be possible to determine how much degradation (aging) of the ferrocyanide has occurred within the waste. This information supports the safe interim storage of the waste and final resolution of the Ferrocyanide Safety Issue.

The Mössbauer program represents a cooperative venture between Westinghouse Hanford Company, the U.S. Department of Energy, and NASA. This small task activity has been in place for approximately one year and is scheduled for completion by mid-year in fiscal year (FY) 1996.

¹ A liquid observation well is a drywell with a closed bottom end and is fabricated of a fiberglass-like material. The LOW fits through a tank riser and extends to the bottom of the tank.

2.0 DESCRIPTION OF ACTIVITIES

2.1 ANALYSIS OF TANK WASTE SIMULANTS

Ten samples of ferrocyanide waste simulants were analyzed by Mössbauer and reflectance spectroscopy in FY 1995. The Mössbauer parameters resulted from the isomer shift (IS) relative to metallic iron foil at room temperature, quadrupole splitting (QS), and hyperfine field (B_{hf}).

All Mössbauer spectra for the In-Farm flowsheet² and $\text{Na}_2\text{NiFe}(\text{CN})_6$ samples are characterized by a singlet whose Mössbauer parameters (see Table 1; average QS = -0.10 mm/s) are characteristic of low-spin iron (II) ferrocyanide compounds. No iron (III) is indicated by the Mössbauer data. The reflectivity spectra for all of these samples are characterized by well-defined band minima near 600 and 1000 nm, which can be attributed to electronic transitions of Ni (II). The low-spin Fe (II) is diamagnetic and will thus not have electronic transitions. The absorptions near 1400 and between 1700 and 2000 nm can be attributed to overtones and combination tones of OH^- and H_2O fundamental vibrations. The much lower reflectivity of the gel form of In-Farm-2, bottom portion simulant, compared to its dried equivalent is a consequence of the high water content of the gel which produces intense absorption with broad bands near 1400 and 1900 nm because of the water present. Essentially, the Mössbauer and reflectivity spectra of the In-Farm simulant samples mimic those for the $\text{Na}_2\text{NiFe}(\text{CN})_6$ sample.

The Mössbauer spectra of the T-Plant, U-Plant, and tank BY-104³ simulants are very different from those of the In-Farm simulants despite the fact that all of them except the tank BY-104 simulant have $\text{Na}_2\text{NiFe}(\text{CN})_6$ as an ingredient. An asymmetric doublet instead of a singlet is present. The sample of tank BY-104 simulant was fit by a doublet with areas constrained equally. Its Mössbauer parameters (see Table 1; IS = 0.31 mm/s and QS = 0.63 mm/s) are consistent with high-spin iron (III); that is, it is not a ferricyanide complex which is low-spin iron (III). Because all the other samples contain $\text{Na}_2\text{NiFe}(\text{CN})_6$ as an ingredient, a singlet and a doublet (with widths and areas constrained equally) were used in the fitting procedures. The Mössbauer parameters are summarized in Table 1. The average IS for the singlet is -0.15 mm/s, which implies low-spin iron (II) associated with the ferrocyanide complex anion. The average Mössbauer parameters for the doublet are IS = 0.38 mm/s and QS = 0.63 mm/s, which imply octahedrally-coordinated, high-spin Iron (III). The average relative area of the iron (III) doublet is 79%. Ferric iron (III) is an

² Three basic flowsheets were used in the 1950s to produce the ferrocyanide waste that was added to the tanks: In-Farm, U-Plant, and T-Plant. Physical and chemical properties of simulants produced for testing are found in Jeppson and Wong (1993).

³ Tank BY-104 simulant is a saltcake simulant produced to mimic the saltcake found in Hanford Site tank 241-BY-104. Saltcake does not contain any ferrocyanide which is a sludge material.

ingredient only for the tank BY-104 and T-Plant, top portion simulants. The mechanism for the formation of the iron (III) in the U-Plant simulants is not known.

Table 1. Summary of Mössbauer Spectrometer Parameters for Tank Waste Simulants.

Sample	Singlet IS	Singlet RA %	Doublet IS	Doublet QS	Doublet RA %	Comments
In-Farm-1T	-.09	100				Fe ⁺² CN
In-Farm-1B	-.10	100				Fe ⁺² CN
In-Farm-1R	-.10	100				Fe ⁺² CN
In-Farm-2T	-.10	100				Fe ⁺² CN
In-Farm-2B	-.10	100				Fe ⁺² CN
T-Plant T	-.17	15	.36	.67	85	Oct Fe ⁺³ , Fe ⁺² CN
U-Plant-1	-.13	27	.38	.60	73	Oct Fe ⁺³ , Fe ⁺² CN
U-Plant-2T	-.15	16	.36	.63	84	Oct Fe ⁺³ , Fe ⁺² CN
U-Plant-2B	-.13	26	.40	.62	74	Oct Fe ⁺³ , Fe ⁺² CN
BY-104			.31	.63	100	Oct Fe ⁺³
Na ₂ NiFe(CN) ₆	-.10	100				Fe ⁺² CN
K ₄ Fe(CN) ₆	-.08	100				Fe ⁺² CN
K ₃ Fe(CN) ₆			-.15	.26	100	Fe ⁺³ CN

2.2 ANALYSIS OF LOW MATERIAL

Samples of two Hanford Site LOW materials were sent to the Johnson Space Center in Houston, Texas for Mössbauer spectroscopy. Both of the LOW materials were found to contain magnetic iron as shown by the hyperfine splitting of the spectra obtained from the measurements. This is both bad and good. The presence of iron in the LOWs is bad, but the fact that the iron shows a significantly different spectrum from the tank simulants means

that it may be still possible to differentiate between the iron in the LOW from that in the tank waste.

Since the iron in the LOW materials is magnetic, its signal shows a six-fold splitting. The iron contained in the tank simulants shows a singlet line shifted slightly upfield from zero. Thus, the iron in the tank waste should still be discernable. However, the LOW material will attenuate the signal by a factor of ~ 100 because of the gamma ray traversing two wall thicknesses. A strong source and longer counting times will tend to obviate these considerations.

2.3 HOT CELL ACTIVITIES

Work within the hot cells commenced at the end of August 1955. Approximately four days were spent working in the hot cell. A number of core segment samples were available for measurement. Samples tested were from tanks 241-BY-110, 241-T-107, and 241-TY-104. These three tanks are all on the Ferrocyanide Watch List (Meacham et al. 1995). All samples were measured as received. In addition, samples from both tank 241-T-107 and 241-TY-104 were dried and then re-measured.

The only good data obtained was the spectra of hematite that was used to confirm that all the equipment was operating properly. Radiation had no apparent effect on the electronics at all.

The primary reason poor spectra were obtained was the fluorescence cause by radioactive strontium and yttrium present in the samples. The gamma-ray line for iron occurs at about 14.4 keV while those for strontium and yttrium occur at 14.1 keV and 14.9 keV, respectively. While looking at shifts in the 14.4 keV line (the Mössbauer effect) the presence of the other two nuclei cause fluorescence and thus obscure the Mössbauer effect. This should be easy to fix since cooling the detector slightly will improve its sensitivity.

Modifications are currently underway at the NASA Johnson Space Center to provide for cooling of the miniaturized Mössbauer spectrometer. The improved instrument should be ready for use toward the end of October or in early November 1955.

3.0 FUTURE ACTIVITIES

The test in the hot cells will be repeated early in FY 1996 once the improved detector is available. A candidate tank known to have received large quantities of ferrocyanide waste in the 1950s will be selected for the first LOW scan. Unfortunately, none of the tanks that received In-Farm flowsheet ferrocyanide waste have an LOW. Most of the BY Farm ferrocyanide tanks, tank 241-TX-118, and tank 241-TY-103 contain LOWs (Borsheim and Simpson 1991). Tank 241-TX-118 will not be selected because it only received a small amount of ferrocyanide.

For the LOW scan activity, the detector will be configured so that the instrument receives the gamma rays from the side rather than from the bottom end. After the successful completion of several LOW measurements, a final report will be written. This will be completed by mid-year in FY 1996.

4.0 REFERENCES

- Borsheim, G. L., and B. C. Simpson, 1991, *An Assessment of the Inventories of the Ferrocyanide Watch List Tanks*, WHC-SD-WM-ER-133, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- Jeppson, D. W., and J. J. Wong, 1993, *Ferrocyanide Waste Simulant Characterization*, WHC-EP-0631, Westinghouse Hanford Company, Richland, Washington.
- Meacham, J. E., R. J. Cash, and G. T. Dukelow, 1995, *Quarterly Report on the Ferrocyanide Safety Program for the Period Ending June 30, 1995*, WHC-EP-0474-17, Westinghouse Hanford Company, Richland, Washington.