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ENGINEERING DATA TRANSMITTAL

1. EDT № 612315

2. To: (Receiving Organization)	3. From: (Originating Organization)	4. Related EDT No.:
Distribution	TWRS Safety Engineering	N/A
5. Proj./Prog./Dept./Div.:	6. Cog. Engr.:	7. Purchase Order No.:
TWRS Safety Engineering	W. S. Callaway	N/A
8. Originator Remarks: This EDT is for approval of WHC-SD-WM-RPT-194, Rev. 0		9. Equip./Component No.: N/A
		10. System/Bldg./Facility: N/A
11. Receiver Remarks:		12. Major Assm. Dwg. No.: N/A
		13. Permit/Permit Application No.: N/A
		14. Required Response Date: N/A

15. DATA TRANSMITTED

(A) Item No.	(B) Document/Drawing No.	(C) Sheet No.	(D) Rev. No.	(E) Title or Description of Data Transmitted	(F) Approval Designator	(G) Reason for Transmittal	(H) Originator Disposition	(I) Receiver Disposition
1	WHC-SD-WM-RPT-194, Rev. 0		0	Scanning Electron Microscopic Analyses of Ferrocyanide Tank Wastes for the Ferrocyanide Safety Program FY 1995	N/A			

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	1. Approved	4 Reviewed no/comment
	2. Releaee	5. Post-Review	2. Approved w/comment	5. Reviewed w/comment
	3. Information	6. Dist. (Receipt Acknow. Required)	3. Disapproved w/comment	6. Receipt acknowledged

17. SIGNATURE/DISTRIBUTION
(See Approval Designator for required signatures)

(G) Reason	(H) Disp.	(J) Name (K) Signature (L) Date (M) MSIN	(J) Name (K) Signature (L) Date (M) MSIN	(G) Reason	(H) Disp.
1	1	Cog.Eng. W. S. Callaway W.S. Callaway 9/29/95			
1	1	Cog. Mgr. R. J. Cash R. J. Cash 9/29/95			
		QA			
		Safety			
		Env.			

18. W. S. Callaway W.S. Callaway 9/29/95
Signature of EDT Originator — Date

19. _____
Authorized Representative for Receiving Organization — Date

20. R. J. Cash R. J. Cash 9/29/95
Cognizant Manager — Date

21. DOE APPROVAL (if required) Ctrl. No.
[1] Approved
[ ] Approved w/comments
[ ] Disapproved w/comments

BD-7400-172-2 (04/94) GEF097

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OCT 03 1995

RELEASE AUTHORIZATION

Document Number:	WHC-SD-WM-RPT-194, REV 0
Document Title:	Scanning Electron Microscopic Analyses of Ferrocyanide Tank Wastes for the Ferrocyanide Safety Program
Release Date:	10/3/95

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 10/3/95

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SUPPORTING DOCUMENT

1. Total Pages 25 22

KMB 10/2/95

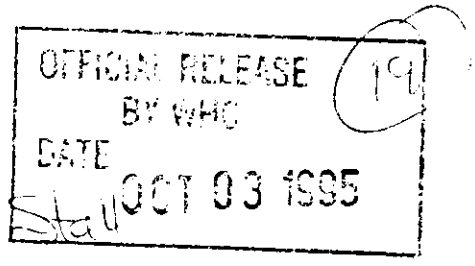
2. Title	3. Number	4. Rev No.
Scanning Electron Microscopic Analyses of Ferrocyanide Tank Wastes for the Ferrocyanide Safety Program	WHC-SD-WM-RPT-194	0

5. Key Words	6. Author
Ferrocyanide Safety Program Scanning Electron Microscopy Characterization	Name: W. S. Callaway W. S. Callaway Signature Organization/Charge Code N2C1L

7. Abstract

This is the Fiscal Year 1995 Annual Report on the progress of activities relating to the application of scanning electron microscopy in addressing the Ferrocyanide Safety Issue associated with Hanford Site high-level radioactive waste tanks. The status of the FY 1995 activities directed towards establishing facilities capable of providing SEM based micro-characterization of ferrocyanide tank wastes is described. A summary of key events in the SEM task over FY 1995 and target activities in FY 1996 are presented. A brief overview of the potential applications of computer controlled SEM analytical data in light of analyses of ferrocyanide simulants performed by an independent contractor is also presented.

8. RELEASE STAMP



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WHC-SD-WM-RPT-194
Revision 0

SCANNING ELECTRON MICROSCOPIC ANALYSES OF FERROCYANIDE TANK WASTES FOR THE FERROCYANIDE SAFETY PROGRAM - FY 1995 REPORT

W. S. Callaway

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

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SCANNING ELECTRON MICROSCOPIC ANALYSES OF FERROCYANIDE TANK WASTES FOR THE FERROCYANIDE SAFETY PROGRAM

FISCAL YEAR 1995 REPORT

ABSTRACT

This is the Fiscal Year 1995 Annual Report on the progress of activities relating to the application of scanning electron microscopy in addressing the Ferrocyanide Safety Issue associated with Hanford Site high-level radioactive waste tanks. The status of the FY 1995 activities directed towards establishing facilities capable of providing SEM based micro-characterization of ferrocyanide tank wastes is described. A summary of key events in the SEM task over FY 1995 and target activities in FY 1996 are presented. A brief overview of the potential applications of computer-controlled SEM analytical data in light of analyses of ferrocyanide simulants performed by an independent contractor is also presented.

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CONTENTS

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LIST OF TERMS

BSE	Backscattered Electron. The intensity of the BSE signal in an electron column instrument is directly proportional to the average Z value of the material upon which the probe beam is impinging.
CCSEM	Computer Controlled Scanning Electron Microscopy
DOE	U.S. Department of Energy
DOH	Department of Health
EDS	Energy Dispersive X-ray Spectroscopy. Elemental analysis technique which separates and quantitates analytical X-ray signals according to their energies. In this case, the beam of an electron column instrument is utilized as a specimen excitation source.
FTIR	Fourier Transform Infrared Spectrometry
FY	Fiscal Year
HTS	Hanford Technical Services
keV	Kilo electron-volt
Personal SEM™	Trademark for the computer controlled scanning electron microscope manufactured by R. J. Lee Instruments, Ltd. (Trafford, PA).
RCT	Radiological Control Technician
SAS	Special Analytical Studies - An organization within WHC
SEM	Scanning Electron Microscope/Microscopy
TWRS	Tank Waste Remediation System
USQ	Unreviewed Safety Question
WDOE	Washington State Department of Ecology
WHC	Westinghouse Hanford Company
XRF	X-Ray Fluorescence Spectrometry
Z	Atomic number

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1.0 INTRODUCTION

1.1 PURPOSE

This year-end report provides a status of activities underway related to the microanalysis of ferrocyanide tank waste materials by scanning electron microscopy (SEM). The SEM activities are being executed as part of the Ferrocyanide Safety Program at the Hanford Site (DOE 1994). This report describes activities which have been completed or initiated in fiscal year (FY) 1995.

1.2 BACKGROUND

The presence of ferro/ferricyanide and nitrate/nitrite salts in tank wastes (Meacham et al. 1995, DOE 1994) on the Hanford Site has been recognized as a potential safety issue. Westinghouse Hanford Company (WHC) has recognized the need for improved characterization of the radioactive ferrocyanide-based tank waste in support of safety, retrieval, and disposal programs. With a reliable characterization database available, scientists and engineers can adequately address the waste tank safety issues and interim safe storage. Characterization of the waste is also required to design appropriate retrieval and process equipment to remove and treat the Hanford high-level waste.

To this end, an extensive amount of modeling, physical testing, and chemical analysis data have been collected on tank waste simulants (Jeppson and Wong 1993). These data have also been supplemented by data from actual tank core samples and in-situ measurement data (Meacham et al. 1995). The Jeppson and Wong report demonstrated that under certain conditions of elevated temperature and little or no moisture a propagating exothermic reaction could occur in some of the simulant materials.

Safety criteria for the Ferrocyanide Watch List Tanks (Postma et al. 1994) have been developed based partially on such data. Postma et al. (1994) concluded that the Hanford Site Ferrocyanide Unreviewed Safety Question (USQ) could be closed and that the Ferrocyanide Safety Issue could be resolved with additional tank waste characterization. There also remains a need to assess the validity of the underlying data, the extent to which in situ waste deviate from the base inferences that have been drawn from simulant testings and significance of any deviations.

The Ferrocyanide Safety Program is attempting to resolve these questions by direct analysis of core samples extracted from selected ferrocyanide tanks. Under severe time constraints, the program must nevertheless produce data and technical interpretations sufficient to validate the physical basis for the current safety margins and establish the degree to which they are either too conservative or provide an inadequate margin of safety.

Microcharacterization of the waste materials by techniques such as SEM can serve two roles. First, it can provide a necessary physico-chemical framework to reconcile various bulk chemical and physical measurements. Microchemical, particle chemistry, particle size, and particle morphology information obtained through SEM measurements should further determination of the relationship(s) between bulk physical characteristics of the wastes (chemical composition, density, homogeneity, moisture content) and bulk waste properties (flammability, rheology, reactivity, drying rate). Second, microcharacterization can validate inferences about structure, precipitation and homogeneity derived from bulk physical and chemical measurement. The ability to more rigorously select the scale of measurement lends microcharacterization data a degree of specificity not accessible by conventional bulk analyses.

1.3 APPROACH

Demonstration of technology and initial ferrocyanide tank waste SEM measurements will utilize techniques originally developed for the analysis of gunshot residue particulates. The R. J. Lee Group, Inc. has performed analyses on several simulant samples utilizing these techniques (R. J. Lee Group 1993a, 1994). WHC has acquired SEM instrumentation and software specifically developed by R. J. Lee Instruments, Ltd. to facilitate CCSEM analyses of this type.

Initial analysis development measurements will utilize tank waste simulant samples. Simulant specimen preparation and SEM methods development activities will be carried out in WHC/SAS non-radiological facilities.

Initial measurements of ferrocyanide tank waste will focus on core samples archived in the WHC 222-S Laboratory facility. Specimen preparation activities will be carried out in the 222-S laboratory. SEM measurements will be performed in a facility at the WHC Weather Station complex meeting applicable radiological requirements (WHC 1994). Initial samples selected for CCSEM analyses will focus on core materials where previous bulk physical or chemical measurements have been of particular interest.

Sample(s) from at least one ferrocyanide tank core will be taken throughout the entire chain from hot cell sampling to CCSEM analysis before conclusion of the Ferrocyanide Safety Program SEM activity.

Initial data interpretation targets will include (1) correlation of sample particle size distributions and particle chemical compositions, (2) detection of target elemental components, and (3) comparison of particle sizes and morphologies determined from different tank waste samples. Given adequate data, interpretations and correlations will address both local variations within a given waste tank sample and variations between waste from different ferrocyanide tanks.

Because of the small size of the specimens actually introduced to the SEM specimen chamber (less than 1 to 2 mg), special attention will be given to establishing criteria to evaluate the applicability of CCSEM results to bulk sample characteristics. The degree to which this applicability may be enhanced by multiple specimen analysis, modifications of specimen preparation procedures and CCSEM analysis protocol will be evaluated.

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2.0 SIMULANT MICROCHARACTERIZATION ANALYSES

Two separate lots of six simulant samples each were submitted to the R. J. Lee Group, Inc. for microcharacterization. Four reports (R. J. Lee Group 1993a, 1993b, 1994; Lee et al. 1994) were generated detailing the results of the simulant microcharacterization analyses. Techniques employed by the R. J. Lee Group included X-ray diffraction (XRD), electron microprobe analysis, FTIR, and CCSEM. The simulant samples analyzed included:

WHC IDENTIFICATION	COLOR and TEXTURE
In-Farm-1	Green slurry
In-Farm-2	Green slurry
U-Plant-1	Olive green slurry
U-Plant-2-18	Olive brown slurry
U-Plant-2-19	Olive brown slurry
Na-Ferrocyanide	Yellow, translucent, granular powder
BY-104 Simulant Saltcake Feed	Brown, wet sediment
U-Plant-1 Cent. Solids	Olive green slurry
U-Plant-2 Top Cent. Solids	Dark green slurry
U-Plant-2 Bottom Cent. Solids	Dark green slurry
T-Plant Top Cent. Solids	Brown slurry
Impure $Na_2NiFe(CN)_6$	Green, granular powder

The completed analyses identified significant effects of variations in the starting chemistries on the resultant simulant reaction products, particle size and physical association. Comparison of earlier XRD data (Bryan et al. 1993) with the R. J. Lee XRD and FTIR measurements also suggests that some changes including hydration and oxidation have probably occurred in the simulants since manufacture. Generally, the results of the R. J. Lee simulants analyses indicate that waste microcharacterization may provide a basis for assessing (1) the variability in the tanks on a local basis, (2) the current physical state of the simulant and tank wastes, and (3) the expected tank waste conditions in the future (i.e., correlation of simulant and tank waste aging).

The CCSEM analyses were found to be particularly applicable in determining the particle by particle distribution of target elements (e.g., sodium, nickel, iron phosphorus, cesium, and bismuth) in the simulant samples. Use of a ternary diagram generator software package developed by the R. J. Lee Group, Inc. was particularly useful in displaying these distributions. For example, though cesium was added to the starting mixtures for both In-Farm-1 and In-Farm-2 a solid cesium phase was only observed in the In-Farm-1 simulant.

The absence of a cesium phase in the In-Farm-2 simulant may result from (1) pH effects on precipitation dynamics and/or (2) inhibition of cesium precipitation by calcium.

General trends in observed crystallite sizes were also noted in the CCSEM data. For example, the In-Farm-1 simulant was observed to have generally larger crystallites indicating relatively slow precipitation. The In-Farm-2 and U-Plant-2 simulants by contrast were observed to be finer grained suggesting more rapid initial precipitation or repeated precipitation and dissolution cycles.

3.0 WHC SCANNING ELECTRON MICROSCOPY ACTIVITIES

3.1 ACQUISITION OF SEM

Budgetary considerations; computer controlled, digital imaging capabilities; and the availability of fully integrated particulate microcharacterization software led to the selection of the R. J. Lee Instruments, Ltd., Personal SEM™[1] as the instrument of choice for the Ferrocyanide Safety Program SEM task activities.

3.1.1 Fiscal Year 1995 Activities

Procurement. Procurement activities for the acquisition of appropriate CCSEM instrumentation was initiated in the last quarter of FY 1994.

August 10, 1994: Requests for Proposal were issued to potential vendors.

September 22, 1994: A Purchase Order was awarded to the R. J. Lee Group, Inc. for the purchase of their Personal SEM™ CCSEM system with associated hardware, firmware, software and support accessories.

November 22, 1994: Original specified delivery date for the CCSEM system.

January 27, 1995: As a result of a series of manufacturing delays, CCSEM system not ready for shipment until late January 1995.

January 30, 1995: WHC cognizant engineer visits R. J. Lee facility January 30 through February 3, 1995 to perform and/or witness pre-shipment acceptance test measurements. Several deficiencies identified and reported to vendor.

February 22, 1995: R. J. Lee CCSEM system received on Hanford Site.

March 13, 1995: R. J. Lee representative arrives on Hanford Site to install CCSEM system at WHC Weather Station Complex.

CCSEM Installation and Testing. The R. J. Lee CCSEM instrument has experienced a series of hardware and software failures which have prevented completion of the installation and testing targets. Major difficulties have included:

[1]Trademark of R. J. Lee Instruments, LTD., Trafford, Pennsylvania.

Imaging Errors: Inaccuracies in magnification calibration and imaging accuracy first identified at vendor facility (January 1995) were found to still be present at installation. Problems apparently resolved with system modifications performed June 6-7, 1995.

Vacuum System: Four system turbomolecular vacuum pumps failed, were returned and replaced over the period of March 14 through August 2, 1995. Problem apparently resolved with installation of fifth pump and replacement of other vacuum system components.

Specimen Stages: Both the manual stage (required for medium to high magnification imaging) and the motorized stage (required for CCSEM particulate analysis protocols) have malfunctioned. Motorized stage was returned to vendor in late August, 1995. Repaired motorized stage received September 6, 1995 and is currently operating acceptably. The manual stage has been returned to the vendor twice and is currently undergoing repairs.

Vibrational Noise: Imaging performance of CCSEM system has been degraded by vibrational noise from numerous sources since installation. Noise sources identified and repaired have included defective vacuum turbo pumps, defective cooling fans, defective stage drive motors and poor turbo pump to backing pump linkage. As of termination of last vendor visit on September 15, 1995, optimum noise minimization seems to have been achieved.

Software: Numerous problems with system software have been encountered and largely resolved through issue of vendor updates or modifications. Only two outstanding software issues to be resolved are currently in vendor's shop.

CCSEM System Upgrade. An upgrade package for the CCSEM system was procured.

The upgrade package:

- Acquired data presentation software developed for presentation of CCSEM particulate microchemical analysis data,
- Acquired a major enhancement in the EDS system software package,
- Upgraded the off-line PC transportable storage media to a level identical to that of the CCSEM instrument computer, and
- Provided WHC access to a magnetic media data base containing data generated during analysis of simulant samples by the R. J. Lee Group, Inc.

The Purchase Requisition for this upgrade was completed April 5, 1995. A Purchase Order to the R. J. Lee Group, Inc. was awarded May 10, 1995. The upgrade package items were received on the Hanford Site August 2, 1995.

Anti-Vibration Mounts. Appropriate vibration dampening mounts for the R. J. Lee SEM system were identified and procured. Slight modification of the mounts (Barry Controls STABL-LEVL[2] SLM Series Air Mounts) were completed to facilitate mounting on the SEM chassis. Installation was completed and reduction of ground mediated, medium to high frequency environmental noise was verified by July 21, 1995.

3.1.2 Actions Planned

- As soon as remaining SEM system hardware and software issues are resolved: Complete "once-through" of all SEM control operations and verify accessibility of all applications software.
- Perform baseline measurements defining basic SEM operational parameters using standards and test materials.
- Complete installation of system upgrade items on off-line data processor and verify accessibility and/or operation of all items.
- Fully test the particulate microcharacterization software package and all associated CCSEM hardware systems to verify proper operation.

3.2 SET-UP OF SEM FACILITY

A facility in which to establish the SEM and carry out the CCSEM analyses of simulant and ferrocyanide tank waste must be established. The facility must

- Adequately support operation of the SEM,
- Meet applicable regulations and requirements associated with the analysis of the radioactive tank wastes,
- Meet applicable WDOE and DOH regulations and requirements associated with emissions and worker safety, and
- Provide minimal specimen handling, specimen storage and data processing facilities.

[2]Trademark of Barry Controls, Brighton, Massachusetts.

The lack of suitable fixed-laboratory facilities on Site and the extremely fluid state of Hanford Site contractor and personnel during FY 1995 has made establishment of a suitable facility problematic.

3.2.1 Fiscal Year 1995 Activities

Cold Testing Facility. Facilities for non-radiological set-up and method development activities were identified in the WHC Weather Station complex (622-G/17). The SEM system was installed in this facility on March 13, 1995.

Radiological Analysis: Fixed Facility. Numerous potential fixed laboratory facilities in the 300, 100-K, 200-W, and 600 (WSCF) Areas of the Hanford Site were investigated. One potential off-site facility was also evaluated. None of these facilities were found to be suitable because of a combination of budgetary, facility leasing, support utility deficiency and radiological control concerns.

Radiological Analysis: Mobile Facility. A 2.5 X 6 meter trailer has been identified (HO-64-5181) and is currently being outfitted in preparation for service as the SEM Microcharacterization facility. The SEM trailer will be located at the Weather Station complex. It is not anticipated that the trailer facility will be transferred to another location with the SEM instrumentation in place.

Appropriate bench space and storage cabinets have been identified in WHC Excess and delivery is anticipated before the close of FY 1995. A portable, recirculating, HEPA capable, laboratory hood unit has also been located and is being refurbished for operation. This hood unit will provide a contamination containment area for open handling of radioactive, tank waste specimens.

SEM Facility: Radiological Control Support. The Radiological Control Organization group in the 200-W area was identified as the cognizant RC organization. Numerous meetings have been held to discuss radiological concerns relating to CCSEM analysis protocols, SEM trailer design and outfitting, issues pursuant to preparation of a SEM Radiological Work Permit, and, proper posting and temporary storage of SEM tank waste specimens.

A member of the WHC SAS organization who was temporarily attached to the ferrocyanide SEM task group to take the lead in resolving all radiological control issues was directly involved in the recent WHC Reduction of Force. Identification of replacement personnel is underway.

Procurement. All SEM maintenance items and operational consumables and support facilities equipment and consumables anticipated to be required to complete the targeted ferrocyanide SEM analysis activities have been procured or ordered as of the close of FY 1995.

3.2.2 Actions Planned

- Complete the outfitting of the SEM Microcharacterization trailer facility.
- Verify that the outfitted trailer and proposed layouts of SEM equipment and support accessories satisfy all radiological concerns of cognizant Radiological Control personnel.
- Obtain a Radiological Work Permit to cover SEM analytical activities in the Microcharacterization trailer.
- Finalize arrangements with cognizant Radiological Control group to obtain the necessary level of RCT coverage and support.
- Verify that the Microcharacterization trailer facility meets applicable WDOE and DOH requirements (e.g., ventilation and air emissions concerns).
- Transfer SEM system and required accessories in Microcharacterization trailer and verify operation of all systems. Repeat and document all baseline measurements.

3.3 TANK WASTE SPECIMEN PREPARATION FACILITY

Both the nature of the target analyses and the radioactive nature of tank waste present challenges to development of adequate SEM specimen preparation procedures. Development efforts based on preparation of simulant specimens will be carried out in non-radiological facilities in the WHC Weather Station complex. Preparation of specimens of the radioactive ferrocyanide tank waste will be carried out in hood(s) in the WHC 222-S laboratory complex.

3.3.1 Fiscal Year 1995 Activities

Procurement. All SEM specimen preparation instrumentation, equipment and consumables anticipated to be required to complete the targeted, ferrocyanide SEM microcharacterization activities have been procured or ordered as of the end of FY 1995.

Duplicates of instrumentation and equipment required for preparation of CCSEM particulate analysis specimens were ordered. The duplicate equipment will

- Allow non-radioactive, specimen preparation, development work to proceed outside of the constraints of a radiologically controlled area,
- Provide identical facilities for preparation of non-radioactive, simulant and standard material specimens, and, radioactive ferrocyanide tank waste specimens,
- Facilitate "Walk-Through" training in SEM specimen preparation protocols and techniques, and,
- Provide back-ups should equipment located within a radiological zone fail prior to completion of targeted ferrocyanide SEM analyses.

Cold Sample Preparation Facility. An area for preparation of non-radiological SEM specimens and test materials was identified and established in building MO-944 in the Weather Station complex.

Initial specimen preparation development activities have been initiated in this facility. To the extent possible, the SEM specimen preparation station in this cold facility is modified to match any operational restrictions which are found to be required for operation in a radiologically controlled area.

Radioactive Sample Preparation Facility. Arrangements are being formalized to perform the specimen preparation activities for the radioactive, ferrocyanide tank waste samples in hood space in the 222-S laboratory complex. The identified hood space is controlled by the TWRS Tank Characterization Program group. Basic filtration station equipment has been transferred to the identified hood space.

Basic 222-S Facility training and application for appropriate supplemental dosimetry has been completed by all involved ferrocyanide SEM task personnel.

The applicable Radiological Work Permit covering the SEM specimen preparation activities in the 222-S facility has been identified (S-401) and evaluation of the impact of radiological control limits and procedures on SEM preparation activities is being evaluated.

A member of the WHC SAS organization, who was attached to the ferrocyanide SEM task group to take the lead in resolving all ferrocyanide SEM specimen preparation issues, was directly involved in the recent WHC Reduction of Force. Redistribution of these activities and identification of possible, replacement personnel is underway.

3.3.2 Actions Planned

- Finalize arrangements necessary to transfer samples from the 222-S hot cell area to the specimen preparation hood area.
- Finalize arrangements with 222-S Radiological Control personnel to obtain appropriate coverage of specimen preparation activities.
- Finalize arrangements for performing specimen preparation activities in the 222-S facility and complete the transfer of the necessary instrumentation and equipment.
- Finalize arrangements necessary to remove prepared SEM specimens from the 222-S facility.
- Finalize arrangements necessary to transport prepared SEM specimens from the 222-S facility to the SEM facility in the Weather Station complex.

- Finalize arrangements for the return of the SEM specimens to the 222-S facility and/or their proper storage or disposal.

3.4 ANALYTICAL PROTOCOL

Successful development of a CCSEM analytical protocol targeted to micro- characterization of ferrocyanide tank waste will require that the following areas be addressed

- Instrument QA/QC monitoring and control,
- Finalization of an applicable specimen preparation procedure which can be executed in a radiologically controlled environment,
- Final definition of target, elemental analytes and target particle size ranges,
- Definition of the degree of analysis standardization practicable and/or required, and
- Determination of specific data interpretation objectives and appropriate presentation formats.

3.4.1 Instrument Monitoring

FY 1995 Activities. A suite of test materials has been assembled to enable the verification and monitoring of basic SEM operational characteristics such as beam spot size, beam current, resolution, magnification calibration, orthogonality and energy calibration of the EDS system.

Actions Planned. After final verification of the complete operational readiness of the R. J. Lee SEM system,

- Baseline measurements of the above properties will be made and documented, and,
- Optimum specimens for routine QA/QC measurements will be selected and the frequencies and protocols for those measurements developed and documented.

3.4.2 Specimen Preparation

Preparation of suitable specimens for CCSEM analysis will be the data quality limiting step. Special care must be taken to preserve important sample components and present them to the SEM in such a manner that the greatest quantity of useful, unbiased, analytical data may be obtained from each measurement run. The small size of the specimens actually presented to the SEM for analysis ($<$ 1 to 2 mg) demands that consideration also be given to representative sub-sampling and the degree to which microcharacterization results may be extrapolated to infer bulk sample properties.

FY 1995 Activities. Two days were spent at the R. J. Lee Group facilities in Monroeville, PA receiving training in their methods for preparation of finely divided solid samples for

SEM particulate analysis. Several discussions were held concerning optional preparation techniques and the use of various solvents, mounting and filter membrane media and specimen stub materials. The specimen preparation targeted for initial ferrocyanide program SEM measurements is based on the R. J. Lee procedure with some modification to accommodate radiological concerns.

A preliminary draft of the proposed specimen preparation procedure was prepared and submitted to WHC 222-S personnel for safety and radiological evaluation. The proposed procedure involves filtration of very dilute isopropanol suspensions of tank waste onto 0.1 micrometer pore size, polycarbonate, filter membranes. The membranes are then appropriately trimmed and affixed to carbon planchets which are attached to 25 mm diameter, aluminum, SEM specimen stubs. A thin coat of carbon is then applied using an evaporative coater (Cressington Model 108[3] Carbon Coater). Modification of this draft procedure in order to (1) respond to 222-S comments, (2) optimize the representativeness and quality of the prepared SEM specimens, and (3) minimize the radiation dose received by personnel is in progress.

Actions Planned.

1. Finalize and document a CCSEM specimen preparation protocol for ferrocyanide tank waste and simulant materials optimizing

   - Representativeness of the sub-sample taken,
   - Evenness and control of the specimen loading of the filter membranes,
   - Stabilization of the tank waste particulates on the filter membrane supports,
   - Reproducibility of the specimen preparation,
   - Practicability of the procedure in a radiological environment, and
   - Personnel safety and radiological ALARA concerns.

2. Finalize design and fabrication of a specimen holder plate for attachment to the SEM, motorized stage, sample table. Evaluate the usefulness and cost effectiveness of the use of the specimen holder plate(s) as a specimen transport device.

3.4.3 Definition of Target Analyses

Definition of the initial CCSEM microcharacterization targets will basically involve

- Determine of a suite of elemental analytes of interest with atomic numbers greater than that of boron,

[3]Trademark of Cressington Scientific Instruments, Inc., Cranberry Township, Pennsylvania.

- Determination whether bulk elemental components or higher Z minor components are of predominant interest,
- Determination of which possible correlations of elemental components (or derived components based on elemental analytes) are of particular interest, and
- Determination of the range of particle sizes of interest or accessible with the Personal SEM™ instrumentation.

FY 1995 Activities. Review of historical data describing chemical composition of tank wastes (De Lorenzo 1994, Meacham et al. 1995) suggests that the initial elemental analyte targets may be selected from the following:

PRIMARY INTEREST

C	P	Sr
N	Ca	Zr
O	Fe	Cs
Na	Ni	Bi

MINOR COMPONENTS OR SECONDARY INTEREST

F	Mn	Hg
Al	Co	Pb
Si	As	Th
Cl	Se	U
K	Ag	Pu
Cr	Cd	Am

For the immediate purpose of performing the ferrocyanide SEM analyses, the target analytes will be C, N, O, P, Na, Fe, Ni and Cs. Correlations of the distributions of these elements with waste particle size will directly address the issue of the presence or absence of a discrete Na,Ni-Ferrocyanide phase in tank waste and the crystallite sizes of such phases should they exist.

Discussions with R. J. Lee Group personnel have suggested that some of the medium to high Z components which may also be of interest can be more effectively measured by setting up separate analysis programs which discriminate against the detection of particles containing only the lower Z, bulk elemental components.

Initial measurements with the Personal SEM™ instrument suggests that the lower limit of particle sizes from which meaningful data may be obtained in a global particulate analysis is approximately 0.2 micrometers. Particles with mean diameters significantly greater than 200 micrometers are to load and retain on the membrane filters. Previous work on simulant samples (R. J. Lee Group 1993a, 1994) indicated that the bulk of the crystallite sizes observed in the simulant samples fall within the range of 0.2 to 100 micrometers.

Actions Planned. Continue to refine the choices of target elemental analytes and target crystallite size ranges as instrumental capabilities are more firmly defined during method development measurements.

3.4.4 Standardization

FY 1995 Activities. An elemental microanalysis standard block and a Faraday Cage were acquired for standardization of the measurement of elemental X-ray signals and for measurement of the stability of the beam current impinging on the specimen respectively.

Actions Planned.

- Determine the time frame over which beam current is sufficiently stable to provide internally consistent analyses,
- Define the semi-quantitative relationship between beam spot size and beam current,
- Determine the approximate correlation between % Spot Size and actual electron beam diameter,
- Define a reproducible procedure for setting detector thresholds for the BSE detector based on the Z values of desired analytes,
- Determine minimum counting times required to acquire significant X-ray signals from potential elemental analytes of interest
- Determine the required frequency of energy calibration of the EDS system, and
- Determine the minimum suite of standardization measurements which must be performed with each CCSEM analysis run.

3.4.5 Data Interpretation

FY 1995 Activities. Actions were completed to acquire the capabilities to manipulate and display CCSEM particulate microcharacterization data in a manner similar to that employed by the R. J. Lee Group, Inc. in their reporting of simulant analyses results (R. J. Lee Group 1993a, 1994). Specifically,

- The proprietary, R. J. Lee Ternary Diagram Generator program was acquired and will be installed on an off-line data processing station. Use of this program allows clear display of microchemical correlations between three elemental analytes (or derived

nodes) for the large numbers of individual particles analyzed for each CCSEM specimen analysis run.

- A 230 Mb magneto-optical drive was acquired and will be installed in the off-line data processing station. An identical drive is located in the SEM console. Addition of this drive will facilitate transfer of data between the SEM console and off-line PC's.

This upgrade of the off-line, data processing station will allow sophisticated data processing and display software to be located on the off-line computer. Sophisticated data and image output peripherals will also be able to be located outside of any radiological areas associated with the actual SEM analysis facility.

Actions Planned.

- Complete installation of above upgrade items in off-line data processor.
- Complete self-training in use of Ternary Diagram Generator.

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4.0 ACTIVITY SCHEDULES

4.1 FISCAL YEAR 1995

Because of the instrumentation and facility difficulties described in Sections 3.1 and 3.2, FY 1995 SEM Task Milestones (Meacham et al. 1995) were not completely met. Milestones and final status are as follows:

- **May 31, 1995.** Westinghouse Hanford Company installs and completes operational acceptance tests on SEM system.

  Milestone Status. Basic installation of the R. J. Lee Instruments Personal SEM™ was completed the week of June 9, 1995. A series of instrument hardware and software problems have prevented completion of basic acceptance tests. Several issues were successfully resolved during vendor repair visit of September 5 - 15, 1995. Balance of issues may be resolved when SEM components currently under repair at vendor facility are returned.

- **September 29, 1995.** Westinghouse Hanford Company issues a report, available for public release, on SEM program results for FY 1995.

  Milestone Status. This FY 1995 Annual Report has been prepared in fulfillment of this milestone.

4.2 FISCAL YEAR 1996

The Ferrocyanide Safety Program SEM activity will be continued in FY 1996. Interim activity targets include:

- **January 19, 1996.** Westinghouse Hanford Company carries out CCSEM analyses of ferrocyanide tank waste samples.

- **February 29, 1996.** Westinghouse Hanford Company issues a report, available for public release, on SEM activity results.

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5.0 REFERENCES

Bryan, S. A., K. H. Pool, S. L. Bryan, R. L. Sell, L. M. P. Thomas, and B. D. Lerner, 1993, *Ferrocyanide Safety Project: Task 3.5, Cyanide Species Analytical Methods Development - FY 1992 Annual Report*, PNL-8399, Pacific Northwest Laboratory, Richland, Washington.

De Lorenzo, D. S., A. T. DiCenso, D. B. Hiller, K. W. Johnson, J. H. Rutherford, D. J. Smith, and B. C. Simpson, 1994, *Tank Characterization Reference Guide*, WHC-SD-WM-TI-648, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

DOE, 1994, *Program Plan for Resolution of the Ferrocyanide Waste Tank Safety Issue at the Hanford Site*, DOE/RL-94-110, Rev. 1, U.S. Department of Energy, Richland Operations Office, 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.

Postma, A. K., J. E. Meacham, G. S. Barney, G. L. Borsheim, R. J. Cash, M. D. Crippen, D. R. Dickinson, J. M. Grigsby, D. W. Jeppson, M. Kummerer, J. M. McLaren, C. S. Simmons, and B. C. Simpson, 1994, *Ferrocyanide Safety Program: Safety Criteria for Ferrocyanide Watch List Tanks*, WHC-EP-0691, Westinghouse Hanford Company, Richland, Washington.

Lee, R. J., G. A. Cooke, and S. K. Kennedy, 1994, *Electron Beam, X-Ray Diffraction and Spectral Studies of Simulated Sludge Samples*, R. J. Lee Group, Inc., Monroeville, Pennsylvania.

R. J. Lee Group, 1993a, *Electron Beam and X-Ray Analyses of Samples for Westinghouse Hanford Company*, Project No. GAH309365, R. J. Lee Group, Inc., Monroeville, Pennsylvania.

R. J. Lee Group, 1993b, *Further Discussion of Electron Beam and X-Ray Analyses of Samples for Westinghouse Hanford Company*, Project No. GAH309365, R. J. Lee Group, Inc., Monroeville, Pennsylvania.

R. J. Lee Group, 1994, *Electron Beam and X-Ray Analyses of Samples for Westinghouse Hanford Company*, Project No. GAH409415, R. J. Lee Group, Inc., Monroeville, Pennsylvania.

WHC, 1994, *Hanford Site Radiological Control Manual*, HSRCM-1, Rev. 2, HSRCM Project, Westinghouse Hanford Company, Richland, Washington.