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16 KEY

Impact Level (F)	Reason for Transmittal (G)	Disposition (H) & (I)
1, 2, 3, or 4 see MRP 5.43 and EP-1.7	1. Approval 2. Release 3. Information 4. Review 5. Post-Review 6. Dist (Receipt Acknow. Required)	1. Approved 2. Approved w/comment 3. Disapproved w/comment 4. Reviewed no/comment 5. Reviewed w/comment 6. Receipt acknowledged

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1	1	Cog./Proj. Eng DM Nguyen	<i>DM Nguyen</i>	6/19/89							
1	1	Cog./Proj. Eng Mgr. NW Kirch	<i>NW Kirch</i>	6/19/89							
1	1	QA M. H. Grandjean	<i>M. H. Grandjean</i>	7/5/89							
1	1	Safety KJ Moss	<i>KJ Moss</i>	7-7-89							

18.

DM Nguyen 6/19/89
Signature of EDT
Originator Date

19

NW Kirch 6-19-89
Authorized Representative
for Receiving Organization Date

20.

NW Kirch 6-19-89
Cognizant/Project
Engineer's Manager Date

21. DOE APPROVAL (if required)

Ltr No. _____
☐ Approved
☐ Approved w/comments
☐ Disapproved w/comments

FERROCYANIDE SAFETY STUDY
TEST PLAN

PACIFIC NORTHWEST LABORATORY

MAY 1989

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FERROCYANIDE SAFETY STUDY
TEST PLAN

WESTINGHOUSE HANFORD COMPANY

MAY 1989

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SST-TP-FECN-1, Rev. 0
May 26, 1989
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FERROCYANIDE SAFETY STUDY
TEST PLAN

1.0 INTRODUCTION

This test plan describes the work which will be done as part of the Pacific Northwest Laboratory's (PNL) Single Shell Tank (SST) Technology Support Program, Project 13924, under the Ferrocyanide Safety Study Task. The task is composed of three subtasks: (1) the energetics laboratory study, (2) the Large-Scale Explosion Study, and (3) the revision of the unclassified PNL report Complexant Stability Investigation Task 1, Ferrocyanide Solids, PNL-5441.

2.0 OBJECTIVE

The overall objective of this study is to investigate the potentially rapid reactions between the ferrocyanide-containing salts, present in the SST's, and oxidants, such as nitrate, also present in the SST's.

The objective of the energetics subtask is to investigate, on a screening basis, SST operational and compositional parameters which could affect the reaction between nickel cesium ferrocyanide, the expected form of cyanide in the SST, and nitrates and/or the nitrate radiolysis product nitrite.

The objective of the large-scale explosion study is to independently confirm the results of the PNL laboratory-scale experiments and to determine the explosive behavior of a large sample of ferrocyanide and oxidant.

The objective of the PNL-5441 revision subtask is to revise the complexant stability report, PNL-5441, to provide a current overview of the Ferrocyanide safety issue and provide information to permit establishment of guidelines for SST management.

3.0 SCOPE

The objective of the energetics subtask will be met by a series of screening experiments using small-scale explosion tests and the thermal analytical techniques: differential scanning calorimetry (DSC), scanning thermogravimetry (STG). The operational and compositional parameters which will be investigated are temperature, waste constituents which could act as catalysts or initiators, nitrate to nitrite ratio, and nitrate/nitrite to ferrocyanide ratio. If funding permits, the effect of non-participating waste constituents may be studied, and/or the kinetic parameters and/or the minimum critical explosion temperature for a specific reaction mixture may be estimated. PNL will prepare a report for public release as a PNL document.

The objective of the large-scale explosion subtask will be accomplished in two phases. In the first phase, Los Alamos National Laboratory (LANL) is scheduled to perform a series of small-scale tests in preparation for performing phase 2, a large-scale explosion test. The Pacific Northwest Laboratory (PNL) will provide LANL with the reaction materials and mixture composition for testing and will interface with LANL experimental personnel. The work will be accomplished via a subcontract between PNL and LANL. PNL will incorporate the results of the LANL reports into the PNL document reporting the results of the PNL laboratory experimental program.

The objective of the PNL-5441 revision will be met by PNL preparing a revised version of the unclassified PNL report Complexant Stability Investigation Task 1, Ferrocyanide Solids, by LL Burger. The new report will include the results of the other two subtasks.

4.0 TASK DEFINITION

This section describes the activities which will be accomplished in the Ferrocyanide Safety Study by subtask. Task Management activities include preparation of monthly reports, the statement of work, test plan, QA plan, waste management plan, technical procedures, safe operating procedures, attendance at program meetings, and meeting with WHC personnel.

4.1 Energetics Study

The Energetics Study will consist of a series of experiments using small-scale explosion (SSX) tests and DSC and STG. Each experiment will be performed in duplicate for confirmation. This experimental study will be comprised of 5 stages.

The first stage of the study will be to evaluate the effect of temperature using nitrate/nitrite eutectics to reduce the melting point below 200°C. This will identify a medium which will provide intimate contact and enhance the interaction between reactants and eliminate physical state as a variable. Also in subsequent stages the use of a low melting point medium will allow identification of the effects of the parameters of interest. Three eutectics will be investigated.

In the second stage the effect of the nitrate to nitrite ratio will be investigated for the range 0 to 0.8. Work performed in FY 88 indicated that the reaction between ferrocyanide and nitrite was more rapid than when nitrate was the oxidant. Three levels of the ratio will be tested.

In the third stage we will evaluate the effect of the five potential catalysts or initiators: ammonium nitrate, hydroxide ion, nickelous ion, EDTA, and TBP/NPH. Ammonium nitrate reacts with itself

exothermally and could act as an initiator for the ferrocyanide-nitrate reaction. Hydroxide ion could cause release of free cyanide ion into the melt which could be more reactive. Nickelous ion has been observed to act as an oxidation catalyst in aqueous systems. EDTA is an organic material which could be oxidized if the temperature increases and thus could initiate the ferrocyanide oxidation; EDTA also is a good complexant and might free the cyanide. TBP/NPH is an organic mixture which could be present in the tanks and could be oxidized when heated. Two concentrations of each catalyst/initiator will be tested.

In the fourth stage, the effect of the oxidant to ferrocyanide ratio will be investigated using only the SSX test. The reaction will occur independently of the amount of oxidant present, however, excess oxidant may have sufficient heat capacity to dissipate the energy released by the reaction without exploding. Three levels of the ratio will be investigated in the range 1.5 to 5 times stoichiometry.

If funding permits, additional stages to determine the affect of non-participating waste constituents, and to measure kinetic parameters and the minimum explosion temperature for a specific mixture will be performed. The non-participating waste constituents to be tested at two concentrations will be alumina and sodium carbonate. The kinetic parameters in the Arrhenius equation will be estimated by performing a series of three isothermal thermogravimetric analyses (ITG). The minimum explosion temperature will be estimated by performing a series of three time-to-explosion experiments using the SSX test procedure.

The constituents selected for stage 3 are based in part on the following:

SD-TI-RE-185, Data Transmittal Package for 241-TY-101 Waste Tank Characterization, RL Weiss and EM Mauss, 1987.

SD-TI-RE-184, Data Transmittal Package for 241-TY-103 Waste Tank Characterization, RL Weiss and EM Mauss, 1987.

Memo, 12715-ASL88-067, "Analysis of Archived Samples from Tanks 241-TY-101 and 241-TY-103 for Total Cyanide", WI Winters to DM Nguyen, 1988.

Memo, 13314-89-025, "Data Analysis of Conditions in Single-Shell Tanks Suspected of Containing Ferrocyanide, " DM Nguyen to NW Kirch, 1989.

4.2 Large-Scale Explosion Test

PNL will be responsible for coordinating and providing technical guidance to LANL; LANL will perform the actual experimental work.

PNL will select the reaction mixture, provide the reaction components and coordinate the transportation, interface with LANL experimental personnel, and incorporate the LANL report into the PNL document describing the results of the energetics study. Included in this activity is travel to LANL to discuss the tests with cognizant personnel.

4.3 Revision of PNL-5441

PNL-5441 will be revised to expand the history of the use of ferrocyanide as a complexant in the SSTs, and will include the results of the PNL energetics study and the LANL large-scale explosion test.

5.0 PRODUCTS

The product of the Energetics Study and the Large-Scale Explosion Study will be a PNL document cleared for release to the public.

The product of the Revision of PNL-5441 will be a PNL document cleared for release to the public.

6.0 PERSONNEL

It is expected that RD Scheele will act as the Task Manager, LL Burger and RD Scheele will serve as the Principal Investigators and Authors, and DL Alexander will be the Technician.

7.0 TEST PROGRAM PREREQUISITES & REQUIREMENTS

7.1 Prerequisites

Personnel Qualifications

The Principal Investigator will have had experience performing and interpreting thermoanalytical results.

Safety Considerations

Quantities of the ferrocyanide will be limited to prevent any hazardous explosions. In the small-scale explosion experiments the amount of ferrocyanide will be limited to < 50 mg and in the thermal analysis experiments the amount of ferrocyanide will be limited to < 10 mg. In addition in the small-scale explosion experiments a plexiglass shield, leather gloves, and tongs will be used when handling heated reaction vessels and during the tests themselves.

Transportation of materials to LANL for the small-scale tests and for the large-scale test will be coordinated with PNL Safety and Transportation personnel. It is anticipated that the materials will be transported to LANL in their special containers.

Measuring and Test Equipment (MT&E)

The following measurements are critical to the success of the work:

- . Temperature (Digital Thermometer/thermocouple, $\pm 2^{\circ}\text{C}$)
- . Temperature (Differential Scanning Calorimeter (DSC), $\pm 5^{\circ}\text{C}$)
- . Temperature (Thermogravimeter (TG), $\pm 2\%$)
- . Mass (Thermogravimeter (TG), $\pm 0.01\text{ mg}$ and Analytical Balance, $\pm 0.1\text{ mg}$)
- . Enthalpy (Differential Scanning Calorimeter (DSC), $\pm 5\%$)

The following equipment will be used for the work:

- . Digital thermometer and thermocouple for small-scale explosion tests which are calibrated on a yearly basis by the Hanford Standards Laboratory.
- . TG and DSC are user calibrated. The calibration will be checked on a monthly basis by using vendor supplied standards. The equipment will be operated according to vendor supplied operations manuals.
- . Analytical Balance capable of measuring 0.1 mg and calibrated on a quarterly basis by the Hanford Standards Laboratory.

Requirements

Pretest Verification

Prior to use the calibrations of the TG and DSC will be confirmed using vendor supplied standards.

Expected Results/Acceptance Criteria

The measurements expected from the DSC studies are the onset temperature, the starting reaction temperature, how long the reaction takes at a given heating rate, the reaction enthalpy, and whether the reaction is exothermic or endothermic. Depending on the complexity of the reaction, these measurements may be quantitative, in any case, the DSC will provide a qualitative measure of when the reaction begins, and how long it takes at a given heating rate. These results will allow a comparison of the effects of different parameters. Interpretation of the results will be supplemented by the TG studies.

The measurements expected from the TG studies will be the onset temperature, the reaction temperature range, and the mass change for a reaction. Depending on the complexity of the reaction, these measurements

will indicate, at least qualitatively, when the reaction begins, how long it will take at a given heating rate, and possibly some indication of the reaction mechanism.

The results expected from the small-scale explosion tests are whether the reaction mixture explodes at a temperature and the time to explosion at a temperature.

Criteria for acceptance of the data will be based on the duplicate analyses performed and compared; a third analysis will be performed if significant differences occur. The discordant analysis will be discarded.

Documentation

The results of all experiments will be recorded in a laboratory records book (LRB). The analyses from each DSC and TG analysis will be saved on flexible diskettes and a hard copy put into the LRB. When filled or at the end of the studies, the flexible diskette will be placed in the Task record files.

Change Control and Test Modifications

This test plan provides a framework for accomplishing the objectives of the Ferrocyanide Safety Study. Because of the investigative nature of the energetics subtask, the principal investigators are free to follow paths that the results or additional information, not available at this time, lead them. Modifications to this test plan which delete a portion of the research described in the Test Plan will require review and approval equivalent to that required for the original. Changes in scope, cost or schedule require the approval of the line manager, project manager and customer.

Data Review

The principal investigator is responsible for analyzing and reviewing the results of the experiments. The EVALUATOR will subsequently review the results. The EVALUATOR shall document the evaluation by dated signature on the test results documentation. For this Task when RD Scheele is the principal investigator, LL Burger will be the EVALUATOR and vice versa. If either LL Burger or RD Scheele should become disabled or no longer work for PNL an alternate EVALUATOR will be appointed by the PROJECT MANAGER.

Test Instructions

The COGNIZANT SCIENTIST is responsible for providing test instructions to the TECHNICIAN.

Applicable Test Procedures and Manuals

- . Technical Procedure LLB-SSX-1 for the SSX experiments.
- . Technical Procedure RDS-TA-1 for the Thermoanalytical experiments.
- . Safe Operating Procedure 325-501-1 for the SSX experiments.

Operating Manuals

- . Model DSC-2, Differential Scanning Calorimeter
- . TGS-2 Thermogravimetric System
- . TGS-2/Thermal Analysis Data Station (TADS) System
- . DSC-2C/Thermal Analysis Data Station (TADS) System
- . System 4 Microprocessor Controller

Waste Disposal Plan

A waste disposal plan will be prepared for the work and will be reviewed with PNL Waste Management/Environmental Control section of Laboratory Safety. The wastes will consist of non-hazardous nickel cesium ferrocyanide (FECN) and milligram quantities of oxides resulting from the oxidation of FECN by nitrates and nitrites.

Ferrocyanide Safety Study

Estimated Schedule

SSF Ferrocyanide Safety Program

Project: FECH1.PJ
06-02-89

Estimated Costs

<u>Activity</u>	<u>FY89, K\$</u>	<u>FY90, K\$</u>	<u>Total, K\$</u>
Preliminary(a)	20	10	30
Energetics Study	60	30	90
LANL (b) Small & Large Scale Explosion Tests	40	60	100
Revision of PNL 5441		60	60
<u>Total</u>	120	160	280

(a) Preparation of Statement of Work (SOW), Test Plan, and communications with WHC and DOE.

(b) Includes both LANL experimental and reporting costs and costs associated with PNL's oversight of LANL activities.