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Program Plan for Evaluation and Remediation of the Generation and Release of Flammable Gases in Hanford Site Waste Tanks

Prepared for the U.S. Department of Energy
Office of Environmental Restoration and
Waste Management

Westinghouse
Hanford Company Richland, Washington

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

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**PROGRAM PLAN FOR EVALUATION AND REMEDIATION OF
THE GENERATION AND RELEASE OF FLAMMABLE
GASES IN HANFORD SITE WASTE TANKS**

G. D. Johnson

ABSTRACT

This program plan describes the activities being conducted for the resolution of the flammable gas problem that is associated with 23 high-level waste tanks at the Hanford Site.

The classification of the wastes in all of these tanks is not final and some wastes may not be high-level wastes. However, until the characterization and classification is complete, all the tanks are treated as if they contain high-level waste.

Of the 23 tanks, Tank 241-SY-101 (referred to as Tank 101-SY) has exhibited significant episodic releases of flammable gases (hydrogen and nitrous oxide) for the past 10 years. The major near-term focus of this program is for the understanding and stabilization of this tank. An understanding of the mechanism for gas generation and the process for the episodic release will be obtained through sampling of the tank contents, laboratory studies, and modeling of the tank behavior. Additional information will be obtained through new and upgraded instrumentation for the tank. A number of remediation, or stabilization, concepts will be evaluated for near-term (2 to 3 years) application to Tank 101-SY. Detailed safety assessments are required for all activities that will occur in the tank (sampling, removal of equipment, and addition of new instruments).

This program plan presents a discussion of each task, provides schedules for near-term activities, and gives a summary of the expected work for fiscal years 1991, 1992, and 1993.

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LIST OF TERMS

AE	acoustic emission
AMS	acoustic monitoring system
AMU	atomic mass units
ANL	Argonne National Laboratory
ARC	accelerating rate calorimetry
CAA	Clean Air Act
CCW	complex concentrate waste
CHM	core hydraulic mockup
CPAC	Center for Process Analytical Chemistry
DNFSB	Defense Nuclear Facility Safety Board
DOE	U.S. Department of Energy
DSC	differential scanning calorimetry
DSS	double-shell slurry
DST	double-shell tank
ED3A	ethylenediaminetriacetic acid
EDTA	ethylenediaminetetraacetic acid
EPA	U.S. Environmental Protection Agency
FAB	fast atom bombardment
FIC	Food Instrument Corporation
FO	fiber optic
FTIR	Fourier Transform Infrared Spectroscopy
FY	fiscal year
GC	gas chromatography
GC/MS	gas chromatography/mass spectrometry
GIT	Georgia Institute of Technology
GTF	Grout Treatment Facility
HEDTA	hydroxyethylenediaminetriacetic acid
HPLC	high-pressure liquid chromatography
HRMS	high-resolution mass spectrometry
HWVP	Hanford Waste Vitrification Plant
IC	ion chromatography
ICP/MS	inductively coupled plasma/mass spectrometry
IR	infrared
ITM	integrating thermal monitors
IWR	interworks requisitions
LANL	Los Alamos National Laboratory
LASL	Los Alamos Scientific Laboratory
LC/MS	liquid chromatography/mass spectrometry
LFL	lower flammability limit
LLNL	Lawrence Livermore National Laboratory
MS/MS	mass spectrometry/mass spectrometry techniques
NEPA	National Environmental Protection Act
NTA	nitrilotriacetic acid
OSR	operational safety requirement
PNL	Pacific Northwest Laboratory
PRC	Planning Research Corp.
RL	U.S. Department of Energy Field Office, Richland
RPM	revolutions per minute

LIST OF TERMS (cont)

SAR	safety analysis report
SEAC	Safety and Environmental Advisory Council
SFE	supercritical fluid extraction
SNL	Sandia National Laboratory
SOW	statement of work
SST	single-shell tank
STG	scanning thermogravimetry
SWS	sludge weight sampler
TBD	to be determined
T/C	thermocouple
TLD	thermoluminescent dosimeter
TOC	total organic carbon
TTX	time-to-explosion
UA	Urban Affairs
USQ	unreviewed safety question
W-ESG	Westinghouse Electronics Systems Group
W-STC	Westinghouse Science and Technology Center
Westinghouse Hanford	Westinghouse Hanford Company

**PROGRAM PLAN FOR EVALUATION AND REMEDIATION OF
THE GENERATION AND RELEASE OF FLAMMABLE
GASES IN HANFORD SITE WASTE TANKS**

1.0 INTRODUCTION

The initial program plan for this activity was issued in September 1990 and was entitled *Safety Improvement Plan - Hydrogen in Waste Tanks*, WHC-EP-0377, Revision 1 (Leggett et al. 1990). This plan provided a program that addressed the problem of hydrogen generation in waste tanks with respect to three main areas: safety analysis, chemistry and tank characterization, and engineered remedies.

The *Safety Improvement Plan - Hydrogen in Waste Tanks* (Leggett et al. 1990) was prepared by the Waste Tank Safety Task Team which was established in March 1990. The Westinghouse Hanford Company (Westinghouse Hanford) subsequently established a program office in July 1990 to address all safety issues associated with the 177 Hanford Site waste tanks. All work on the flammable gas problems is currently being directed by the Waste Tank Hydrogen Stabilization Program.

This program plan describes the major activities being performed for the resolution of the flammable gas problem. Resources and talents, not only of the Hanford Site contractors, but also those of other U.S. Department of Energy (DOE) sites, universities, and private companies, are being applied to this program. Some aspects of the program plan are still being developed, so additional information will be received, evaluated, and added in subsequent revisions. This program plan will be updated annually unless significant scope change warrants that it be released earlier.

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2.0 BACKGROUND

In March 1990, the potential for a large quantity of hydrogen and nitrous oxide to exist as an explosive mixture within the waste was declared an unreviewed safety question. This designation set in motion a series of actions under *Safety of Nuclear Facilities*, DOE Order 5480.5 (DOE 1986), that normally culminates in an updated safety analysis report (SAR) and new operating restrictions.

A detailed review of each waste tank was performed to evaluate the potential for hydrogen generation and trapping within the waste (using existing data). As a result of this and previous reviews, 5 double-shell tanks (DST) and 18 single-shell tanks (SST) have been placed on a "Watch List." These tanks are listed because a potential ignition of flammable gases vented from the tank could result in a "potential for release of high-level waste due to uncontrolled increases in the temperature or pressure." The condition in these tanks has been declared an unreviewed safety question (USQ) because of the potential consequences of a radiological release resulting from ignition of an accumulated mixture of nitrous oxide and hydrogen under the waste crust, an event not analyzed in any previous safety analysis. Further operating restrictions were implemented for these tanks to reduce the potential for sparks and ignition sources. These restrictions are implemented through interim operational safety requirements (OSR). The following activities are restricted:

- Waste transfers into and out of tanks
- Waste core sampling
- In-tank photography
- Work in primary tank air space or on the associated ventilation/exhaust systems
- Work in tank annulus or on associated annulus peripheral equipment
- Work in the vicinity of the tank or exhaust systems.

Additional requirements have been imposed on the following activities:

- Hydrogen/flammable gas monitoring
- Special briefings
- Increased supervision
- Management approval of waivers of any of the special requirements or restrictions.

The Watch List was developed for tanks that have a potential for ignition of flammable gases. Recently, Westinghouse Hanford provided information concerning the identification and monitoring of these tanks to the DOE in response to Public Law 101-510, Section 3137.

concerning the identification and monitoring of these tanks to the DOE in response to Public Law 101-510, Section 3137.

Table 2-1 provides a listing of the 23 flammable gas Watch List tanks with a summary of the current monitoring capability. The near-term efforts of this program are being focused on Tank 241-SY-101, commonly referred to as Tank 101-SY. This tank has been judged to be the tank with the greatest flammable gas safety concern of the 23 flammable gas tanks.

Table 2-1. Flammable Gas-Generating Tanks.

These tanks are listed because a potential ignition of flammable gases vented from the tank could result in a "potential for release of high-level waste due to uncontrolled increases in the temperature or pressure." The condition in these tanks has been declared a USQ because of the potential consequences of a radiological release resulting from ignition of an accumulated mixture of nitrous oxide and hydrogen under the waste crust, an event not analyzed in any previous safety analysis. The monitoring capability indicated denotes coverage for the listed tank and not a location (i.e., one monitor may cover more than one tank).				
Tank number	Environmental monitoring		Temperature monitoring	Pressure monitoring
	Tank	Area		
Single-shell tank				
101-A	None	X	X	None
101-AX	None	X	X	None
103-AX	None	X	X	None
102-S	None	X	X	None
111-S	None	X	X	None
112-S	None	X	X	None
101-SX	X	X	X	X
102-SX	X	X	X	X
103-SX	X	X	X	X
104-SX	X	X	X	X
105-SX	X	X	X	X
106-SX	X	X	X	X
109-SX	X	X	X	X
110-T	None	X	X	None
103-U	None	X	X	None
105-U	None	X	X	None
108-U	None	X	X	None
109-U	None	X	X	None
Double-shell tank				
103-AN	X	X	X	X
104-AN	X	X	X	X
105-AN	X	X	X	X
101-SY	X	X	X	X
103-SY	X	X	X	X

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3.0 PROGRAM OBJECTIVES AND APPROACH

3.1 OBJECTIVES

The major objective for the Waste Tank Hydrogen Stabilization Program is to develop and implement methods to control the generation and/or release of these gases so that the tanks are maintained in a condition that is safe for site workers and the general public. As the work proceeds towards achieving this goal, two other objectives must be met. First, it is necessary to ensure that continued operation of the facility does not lead to any condition that could create an accident. Second, to facilitate this objective, the monitoring (instrumentation) of the tanks must be upgraded.

The approach for accomplishing the program objectives is provided in Figure 3-1. The two columns on the right show potential methods for achieving the main objective. Near-term remediation (or stabilization) concepts would change the tank from a mode of episodic gas release to one of a continuous release. Long-term remediation would eliminate the generation of gases or, at least, reduce the production to a very low level. Both actions are designed to keep the tank safe until its contents are subject to final disposal.

In the initial phase of the program the work scope is focused to acquire knowledge on the tank and contents, upgrade the monitoring and control of the tank, and develop remediation strategies. Figure 3-1 shows the inter-relationship between these activities. All of the tank upgrades, waste characterization, and remediation concept development will require input from safety evaluations. The work in the program activities will be directed to a decision of when and how to implement a remedial action. This, in turn, may require the construction of interim tank space and treatment facilities. A variety of concepts for remediation have been proposed and they are discussed in Section 4.10.

As indicated above, it is necessary to upgrade the monitoring of the tanks and their contents. The activities associated with the characterization, modeling, and the operation of the facility require detailed information for parameters such as temperatures, pressure, gas flow, gas composition, and surface level. First, aging instrumentation for Tank 101-SY is being upgraded. Second, additional instrumentation is being added to the tank to improve knowledge about the tank contents. Similar upgrades will be conducted for other Watch List tanks.

Resolution of the generation and release of flammable gases requires detailed characterization of the waste. As discussed in the *Safety Improvement Plan - Hydrogen in Waste Tanks* (Leggett et al. 1990) the primary means for waste characterization occurs through core sampling. Issues associated with ignition of flammable gases, chemical reactions in the crust, and ventilation/inertion of Tank 101-SY were not sufficiently resolved to permit core drilling of Tank 101-SY in 1990.

Figure 3-1. Hydrogen Gas Remediation.

SA = Safety Analysis
 OSR = Operational Safety Requirements
 SAR = Safety Analysis Report

Before core sampling of Tank 101-SY was conducted, two near-term issues were resolved:

- Assessment of the potential for a "dome gas burn"
- Assessment of the potential for a "crust burn."

During release of flammable gases from Tank 101-SY, some portion of the mixture of hydrogen and nitrous oxide always exceeds the lower flammability limit (LFL) in the tank dome space. The chemical nature of the gas mixture formed and the amount of gas released is such that a volume of gas will always exceed the LFL at the release site regardless of the ventilation rate or the tank inerting. The approach developed by Westinghouse Hanford is to "manage the risk." That is, the ventilation system will be sized to maintain the volume of gas that, if ignited, will not produce adverse environmental or radiological consequences. A detailed study of the ventilation requirements for Tank 101-SY was provided to DOE in February 1991 (Burgess and Homan 1991); this study is discussed further in Section 4.12.

The term "crust burn" refers to the potential for chemical reactions in the crust to lead to unacceptably high temperatures as a result of heat applied to the crust from core drilling or from a burn of the gases. The crust contains organic carbon compounds (fuel) and oxidizers (nitrates/nitrites). A detailed study on this topic is being conducted and a preliminary report issued. It should be noted that results obtained from a limited amount of crust material in November 1990 indicate that the crust is moist, contains inert compounds, and has a low value for organic carbon. Final closure of this issue will require additional crust samples to provide some statistical confidence that the crust composition, especially its thermal behavior, could not lead to a crust burn. Additional discussion on the resolution of safety issues is given in Section 4.1.

A key step towards successful resolution of the gas problem involves determination of the mechanism(s) for the production and release of the gases. Laboratory studies on synthetic and actual waste will provide the requisite information. In addition, detailed analytical models are being prepared to estimate the flow patterns from release of gas in the tank system and for assessing the thermal-physical behavior of the tank contents both during "steady state" conditions and during the gas release event. Results of the characterization and modeling will be used to formulate both near-term and final remedial actions.

All proposed work in and around Tank 101-SY must be conducted in a safe manner to ensure that postulated accidents have a very low probability of occurrence. Detailed safety analyses have been and continue to be conducted for a postulated burn in the tank dome space (Fox et al. 1990), and safety assessments will be conducted for all proposed activities associated with any Watch List tank. Such safety analyses will be updated as characterization and monitoring information redefine the safety envelope. Furthermore, a plan is being prepared for response to any tank event that involves a temperature rise, pressure increase, fire, or explosion. Finally, integrity assessments will be conducted for the tanks to determine the actions required to ensure

continued safe storage of the waste until pretreatment and final disposal (e.g., Hanford Waste Vittrification Plant [HWVP], Grout Treatment Facility [GTF]) can be implemented.

3.2 PROGRAM MANAGEMENT AND WORK BREAKDOWN STRUCTURE

All activities will be coordinated through individual program manager(s). Program management activities will provide for the planning, direction, scheduling, and financial tracking of the program. It will also provide a focal point for the integration of activities of this program with Westinghouse Hanford Tank Farm Project Engineered Applications, the SST program, the DST waste disposal program, Safety, Quality Assurance (QA), other contractors, the U.S. Department of Energy Field Office, Richland, and other site programs as necessary. External reviews will also be coordinated through this function.

The work breakdown structure is presented in Table 3-1. The relationship between the work breakdown structure and other portions of the Waste Tank Safety program are described in WHC-EP-0426, *Waste Tank Safety Programs Overview Plan*, W1W End Function.

Table 3-1. Work Breakdown Structure.

Cost account plan numbers	Title
1W1W7	Flammable Gas Waste Tank Stabilization
1W1W7A	Chemistry
1W1W7B	Instrumentation
1W1W7C	Ventilation
1W1W7D	Remediation
1W1W7E	Tank Farms Support

3.3 KEY ASSUMPTIONS

3.3.1 Funding Assumptions

3.3.1.1 Fiscal Year 1991 Appropriations Case. The "appropriations" case for fiscal year (FY) 1991 assumes that the entire Waste Tank Safety Program receives \$17.5 million. This level requires reprogramming of \$4.6 million of existing FY 1991 funds.

3.3.1.2 Fiscal Year 1991 Intermediate Case. An intermediate FY 1991 case of \$22 million for the total program is also presented.

3.3.1.3 Fiscal Year 1991 Baseline Case. The FY 1991 "baseline" case assumes that the total Waste Tank Safety Program receives \$34 million.

3.3.1.4 Fiscal Year 1991 Incremental Case. An incremental FY 1991 case is considered (at \$45 million) which assumes no funding limitations exist to accomplish the total identified workscope.

3.3.1.5 Fiscal Year 1992 Guidance Level. The FY 1992 guidance level assumes that the program receives basic escalation (5%) only over the FY 1991 appropriation level (\$18.4 million). It is assumed that the lower budget values do not change the overall requirement, but rather stretch out the overall schedule of the program.

3.3.1.6 Fiscal Year 1992 Baseline Planning Level. The baseline planning level for FY 1992 is \$35.7 million (\$34 million escalated).

3.3.2 Documentation

All deliverable documents prepared under this program shall be Westinghouse Hanford or DOE Field Office, Richland (RL) external documents and cleared for public release.

3.3.3 Technology

In general, no new breakthroughs in technology are considered a prerequisite to achieving remediation. However, considerable laboratory research is necessary to answer basic issues of this program. Should new or novel technology be discovered during course of work, DOE patent protection will be sought in accordance with Westinghouse Hanford procedure.

3.3.4 Waste Tank Flammable Gas Stabilization

3.3.4.1 Field Work. Field work on Waste Tank Flammable Gas Stabilization will be confined to Tank 101-SY in FY 1991. Other tanks may be used for demonstrations of activities only if it is safe and expedient to do so.

3.3.4.2 Scheduling. For initial scheduling purposes, the nominal interval between Tank 101-SY gas releases is assumed to be 98 days.

3.3.4.3 Gas Release. Three successive time periods or intervals follow a gas release in Tank 101-SY: (1) an interval of up to 5 days in which the tank crust level stabilizes, (2) an interval of 20 days (i.e., a "window" of time) in which crust-intrusive activities are completed, and (3) an interval of 10 days beyond the 20-day window in which nonintrusive activities are completed.

3.3.4.4 Parametric Analysis. A detailed parametric analysis core sampling in Tank 101-SY can be completed using the present ventilation system; upgrades for this effort are not required in FY 1991 (Burgess and Homan 1991).

3.4 DRIVERS

For the DOE, Hanford Site waste tank safety is the foremost safety concern. Waste tank safety has been given top priority at Westinghouse Hanford, RL, and by the Secretary of the DOE. The activities identified in this plan are the critical activities necessary to close flammable gas safety concerns related to both SSTs and DSTs at the Hanford Site.

3.5 PROGRAM OVERVIEW SCHEDULES

As mentioned in Section 1.0, some parts of the program are still being defined. It is possible that some program activities can be accelerated, and likewise, some portions may require additional resources and time for successful completion. A preliminary schedule for the program is shown in Figure 3-2. One of the pivotal schedule related decisions is the decision on the upgrade of the ventilation system and how it affects the core drilling. The schedule shown in Figure 3-2 assumes no impacts on the core drilling operations. Sampling of the tank contents will occur first by crust sampling, then by core drilling. This is required to ensure that operations on the tank will not lead to a "crust burn" (chemical reactions) situation. Because of the time required for analyses of core samples and for the detailed laboratory studies on mechanisms for gas generation, it is anticipated, at this time, that interim treatment (near-term remediation) of the tank will not occur until late 1993.

An overview schedule for the near-term activities is shown in Figure 3-3. This schedule is based on "windows" in which work can be performed in the tank. A 20-day window was established for intrusive activities, that is, the tank contents are disturbed. For nonintrusive work, a 30-day window applies. This includes installation of new equipment on the risers, such as a television camera. The schedule in Figure 3-3 was set up from the time of the venting that occurred in October 1990. The in-tank work time period immediately after that release was designated as "Window A." Successive windows are also labeled alphabetically (e.g., B, C). The proposed activities are shown for each window. The schedule was established for the near-term work in Windows B and C. Final details for the remaining windows are still being formulated.

Detailed schedules for all activities are given in Appendix E.

Figure 3-2. Flammable Gas Tank Stabilization.

Figure 3-3. Tank 101-SY Sampling Plan.

Total: Schedule Assumes 38 Days Between Gas Releases and then 6 Days for the Crust Level to stabilize

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4.0 PROGRAM PLAN TASKS

The Waste Tank Hydrogen Stabilization Program Plan has been structured to reflect the objectives discussed in Section 3.0. Major features address each objective:

- Accident prevention
 - Safety analyses
 - Environmental assessments
 - Tank integrity assessments
 - Watch List evaluation.
- Problem resolution
 - Waste sampling
 - Waste characterization
 - Tank monitoring and special surveillance
 - Waste modeling
 - Laboratory studies (mechanisms)
 - Tank database
 - Remedial actions.
- Tank facilities upgrade
 - Monitoring instrumentation upgrade
 - Ventilation upgrade
 - Data collection and management upgrade.

In addition to these items, support activities include independent safety reviews, QA, operations, monitoring, and maintenance.

4.1 SAFETY ANALYSES

This activity will provide the following:

- Safety analyses required to determine the acceptability of the consequences of the accidents that are now recognized as possible within the tank farms
- Updated preliminary OSRs SST
- Upgraded SARs/OSRs for the DSTs, SSTs, and double-shell aging waste tanks
- Written "safety assessments" and environmental assessments that are required to document the acceptability of in-tank intrusive operations in a form suitable for submittal to DOE for approval as required by DOE Order 5480.5 (DOE 1986)
- Safety documentation for interim remediation.

Safety analysis effort is initially focused on establishing the safety of interim tank-intrusive activities that are being performed to characterize the waste. Figure 4-1 shows the relationship between the safety areas associated with the tank and the various elements of the current program plan. The left column, labeled "safety areas," shows the major areas, the right column shows the various activities and analyses that make up the program, and the middle column shows the criteria that will be used to measure success.

4.1.1 Safety Analyses

The analyses that are required to establish the safety of the tanks that contain flammable gas mixtures are organized on a topical basis. Among others, safety analyses are being performed to determine the consequences of accidents related to in-tank activities performed for the resolution of the following areas:

- Ventilation system upgrade requirements
- Crust burning issue elimination
- Core drilling
- Remediation method selection.

The resolution of each of these safety areas will be provided in the form of topical reports suitable for DOE review and approval. These topical reports will form the technical basis for decisions regarding tank intrusive safety assessments as well as provide specific input into subsequent SAR upgrade efforts and interim OSR generation.

A risk assessment has also been initiated to systematically determine the risk from tank farm operations. The Risk Assessment Program is a first step in the development of an upgraded SAR and consists of the following program elements:

1. Facility evaluation
2. Hazard and mitigating system identification
3. Accident sequence analysis
4. Consequence analysis.

This four-step approach to risk assessment leads to a logically organized accident analysis that will be included in the SAR. The first step, "facility evaluation," provides for the collection and evaluation of available information about facility design, operation, and storage procedures and existing safety analyses. The second step, "hazard and mitigating system identification," uses the above information to identify the systems that are available to prevent and/or mitigate accidents. The third step, "accident sequence analysis," uses event trees and fault trees to systematically identify the potential initiating events, evaluate the manner in which the facility responds to the initiating events, and assemble the sequences into bins (groups) for subsequent consequence analysis. The fourth step, "consequence analysis," provides the consequences of each sequence bin.

Figure 4-1. Flammable Gas Safety Issues Resolution.

SAFETY AREAS	STABILIZATION CRITERIA	TEST AND ANALYSES (FROM PROGRAM PLAN)
1. Flammable Vapors in Tank Dome Space - Release Rate - Composition/Burn Properties	Maintain Vapor Space < 1/X LFL (long term) Minimize time that vapor > LFL (interim)	Gas Analysis Ventilation Study Flammability Studies TV Camera Waste Characterization Instrumentation Upgrades
2. Flammable Crust - Spontaneous Reactions - Initiated Reactions	Crust composition/moisture above X Assure TOC < X Assure moisture > Y	Crust Samples Crust Characterization TV Camera Calorimetry
3. Flammable Vapor Below Crust - Quality - Composition/Burn Properties	Maintain vapor space < 1/X LFL (long term) Minimize time that vapor > LFL (interim)	Tank Model Core Sample
4. Tank Structural Integrity - Normal Conditions - Natural Phenomena - Combustion Accident	Maintain confinement Maintain post accident confinement Maintain consequential P < X	Tank Structural Analysis

X = To be determined "standard"

P = Pressure

LFL = Lower Flammability Limit

4.1.2 Safety Analysis Report Upgrades

In parallel with the above effort, significant activities are undertaken to begin the SAR upgrade effort. The SAR upgrade effort consists of the following program elements:

1. Identification of engineering, operations, and design data and analysis needs
2. Development of SAR annotated outline
3. Development of SAR review/acceptance criteria document
4. Preparation and review of chapter.

These program elements lead to a logical buildup of the SAR using a disciplined approach to the identification of SAR acceptance criteria, which requires the clear identification of facility features and analyses for use in preparing the risk assessment and subsequent SAR. The first step, "identification of engineering, operations, and design data and analysis needs," provides for the specific development, on a chapter-by-chapter basis, of what reports and other technical data and information are required from the plant. This data and information are used to develop the descriptive material that is presented in the SAR. The second step, "development of SAR annotated outline," will provide the format and content guidance in a specific document that will be used by the SAR writer as a checklist of what sections and details must be included in the SAR. This same document will be useful to the various SAR reviewers as well. The plan is to secure approval of this document by review agencies, including DOE, so that the review process can be made more predictable.

The third step, "identification of SAR acceptance criteria," will provide selected specific acceptance criteria of the requirements of Regulatory Guide 3.26 that can be used to judge the adequacy of each section of the SAR. As in the second step, this acceptance criteria document will be presented to all reviewing functions for approval before the SAR upgrade. This identification of SAR review/acceptance criteria and preapproval of the review functions will enhance the predictability of the review and approval process. Following the completion of the above three activities, drafting of the upgraded SAR will begin. This fourth step includes the preparation of draft SAR material and review and approval of the SAR, both internally and externally.

4.1.3 Safety Assessments

The final activity is the preparation of safety assessments in support of the in-tank intrusive operations that are required to characterize the tank contents and to add instrumentation and other items into the tank. These safety assessments are really mini-SARs that provide (1) a systematic assessment of the safety of the operation, (2) an identification of the consequences of accident sequences that have been postulated, and (3) a clear delineation of the additional controls that are imposed on the operation. These safety assessments are prepared in accordance with Westinghouse Hanford

procedures. The safety assessments will be prepared for those in-tank intrusive activities identified in other portions of this program.

4.1.4 Safety Reviews

Reviews of safety assessments will include internal Westinghouse Hanford reviews and reviews by the DOE. Westinghouse Hanford reviews will include functional reviews by the program office, engineering, tank farm operations, independent nuclear safety, and the Safety and Environmental Advisory Council (SEAC). In addition to the reviews of specific documents, periodic briefings will be held on request with the Defense Nuclear Facility Safety Board and the Advisory Committee on Nuclear Facility Safety.

4.1.5 Fiscal Year 1991 Work Scope (Current Year)

4.1.5.1 Expanded Outline and Acceptance Criteria.

- Prepare detailed outline and guide to content for waste tank SARs.
- Prepare acceptance criteria document for use by reviewers and authors in preparing complete sections.
- Obtain internal and external approval on expanded outline and acceptance criteria.
- Separate the expanded outline into categories of source organizations and notify them of SAR inputs required.

4.1.5.2 Aging Waste Safety Analysis Report.

- Perform evaluation for compliance with DOE Order 6430.1A.
- Resolve and close out existing comments on draft SAR Chapters 4, 5, 6, and 7.
- Perform review of expanded outline.

4.1.5.3 Single-Shell Tank Safety Analysis Report.

- Perform evaluation for compliance with DOE Order 6430.1A.
- Prepare 50% of text for Chapters 5 and 9.

4.1.5.4 Double-Shell Tank Safety Analysis Report.

- Perform evaluation for compliance with DOE Order 6430.1A.
- Prepare 50% of text for Chapters 5 and 9.

4.1.6 Fiscal Year 1992 Work Scope (Budget Year)

4.1.6.1 Prepare Operational Safety Requirements on Single-Shell Tank and Aging Waste Facility.

4.1.6.2 Aging Waste Safety Analysis Report.

- Rewrite, per expanded outline, Chapters 1 through 10 and 80% of Chapters 11 and 12.
- Perform peer review of Chapters 1, 4, 5, 6, 7, 8 and 9.
- Resolve comments on Chapters 4 through 9.

4.1.6.3 Single-Shell Tank Safety Analysis Report.

- Complete text preparation on Chapters 5 and 9.
- Prepare text for Chapters 4 and 6.
- Complete peer review and comment resolution for Chapter 4.

4.1.6.4 Double-Shell Tank Safety Analysis Report.

- Complete text preparation on Chapters 5 and 9.
- Prepare text for Chapters 4 and 6.
- Complete peer review and comment resolution for Chapter 4.

4.1.7 Fiscal Year 1993 Work Scope (Plan Year)

4.1.7.1 Aging Waste Safety Analysis Report.

- Complete remainder of Chapters 11 and 12 text.
- Perform peer review of Chapters 2, 3, 10, 11 and 12.
- Resolve comments for Chapters 1, 2, 3, 10, 11, and 12.
- Perform functional review and SEAC review of total SAR.

4.1.7.2 Single-Shell Tank Safety Analysis Report.

- Prepare Chapters 2, 7, 8, and 11, including peer review and comment resolution.

4.1.7.3 Double-Shell Tank Safety Analysis Report.

- Prepare Chapters 2, 7, 8, and 11, including peer review and comment resolution.

4.2 TANK INTEGRITY ASSESSMENTS

This task is covered by the Waste Tank Properties and Contents Activity (1W1W5) which is another major activity in the overall waste tank safety program. Because the results of analyses on Tank 101-SY could impact the tanks on the hydrogen Watch List, a brief summary of the applicable work is described in this program plan.

This work will evaluate the structural integrity of both the DSTs and SSTs, including those that contain potentially hazardous hydrogen buildup. Tanks on the Watch List will be prioritized for remedial actions in the specific evaluations. State-of-the-art analytical methods will be used. The following specific activities are either planned or under way:

- Complete Tank 101-SY (DST) hydrogen explosion analysis
- Evaluate impacts of waste tank hydrogen explosion on two types of SSTs (500,000-gal- and 1,000,000-gal-capacity tanks)
- Provide a structural accident assessment for all SSTs and DSTs on the Watch List
- Update seismic assessments to latest DOE standards
- Evaluate all tanks, on a tank-by-tank basis, considering effects such as thermal cycling, material aging, and corrosion, to estimate useful tank life
- Determine and implement program for monitoring tank structural properties, such as concrete strength and liner corrosion rates.

4.2.1 Work Scope for Fiscal Years 1991, 1992, and 1993

This information is provided in the *Waste Tank Properties and Contents Program Plan* (DeFigh-Price 1991).

4.3 EVALUATION OF WASTE TANK WATCH LIST

Twenty-three tanks (5 DST, 18 SST) were declared to represent a USQ because of their potential for generating hydrogen which, in turn, may lead to a potential release of waste as a result of uncontrolled increases in tank temperature or pressure. These tanks were also placed under restrictive controls using interim OSRs.

The objective of this activity is to develop and implement a technical evaluation process whereby the tanks on the hydrogen generation Watch List (other than Tank 101-SY) can be dispositioned. The evaluation process will identify those tanks that can be assigned to a lower category to remove operating restrictions on a near-term basis. For the remaining tanks on the Watch List, recommendations will be made for characterization activities and enhanced long-term surveillance whose result is expected to result in removal from the Watch List. The activities of this task will be coordinated with the Waste Tank Properties and Contents Program.

One of the first activities will be to collect and review existing documents relating to the development of the Watch List and tank ranking evaluations. Historical data judged to be relevant to hydrogen generation and release will be collected and documented in a single report.

Next, the reason or cause for a given tank to be on the Watch List will be reviewed. Also, current tank data will be reviewed to determine if the original reason is still valid. If the original reason for including the tank on the Watch List is no longer valid, a report will be prepared documenting the information and recommending a change in category for the tank. If the results of the data reviews indicate that a tank should at least temporarily stay on the Watch List, then the engineering evaluation will include a recommendation as to what additional information/surveillance data collection is appropriate. After added data are collected, another evaluation will be conducted. If justified, a recommendation for a category change will be made and documented as above. If a category change is not justified, long-term surveillance will be recommended and/or remedial action options will be developed and implemented.

4.3.1 Fiscal Year 1991 Work Scope (Current Year)

This activity will occur only if the incremental FY 1991 case budget is approved. It is assumed that this activity will be delayed until FY 1992.

4.3.2 Fiscal Year 1992 Work Scope (Budget Year)

The work scope for FY 1992 is listed below.

- Define needed historical data.
- Document criteria for changing Watch List.
- Define requirements for new data and associated instrumentation.
- Prepare report on historical data for 23 flammable gas Watch List tanks.
- Gather and document new data.
- Complete comparison of existing data to criteria.
- Prepare documentation recommending removal from Watch List based on historical data.
- Prepare documentation recommending characterization/long-term surveillance.
- Prepare final summary report.

4.3.3 Fiscal Year 1993 Work Scope (Plan Year)

All activities will be conducted as part of the *Waste Tank Properties and Contents Program Plan* (DeFigh-Price 1991).

4.4 WASTE SAMPLING

The chemical and physical properties of the waste material are central to resolving tank safety issues. An understanding of these properties may be obtained by retrieving and analyzing waste samples from the tank in question. Data requirements for safety analyses, remedial actions, and modeling activities are listed in Table 4-1.

In particular, additional samples of the liquid and slurry layers beneath the crust must be collected and analyzed to better understand the mechanisms by which hydrogen and other gases are generated and periodic "rollover" of the layers occurs. However, as a result of safety concerns about possible flammability and secondary chemical reactions in the crust, these lower layers cannot be sampled by existing methods (e.g., rotary core drilling) until additional data and analyses are completed on the crust material.

Analyses of representative crust samples of adequate size for thermal analysis and from various locations in the same tank would provide a reliable characterization of the crust. Additional results expected from these analyses include defining a better simulation of the crust material for drilling tests, information on crust surface radionuclide source terms, guidance on crust solubility, and input for design and use of crust sampling devices and a penetrometer. In short, these analyses would help to answer safety concerns and permit more complete sampling of the tank's contents by core drilling.

Methods for retrieving waste samples include core drilling and removal of crust material adhering to existing instruments and other equipment removed from the tanks. Also discussed are design efforts currently under way to provide simpler or more versatile, intrinsically safe, means of sampling or providing information about the crust material. These include a sludge weight crust sampler, an auger crust surface sampler, and a penetrometer.

Proposed schedules for obtaining samples are shown in Figures 3-2 and 3-3.

4.4.1 Core Drilling of Tank Waste

The reference method for obtaining samples from the waste tanks is by drilling a core from top to bottom of the tank contents. The basic operation of this approach is discussed in *Safety Improvement Plan - Hydrogen in Waste Tanks* (Leggett et al. 1990). Recent tests with the drill rig on simulated hard waste forms lead to temperatures in the drill bit which, without a better understanding of the crust properties, could pose a fire or explosion hazard. Efforts are under way to redesign the drill bit to eliminate this problem, but until this situation has been corrected, other methods are being considered to characterize the crust and retrieve samples from the tank.

One method is to use the existing core drilling equipment in a "push mode" (i.e., pushing the drill bit through the crust without rotating it) so that less friction and heat are generated. Pieces of the crust adhering inside the drill bit can then be recovered. This mode of operation may not

Table 4-1. Data Requirements. (sheet 1 of 2)

Safety analysis requirements
<p>Characterize physical and chemical properties of the crust to support modeling of crust movement during gas generation and migration and to assess the potential consequences of a gas explosion.</p> <p>Quantitatively identify toxicological components and aerosols (subject to release) in the crust, liquid, and slurry layers for analysis of the consequences of an explosion.</p> <p>Identify reactive materials (chemicals) in the crust to evaluate the potential for a secondary crust reaction.</p>
Engineering remedies requirements
<p>Evaluate liquid and slurry layer characteristics to support evaluation of pumps and mixers suitable for waste transfers:</p> <p>Specific gravity Percent settled solids Solids settling rate Shear stress versus shear rate rheogram Particle size distribution pH Composition (anions, cations, organics, radionuclides)^a</p>
<p>Evaluate liquid and slurry layer characteristics to support sizing of pumps and mixers suitable for waste transfers:</p> <p>Specific gravity Solids settling rate Percent settled solids pH Weight percent and volume percent centrifuged solids Shear stress versus shear rate rheogram Particle size distribution Shear strength Penetration resistance Abrasive--Miller number Composition (anions, cations, organics, radionuclides)^a</p>
<p>Evaluate crust characteristics to support the design of "crustbusters" (currently given lower priority):</p> <p>Density Thickness Compressive strength Penetration resistance Dissolution properties (in 1 molar and 2 molar caustic water)</p>

Table 4-1. Data Requirements. (sheet 2 of 2)

Mechanistic modeling requirements
<p>Evaluate crust characteristics and composition to support evaluation of the gas release mechanism:</p> <ul style="list-style-type: none"> Composition (anions, cations, organics, radionuclides) Density Percent water Differential scanning calorimetry (performed from ambient to 450 °C) Thermal conductivity^b Porosity^b (i.e., permeability)
<p>Evaluate liquid layer thermal and rheological properties to support development of a thermohydraulic model of the tank:</p> <ul style="list-style-type: none"> Composition Solids settling rate Density (solids and liquid phases) Specific heat Thermal conductivity^b Shear stress vs. shear rate rheogram Surface tension Gas generation rate and composition Coefficient of thermal expansion
<p>Evaluate slurry layer thermal and rheological properties to support development of a thermohydraulic model of the tank:</p> <ul style="list-style-type: none"> Composition Solids settling rate Percent settled solids Density Thermal conductivity^b Specific heat Particle size distribution Shear strength Shear stress vs. shear rate rheogram Gas generation rate and composition Coefficient of thermal expansion Surface tension

^aChemical and radiochemical data required to evaluate compatibility with Tank 102-SY and Tank 103-SY waste.

^bFurther methods development is required.

generate a representative profile of the tank crust contents, but will possibly help augment existing knowledge of the crust properties. This method provides profile information on the waste below the crust once the crust penetration occurs. This push mode method was used during Window C.

4.4.2 New Core Drilling System

The new core drilling system represents a modification of the existing core drilling system to improve drilling performance, to drill within a specified drill bit maximum temperature limit, and to improve the display and recording of important drilling parameters. The need for these changes was identified by tests with the existing system in simulated hard waste material. The new system includes several design features:

- A new drill bit with improved drilling performance in hard waste materials. The drill bit may include three thermocouples for the direct measurement of drill bit temperature. The drill bit will also be compatible with the use of a purge gas for the removal of fines and cooling of the drill bit.
- A system to provide an online display and recording of the output of the three thermocouples installed in the drill bit. This system includes high-temperature alarms to signal the operator to stop the drill string rotation if temperature limits are exceeded.
- A system to provide a controlled flow of nitrogen purge gas to the drill bit for the removal of fines and cooling the drill bit. The need for a purge flow will be determined before drilling operations; the new core drilling system will have the capability to drill with or without purge flow.
- A system to provide for the measurement, high- and low-alarm indication, online display, and recording of the following additional parameters: gaseous nitrogen purge flowrate, pressure, and temperature; the torque imposed on the drill string; the revolutions per minute (RPM) of the drill string; the downward force applied to the drill string; and the downward drill string displacement.

4.4.2.1 Fiscal Year 1991 Work Scope (Current Year). A two-part testing program will be performed. The first test series consists of engineering tests to select the optimum drill bit and drilling parameters for a range of simulated tank crust materials. The second test series will use a simulated tank riser and waste tank to test the operational performance of the new drilling system and to perform training of the drill crews.

The engineering test will be performed in two parts. In the first part, the drilling performance of up to four new drill bits will be checked against the performance of the standard drill bit to select the optimum drill bit.

These tests will be conducted with the Sulfur K-Mag¹ simulant which was used to conduct the previous drill tests. In the second part, the selected drill bit will be tested using five specially selected material simulants, reflecting a spectrum of salt cake properties, to determine optimum drilling parameters based on analog drilling performance keeping the maximum drill bit temperature less than 180 °C. The five specially selected material simulants were based on samples previously obtained from a number of waste tanks including Tank 101-SY. The engineering tests will be conducted with and without purge flow and will also be used to determine the optimum purge flow. The performance of the core sampling equipment will also be evaluated during these tests.

The operational test will use the new drilling system to perform a checkout using a simulated Tank 101-SY riser and tank section. The tank section will simulate the elevation of the top of the crust relative to the top of the riser. The depth of the waste in the simulated tank will be sufficient to take several core samples. A second objective of the test will be to train the operating crews to use the new core drilling system.

4.4.2.2 Fiscal Year 1992 Work Scope (Budget Year). Modifications started in FY 1991 will be completed in FY 1992. This will include the installation of instruments to monitor drilling parameters (RPM, torque, travel, load, and the incorporation of alarms for high and low signals). Final checkout of the new core drill system will include a full operational test and training of operations.

4.4.2.3 Fiscal Year 1993 Work Scope (Plan Year). No activities are planned for FY 1993. All work will be completed in FY 1992.

4.4.3 Retrieval of Samples from In-Tank Equipment

Photos from inside the tanks indicate that crust material adheres to instruments and other in-tank equipment, sometimes forming a hard solid mass or "lollypop." In November 1990, in an attempt to gain insight of the chemical nature of the crust in Tank 101-SY, an effort was initiated to remove the Food Instrument Corporation (FIC) probe, the manual tape probe, and the sludge weight from the tank. Samples of crust material were retrieved from these items for laboratory analysis, and the results are forthcoming.

A comprehensive plan and schedule is being prepared for removal, packaging, and disposal of the lances and cleanout of the risers to provide access for new instrumentation to be installed in the tank. In addition, an overall plan for removal of other unused equipment and cleanout of risers is being prepared. These activities may provide opportunities to obtain additional crust samples.

4.4.3.1 Fiscal Year 1991 Work Scope (Current Year). Samples were obtained from the FIC probe, manual tape plummet, sludge weight, auger sampler, and the sludge weight sampler.

¹Sulfur K-Mag is a tradename of Duval Corporation.

4.4.3.2 Fiscal Year 1992 Work Scope (Budget Year). A plan will be prepared for obtaining samples from the air lance tubes as they are removed to provide more risers for sampling and instrumentation.

4.4.4 Sludge Weight Sampler

One of the crust sampling devices under development is called a sludge weight sampler (SWS). The SWS is so named because it will be a modification of an existing design for a sludge weight, a weighted device presently used to measure sludge levels in the tanks. The SWS will offer a higher probability of success in obtaining crust samples of adequate size than the existing sludge weight design and will meet the current design and operating restrictions for equipment used in Tank 101-SY. While the SWS can only be used to sample the top surface of the crust, procedures now in place at tank farms (for operating the sludge weight device) can be adapted with relative ease. Therefore, the SWS can be put to use without extensive procedure development and delays. The SWS can be used to obtain samples of crust material from up to five locations within Tank 101-SY.

4.4.4.1 Fiscal Year 1991 Work Scope (Current Year). The SWS will be designed for fabrication at the Hanford Site. At least four design concepts will be developed and fabrication sketches prepared for proof of concept testing. This initial testing will determine which design features will be incorporated into a final design. The design will then be finalized and verified before use by the necessary safety, QA, and readiness reviews and by testing to demonstrate the reliability of the device and its compatibility with Tank 101-SY risers and sludge weight removal reels.

In operation, the SWS will be lowered into the tank until it contacts the crust surface; it will then be raised up a predetermined distance and dropped. The energy of impact should allow the device to penetrate the crust surface and capture a sample. The SWS will then be retracted into a removal reel and a determination made as to whether or not a sample of adequate size has been obtained. This determination will be based on measuring the radiation field around the reel. If measurements indicate that the sample size is inadequate, the procedure will be repeated using a second SWS and removal reel assembly. The sample(s) will be left intact inside the SWS(s), removed from the tank, and transported to the laboratory for analysis.

The results will be used to supplement the limited data obtained from the FIC probe, manual tape, and sludge weight removed earlier. Specifically, the data will be factored into the safety evaluations for crust burn and intrusive crust sampling (auger, penetrometer, push mode core sampling, and core drilling) and will be useful as a nonintrusive precore sampling crust characterization opportunity.

4.4.4.2 Fiscal Year 1992 Work Scope (Budget Year). It is not anticipated that this technique will be applied to other tanks. Thus, there is no work scope for FY 1992.

4.4.4.3 Fiscal Year 1993 Work Scope (Plan Year). No sludge weight sampling is planned for FY 1993.

4.4.5 Auger Crust Surface Sampler

Another crust sampling device under development is an auger which will sample the crust up to 6 in. beneath the top surface for analysis, with the sampling depth adjustable inside this range. Advantages of the auger over the SWS will include the ability to capture samples deeper within the crust and with a minimum of downward force applied on the crust. The auger will be designed with few moving parts and will be operated manually to help minimize any possibility of igniting the waste. The auger will require specific procedures to be developed for its operation and will be available by May 1991, in time for the scheduled Window C.

4.4.5.1 Fiscal Year 1991 Work Scope (Current Year). Design concepts for the auger have been derived and evaluated based on compatibility with sample handling equipment at the 222-S Laboratory and expected properties of the crust, which were, in turn, based on characterization studies that were conducted on Tank 101-SY waste in 1986. The design will be finalized and verified before use by the necessary safety, QA, and readiness reviews and by testing to demonstrate the operability of the device.

In operation, the auger will be lowered through a tank riser to the crust surface, manually operated, and then pulled into a container where the sampled material is deposited. The approximate sample size will be determined by measuring the radiation field around the container. If measurements indicate that the sample size is inadequate, the auger will be again lowered to the crust surface, any necessary adjustment made, and the process repeated until a sample of adequate size is obtained. The sample will then be removed from the riser and shipped in its container to the laboratory for analysis.

4.4.5.2 Fiscal Year 1992 Work Scope (Budget Year). The technique of obtaining samples with the auger sampler will be used for other tanks that may generate flammable gases. Two of these tanks are 103-SY and 104-AN. Both tanks have shown a history of slurry growth and collapse.

4.4.5.3 Fiscal Year 1993 Work Scope (Plan Year). Additional tanks on the Watch List may be sampled by this technique depending upon the results of FY 1992 sampling activities.

4.4.6 Penetrometer

One device that will provide information on the mechanical properties of the crust without requiring a sample to be drawn is a penetrometer. This instrument measures the penetration resistance or hardness of the crust. A penetrometer is under development for use in the tanks and will be designed to take readings from the crust surface and, if needed, to a depth of up to 36 in. beneath the surface. Penetrometer data will assist in the design of drill bits and other core drilling equipment because it will provide a means of correlating the properties of simulated crust material, used for equipment testing, with those of the actual crust in the tank. Penetrometer data may also be useful in estimating crust depth. The penetrometer will be available for in-tank testing in time for Window C, scheduled for May 1991, at which time only readings of the crust top surface will be taken. Additional penetrometer readings may be taken later within the crust profile.

4.4.6.1 Fiscal Year 1991 Work Scope (Current Year). The design will be based on studies to identify materials and fabrication methods to be used. The penetrometer design will be finalized and verified before use by the necessary safety, QA, and readiness reviews. Testing to demonstrate the operability of the device is scheduled to be conducted in Tank 101-SY.

In operation, the penetrometer will be lowered through a tank riser until the crust surface is contacted and activated to obtain a reading. If additional readings are taken later, these may be done at various depths beneath the crust surface to a maximum depth of 36 in., thus generating a vertical profile of the crust. Extensions would be added to the device as needed as successive readings are made. The depth below the crust surface would be determined before each penetrometer reading. Tip assemblies of the penetrometer, which contact the crust during operation, as well as any parts of the device which come into contact with the sludge in the tank and become radioactively contaminated, will be discarded after each test.

4.4.6.2 Fiscal Year 1992 Work Scope (Budget Year). The penetrometer is designed to be used in conjunction with the auger sampler. Thus, it will be used for the same tanks as the auger sampler (Section 4.4.5.2).

4.4.6.3 Fiscal Year 1993 Work Scope (Plan Year). Additional tanks on the Watch List may be sampled by this technique depending upon the results of FY 1992 sampling activities.

4.4.7 Other Methods

Several methods for sampling the tank waste in addition to the above have been evaluated for possible use on Tank 101-SY. Of these, the following may be investigated further and used at a later date if it is still necessary: drop bottle, packer system for existing air lance, and an in-tank densitometer. For many reasons none of these is as desirable as the options discussed above.

In addition, there are several methods under consideration which, like the penetrometer, do not obtain a sample but characterize the waste in place. These methods are discussed elsewhere and include gas sampling or monitoring and various remote-sensing methods employing sonic, ultrasonic, radar, infrared, electromagnetic, and radiological technology.

One item being considered is a sampling bottle that will obtain a liquid sample that retains the gas at its hydrostatic pressure.

4.5 WASTE SAMPLE ANALYSIS

Analyses to be performed on all waste samples retrieved from the tank have been described in the *Safety Improvement Plan - Hydrogen in Waste Tanks* (Leggett et al. 1990). Table 4-2 provides a brief summary of the analyses to be performed. A detailed analytical chemistry plan was developed in August 1990 and was issued as an internal Westinghouse Hanford document.

Table 4-2. Core Sample Analyses.

Physical and rheological
Photographs Color, description of sample Volume, weight Particle size Density Weight percent water Weight and volume percent solids Solid settling rate Differential scanning calorimetry Thermogravimetric analysis Polarized microscopy Shear strength Shear stress-shear rate rheograms Penetration resistance X-ray diffraction
Radiochemical
Transuranics (^{241}Am , $^{239/240}\text{Pu}$, ^{237}Np) Gamma energy analysis (^{137}Cs) Total alpha Total uranium ^{90}Sr
Chemical
Inductively coupled plasma (metals) Anions (NO_2 , NO_3 , CO_3 , SO_4 , PO_4 , F , Cl) Ammonia/ammonium ion Cyanide pH Total organic carbon (TOC) Volatile organic analysis (VOA) Semivolatile organic analysis Complexants (ethylenediaminetetraacetic acid [EDTA], hydroxyethylenediaminetriacetic acid [HEDTA], nitrilotriacetic acid [NTA], ethylenediaminetriacetic acid [ED3A]) (See Figures 4-2 and 4-3.)

Figure 4-2. Probable Source ED3A.

*Detected by GC-MS and GC-FTIR

Figure 4-3. Chelating/Complexing Agents^(a) and Their Degradation Product Wastes.

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The majority of the analyses will be performed by Westinghouse Hanford. However, support will be provided by Pacific Northwest Laboratory (PNL) for certain types of characterization of gaseous, liquid, and solid samples from the tank. This support will include organic compound analyses, radionuclide analyses, gas phase analysis, and characterization of physical properties.

The organic characterization will include analyses for volatile and semivolatile organics, as well as chelators and their degradation products. The analyses for volatile and semivolatile compounds will be performed by gas chromatography/mass spectrometry (GC/MS) methods that are in place and used on a routine basis. Analytical methods for the chelators are not yet in place (the development of needed analytical methods is covered in Section 4.5.2 of this plan). The gas phase analysis will include the determination of both nonhydrocarbon gases and hydrocarbons (including the determination of volatile organic compounds that have been cryogenically trapped). The analyses for the nonhydrocarbon gases and light hydrocarbons will be performed by quantitative mass spectrometry. The cryogenically trapped samples will be analyzed by GC/MS.

The radionuclide analyses include determinations of ^{241}Am , ^{79}Se , ^{63}Ni , ^{94}Nb , and ^{237}Np . These analyses involve conventional ion-exchange separations and scintillating counting for the selenium, nickel, and niobium, and solvent extraction separation followed by alpha energy analysis for the americium and neptunium. The physical property characteristics will include measurements of density, shear strength, solid settling rate, and percent settling of solids.

To provide the requisite data for safety analyses, modeling, and remedial studies, a number of tests must be developed. They are discussed below.

4.5.1 Development of Physical Chemical Property Tests

The following tests are being developed for use in the Hanford Site hot cell facilities: adiabatic calorimetry, surface tension, thermal expansion, crust strength, porosity, thermal conductivity, and explosivity.

4.5.2 Development of Methods for Analysis of Organics (Pacific Northwest Laboratory)

Critical to the understanding of the chemical mechanism by which hydrogen is being generated in Tank 101-SY is the analysis of the organic chemicals that are present in the waste. When the waste was first generated, there were a limited number of organic chemicals in the waste stream from the chemical processes at the Hanford Site. These organic chemicals included the chelators hydroxyethylenediaminetriacetic acid (HEDTA) and ethylenediaminetetraacetic acid (EDTA), a buffering agent glycolic acid (hydroxyacetic acid), and trace amounts of solvents from the solvent extraction processes. It is expected that the solvents were steam stripped when the wastes were treated in the crystallizer-evaporators. However, HEDTA, EDTA, and glycolic acid are expected to have survived the crystallizer-evaporator process and are now found in the DSTs. Early work by Delegard (1980) suggests that these organics decompose, in contact with solutions that simulate the waste in Tank 101-SY, to liberate the same gases that are detected during a gas release event from

Tank 101-SY plus unspecified organic decomposition products. Later, a waste containing complexants was analyzed and a large fraction of the organic constituents determined (Strachan et al. 1986). However, no such analysis has been attempted for the wastes in Tank 101-SY.

Work being carried out under Section 4.8, "Synthetic Waste Studies," will focus on the chemical mechanisms for the reaction between the organic chemicals known to have been added in the chemical process at the Hanford Site and simulated wastes. To confirm the results from these studies and to understand the mechanism of hydrogen production, samples will be collected from Tank 101-SY and analyzed for the organic constituents.

Appropriate separations methodology and sample preparation techniques will be used to separate the organics into volatile, semivolatile, and nonvolatile fractions. The development of these separation methods is described in Section 4.5.2.1. Most analyses for volatile and semivolatiles will be conducted using existing GC/MS procedures. However, for certain of these compounds, more advanced techniques may be required. The development of these techniques is described in Section 4.5.2.2. The development of methods for the analysis of chelators is described in Section 4.5.2.3. In the case where the sum of the analyzed organic carbon obtained from the analysis of volatile, semivolatiles, and the chelators does not account for 100% of the total organic carbon (TOC) analysis, additional analytical techniques will have to be used to account for the remainder. The development of these techniques is described in Section 4.5.2.4.

The methods and techniques whose development is described in the following sections could also be used for the analysis of similar tanks or mixed hazardous wastes.

4.5.2.1 Separations Methodology and Sample Preparation. Strachan et al. (1986) analyzed the organic components in Tank 107-AN, a tank that contained complexant concentrate. The objective was to determine all of the organic species such that the sum of the organic carbon analyzed equaled the TOC of the sample. Before the project ended they had a recovery of 75% relative to the TOC analysis. The methodology used in this study emphasized the need to separate the organic constituents by broad compound classes such as volatile, semivolatile, and nonvolatile organics. However, Toste et al. (1988) was only able to account for approximately 2% of the TOC in a double-shell slurry (DSS) waste sample. The methodology developed in 1986 will be further developed in this task, and our ultimate goal is to identify as much of the TOC as possible.

To achieve nearly 100% agreement between the sum of the analyzed organic carbon and the TOC analysis, an alternate scheme for separating the organic constituents in Tank 101-SY must be developed. The organic constituents will be separated into volatile, semivolatile, and nonvolatile components. The fractions will be further separated into polar and high-molecular weight components. In this task, selective solvent extraction and open column chromatography will be used to achieve a separation of the classes of organic constituents. Other techniques such as supercritical fluid extraction (SFE) and solid phase extraction may be required to provide suitable fractionation. Additional sample preparation may be required before actual analysis. In the

method developed in 1986, the water-soluble organics were first converted to water-insoluble, organic extractables. These methods will provide material to be analyzed using other analytical techniques.

4.5.2.2 Enhanced Analysis for Volatile and Semivolatile Organics Using High-Resolution Mass Spectrometry and Tandem Mass Spectrometry Techniques.

One of the difficulties with organic analyses is the number of possibilities that exist for any given response from the analytical instrument. Thus, a given mass spectrum could result from any number of organic molecules with similar structures present in the sample. As an example, C_4 -benzothiophene ($C_{12}H_{14}S$) and 4,5-methanophenanthrene may have identical mass spectra, but can be distinguished by accurate mass measurements. The C_4 -benzothiophene has a molecular weight of 190.0816 and 4,5-methanophenanthrene has the same nominal molecular weight but an exact mass of 190.0782. Although there may be ambiguity in the mass spectra for certain volatile and semivolatile organic species, accurate mass measurements can lead to a suite of fingerprints for the organic constituents that make up the volatile and semivolatile organics in this waste. In addition, for those components for which no reference mass spectrum exists in the library, accurate mass measurements will be used to unambiguously identify that component.

Tandem mass spectrometry, for which the acronym MS/MS has been coined, emulates GC/MS in replacing the chromatograph by a mass separator. In a tandem mass spectrometer, primary ions of a compound or a mixture of compounds are generated in the ion source. The primary ions are mass selected in the first stage (MS-1). A given ion filtered or selected out by MS-1 will undergo decomposition reactions on its path to the second stage (MS-2) where mass analysis of these secondary fragment ions is performed. An obvious advantage of this is speed: GC/MS is limited by the time required for chromatographic separation (usually many minutes), while the second MS only requires an additional ion transit time of milliseconds. In addition to the obvious specificity improvements, the sensitivity attainable can also be improved substantially. Tandem mass spectrometry techniques have been used to identify components in complex mixtures such as coal tars and pharmaceutical solutions. The MS/MS techniques may be applicable for the analysis of specific components in the complex mixtures from Tank 101-SY.

4.5.2.3 Methods Development for Chelators and Chelator Fragments. Methods will be developed or adapted for the analysis of chelators and chelator fragments. Complementary methods will be developed, including derivatization GC/MS, liquid chromatography (LC), and liquid chromatography/mass spectrometry (LC/MS).

Two derivatization GC/MS methods will be applied to the analysis of chelators: (1) reaction with boron trifluoride/methanol, (2) reaction of HCl/butanol to produce the butyl esters. The LC/MS method to be developed involves the use of a RP 2 Lichrosorb column with ammonium acetate as the mobile phase and the thermospray interface. The LC method to be examined requires reverse-phase, ion-pair chromatography with Cu(II) and ion-pair reagent in the mobile phase. This method was originally developed by W. R. Grace. Alterations will be made to this method to provide the desired chromatographic separation and quantitation.

4.5.2.4 Methods Development for Thermally Labile, Polar, and Nonvolatile Components. As described in Section 4.5.2.3, methods for determining the chelators and some of the chelator fragments are being developed. However, there are other classes of nonvolatile organics that are not amenable to the U.S. Environmental Protection Agency (EPA)-accepted analytical techniques (GC or GC/MS). These nonvolatile organic species will require advanced organic analytical techniques to determine their concentrations in Tank 101-SY waste. Some of these organics were listed in the 1986 analysis of Tank 107-AN waste as "MW-247," for example. The determination of these organic species may be amenable to complementary analytical techniques such as supercritical fluid chromatography/mass spectroscopy (SFC/MS), LC/MS, microcolumn LC/MS, derivatization GC/MS, MS/MS, and fast atom bombardment (FAB). Organometallics will be analyzed by LC/MS-inductively coupled plasma/mass spectrometry (ICP/MS). This will enable the organic moiety and the associated metal to be determined simultaneously. These techniques have not yet been applied to the analysis of nonvolatile species in mixed hazardous wastes, but will be developed in this task.

4.5.3 Deflagration Studies

Analyses of various postulated hydrogen burns have been conducted to support the work on the evaluation of the ventilation system and to support safety analyses for accidents that might occur as a result of activity in the tank. Because data for deflagrations are incomplete, a study has been initiated with the Pittsburgh Research Center of the U.S. Bureau of Mines.

The purpose of the deflagration study is to determine risks of the hydrogen, nitrous oxide, nitrogen, and oxygen system. To be determined are pressure and temperature as a function of composition of reacting gases and the concentration of gases before and after the combustion event. Analyses of gases after the combustion event will be restricted to those tests that had an initial concentration of $\leq 8\%$ hydrogen. This information will be used to evaluate safety issues related to periodic slurry growth and flammable gas releases from Tank 101-SY. The conditions to be evaluated will simulate gases in the vapor space above the saltcake as well as gases that potentially are trapped in pockets within/under the waste.

A copy of the statement of work for these studies is provided in Appendix A.

4.5.4 Fiscal Year 1991 Work Scope (Current Year)

4.5.4.1 Waste Analyses. Analyses will be performed on samples retrieved by the methods described in Section 4.4, which includes samples from tank instruments (Section 4.4.3), the SWS (Section 4.4.4), the auger sampler (Section 4.4.5), and the core drill (Section 4.4.1). In addition, analyses will be conducted of the gases released from each venting cycle.

4.5.4.2 Development of Tests. The physical property tests listed in Section 4.5.1 will be developed for the 222-S Hot Cell Facility in the 200 West Area of the Hanford Site.

The development of techniques for analysis of organics will include functional group analysis by gas chromatography/Fourier Transform Infrared Spectroscopy (GC/FTIR), total chelation, chelator analysis by the complementary method derivatization GC/MS, LC/MS, capillary electrophoresis-electrospray, LC/ICP/MS (for chelators and organometallics), high-pressure liquid chromatography/ultraviolet (HPLC-UV), and HPLC. Although not part of the organic methods development, efforts are also under way to provide a method for peroxide analysis.

4.5.5 Fiscal Year 1992 Work Scope (Budget Year)

4.5.5.1 Waste Analyses. Analyses on additional core samples from Tank 101-SY will be conducted. Analyses will continue on gases released from the various venting cycles. Analyses will be initiated on core samples from other Watch List tanks. These tanks have not yet been identified because of the emphasis on Tank 101-SY, but evaluations conducted in late FY 1991 and early FY 1992 will determine which tanks will be sampled.

4.5.5.2 Development of Tests. It will be necessary to check out the newly developed tests for physical properties and organic compounds with actual waste from some of the tanks. Some trial runs will be conducted to verify the techniques on radioactive samples. If needed, methods will be developed for the analysis of high molecular weight compounds that are not amenable to the methods developed in the chelator analysis. As these test methods become qualified, they will be incorporated into the routine analyses.

4.5.6 Fiscal Year 1993 Work Scope (Plan Year)

4.5.6.1 Waste Analyses. Analyses will be conducted on core samples from other Watch List tanks.

4.5.6.2 Development of Tests. All development activities will be completed in FY 1992.

4.6 DEVELOPMENT OF ADDITIONAL APPROACHES IN CHARACTERIZING HYDROGEN TANKS

The primary means for characterization of tank waste is through analyses of samples obtained from core drilling. As indicated in Section 4.4.2, additional work is required to get the drill system ready for use in Tank 101-SY. Additional technologies for in situ waste characterization are being examined for application to Tank 101-SY and other Watch List tanks to determine whether information on the chemical and physical nature of the waste can be obtained in a more efficient and cost-effective manner.

4.6.1 Tank Gamma Scans

Gamma scans are being conducted in five separate tank risers in the annulus of Tank 101-SY using existing equipment routinely used to determine the interstitial liquid level in other tanks. Gamma scans in the tank annulus

are being conducted at 2- to 3-week intervals in an attempt to correlate gamma levels to tank waste material interfaces, depths, levels, and movement relative to the hydrogen release dynamics. A gamma scan soon after the Window B release event will allow data comparisons following a waste content rollover, where temperature profiles are seen to reverse. Gamma spectroscopy at 17 vertical points in two riser locations in the annulus is also planned using a cadmium-telluride detector in the actual tank environment. A final report was issued in April (WHC-EP-0428) (Leggett et al. 1991).

4.6.2 Development and Application of Other Technologies

A wide variety of technologies exist for the physical and chemical characterization of materials. A number of meetings at the Hanford Site have been conducted to determine which methods warrant investigation. The methods were categorized as evaluation of the physical condition of the tank and the contents, physical properties of the waste forms, and chemical information for the waste. Several methods are being examined:

- Infrared thermographic scanning of the surface of the waste tank contents is being investigated to verify the analytical model. Activities supporting procurement of a commercial system have been initiated.
- Fiber Optic (FO) instrumentation, specifically FO chemical sensors, are of some interest for Tank 101-SY as a result of their being intrinsically safe. A task team has been evaluating the maturity of the technology and surveying the available resources and methods. National laboratories (Lawrence Livermore National Laboratory [LLNL], Los Alamos Scientific Laboratory [LASL], Sandia National Laboratory [SNL], and PNL) are being consulted. A private consultant has been contacted in the area of FO sensors in hostile environments. Several not-for-profit organizations and federal agencies have been contacted relative to their capabilities. The Westinghouse Science and Technology Center (W-STC), has also been engaged to provide assistance in this area.
- Novel potential in situ chemical sensors including piezoelectric resonators, the PNL-developed spectrometer-on-a-chip which is based on absorption spectra, and LANL-developed probes for NO₂ detection and absorption spectra measurements.

Support is being obtained from W-STC. A specific scope of work, addressing near-term needs, was mutually agreed to between W-STC and Westinghouse Hanford during a 2-day workshop at the Hanford Site. Appendix B provides a copy of the statement of work.

Support is being obtained from the U.S. Bureau of Mines in Pittsburgh. Discussions have been held relative to explosivity classification and testing, intrinsic safety, instrumented drill string instrumentation, and FO gas sensors. A scope of work was prepared which includes bringing key U.S. Bureau of Mines resources to the Hanford Site for several days of technical assistance.

4.6.3 Development of New Approaches for Waste Characterization (Pacific Northwest Laboratory)

The focus of this activity is to develop in situ measurement methods for physical properties that are important to understanding waste behavior and dynamic processes, but which cannot be obtained through core sampling and laboratory testing. In situ measurements must be performed when (1) the property, such as location and size of gas bubbles, is a property of the bulk waste and is not preserved in a core sample, and (2) the time dependence or variation of a property is required. Understanding the time variation of certain properties just before and after a hydrogen release may be particularly important in understanding the hydrogen-generating mechanism and the waste dynamics.

The following four in situ sensors and measurement methods may be developed to measure the indicated properties and characteristics:

- Acoustic probe for bubble characterization (size and location)
- Torsional waveguide for density and viscosity measurement
- Eddy current probe for mapping of interfaces
- Acoustic waveguide for temperature profiling (which will provide an alternative method for confirming thermocouple measurements).

To understand the behavior of the tank contents it may also be important to know the values for certain other properties. The need for these values will be identified as a result of the activities of Activity 4.7. Generally, these properties should be obtained by core sampling and laboratory testing. These properties include mass density, specific heat, thermal conductivity, permeability of the crust for hydrogen (H_2) and nitrous oxide (N_2O), particle size distribution of the sludge, solubility of H_2 and N_2O in the sludge, electrical conductivity, magnetic permeability, and acoustic properties (velocity and attenuation). Equipment is commercially available to obtain these measurements, except for the acoustic properties which require special fixturing and analysis.

Therefore, in addition to development of the four in situ methods described above, this activity also may address the development of a laboratory system to measure acoustic properties.

4.6.4 Fiscal Year 1991 Work Scope (Current Year)

A task team was established for reviewing the potential applications of FO sensors. They will provide a recommendation for areas that would benefit from the application of this technology. In addition, a cost estimate for the development activities will be prepared for a broad range of applications to tank farm issues.

A contractual agreement will be established with the W-STC division to provide support in the assessment of various methods to gather information from the tank. This will include new approaches for measurement of temperature and other process parameters.

The PNL started an assessment of various in situ methods in FY 1990. This year PNL will complete the assessments. Many of the methods involve determination of physical properties.

4.6.5 Fiscal Year 1992 Work Scope (Budget Year)

From the studies conducted in FY 1991, several technologies providing a near-term benefit will be selected for application to the waste tanks. Laboratory tests will be conducted to verify the techniques and engineering plans will be prepared for the fabrication and installation of the devices on selected tanks.

4.6.6 Fiscal Year 1993 Work Scope (Plan Year)

Instruments prepared in FY 1992 will be operated in the field and the data will be analyzed.

4.7 TANK MODELING

The reduction and eventual mitigation of the flammable gas accumulation and release requires an understanding of the mechanisms involved in each step of the process.

4.7.1 Thermo-Physical Modeling

The focus of this activity is the development of mathematical models for the thermo-physical processes occurring in Tank 101-SY and the incorporation of these models into an appropriate computer code. The approach to be taken will include the assembly and correlation of available data, the development and refinement of mathematical models of the mechanisms involved, and the development of physical models to demonstrate mechanisms and to verify analyses. This activity will be conducted by PNL under the direction of Westinghouse Hanford.

4.7.1.1 Mathematical Modeling. Mathematical models of the likely mechanisms leading to the periodic increase and/or decrease in waste volume and the concomitant release of flammable gases from Tank 101-SY will be developed and/or refined. One of these models is the thermal model that will be used to calculate the thermal profile in the tank before and after a gas release. Other models will be developed for the bubble dynamics and fluid dynamics. Specialists and consultants in various fields will be used to develop these models.

The results from these individual modeling efforts will be analyzed to verify the applicability to Tank 101-SY and modified as appropriate. These individual models will be brought together to provide the comprehensive model of Tank 101-SY upon which computer simulations will be made.

4.7.1.2 Computer Modeling. Existing computer codes that model convective turnover of a fluid do not include all of the mathematical factors needed to explain the physical processes that are taking place in Tank 101-SY. For instance, bubble formation and dynamics and the action of the solids will be needed to simulate the periodic gas release in the tank. The mathematical models that describe these processes, as well as sludge rheological properties, will be programmed into an appropriate computer code. It is expected that the upgraded computer code will provide an important demonstration of integrated modeling of Tank 101-SY. The code will be capable of dealing with the simultaneous interactions of the fluid dynamic forces and provide a graphic depiction of what is happening in the waste tank liquid during gas release.

4.7.1.3 Physical Modeling. As the computer models are developed, there will be a need to validate them against measurements made in the actual tank and in model systems. With the current safety concerns and the limitations that radioactive wastes place on the type of measurements that can be made in Tank 101-SY, there is a need to develop physical models of the tank. In this equipment, parameters can be adjusted according to the needs of the mathematical model and the results of various experiments compared with the results of the computer simulations. Likewise, there will be portions of the mathematical models which may require development through testing of physical models.

The physical modeling experiments are envisioned to be performed in proportionally scaled vessels. For this effort, 1/4- and 1/12-scale tanks are available, but the sizes of many tests are expected to be smaller, laboratory scale (some at other sites). The vessels will be scaled according to the model being investigated and such that dimensionless properties can be obtained for use in the models.

4.7.1.4 Crust Modeling. Overlying the liquid in Tank 101-SY is a crust estimated to be up to 4 ft thick. The role this crust plays during the release of gases from the tank has not been determined. However, the data on the gas volumes and waste volume increases suggest that the gases do not accumulate under the crust. In this subtask, at least three models for the crust will be investigated: (1) the crust acts as an impermeable layer that fractures during a release event, (2) the crust acts as a permeable layer through which the gas is throttled, and (3) the rigid crust tilts during an event. In this subtask, estimates of the thermal and mechanical properties of the crust will be made and used in the models to determine which is the most probable role the crust plays in the release of the gases from the tank. These models will be refined as data on the crust become available from the characterization of tank crust (both ex- and in-tank measurements) and from the characterization of synthetic crusts produced in laboratory experiments.

4.7.2 Gas-Flow Model

Analytical models have been developed to describe the transport and distribution of the vented slurry gases within the tank dome and throughout the ventilation system. This thermal-hydraulic modeling of Tank 101-SY gas space and ventilation system is being performed with a finite-difference code which solves the conservation equations for mass, energy, and momentum. The code uses a flexible noding scheme that allows it to be run in a lumped-parameter mode or in a one-, two-, or three-dimensional mode. Both lumped-parameter and three-dimensional models have been developed. The initial model was developed using the lumped-parameter modeling option (i.e., each waste tank was modeled as a single, perfectly mixed volume; Tanks 102-SY and 103-SY are included because they connect to the same ventilation system as Tank 101-SY). This model has been used to estimate the gas injection volume and rate required to reproduce the observed pressure pulse in Tank 101-SY. The analysis also provides a calculated hydrogen concentration as a function of time in the tank as well as points downstream in the ventilation system (based on the perfectly mixed tank assumption). This model has been used to simulate each of the gas release events that has occurred since April 1990. This effort has contributed significantly to the understanding of these events. These analyses will continue to be performed for each gas release event in Tank 101-SY.

As stated above, a three-dimensional model of the tank gas space has also been developed. This model has been used to demonstrate that good mixing in the tank dome is anticipated under most conditions. However, the analyses have also identified thermal stratification caused by high ambient temperature as a potential mechanism leading to poor mixing and locally high hydrogen concentrations. The three-dimensional model has also been used to evaluate postulated releases (e.g., during core sampling) and proposed mitigating actions (e.g., local nitrogen purge). These activities are expected to continue to support various planned operating evolutions. Parametric sensitivity studies will be performed to evaluate the impact of several assumptions made in developing the model (e.g., physical description and location of the gas release path through the crust).

These models also are being used as integral part of the ventilation system studies as described in Section 2.2. Finally, similar modeling activities are anticipated for other flammable gas-generating tanks as the requirements are identified.

4.7.3 Fiscal Year 1991 Work Scope (Current Year)

4.7.3.1 Gas Flow Modeling Work Scope. Planned FY 1991 activities related to gas-flow modeling in flammable gas-generating tanks include the following:

- Perform sensitivity studies to evaluate the impact of various assumptions made in the existing gas flow/mixing model of Tank 101-SY. Items to be studied include the effect of increasing the number of nodes in the three-dimensional model of the dome space and various assumptions related to the gas-release location (e.g., single point versus distributed release).

- Analyze gas-release events which occur in Tank 101-SY during FY 1991 to evaluate gas-release quantities and rates.
- Evaluate gas-release events in other tanks. This activity is not well defined yet, but some evaluation of gas-release events in other tanks on the Watch List may be initiated this year.
- Support the Tank 101-SY ventilation system upgrade sizing study/ conceptual design as necessary.

4.7.3.2 Thermo-Physical Modeling Work Scope. The principal activity in this area during FY 1991 will be the compilation of data from Tank 101-SY and the development of initial conceptual models to explain the observed response. Various theories will be tested against the available data using relatively simplistic modeling techniques. In addition, the development of more detailed hydrodynamic computer models will be initiated as the understanding of the phenomenon increases. Finally, detailed planning for future activities, including physical experiments and the identification and collection of necessary data, will be performed.

4.7.4 Fiscal Year 1992 Work Scope (Budget Year)

4.7.4.1 Gas Flow Modeling Work Scope. Planned FY 1992 activities related to gas-flow modeling in flammable gas-generating tanks include the following:

- Analyze gas-release events which occur in Tank 101-SY during FY 1992 to evaluate gas-release quantities and rates.
- Perform analyses of gas-release events in other tanks as deemed appropriate.
- Support the detailed design of the Tank 101-SY ventilation system upgrade.

4.7.4.2 Thermo-Physical Modeling Work Scope. The analytical modeling of Tank 101-SY waste behavior will continue to be refined and tested against new data. Physical model testing will be performed to demonstrate the postulated gas accumulation/release phenomenon and results from this testing will be used to validate and upgrade the mathematical model. Evaluation of data from other tanks is anticipated. Finally, proposed remediation techniques will be evaluated.

4.7.5 Fiscal Year 1993 Work Scope (Plan Year)

To be determined.

4.8 SYNTHETIC WASTE STUDIES

An initial approach for conducting tests on synthetic wastes was given in the *Safety Improvement Plan-Hydrogen in Waste Tanks* (Leggett et al. 1990). Since the Plan was issued, the Tank Waste Science Panel has provided some

recommendations on an expanded program. Detailed task statements have been prepared for review by the various participating organizations. A summary of the program will be given below.

The synthetic waste studies provide a key element in the approach for understanding the mechanisms for gas generation and accumulation. In addition, these studies will provide valuable information for safety analyses and the studies being conducted for remedial actions.

There are four participants in the synthetic waste studies: PNL, Westinghouse Hanford, Argonne National Laboratory (ANL), and the Georgia Institute of Technology (GIT). When this document was prepared, negotiations were still under way with GIT. Table 4-3 shows a summary of the lead and supporting roles for each participant.

4.8.1 Development of Methods for Producing Synthetic Wastes

Information relevant to the flammable gas Watch List tanks will be obtained and assembled. This will include reports on (1) the history of these tanks, (2) measured and predicted compositions of the waste in these tanks and other tanks containing complex concentrate waste (CCW) and DSS, and (3) chemical reaction studies to date. In addition to the reports, personnel familiar with pertinent tank issues and history will be contacted.

Of most interest is the waste present in Tank 101-SY because this tank is showing the largest fluctuations in surface level. However, similar organic-bearing wastes were added to other Hanford Site waste tanks. It is, therefore, important to investigate the behaviors of a range of waste compositions.

The synthetic waste compositions tested will be based on an understanding of the wastes added to these tanks as well as the results from the chemical analyses of actual waste from tanks (101-SY, 103-SY, 103-AN, 107-AN). Based on these analyses and on the process operations, recipes and methods for producing simulated wastes will be developed. To determine a reference waste composition, Hanford Site personnel responsible for chemical analyses and preparation of synthetic wastes representative of slurry growth tanks will be contacted to obtain copies of pertinent reports and recipes.

4.8.2 Crust Formation and Properties

In Tank 101-SY, crust formation and behavior may impact retention and release of the generated H_2 and N_2O . Knowledge about the chemical composition, physical properties, physical behavior, and reactivity of the crust is important in making decisions with respect to potential remediation and disposal operations.

Using various synthetic wastes, the impact of waste variability on crust formation and on selected physical and chemical properties of the crust will be determined. The results of these synthetic crust characterizations will be compared with results obtained from the characterization of actual crust material. These comparisons will allow an assessment of the validity of the

Table 4-3. Synthetic Waste Studies--Hydrogen Issue.

Task	Pacific Northwest Laboratory	Westinghouse Hanford Company	Georgia Institute of Technology	Argonne National Laboratory
Synthetic recipe	Independent evaluation Variations around base	LEAD Base point Update given Core sample	--	--
Crust--rate of formation, solubility, hardness, permeability, reaction potential, constituents, effect of synthetic recipe variations	LEAD	Observations Adiabatic calorimeter tests	Limited studies	Limited studies
Gas generation-rate, constituents, effect of waste variations (viscosity, temperature, constituents)	Observations Biology	LEAD Effects of slurry composition, temperature, organic functional groups Corrosion Pilot tests	Limited studies	Limited studies
Chemical reactions--tracers to identify reactions and source of gases--waste constituents versus time	Evaluation by Science Panel	Observations	LEAD Heat generated by reaction Radiation effects (limited studies)	--

Table 4-3. Synthetic Waste Studies--Hydrogen Issue. (cont)

Task	Pacific Northwest Laboratory	Westinghouse Hanford Company	Georgia Institute of Technology	Argonne National Laboratory
Radiation effects waste g-factor and principal things affecting it	--	--	--	LEAD Literature search
Synthesis of results reports, suggested remedies	LEAD Science Panel input Crust remedies Summary of relevant tank data	Additives and temperature remedies	Chemical remedies	Chemical remedies

results obtained from the characterization of the synthetic crusts. The synthetic crusts will be grown at the temperature of Tank 101-SY (about 60 °C). The following activities will be completed:

- The rate of crust formation, as measured by the thickness, will be determined.
- Selected physical properties including shear strength, penetration resistance, density, and weight percent water and nonorganic material (as oxides) will be determined for recovered crust.
- Selected physical properties including density, weight percent water and nonorganic material, viscosity (viscosity versus shear rate) and percent centrifuged solids will be determined for the composite slurry, any aqueous phase(s), and any sludge.
- Selected chemical analyses including anions available by inorganic ion chromatography (IC), elements by ICP atomic emission spectrometer, TOC, total inorganic carbon, and organic complexants will be determined for the crust, the aqueous phase(s), the sludge, and the composite slurry.
- The solubility of the crust in selected aqueous media will be determined.
- The reactivity of the crust and aqueous phases will be measured using various analytical methods which will include time-to-

explosion tests (TTX), differential scanning calorimetry (DSC), scanning thermogravimetry (STG), and accelerating rate calorimetry (ARC).

4.8.3 Gas Generation Reaction Mechanisms and Kinetics

A lack of knowledge about the mechanism(s) by which gases are generated in Tank 101-SY has weakened the basis for the safety analyses for this tank. Adequate safety analyses will be required before safe remediation of this tank can be undertaken.

The objective of this subtask is to determine the stoichiometry, mechanism, and kinetics of the gas-generating reaction(s). Experimental studies will be performed to determine the basic information about the reaction(s) in the wastes:

- The important parameters affecting the gas generation (based on a screening study of compositional and radiation effects)
- The chemical mechanisms which produce the reactive gases (primarily H_2 and N_2O)
- The part that radiation plays in effecting gas generation.

Experiments will be performed to determine the importance of various factors on the gas-generating reactions. A statistically designed screening study will be used to identify waste constituents that influence or participate in the gas-generating reaction(s).

Based on the work of Delegard (1990) and others, the following are being considered as potential factors for inclusion in the screening study: $NaNO_3$, $NaNO_2$, $NaAlO_2$, EDTA, HEDTA, Cl^- , Ni^{2+} , Fe^{2+} , Fe^{3+} , NaOH, platinum, ruthenium, rhodium, palladium. Radiation effects will also be assessed. The results from the screening study will provide some of the basis for follow-on activities.

4.8.4 Stoichiometry, Kinetics, and Mechanisms of Reactions

In this task, the stoichiometry, kinetics, and mechanism(s) of the gas-generating reaction(s) will be investigated. The direction for this work will be based partially on the information gained from the screening studies identified above. It is anticipated that researchers at the GIT will perform this work. Contract negotiations are under way for this activity. The following approach will be used:

- The stoichiometries of the reaction(s) will be determined by using simple systems of critical reactants (e.g., $NaNO_2$ and HEDTA). The goal will be to identify and determine the amount of gaseous, solid, and soluble organic and inorganic products produced per mole of reactant(s).

- The reactivities of functional groups present in the reactive complexants will be isolated by using simple model compounds and isotopic tracers. For example HEDTA, identified by Delegard (1990) as a reactive complexant, is composed of alcohol, amine, and carboxylate groups; the reactivities of these groups will be investigated using simple molecules and ^{13}C , ^2H , and ^{15}N labeled functional groups.
- Functional groups in the reactive complexants themselves will be traced with isotopic labels and behavior determined. The behavior will be compared with the model compounds.
- The kinetics of the reaction(s) will be investigated using pseudo first-order conditions to allow examination of the effect of changing the concentration of one particular reactant. Each of the critical reactants or factors will be investigated.
- The kinetic parameters of the Arrhenius equation will be determined by changing the temperature of the reaction(s).

In these experimental studies, various measurements will be performed to follow the progress of the reaction. These measurements include the volume of gas produced, the composition of the gas produced, the increase in system pressure resulting from gas production, and the composition of the slurry.

4.8.5 Determination of the Effects of Radiation

The wastes in Tank 101-SY are highly alkaline and have been in the DSTs for approximately 15 years (and thus exposed to a radiation field). In that environment, many reactions can occur which will change the chemical nature of the constituents in the waste. It is, therefore, important to determine the effect of long-term exposure of the wastes to radiation. Researchers at ANL will conduct this work.

To investigate the effects of gamma radiation (1) pertinent literature will be reviewed, (2) external radiation will be included as one of the factors evaluated in the screening study, and (3) experimental studies will be performed to determine the effect of radiation on gas generation.

In the literature review, reports on the effects of radiation on the Hanford Site waste constituents (including complexants) and on their reactions will be assembled and evaluated. Of prime interest will be gas-producing reactions, in particular, those reactions producing the reactive gases such as hydrogen, nitrous oxide, and the oxides of nitrogen.

Experimental studies will be performed to assess the effects of radiolysis on gas generation. Experiments will be performed to determine if the chemical generation is enhanced by the presence of radiolytic generated reaction intermediates or if the two processes, chemical and radiolytic, are

more-or-less independent. Another goal for these experiments is to measure the G values (molecules of gas/100 eV of deposited energy) for the generated gases, such as H_2 and O_2 , and the importance of these gases on the degradation mechanism.

Appendix C provides the detailed statement of work for this activity.

4.8.6 Testing of Actual Wastes

Finalization of the treatment and/or remediation strategies for the gas-producing and gas-retentive wastes is dependent on chemical and physical characterization and determination of behaviors, reactivities, and sensitivities of actual wastes. Such testing is required to validate studies with synthetic wastes and any treatment methods that arise from these studies.

Testing of the actual wastes could include studies to determine (1) the composition of gases generated and the gas-generation rate and (2) the chemical composition, the physical properties, the reactivities, and the sensitivities of crusts.

4.8.7 Synthesis of Results

A working group of the participants for Sections 4.8.2 through 4.8.5 will hold regular meetings to review the status of work and to ensure a close interaction of each organization. Status reports will be issued on these tasks and will provide up-to-date answers on the issues of gas generation.

4.8.8 Tank Waste Science Panel

Because of the potential for explosion and attendant release of hazardous materials into the environment, Westinghouse Hanford and the DOE realized the need for knowledge about the chemical and physical processes occurring in Tank 101-SY that lead to generation of the gases and their episodic release. In June 1990, PNL, with support from Westinghouse Hanford, began assembling a panel of senior scientists and engineers to develop a better understanding of the physical and chemical processes in Tank 101-SY leading to gas formation and release. This knowledge is necessary to provide a technically defensible basis for stabilization and mitigation of the present problem as well as future remediation of the tank and its contents. The Tank Waste Science Panel includes scientists from DOE laboratories, various companies, and universities; the panel includes experts in theoretical chemistry, separations chemistry, organic chemistry, radiation chemistry, analytical chemistry, nuclear chemistry, chemical engineering, process chemistry, mechanical engineering, and fluid dynamics. Other experts will be added to the Panel as the situation dictates.

To accomplish its mission the Panel will accomplish the following activities:

- Compile the data available on Tank 101-SY pertinent to the generation and subsequent release of gases.

- Analyze the available data on Tank 101-SY to establish, if possible, preliminary models of the chemical processes resulting in the formation of H_2 and the physical processes giving rise to the episodic release of the gases.
- Provide recommendations on the research program to address the outstanding issues identified in the analysis of the data on Tank 101-SY.
- Review new information about Tank 101-SY and the results of the research program on a periodic basis and recommend further work as required.

4.8.9 Fiscal Year 1991 Work Scope (Current Year)

In FY 1991, studies are being directed towards (1) developing methods to prepare synthetic wastes suitable for use in gas-generation studies, (2) determining crust growth behavior, crust composition, physical properties, and reactivity, (3) initiating a systematic investigation to determine the thermally driven chemical mechanisms responsible for gas generation, and (4) initiating a systematic investigation of the role of radiation in gas generation. The Tank Waste Science Panel, a multidisciplinary group comprising scientists from DOE laboratories, universities, and industry, was established to provide technical oversight and recommendations for further research.

Recipes and methods for producing synthetic tank wastes will be developed, based on a review of available literature and other resources. A report will be prepared by PNL that critically reviews available waste composition data for DSTs on the hydrogen or flammable gas Watch List. This report will also review synthetic waste compositions that have been used in past studies and assess possible waste compositional effects on gas generation.

The rates of generation, composition, physical properties, and reactivity of crusts formed on synthetic wastes will be assessed at PNL. The composite slurry, aqueous phases, and bottom saltcake will also be characterized. Selected physical properties include shear strength, penetration resistance, viscosity, density, volume percent centrifuged solids, weight percent water and oxides. Compositional analyses include TOC, total inorganic carbon, elemental analysis by ICP, and anion analysis by IC. The reactivity of the crust and aqueous phases will be assessed by TTX, DSC, and STG. For a selected subset of these tests, the rate and stoichiometry of gases generated during crust growth will be evaluated.

Laboratory tests are to be conducted at GIT to determine chemical mechanisms responsible for the generation of hydrogen and other gases from Tank 101-SY. The studies will focus on identification of the product, identification of the source of carbon, nitrogen, and hydrogen for the formation of CO_2 , H_2 , N_2O , and NH_3 , determination of the stoichiometry and kinetics of the reactions, and identification of any key intermediates formed in the reactions. A test plan will be prepared by GIT and approved by Westinghouse Hanford before beginning actual experiments. Initial studies

will consider glycolic acid, HEDTA, and inorganic constituents to be identified by Westinghouse Hanford. Methods will be developed to analyze gas mixtures, gas anions, and gaseous degradation products of organic constituents of the waste. Studies will be initiated to determine the rate of gas evolution as a function of organic concentration and temperature, with the goal of developing kinetic rate expressions for each important liquid phase and gaseous specie.

Studies to determine the role of radiation on the production of hydrogen and other gases from Tank 101-SY will be performed at ANL. Initially, a literature survey will be conducted concerning the rates of gas generation by the radiolysis of water and organics of interest. Results of the literature survey will be used to calculate the expected overall yields for radiolysis products in Tank 101-SY; an open literature report will be issued by ANL on this subject. Irradiation tests will be conducted on synthetic waste samples to measure gas generation rates and products. Tests will be conducted to identify whether hydrogen is a primary product and/or the result of secondary reactions. Radiolytic yields, or G values (molecules/100 eV), will be determined for specific reactions. A test plan will be prepared by ANL and approved by Westinghouse Hanford before beginning actual experiments.

Integrated gas-generation studies will be conducted by Westinghouse Hanford with the purpose of testing hypotheses resulting from studies conducted at ANL, GIT, PNL, and elsewhere. Initial tests using simulated wastes will assess the relative importance of gamma radiolysis, thermal decomposition, and mild steel corrosion on the rate and stoichiometry of gas generation. Using the reference synthetic waste composition, these initial tests will be aimed primarily at establishing the N_2O/H_2 ratio characteristic of thermally driven versus radiolytic reactions.

A summary report will be prepared that discusses the results of synthetic waste studies conducted during FY 1991. This report will be compiled by PNL, but will include contributions from ANL, GIT, PNL, Westinghouse Hanford, members of the Tank Waste Science Panel, and others, as is appropriate.

4.8.10 Fiscal Year 1992 Work Scope (Budget Year)

Synthetic waste studies will be aimed at determining the sources, retention, and eventual release of reactive gases from certain Hanford Site waste storage tanks and identifying possible remedies that might be used to mitigate this gas buildup. The studies will consist of (1) basic studies of the stoichiometry, kinetics and mechanisms of gas generation by chemical decomposition, using simplified synthetic wastes, to be conducted at GIT, (2) basic studies on the role of gamma radiolysis on the stoichiometry, kinetics and mechanisms of gas generation, to be conducted at ANL, and (3) integrated gas-generation studies, to be conducted at PNL, which will consider the overall effects of chemical decomposition, radiolysis, and steel container corrosion. Activities of the Tank Waste Science Panel, which provides technical review and recommendations for future studies, is also included.

Studies to be conducted at GIT will emphasize the stoichiometry, kinetics, and mechanisms of gas generation by chemical decomposition.

Reactivities of functional groups present in complexants will be isolated using simple model compounds and isotopic labeling (^2H , ^{13}C , ^{15}N) of specific functional groups where appropriate. Behavior of the simple model compounds will then be compared to reactive complexants themselves. This effort will include identification of decomposition products of the complexants remaining in the aqueous/solid phases and may require development of advanced analytical methods.

Studies to be conducted at ANL will emphasize radiolytic decomposition of complexants to produce hydrogen and other gases. Radiolytic yields will be determined for gaseous products of interest. It will be determined whether degradation products are generated directly from complexants such as HEDTA, or from degradation products. Studies will also address whether hydrogen generation requires both radiolytic and chemical processes. A principal objective is to determine the rate of generation of primary radicals, identify subsequent reaction pathways, and assess the viability of radical scavengers as a means to suppress hydrogen generation from radiolysis.

Integrated gas generation studies, to be conducted at Westinghouse Hanford, will consider the combined effects of gamma radiolysis, chemical decomposition pathways, and steel container corrosion of the production of hydrogen, nitrous oxide, and other gases. Possible reaction mechanisms identified in basic studies at ANL and GIT, as well as those proposed by the Tank Waste Science Panel, will be tested using synthetic wastes more closely resembling actual tank compositions than those used in basic studies. In addition to gamma ray intensity and temperature, the sensitivity of gas-generation rates and stoichiometry to components such as NaNO_3 , NaNO_2 , NaAlO_2 , and Cl^- , first-row transition metals (Ni^{2+} , Fe^{2+} , and Fe^{3+}), second-row transition metals (platinum, ruthenium, rhodium, and palladium), key organic complexants and their breakdown products, and atmospheric oxygen, will be investigated.

4.8.11 Fiscal Year 1993 Work Scope (Plan Year)

Gas-generation studies using synthetic wastes will be expanded to consider a broader range of organic components present in actual tank wastes, many of which remain to be identified. The GIT will continue to lead the efforts to determine the kinetics, mechanisms, and stoichiometry of gas generation by chemical pathways; ANL will continue to lead efforts to assess the role of radiolysis on gas generation; and Westinghouse Hanford will serve as leader of integrated gas-generation studies. Emphasis of these studies will shift towards identifying and testing possible means of mitigating the episodic release of flammable gases from the DSTs.

4.9 TANK DATABASE

This task is part of the Waste Tank Properties and Contents Activity (1W1W5) referenced in Section 4.2. It is discussed here to show how the data described in this program plan will be collected, analyzed, and archived.

The entire Waste Tank Safety Program requires real-time access to quality controlled, traceable data. These data include operational information

(e.g., temperatures, liquid levels), waste inventory data (based on both historical records and laboratory analyses), and historical information such as structural and construction information, operating records, safety evaluations, engineering evaluations, nonconformance reports, engineering change notices, laboratory studies, and all company correspondence related to tanks.

To respond to the widely varying requests for information from different internal and external groups, a tank history organization has been established, in the Waste Management Technology organization, to network the existing computerized databases and to compile the critical historical information into a centralized spot. This group will ensure that adequate quality control is maintained over the data. This group is funded through activity W1W5, to ensure that all critical tank safety data, including that related to flammable gas generation, are adequately controlled and accessible. A centralized "library" of information has been established in Building 2750-E of the 200 East Area to serve as a collection and resource center of information for individuals to use while analyzing the tanks. This organization will also become the centralized group to respond to requests for existing information on tanks.

The work scope for FYs 1991, 1992, and 1993 are described in *Waste Tank Properties and Contents Program Plan* (DeFigh-Price 1991).

4.10 REMEDIAL ACTIONS

Development of an acceptable remedial action requires a number of steps, as shown in Figure 4-4, which all lead to control of the tank. The process starts with the identification of criteria for remediation; for example:

1. Maintain the tank dome space at a value that is less than XX% of the lower flammability limit.
2. Maintain a negative pressure in the dome space.
3. Prevent a "crust burn."
4. Prevent uncontrolled reactions of the gas and waste.
5. Maintain tank integrity.
6. Maintain disposal and retrieval options.
7. Prevent unacceptable releases of toxic or radiological substances.
8. Prevent unacceptable alteration of crust and/or liquid waste properties.
9. Prevent buildup of gas pockets under the crust that exceed X cubic feet.
10. Prevent buildup of gas in the slurry that exceeds X cubic feet (STP).

Figure 4-4. Remediation Logic.

11. Maintain ease of maintenance and operation.
12. Minimize overt actions (i.e., be passive to extent that is possible).

Selection of any near-term remediation concept also must consider the following:

1. "Timing" (i.e., When will the concept be ready for use?)
2. Reliability
3. Minimum impact on long-term remediation
4. Maintain surveillance options
5. Allow for test/demonstration of other concepts
6. Attempt to mimic natural phenomenon.

A process that will occur in parallel to the criteria definition is the proposal of possible concepts. Table 4-4 lists some of the concepts discussed to date. For each concept the table provides a short listing of the features of the proposed concept, the possible approaches to effect the concept, the information required for evaluating the concept, the potential issues that require resolution, and finally, the means by which the program will acquire the requisite data and analyses to solve the issues and provide the knowledge required for the evaluation studies. The last row of the table also provides a reference to the program plan section that provides the necessary information for each concept. A more detailed list of the sections on required knowledge, issues, and means to obtain knowledge and solve issues is given in Appendix D.

As shown in Figure 4-1, the concepts will be evaluated against the criteria. If any of the concepts meet the criteria, they can be selected for detailed engineering evaluations. Once a concept has been selected, the concept can be turned into a project for design fabrication and implementation. Figure 4-1 also shows that various steps in the process will require data from tank waste analyses, laboratory studies, and analyses. Safety and environmental evaluations are also part of the process.

4.10.1 Fiscal Year 1991 Work Scope (Current Year)

Activities in FY 1991 will be directed to the development of the criteria and "brainstorming" for concepts.

4.10.2 Fiscal Year 1992 Work Scope (Budget Year)

Evaluations of the concepts will be conducted and engineering studies will be initiated.

Table 4-4. Remediation Concepts. (sheet 1 of 2)

	Dilution of tank contents	Circulation of tank contents	Transfer of tank contents	Sparge with inert gas
Features	<ul style="list-style-type: none"> • Lower gas-production-per-unit volume • Enhance release of gas because of lower viscosity 	<ul style="list-style-type: none"> • Promote continuous release of gas • Retard crust buildup • Dissolve crust 	<ul style="list-style-type: none"> • Reduce volume of waste, thereby lowering total gas production 	<ul style="list-style-type: none"> • Lower gas production <ul style="list-style-type: none"> - Circulation - Removes other gases (O_2, N_2O)
Approach(es)	<ul style="list-style-type: none"> • Dilute with water • Dilute with other waste 	<ul style="list-style-type: none"> • Pump waste; options include bottom-to-top and bottom only • Mechanical stirring 	<ul style="list-style-type: none"> • Pump waste to another tank 	<ul style="list-style-type: none"> • Install lances • Circulate waste to a location (some other position) for gas injection and return.
Required knowledge	<ul style="list-style-type: none"> • Solubility of waste • Compatibility with other waste • Chemistry of waste • Depth of various layers • Mechanism of gas generation 	<ul style="list-style-type: none"> • Physical properties of waste and crust • Chemistry of waste • Depth of various layers • Mechanism of gas generation • Efficiency of mixing and circulation • Method for circulator 	<ul style="list-style-type: none"> • Physical properties of waste • Compatibility with other waste • Mechanism of gas production • Depth of various layers • Available tank space • Method of pumping 	<ul style="list-style-type: none"> • Physical properties of waste • Gas content in slurry and sludge • Mechanism of gas production • Solubility of gas
Issues	<ul style="list-style-type: none"> • Presence of crust • No free space in Tank 101-SY • Gas generation of diluent • Verify that the method works 	<ul style="list-style-type: none"> • Presence of crust • Pump life-time • Growth/dissolution of crust • Pump requirements • Verify that the method works 	<ul style="list-style-type: none"> • Tank space • Gas generation of transferred waste • Verify that the method works 	<ul style="list-style-type: none"> • May need to dilute the waste • Number and location of lances • Effect on ventilation system • Verify that the method works • Distribution of gassy waste
Means to obtain knowledge and solve issues (Program Plan section)	<ul style="list-style-type: none"> • Sample waste in tank (4.0, 4.5) • Evaluate data for other tanks (4.9) • Build new tanks • Characterize tank (4.6, 4.11) • Evaluate mechanisms for gas production (4.8) • Tank models (4.7) • Tank instrumentation (4.11) 	<ul style="list-style-type: none"> • Sample waste (4.4, 4.5) • Characterize tank (4.6, 4.11) • Model tank (4.7) • Evaluate mechanisms (4.8) • Design study (4.10) 	<ul style="list-style-type: none"> • Sample waste (4.4, 4.5) • Characterize tank (4.6, 4.11) • Evaluate mechanisms (4.8) • Build new tanks • Evaluate data on other tanks (4.9) • Engineering study (4.10) 	<ul style="list-style-type: none"> • Sample waste (4.4, 4.5) • Evaluate mechanisms (4.8) • Tank modeling (4.7) • Ventilation study (4.12) • Design and engineering study (4.17) • Tank instrumentation (4.11)

Table 4-4: Remediation Concepts. (sheet 2 of 2)

	Ultrasonic agitation	Transfer, dilute, and agitate	Chemical treatment	Thermal treatment
Features	<ul style="list-style-type: none"> • Cause release of gases at desired timing intervals 	<ul style="list-style-type: none"> • Control release of gases 	<ul style="list-style-type: none"> • Destroy or remove compounds that produce gases • Dissolve crust 	<ul style="list-style-type: none"> • Change reaction rate that generates gas for gas generation
Approach(es)	<ul style="list-style-type: none"> • Use ultrasound to enhance bubble transport and release 	<ul style="list-style-type: none"> • Transfer 100,000 gal of slurry • Dilute with 10,000 gal of water • Maintain opening in crust • Provide mechanical energy to trigger release of gas 	<ul style="list-style-type: none"> • In situ application • Transfer waste to treatment facility • Add gas absorber 	<ul style="list-style-type: none"> • Cool the tank (reduce rate) • Heat the tank (destroy compounds)
Required knowledge	<ul style="list-style-type: none"> • Required frequency • Number of transducers • Time application (pulsed or continuous) • Mechanism of gas production • Bubble behavior 	<ul style="list-style-type: none"> • Solubility of waste • Crust properties • Waste compatibility • Amount and location of "mechanical energy" • Efficiency of mixing and circulation • Mechanism of gas production 	<ul style="list-style-type: none"> • Characterization of waste • Mechanism of gas production • Identify gas absorbers 	<ul style="list-style-type: none"> • Mechanism of gas generation • Chemistry of waste • Method to heat or cool tank
Issues	<ul style="list-style-type: none"> • Heat deposited in waste • Means to attach transducers • Verify that the method works 	<ul style="list-style-type: none"> • Presence of a crust • No free space in Tank 101-SY • Verify that the method works 	<ul style="list-style-type: none"> • Construction of a treatment facility • Mixing of materials in the waste • Verify that the method works 	<ul style="list-style-type: none"> • Tank corrosion • Effects of thermal change • Verify that the method works
Means to obtain knowledge and solve issues (Program Plan section)	<ul style="list-style-type: none"> • Evaluate mechanisms (4.8) • Tank modeling (4.7) • Laboratory testing and analyses and demonstration • Tank instrumentation (4.11) 	<ul style="list-style-type: none"> • Sample waste (4.4, 4.5) • Evaluate mechanisms (4.8) • Tank modeling (4.7) • Evaluate data on other tanks (4.9) • Design an engineering study (4.10) • Build new tank space • Tank instrumentation (4.11) 	<ul style="list-style-type: none"> • Sample waste (4.4, 4.5) • Evaluate mechanisms (4.8) • Design an engineering study (4.10) • Tank instrumentation (4.11) • Pilot plant studies 	<ul style="list-style-type: none"> • Sample waste (4.4, 4.5) • Evaluate mechanisms (4.8) • Design an engineering study (4.10) • Tank instrumentation (4.11) • Pilot plant studies

4.10.3 Fiscal Year 1993 Work Scope (Plan Year)

Detailed design work will be initiated on the most promising near-term remediation concept.

4.11 UPGRADE OF TANK INSTRUMENTATION

A major effort is being conducted for upgrading the instrumentation and the ventilation system for Tank 101-SY.

4.11.1 Gas Monitoring System

A gas monitoring system was developed for the characterization of Tank 101-SY vapor space. The system performs two primary functions on gas sample streams from three locations within the tank vapor space and a fourth location in the exhaust header:

- Real-time monitoring of hydrogen
- Real-time characterization of gas constituents.

Each vapor space location consists of a sample probe assembly installed in a 4-in.-diameter tank riser. Each assembly has three individual probes of different lengths: one probe near the top of the vapor space, one near the crust, and one in between. Only one probe on each assembly is in use at a time; it is remotely selected. The sample locations within the tank help to characterize the gases during an event as well as during normal operations.

The gas monitor system includes H₂ specific monitors, gas spectrum analyzers, grab sample stations, data acquisition systems, and all supporting instrumentation and hardware.

The percentage of H₂ in each gas sample can be monitored continuously, with an operating range of 0 to 100 vol% H₂, a resolution of 0.2 vol% H₂, and a repeatability of 0.1%. The maximum response time between when the gas enters the end of a sample probe until the instrumentation shows its H₂ concentration is 120 seconds. There will be an adjustable alarm with a setpoint of between 0.1% and 4.0%.

The gas spectrum analyzer has a resolution of 2 to 100 atomic mass units (AMU), scanning speed variable from 10 ms to 10 s per AMU, with a minimum detectable partial pressure of 5×10^{-12} torr. It is assumed that gases will be detectable to 200 ppm. The stability will be ± 0.1 AMU for mass and $\pm 2\%$ peak height after a 30 min warmup. The data interface to the data logger is RS-232.

The grab sample station will consist of four 75-cc sampling cylinders connected in series in a sample line.

The differential pressure between the tank/ventilation header and atmosphere is measured and logged for each of the four sample systems.

The range of the differential pressure transmitters is -5 to +20 in. water gauge. The header location is also instrumented to measure temperature, humidity, and gas flow rate as described in Section 2.3.

Information from all of the instrumentation is captured digitally on a data logger system. Data can be removed from the logger and taken elsewhere for off-line analysis. The data logger and mass spectrometers are housed in an instrument trailer which is located close to the tank.

The in-tank installation of the gas sampling and hydrogen monitoring equipment was completed at riser 17B for Window C. Dome space monitoring of hydrogen concentration and dome pressure will allow for characterization of the hydrogen/nitrous oxide release mechanisms in the dome. The data will be used to further validate and improve the gas flow models currently being used to assess the hydrogen release safety concerns and operating risks. The three-dimensional data will be factored into the safety analysis assumptions for hydrogen concentration as a function of time and space.

4.11.2 Tank Process Instrumentation

Upgrades are being made to the instrumentation used to monitor the operation of Tank 101-SY. These upgrades include the replacement and addition of instruments to the tank.

4.11.2.1 Exhaust Header Instrumentation. Instrumentation upgrades for Tank 101-SY exhaust header include temperature, pressure, flow and humidity.

The exhaust gas temperature is normally in the range of 90 to 130 °F. The temperature monitoring will cover the range of 32 to 200 °F to ensure data capture during the tank venting process.

The velocity measurement system, located in the 12-in.-diameter schedule 40 steel exhaust duct, will monitor flow velocity in the range from 509 to 5,093 ft/min (i.e., this equates to a normal volume flow rate of 400 to 4,000 ft³/min for gases in a 12-in.-diameter pipe when combined with temperature and pressure data). This flow range extends below the normal exhaust duct flow velocity of nominally 828 ft/min (650 ft³/min) and above the highest postulated flow velocity to date, which ranged between 2,546 and 3,820 ft/min (2,000 and 3,000 ft³/min). The range of the current flow monitoring system will also be widened to encompass the required flow range.

The dome space pressure measurement is currently used to calculate the actual exhaust duct volumetric flow as well as provide valuable data concerning the gas-release venting process. The pressure instruments will provide for monitoring in the range from -5 to +20 in. H₂O. This range extends below the normal tank pressure of nominally -2 in. H₂O and above the highest evaluated gas release pressure, to date.

The humidity measurement is used to determine the heat-carrying capacity and the relative flammability of the exhaust duct gases. It is also used to determine the evaporation rate of the tank contents. The humidity monitor will provide temperature compensated relative humidity measurements in the range of 10% to 90%.

4.11.2.2 Instrument Tree. A new instrument tree is being designed for installation in Tank 101-SY; it will accommodate a variety of measurement sensors. This multifunction instrument tree will provide above-surface and in-waste monitoring during normal operations and during a hydrogen release. The operating mode monitoring will provide enhanced information on temperature, gas and waste pressure, and hydrogen and other gas concentrations to establish nominal conditions. The same data during a hydrogen release will help characterize these parameters for the transient conditions, aiding in separating the causing from the resulting constituents within the waste. The instrument tree will consist of a group of tubes fitted to a riser adapter flange. Both open- and closed-ended tubes will be included to accommodate the measurement of temperature, both above and within, the tank residuals, gas sampling, in the vapor space and vapor space gas pressure. The instrument tree will be connected to a new signal-conditioning and data-acquisition system.

The design requirements for the instrument tree are listed below:

1. Measurements

a. Temperature

- (1) Measure temperatures at fixed elevations approximately 2 ft apart.
- (2) Measure temperatures in and above the waste.
- (3) Ensure that time response of temperature measurements is comparable to existing in-tank trees which is estimated to be approximately 10 seconds for a 63% change resulting from a step in temperature.
- (4) Because individual temperature sensors will not be replaceable, provide other methods of achieving reliability and verifiability.
- (5) Allow user selection of temperature measurement elevations before fabrication (adaptable dimensions).
- (6) Prove a single moving temperature detector for verification of measurements from fixed elevation sensors. This includes design of guide tube and feed mechanism.

b. Pressure--Provide above-waste and in-waste pressure measurement ports. This will measure in-tank dome pressure relative to atmosphere.

c. Gas Sampling--Provide gas sampling ports at three fixed elevations to be determined before fabrication. Typically, locations should be near the tank top, near the waste surface, and midway in between.

2. Mechanical

- a. Provide a generic design that can be adapted in overall length by fabrication to specific tank depths.
- b. Ensure that the tree fits into any tank riser down to a 4-in.-diameter nominal pipe size. Appropriate riser adapters may be used for larger risers.
- c. Define a "best" diameter requirement to pass through typical distorted tank risers and consider the core drill diameter.
- d. Address the inability to fully insert a tree into a tank resulting from unforeseen obstructions.
- e. Penetrate crusts of varying hardness and thickness.

3. Reliability

- a. Use high-quality components, redundancy, and other means determined by design, to ensure reliability, verifiability, and known accuracy.

4. Interfacing

- a. Define physical and instrument/electrical interfaces.
- b. Ensure that instrumentation used is consistent and compatible with existing and planned data acquisition systems.

4.11.2.3 Surface Level. Testing was done to determine the feasibility of alternative methods of measuring the surface level of the waste crust. The currently installed equipment required physical contact with the crust and also required that the contacted crust be electrically conductive. A new surface-measuring device which operates on radar technology was procured and tested. The test and recommendations for implementation were completed in March 1991 and a radar gauge was installed during Window C.

4.11.2.4 Television Camera. A television camera and lighting system was prepared for installation in Tank 101-SY during the Window C activities. The camera provides for a visual assessment of the tank surface and general condition of the tank. The last still pictures were taken in April 1989. The television camera will be used to observe the behavior of the crust. The nature and location of the gas release is required for safety assessments and for the modeling activities.

The television camera allows for real-time monitoring of sampling activities, core drilling (push mode and rotational mode) and penetrometer tests. This will support the activities from an operational viewpoint and from a safety perspective. This camera will be a valuable tool for other installation and removal activities.

Eventually, lances may have to be removed to free up space for the other instruments. Lance removal will be a difficult task and the camera is essential to this proposed operation. Finally, the television camera will aid assessment of the integrity of the tank. Other imaging techniques being considered include photography periscopes and optical fibers, using the lighting system designed for the television camera.

4.11.3 Tank Process Instrumentation (Pacific Northwest Laboratory)

Efforts are under way to upgrade the instrumentation used to monitor tank operation. This includes temperature, surface level, pressure, gas flow rate, and waste behavior and composition. Gamma scans have been conducted to characterize the tank's contents and a schedule for routine monitoring is being developed. Other technologies being evaluated include television cameras, periscopes, infrared thermography, photogrammetry, radar, acoustic monitoring, laser imaging, and multisensor image enhancement.

The work described in this section of this plan is being performed by PNL under the direction of Westinghouse Hanford. This work is being conducted using a two-phase approach. The overall objective of the initial phase is to investigate and/or evaluate a wide variety of potential instrumentation processes, devices, and techniques that could be used to monitor the behavior, and characterize the form and/or composition, of the tank contents.

For those instrumentation processes, devices, and techniques for which development work is warranted, a second phase will be completed. During the second phase, work is conducted to develop conceptual designs, procure and assemble prototype instrumentation systems, and conduct laboratory and mockup tests and provide the prototype system to the site contractor.

4.11.3.1 Temperature Monitoring. An engineering assessment of the operational integrity of the currently installed thermocouple (T/C) trees has been conducted. The existing T/C system in Tank 101-SY was evaluated, and recommendations were made relative to continued use of the existing system and/or design of replacement systems. Operational and functional criteria for the T/C systems were defined with respect to expected temperature range, accuracy, transient response, steady-state response, design life, reliability, and maintainability. This activity focused on waste Tank 101-SY in an effort to establish environmental conditions and instrument configurations, and to assess their impact on the operational performance of the T/C systems.

Literature regarding the effect of irradiation on T/C performance was reviewed as a basis for extrapolating existing data to the tank environments. The draft PNL report on this activity addressed the scope of the investigation, methodology to assess the operational status of the existing T/C systems, importance of sustained exposure to radiation environment on T/C performance, and recommendations to Westinghouse Hanford regarding the possibility of on-line calibration and/or standardization.

The accuracy and integrity of the thermocouples presently installed in tanks 101-SY, 102-SY, and 103-SY are to be evaluated based on field activity. The procedure will use electronic instruments to measure the loop resistance

of various thermocouple configurations of installed and new comparison thermocouples. In addition, the tests measure the output of installed and new comparison thermocouples using an electronic thermometer.

4.11.3.2 Stereographic Surface Topography. A survey has been completed of commercially available photogrammetric systems that might be used to analyze the surface topography of waste materials stored in Tank 101-SY. Approximately 50 suppliers of photogrammetric systems were contacted, and these results were summarized in a draft PNL report.

Two basic techniques of photogrammetry appear applicable for analyzing the surface topography of the waste tank contents. These are known as the (a) stereographic and (b) convergent techniques. The stereographic technique allows images of the surface to be obtained which, when properly viewed, indicate depth. The convergent technique does not produce a three-dimensional image, but does permit increased accuracy in measuring the three-dimensional coordinates of a feature.

By performing photogrammetric analysis of the surface crust in a waste tank, localized movements of the surface crust may be detected. In the draft report issued on this activity, it was recommended that the use of photogrammetric analysis for monitoring the surface level of waste tank contents be further pursued.

4.11.3.3 In Situ Surface Topography Methods. A literature search, augmented with laboratory testing, is being conducted to evaluate methods that can be used for determining the waste surface topography in the storage tanks. Potential methods include range finder techniques, optical triangulation techniques, optical phase detection techniques, diffractive ranging techniques, and a grid projection technique. Each of these methods is being evaluated as a means for determining surface topography.

Commercial suppliers of candidate systems are being contacted to identify equipment that meets these waste tank requirements. When possible, laboratory tests will be conducted to evaluate the feasibility and limitations of the most promising techniques.

Functional requirements for a field-applicable measurement system are being defined. A PNL report will be prepared that will summarize the constraints for such measurement systems, the techniques that were investigated, the advantages and disadvantages of each technique, and the probable cost and delivery for obtaining a commercial system or developing a customized system.

4.11.3.4 In Situ Passive Acoustic Monitoring Methods. An assessment of available passive acoustic monitoring technology was conducted. These techniques are based on detecting and analyzing the acoustic energy produced by dynamic, mechanical processes in the waste. The technology appears to be well suited for detecting shifting and cracking in the solid waste layer in the tanks. Previous experience in leak detection using acoustic emission technology suggests that this method may also be useful for detecting gases escaping through cracks in the solid crust.

During a Phase I feasibility study, the general requirements for access, temperature, radiation field, sensitivity, and sensor attachment were identified. Technology and equipment to meet these needs were defined and documented in a draft PNL report. The objective of the second phase of this work is to develop or procure a prototype acoustic monitoring system, verify operability, and provide this system to Westinghouse Hanford for installation on waste Tank 101-SY. The PNL will select, procure, and assemble an acoustic monitoring system based on off-the-shelf components. Presently, the system concept consists of microphones operating in the audible range, used in conjunction with conventional stripchart and/or magnetic tape recording equipment.

To satisfy near-term tank monitoring needs, a prototype microphone system will be designed for installation in the annulus between the primary and secondary tank shells to detect crust-related and other signal sources in the audible frequency range. Signal processing and data reduction/analysis will be performed as a follow-on activity. The goal of the follow-on work will be to associate detected acoustic signals with the tank/waste processes and behavior that caused the detected signals. Conventional signal processing techniques may be applied to reduce the effects of interfering background noises.

Alternative approaches include geophone or hydrophone techniques to detect low-frequency sources, acoustic emission (AE) techniques to detect high-frequency sources, and microphones installed in the vapor space above the waste to detect audible airborne sources. A geophone array could be installed in the access passages below waste Tank 101-SY to detect subaudible sources such as tank content movements or gas bubble generation and coalescence. One or more AE sensor arrays could be attached to the outer wall of the inner tank to detect ultrasonic sources such as crust/tank rubbing, and possibly to also provide early warning of potential loss of tank wall integrity.

In-place testing of sensor response, using a simulated signal source or other excitation technique, is needed to confirm reliable operation of the acoustic monitoring system. Conceptual design and feature testing of field-implementable geophone, hydrophone, acoustic emission, in-tank microphone, and source simulation equipment is needed to evaluate the practicability and utility of these various methods.

4.11.4 Hanford Hazardous Waste Tank Instrumentation Panel

The Hanford Hazardous Waste Tank Instrumentation Panel is established, under the direction of the Vice President, Waste Tank Safety Operations and Remediation, to identify, evaluate, and recommend new instrumentation technologies for use within the Tank Farm Complex at the Hanford Site. This effort will focus on identifying technologies which will support surveillance and characterization instrumentation needed for the Hazardous Waste Storage Tanks with unreviewed safety questions (DOE 1986).

The Panel will coordinate activities of Westinghouse Hanford, PNL, other DOE laboratories and operations, universities, and other organizations participating in the work.

4.11.5 Fiscal Year 1991 Work Scope (Current Year)

4.11.5.1 Fiscal Year 1991 Work Scope for Westinghouse Hanford. The following activities are being carried out to support the upgrade of tank instrumentation:

- Initiate the installation design for the data acquisition system equipment required for thermocouple monitoring for Tank 101-SY.
- Initiate design of a new generic multifunction instrument tree.
- Provide the installation design for the drill bit temperature monitoring and data acquisition system equipment required for the New Core Drilling System.
- Provide the design and testing services for installation of the radar surface level gauge in Tank 101-SY.
- Begin to assess the current status (utility) of instrumentation currently in use on the Watch List waste tanks.
- Investigate usefulness of gamma and neutron probe measurements on the Watch List hazardous waste tanks.
- Establish interface activities between the Hanford Hazardous Waste Tank Instrumentation Panel, the Watch List Waste Tank Review Task Team, the Tank Waste Science Panel, the Fiber Optic Chemical Sensor Task Team and other task teams commissioned to investigate special sensing and measurement functions for hazardous waste tanks instrumentation.
- The Hazardous Waste Tank Instrumentation Panel will begin to monitor and coordinate the evaluation and assessment of remote sensing technologies which could provide measurements of physical properties and chemical properties of waste within the Hazardous Waste Tanks. This includes the following remote sensing methods: (1) sonic, (2) ultrasonic, (3) radar, (4) infrared, (5) electromagnetic, (6) optical and (7) radiological.
- Select and evaluate new measurement devices and instrumentation systems to implement additional tank and tank waste parameter measurement requirements as identified by the Waste Tank Watch List Review task Team.
- Identify and assess intrinsically safe equipment which may be installed in flammable gas hazardous waste tanks.
- Begin planning installation designs for instrumentation of the balance of the Watch List Hazardous Waste Tanks using lessons learned from the instrumentation of Tank 101-SY.
- Provide long-term planning efforts for upgrades to the electrical, instrumentation, and control systems within the Tank Farm complex.

- Provide engineering studies as applicable to support the long-term planning efforts for upgrades to the Tank Farms electrical, instrumentation, and control systems.

4.11.5.2 Fiscal Year 1991 Work Scope for Pacific Northwest Laboratory.

A literature search and laboratory investigation will be conducted to evaluate methods for determining the surface topography of the top layer in the waste storage tanks. The methods to be evaluated are listed below:

- Range finder techniques where beams of energy such as acoustic, light (LIDAR), microwave (radar), or millimeter waves, are projected onto a surface and the time of flight provides a measure of surface position.
- A photogrammetric technique, using stereoscopic photographic techniques.
- Optical triangulation and phase detection using the reflected light from a scanned laser beam.
- Grid projection where the shape of lines projected onto the tank contents indicates the surface contour.
- Diffractive ranging where the curvature of a wavefront reflected from the surface is measured through a diffraction gating.
- A mask camera technique using a video camera and two slits placed in a mask.

A prototype acoustic monitoring system (AMS) will be developed, procured, and installed on Tank 101-SY. This system will use microphones operating in the audible range, in conjunction with conventional stripchart and magnetic tape recording equipment. Signal processing and data reduction/analysis will be performed. The objective is to associate detected acoustic signals with the tank/waste processes and behavior that caused the detected signals.

4.11.6 Fiscal Year 1992 Work Scope (Budget Year)

4.11.6.1 Fiscal Year 1992 Work Scope for Westinghouse Hanford. The following activities are planned to support the upgrade of tank instrumentation.

- Continue to provide support for the new core drilling system instrumentation and data acquisition systems.
- Continue to assess the current status (utility) of instrumentation currently in use on the Watch List waste tanks.
- Provide engineering support for the installation of the instrumentation and control systems required by the ventilation system upgrade.

- Provide interface activities between the Hanford Hazardous Waste Tank Instrumentation Panel, the Watch List Waste Tank Review Task Team, the Tank Waste Science Panel, the Fiber Optic Chemical Sensor Task Team and other task teams commissioned to investigate special sensing and measurement functions for hazardous waste tanks instrumentation.
- The Hazardous Waste Tank Instrumentation Panel will coordinate the evaluation and assessment of remote sensing technologies which could provide measurements of physical properties and chemical properties of waste within the Hazardous Waste Tanks. This includes the following remote sensing methods: (1) sonic, (2) ultrasonic, (3) radar, (4) infrared, (5) electromagnetic, (6) optical, and (7) radiological.
- Assess the engineered feasibility of identified new remote sensing instrumentation technologies for installation into hydrogen-bearing waste tanks with respect to intrinsic safety and other installation and operational concerns.
- Select and evaluate new measurement devices and instrumentation systems to implement tank structural parameter measurement requirements.
- Develop new remote-sensing instrumentation systems for installation into Hazardous Waste Tanks.
- Plan installation designs for the balance of the Watch List Hazardous Waste Tanks using lessons learned from the instrumentation of Tank 101-SY. Provide support activities to implement the upgrade of the instrumentation used on the other Watch List tanks.
- Provide long-term planning efforts for upgrades to the electrical, instrumentation, and control systems within the Tank Farm complex.
- Provide engineering studies as applicable to support the long-term electrical, instrumentation, and control systems planning effort.
- Provide new instrumentation system designs to implement additional parameter measurement requirements.

4.11.6.2 Fiscal Year 1992 Work Scope for Pacific Northwest Laboratory.

Proposed in situ waste characterization methods will be evaluated using core samples removed from Tank 101-SY and in small-scale tank models containing simulated waste. These tests will help determine which proposed methods appear most practical for further development. These studies will also provide input data to the thermo-physical tank model described in Section 4.7.1.

Experimental evaluation of the millimeter wave and/or modified infrared laser range finder techniques for waste tank surface topography determinations will be completed. Scanning systems and computer softer for receiving and displaying the signals will be developed. Conceptual system designs will be developed for both the millimeter wave approach and the infrared laser range

finder technique, and key design features will be mockup-tested to confirm applicability and performance characteristics. For tanks where fog and haze are not a problem, the photogrammetric technique and/or time-lapse photography using a low-power laser beam appear applicable. These techniques will be subjected to laboratory evaluation and testing.

Data obtained during acoustic monitoring of Tank 101-SY will be reduced and analyzed to identify potentially significant acoustic events. Continuing field support will be provided to maintain the existing AMS, and to support installation and checkout of additional channels. Additional monitoring channels will be developed, evaluated, and incorporated into the AMS to add high-frequency (acoustic emission) and low-frequency (accelerometer/geophone) monitoring capability to the present audible-range system. Prototype sensor holding fixtures will be designed, fabricated, and feature tested. The ultimate objective is to provide reliable instrumentation for monitoring the behavior of the tank contents.

4.11.7 Fiscal Year 1993 Work Scope (Plan Year)

4.11.7.1 Fiscal Year 1993 Work Scope for Westinghouse Hanford. The following activities are planned to support the upgrade of tank instrumentation:

- Continue to assess the current status (utility) of instrumentation currently in use on the Watch List waste tanks.
- Plan installation designs for the additional hazardous waste tanks. Provide support activities to implement the upgrade of the instrumentation utilized on the other Watch List tanks.
- The Hazardous Waste Tank Instrumentation Panel will continue to coordinate the valuation and assessment of remote sensing technologies which could provide measurements of physical properties and chemical properties of waste within the hazardous waste tanks.
- Assess the engineered feasibility of identified new remote sensing instrumentation technologies for installation into hydrogen-bearing waste tanks.
- Develop new remote sensing instrumentation systems from newly identified technology for installation into hazardous waste tanks.
- Provide long-term planning efforts for upgrades to the Electrical Instrumentation and Control Systems with the Tank Farm Complex.
- Provide Engineering Studies as applicable to support the long-term Electrical, Instrumentation, and Control Systems planning effort.
- Provide new instrumentation system designs to implement additional parameter measurement requirements.
- Assist in the evaluation of concepts, related to Tank Farm Instrumentation and Control systems, required to effect chosen remedial actions and carry out Engineering Studies as appropriate.

4.11.7.2 Fiscal Year 1993 Work Scope for Pacific Northwest Laboratory. Those in situ characterization techniques, developed and evaluated in FYs 1991 and 1992, that show promise for determining and monitoring the desired physical properties in Tank 101-SY and similar tanks, will be engineered for deployment inside the selected tank. Safety, reliability, and maintainability criteria will be developed and applied, and prototype systems will be fabricated and evaluated during laboratory and field tests.

The conceptual designs for in situ lapographic measurements developed during FY 1992 will be finalized, and prototype hardware will be designed and developed. Commercially available instruments will be tested using laboratory fixtures and simulated waste samples to determine performance under laboratory conditions. Prototype systems will be assembled and deployed for full-scale mockup and/or field testing on benign tanks. Feature testing will be used to confirm probe performance with respect to the individual temperature, humidity, radiation, and intrinsic safety criteria; a complete mockup test will be conducted to confirm that the required performance criteria are met under the combined environmental effects. Feedback regarding design features will be provided to the commercial equipment suppliers, as appropriate, toward upgrading the instrumentation to meet tank monitoring needs.

Computerized data reduction and analysis concepts will be developed and implemented for the passive acoustic monitoring system. The prototype equipment will be reduced to field designs that can be placed on other tanks. Field support activities will be continued, and data from tanks other than Tank 101-SY will be analyzed, if available.

4.12 UPGRADE OF TANK VENTILATION

The current SY farm ventilation system serves Tank 101-SY and two other tanks. The system was designed to provide for radiological control and tank cooling only and is not adequate to ventilate a rapid release of gas and to maintain a negative pressure in Tank 101-SY and the other two tanks during periodic gas releases. Evaluations have been performed and they have concluded that a new ventilation system should be installed on Tank 101-SY and at that time Tank 101-SY should be isolated from the other two SY farm tanks.

A study was issued (Burgess and Homan 1991) that concluded that the new ventilation system should have a nominal inlet design purge flow of 5,000 ft³/min with the capability to exhaust at a rate higher than 5,000 ft³/min. It was further concluded that inerting or increasing the purge flow higher than 5,000 ft³/min would not result in a significant risk reduction and that increased ventilation above the current 620 ft³/min during window periods would also not result in a significant risk reduction.

A waste tank ventilation system upgrade plan is being prepared. Implementation of this plan will provide a new Tank 101-SY ventilation system by the end of FY 1992. The major activities during FY 1991 are the preparation of National Environmental Protection Act (NEPA) and Clean Air Act (CAA) documentation, preparation of design drawings and specifications, preparation of testing procedures, and, if appropriate, initiation of procurement. Installation, checkout, and startup of the new ventilation system are in FY 1992.

4.12.1 Fiscal Year 1991 Work Scope (Current Year)

The following tasks are planned for FY 1991:

- Perform preconceptual Tank 101-SY ventilation system evaluations.
- Issue WHC-EP-0406, *Ventilation Flow Recommendations for Waste Tank 241-SY-101* (Burgess and Homan 1991).
- Reach agreement with the DOE on the isolation of Tank 101-SY from the other two SY farm tanks before installation of a new ventilation system.
- Prepare planning for the design, procurement, and installation of a new Tank 101-SY ventilation system.
- Prepare functional design criteria for the new Tank 101-SY ventilation system.
- Prepare the conceptual design report for the new Tank 101-SY ventilation system.
- Based upon funding availability, initiate the detail design of the new Tank 101-SY ventilation system
- Based upon funding availability, prepare and submit NEPA and CAA documentation for the new Tank 101-SY ventilation system.
- Based upon funding availability and NEPA and CAA requirements, initiate the procurement and fabrication of components for the new Tank 101-SY ventilation system.
- Perform scale-model tests of the new ventilation system features to evaluate design features crucial for mixing and control stability.
- Initiate the preparation of procedures to test the new Tank 101-SY ventilation system components and subsystems.

4.12.2 Fiscal Year 1992 Work Scope (Budget Year)

The following tasks are planned for FY 1992:

- Complete the detail design of the new Tank 101-SY ventilation system.
- Obtain NEPA and CAA approval for the installation of the new Tank 101-SY ventilation system.
- Complete procurement of equipment and components for the new Tank 101-SY ventilation system.
- Complete subsystem testing of the new Tank 101-SY ventilation system.

- Install the new Tank 101-SY ventilation system.
- Complete operating procedure preparation and operator training.
- Isolate Tank 101-SY from the other two SY farm tanks and start up the new Tank 101-SY ventilation system.

4.12.3 Fiscal Year 1993 Work Scope (Plan Year)

To be determined.

4.13 ENVIRONMENTAL PLAN

4.13.1 Purpose

This section is a plan containing a summary of the objectives and methods, which are either in place or will be developed, to ensure that the investigative aspects of Tank 101-SY characterization comply with existing regulations and requirements for protecting the population, workers, and environment at the Hanford Site.

4.13.2 Scope

This plan covers activities for the installation of monitoring equipment and collection of waste characterization samples inside Hanford Site Tank 101-SY. This plan draws from the various Hanford Site organizations associated with Environment, Health, and Safety. Some of the requirements may appear to cross organizational boundaries. This plan does not cover remediation or contingencies from unplanned events.

Protection of the environment is governed by DOE Orders, plus federal and Washington State regulations. Hanford Site environment is controlled primarily by RL orders, amplified in the controlled manuals of the site contractor(s). The occupational environment is controlled additionally by various Occupational Safety and Health Administration guidelines, which are given detailed application in internal Hanford operational manuals and procedures. This plan summarizes the primary references, and lists the detailed manuals and procedures when there is a significant potential impact due to the in-tank activity.

4.13.3 Requirements

Hanford Site operations with potential environmental impacts are controlled by WHC-CM-7-5, *Environmental Compliance* (WHC 1991). This manual collects and summarizes all applicable DOE, EPA, State, and Federal environmental requirements. In addition, the site *Industrial Safety Manual*, WHC-CM-4-3 (WHC 1989), controls worker protection requirements.

Detailed environmental requirements will be included in individual procedures for the specific tank intrusive activities. Where these are covered in existing procedures, they will be included by reference only. A prejob analysis will be used as the basis to mitigate those probable impacts which are not so covered.

4.13.4 Methods

Environmental monitoring to comply with requirements in WHC-CM-7-5, *Environmental Compliance* (WHC 1991), will continue under existing procedures at existing frequencies and locations throughout the implementation of the tank characterization. Detailed supplemental monitoring will be provided on a task-by-task basis following final review of work plans by Health Physics and Environmental Protection organizations.

Mitigation requirements (engineering and administrative controls) for both site occupational and offsite populations will be included in work permits under the existing site procedures, as a result of the task safety analyses.

Detailed responsibilities (outside the controlled manual system), which apply to other organizations will be determined before the final readiness review and a notification letter issued as an addendum to the specific task work plan, by the project director.

4.13.5 Reporting and Documentation

Environmental Protection currently administers the effluent monitoring and near-field environmental surveillance programs. Releases of contamination, both hazardous and radioactive substances, are documented in standard reports to RL and State of Washington oversight agencies. Any unusual occurrence is further reported via the Occurrence Reporting Center, in accordance with site procedures (WHC-CM-1-3, MRP 5.14) (WHC 1988).

Tank Farm Operations provides facility reports on tank status. Industrial Health and Safety provides data on worker occupational data. Health Physics, in cooperation with the PNL and the Hanford Environmental Health Foundation, maintains occupational medical data on all workers.

Environmental Assurance will review environmental monitoring data and document the pedigree of that data, through a compliance audit, if deemed necessary.

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5.0 TASK MILESTONES AND SCHEDULES

Schedules are presented for most of the activities discussed in Section 4.0. Exceptions are noted below:

- Section 4.1, "Safety Analyses"--Safety Analyses are shown for each specific activity where they are required (e.g., Section 4.4.4, "Sludge Weight Sampler"). The SAR upgrades cover all of the tank farm facilities and the details are given in WHC-SD-WM-PLN-001, *Program Plan for Tank Farms Safety Analysis Reports* (Swanson 1991).
- Section 4.2, "Tank Integrity Assessments," and Section 4.9, "Tank Data Base"--These activities are covered in the *Waste Tank Properties and Contents Program Plan* (DeFigh-Price 1991).
- Section 4.13, "Environmental Plan"--This is a support activity similar to Section 4.1 and the schedules for those activities requiring these analyses.

See Appendix E for copies of preliminary schedules.

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6.0 PROGRAM FUNDING

6.1 EXPENSE

Table 6-1 summarizes the expense costs.

Table 6-1. Expense Cost Summary.

Activity	FY (\$000)		
	1991	1992	1993
Program management and work breakdown structure (3.2 ^a)	477	600	670
Safety analyses (4.1)	1,300	1,400	1,400
Tank integrity assessments (4.2)	^b	^b	^b
Evaluation of waste tank Watch List (4.3)	65	300	0
Waste sampling (4.4) ^c	3,315	3,750	2,800
Waste sample analysis (4.5)	3,507	4,370	4,160
Development of additional approaches in characterizing hydrogen tanks (4.6)	312	500	300
Tank modeling (4.7)	705	600	500
Synthetic waste studies (4.8)	2,778	3,080	2,200
Tank database (4.9)	^b	^b	^b
Remedial actions (4.10)	0	1,300	5,920
Upgrade of tank instrumentation (4.11)	929	1,500	900
Upgrade of tank ventilation (4.12)	647	600	150
Program support (4.8.8, 4.13, 7.0)	716	1,000	1,000
Total	14,751	19,000	20,000

^aParenthetical notation refers to section of document within which the listed activity is addressed.

^bDeFigh-Price (1991).

^cIncludes support for Tank Farm Operations.

6.2 CAPITAL EQUIPMENT

Table 6-2 summarizes the capital costs.

Table 6-2. Capital Cost Summary.

Activity	FY (\$000)		
	1991	1992	1993
Waste sampling (4.4 ^a)	1,740	1,200	750
Waste sample analysis (4.5)	1,415	875	400
Development of additional approaches in characterizing hydrogen tanks (4.6)	--	300	100
Tank modeling (4.7)	--	500	100
Synthetic waste studies (4.8)	--	500	--
Remedial actions (4.10)	--	2,500	3,800
Upgrade of tank instrumentation (4.11)	930	2,000	3,000
Upgrade of tank ventilation (4.12)	0	7,000	1,000
Total	4,085	14,875	9,150

^aParenthetical notation refers to section of document within which the listed activity is discussed.

7.0 QUALITY ASSURANCE

Quality Assurance is an integral part of any successful program. It provides for independent oversight at the planning, implementation, and completion stages to assure appropriate management that stated objectives and goals are achieved.

At the Hanford Site, the DOE has primary responsibility to ensure that activities as performed are handled in an efficient and cost-effective manner. To control the quality of these activities, the DOE has imposed Order 5700.6B, *Quality Assurance*, and for DOE-RL, through Order RL-5700.1A, *Quality Assurance*. These orders require the selective and judicious application of requirements from the national consensus standard ASME NQA-1, *Quality Assurance Requirements for Nuclear Facilities*.

For environmental programs at the Hanford Site, the quality program requirements are imposed by the *Hanford Federal Facility Agreement and Consent Order* (referred to as the Tri-Party Agreement). The Tri-Party Agreement specifies that all parties shall use procedures for QA and Quality Control in accordance with EPA methods. Two EPA documents that define guidance to this methodology are QAMS 005/80, *Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans*, and EPA/540/G-87/003, *Data Quality Objectives for Remedial Response Activities*.

Westinghouse Hanford Company directs compliance with DOE quality requirements in WHC-CM-4-2, *Quality Assurance*. This imposes the criteria of ASME NQA-1 on all quality-affecting activities performed by personnel. The EPA quality requirements are specified in the existing quality programs to ensure overall compliance with the Tri-Party Agreement.

The QA interface shall ensure that program activities are defined, controlled, and documented in accordance with approved procedures. These controls and oversight provide confidence that the stated goals and objectives have been satisfied.

WHC-EP-0416

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8.0 REFERENCES

- Burgess, D. M., and J. L. Homan, 1991, *Ventilation Flow Recommendations for Waste Tank 241-SY-101*, WHC-EP-0406, Westinghouse Hanford Company, Richland, Washington.
- Carothers, K. G., et al., 1991, *Evaluation of April 19, 1990 Tank 241-SY-101 Gas Release Event*, WHC-SD-WM-PE-039, Westinghouse Hanford Company, Richland, Washington.
- DeFigh-Price, C., 1991, *Waste Tank Properties and Contents Program Plan*, WHC-EP-0403, Westinghouse Hanford Company, Richland, Washington.
- Delegaard, C., 1980, *Laboratory Studies of Complex Waste Slurry Volume Growth in the Tank 241-SY-101*, RHO-LD-124, Rockwell Hanford Operations, Richland, Washington.
- DOE, 1986, *Safety of Nuclear Facilities*, DOE Order 5480.5, U.S. Department of Energy, Washington, D.C.
- Fox, G. L., D. A. Himes, L. J. Julyk, J. Mishima, C. J. Moore, H. Padilla, B. V. Winkel, and D. D. Stepnewski, 1990, *Response of Tank 241-SY-101 to a Postulated Hydrogen Burn*, WHC-SD-WM-TI-426, Westinghouse Hanford Company, Richland, Washington.
- Gaspar, K. A., and I. E. Reep, 1991, *Waste Tank Safety Programs Overview Plan, W1W End Function*, WHC-EP-0426, Westinghouse Hanford Company, Richland, Washington.
- Leggett, W. D., D. G. Baide, M. V. Berriochoa, R. M. Black, W. T. Dixon, G. L. Dunford, G. D. Johnson, N. W. Kirch, L. G. Morgon, R. E. Raymond, M. H. Shannon, D. D. Stepnewski, J. B. Waldo, D. D. Wodrich, 1990, *Safety Improvement Plan - Hydrogen in Waste Tanks*, WHC-EP-0377, Revision 1, Westinghouse Hanford Company, Richland, Washington.
- Leggett, W. D., W. F. White, R. D. Crowe, F. A. Schmittroth, and G. L. Troyer, 1991, *Gamma Scans in the Annulus of Tank 241-SY-101*, WHC-EP-0428, Westinghouse Hanford Company, Richland, Washington.
- Lokken, R. O., R. D. Scheele, D. M. Strachan, A. P. Toste, 1986 (September), *Complex Concentrate Pretreatment FY 1986 Progress Report*, Prepared by Pacific Northwest Laboratory, for Rockwell Hanford Operations and the U.S. Department of Energy, Richland, Washington.
- Strachan, D. M., R. O. Lokken, R. D. Scheele, and A. P. Toste, 1986, *Complex Concentrate Pretreatment FY 86 Progress Report*, PNL-7687, Pacific Northwest Laboratory, Richland, Washington.
- Toste, A. P., T. J. Lechner-Fish, D. J. Hendren, R. D. Scheele, and W. G. Richmond, 1988, *Journal of Radioanalytical and Nuclear Chemistry*, Vol. 123, pp. 149-166.

WHC, 1988a, *Management Requirements and Procedures*, WHC-CM-1-3, Westinghouse Hanford Company, Richland, Washington.

WHC, 1988b, *Quality Assurance*, WHC-CM-4-2, Westinghouse Hanford Company, Richland, Washington.

WHC, 1989, *Industrial Safety*, WHC-CM-4-3, Westinghouse Hanford Company, Richland, Washington.

WHC, 1991, *Environmental Compliance*, WHC-CM-7-5, Westinghouse Hanford Company, Richland, Washington.

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APPENDIX A .

TEST PLAN: DEFLAGRATION STUDIES ON WASTE TANK 101-SY

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WHC-EP-0416

TEST PLAN

DEFLAGRATION STUDIES ON WASTE TANK 101-SY

**PHASE I. LABORATORY FLAMMABILITY STUDIES OF MIXTURES
OF HYDROGEN, NITROUS OXIDE, AND AIR**

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INTRODUCTION

Waste slurries produced during the recovery of plutonium and uranium from irradiated fuel are stored in underground storage tanks. While a variety of waste types have been generated, of particular concern are the wastes stored in Tank 101-SY. A slurry growth-gas evolution cycle has been observed since 1981. The waste consists of a thick slurry, consisting of a solution high in NaOH, NaNO_3 , NaAlO_2 , dissolved organic complexants (EDTA, HEDTA, NTA, and degradation products), other salts (sulfates and phosphates), and radionuclides (primarily cesium and strontium). During a gas release the major gaseous species identified include: hydrogen and nitrous oxide (N_2O). Significant amounts of nitrogen may also be present. Traces of ammonia, carbon oxides, and other nitrogen oxides are also detected. Air and water vapor are also present in the tank vapor space.

OBJECTIVE

The purpose of the deflagration study is to determine risks of the hydrogen, nitrous oxide, nitrogen, and oxygen system. To be determined are pressure and temperature as a function of composition of reacting gases and the concentration of gases before and after the combustion event. Analyses of gases after the combustion event will be restricted to those tests that had an initial concentration of $\leq 8\%$ hydrogen. This information will be used to evaluate safety issues related to periodic slurry growth and flammable gas releases from Tank 101-SY. The conditions to be evaluated will simulate gases in the vapor space above the salt cake as well as gases that potentially are trapped in pockets within/under the waste. The deflagration study will relate experimental laboratory results to conditions in the existing tanks.

The Pittsburgh Research Center (PRC) will conduct all the tests in either a 20-L or 120-L chamber using standard flammability test procedures developed by the PRC for similar studies. Flammability data include: lean flammability limits, peak explosion pressures, maximum rates of pressure rise, calculated and/or measured temperatures, calculated burning times or flame speeds, and calculated and/or measured hydrogen fraction burned. The tests will be performed at ambient temperature and pressure under both turbulent and quiescent conditions, with the turbulent conditions being employed only for lean mixtures ($\leq 8\%$ initial hydrogen).

KEY TECHNICAL PERSONNEL AND ORGANIZATION CHARTS

The work described in this Test Plan will be conducted by the Fires and Explosions Group of the Pittsburgh Research Center, Bureau of Mines, U.S. Department of the Interior. Organization charts of the Pittsburgh Research Center and of the Fires and Explosions Group are in appendix A. Resumes of the key personnel who will supervise and conduct the research are listed in appendix B.

ESTIMATED TIME SCHEDULE FOR TESTS

Phase I. Laboratory Flammability Studies of Mixtures of Hydrogen, Nitrous Oxide, and Air started on May 29, 1991 and will end on June 30, 1992.

The detailed lists of experimental tests for the mixtures of hydrogen, nitrous oxide, and air are listed in tables 1-5 in Appendix C and in the Interagency Agreement. Tables 1 and 2 are for two ratios of hydrogen to nitrous oxide diluted with air. We will measure the maximum pressures and rates of pressure rise for the undiluted mixtures and then the amount of air to dilute each mixture below the lean flammability limit. Table 3 is for similar data for hydrogen in air. Table 5 lists a specific run with a mixture of hydrogen, nitrous oxide, nitrogen, and air. Table 4 deals with the lean flammability limits of various mixtures. We will do the tests listed in table 4 and any other additional tests that are necessary to characterize the lean flammability limits of the hydrogen and oxidizer mixtures. There will also be a limited number of tests to evaluate the effects of water vapor at a temperature of 54 °C. In addition to the tests listed in the tables, we will do some preliminary tests on hydrogen and nitrous oxide mixtures inerted with argon.

All of these experimental tests should be completed within six months after approval of the Test Plan. The exact order of the tests will be determined as the work proceeds.

Our estimated schedule is:

early August, 1992	test chamber, control circuitry, instrumentation, and data acquisition system ready for testing
mid August, 1992	begin tests in Appendix C (assuming Test Plan is approved)
September, 1992 to November, 1992	complete majority of tests listed in Appendix C
December, 1992	review flammability data
January, 1992 to February, 1992	complete any remaining tests
March, 1992	write draft final report
April, 1992	review of draft final report by DOE and Westinghouse
May, 1992	revise final report

CALCULATED ADIABATIC DATA

The adiabatic flame temperatures for the various hydrogen, nitrous oxide, and air mixtures will be calculated using the NASA-Lewis computer code, CEC 80, using thermodynamic properties taken from the JANAF tables. It will also be possible to assess the effects of small amounts of added ammonia or the efficiency of various inerting gases by using this computer code.

TEST CHAMBERS, DETAILED TEST PROCEDURES, AND OUTPUT DOCUMENTATION

The tests will be conducted in two Bureau of Mines chambers: one with a volume of 20 L and one with a volume of 120 L. The 20-L chamber is a near-spherical vessel that can be used for the testing of either gases or dusts. It has a pressure rating of 20 bar (300 psig) and is described in the publications in appendixes D and E. The 120-L chamber is a spherical vessel used for the testing of gases. It has a pressure rating of 69 bar (1000 psig) and is described in the publication in appendix E. The flame propagation criteria used for the lean flammability limit measurements in the two chambers are also listed in appendix E. Instrumentation for the chambers will include two pressure transducers to measure the explosion pressure and, at least for some runs, a fine thermocouple to measure the explosion temperature.

Data will be recorded using a high speed analog-to-digital (A/D) board in a personal computer (PC). It can sample several data channels at speeds greater than 20 kHz per channel. In addition, the data will also be recorded on a high speed strip chart recorder. The direct data will include the starting pressure, maximum explosion pressure, maximum rate of pressure rise, and maximum temperature (if the thermocouple is used). In addition, the explosion temperature will be calculated from the maximum explosion pressure using the ideal gas law, the maximum burning velocity will be calculated from the maximum rate of pressure rise, and the fraction of hydrogen burned will be calculated from the final pressure after the explosion products have cooled. Gas samples will also be collected from some of the tests. The samples will be analyzed by standard gas chromatography for hydrogen, nitrous oxide, nitrogen, and oxygen.

The general testing procedures are:

1. Standard Bureau safety precautions will be followed. For example, no smoking or open flames are permitted in the test area.
2. When changing gas cylinders, the gas feed lines to the chamber must be thoroughly flushed before the start of the tests.
3. Tests of hydrogen at near stoichiometric concentrations will be made in the 120-L chamber. The chamber will be located in a bomb-proof and will be operated remotely from the observation room.

The detailed procedures for each test (for either chamber) are:

1. Evacuate the chamber to ≤ 0.01 bar (≤ 0.1 psia).
2. Add hydrogen by measuring the partial pressure in the chamber with a sensitive pressure transducer (0 to -20 psia).
3. Add the other gases by partial pressures.
4. Mix the gases with an internal fan. (First, the mixing time necessary for each chamber will be determined by sampling at various time intervals while the gases are mixing.)
5. Collect sample of initial test mixture if desired. (Samples will be collected from the initial tests to confirm the partial pressure mixing procedure. Later, mixtures will be spot checked.)
6. After mixing, the initial pressure before the test should be -1 bar.
7. After turning off the fan, wait 30 sec so that the gas mixture is quiescent before the test. (If the test is to be made under turbulent conditions, leave the fan on.)
8. If using electric spark ignition, charge the capacitor to the proper voltage. If using chemical ignitor, remove the shunt and connect the leads.
9. Push "start" button to begin test and data acquisition.
10. After test, collect gas sample of products if desired. (This may be difficult if the final chamber pressure is significantly below atmospheric due to the condensation of water vapor.)
11. Record the starting pressure, maximum explosion pressure, maximum rate of pressure rise, and maximum thermocouple temperature (if used) in the daily data notebook. The pressure data recorded by the PC can also be compared to those from the strip chart recorder.

An example of the computer output data for a test run is in appendix F. This is typical of the data that will be produced for each test run. In addition to the hard copies that we send you, we will also make the data available to you on floppy disks, along with a computer program to display the data. The data for each run will also be recorded in a daily notebook, along with instrument calibration data. A copy of the notebook entries will also be made available to you.

CALIBRATION OF EQUIPMENT AND QUALITY ASSURANCE

The primary check of the calibration of the entire test system will be repeat tests of standard mixtures of gases (e.g., 10% methane in air or 20% hydrogen in air). These calibration tests will be run at least once a week during the testing. These tests will assure that there are no changes in the entire system, including test chamber, gas measurement and mixing procedures, pressure transducers, and PC data acquisition and analysis system. The data compared for these calibration tests will include maximum pressure and maximum rate of pressure rise.

One strain gauge pressure transducer (0-20 psia) will be used to measure the mixing of the gases by partial pressures. Two strain gauge pressure transducers (0-200 or 0-300 psia) will be used for all flammability tests. Each of these transducers has a calibration check built in by the manufacturer (appendix G). The transducers will be checked each day with their built-in calibration before the start of the gas tests. In addition, the Bureau has a dead weight tester (appendix H) as a primary pressure standard. This will be used to check the calibration of the two transducers once at the start and once at the end of the testing program. The calibration data will be recorded in the daily notebook.

The computer program will print out the data for each pressure transducer (appendix F). It will also compare the data from the two transducers and will display the average of the two on the summary data sheet if the data agree to within 5%. If the two transducers do not agree to within 5% for a run, they will both be checked with their built-in calibration standard. If the calibration is incorrect, it will be corrected or the transducer will be replaced.

For at least some of the tests, a platinum-rhodium thermocouple will be installed in the chamber to measure the explosion temperature as a function of time. The temperature will be calculated from the measured voltage by an equation that matches the data in standard thermocouple reference tables, such as those in the Omega Engineering Temperature Measurement Handbook.

The gas samples will be analyzed by standard gas chromatography (GC). The GC will be calibrated daily with Matheson primary standard gases (appendix I) or the equivalent. The calibration gases will include hydrogen, nitrous oxide, oxygen, and nitrogen. The GC will be used to analyze gas samples from the hydrogen, nitrous oxide, nitrogen, and air cylinders used to produce the gas mixtures for the tests. In addition, the GC will be used as necessary to measure gas samples from the test chambers before the runs to verify the mixture concentrations. After the runs, gas samples analyzed by GC could determine any unreacted hydrogen or gaseous products of combustion.

DELIVERABLES

Monthly reports	by 15th of month
Test data on floppy disks	by March 1, 1992
Final report -- draft	by April 1, 1992
-- final	by June 1, 1992

Appendix A: Organization Charts
for Pittsburgh Research Center, Bureau of Mines

(NOT INCLUDED FOR THIS DOCUMENT)

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Appendix 3: Key Personnel

(NOT INCLUDED IN THIS DOCUMENT)

WHC-EP-0416

Appendix C: List of Flammability Tests

(NOT INCLUDED IN THIS DOCUMENT)

Hydrogen-Nitrous Oxide-Air Deflagration Tests

Measure flammability of gas mixtures with fixed ratios of nitrous oxide to hydrogen as a function of dilution with air. The mixtures of interest correspond to ratios of $N_2O:H_2$ generated in the tanks (nominally $N_2O/H_2 = 0.77$). The gas composition range of interest is bracketed by values shown in Tables 1 and 2. A limited number of tests is to be defined by PRC to evaluate the effects of water vapor at a concentration which corresponds to the temperature in the wastes ($54^\circ C - 130^\circ F$).

Table 1
Hydrogen/Nitrous Oxide/Air Tests
($N_2O/H_2 = 1$)

Test #	----- Volume % -----		
	H_2	N_2O	Air
1	4	4	92
2	6	6	88
3	8	8	84
4	10	10	80
5	12	12	76
6	15	15	70
7	20	20	60
8	30	30	40
9	40	40	20
10	50	50	0

Table 2
Hydrogen/Nitrous Oxide/Air Tests
($N_2O/H_2 = 0.67$)

Test #	----- Volume % -----		
	H_2	N_2O	Air
1	4	2.7	93.3
2	6	4.0	90.0
3	8	5.3	86.7
4	10	6.7	83.3
5	12	8.0	80.0
6	15	10.0	75.0
7	20	13.3	66.7
8	30	20.0	50.0
9	40	26.7	33.3
10	50	40.0	0

Hydrogen/Air Tests

Measure combustion of a select mixture of hydrogen and air as shown in Table 3 to provide data for WHC to compare these results with values in the literature.

Table 3
Hydrogen//Air Tests

Test #	----- Volume % -----	
	H ₂	Air
1	6	94
2	8	92
3	10	90
4	12	88
5	30	70

Lean Mixtures Tests

Measure combustion near the flammability limit of hydrogen, nitrous oxide, oxygen, and nitrogen mixtures under turbulent and quiescent conditions at ambient temperature and pressure. (This will allow comparison to combustion experiments performed using the "standard" flammability-limit test apparatus). Proposed compositions are shown in Table 4.

Table 4
Hydrogen/Nitrous Oxide/Air

Test #	----- Volume % -----		
	H ₂	N ₂ O	Air
1	3.0	97.0	0.0
2	3.5	96.5	0.0
3	3.0	87.0	10.0
4	3.5	86.5	10.0
5	3.0	77.0	20.0
6	3.0	3.0	94.0
7	3.5	3.5	93.0
8	3.5	2.3	94.2
9	3.0	2.0	95.0

Hydrogen/Nitrous Oxide/Nitrogen/Air

There is some evidence that nitrogen may also be included in the generated gases. One test is proposed to examine this event which is shown in Table 5.

Table 5
Hydrogen//Nitrous Oxide/Nitrogen/Air

Test #	----- Volume % -----			
	H ₂	N ₂ O	N ₂	Air
1	33	25	20	22

Based on the results of the initial testing program additional experiments may be required and warranted. Tests may be required in the PRC's larger explosion chamber and/or other equipment developed by the PRC for similar testing programs.

Appendix D: Reference Publication

(NOT INCLUDED IN THIS DOCUMENT.)

20-l explosibility test chamber for dusts and gases

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The Bureau of Mines has designed a 20-l test chamber for the explosibility testing of dusts, gases, and their mixtures. It can be used to measure lean and rich limits of flammability, explosion pressures and rates of pressure rise, minimum ignition energies, minimum oxygen concentrations for flammability, and amounts of inhibitor necessary to prevent explosions. The 20-l chamber can be used at initial pressures that are below, at, or above atmospheric as long as the maximum explosion pressure is less than 21 bar, which is the rated pressure of the chamber. The chamber instrumentation includes a pressure transducer, optical dust probe, an oxygen sensor, and multichannel infrared pyrometers. Ignition sources used include electric sparks and electrically activated chemical ignitors. Examples of the various types of data that can be obtained for dusts and gases are shown.

INTRODUCTION

An accurate knowledge of the explosion hazards of dusts and gases is necessary for their safe handling in mining, manufacturing, electric power generation, and transportation. The 20-l chamber described in this paper was designed primarily for dust explosibility testing, but it can also be used for testing flammable gases and dust-gas mixtures.

The 1.2-l cylindrical Hartmann bomb was developed at the Bureau of Mines in the 1930's and became a standard dust explosibility test apparatus¹⁻³ that has generated data for many dusts.⁴ Over the intervening years problems have surfaced with the apparatus, including nonuniform dust dispersion,⁵ lack of agreement with large-scale tests for rates of pressure rise,^{6,7} and the inadequacy of the spark ignition source for many dusts.⁸ To correct those problems, European researchers have developed several larger, more spherical test chambers. A 1-m³ chamber designed by Bartknecht^{9,10} is now the standard in much of Europe for measuring pressures and rates of pressure rise for dust explosions. Also available is a 20-l spherical chamber designed by Siwek¹¹ which gives comparable data for rates of pressure rise.

Over the past decade, the Bureau of Mines renewed its development of laboratory size chambers which produce data that agree well with full-scale mine explosion testing results. An 3-l chamber¹ produced much valuable data¹²⁻¹⁴ but was limited somewhat by the maximum ignition energy that could be realistically used.

Recently, the Bureau has designed a 20-l chamber that permits the use of very strong ignitors which are necessary for hard-to-ignite dusts and for dust-inhibitor mixtures. Some preliminary 20-l data on the explosion hazards of oil shale dust¹⁵ have been presented, but this paper is the first complete documentation of the 20-l chamber and its capabilities.

The Bureau of Mines' main concern is explosion prevention and protection in underground mines and related surface facilities and processing plants. Accordingly, the primary characteristics of dusts that are measured are lean limits of flammability and amounts of inhibitor necessary to

inert those flammable dusts. Therefore, the optical dust probe developed to monitor the uniformity of the dust cloud dispersion were of critical importance to the design of the chamber and the testing procedures. Other researchers, whose primary interest is the measurement of maximum pressures and rates of pressure rise necessary for venting calculations, are not as concerned with the uniformity of the dust dispersion in their chambers. Generally, they have not routinely monitored the dust dispersion with optical probes or other means. Although the Bureau of Mines' 20-l chamber and Siwek's 20-l chamber were designed primarily to study different aspects of dust explosion hazards, both can be used to measure most of the explosion characteristics of dusts.

1. 20-l CHAMBER AND INSTRUMENTATION

A photograph of the Bureau's 20-l explosibility test chamber and associated instrumentation is shown in Fig. 1. The chamber was designed to allow maximum flexibility in the positioning of current instrumentation and for the possi-

Fig. 1. 20-l explosibility test chamber and associated control circuitry and recorder.

Fig. 1. Vertical cross section of 20-l explosibility test chamber, showing dispersion nozzle.

Fig. 2. Horizontal cross section of 20-l explosibility test chamber.

ble addition of new instrumentation. The 20-l chamber is a near-spherical vessel constructed of type 304 stainless steel and its pressure rating is 21 bar. Vertical and horizontal cross-section drawings of the chamber are shown in Figs. 1 and 2, respectively. Note that there are several ports for gas inlet valves, etc., shown in the photograph (Fig. 1) but omitted from the drawings (Figs. 1 and 2). The chamber top is hinged and opens across the full chamber diameter allowing easy access to the interior for positioning instruments and for cleaning. The bolts that hold the top down are shown in the photograph (Fig. 1) but are omitted from the cross section (Fig. 2). During routine operation at two to four tests per hour, the thick (1.3 cm) walls of the chamber provide sufficient heat sink for the postexplosion gases and particles to cool to room temperature without the need for water cooling of the chamber.

Three sapphire windows permit observations of the explosion in the ultraviolet, visible, or infrared regions of the spectrum. By observing through these windows, several multichannel infrared pyrometers³⁻⁵ developed at the Bureau of Mines can measure dust explosion temperatures. The two sapphire windows on opposite sides of the chamber can also be used with an infrared source and one of the multichannel pyrometers for emission-transmission temperature measurements of either dust or gas explosions.³

The pressure transducer measures the explosion pressure and a differentiator amplifier allows the direct measure of the rate of pressure rise. An oxygen sensor measures the residual oxygen concentration after the explosion. The optical dust probes⁶⁻¹¹ developed at the Bureau of Mines and shown in Figs. 1 and 2 measure the uniformity of the dispersed dust cloud. Each probe measures the transmission

through a 103-cm path length in the dust cloud. Data are recorded on a high-speed, multichannel strip-chart recorder.

In the operating procedure for quiescent gas explosion tests, the chamber is evacuated and the flammable gas to be tested is added slowly through a valve into a side port of the chamber. Then air is added slowly to bring the final pressure to 1 atm absolute. The gases are mixed by a fan (not shown). After mixing, the fan is shut off, and after a delay to allow the turbulence to dissipate, a spark or chemical ignitor initiates the explosion test. For turbulent gas explosion tests, the air may be added rapidly through the dispersion nozzle after the flammable gas has been added through the side port.

All of the dust explosion tests are at least somewhat turbulent, because turbulence is necessary to keep the dust in suspension. The standard test procedure for dusts is to open the chamber top, remove the dispersion nozzle, and then place the dust in the reservoir as shown in Fig. 1. After replacing the nozzle and bolting on the top, the chamber is evacuated to about 0.1 atm. Then a short pulse of air (0.3-4 duration at 11 bar from a 16-l reserve tank) disperses the dust through the nozzle and raises the chamber pressure to 1 atm absolute. The dispersion uniformity in both space and time is measured with the optical dust probes. The ignition source is normally activated at 0.1 s after the end of the dispersion pulse, at which time there is still a moderate level of turbulence in the chamber. Ignition sources used include electric sparks and chemical ignitors that are activated electrically. This is the standard procedure for dust tests at a moderate turbulence level; the procedure can also be modified to achieve high or low turbulence levels.

If there is too much dust to fit in the reservoir, the dust

FIG. 4. Alternate dispersion system for 20-l chamber.

is placed on top of the nozzle. In a series of experiments with various dust concentrations, no difference in the dispersion uniformity was found between tests with dust placed in the reservoir and those with dust placed on top of the nozzle, so either procedure may be used. An alternate dispersion system is the cone disperser shown in Fig. 4. It is similar to the dispersion system in the 1.2-l Hartmann bomb and the 3-l chamber developed previously at the Bureau of Mines. For this system, the dust is placed around the cone at the bottom of the chamber and the air pulse that comes out around the circumference of the cone disperses the dust.

Examples of the dispersion pulse pressure history and dust probe transmission traces for the dispersion of coal dust using the nozzle configuration and standard procedure are shown in Fig. 5. For these data, the dust was dispersed but not ignited. The concentrations listed are the mass of dust placed in the chamber divided by the 20-l volume. The optical probes measure the uniformity of the dispersion to assure that this nominal concentration is actually dispersed as the true concentration in the chamber. As described previously, the dispersion procedure involves the evacuation of the chamber to about 0.2 atm absolute, then the 0.3-s air pulse disperses the dust and brings the pressure back to 1.0 atm absolute as shown in Fig. 5(a). The transmission traces from

FIG. 5. Coal dust dispersion in the 20-l chamber. (a) Pressure trace showing air dispersion pulse. (b) Optical dust probe traces at two heights H for concentrations of 175 and 400 g/m^3 , respectively.

FIG. 6. Optical dust probe dispersion data for Purple K powder in the 20-l chamber.

the two dust probes are shown for dispersions of two different concentrations in Figs. 5(b) and 5(c). The traces show a relatively constant transmission for at least 1 s after dispersion. The slight increase in transmission with time for the higher concentration (400 g/m^3) is probably due to agglomeration of the dust particles because the same effect is seen for the dust probes at both heights. If the increase in transmission were due to settling of the dust, the effect would be more pronounced for the probe in the top part of the chamber at the 29-cm height.

The effectiveness of the dust dispersion was studied by measuring the average transmission over a 0.2-s time interval starting at the end of the dispersion pulse. The data from the two dust probes at two heights in the 20-l chamber for the dispersion of Purple K (a dumdized fire extinguishant powder) are shown in Fig. 6. The data follow a linear relationship between the logarithm of the transmission T and the mass concentration C_m as expected from the Bouguer law:

$$T = \exp\left(-\frac{3QC_m l}{2\rho D_p}\right),$$

where Q is a dimensionless extinction coefficient, l is the path length, ρ is the density of a particle, and D_p is the surface weighted mean particle diameter. A detailed discussion of the optical dust probes and the Bouguer law is found in Refs. 3 and 10.

Optical dust probe dispersion data from three heights in the 20-l chamber for Pittsough seam bituminous coal dust are shown in Fig. 7. The data show good agreement in the measured transmissions at different heights, showing good dispersion uniformity. At the higher dust concentrations studied there is a slight upward divergence from the expected linear relationship on the semi-logarithmic graph. This is

FIG. 7. Optical dust probe dispersion data for coal dust in the 20-l chamber.

probably due to increased agglomeration of the coal dust particles resulting in a larger mean diameter at the higher concentrations compared to the lower concentrations.

II. DUST AND GAS EXPLOSION DATA

Examples of the pressure history data for coal dust explosions at a moderate turbulence level in the 20-l chamber are shown in Fig. 8 for two different mass concentrations. In this graph the time scale starts at the end of the dispersion pulse [equivalent to a time of 0.3 s in Fig. 5(a)], after the pressure has returned to 1 atm absolute. The ignitor is energized at about 0.1 s and the resulting explosion pressures (absolute) and rates of pressure rise are recorded as a function of time. The ignition sources used for the dust tests are strong chemical ignitors that are activated electrically. At the lower concentration, 100 g/m³, there is a slow rise to maximum pressure [Fig. 8(a)] because this concentration is approximately at the lean flammability limit for this dust. The rate of pressure rise trace [Fig. 8(b)] shows an initial spike due to the ignitor and then a fairly steady rate of about 6 bar/s for the slowly propagating dust explosion. The pressure trace [Fig. 8(c)] for the strong explosion at a 500-g/m³ concentration shows a rapid rise to a maximum pressure that is about 6 bar above ambient. The rate of pressure rise [Fig. 8(d)] is much faster at this concentration, with a maximum of about 120 bar/s. Both of these tests were done with the standard dispersion procedure which results in a moderate level of turbulence due to the 0.3-s dispersion and 0.1-s delay before ignition. A more rapid dispersion and shorter ignition delay would result in a higher level of turbulence and higher rate of pressure rise.

FIG. 8. Explosion pressure (absolute) and rate of pressure rise traces for coal dust explosions at 100 and 500 g/m³.

FIG. 9. Explosibility data for Pittsburgh seam bituminous coal dust in air at a moderate turbulence level.

A complete summary of the explosibility data for Pittsburgh seam bituminous coal at a moderate turbulence level in the 20-l chamber is shown in Fig. 9. These data were obtained using the strong chemical ignitors which had calorimetric energies of 1000 or 2500 J. The pressure ratio [Fig. 9(b)] is the maximum explosion pressure (absolute) divided by the pressure at ignition (1 atm absolute), and it corresponds approximately to the absolute explosion pressure in atm or bar. At the lowest concentrations, there is only a small pressure rise due to a small amount of burning around the ignitor, and the dust is considered nonexplosive. At slightly higher concentrations, every test results in an explosion. Based on the previous criterion^{1,12} of a pressure ratio of two, the lean flammability limit is 90–100 g/m³ for this coal dust. There is no evidence of a rich flammability limit even at the highest dust concentrations tested.

In full-scale tests^{1,2,4} in the Bureau Experimental Mine, the lean limit is about 60 g/m³ for a coal dust loading on the floor and walls that is dispersed by the propagating flame. However, this is a nominal concentration since the actual dust concentration varies continuously in space and time.^{19,20,26} In some preliminary tests²² of predisposed coal dust in the Experimental Mine, the lean limit was approximately 150 g/m³. Therefore, within the accuracy of the measurements, there is good agreement in the data from the 20-l laboratory chamber and the full-scale mine tests.

The rate of pressure rise (dP/dt) data in Fig. 9(a) are shown as the cubic law index,³

$$K_{St} = \left(\frac{dP}{dt} \right)_{\max} V^{1/3}, \quad (2)$$

where the maximum of dP/dt is multiplied by the cube root of the chamber volume V . K_{St} should be independent of the size of the test chamber if the turbulence level and the corresponding flame speed are the same in the various chambers.³

The subscript *St* comes from the word "Staub," which is German for dust. The maximum value of K_{St} for the coal dust in Fig. 9a is about 30 bar m/s. This is for the moderate level of turbulence generated by the standard dispersion procedure. Because of their dependence on turbulence level, the K_{St} data shown here should only be used for relative comparisons among different dusts. As discussed previously, a higher level of turbulence from a more rapid dispersion and shorter delay before ignition would result in a much higher value of K_{St} . Standards organizations are currently trying to reach agreement on a turbulence level (or equivalently, a dust dispersion procedure) for 10-l chambers that would yield a value of K_{St} that could be used for realistic venting design for large-scale structures.

Additional comparisons between the 10-l chamber and the Experimental Mine were made for various grades of oil shale dust.¹³ In both the laboratory and full-scale tests, the lowest grade or assay of fine-size oil shale that would propagate a dust explosion was about 35 ml/kg (≈ 10 gal/ton).

Explosion data for quiescent methane gas in air are shown in Fig. 10. The ignition source was a strong electric spark, which is generally adequate for gases. The lean and rich limits of flammability [from Fig. 10(b)] in the constant-volume 10-l chamber are about 5 and 16 vol %, respectively. The lean limit is the same as that determined in flammability tubes, but the rich limit is slightly higher than the 15-vol % value measured in flammability tubes.¹² Using the stronger 500-J electrical ignitors in the 10-l chamber, the lean limit is

FIG. 10. Explosion data for quiescent methane-air.

FIG. 11. Spark ignitability data for Pittsburgh coal dust.

only slightly lower, but the rich limit extends to about 17 vol %. The maximum explosion pressures [Fig. 10(b)], reached at near stoichiometric concentrations, are slightly over 90% of the calculated, adiabatic values. The rate of pressure rise data [Fig. 10(a)] are plotted as the index K_{St} , defined similarly to Eq. 21, but for gases. The maximum value, $K_{St} \approx 68$ bar m/s, is reached at a near stoichiometric concentration. This agrees well with the 60, 71, and 80 bar m/s K_{St} values for 10% methane (quiescent) in large chambers of 190-, 370-, and 1900-l volume, respectively.¹³ Turbulent methane-air would have much higher K_{St} values.

Previous figures have shown the basic explosion data (flammability limits, pressures, and rates of pressure rise) for a dust and a gas. Another aspect of the explosion hazard is the ignitability of the mixture. Figure 11 shows data on the minimum electrical spark energies necessary to ignite the various concentrations of Pittsburgh coal dust. The effective energy¹⁴ plotted as the ordinate is a measure of the fraction of the stored circuit energy that is deposited into the gas in the spark gap. The minimum in spark ignition energy occurs at a very high dust concentration, approximately eight times the lean limit concentration. For these data, the ignition delay was increased from the standard 0.1 s to 0.5 s to reduce the turbulence level somewhat. (It should be noted that such ignition energies are dependent on the turbulence in the chamber, and that an even lower turbulence would probably give a lower minimum ignition energy. Therefore, the minimum ignition energies measured in the 10-l chamber using a certain dispersion procedure and turbulence level should not be considered as absolute values but as only relative values for the comparison of the various dusts tested. This is the same conclusion as for the rates of pressure rise. Hopefully, some standards organizations will reach agreement on a standard testing procedure for these values so that various laboratories can compare results.)

One of the primary methods of reducing the dust explo-

Fig. 12. Explosion pressures for pure coal dust compared to those for coal-inertor mixtures containing the listed percentages of limestone rock dust.

tion hazard in coal mines is the addition of inert rock dust to the coal dust that accumulates on the walls and floor of the mine. Therefore, it is important to be able to measure the amount of an inhibitor dust that must be mixed with coal dust in order to render it nonexplosive. Previously, relatively good agreement was achieved between the data in the 3-ft chamber and the experimental mine in terms of the amounts of various inhibitor dusts necessary to inert coal dust.¹²⁻¹⁴ The use of stronger chemical ignitors in the 10-ft chamber has given even better agreement. In the 3-ft chamber, 50-55 wt. % of limestone rock dust in a coal-inertor mixture would inert the dust.¹²⁻¹⁴ In the 10-ft chamber, using the stronger ignitors, 70 wt. % of rock dust is required, as shown in Fig. 12. The addition of limestone rock dust to the Pittsburgh coal dust raises the coal's lean flammability limit and reduces the maximum explosion pressure. At 70% rock dust in the mixture, there is only a negligible pressure rise due to the small amount of burning around the ignition source. Since there is no propagation beyond the ignition region, this mixture is considered nonexplosive. In the full-scale Experimental Mine tests, using a large methane-air volume as the ignition source, about 70-75 wt. % of limestone rock dust is necessary to inert Pittsburgh coal dust.¹²⁻¹⁴

Another type of test that can be conducted in the 10-ft chamber is the measurement of lean flammability limits for dusts or gases at reduced and elevated initial pressures. Previous measurements for saturated hydrocarbon gases have shown that the lean limit expressed in volume percent is relatively independent of initial pressure.¹⁵ Therefore, for such gases, if the lean limit is expressed as mass concentration of dust per unit volume, it would vary linearly with initial pressure. The data in Fig. 13 are for polyethylene dust dispersed in the 10-ft chamber and ignited at various initial pressures. The measured lean flammability limit for the dust varies roughly linearly with pressure, the same is for gases when expressed in mass concentration.

Fig. 13. Lean explosion limits for polyethylene dust as a function of initial pressure (absolute).

III. DISCUSSION

A 10-ft chamber has been designed at the Bureau of Mines for the explosibility testing of dusts, gases, and their mixtures. Because of its larger volume, stronger ignition sources can be used than in the previous 3-ft chamber. However, the 10-ft chamber can still be easily operated by one person. Much less time and much smaller dust samples are required for tests in the 10-ft chamber compared to the 3-ft chambers that are used for dust explosion testing.

The 10-ft chamber can measure various aspects of the hazards of combustible dusts and gases. These include flammability limits, explosion pressures, rates of pressure rise, minimum ignition energies, minimum oxygen concentrations, and amounts of inhibitor necessary to inert a mixture. The data obtained in the 10-ft chamber, and particularly the data on the amounts of inhibitor powders necessary to inert coal dust, have shown good agreement with full-scale experimental mine explosion data. Therefore, the 10-ft chamber can be used for preliminary testing before full-scale mine tests. It can also be used for tests that cannot be easily conducted in the experimental mine such as the explosibility of dust-gas mixtures, minimum oxygen concentrations for flammability, and the effects of initial pressures that are below or above atmospheric.

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1. H. G. Dorsett, Jr., M. Jacobson, J. Nary, and R. P. Williams, U.S. Bureau of Mines RI 6214, 1960.
2. J. Nary and R. P. Williams, *Development and Control of Dust Explosions* (Marcel Dekker, New York, 1963).
3. American Society for Testing and Materials, E779-41, in 1963 *Annual Book of ASTM Standards* (ASTM, Philadelphia, 1963), Vol. 4.02, pp. 157-176.
4. National Fire Protection Association, *Fire Protection Handbook*, 4th ed. (NFPA, Boston, 1976), Sec. 1, Chap. 3, pp. 1-100 to 1-113.
5. H. A. Explosion and A. J. Pryor, *Fire Technol.* 1, 17 (1967).

- ¹⁰W. Bertschert, *Staub-Remass*, Luft 31, 112 (1971) pp. 29-40 in English translation.
- ¹¹R. Z. Schindl, *Staub-Remass*, Luft 37, 110 (1977).
- ¹²M. Hertzberg, K. L. Casadolar, and J. J. Oberman, U. S. Bureau of Mines RI 1360, 1979.
- ¹³W. Bertschert, *Explosionen: Cause, Prevention, Protection* (Springer, New York, 1981).
- ¹⁴Verein Deutscher Ingenieure (Association of German Engineers), *Druck-messung von Schmelzexplosionen* (Pressure Release of Dust Explosions), VDI 1671, VDI-Handbuch Messung der Luft, Vol. 2, 1983, 31 pp.
- ¹⁵R. Stenz, *20-L-Laborapparat für die Bestimmung der Explosionscharakteristika von explosiblen Stäuben* (20-Liter Laboratory Apparatus for the Determination of the Explosion Characteristics of Flammable Dusts), Chem-Ges. AG (Basel/Winterthur Engineering College, Winterthur, Switzerland, 1977).
- ¹⁶M. Hertzberg, K. L. Casadolar, and C. P. Lutzner, in *Explosion Symposium (International) on Combustion* (The Combustion Institute, Pittsburgh, 1981), pp. 717-729.
- ¹⁷M. Hertzberg, K. L. Casadolar, C. P. Lutzner, and A. C. Smith, U. S. Bureau of Mines RI 1708, 1982.
- ¹⁸K. L. Casadolar, M. Hertzberg, and J. K. Richmond, in *Proceedings of the 10th International Conference of Safety in Mines Research Institute*, Sheffield, England, 3-7 October 1983, paper F4.
- ¹⁹K. L. Casadolar, M. Hertzberg, and R. S. Conn, in *17th Oil Shale Symposium Proceedings* (Colorado School of Mines, Golden, Colorado, 1984), pp. 243-254.
- ²⁰K. L. Casadolar, *Appl. Opt.* 18, 2595 (1979).
- ²¹K. L. Casadolar and M. Hertzberg, *Opt. Eng.* 21, 32 (1982).
- ²²K. L. Casadolar and M. Hertzberg, in *Temperature for Measurement and Control in Science and Industry, Vol. 5*, edited by J. F. Schooley (American Institute of Physics, New York, 1982), pp. 453-463.
- ²³L. Lieberman, R. S. Conn, and K. L. Casadolar, *Rev. Sci. Instrum.* 48, 1314 (1977).
- ²⁴K. L. Casadolar, L. Lieberman, and R. S. Conn, U. S. Bureau of Mines RI 1542, 1981.
- ²⁵R. S. Conn, K. L. Casadolar, and L. Lieberman, *Rev. Sci. Instrum.* 53, 311 (1982).
- ²⁶M. G. Lissman, U. S. Bureau of Mines Bulletin 627, 1965, pp. 21, 25-27.
- ²⁷M. Hertzberg, R. S. Conn, and K. L. Casadolar, in *Fourteenth Symposium (International) on Combustion* (The Combustion Institute, Pittsburgh, 1984).
- ²⁸J. K. Richmond, L. Lieberman, A. E. Brustas, and L. F. Miller, in *Seventeenth Symposium (International) on Combustion* (The Combustion Institute, Pittsburgh, 1979), pp. 1257-1267.
- ²⁹J. K. Richmond, M. J. Sasse, L. F. Miller, and L. E. Davenport, in *14th Oil Shale Symposium Proceedings* (Colorado School of Mines, Golden, Colorado, 1981), pp. 61-74.
- ³⁰T. P. Gillis (personal communication).

Appendix E: Reference Publication

(NOT INCLUDED IN THIS DOCUMENT)

FLAMMABILITY LIMIT MEASUREMENTS FOR DUSTS AND GASES: IGNITION ENERGY REQUIREMENTS AND PRESSURE DEPENDENCES

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Data are presented for the flammability limits of Pittsburgh Seam bituminous coal dust, polyethylene powder, and methane in air at pressures in the range 0.5 to 3 bar. Explosibility test chambers of 20 and 120 L were used, and ignition limitations were overcome with efficient pyrotechnic ignitors with nominal energies of 500 to 5,000 J. The propagation criterion used was based on the maximum explosion pressure and the size-normalized maximum rate of pressure rise. The latter is a dynamic criterion that tends to minimize "overdriving" effects as the 20-L data are taken to their asymptotic limits at high ignition energies. The measured lean limits in air at atmospheric pressure are 90 g/m³ for the coal dust, 35 g/m³ for polyethylene, and 4.9 vol pct for methane. The rich limit for methane is 18-19 vol pct, whereas the dusts have no rich limits out to concentrations as high as 4,000 g/m³.

A linear, lean-limit pressure dependence was measured for the dusts which was essentially the same as the pressure dependence measured for methane when all are expressed in comparable units; namely, mass concentration of fuel per unit volume of air. This observation further confirms a lean limit dust flame propagation mechanism that is controlled by the gas-phase reaction rate. The limit concentrations are then determined by the dust loading required to generate a lean limit concentration of pyrolysis products in the volatiles-air mixture, and the dust behaves as an equivalent "homogeneous," premixed gas, regardless of the initial pressure.

Introduction

An accurate knowledge of the flammability behavior of substances is essential for a realistic appraisal of the fire and explosion hazards involved in their industrial manufacture and use. Explosion hazards are quantifiable in terms of the product of the probability of the existence of a flammable mixture with the separate probability of the presence of an adequate ignition source. The former condition is traditionally specified in terms of lean (lower) and rich (upper) limits of flammability. Any region of space whose composition is between the lean and rich limits is explosive, and the former probability is simply quantified as the fraction of time the system exists within that composition domain. Lean and rich limits are thus boundaries defining the extent of a composition domain of explosibility at room temperature and ambient pressure within which explosion is possible in the presence of an adequate ignition source, but beyond which explosion is impossible regardless of the strength of the ignition source. For fuel substances in air, the wider that domain, the more hazardous the substance.

For gases and vapors that mix homogeneously with air, the available experimental results are summarized and analyzed in a series of Bureau of Mines Bulletins.¹⁻⁴ For heterogeneous mixtures of dusts⁵⁻⁷ dispersed in air, our state of knowledge is less satisfactory. There are three major reasons for the difficulties with dusts. The first deals with the composition variable and the necessity of adequately defining that variable on the appropriate microscopic scale when considering dusts. For gaseous components, mixing of fuel with oxidant is on the molecular scale and the resultant system is homogeneous, containing only one phase—a gas. For a two phase mixture of a dust in air, such perfect mixing is impossible, and at least one additional variable is required in order to define its composition on the microscopic scale that determines its combustion behavior. For spherical, monodispersed dusts, that additional variable is the particle diameter. For example, a 1 kg lump of coal suspended in a 1 m³ container presents no explosion hazard whatever; however, that same mass, when pulverized into a fine dust of less than 100 μ m in diameter and uniformly dispersed in that same volume, is an explosive

mixture. The thermodynamic states (more accurately, the *thermodynamic* states) of those two systems are essentially identical, but their dynamic behavior is vastly different. Thus, while a uniform mixture of gases is homogeneous for scales beyond its molecular dimensions, a dust dispersion is not only phase-heterogeneous, it is necessarily compositionally heterogeneous on the scale of its particle diameter. The state of the heterogeneous system is thus not uniquely defined by its macroscopic composition, temperature, and pressure. The particle diameter is critical in defining the fuel concentration on the microscopic scale that determines its dynamic combustion behavior.³

The second major reason for the difficulties in obtaining reliable data for dusts is that the composition variable, by itself, may be nonuniform on the larger scale. A homogeneous gas, once mixed, remains premixed indefinitely; however, that is not so for heterogeneous mixtures. The initial dispersion of a heterogeneous mixture is complicated by agglomeration, and the everpresent gravitational force tends to segregate the denser dust from the less dense air. Those processes are the major causes of the uncertainty in most dust explosibility studies¹ since they generate spatial and temporal nonuniformities in dust concentration on the macroscopic scale. Those uncertainties are present in laboratory systems,² in full-scale mine experiments,^{3,9} or in large grain silos.¹⁰ Intense, turbulent airflows are required to disperse dusts and to maintain a uniformly dispersed mixture during the course of an experiment. Only when the dust is adequately and uniformly dispersed and the dispersion is maintained and monitored in time and space, can the dust concentration be considered to be controlled sufficiently to yield reproducible data.^{1,3,9}

These first two difficulties characterize all condensed-phase fuels and have been addressed in previous studies.^{3,9} It is the third difficulty, which is not limited to dusts, that is a main subject of this paper, and it deals with ignition source strength requirements. The necessary precondition for determining whether flame can propagate freely in any given system is the requirement that a combustion wave be present initially. Clearly, a combustion wave front must exist initially before one can determine whether the medium being studied can be activated by the wave to sustain its propagation. The failure of flame propagation in a given experiment can be explained as being due to the presence of a nonexplosive mixture with a concentration beyond the flammability limits only if one is certain that the ignition source was strong enough to

have initiated a potential combustion wave. The source strength must be as strong as necessary to ensure that the result is independent of ignition energy; a true flammability limit should therefore be independent of ignition energy.

This ignition energy problem is not a purely academic one. From its very establishment in 1910, the earliest measurements made in the Bureau of Mines' full-scale experimental mine showed that the explosive properties of test mixtures of coal dust with inert rock dust displayed a sensitivity to the strength of the initiation source.^{10,11} Even before 1910, it was the lack of understanding of such ignition source strength requirements that led to the deadly misapprehension that pure coal dust was nonexplosive, and mine explosion disasters near the turn of the century were consequently attributed entirely to methane gas ("grisou," "firedamp," or "schlagwetter"). Although that misapprehension regarding the explosivity of coal dust was corrected in 1891 by a Royal Commission,¹² the knowledge was slow to diffuse across the Atlantic. For some 20 years after the Commission's findings were published, it was still a common practice in U.S. mines to pack borehole explosives with loose coal dust in order to "stem" such shots.¹³ That misconception thus played a major role in the high fatality rates from coal mine disasters during the first decade of this century.¹³

For the measurement of flammability limits in gases, ignition source strength requirements are much less severe than for dusts; however, data will be presented here for methane that show that the "standard" flammability tube test method,¹⁴ which relies on electric spark initiation, does not necessarily ensure that results are independent of ignition energy, even for gaseous mixtures.^{15,16}

The second main topic of this paper deals with the extent to which the flammability limits vary with initial ambient pressure. New data will be presented for the pressure dependence of the limits of flammability for coal dust, polyethylene, and methane.

Apparatus. Experimental Method. Ignitors

Most of the data to be presented here were obtained with the Bureau of Mines 20-L explosibility test chamber which is shown in Fig. 1. The chamber is nearly spherical in shape, is constructed of type 304 stainless steel, and has a pressure rating of 21 bar. The details of its development, the description of associated instrumentation, the measurements of the uniformity of dust dispersion, the experimental

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FIG. 1. Vertical cross section of the Bureau of Mines 20-L explosibility test chamber.

procedures used, and its general performance are described in reference 9.

For dust flammability measurements, the turbulence necessary to keep the dust in suspension is achieved by an airblast of 0.3 s duration. The dust dispersion uniformity is monitored in space and time with the two dust probes² shown in Fig. 1. Some 0.1 s after the dispersion pulse is turned off, the ignitor is activated. The ignition sources used are listed in table 1. The electric

spark, which was used only for methane, has an effective energy of 1.6 J. It was delivered from a capacitor whose stored energy was 17 J. The details of the discharge circuit and the method used to measure the effective ignition energy are described elsewhere.^{10,17} The stronger ignition sources were chemical ignitors manufactured by Fr. Sobbe, GmbH. (Reference to trade names does not imply endorsement by the Bureau of Mines.) They contain a pyrotechnic powder mixture of 40 pct by weight zirconium, 30 pct barium nitrate, and 30 pct barium peroxide. Varying masses of powder, from 0.12 to 1.2 g of the mixture, are used to generate the nominal calorimetric energies listed in table I. The effective energies were calculated from the measured pressure rise, Δp , generated by the ignitor itself, in air at 1 atm, in the test chamber volume of $V_0 = 20$ L. The pyrotechnic ignitor reaction is approximated by the chemical reaction:

This strongly exothermic reaction is capable of generating an adiabatic flame temperature of 3870 K. The ignitor mixture is slightly fuel rich with an equivalence ratio of 1.17. Since the products are mostly hot, condensed-phase particulates, they do not dilute the test mixture, and they are probably therefore more efficient in ignition than gaseous combustion products. The Soobee ignitors are activated electrically with an internal fuse wire.

Pressure rise measurements from the probe ignitors themselves were made during their

TABLE :
Ignition source strengths

Source	Stored electrical energy (Joule)	Nominal calorimetric energy (Joule)	Pressure rise (mm Hg)	Effective energy (Joule) = 1.2 V (mm Hg)
Electric spark	10	—	8.3	10 = 10.2
Source chemical ignitor	—	500	50	250 = 45
	—	1000	100	350 = 80
	—	2500	250	1250 = 160
	—	5000	500	2500 = 220

ignition in air, nitrogen, argon, and a vacuum. The air values in millibars are shown in table I. In nitrogen, the measured Δp values were systematically about 10 pct lower than the values in air. There is an additional exothermicity from various excess fuel components in the ignitors, and their reaction with ambient oxygen near the ignition volume generates a higher Δp when the mixture is initiated in air than when it is initiated in pure nitrogen. In argon, the measured Δp was some 50 pct higher than the value measured in nitrogen, as expected from the lower heat capacity of the monatomic gas. The absence of rotational degrees of freedom for the monatomic gas causes a higher temperature to be generated within the ignition volume, which is sensed as a higher Δp . In a vacuum, there is no surrounding mass of gas to be compressed by the expanding ignition volume, and the measured pressure rise was due only to the gas generated during the chemical reaction. In a vacuum, that pressure rise was only 16 mbar for the 5,000 J ignitor. In this paper, the Sobbe ignitors are usually referred to in terms of nominal calorimetric energies; however, when the data obtained with them are plotted graphically, the figure axes indicate both nominal and effective energies. The data in table I show that from 40 to 60 pct of the nominal calorimetric energy of the ignitors is converted into effective internal energy within the ignition volume.^{16,17}

In addition to 20-L data, methane-air data were also obtained in a larger, 120 L volume (a 60 cm diameter sphere).¹⁸ The pressure range of the larger sphere was 69 bar, and the chemical ignitors used therein were positioned slightly below center. For methane studies in both chambers, gas compositions were controlled by partial pressures of methane and air added to an initially evacuated system. Internal fans were used to mix the gases, but were turned off prior to ignition so that the gases were initially quiescent.

Flammability Data and Limit Criteria

Methane in Air

The data for methane in air in the 20-L chamber are shown in Fig. 2. Measured maximum explosion pressure ratios, π_{max} , are shown in 4, and K_{st} values are shown in 5. The former is the maximum explosion pressure corrected to the Δp of the ignitor divided by the initial pressure. Since the initial pressure is near 1 bar absolute, the π_{max} values shown are approximately equal to the final explosion pressures in

FIG. 2. Flammability limit data for methane in air for various ignition source strengths in the 20-L chamber.

bars absolute. The K_{st} -value is the size-normalized maximum rate of pressure rise. Size normalization is achieved by multiplying $(dp/dt)_{max}$ by $V^{1/3}$. For clarity, the methane concentration scale is magnified for the lean mixtures below 6 pct methane. Several curves corresponding to the first four ignitors listed in table I are shown and are drawn through their appropriate data points. As expected, there is a widening of the apparent domain of flammability with increasing ignition energy.

Surprisingly, however, for the near-stoichiometric mixtures, both π_{max} and K_{st} are somewhat higher for the spark source than for the more energetic chemical ignitors. The result is an artifact of the differences in the source geometries: the spark is a point-source, whereas the chemical ignitor approximates a line source. The spark generates a spherical wave front that contacts the wall almost simultaneously everywhere along the flame front surface at the instant combustion is complete. For the line-source chemical ignitors, the wave front is not spherical and the wave surfaces initiated near ends of the line contact the wall before other

volume elements are consumed. As a result, combustion from the line source is less adiabatic, resulting in slightly lower π_{max} and K_{st} values. This source geometry effect is not significant for the near-limit mixtures. Their structures are dominated by buoyancy forces and are thus markedly distorted by gravity.^{12,13} For the near limit mixtures the domain of flammability is broadened substantially as the energy of the ignitors increases.

The major problem to be resolved is to determine how much of that broadening is real and how much is only apparent, caused by an "overdriving" of the system. As indicated earlier, the way to ensure that a combustion wave is present initially in such non-steady-state flammability tests is to increase the ignition source strength until an invariant result is obtained. But if the test volume is finite, increasing the source strength can alter the initial state of the system being tested. If the source is too large and too strong relative to the size of the test volume, the system will be "overdriven"; that is, it is preheated and prepressurized.

The pressure-time evolution in a constant volume, spherical explosion is proportional to the fractional volume $V(t)$ occupied by the fireball during the time of propagation, i.e. Thus

$$p(t) - p_0(p_{max} - p_0) = kV(t)/V_0 \quad (1)$$

where k is a correction factor related to the differences in compressibility between burned and unburned gases. For spherical propagation from a point source

$$V(t)/V_0 = [r(t)/r_0]^3 = [S_0 t/r_0]^3 \quad (2)$$

where S_0 is the flame speed and is given by

$$S_0 = ar(t)/dt = (p_0/p_0)S_0 \quad (3)$$

The burning velocity is S_0 , and p_0/p_0 is the density ratio of unburned to burned gases (at constant pressure). Differentiating equation (1) with respect to time and substituting equations (2) and (3) into the result, gives:

$$dp(t)/dt = 3k(p_{max} - p_0)(p_0/p_0)S_0 r(t)/r_0^3 \quad (4)$$

Equation (4) shows that the maximum rate of pressure rise should occur at the instant the wave front contacts the wall; that is, at $r(t) = r_0$.

At that instant the proportionality factor k is unity. Setting $r(t) = r_0 = W/4\pi r_0^2$ and letting $p_0/p_0 = T_0/T = p_{max}/p_0$ gives:

$$\begin{aligned} dp(t)/dt|_{max} V_0 &= K_{st} \\ &= 3/4 \pi (p_{max} - p_0) p_0 p_{max} S_0 \end{aligned} \quad (5)$$

Equation (5) is the "cubic law" used to generate K_{st} . Because it is size normalized, K_{st} is the parameter used in the design of venting systems for the relief of explosion pressures.¹⁴ It will be used here in order to develop a dynamic propagation criterion, in combination with the pressure criterion ($\pi_{max} = 2$) used in previous studies.^{15-17,20,21} Strong ignition sources generate large ignition volumes, and localized burning or even marginal propagation in the highly perturbed region adjacent to the ignition source volume can sometimes generate pressure ratios that exceed the criterion of $\pi_{max} = 2$, even though propagation may not extend much beyond the source volume. This "overdriving" problem can be solved by using still larger test volumes or by modifying the propagation criterion through the choice of an additional criterion based on K_{st} . The new, combined criterion is more representative and realistic because it is also based on the rate of flame propagation in regions that extend farthest from the source. One chooses a limit velocity for upward flame propagation^{22-24,25} of $S_0 = (S_{0,lim}) = 3.0$ cm/s. The choice of a limit flame temperature of 1450 K for methane gives: $p_0/p_0 = T_0/T = p_{max}/p_0 = 5$. Substituting these into equation (5) gives $(K_{st,lim}) = 3$ bar m/s as an ideal dynamic limit criterion for spherical propagation. However, propagation is not spherical as the limit concentrations are approached because buoyancy forces, which are responsible for the very existence of limit concentrations, markedly distort the shape of the flame front.¹² The K_{st} criterion used should therefore be less than 3 bar m/s. For the methane data obtained with weaker ignition sources, the average K_{st} value at $\pi_{max} = 2$ is about 1.5 bar m/s in the 20-L chamber. Accordingly, that value is chosen as an additional criterion to be used with the stronger ignitors.

Using this combined criterion of $\pi_{max} \geq 2$ and $K_{st} \geq 1.5$ bar m/s, the lean and rich limit data for methane shown in Fig. 2 are replotted in Fig. 3 as a function of ignition energy. The effective energy is shown on the left axis and the nominal calorimetric energy is shown on the right axis, where the scale is nonlinear and approximate. In order to insure that the system was not overdriven, at the highest energies data were also obtained in the 120-L chamber, and those results are also plotted in Fig. 3. Since true limits should be independent of ignition energy, they are given by the vertical asymptotes. The extent to which too soft a propagation criterion relative to the strength of the ignition source can result in an "overdriven" system is shown by the outward bowing of the curves at the higher energies, indicated at

FIG. 3. Effects of ignition energy and chamber volume on the apparent flammability limits of methane in air.

the smaller chamber. Their failure to maintain the asymptotic values reached at intermediate energies is a reflection of such overdriving.

In addition to the overdriving complication, the data are sensitive to buoyancy effects and to turbulence. Buoyancy phenomena involve distinctions between the three propagation directions: upward, horizontal and downward. Even though the gas mixture is initially static, turbulence effects are present because of the flow disturbance induced by the ignitor transient. The magnitude of the ignitor-induced turbulence is a function of the ignitor energy relative to the chamber volume. The more energetic the ignitor and the smaller the test volume, the greater is the ignitor-induced turbulence level. This same combination of small test volume and strong ignitor, if carried still further, will also cause the system to be strongly overdriven.

There is a complex interaction between turbulence and buoyancy. Buoyancy effects induce severe limitations on the fraction of chamber volume that can be consumed by combustion when ignition is central and propagation is limited to the upward and horizontal directions only. Turbulence distributes ignition sources randomly throughout the test volume and thus counteracts those gross geometric limitations of buoyancy.¹¹ A detailed consideration of that complex interaction between turbulence and buoyancy for near-limit mixtures is beyond the scope of this paper; however, the interaction has a profound effect on the selection of a least-limit criterion. Surface

to say that the additional criterion of $K_G \geq 1.5$ bar m/s, which was realistic for the 20-L system where turbulence was strong and buoyancy limitations were small, is no longer realistic in the 120-L system where turbulence is less significant and buoyancy effects dominate. Accordingly, for the 120-L system only the $\pi_{max} \geq 2$ propagation criterion is used. In the larger volume that criterion corresponds to propagation that is limited to the upward and horizontal direction only, at a cone half angle of about 45° from the vertical.^{11,14,23}

The asymptotic limits reached in the 20-L volume correspond to upward propagation limits in a system in which buoyancy effects are suppressed by turbulence. The values reached in the 120-L system are closer to horizontal propagation limits. In any case, the overdriving effects in the 20-L system are observable from the data in Fig. 3, where the apparent lean limit recedes outward after reaching its asymptotic level at intermediate energies. At those same energies in the larger 120-L system there is no overdriving and the curve remains at the asymptotic value. There is a slight widening of the apparent limit even in the 120-L system between 2,500 and 5,000 J calorimetric energy, but that is associated more with the onset of significant turbulence than with overdriving. The propagation criterion of $\pi_{max} \geq 2$ is a condition that, in a laminar system, requires propagation both upward and horizontal; however, that same condition can be satisfied by only upward propagation when the system becomes more turbulent.

Combining the 20-L data at intermediate energies with the 120-L data at the highest energies gives an asymptotic value of 4.9 ± 0.1 pct for the lean limit of methane in air. The commonly accepted value for the lean limit is 5 pct methane² obtained with spark sources in flammability tubes, but the data in Fig. 3 give a higher value, nearer to 4.8–4.9 pct. That higher rich limit measured here is an example of the ignitability limitations of electric spark sources. Such spark-ignitability limitations can be present even in homogeneous gases. A similar case involved the inerting limit for C.F. Braddon to methane-air.¹¹

Coal Ignition in Air

The data on Pittsburgh Seam bituminous dust in air are shown in Fig. 4. This dust has a broad size distribution with a surface mean diameter of 7.2 μ m and a mass mean diameter of 10 μ m. The measured maximum explosion pressure values are shown in A, and the K_{St} values are shown in B, for dusts in

FIG. 4. Flammability data for pulverized Pittsburgh Seam coal dust in air for various ignition source strengths.

subscript *St* (Staub, the German word for dust) is used for the *K*-value.²² The data are plotted as a function of coal dust concentration, and for clarity the scale is magnified for lean concentrations below 200 g/m³. Curves are drawn through the data points corresponding to the various ignitors. As with methane, the lean limit for coal dust is reduced at the higher energies. In the case of the dust, however, a "normal" rich limit is absent, as the data in Fig. 4 show. Tests were also made out to concentrations of 4,000 g/m³, and no rich limit was found, in agreement with the previous studies of others.²³ The coal lean limit data are plotted in Fig. 5 as a function of ignition energy. The error bars indicate the precision of the measurements. One curve uses the same combination of limit criteria as used earlier for methane ($\pi_{max} = 2$ and $K_{st} = 1.5$ bar-m/s), as an example of the extent to which the data may be sensitive to criteria chosen; another curve is shown that uses a more stringent criterion ($\pi_{max} = 3$ and $K_{st} = 3$ bar-m/s).

For dusts, as the limit concentrations are approached, flame propagation is never as spatially contiguous as it is for homogeneous gases. The microscopic and macroscopic inhomogeneities in the dust concentration inevitably

FIG. 5. Effects of ignition energy on the apparent lean flammability limit of coal dust in air using different propagation criteria.

generate noncontiguous flame fronts, and propagation occurs in streaky filaments or patches of flame that follow those regions that have slightly higher dust concentrations.²⁴ Based on such considerations and an evaluation of the data for many different dusts and their comparison with full scale mine data, a K_{st} -value of 1.5 bar-m/s is considered to be a realistic and conservative criterion for the flame propagation limit of dusts in the 20-L system. Adding that criterion to the previously used criterion of $\pi_{max} = 2$ gives a lean limit of flammability for Pittsburgh Seam coal dust of 90 ± 10 g/m³.

Other Dusts

In Fig. 6, the final result for coal dust is compared with similar data for two other dusts: polyethylene and an oil shale dust (oil assay, 140 mL/kg). The polyethylene has a surface mean diameter of 27 μ m and a mass mean diameter of 37 μ m; the oil shale has a surface mean diameter of 22 μ m and a mass mean diameter of 60 μ m. The completely volatilizable polyethylene is a solid hydrocarbon that is more flammable than coal dust, with a lean limit of about 35 g/m³. That value is comparable to the lowest of the lean limit concentrations observed for the more reactive hydrocarbon gases.²⁵ The oil shale dust with a combustible volatile content of only 15 pct is much less flammable than coal dust; its lean limit is about 250 g/m³ at the highest ignitor energy tested. To a first ap-

FIG. 6 Effect of ignition energy on the apparent lean limits of flammability for polyethylene, coal, and oil shale dusts.

proximation, these data show that the product of the lean limit concentration and the combustible volatile yield is constant: a reflection of a common overall propagation mechanism for the dusts that involves devolatilization of the dust followed by gas-phase combustion of the volatile-air mixture.

The data in Fig. 6 show that while polyethylene and coal dust reach their asymptotic limits at effective energies in the kilojoule range, the shale dust still shows a sensitivity to ignition strength even in that high an energy range. If the experimental system were limited to effective ignition energies in the 10 to 100 J range, while one would not obtain the true values for the lean limits of polyethylene or coal dust, one would nevertheless correctly observe that those dusts are capable of propagating dust explosions. By contrast, for the oil shale dust, energies in the 10 to 100 J range are so inadequate that they would lead to the dangerous misconception that the dust is nonexplosive. One reason for many of the past discrepancies between the results obtained in full scale mine explosion tests and those obtained in laboratory studies is attributable to this problem of the ignition energy limitation. Another reason deals with the problem of the uniformity of dust dispersion that was mentioned in the Introduction.

In full-scale mine tests, the necessity of having to disperse the dust into the mine

volume after its initial loading on surfaces or shelves requires a strong aerodynamic disturbance. That disturbance is usually generated with a flammable methane-air ignition zone of 10 to 30 m³, initiated at the closed end of the mine. The use of such a gas ignition zone not only disperses the dust into the mine volume but it simultaneously ensures the preexistence of a free flame at the beginning of the dispersed dust zone. If the laboratory-scale tests are taken to their asymptotic limits at high ignition energies, so that one can be equally confident that a free flame preexists in the test mixture, then the laboratory results are in good agreement with mine test results.^{9,29,37}

Pressure Dependences

Data obtained for the pressure dependences of the flammability limits for methane, polyethylene, and coal dust are shown in Fig. 7. The absolute values for the lean limit concentrations of polyethylene are virtually identical at all pressures to those of methane when the methane values are expressed in the same concentration units: mass of methane per unit volume of air. Both methane and polyethylene show the same linear pressure dependence. These obser-

FIG. 7 Effect of initial pressure on the flammability limits of methane, polyethylene dust, and coal dust in air.

uations further justify the viewpoint that the combustion behavior of the fine dust at its lean limit concentration approaches that of an equivalent, homogeneous, premixed gas. The overall flame propagation mechanism in the dust cloud becomes controlled by the gas-phase reaction rate. Its lean limit concentration is then determined by the dust loading required to generate a lean limit concentration of pyrolysis products in the volatiles-air mixture, regardless of the initial pressure. Although the coal dust lean limit curve shown in Fig. 7C also varies linearly with pressure, it appears to have a finite intercept. The coal dust data are explainable in several alternative ways: the appearance of a mixing limitation for the coal volatiles at high pressures; a pressure dependent ignitability limitation for the more difficult to ignite coal dust; or a possible variation of volatility yield with pressure.

If the methane data are expressed in volume percent, they show a lean limit that is invariant with pressure. In the pressure range of 1 to 3 bar, that lean limit value is 4.9 ± 0.1 vol pct methane. That measured pressure independence for the vol pct lean limit is in agreement with the data of previous investigators.¹⁴ For the rich limit pressure dependence below 3 bar, literature data are somewhat contradictory.¹⁴ The results obtained here for the rich limits (Fig. 7A) show that if they are expressed in volume percent, they are independent of pressure from 0.5 to 2 bar at a value of 18 to 19 vol pct methane.

Although the exact values of the measured lean and rich limits show some dependence on ignitor strength and propagation criterion, once those factors are fixed, the limit values, if expressed in g/m^3 , display a linear pressure dependence. Apart from the pressure dependence, it should be noted that the absolute magnitude of the rich limit measured here, 18 to 19 pct methane, is substantially higher than that previously reported.

REFERENCES

1. COWARD, H. F., AND G. W. JONES. Bureau of Mines Bulletin 303, 1952.
2. ZABETAKIS, M. Bureau of Mines Bulletin 627, 1965.
3. HERTZBERG, M., K. L. CASHDOLLAR, AND I. J. OFFERMAN. Bureau of Mines Report of Investigations 8360, 1979.
4. HERTZBERG, M., K. L. CASHDOLLAR, AND C. P. LAZZARA. Eighteenth Symposium (International) on Combustion, p. 747, 1982.
5. HERTZBERG, M., K. L. CASHDOLLAR, D. L. NG, AND R. S. CONTI. Nineteenth Symposium (International) on Combustion, p. 1169, 1982.
6. RICHMOND, J. K., I. LIEBMAN, A. E. BRUSZAK, AND L. F. MILLER. Seventeenth Symposium (International) on Combustion, p. 1257, 1979.
7. ECKHOFF, R. K. First International Colloquium on Explosibility of Industrial Dusts, p. 63. Baranow, Poland, Nov. 8-10, 1984.
8. CASHDOLLAR, K. L., I. LIEBMAN, AND R. S. CONTI. Bureau of Mines Report of Investigations 8542, 1981.
9. CASHDOLLAR, K. L., AND M. HERTZBERG. Rev. Sci. Instrum. 56, p. 596 (1985).
10. RICE, G. S. U.S. Geological Survey Bulletin 425, p. 1911.
11. RICHMOND, J. K., I. LIEBMAN, AND L. F. MILLER. Bureau of Mines Report of Investigations 8077, 1975.
12. CHAMBERLAIN, J., M. P., LORD RAYLEIGH, AND OTHERS. First Report of the Royal Commission on Explosions from Coal Dust in Mines. HMSO London, 1891.
13. HUMPHREY, H. B. Bureau of Mines Bulletin 589, 1960.
14. HERTZBERG, M. Fuel-Air Explosions, p. 3. University of Waterloo Press, 1982.
15. HERTZBERG, M., K. L. CASHDOLLAR, I. ZLOCHOWER, AND D. L. NG. Twentieth Symposium (International) on Combustion, p. 1691, 1985.
16. HERTZBERG, M., R. S. CONTI, AND K. L. CASHDOLLAR. Twentieth Symposium (International) on Combustion, p. 1681, 1985.
17. HERTZBERG, M., R. S. CONTI, AND K. L. CASHDOLLAR. Bureau of Mines Report of Investigations 8988, 1985.
18. HERTZBERG, M. Twentieth Symposium (International) on Combustion, p. 1967, 1985.
19. BARTKNECHT, W. Explosions: Course, Prevention, Protection. Springer, NY, 1981.
20. Association of German Engineers (VDI): Pressure Relief of Dust Explosions, VDI 3673, VDI-Handbuch Reinhaltung der Luft, 6, 1983.
21. LeCHATELIER, H. Annales des Mines, 19 Ser 3, 398 (1891).
22. LINNETT, J. W., AND C. J. S. M. SIMPSON. Sixteenth Symposium (International) on Combustion, p. 20, 1957.
23. BURGESS, D. S., A. L. FURNO, J. M. KUCHTA, AND K. E. MURA. Bureau of Mines Report of Investigations 8709, 1982.
24. DEGUINGAND, B., AND S. GALANT. Eighteenth Symposium (International) on Combustion, p. 705, 1981.
25. GRUNER, J. Fifteenth Symposium (International) on Combustion, p. 103, 1975.
26. CASHDOLLAR, K. L., I. ZLOCHOWER, AND M. HERTZBERG. Bureau of Mines Report of Investigation, in process.
27. CASHDOLLAR, K. L., M. J. SAKPO, E. S. WEISS, AND

COAL COMBUSTION

28. HERTZBERG, Laboratory and Mine Dust Explosion Research at the Bureau of Mines. Symposium on Industrial Dust Explosions, June 1986. Pittsburgh, PA.

29. JOHNSON, A. L., A. L. FURNO, AND J. M. KUCHTA. Bureau of Mines Report of Investigations 5246. 1977.

WHC-EP-0416

Appendix F: Data Examples

(NOT INCLUDED IN THIS DOCUMENT)

90/11/07 14:46:48

20-L CHAMBER, PITTSBURGH RESEARCH CENTER, BUREAU OF MINES
Summary Report - Test Number 900505

Fuel: HYDROGEN H2 2nd Gas : NITROUS OXIDE N2O

Concentration: 12.1 % Concentration: 12.1 %

Remainder Gas: air

Ignitor : 138 J.

Dispersion Time: 0.000 c
Total Delay Time: 0.122 sec
Ignition time: 0.540 s

P1 Smoothing 3, 11
Pressure at Ignition: 14.7 psia
P max: 76.1 psia at 0.10 s
Pressure Ratio: 5.15

Max dP/dt: 1273.9 psi/s at 0.08 s
Kg : 23.95 bar m/s

Mixing: fan mixing

Sample Rate: 2000 Hz

<CR> - continue

F3 - print screen

Pressure Transducer 1

004505

Max pressure 75 at 1.64 sec

Press. at ignition 14.7

Max IP/45 1274 at 1.64 sec

IP/45 = 1.64 sec

IP/45

IP/45 = 1.64 sec

WHC-EP-0416

Appendix G: Pressure Transducers

(NOT INCLUDED IN THIS DOCUMENT)

Viatran

PRODUCT BULLETIN NO. 53

Model 218 Pressure Transducer

Output : 0-5V DC
 Pressure Ranges : 0-5 thru 0-15,000 PSI
 Supply Input Voltages: 12V, 24V, 28V, or ± 15 V DC
 Type : 4-wire

The Model 218 utilizes field-proven single element strain gage technology coupled with DC signal conditioning to provide 0-5V DC signal in ranges of 0-5 thru 0-15,000 PSI G, A, V, or D. With standard compensated temperature limits of -30°F to -180°F , the Model 218 will suit the majority of applications without special installation procedures.

All stainless steel construction of both pressure cavity and housing assures the maximum protection

against corrosion and environmental contamination during normal operation. Electrical connection is made through a standard six pin screw-type connector. Viatran's unique calibration circuit facilitates field calibration without a pressure source.

The Model 218, through many years of varied application and dependable service, has proven itself in severe industrial environments.

Dimensions

Specifications

Pressure Ranges	0-5, 10, 15, 20, 25, 30, 50, 75, 100, 200, 300, 400, 500, 750, 1000, 1500, 2000, 3000, 4000, 5000, 7500, 10,000, and 15,000 PSI range, absolute, vacuum, differential.	Ripple	Not Applicable
Differential Base Pressure	2000 PSI Maximum	Circuit Protection	Not Applicable
Measure and Fluids	Any fluid compatible with 316 SS and Buna N O-rings standard. Alternate materials available optionally. Differential units require a clean, dry gas as a reference medium.	Insulation Resistance	Better than 1000 megohms at 50V DC
Supply Voltage	Model 218-12 12V DC $\pm 2V$ DC Model 218-24 24V DC $\pm 2V$ DC Model 218-28 28V DC $\pm 2V$ DC Model 218-15 15V DC $\pm 1V$ DC	Proof Pressure	10 times rated range (15,000 PSI maximum). M5 provides increased overpressure capability.
Regulation	Less than $\pm 0.1\%$ FSO over supply voltage range.	Burst Pressure	5 times rated range (20,000 PSI maximum)
Output Signal	0-5V DC. M18 provides 0-10V DC.	Long-Term Stability	Better than $\pm 0.05\%$ FSO over 6 months.
Load Impedance	500 ohms nominal	Resolution	Infinite
Static Error Band	Better than $\pm 0.4\%$ of calibrated span, including errors due to linearity, hysteresis and repeatability. M19 provides improved accuracy.	Position Sensitivity	Mounts in any position with no effect on zero.
Combined Zero & Span Temperature Effects on Accuracy	Less than 2% FSO per 100°F. M11 provides improved temperature performance.	Response Time	Less than 1 millisecond to reach 90% of full scale.
Operating Temperature Limits	-50°F to +200°F	Frequency Response	0 KHz for 0-5 PSI range extending up to 20 KHz for 0-15,000 PSI range.
Range Adjustment	$\pm 10\%$ FSO	Shock & Vibration	Less than 0.25" W.G. per G in plane normal to diaphragm. Negligible error in remaining two planes.
Range Calibration Signal	100% FSO calibration circuit operated by shorting pins 5 (E) and 6 (F).	Pressure Capsule Material	302 SS, 316L SS and Buna N O-rings. Includes materials wetted by process fluids. Alternate materials available optionally.
Range Calibration Signal Accuracy	Better than $\pm 1.0\%$ FSO. Exact pressure-to-output correlation data provided on calibration data card shipped with unit.	Process Pressure Port (M1)	1/4" NPT female. M2 provides alternate pressure port.
Zero Adjustment	$\pm 10\%$ FSO screwdriver adjustable.	Reference Pressure Port (M2)	1/4" NPT female. Differential pressure units only.
Interaction Between Zero & Span	Less than $\pm 1.0\%$ FSO over full adjustment range.	Electrical Connection	WK8-12S. M1 provides alternate connectors.
		Mounting	May be supported by process piping or supplied with optional mounting bracket A1.
		Enclosure	High quality stainless steel. All electrical components protected against adverse environmental conditions.
		Material	Stainless steel, welded to transducer body.
		Weight	22 ounces, nominal (622.7 grams)

Ordering: Specify model, input voltage, and pressure range and indicate modifications or accessories required. Refer to Catalog No. 58 for details.

Viatran CORPORATION
1111 INDUSTRIAL BLVD. - SPRING HOUSE, PA 15141
TEL: 412-261-1111 FAX: 412-261-1150

1283-10M

trans metrics

High Output Pressure Transducer Model P21 E Type

three terminal operation from dual power supplies

Features:

- ranges 0-15 psi through 0-15,000 psi absolute, gage and vacuum
- compatible with most liquids and gases
- output signal 0-5 VDC standard
- excitation = 12 to = 15
- three accuracy classes — 0.15 - 0.5 - 1.0
- static and dynamic measurements
- field adjustable zero and span
- temperature compensated

DESCRIPTION:

The P21E type was specifically designed to operate with excitation being supplied by dual power supplies (= 12 to = 15) with the output signal referenced to ground or power supply common; however, this unit will also operate with a single power supply and will produce a phantom ground. When operating from a single supply either the power supply low or signal low may be grounded, but not both.

The P21E type includes all the necessary electronics including an instrument amplifier to provide a high level output signal (0 to 5 VDC is standard). These units have internal potentiometers to adjust the zero and span settings (these potentiometers are behind plugs).

P21E types are available in three accuracy classes and prices to match various requirements. All are carefully tested, compensated and calibrated with NBS traceable standards to assure compliance with specifications. A certificate of calibration is supplied with each unit giving the exact sensitivity of that unit.

The P21E type pressure

transducers employ a four-arm strain gage bridge bonded to the reference or non-wetted side of a stainless steel diaphragm. This diaphragm type pressure sensor is machined from 17-4 PH stainless steel bar so that there are no joints or pockets in the stressed areas near the diaphragm. This construction yields a highly reliable transducer with long life and with low errors due to hysteresis and non-repeatability. The stainless steel pressure cavity of the P21 transducers has a low volume that is highly corrosion resistant to most liquids and gases. There are no adhesives, plastics or O-rings used in the P21's pressure cavity.

The P21E type can be provided in virtually any pressure range between one atmosphere and 15,000 PSI in any desired units. All P21's may have a vacuum applied to their pressure port and will indicate this with a negative output signal. In addition to the usual true gage (relative) reference types, the P21 is available for sealed gage, absolute, compound, vacuum and wet-dry measurements. Consult factory application engineers for help with your requirements.

Circuit Diagram

3-wire circuit

Dimensions

0.75 in. diam.
19 mm
0.75 in. diam.
19 mm
0.75 in. diam.
19 mm

0.75 in. diam.
19 mm
0.75 in. diam.
19 mm
0.75 in. diam.
19 mm

trans-metrics, Inc. • 5325 Nairman Pkwy. • Solon, Ohio 44139 • Phone: (216) 248-2229 • Telex/TWX 310-427-2059

Specifications — Model P21 E Type

PRESSURE RANGES 0-15, 25, 50, 100, 150, 200, 300, 500, 750, 1000, 1500, 2000. Other ranges and units may be 2500, 3000, 5000, 10000, 15000 PSIG, PSIA, PSIV or PSIS available

INDIVIDUAL CHARACTERISTICS

		P21EA	P21EB	P21EC
FULL SCALE OUTPUT	VDC (field adjustable)	0 to 5.0 = 0.025	0 to 5.0 = 0.05	0 to 5.0 = 0.1
ZERO BALANCE	1/2 FSO Maximum (field adjustable to zero)	= 1.0	= 2.0	= 2.0
STATIC ERROR BAND	1/2 FSO (nonlinearity, hysteresis, and nonrepeatability)	= 0.15	= 0.50	= 1.0
NONREPEATABILITY	1/2 FSO	0.1	0.1	0.2
THERMAL EFFECTS	1/2 FSO/100°F 1/2 FSO/50°C	= 1.0	= 2.1	= 5.0 typical
OPERATING TEMPERATURE RANGE		-65 to +250°F -54 to +125°C	-30 to +180°F -35 to +80°C	0 to +160°F -20 to +70°C

COMMON CHARACTERISTICS

COMPENSATED TEMPERATURE RANGE 0 to +160°F
-20 to +70°C
= 12 to +15 VDC
1/2 FSO
EXCITATION
EXCITATION REGULATION
RESOLUTION Infinitesimal
PROOF PRESSURE 2x rated pressure or 20,000 PSI,
whichever is less
BURST PRESSURE 4x rated pressure or 25,000 PSI,
whichever is less
LIFE Over 10 million cycles between zero and
rated pressure
FREQUENCY RESPONSE Flat to 2500 Hz

MATERIAL Sensing cavity 17-4 PH stainless steel
housing 304 stainless steel
PRESSURE FITTING 7/16-20 UNF-2B straight thread
for O-ring seal with 1/4 in. tube fittings (SAE type)
ELECTRICAL CONNECTOR Bendix PTH-10-6P or
equivalent
NOISE 10 millivolts 0-5
OUTPUT CURRENT 5 milliamperes maximum
CURRENT CONSUMPTION 35 milliamperes typical
ACCELERATION EFFECT, STATIC 1 mg
WEIGHT 5 oz.
SOURCE INDEPENDANCE less than 50.0ms
CAVITY VOLUME, less thread 0.02 cu. in.

HOW TO ORDER:

Specify the model, pressure range, units and type (gauge, absolute, sealed gauge, differential, or vacuum)

List any options or modifications.

Include any accessories as a separate item. Note that mating electrical connectors are not included with transducers and should be ordered as a separate item if required.

For special application, please consult the factory.

*The standard pressure fitting on the P21 is the SAE straight thread O-ring type with 7/16-20 thread. This fitting can be interfaced with many Parker and Swagelok fittings as well as those of many other companies so that connections may be made in almost any situation. Trans Metrics stocks many of these fittings for your convenience. The P21 can also be provided with a 1/4-13 NPT internal pipe thread, MS 32649 internal straight thread fluid connection, or the MS 32655 external 1/4 flare tube fitting for 1/4 O.D. tubing.

3325 Naiman Parkway, Solon, Ohio 44139
Phone 216/248-2229

Telex/TWX 310-427-2059, Cable: Transmtrix Solon
2715 Printed in U.S.A. 1/83

Appendix H: Pressure Calibration Standard

(NOT INCLUDED IN THIS DOCUMENT)

Consolidated Electrodynamics Corporation CEC

Primary Pressure Standard #6-201

GENERAL DESCRIPTION

A. INTRODUCTION

The Primary Pressure Standard (Fig. 1A) is a high-accuracy pneumatic dead-weight tester used for measuring gas pressure. It is a true primary instrument in that it uses as its references the fundamental quantities of mass, length, and time. The 6-201-0001 is ideally suited for accurately calibrating other pressure-measuring instruments. Both gage and absolute pressure measurements may be made.

B. PRINCIPLE OF OPERATION

The simplicity of the principle of operation of the 6-201-0001 is apparent in the schematic diagram shown in Fig. 1B. The gas whose pressure is to be determined is admitted through Port A. When this pressure causes the piston (P) with its weights (W) to rise to a point of equilibrium, balance is achieved. Since the effective diameter (d) of the piston-cylinder combination and the weight of the piston, plus the added weights, are accurately determined, the total weight (lbs) divided by the effective area (sq in) provides the actual pressure in pounds per square inch. Friction between the piston and cylinder is negligible in the 6-201-0001, as their surfaces are polished to a microfinish and the piston is rotated on an air film during operation, thereby reducing static friction to a minimum.

C. APPLICATIONS

The 6-201-0001 Primary Pressure Standard represents the latest development in pressure-measuring devices. Some of the several possible applications are listed below. The user will undoubtedly discover additional applications not given here.

1. Calibration of absolute and gage-type pressure-measuring instruments.
2. Checking mercury manometers.
3. Calibration of CEC Electromanometer Secondary Pressure Standards.

A unique feature of the 6-201-0001 is its capacity for direct calibration of absolute type transducers. The chamber within the cover glass (see Fig. 1A) can be easily evacuated for this purpose. The pressure drop across the piston-cylinder area is thus referenced essentially to zero absolute pressure rather than ambient pressure. It is for this reason, principally, that the motor drive (Item 2, Fig. 3) is provided; rotation of the piston could not be

6-201-0001
21.4 1-63

TYPE 6-201-0001 PRIMARY PRESSURE STANDARD

FIG. 1A

SCHEMATIC - TYPE 6-201-0001 PRIMARY PRESSURE STANDARD

FIG. 1B

6-201-0001
2114 3-63

TYPE 5-201-0001 SET-UP FOR CALIBRATION WITH
TYPE 5-003-0001 CALIBRATION PRESSURE CONTROLLER

FIG. 2A

5-201-0001
2114 3-63

4834-111
2371-4191

TYPE 6-201-0001 SET-UP FOR GAGE CALIBRATION

FIG. 2 B

TYPE 6-201-0001 SET-UP FOR ABSOLUTE CALIBRATION

FIG. 2 C

accomplished by hand. A typical system for absolute calibrations is shown in Fig. 2B. In Fig. 2A is shown a typical system for calibrating gage-type transducers.

D. SPECIFICATIONS

1. Operational Characteristics

- a. Accuracy: 0.015%* of reading
- b. Pressure ranges: 0.3-1.5, 0.3-5, 1.5-15, 1.5-50, 15-150, 15-500
- c. Resolution: Better than 0.002% of reading
- d. Temperature range: 60°F to 100°F
- e. Standard ambient temperature: 75°F
- f. Humidity: 0 to 80% of relative humidity
- g. Thermal coefficient of sensitivity: -0.0012% of reading/°F
- h. Power requirement: 105-125 volts, 60 cps, 10 watts to the motor through a momentary contact manual switch

2. Mechanical Characteristics

- a. Size: 10 1/2" long, 8 1/2" wide, and 7 1/2" high nominal
- b. Weight: Approximately 22 pounds complete
- c. Mounting: Three leveling screws in tapped holes in base may be used as intended or replaced for more permanent installation.
- d. Finish: Dark blue painted base, medium blue painted case, glass cover
- e. Electrical connection: A detachable 3-prong cord set is supplied to match a standard Cannon connector in the instrument base.
- f. Pressure connection: Under side of piston pressurized from standard 1/4" Swagelok fitting in the base. Case vented to atmosphere (gage pressure) or evacuated (absolute pressure) through a fitting capable of receiving a standard 1/2" I. D. vacuum pump hose.
- g. Fluids applicable to parts: Clean, dry, noncorrosive gases only.

*For ranges of 15-150 and 15-500 psi the accuracy is 0.025% of reading.

6-201-0001
2114 3-63

Part I
-2-

PART II

OPERATING INSTRUCTIONS

A. INITIAL SET-UP

NOTE: The Type 6-003-0001 Pressure Calibration System provides a convenient factory available set-up for use with the Type 6-201-0001 Pressure Standard. Refer to the Operation and Maintenance Manual of the Type 6-003-0001 Pressure Calibration System for proper instructions in its use with the Type 6-201-0001 Primary Pressure Standard.

1. Remove the Primary Pressure Standard from its container and place it on a flat, firm surface at the operating site. Using the knurled leveling screws, level the instrument so that the bubble in the spirit level is in the center of its circle.
2. Select the appropriate piston-cylinder combination for the desired pressure range. (See Part III, Pressure Table.) Using the spanner wrench provided, tighten the piston or cylinder down until an air-tight seal is made with the "O" ring in the adapter. See "Precautions", Section C.
3. Attach the power cable to the receptacle at the base of the instrument and to a 105-125 volt, 60-cycle power source.
4. Connect the pressure line (DO NOT apply pressure at this time) to the instrument lower male fitting labeled (+).

If absolute pressure measurements are to be made, connect the vacuum line to the upper male fitting labeled (-).

Leak-free connections are essential if accuracy is to be maintained. When making connections to the pressure and reference ports of the Primary Pressure Standard, care should be taken to avoid twisting the fittings and thus causing a loss of seal.

5. Before making absolute measurements, during which the chamber within the cover glass is evacuated, apply a thin coat of vacuum grease to the ring gasket on which the cover glass rests.
6. Select the appropriate weight set for the pressure range desired and place the required weights on the piston cylinder as shown in Fig. 4. Also see Section B, 4 of Part II.

Note that the pressure stop swings to one side to allow placing of the weights. Be certain that the pressure stop is returned to its position above the weights before applying pressure to the instrument.

6-201-0001
211 1-63

TYPE 8-201-0001 PRIMARY PRESSURE STANDARD, EXPLODED VIEW

FIG. 3

8-201-0001
2114 3-63

7. Place the cover glass in position as shown in Fig. 1A. The cover glass should always be in the position shown even when making gage measurements, as it shields the weights against air currents which may affect instrument accuracy.

B. OPERATION

NOTE: It is mandatory that the pistons, cylinders, and weights be thoroughly cleaned before operation of the unit (see Part II, C PRECAUTIONS, 4).

1. Feed air pressure into the instrument until piston and weights rise to approximately 1/8 inch from the pressure stop. Maintain the pressure at this level.
2. Depress motor starter button to rotate piston and weights. When the piston has reached proper speed, the motor will automatically disengage and the piston (or cylinder) will spin freely. The time required to reach proper speed before disengaging will vary with the number of weights being used.
3. Weights may be added or removed to obtain range of pressures for the measurements desired (see Part III, Pressure Table).
4. Six pressure ranges are currently available. These are shown below with the appropriate piston-cylinder combinations and weight sets required. The values of the weight sets are such that equal increments of 1% full-scale can be measured starting with the lowest pressure point indicated in the table below.

<u>PRESSURE</u> <u>RANGE</u>	<u>INCREMENTS</u>	<u>PISTON-CYL NO.</u>	<u>USE</u> <u>&</u>	<u>WEIGHT SET NO.</u>
0.3 - 1.5 psi	0.015 psi	6-001-0001		6-002-0001
→ 0.3 - 5 psi	0.05 psi	6-001-0001		6-002-0002
1.5 - 15 psi	0.15 psi	6-001-0002		6-002-0001
→ 1.5 - 50 psi	0.50 psi	6-001-0002		6-002-0002
15 - 150 psi	1.50 psi	6-001-0003		6-002-0001
→ 15 - 500 psi	5.00 psi	6-001-0003		6-002-0002

The lower limit of each range is determined by the weight of the piston or cylinder, whichever is the item lifted by the incoming air pressure. In the two lowest ranges, where the largest diameter piston-cylinder is utilized, the cylinder is the suspended, revolving member. This is piston-cylinder combination No. 6-001-0001. The weight of this cylinder is 0.00 ounces which provides a minimum pressure measurement of 0.3 psi.

6-201-0001
1114 5-63

Part II
-2-

LEVELING THE 6-201-0001 PRIMARY PRESSURE STANDARD

FIG. 4

6-201-0001
2114 3-83

2071-2

In the four highest ranges, the piston is the suspended, revolving member. This is piston-cylinder combination No. 6-001-0003, and the weight of the piston is 3.00 ounces, providing a minimum pressure measurement of 15 psi.

Using the weight sets provided, the pressure may be varied in 1% increments over the range.

Piston-cylinder combinations have the following dimensions:

PISTON-CYLINDER NO.	NOMINAL DIAMETER	AREA
6-001-0001	1.26 in.	1.25 sq in. $\pm 0.01\%$
6-001-0002	0.400 in.	0.125 sq in. $\pm 0.01\%$
6-001-0003	0.126 in.	0.0125 sq in. $\pm 0.02\%$

Weight sets are supplied in the following combinations:

WEIGHT SET NO.	WEIGHT VALUE & NUMBER OF WEIGHTS
6-002-0001	(9) 0.3 oz $\pm 0.005\%$ (9) 3.0 oz $\pm 0.005\%$
6-002-0002	(9) 1.0 oz $\pm 0.005\%$ (1) 4.0 oz $\pm 0.005\%$ (1) 7.0 oz $\pm 0.005\%$ (9) 10 oz $\pm 0.005\%$

The 4- and 7-ounce weights in Weight Set No. 6-002-0002 provide a means for easily making pressure measurements not possible with the 1- and 10-ounce weights (see Part III, Pressure Table).

5. The primary pressure standard has been calibrated in CEC's laboratory at an ambient temperature of approximately 75°F. The value marked on each weight and piston-cylinder combination is based on standard gravity at 45° latitude (980.665 Cm/sec^2 or $32.174 \text{ ft/sec/sec}$ at SEA LEVEL).

At the user's location, temperature, altitude, and latitude may, of course, differ. Therefore, certain correction factors must be applied to obtain maximum accuracy. The nomograph included in this manual (Fig. 5) can be used to obtain the correction factor for these three variables. Instructions for use of the nomograph are found on the figure.

Upon obtaining the proper correction factor, the following formula should be applied:

6- 1-0001
21 3-63

Part II
-3-

$$P_1 = P_0 (1 + \text{Correction Factor})$$

Where

P_1 = Actual Pressure

P_0 = Indicated Pressure (according to weights and piston area)

The nomograph of Fig. 5 is based upon the thermal coefficient of sensitivity given in the specifications and in the following formula for gravity computation:

$$*g = 32.174 - 0.085 (\cos 2 \phi) - 0.000094 (h)$$

Where

g = ft/sec/sec

ϕ - latitude in degrees

h = altitude in feet

C. PRECAUTIONS

Because of the high accuracy of the 6-201 Primary Pressure Standard, mechanical tolerances are exceedingly small. All components, therefore, must be kept scrupulously clean at all times. If the following rules are diligently observed whenever handling the instrument or its components no difficulties will be experienced:

1. Keep weights clean and in their storage cases when not in use, and exercise caution in handling so that they are not dropped or scratched.
2. Install and handle pistons and cylinders with utmost care. Surfaces should be maintained free of scratches and dents. Working surfaces are microhoned and clearances measured in microinches. DO NOT touch these surfaces with dirty fabrics or corrosive materials. Perspiration from the hands may etch the polished surfaces.
3. If piston or cylinder do not rotate freely, or if a metallic rubbing sound is heard when they are rotating, stop operation of the instrument immediately. This is an indication of unclean piston or cylinder surfaces.
4. To clean piston and cylinder, wipe carefully with an optical quality cleansing tissue, such as "Kimwipes", which has been wet with a non-filming solvent** (acetone or methyl ethyl ketone are ideal). Repeat

* Ref.: National Bureau of Standards Nomograph #8, Section 11.

** These materials give off toxic vapors. Handle accordingly.

CHART I GRAVITY CORRECTION (C₁)

FIG.5

CHART II TEMPERATURE AND AIR BUOYANCY CORRECTION (C₂)

$$\text{ACTUAL PRESSURE} = \text{INDICATED PRESSURE} (1 + C_1 + C_2)$$

FIG. 5A

several times to insure cleanliness. This cleaning process should be done before each operation of the unit to assure the freedom of the surfaces from dirt, grease, or lint.

5. Be certain that the pressure stop is in the position shown in Fig. 1A before applying pressure to the instrument.

6. When making measurements, either gage or absolute, make certain that the piston or cylinder is freely floating between the pressure stop and the lower travel limit.

7. Replace the cover glass as shown in Fig. 1A when making measurements. Failure to do so may introduce errors because of air currents flowing about the weights.

8. Normal maintenance of the 6-201-0001 consists principally of maintaining its components in a condition of cleanliness at all times. To replace damaged components, consult the parts list in this manual and contact your nearest CEC office.

9. Errors in pressure measurement with this instrument can be introduced if the piston or cylinder becomes magnetized. They have been demagnetized before shipment and should normally remain so. If the parts are exposed to a magnetic field, however, they may be partially remagnetized. Therefore, as precautionary maintenance, it is recommended that pistons and cylinders be occasionally demagnetized.

D. SPECIAL INSTRUCTIONS FOR 6-001-0003

Because of the extremely small mechanical tolerances of the 6-001-0003 Piston-Cylinder Combination, special care must be taken in handling this component. A very thin film of special oil must be applied to the mating surfaces before the piston is allowed to rotate in the cylinder.

The following procedure is recommended for cleaning and lubricating the 6-001-0003 Piston-Cylinder Combination:

1. Materials Needed

- a. Methyl-Ethyl-Ketone (MEK) to be used as a cleaning agent. The final cleaning should always be done with fresh uncontaminated MEK.
- b. Lint-free, optical quality, cleaning tissue.
- c. Special lubricating oil (CEC A84309-3) supplied with instrument.
- d. Nylon short-stem brush.

- e. Reagent quality-pure ethyl alcohol to be used for final rinsing.

2. To Clean and Lubricate Piston

- a. Wet a clean, dry, cleansing tissue with MEK and carefully wipe the piston clean.
- b. Repeat again, using fresh, uncontaminated MEK.
- c. Repeat 2, a, using reagent quality-pure ethyl alcohol.
- d. Apply several drops of the special oil to a clean, dry tissue, and apply a uniform film of oil to the surface of the piston.
- e. Wipe the surface of the piston with a clean, dry tissue. Repeat twice, wiping as dry as possible.

3. To Clean Cylinder

- a. Dip brush in MEK and scrub the cylinder several times.
- b. Flush the cylinder with fresh, uncontaminated MEK. Repeat, using fresh, uncontaminated MEK.
- c. Repeat 3, b, using reagent quality-pure ethyl alcohol.
- d. Blow dry air or nitrogen through the cylinder until the surface is dry.
- e. Do not apply lubricating oil to the cylinder surface.

E. CALIBRATION

If calibration certification is required, or for periodic recalibration, the CEC factory should be consulted.

Appendix I: Calibration Gases for
Gas Chromatography

(NOT INCLUDED IN THIS DOCUMENT)

Calibration Gas Mixtures

Calibration Gas Mixtures

Matheson pioneered in the preparation and analysis of gas mixtures and today is the recognized leader in the field. Virtually every significant advance in gas mixture technology was developed in Matheson's laboratories. This dominant position is based on creative competence, a dedication to excellence, a commitment to customer satisfaction, and on a broad experience — the most important single requirement for the development and processing of gas mixtures. Matheson experience — unequalled and unsurpassed — is your guarantee of the best in existing mixtures and in formulating new mixtures to precise customer-furnished requirements.

A continuing research program supports this experience and has provided valuable information on the techniques necessary to prepare accurate, stable and economical gas mixtures.

To achieve this we use both steel and aluminum cylinders combined with a variety of internal cylinder preparations. Rely on Matheson technology to pick the right combination. Tell us what you need; we'll do the rest.

It is important to note that the degree of difficulty in achieving mixture consistency increases with the number of components. There is also some inherent instability with certain components. Matheson's expertise is available to discuss your particular needs. Just ask!

To permit simple selection of the proper mixture for a specific application, Matheson mixtures are divided into the three categories described on this page.

Tighter Preparation Tolerances

Matheson is aware of certain special applications that do not require the extremely close tolerances of Primary Standards, but do require preparation tolerances exceeding those of Certified Standards. In the process control industry, for example, consistent minor component concentrations are at least as important as the accuracy of the certification. With these thoughts in mind Matheson has developed a *dynamic blending system* that delivers mixtures with tighter preparation tolerance than those listed for Certified Standards at economical prices.

Dynamic gas blending, a real time gas blending process, is a more complete gas mixing than other blending processes. This enables Matheson to produce identical gas mixtures in as many cylinders as necessary — gas mixtures in separate cylinders allows the user to connect a number of cylinders to a common manifold and/or using identical mixtures at separate locations. Think of the possibilities — assurances of consistency and elimination of re-analysis of each cylinder.

Primary Standards

Primary Standards should be used whenever you need the most accurate calibrations of an instrument, or in those applications where the knowledge of the gas concentration is critical.

Matheson Primary Standards are used wherever science requires the highest accuracy and reliability available in gas mixtures. These mixtures are precisely blended by weighting the gas components on a high load, high sensitivity analytical balance. All weights used on this balance are traceable to the National Bureau of Standards. The accuracy of weighing generally exceeds any analytical instrument accuracy. Routine quality control is used to insure the accuracy of the mixtures. Complete specifications are given on the following page.

Certified Standards

Certified Standards are the workhorses of science and industry. Applications include instrument calibration, biological, environmental and medical studies, and process simulation control and purification.

Certified Standards are calibration gas mixtures prepared by a variety of gravimetric, partial pressure and volumetric techniques. Component certification is provided through the use of NBS Standard Reference Materials, Matheson Primary Standards, certified weights, or wet chemical methods. Complete specifications are given on the following page.

Unanalyzed Mixtures

These mixtures are used in applications which do not require a mixture of accurately known composition. These mixtures are prepared by the same composition. These mixtures are prepared by the same gravimetric, partial pressure and volumetric techniques used to prepare the Certified Standards. They are not analyzed or adjusted, and the preparation tolerance cannot be guaranteed. Complete specifications are given on the following page.

Special Accuracy Mixtures

When a lack suitable standards exists or a standard proves impractical, Matheson will prepare a gas or liquid phase mixture gravimetrically on one of its many precision balances. These mixtures will not be given the Matheson Primary Standard label but they are expected to be of the highest accuracy possible.

May 1, 1991

Burns & Roe Services
Cylinder Pad
Cochran Mill Road
Bruceeton, Pennsylvania 15236

Reference P.O.#: 3273-070-REL-#99A

Gentlemen:

Below are the results of the analysis you requested, as reported by our laboratory. Results are in volume percent, unless otherwise indicated.

CYLINDER NUMBER: 390

<u>COMPONENT</u>	<u>REQUESTED</u>	<u>ACTUAL</u>
CARBON DIOXIDE, COLEMAN	12.00%	11.986%
CARBON MONOXIDE, MATHESON	1.00%	1.002%
HYDROGEN, MATHESON	5.00%	5.002%
METHANE, MATHESON	12.00%	12.025%
ETHANE, RESEARCH	1.00%	1.004%
NITROGEN, MATHESON	BALANCE	BALANCE

Sincerely yours,
MATHESON GAS PRODUCTS, INC

Wray LaFond
Branch Manager

WL/sad

1650 Enterprise Parkway
P.O. Box 353
Twinsburg, Ohio 44087
Phone (216) 425-4406
Toll Free (800) 425-9427

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WHC-EP-0416

APPENDIX B

**STATEMENT OF WORK FOR WESTINGHOUSE SCIENCE
AND TECHNOLOGY CENTER SUPPORT**

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APPENDIX B

STATEMENT OF WORK FOR WESTINGHOUSE SCIENCE AND TECHNOLOGY CENTER SUPPORT

1.0 SUMMARY

In October 1990, Westinghouse Hanford Company began discussions with the Westinghouse Science and Technology Center (W-STC) to determine how work on Hanford Site waste tanks could be improved. This led to a contract (a \$90,000 Interworks Requisition, implemented in February 1991) for W-STC to carry out five tasks. Our technical point of contact at W-STC is David F. McLaughlin (412-256-2138). The draft reports covering Tasks 1 through 4 were completed by June 1, 1991.¹

The tasks are summarized as follows:

1. In-Tank Topographic Methods. Evaluate technologies for mapping of waste tank surface crust topography to map surface temperature distribution of tank contents, including an evaluation of commercially available hardware.
2. Interior Surface Crust Temperature Mapping. Evaluate use of infrared thermography to map surface temperature distribution of tank contents, including an evaluation of commercially available hardware.
3. On-Line Gas Detection Using Raman Scattering. Determine feasibility of remote, continuous, in situ fiber optic monitoring of gas composition in the waste tank vapor space, using state-of-the-art spectroscopic techniques, including an evaluation of currently available hardware.
4. Passive Temperature and Gamma Ray Monitoring. Evaluate the applicability of Westinghouse Hanford's High-Dose thermoluminescent dosimeter (TLD) Gamma Detection Technology and passive Integrating Thermal Monitors (ITM) for determination of both localized temperature history of the waste tanks and identification of temperature and radiation field hot-spots within the double-shell tank annulus.
5. General Technical Assistance. Provide Westinghouse Hanford with general technical assistance, including peer review of selected documents, onsite visits on an as-needed basis, and telephone/telefacsimile (FAX) consulting services.

¹The scheduled completion date was changed from March 1, 1991, to June 1, 1991, because of the delay in placement of the contract. Tasks 1 through 4 (drafts) were completed as scheduled. Task 5, which was not in the original scope of work, has been extended until January 1, 1992.

Tasks 1 through 4 are generally of about one manmonth's duration and consist of survey of available technology and preparations of a recommendation on acquisition to meet Westinghouse Hanford needs. Task 5 is provided as needed.

Tasks 1 through 4 have been completed and task 5, because of urgently needed support, has been extended until January 1, 1992.

2.0 DETAILED TASK DESCRIPTIONS

2.1 IN-TANK TOPOGRAPHIC DESCRIPTIONS

2.1.1 Objective

Perform preliminary engineering required to define Westinghouse Hanford needs and assess resources available to develop in-tank topographic mapping methods.

2.1.2 Approach

The W-STC is a leader in state-of-the-art vision technology with proven system integration experience. The Control and Machine Vision organization at W-STC will assess vision sensor technologies that offer potential for performing 3-dimensional mapping of the waste tank surface. The W-STC has significant experience with several vision techniques for accomplishing surface mapping including structured light imaging, raster scan laser ranging, radially scanning laser range finding, range from focus, and stereo vision.

The primary concern for the application of this technology to the Hanford Site problem relates to the image quality that can be expected to be reflected from the waste tank surface. The first priority is to conduct experiments at W-STC to determine the viability of specific machine vision techniques for this application. If the experimental results are favorable, Westinghouse Hanford and W-STC will define the mapping system functional requirements (e.g., sensor size, weight, resolution, accuracy, radiation hardness, mapping speed, delivery system interface); and configure a program to select commercially available devices for accomplishing the task and perform system integration for development of a useable tool that serves Westinghouse Hanford needs. It is suggested that Westinghouse Hanford consider visiting the W-STC facilities during this project cycle to review experimental results from the feasibility tests and work in concert with W-STC personnel to establish the system functional requirements.

2.1.3 Deliverables

- Identify Westinghouse Hanford topography mapping needs and constraints.

- Conduct reflectivity experiments to demonstrate feasibility.
- Prepare implementation plan including resource estimates for implementing an in-tank topographic mapping system.

2.2 INTERIOR SURFACE CRUST TEMPERATURE MAPPING

2.2.1 Objective

The objective is to prepare a workscope for the development of an optical infrared temperature mapping system to be used inside the nuclear waste tanks at the Hanford Site.

2.2.2 Approach

Nonelectrical sensing technologies offer a preferred approach to nuclear waste storage monitoring. Given the volatile nature of the waste, explosion-proof sensing is required to ensure proper safety. For intra-tank temperature monitoring of the waste, optical sensing techniques are good candidates. In particular for the requirement on nonintrusive temperature mapping, Westinghouse Hanford views a sensitive optical infrared (IR) scanner as having good potential of accomplishing this task. Because a surface crust blocks direct viewing of the waste underneath, the monitor will need to infer the temperature distribution of the waste by the temperature mapping of the surface crust.

An important factor when considering IR temperature sensing is the emissivity. Although the relation between IR radiation and temperature is well-known and straightforward, it is dependent on the emissivity of the object, which varies with different materials and also with different states of the same material. The preferred approach, therefore, is to use a dual-wavelength comparative technique that eliminates the need of knowing the emissivity of the object of interest.

Using the extensive expertise the Westinghouse Electronics Systems Group (W-ESG) has in both extremely sensitive IR scanning systems and in high-tech image processing, a versatile, highly sensitive temperature mapping system can be conceptualized for use in the nuclear waste application. The design would be capable of undergoing a two-level test schedule, first in the laboratory with simulated conditions followed by measurements on the Hanford Site inside an actual tank.

2.2.3 Deliverables

- Consult with Westinghouse Hanford concerning the conditions and problems associated with temperature monitoring inside the tanks.
- Meet and discuss with W-ESG experts on the state-of-the-art in IR sensing and image processing technologies and applicability to Westinghouse Hanford needs.

- Determine the conceptual design of the IR temperature mapping system.
- Contact suppliers to determine the availability and cost to construct such a system.
- Write a report recommending the design of such a system and the equipment and cost required to construct and test the system under both simulated and actual conditions.

2.3 ON-LINE GAS DETECTION USING RAMAN SCATTERING

2.3.1 Objective

The objective is to evaluate techniques for continuously measuring concentrations of the gases species in the tank, requiring that no material is to be removed and measurement is to be carried out with no explosion risk.

2.3.2 Approach

Preliminary evaluation of the Hanford Site gas detection requirements indicate that the best approach is the use of a remote Raman detection system. The system will consist of a single-ended optical sensor, composed of optical lenses, which is connected by fiberoptic cable to the remotely located spectrum analyzer. The analyzer feeds the information to a data processor (a personal computer) that calculates and displays the concentration of the gases of interest. The Raman scattering from the gas molecules is activated by a small, frequency doubled, YAG laser which can also be remotely located with the beam guided to the optical sensor by the fiberoptic cable. The power density can be maintained well below the levels required to initiate an explosion. The sensor will be hermetically sealed and contains only passive optical components such as lenses and mirrors, but no electronics. It can be designed to measure the gas concentration within a centimeter of the sensor, or over a pathlength of several meters. Multiple optical sensors can be used to measure gas concentrations at a number of locations within the tank, and/or in multiple tanks while sharing the same processing optics and electronics. An advantage of the system is that it can detect a number of gases such as H_2 and O_2 not measurable with other optical techniques. The system can be calibrated by comparing the signal strength of trace gases to the strength of a gas with known concentration such as N_2 , and the results are independent of a number of other factors that can influence optical measurements.

A preliminary calculation of instrument sensitivity using a frequency-doubled YAG laser, operating at 0.53 μ m with 1 mJ output per pulse, shows a signal-to-noise ratio of 1,000 for detecting the presence of 0.1% H_2 in 1 atmosphere of gas. Other gases such as O_2 have similar cross-sections. Gases such as N_2O , NO_x , NH_3 , CO , CO_2 , and benzene are expected to have similar cross-sections and should, therefore, be equally detectable.

2.3.3 Deliverables

- Contact suppliers to establish the availability of commercial equipment, such as lasers, Raman analyzers, and data processing, hardware and software, that can be incorporated into the proposed system.
- Evaluate suitability for use in radioactive and potentially explosive environments.
- Determine the Raman cross-sections for all gases of interest (from the literature).
- Refine the conceptual instrument design outlined above and calculate the instrument sensitivity for gases of interest.
- Recommend a course of action for testing the technology in a simulated environment and a permanent installation.

2.4 PASSIVE TEMPERATURE AND GAMMA RAY MONITORING

2.4.1 Objective

The objective is to evaluate the applicability of passive Integrating Thermal Monitors and high-dose passive gamma detectors for identification of temperature and radiation fields and potential hot-spots in high-level nuclear waste storage tanks.

2.4.2 Approach

A new passive for temperature monitoring has been recently developed at W-STC. These devices, ITMs, consist of materials whose optical properties change gradually as a function of time and temperature. The ITMs are deployed in a thermal environment for a time sufficient to provide a measurable response and are then retrieved and analyzed. The ITMs were developed for temperature surveillance in nuclear reactor containment environments where 2 to 5 yr exposures in 30 to 65 °C temperature range are typical. However, an extensive and general temperature calibration data base has been developed that will allow accurate temperature measurements to be carried out during exposures of 1 to 100 days at temperatures of 30 to 200 °C (86 to 392 °F), and, if necessary, additional measurements can be carried out to extend coverage to higher temperatures.

The ITMs used for thermal environment surveillance at nuclear power reactors have dimensions of 1 cm by 1 cm by 0.1 cm. This size was chosen for handling convenience, and ITMs can be miniaturized if required for a particular temperature surveillance application. The low cost of ITMs makes 2-dimensional or 3-dimensional monitoring of temperature gradients (including locating possible hot spots) a practical consideration. The ITMs are completely insensitive to B/7 fields and can be retained as a permanent record

of surveillance of a particular thermal environment. All procedures for manufacture and readout of ITMs have been reviewed through quality assurance audits and have been found to be in compliance with nuclear industry requirements. The temperature measurements carried out during all ITM calibrations are traceable to National Institute of Standards and Technology Temperature standards.

Additional information as to tank contents and distribution can be achieved by passive gamma ray detection. Passive measurements of integrated gamma (or beta-gamma) doses can be made to uncertainties of less than -10% over a wide range of gamma intensities. The production of optical centers in crystals by ionizing radiation is used to make measurements in the higher integrated dose ranges. The optical crystals are read by measuring the amount of optical absorbance at wavelengths that correspond to the various color centers of interest. The dose range of the optical crystals developed at Westinghouse is from 3×10^3 to 10^{10} rads. The response of the optical crystals has been shown to be independent of temperature over this range.

Doses less than 3,000 rads can be measured with conventional TLD devices. Specially developed TLD reading methods are used at Westinghouse Hanford to avoid information loss resulting from thermal fading. These passive devices can be deployed in the radiation field of interest for a time consistent with the response sensitivity range and retrieved to determine the integrated dose during that time interval. Because of their low cost, passive gamma ray dosimeters can be deployed in 2-dimensional or 3-dimensional arrays to map radiation field gradients or to locate possible radiation "hot spots."

2.4.3 Deliverables

- Evaluate applicability of ITMs to monitoring of local temperatures in waste tank applications, including evaluation of device sensitivity, logistics and deployment, and interpretation of response.
- Prepare evaluation of specially developed passive gamma ray dosimeters for mapping of radiation fields in waste tanks, and identification of "hot spots."
- Develop a program of implementation of ITM and passive gamma detector technology consistent with the needs of Westinghouse Hanford.

2.5 GENERAL TECHNICAL ASSISTANCE

The W-STC will provide Westinghouse Hanford with general technical assistance, including peer review of selected documents, onsite visits on an as-needed basis, and FAX consulting services.

WHC-EP-0416

APPENDIX C

**STATEMENT OF WORK FOR ARGONNE NATIONAL LABORATORY
ACTIVITIES ON SYNTHETIC WASTES**

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Statement of Work
for
**"RADIOLYTIC GENERATION OF GASES FROM SYNTHETIC
WASTE"**

Chemistry Division
Argonne National Laboratory

Principle Investigator

Dan Meisel¹

Task Force Investigators

M. C. Sauer², C. D. Jonah², J. C. Sullivan³, M. S. Matheson¹, E. P. Horwitz⁴

1.0 Objective:

The primary objective of this program is to identify the role of radiation in the production of hydrogen and other gases in waste tank 241-SY-101.

A secondary objective is the identification of remedies, based on the work described below, which could be used to mitigate the build-up of hydrogen, nitrous oxide and/or other, presently unknown, but undesirable gasses in waste tank 241-SY-101.

2.0 Background:

2.1 The Tank:

The problems associated with tank 241-SY-101, as reflected in the Science Panel report, are outlined in this section. Similar problems were identified in other tanks. Slurry growth and collapse cycles have occurred in wastes of this tank since 1981. The rapid decrease in the surface level of the tank is accompanied by a release of gas that is mainly composed of hydrogen and nitrous oxide. The radioactive material in the tank is in the form of a crust, a slurry and a sludge. The tank 241-SY-101 was filled with concentrated aqueous radioactive waste from 1977 to 1980. The major source of radioactivity in this waste is ¹³⁷Cs. It is an established fact that hydrogen gas can be produced by radiolysis of water. Earlier work conducted at Hanford on synthetic waste showed that there is also a chemical process for the generation of hydrogen and other gases. Thus, the hydrogen may arise from both chemical and radiolytic processes. There are no data on the specific organic species currently in tank 241-SY-101, but based on the material placed in the tank, it is likely that radiation may also produce hydrogen gas from the reaction of organics with hydrogen atoms produced by the radiolysis of water. This statement of work has been prepared to assess the importance of radiation-produced hydrogen and other gases in tank 241-SY-101.

¹Electron Transfer and Energy Conversion Group, CHM. ²Radiation Chemistry and Reactive Intermediates Group, CHM. ³Heavy Elements Group, CHM. ⁴Separations Group, CHM.

2.2 Radiolytic Sources for Hydrogen Generation.

Discussion among the authors of this proposal led to several working hypotheses that may provide explanations to the radiolytic sources of the generation of gases. We hasten to emphasize that the currently available information can only provide very crude starting positions. The concentrated solutions in the tank are "approximated" here to water; this approximation is highly inaccurate and leads to many of the uncertainties which will be addressed by the proposal.

The interaction of ionizing radiation with water produces ionization (electrons and holes) and excitation events in localized regions of energy deposition labeled "spurs". Little can be done to affect the distribution of the energy deposition and of the initial products, short of changing the material in which the energy is deposited. Therefore, this stage of the energy deposition will not be addressed by this proposal (except in the tangential manner mentioned in task 3 below). Excitation of water molecules may lead directly to the production of molecular hydrogen. Little can be done to avert this possible source for molecular hydrogen but this does not seem to pose a serious problem because these yields are very low; low enough to preclude this mechanism as the cause for the problem. Thus, if radiation is a major source of H_2 it must come from H atoms.

In subsequent stages of the interaction of the radiation with water electrons thermalize, solvate and react with the local high concentrations of protons (produced by the dissociation of holes) within the spurs to give hydrogen atoms. In addition, some hydrogen atoms may be produced by the fragmentation of excited water molecules. The reactions of the hydrogen atoms will be the focus of this proposal. In the absence of organics, most of the hydrogen atoms would react with the nitrite and nitrate which exist in the tank at high concentrations. However, the organic substrates, at the concentration levels present in the tank, will compete for these hydrogen atoms to produce directly H_2 by an hydrogen abstraction reaction. Furthermore, the organic radicals, which are the other product of the same hydrogen abstraction reaction, are often strong reductants. There are well documented pathways for such radicals to produce molecular hydrogen (e.g. catalysis on metallic particles which may well be present in the tank). It is also conceivable that the organic radicals, via their reactions with nitrite and nitrate, are the source of the observed N_2O .

Similar considerations may be applied to the oxidizing equivalents produced by the deposition of energy in water (eventually OH radicals from hole dissociation). For the sake of brevity, these considerations will not be reiterated here; they seem irrelevant to the production of reduced products. However, in the presence of organic substrates they may produce similar radicals, hence concerns similar to those mentioned above for the hydrogen atom reactions arise. A major effort in this proposal will therefore be directed to study the effects of organics on the yield of gases.

3.0 Approach:

To address the objectives stated above, a task force including the CHM/ANL personnel listed above, with expertise in radiation chemistry as well as familiarity with the problem of tank 241-SY-101, has been assembled. To adequately assess the role of radiolysis in the generation of H_2 and N_2O in the tank, the program described below is proposed. The design of this experimental program is limited by the scarcity of accurate information on the composition of the wastes, its physical condition (i.e., slurry, solid, solution, sludge), the distribution of radioactivity and the organic compounds in the tank. The plan is based, therefore, on "best guesses" concerning the conditions in the tank and on our ability to perform meaningful experiments which will improve our understanding of radiolytic processes in the tank. Analysis of the tank contents should provide guidance on these questions. The experimental program will be adjusted to reflect the increased information on the condition of the waste as the program proceeds.

3.1 Task 1: (J. C. Sullivan)

There exists a large data base of G-values (yield of molecules/100ev absorbed radiation) and rates of production and subsequent reactions of primary radicals produced by radiation. Because most of these G-values are measured at low concentrations, they provide only a zero-order approximation to the processes occurring in Tank 241-SY-101. It will facilitate the experimental program to conduct a literature survey of published radiolysis data to obtain information relevant to the composition of the solution in Tank 241-SY-101. The survey will be focused on available information on yields of hydrogen and nitrogenous gases and on rates of primary radicals with components of the waste in highly concentrated solutions of hydroxide, nitrate, nitrite, aluminate and carbonate. The available computer data bases will be accessed and evaluated for the existence of yield and reaction rate data for relevant reactions of importance. This will provide the basis for the development of a model that has two purposes: (1) to predict yields and assess production rates of H_2 gas and, (2) to suggest directions for static radiolysis studies. A report on the results of the literature search will be provided to WHC within three months after authorization has been given for the ANL work to proceed.

The above-collected data will be used to develop a preliminary model to show the consequences of the present knowledge base. Computer codes have been developed and utilized at CHM over the years to integrate the appropriate differential equations. However, the systems relevant to the tank problems are inherently "stiff" (the rate parameters are very fast, picosecond time scale, but the final processes occur on long time scales). This may require significant modifications to the utilization of the integrating algorithms and careful tests for their efficient responsiveness. Because of the incomplete nature of the data, this model will provide only a first

approximation for the H₂ yields seen in Tank 241-SY-101. The role of high salt concentrations on rate constants will be estimated using models that have been successfully used at ANL to explain and predict electron reactions. Unknown rate constants will be estimated from rates of analogous reactions as obtained in the literature survey. A sensitivity analysis will be done on unknown rate parameters to assess their impact on the complete system and to guide the work of Tasks 2 and 3. As results become available from Tasks 2 and 3, the new parameters will be incorporated into the expanded model.

3.2 Task 2: (M. C. Sauer)

Solutions simulating the composition of the "convecting liquid phase" of Tank 241-SY-101 will be irradiated at room temperature with ⁶⁰Co gammas. Yields (G-values, in units of molecules per 100 eV) of gas components (primarily H₂ and N₂O, but also other components if detected) will be determined by gas chromatography and/or mass-spectrometry. Independently, total gas yields will also be determined by volumetric measurements. These G-values will be measured as a function of irradiation time and thus will provide information on initial G-values which are necessary for computer modeling. These experimental data also will test the predictions of the G-values as a function of irradiation time determined from the models we develop. While no significant dose-rate effects are expected, a series of experiments will be conducted to verify this expectation. For this phase of the experimental program, the required techniques have already been utilized in our laboratories; hence, a prolonged "startup" time is not expected.

The composition of the simulated "convecting liquid phase" will be designed to resemble the liquid phase and yet provide a chemically well-defined system. Solutions will generally include, therefore, NaOH, NaAlO₂, NaNO₂, NaNO₃ at concentrations near the solubility limit. The irradiation of the above solutions will provide a baseline level for the G-values of the gases and is expected to exhibit a very low G-value for H₂. The measured G-values can be compared with the predictions of the model developed in Task 1. The yield of N₂O cannot be predicted at the present time since no known mechanism is available for its radiolytic production. Existing experimental evidence suggests that a significant source for the release of H₂ is the reaction of hydrogen atoms with organic substrates. The effect of controlled addition of organic functionalities, specifically acetate, oxalate, ethanol, citrate, ethylenediamine, HEDTA and EDTA at high concentrations (probably 1M or so) on the G-values will be measured. Because the exact speciation of the organic content of Tank 241-SY-101 is presently unknown, we plan to study the effect of the representative functionalities listed above. Emphasis will be placed on measuring the effect of one organic component at a time but the effect of mixtures will be studied to check additivity.

After any practical problems have been solved and reproducible data can be obtained at room temperature, the effect of temperature on the G-value will be examined. Only the temperature range pertinent to Tank 241-SY-101 will be studied (25°C to 60°C). Irradiation will be performed at an elevated temperature, but measurements of yields of the gases will be done at room temperature.

Concerns have been raised in preliminary discussions of the task force assembled at CHM/ANL on how to address the effect of slurries on gas production in Tank 241-SY-101. It was concluded that within the time frame and resources allocated to this statement of work, detailed analysis of the effect of slurries would be unrealistic. Nevertheless, we believe that it is important to establish the effect of alumina-silicate particles dispersed in the solution and we plan to conduct a series of experiments to test the influence of solid particles on the yields. If the procedure now being utilized for G-value measurements in solutions is inadequate, a procedure for measuring G-values of gas production from slurries will be developed.

3.3 Task 3: (C. D. Jonah)

To enhance the predictive utility of the model calculations of Task 1 and to provide a physico-chemical basis for the understanding of the radiolytic production of H_2 and N_2O , we will perform pulse radiolysis experiments if such are suggested by the results in Task 2 or to verify pathways developed in Task 4. These experiments will be designed to determine rate parameters for the primary-radical reactions with the components of the solutions described in Task 2 above. Rate parameters for reactions of e_{aq}^- (solvated electrons), H , and OH with the components described in Task 2 may be measured. It is also expected that the identity of the primary radicals could be modified by the high concentrations existing in the solutions. For example, reactions of "dry" electrons (prior to their solvation) are expected to differ substantially from those of solvated electrons which dominate in dilute solutions. Such new pathways may be revealed by the pulse radiolysis experiments. In addition, these studies may provide information on the identity of secondary radicals and therefore will outline pathways for reactions subsequent to the reactions of the primary radicals. The viability of remedies to be proposed in Task 4 below will be assessed in light of the rate parameters and mechanistic information supplied by these experiments.

The high concentrations of solutes in the simulated tank solutions will require time resolution in the picosecond regime (e.g., 1M nitrate will react with e_{aq}^- in less than 100 psec). For this purpose, we propose to use both the ANL Stroboscopic Pulse Radiolysis system (50 ps - 3 ns) and/or the fast single pulse system (500 ps - long times). Once information is collected in these experiments, the results will be fed into the modeling codes developed in Task 1 to provide more realistic predictions.

3.4 Task 4: (D. Melsel)

The role of radiolysis in the production of gases, if any, will be assessed. If significant radiolytic contributions are identified, strategies to eliminate or minimize the radiolytic production of H₂ will be suggested based on the information and insight gained through the activities of Tasks 1-3. Optimally, any recommendations for such actions should be tested but within the time frame of this proposal testing seems unrealistic.

ANL/WHC Contacts:

The PI will act as the liaison to WHC and will be responsible for the execution of the program and reporting to WHC through all phases of the program. Scientific personnel included in the task force is identified at the heading of this proposal and personnel responsible for each task is identified at the heading of the specific task. Periodic coordination meetings will be established as necessary. Travel costs were calculated to reflect 5 man-trips and 15 man days travel during the program period.

Deliverables and Time Table:

Time table for execution and significant milestones of the program are indicated in the enclosed appendix.¹ In addition the following items will be delivered:

1. Monthly progress reports in a letter format by the last day of each month. The progress reports will include significant experimental result, technical conclusions and summary of funds expended on each task during the monthly period.

2. Summary report of task 1 literature survey will be submitted no later than 3 months following authorization. This report will provide the basis for an open literature report.

3. A preliminary final report will be issued to WHC no later than September 30, 1991. A final report, suitable for external release, will be issued no later than 6 weeks following receipt of WHC comments.

¹See Appendix E, Section 4.8.5.

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APPENDIX D
REMEDIATION CONCEPTS

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APPENDIX D

REMEDIATION CONCEPTS

Dilution of Tank Contents

Features

- Lower gas production per unit volume
- Enhance release of gas because of lower viscosity.

Approach(es)

- Dilute with water
- Dilute with other waste.

Knowledge Required

- Identify correct solvent (water, NaOH?)
- Chemical compatibility with other wastes (i.e., what happens when they are mixed - gases generated, precipitate formed?)
- Sufficient understanding of gas generation mechanisms to predict
 - Impact of pumping on gas generation in Tank 101-SY
 - Impact of dilution on gas generation in Tank 101-SY
 - Impact of mixing wastes on gas generation in transfer tank
 - Gas generation behavior of waste transferred to an empty tank
- Sufficient understanding of gas retention/release behavior to predict
 - Impact of pumping on gas retention/release in Tank 101-SY
 - Impact of dilution on gas retention/release in Tank 101-SY
 - Impact of mixing wastes on gas retention/release in transfer tank
 - Gas retention/release behavior of waste transferred to an empty tank
- Is the crust's "gas throttling" action required? If so, impact on crust's gas release properties
- What will happen to the crust?
- Method of mixing diluent with waste
- Method of pumping waste out of tank

Physical properties of undiluted waste (required for designing pumping and dilution/mixing system) - viscosity and density as functions of temperature, viscosity as a function of shear rate

Locations and sizes of bubbles (required for modeling effects of pumping and dilution/mixing)

Physical properties of diluted waste (for modeling diluted Tank 101-SY) - viscosity and density as functions of temperature, viscosity as a function of shear rate

Effect on tank wall integrity

Issues

Need means to penetrate crust

No free space in Tank 101-SY; where will waste be put?

What is the likelihood that additional tank space can be made available in a timely manner, or that mixing of wastes will be allowed

Are appropriate risers available?

Verify that the concept works.

Means to get Knowledge/Resolve Issues

Crust and slurry data from Tank 101-SY (including crust data pertinent to choosing appropriate means of penetrating crust)

Waste data from other tanks (records, sampling)

Chemistry studies on Tank 101-SY and appropriate other wastes (synthetic, actual wastes) to determine compatibility, appropriate solvent for Tank 101-SY waste, properties of dissolved waste (viscosity and density as functions of temperature, viscosity as a function of shear rate)

Gas generation studies with synthetic (and actual) wastes to resolve gas generation questions

Use of tank modeling (mathematical, physical, computer) to resolve gas retention/release questions, question about fate of crust, test concept

Tank instrumentation to obtain in situ waste characteristics data - viscosity and density as functions of temperature, viscosity as a function of shear rate, locations and sizes of bubbles

Evaluation of tank wall effects (experimental if necessary)

Circulation of Tank Contents

Features

Promote continuous release of gas

Retard crust buildup

Dissolve crust

Approach(es)

Pump waste; options include bottom to top and bottom only

Mechanical stirring

Knowledge Required

Sufficient understanding of gas generation mechanisms to predict impact of circulation on gas generation in Tank 101-SY

Sufficient understanding of gas retention/release behavior to predict impact on gas retention/release in Tank 101-SY

Is the crust's "gas throttling" action required? If so, impact on crust (e.g. ablation of crust)

What will happen to the crust?

Physical properties of waste (required for designing circulation system and for modeling of tank contents) - viscosity and density as functions of temperature, viscosity as a function of shear rate.

Locations and sizes of bubbles in the slurry layer

Most appropriate system for inducing circulation (pumping, stirring, sparging?) as well as how system will be deployed (number of spargers or pumps, locations, sizes, etc)

Any effect on waste volume?

Any enhanced erosion/corrosion of tank walls?

Issues

Is tank space adequate (i.e., would waste transfers be required)

Crust behavior

Installation through crust

Pump lifetime

Appropriate risers available?

Verify that the concept works

Means to get Knowledge/Resolve Issues

Crust and slurry data from Tank 101-SY (including crust data pertinent to choosing appropriate means of penetrating crust)

Gas generation studies with synthetic (and actual) wastes to resolve gas generation questions

Use of tank modeling (mathematical, physical, computer) to resolve gas retention/release questions, questions about fate of crust and effects on waste volume, test design concepts

Tank instrumentation to obtain in situ waste characteristics data - viscosity and density as functions of temperature, viscosity as a function of shear rate, locations and sizes of bubbles in the slurry layer

Evaluation of tank wall effects (experimental if necessary)

Transfer Waste

Features

Reduced volume of waste thereby lowering total gas production

Approach(es)

Pump waste to another tank

Knowledge Required

Chemical compatibility with other wastes (i.e., what happens when they are mixed - gases generated, precipitate formed?)

Sufficient understanding of gas generation mechanisms to predict

- Impact of pumping on gas generation

- Impact of mixing wastes on gas generation in transfer tank

- Gas generation behavior of waste transferred to an empty tank

- Gas generation behavior of waste left in tank

Sufficient understanding of gas retention/release behavior to predict

- Impact of pumping on gas retention/release in Tank 101-SY

- Impact of mixing wastes on gas retention/release in transfer tank

- Gas retention/release behavior of waste transferred to an empty tank.

- Gas retention/release behavior of waste left in tank

Is the crust's "gas throttling" action required? If so, impact on crust's gas release properties

What will happen to the crust?

Method of pumping waste out of tank

Physical properties of waste (required for designing pumping system and for modeling of tank contents) - viscosity and density as functions of temperature, viscosity as a function of shear rate

Locations and sizes of bubbles in the slurry layer (required for modeling the effects of pumping and the behavior of waste remaining in tank)

Issues

Need means to penetrate crust

No free space in Tank 101-SY; where will waste be put?

What is the likelihood that additional tank space can be made available in a timely manner, or that mixing of wastes will be allowed

Are appropriate risers available?

Verify that the concept works

Means to get Knowledge/Resolve Issues

Crust and slurry data from Tank 101-SY (including crust data pertinent to choosing appropriate means of penetrating crust)

Waste data from other tanks (records, sampling)

Chemistry studies on Tank 101-SY and appropriate other wastes (synthetic, actual wastes) to determine compatibility

Gas generation studies with synthetic (and actual) wastes to resolve gas generation questions

Use of tank modeling (mathematical, physical, computer) to resolve gas retention/release questions, question about the fate of the crust

Tank instrumentation to obtain in situ waste characteristics data - viscosity and density as functions of temperature, viscosity as a function of shear rate, locations and sizes of bubbles in the slurry layer

Sparge (Dilute Released Flammable Gases?) With Nitrogen

Features

Lower gas production

Circulation

Removes other gases (O_2 and N_2O)

Approach(es)

Install lances

Circulate the waste to a pump pit, inject gas, and circulate back to lower part of tank

Knowledge Required

Sufficient understanding of gas generation mechanisms to predict impact of sparging on gas generation in Tank 101-SY

Sufficient understanding of gas retention/release behavior to predict impact of sparging on gas retention/release in Tank 101-SY (e.g., will sparging effect circulation of waste?)

Is the crust's "gas throttling" action required? If so, impact on crust

What will happen to the crust?

Physical properties of waste (required for modeling of tank contents) - viscosity and density as functions of temperature, viscosity as a function of shear rate

Locations and sizes of bubbles in the slurry layer and solubility of gas in the slurry

Behavior of sparge gas (bubble sizes, gas distribution)

Amount of gas needed

Most appropriate system for sparging (numbers, locations, heights of lances, rate of bubbling)

Any effect on waste volume?

Any tank wall erosion/corrosion effects?

Issues

Installation through crust

Verify that the concept works

Appropriate risers available?

Means to get Knowledge/Resolve Issues

Crust and slurry data from Tank 101-SY (including crust data pertinent to choosing appropriate means of penetrating crust)

Gas generation studies with synthetic (and actual) wastes to resolve gas generation questions

Use of tank modeling (mathematical, physical, computer) to resolve gas retention/release questions, questions about fate of crust and effect on waste volume, test design concepts

Tank instrumentation to obtain in situ waste characteristics data - viscosity and density as functions of temperature, viscosity as a function of shear rate, locations and sizes of bubbles in the slurry layer

Evaluation of tank wall effects (experimental if necessary)

Transfer, Dilute, Mechanical Trigger

Features

Control release of gases

Approach(es)

Transfer 100,000 gal of slurry

Dilute with 10,000 gal of waste

Maintain opening in crust

Provide mechanical energy to trigger release of gas

Knowledge Required

Identify correct solvent (water, NaOH?)

Chemical compatibility with other wastes (i.e., what happens when they are mixed - gases generated, precipitate formed?)

Sufficient understanding of gas generation mechanisms to predict

Impact of pumping on gas generation in Tank 101-SY

Impact of dilution/circulation on gas generation in Tank 101-SY

Impact of mixing wastes on gas generation in transfer tank

Gas generation behavior of waste transferred to an empty tank

Sufficient understanding of gas retention/release behavior to predict

Impact of pumping on gas retention/release in Tank 101-SY

Impact of dilution/circulation on gas retention/release in Tank 101-SY

Impact of mixing wastes on gas retention/release in transfer tank

Gas retention/release behavior of waste transferred to an empty tank

Is the crust's "gas throttling" action required? If so, impact on crust's gas release properties

What will happen to the crust?

Method of mixing diluent with waste

Method of pumping waste out of tank

Physical properties of undiluted waste (required for designing pumping and dilution/mixing system) - viscosity and density as functions of temperature, viscosity as a function of shear rate

Locations and sizes of bubbles (required for modeling effects of pumping and dilution/mixing)

Physical properties of diluted waste (for modeling diluted Tank 101-SY) - viscosity and density as functions of temperature, viscosity as a function of shear rate

Most appropriate system for inducing circulation (pumping, stirring, sparging?) as well as how system will be deployed (number of spargers or pumps, locations, sizes, etc)

Any enhanced erosion/corrosion of tank walls?

Issues

Need means to penetrate crust

No free space in Tank 101-SY; where will waste be put?

What is the likelihood that additional tank space can be made available in a timely manner, or that mixing of wastes will be allowed

Appropriate risers available?

Verify that the concept works

Means to get Knowledge/Resolve Issues

Crust and slurry data from Tank 101-SY (including crust data pertinent to choosing appropriate means of penetrating crust)

Waste data from other tanks (records, sampling)

Chemistry studies on Tank 101-SY and appropriate other wastes (synthetic, actual wastes) to determine compatibility, appropriate solvent for Tank 101-SY waste, properties of dissolved waste (viscosity and density as functions of temperature, viscosity as a function of shear rate)

Gas generation studies with synthetic (and actual) wastes to resolve gas generation questions

Use of tank modeling (mathematical, physical, computer) to resolve gas retention/release questions, question about fate of crust, test concept

Tank instrumentation to obtain in situ waste characteristics data - viscosity and density as functions of temperature, viscosity as a function of shear rate

Evaluation of tank wall effects (experimental if necessary)

Ultrasonic Agitation

Features

Cause release of gases at desired timing intervals

Approach(es)

Use ultrasound to enhance bubble transport and release

Knowledge Required

Sufficient understanding of gas generation mechanisms to predict impact of UA on gas generation in Tank 101-SY (including "sonic chemistry")

Sufficient understanding of gas retention/release behavior to predict impact on gas retention/release in Tank 101-SY

Is the crust's "gas throttling" action required? If so, impact on crust (e.g. ablation of crust)

What will happen to the crust?

Physical properties of waste (required for modeling of tank contents) - viscosity and density as functions of temperature, viscosity as a function of shear rate

Acoustic properties of waste (attenuation distance as a function of frequency)

Locations and sizes of bubbles in the slurry layer

Most appropriate system for inducing UA (frequency, amplitude, numbers and locations of emitters)

Method for deploying emitters and number required

Any effect on waste volume?

Any enhanced erosion/corrosion of tank walls?

Effect of ultrasonic energy on tank integrity (walls, concrete structure) and surrounding structure

Issues

Is tank space adequate (i.e., would waste transfers be required)

Are appropriate risers available (access to annulus)

Verify that the concept works

Means to get Knowledge/Resolve Issues

Crust and slurry data from Tank 101-SY

Gas generation studies with synthetic (and actual) wastes to resolve gas generation questions

Use of tank modeling (mathematical, physical, computer) to resolve gas retention/release questions, questions about fate of crust and effects on waste volume, test design concepts

Tank instrumentation to obtain in situ waste characteristics data - viscosity and density as functions of temperature, viscosity as a function of shear rate, locations and sizes of bubbles in the slurry layer, acoustic properties of waste

Evaluation of tank wall, tank integrity effects (experimental if necessary)

Identify appropriate emitters and method of deploying them

Demonstration of concept

Chemical Treatment

Features

Destroy or remove compounds that produce gases

Dissolve crust

Alter chemicals/substances that hold gases

Approach(es)

In situ application

Transfer waste to treatment facility

Add gas absorber

Add surfactants

Knowledge Required

Appropriate chemical treatment (complexant destruction, Cs removal, scavenging radical, chemical "suppressant," gas absorber)

Is tank space sufficient for anticipated in situ treatments

Sufficient understanding of gas generation mechanisms to predict

Impact of treatment and its implementation on gas generation in Tank 101-SY

Impact of pumping on gas generation in Tank 101-SY (if removal is required)

Knowledge of surfactants and their interactions with chemicals in the tank

Sufficient understanding of gas retention/release behavior to predict

Impact of pumping on gas retention/release in Tank 101-SY (if removal is required)

Impact of implementing treatment on gas retention/release in Tank 101-SY

Is the crust's "gas throttling" action required during implementation? If so, impact on crust's gas release properties

What will happen to the crust?

Method of mixing chemical treatment with waste

Method of pumping waste out of tank (if needed)

Physical properties of waste (required for designing pumping and/or mixing system and for modeling tank behavior) - viscosity and density as functions of temperature, viscosity as a function of shear rate

Locations and sizes of bubbles in slurry layer (needed for modeling of waste behavior during implementation)

Effect on tank wall integrity

Any effect on waste volume?

Issues

Mixing behavior of materials in the waste

Need means to penetrate crust

No free space in Tank 101-SY; where will waste be put if free space needed?

What is the likelihood that additional tank space can be made available in a timely manner, or that additions to tank will be allowed

Are appropriate risers available?

Verify that the concept works

Means to get Knowledge/Resolve Issues

Crust and slurry data from Tank 101-SY (including crust data pertinent to choosing appropriate means of penetrating crust)

Gas generation studies with synthetic (and actual) wastes to test concept and resolve gas generation questions

Use of tank modeling (mathematical, physical, computer) to resolve gas retention/release questions, question about fate of crust and effects on waste volume, test concept

Tank instrumentation to obtain in situ waste characteristics data - viscosity and density as functions of temperature, viscosity as a function of shear rate, locations and sizes of bubbles in the slurry layer

Evaluation of tank wall integrity effects (experimental if necessary)

Pilot plant studies

Thermal Treatment

Features

Change reaction rate for gas generation

Approach(es)

Cool the tank (reduce the rate)

Heat the tank (destroy compounds)

Knowledge Required

Sufficient understanding of gas generation mechanisms to

Determine how hot or cool the waste should be maintained

Predict impact of chosen heating or cooling process on gas generation in Tank 101-SY

Sufficient understanding of gas retention/release behavior to predict

Impact of heating or cooling on gas retention/release in Tank 101-SY

Predict impact of chosen heating or cooling process on gas retention/release in Tank 101-SY

Is the crust's "gas throttling" action required? If so, impact on crust (e.g. ablation of crust)

What will happen to the crust?

Thermal and physical properties of waste (required for designing cooling or heating system and for modeling of tank contents) - viscosity and density as functions of temperature, viscosity as a function of shear rate, specific heat, thermal conductivity

Locations and sizes of bubbles in the slurry layer (needed for modeling effects of cooling/heating on gas release)

Most appropriate system for inducing heating or cooling as well as how system will be deployed (number of coils, locations, sizes, etc)

any effect on waste volume?

Any enhanced erosion/corrosion of tank walls?

Effect of heating or cooling on tank integrity

Issues

Is tank space adequate (i.e., would waste transfers be required if waste is to be heated)?

Tank corrosion

Appropriate risers available?

Verify that concept works

Means to get Knowledge/Resolve Issues

Crust and slurry data from Tank 101-SY

Gas generation studies with synthetic (and actual) wastes to resolve gas generation questions

Use of tank modeling (mathematical, physical, computer) to resolve gas retention/release questions, questions about fate of crust and effects on waste volume, test design concepts

Tank instrumentation to obtain in situ waste characteristics data - viscosity and density as functions of temperature, viscosity as a function of shear rate, locations and sizes of bubbles in the slurry layer

Evaluation of tank wall effects (experimental if necessary)

Evaluation of tank integrity effects

Pilot plant studies

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APPENDIX E
PRELIMINARY SCHEDULES

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4.3 Evaluation of Waste Tank Watch List

Evaluation of Waste Tank Watch List

4.4.1 Sheet 1 of 3

4.4.1 Sheet 2 of 3

4.4.1 Sheet 3 of 3

4.4.2 Core Drilling (Sheet 1 of 3)

4.4.2 Core Drilling (Sheet 2 of 3)

4.4.2 Core Drilling (Sheet 3 of 3)

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4.4.3

Activity Completed in November 1990.

4.4.4 (Sheet 2 of 2)

4.4.5 (Sheet 2 of 3)

4.4.5 (Sheet 3 of 3)

4.4.6 (Sheet 1 of 3)

4.4.6 (Sheet 2 of 3)

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4.4.7

In Development

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4.5

Waste Sample Analysis
(Shown in Figure 1)

4.5.1 Development of Physical Property Tests

Adiabatic Calorimetry

	<u>Completion Date</u>
Identify non-radioactive set-up area for calorimeter	11/30/90
Instrument operability checks	12/15/90
Approve non-radioactive test plan	02/30/91
Test non-radioactive synthetics	07/31/91
Approve radioactive test plan and site	09/30/91

Other Physical Tests

(Thermal expansion, surface tension, porosity, thermal conductivity, crust strength)

Identify required instrumentation	01/15/91
Identify work area	01/15/91
Receive instrumentation	03/15/91
Install instrumentation	05/15/91
Demonstrate operation	06/15/91
Develop specific procedures	08/15/91
Approve procedures	09/30/91

4.5.2 Development of Organic Methods (PNL)

Deliverables

TBD	Open literature publications (subjects, journal, TBD).
2/91	Obtain samples from Tank 101-SY for use in test method development/validation.
3/91	Procure new data system for High Resolution Mass Spectrometry (HRMS).
5/91	Assess suitability/adaptability of current separation methodology for application to Tank 101-SY.
8/91	Assess applicability of methods for non-volatile thermally labile and polar components.
10/91	Develop/implement new separations methodology as needed.
1/92	Develop methods as needed.
9/92	Continue method development effort.
9/93	Continue method development effort.

Analytical Method Development

11/15/90	Peroxide analysis
11/15/90	Functional group analysis by GC/FTIR
12/01/90	Total chelation
12/01/90	Chelator analysis by derivatization-GC/MS
01/01/91	Chelator analysis by LC/MS
02/01/91	Chelator analysis by capillary electrophoresis/electrospray
02/01/91	Chelator and organometallics analysis by LC/ICP/MS
12/01/91	Chelator analysis by HPLC-UV
10/31/90	Chelators by HPLC
10/31/90	Gas Analysis Mass Spectrometer
12/15/90	Radiochemistry procedure write up

4.6.2

4.6.3 Development and Application of Other Technologies

Development And Application of Other Technologies

Fiscal Year 1991

ACTIVITY/TASK	OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEPT
1. Fiber Optic Technology (a) Assess needs and provide recommendations (b) Issue schedule for development of sensors												
2. Support from W-STC (a) Assess topographic methods (b) Assess crust temperature mapping (c) Assess on-line gas monitoring with random scattering (d) Assess passive temp and gamma monitoring												
3. Infrared Scanning (a) Assesses feasibility												

4.6.4 Development of New Approaches for Waste Characterization (PNL)

Deliverables

FY 1991

- 3/91 Develop detailed FY 1991 Work Plan
- 9/91 Interim report on demonstration of acoustic concepts and progress in development of chemical sensors.

FY 1992

- 7/92 Design review of prototype system
- 9/92 Interim report describing system design and report of progress in procurement and fabrication

FY 1993

- 9/93 Final report and system documentation describing the performance of a prototype hydrogen detection and waste characterization system (as evaluated on simulated wastes)

4.7.1 Thermo-Physical Modeling (PNL)

Deliverables

- 11/90 Document results of modeling efforts performed to date
- 1/91 Evaluate proposed gas release theories with respect to their consistency with release data and the physical properties of tank contents.
- 3/91 Document model development needs.
- 6/91 Complete initial upgrades to hydrodynamic code to include capabilities required for modeling Tank 101-SY.
- 8/91 Complete initial mathematical modeling of tank behavior.
- 7/92 Complete physical modeling of tank.
- 9/92 Complete final development of computer model of tank behavior.

4.7.2 Gas Flow Models (Westinghouse Hanford)

Deliverables

2/91	Provide input to the Tank 101-SY ventilation system upgrade sizing report.
7/91	Document results of gas flow model sensitivity studies performed.
9/91	Document results of analyses of gas release events which occurred in FY 1991.
7/92	Document results of the detailed analyses performed in support of the Tank 101-SY ventilation system upgrade.
9/92	Document results of analyses of gas release events which occurred in FY 1992.

4.8.1 Development of Methods for Producing Synthetic Wastes

Deliverables

05/10/91	Issue letter report on Westinghouse Hanford method and formula for preparation of synthetic waste.
10/26/90	Issue letter report on PNL method of producing synthetic waste.

4.8.2 Crust Formation and Properties (PNL) (Sheet 1 of 2)

Deliverables

Subtask 5.1

10/26/90 Produce five synthetic wastes (one reference and four variants) and issue a letter report on the method of producing these simulated wastes, the basis for the choices made, and questions in this area which deserve further investigation.

Subtask 5.2

11/30/90 A status report will be prepared that describes the end-of-November status of the work of this task and briefly summarizes the results obtained through mid-November.

12/14/90 A letter report will be issued that documents the interim results (results after three weeks of crust growth/gas generation testing) of 1) the physical and chemical characterization of crusts that have formed on synthetic wastes, as well as the slurries and salt cake layers, and 2) gas generation behavior.

2/28/91 An addendum to this task description will be prepared that proposes follow-on work (including costs and deliverables) directed toward identifying crust formation mechanisms.

3/8/91 The final draft of a PNL Topical Report describing the results of gas generation testing and the physical and chemical characterization of reference synthetic waste crusts, slurries, and salt cake layers will be submitted to DOE-RL for clearance. This report will be submitted to Westinghouse Hanford as a comment draft by 2/18/91 and comments will be received from Westinghouse Hanford by 2/25/91.

Subtask 5.3

12/14/90 A letter report will be issued that documents the information assembled that provides the basis for the choice of synthetic waste used for the work identified in this SOW.

Subtask 5.4

11/30/90 A letter report will be issued that will provide an assessment of whether microorganisms are a likely source of gas generation in Hanford Site DSTs. This report will either state that this effect can be ruled out as a gas generation mechanism, or propose testing to be conducted to determine the extent to which microorganisms may contribute to gas generation in these tanks.

4.8.2 Crust Formation and Properties (PNL) (Sheet 2 of 2)

Subtask 5.5

2/28/91 An addendum to this task description will be prepared that proposes follow-on work (including costs and deliverables) directed toward testing the validity of gas generation mechanism hypotheses identified (and initially tested) by GIT and ANL.

Subtask 5.6

9/30/91 A status report will be prepared that summarizes the current understanding of gas generation and crust formation mechanisms based on the FY 1991 work of GIT, ANL, Westinghouse Hanford, and PNL.

4.8.3 Gas Reaction Mechanism and Kinetics

TBD- Dan Herting

4.8.4 Stoichiometry, Kinetics, and Mechanisms (Sheet 1 of 5)

Contract not yet in place. See proposed schedule.

(1) Product Identification

4.8.4 Stoichiometry, Kinetics, and Mechanisms (Sheet 2 of 5)

(2) Source of Carbon, Hydrogen and Nitrogen in the Formation of CO_2 , H_2 , N_2O and NH_3

4.8.4 Stoichiometry, Kinetics, and Mechanisms (Sheet 3 of 5)

4.8.4 Stoichiometry, Kinetics, and Mechanisms (Sheet 4 of 5)

(4) Kinetics of the Reactions

- ① Develop procedures and line-tune apparatus for measurements of gas evolution.
- ② Measure rates of gas evolution as a functions of
 - a. concentrations of reactants
 - b. temperature
- ③ Evaluate kinetic rate expressions for evolution of gas from initial rate studies
- ④ Identify gas composition - evaluate the production of each gas component as a function of time
- ⑤ Develop kinetic rate expressions for the formation of each of the gas components

4.8.4 Stoichiometry, Kinetics, and Mechanisms (Sheet 5 of 5)

(5) Isolation of Key Intermediates

Combinations of NO_2^- , NO_3^- , NaAlO_2 , HEDTA, OH⁻
 IR, ^{15}N , ^{27}Al NMR
 Isotopic labeling (D , ^{15}N)

Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

4.8.5 Determination of the Effects of Radiation (ANL)

Time Table and Milestones

4.8.6 Testing of Actual Wastes

TBD

4.8.7 Synthesis of Results

[illegible]

4.8.8 Tank Waste Science Panel

Deliverables

- 1/91 The final meeting minutes for the September Tank Waste Science Panel Meeting will be transmitted to Westinghouse Hanford.
- 2/91 A cleared PNL Topical Report will be transmitted to Westinghouse Hanford that contains a compilation of the data available on Tank 101-SY pertinent to the formulation and subsequent release of gases.
- 2/91 A cleared PNL Topical Report will be transmitted to Westinghouse Hanford that 1) documents an analysis of the available data on Tank 101-SY to establish preliminary models of the chemical processes resulting in the formulation and episodic release of H₂ and N₂O, and 2) formulates a research program to address issues identified in the analysis of the data.
- 3/15/91 The final meeting minutes for the February Tank Waste Science Panel Meeting will be transmitted to Westinghouse Hanford.
- 6/15/91 The final meeting minutes for the May Tank Waste Science Panel Meeting will be transmitted to Westinghouse Hanford.
- 9/15/91 The final meeting minutes for the August Tank Waste Science Panel Meeting will be transmitted to Westinghouse Hanford.

4.10 Remedial Actions

The Remedial Actions schedule is being developed. A preliminary schedule is shown in Figure 1.

4.11.1 Gas Monitoring System (Sheet 1 of 3)

4.11.1 Gas Monitoring System (Sheet 2 of 3)

4.11.1 Gas Monitoring System (Sheet 3 of 3)

4.11.2.2

4.11.2.3 Surface Level

Enraf Nonius Model 872 Radar Gauge System

The scheduled milestones are as follows:

11/1/90	Equipment received, procurement complete
12/7/90	Issue Work Plan
12/14/90	Issue Test Plan
1/18/91	Testing complete in 305 Building, 300 Area
2/8/91	Issue Enraf Nonius Radar Gauge Report

This schedule applies only to installation and testing activities inside of the 305 Building.

4.11.2.4 Assessment of Thermocouples

3/15/91	Issue Test Procedures for Integrity and accuracy assessment of thermocouples.
TBD	Complete assessment of Tank 101-SY.
TBD	Complete Assessment of Tank 102-SY.
TBD	Complete assessment of Tank 103-SY.

E-50

4.11.2.4 (Sheet 2 of 2)

4.11.3 Tank Process Instrumentation (PNL)

Deliverables

11/90	Issue letter report assessing Tank 101-SY temperature monitoring system.
11/90	Issue draft report (for Westinghouse Hanford comment) on feasibility of materials characterization monitoring methods.
11/90	Issue report on survey of commercially available stereographic surface topography analysis systems.
11/90	Issue draft report (for Westinghouse Hanford comment) that identifies appropriate methods and equipment for detection and/or analysis of acoustic phenomena occurring in Tank 101-SY.
1/91	Develop and procure a prototype acoustic monitoring system, verify operability, and provide the system to Westinghouse Hanford for installation on Tank 101-SY.
3/91	Issue draft report (for Westinghouse Hanford comment) that documents an evaluation of various methods for determining surface topography in Tank 101-SY.

4.12 Upgrade of Tank Ventilation

- 2/28/91 Issue report on recommended approach for upgrading Tank 101-SY ventilation system.
- TBD Develop conceptual design.
- TBD Conduct preliminary design review.

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