

# memorandum

M-32  
Idaho Operations Office  
West Valley Project Office

DATE: July 10, 1990

SUBJECT: Assessment of Chemical Reaction Hazards - West Valley Demonstration Project  
(WVDP) Waste Tanks

TO: J. E. Solecki, Acting Assistant Manager  
for Environmental Restoration  
and Waste Management

Attached for your information and use is a copy of the West Valley Nuclear Service Co. Inc. (WVNS) assessment of chemical reaction hazards which may be applicable to the WVDP high level waste tanks.

This assessment concludes that for each potential chemical hazard evaluated in connection with WVDP waste storage tanks, the plausibility of an adverse chemical reaction is very low to nonexistent. Note that the format used in the assessment is patterned after the review conducted on the Hanford high level waste tanks by an adhoc chemist panel. Also included in the attachment is the review of the hydrogen generation issue for the West Valley high level waste tanks and Supernatant Treatment System (STS). That analysis also concluded hydrogen generation potential at West Valley is very low. The hydrogen data was previously sent to you on May 3, 1990.

Please call E. Maestas at FTS 473-4314, if you have questions.

*Tom Rowland*  
for W. W. Bixby, Director  
West Valley Project Office

Attachment

cc: T. W. McIntosh, DOE-HQ (w/att.)  
G. Braken, DOE-RL (w/att.)

SWM:013:90 - 1397:90:10

SWM:am



West Valley  
Nuclear Services Company  
Incorporated

P.O. Box 191  
West Valley, New York 14171-0191

June 29, 1990

Dr. W. W. Bixby, Director  
Mail Stop - DOE  
West Valley Project Office  
U.S. Department of Energy  
P.O. Box 191  
West Valley, New York 14171-0191

Dear Dr. Bixby:

Attention: Mr. E. Maestas

SUBJECT: Assessment of Chemical Reaction Hazards - West Valley Demonstration  
Project (WVDP) Waste Tanks

- Reference:
- 1) Letter WFB:90-19, W. F. Brehm, FFTF MASF and Plant Systems Engineering to D. G. Baide et al, "Senior Chemists' Panel Report," dated May 15, 1990.
  - 2) Letter FH:90:0051, T. F. Kazmierczak to J. M. Pope, "NaNO<sub>2</sub> addition into 8D-1," dated May 4, 1990.
  - 3) Letter SG:88:0049, D. K. Ploetz to R. E. Lawrence, Jr., "Hydrogen Generation in the STS Process," dated May 19, 1988.
  - 4) Letter W. H. Griest, ORNL to C. W. McVay, "Organic Analyses of Your Sample 8D-2 Decon Supernate," dated April 19, 1988.
  - 5) Letter WD:90:0399, D. K. Ploetz to W. W. Bixby, "Assessment of Hydrogen Generation at the WVDP," dated April 9, 1990.

Eli Maestas of the WVPO has made WVNS cognizant of additional concerns related to the potential for a chemical reaction within HLW storage tank 101-SY at Hanford. WVNS is sensitive to this situation and has specifically evaluated each of the chemical reactions described in Reference 1 for applicability to the HLW stored at West Valley. The potential for any of these chemical reactions described in the reference occurring in the HLW storage tanks at West Valley is judged to be very low to nonexistent, as shown in Table 1.

Very truly yours,

*R. F. Itzo*

R. F. Itzo, Senior Engineer  
Mail Stop - 218  
IRTS Engineering  
West Valley Nuclear Services Co., Inc.

*J. C. Meess* for D.C. Meess 6-29-90

J. C. Meess, Manager  
Mail Stop - 218  
IRTS Engineering  
West Valley Nuclear Services Co., Inc.

CJ:90:0041  
DKP:bls

BLS0039

Attachments: A) Table 1 - Assessment of Chemical Reaction Hazards - WVDP HLW  
Storage Tanks

B) Reference (1), (2), (3), (4), and 5

ATTACHMENT A  
TABLE 1 - ASSESSMENT OF CHEMICAL REACTION HAZARDS - WVDP WASTE STORAGE

POTENTIAL HAZARD	WASTE STORAGE TANK			COMMENTS
	8D-1	8D-2	8D-4	
1. Nitrate/Nitrite Organic Reaction	Very low	Very low	Very Low	Organic levels not significant <sup>(4)</sup> ; waste temperature well below ignition temperature. <sup>(2)</sup>
2. Reaction of H <sub>2</sub> with N <sub>2</sub> O	Very low	Very low	Very low	No detectable H <sub>2</sub> present. <sup>(3)</sup>
3. NPH Combustion	N/A	N/A	N/A	No NPH present (unique to core drill being used to sample crust at Hanford); no ignition source exists.
4. Reactions with Ammonium Nitrate	Very low	Very low	Very low	No ammonium compounds detected.
5. "Red Oil" Reactions	N/A	N/A	N/A	Presence of red oil not likely; total organic carbon content insufficient to be a hazard. <sup>(4)</sup>
6. Reactions of H <sub>2</sub> with higher NO <sub>x</sub>	Very low	Very low	Very low	No detectable H <sub>2</sub> present. <sup>(3)</sup>
7. H <sub>2</sub> /N <sub>2</sub> O Pressure Pulse	N/A	N/A	N/A	Gas "pocketing" not likely; waste is permeable, no "crust" formation. <sup>(5)</sup>
8. Toxic Gas Release	N/A	N/A	N/A	Presence of significant accumulations of NH <sub>3</sub> , CO, Cl <sub>2</sub> , NO <sub>x</sub> unlikely due to constant ventilation.
9. Chain Reactions	N/A	N/A	N/A	Insufficient organic present <sup>(4)</sup> , ignition source absent.
10. Hydrazine Reactions	N/A	N/A	N/A	Hydrazine presence unlikely; no ignition source exists.

- Reference: 1) Letter WFB:90-19, W. F. Brehm, FFTF MASF and Plant Systems Engineering to D. G. Balde et al, "Senior Chemists' Panel Report," dated May 15, 1990.
- 2) Letter FH:90:0051, T. F. Kazmierczak to J. M. Pope, "NaNO<sub>2</sub> addition into 8D-1," dated May 4, 1990.
- 3) Letter SG:88:0049, D. K. Ploetz to R. E. Lawrence, Jr., "Hydrogen Generation in the STS Process," dated May 19, 1988.
- 4) Letter W. H. Griest, ORNL to C. W. McVay, "Organic Analyses of Your Sample 8D-2 Decon Supernate," dated April 19, 1990.
- 5) Letter WD:90:0399, D. K. Ploetz to W. W. Bixby, "Assessment of Hydrogen Generation at the WVDP," dated April 19, 1990.



Westinghouse  
Hanford Company

ATTACHMENT B

Reference 1  
CJ:90:0041

Internal  
Memo

From: FFTF MASF and Plant Systems Engineering  
Phone: 6-0000, N2-01  
Date: May 15, 1990  
Subject: SENIOR CHEMISTS' PANEL REPORT

WFB:90-19

To:	D. G. Baide	R1-51	G. D. Johnson	L5-03
	M. V. Berriochoa	D3-30	N. W. Kirch	R2-11
	J. C. Diagini	R1-51	R. D. Marusich	R3-02
	R. M. Black	R1-19	J. Mishima	K6-03
	Il. R. Brager	L5-03	L. D. Muhlestein	N1-28
	E. J. Campbell	B3-26	A. Padilla	H0-32
	K. G. Carothers	R1-51	R. E. Raymond	R1-62
	R. P. Colburn	L4-55	D. A. Reynolds	R2-11
	H. F. Daugherty	R2-53	M. H. Shannon	B1-35
	W. T. Dixon	B2-35	A. R. Schade	B1-35
	G. L. Dunford	R1-51	W. J. Schuck	N2-01
	F. D. Fisher	T5-12	D. D. Stepnewski	N1-31
	W. H. Hamilton	R2-40	H. H. VanTuyt	P7-22
	M. S. Hanson	K1-51	J. B. Waldo	N2-51
	D. L. Herting	T6-50	O. S. Wang	H0-31
	U. F. Hicks	N2-01	D. D. Wodrich	R2-23
	D. K. Holsten	N2-01	File T1-1	

cc: WFB File/LB

The report of the Senior Chemists' Panel meetings regarding issues for core drilling in Tank 101-SY is attached. The panel concluded that if the potential for producing a spark in the gas space during drilling operations could be eliminated, then the risk of a frequent...

W. F. Brehm, Panel Chairman  
MASF and Plant Systems Engineering

dev

Attachment

## REPORT OF SENIOR CHEMISTS' PANEL

### ASSESSMENT OF CHEMICAL REACTION HAZARDS FROM CORE DRILLING IN TANK 101-SY

May 1990

#### INTRODUCTION

The Senior Chemists' Panel was convened at the request of L. D. Muhlestein and W. D. Leggett to review possible chemical reactions in Hanford waste tanks, in order to enhance confidence in the safety of sampling and other operations in the tanks. Two more detailed lists of activities for the panel have been established; these lists are included as Attachments A and B to this report.

Members of the panel are:

W. F. Brehm, FFTF MASF and Plant Systems Engineering, Chairman  
R. P. Colburn, Chemical and Waste Process Applications  
D. L. Herting, Process Chemistry and Engineering Laboratories  
F. D. Fisher, Plutonium Process Support Laboratory  
H. H. Van Tuyl, PNL Analytical Chemistry Laboratory  
J. Mishima, PNL Aerosol Science and Applied Meteorology

Three meetings were held April 27 and 30, and May 1, with a specific objective of defining chemical reaction hazards that must be considered before core drilling in tank 101-SY. Dr. Chester Grelecki of Hazards Research, Inc., consultant to Westinghouse Hanford Company on the waste tank program, reviewed the panel's recommendations and provided additional information at the May 1 meeting.

R. P. Colburn served as chairman for the April 30 meeting, and assisted in preparation of this report. This report documents the panel discussions and conclusions. Additional information that became available between the May 1 meeting and the issuance of this report has been factored in as appropriate.

#### SUMMARY AND CONCLUSIONS

The panel concluded that the single greatest perceived risk is that of a spark during the drilling operation that would ignite the gas mixture. If that concern is absent or can be mitigated, the risk of an event during the core drilling operation from chemical reaction is quite low.

This conclusion is based on the discussions described below, but includes the following caveats and prerequisites:

The core drilling should begin shortly after a gas release event ("burp"). Analysis of the exhaust gas from Tank 101-SY must indicate only background levels of hydrogen, measured by gas chromatograph or thermal conductivity detector.

Samples of complexed concentrate available in the 200 Area laboratory should be analyzed for reactivity by differential scanning calorimetry or other methods before drilling is started. The results of this analysis will determine whether it is necessary to flood the crust at least in the region adjacent to the drill with water before core drilling (recognizing that the integrity of crust samples would be decreased).

No normal paraffin hydrocarbon (NPH) or other flammable liquid is to be used as a pressure equalizing fluid during the drilling operation.

Ventilation air flow in the exhaust duct is to be maintained. An alarm ~~indicating loss of ventilating airflow is required.~~ Samples are to be taken from Tank 101-SY, and the HEPA filters in the common duct, to verify that the amount of ammonium nitrate is insignificant. It is recommended that these samples also be analyzed for radioactivity.

Analysis of exhaust gas for ammonia and hydrazine is recommended.

NOTE: At the May 8 Waste Tank Safety Task Team meeting, attended by H. H. Van Tuyl and W. F. Brehm, there was considerable discussion regarding the necessity of flooding the crust, or at least the region adjacent to the drill, regardless of the outcome of the calorimetry testing. Doing so would further retard the potential for spark formation during drilling. The rationale for doing so is that if a hydrogen burn is initiated, there is no way to absolutely guarantee that temperatures in the range sufficient to ignite the mixtures in the dry crust (which in turn would lead to energy releases that are beyond the capacity of the system to absorb) cannot be generated; therefore, the flooding of the crust would be required in all cases. The panel agrees that the extra measure of safety is provided by flooding the crust adjacent to the drill during drilling operations, but notes that some information concerning physical properties of solid crust will be lost in doing so. As of this writing (May 14), it appears that the water flooding on the crust in the vicinity of the drill will be done.

#### MEETINGS

D. A. Reynolds of Tank Farm Process Technology briefed the panel on the addition sequence of double shell slurry (DSS) and complexed concentrate (CC) to Tank 101-SY. Reynolds emphasized that the DSS material put into tank 101-SY is the most concentrated that had been processed through the evaporator. Samples were taken of the slurry (not the crust) from Tank 101-SY in 1986, and these results were discussed. J. C. Biagini of Tank Farm Support Process Engineering provided a detailed description of the core drilling operation. A key point in his presentation was that the actual cutting surface at the end of the drill is a material that cuts the crust on top of the slurry, but will not cut through the bottom of the tank. The drill rotates slowly (tens of rpm). He mentioned the use of NPH as a pressurizing fluid inside the drill string, and that the maximum temperature observed during core drilling operations is estimated to be 120°C (250°F). He also mentioned that Tank 101-SY has never been sampled by core drilling. Varying opinions on the

probability of successfully obtaining core samples from solid crust were expressed by the meeting attendees.

The panel discussions quickly focused on the potential for producing sparks during the penetration of the hard crust, either from the actual cutting, or striking a hard object in the crust (several objects have been used as projectiles in an attempt to break the crust, and left in the tank). Other concerns were also brought up and discussed. At the conclusion of the April 27 meeting, the panel developed a list of nine items associated with perceived hazards of chemical reactions that would impact core drilling operation in Tank 101-SY. The April 30 meeting generated a discussion of each issue with emphasis on information that could alleviate the concern. The May 1 meeting continued the review, with additional input from C. Grelecki and members of the Safety Support organization. A tenth item was added to the perceived hazards list on May 1.

## DISCUSSION

This list of perceived hazards was developed:

1. Reaction of Nitrate/Nitrite Salts with Organic Material
2. Reaction of H<sub>2</sub> with N<sub>2</sub>O
3. Residual NPH on Tank Surfaces
4. "Red Oil" Reactions
5. Hydrogen Reactions with Higher Oxides of Nitrogen
6. Tank Burp During Core Sampling
7. Toxic Gas Releases
8. Chain Reactions: one reaction supplies enough heat to initiate a different class of reaction
9. Reactions of hydrazine

The resolution of each of these items is discussed below.

### 1. Reaction of Nitrate/Nitrite Salts with Organic Material

~~The presence of organic material in the tank~~ in the tank have a potential as an explosive mixture. Condensed-phase reactions can be more damaging than gas-phase reactions because of the higher concentration of the reactants. Several organic species including the chelating agents citric acid, N-(2-hydroxyethyl)ethylenediaminetriacetic acid (HEDTA), ethylenediaminetetraacetic acid ~~and~~, hydroxyacetic (glycolic) acid, and chelating agent fragments resulting from reactions of the chelating agents, are present in ~~the tank~~ throughout the tank.

~~However, the mixture of sodium nitrate and sodium nitrite with sodium acetate~~ ~~is not explosive at 260°F (126°C) and 6°F (33°C) and is not considered for initiation of a nitrate-sodium acetate reaction. Even the much more sensitive mixture of equal parts of sodium nitrate and sodium nitrite with sodium acetate becomes explosive only at temperatures above approximately 260°F (500°F). Frictional heating or impact of the core drilling device with the crust were considered very unlikely as adequate sources for ignition. The hazard from this type of~~



reaction is limited to the dried portion of the crust; the presence of water in the slurry under the crust will inhibit the reaction and absorb energy through the heat of vaporization of water.

~~Table 1.1 identified three components in the tank, the agents and the fragments as possibly having been present at one or more of the temperatures mentioned as necessary for starting the nitrate/nitrite-organic reaction. These components were sampled from Tank 107-AN and reported in a 1986 end-of-year report on complexed concentrates. (Ref. W. F. Brehm and D.L. Strachan, PNL, personal communication May 2, 1990). A copy of the table is included as Attachment D. The three components are Nitrilotriacetic acid (NTA), N-(2-hydroxyethyl)iminodiacetic acid (HEIDA), and Iminodiacetic acid (IDA).~~

Some complexed concentrate material from Tank 107-AN is available. The panel established that this material must be analyzed by Differential Scanning Calorimetry (DSC) for both reaction temperatures and rate of temperature increase before core drilling is done. Other possible analysis methods are Differential Thermal Analysis (DTA), Thermogravimetric Analysis (TGA), and testing for impact sensitivity (which would probably be done at Los Alamos). If increased reaction potential is observed, then the required conditions and prerequisites for core drilling may need to be made more rigorous (water flooding on the crust, etc.).

NOTE: At the May 1 meeting, C. Grelecki cautioned against use of water spray techniques, since they can be a source of static electricity and sparks. Flooding techniques should be used if water additions on the crust are required.

However, there remains a lack of knowledge of the physical nature of the crust surface and its interaction with the drill tip. Use of cameras or videotapes during the drilling operation could increase the knowledge. Methods of visually recording events inside the tank, which satisfy rigorous safety requirements, are now being developed so that the present restrictions on photography and light sources inside the tank may be lifted.

## 2. Reaction of H<sub>2</sub> with N<sub>2</sub>O

Both hydrogen (H<sub>2</sub>) and nitrous oxide (N<sub>2</sub>O) have been identified as ~~components~~ components in the gases released from the tank. There is concern regarding ~~concentrations~~ concentrations of these gases in a pocket below the crust, and ~~high~~ high concentrations of these gases next to the surface above the crust. ~~The~~ potential for ignition due to frictional heating or sparking during core drilling was ~~considered~~ considered extremely low based on J. C. Biagini's presentation. However, as mentioned above, a more accurate knowledge of the physical nature of the crust and composition of the drill tip would be useful for further evaluation of this potential. The potential for triggering ignition was considered to be lower as the drilling was extended into the slurry below the crust because of the large amount of water present. It was speculated that the collection of gases below the crust may be a "froth" which would reduce the potential for rapid spread of the reaction even if ignition did occur at

some point. However, the actual nature of the gas below the crust remains speculative. The panel concluded that the overall potential hazard was low.

### 3. Normal Paraffin Hydrocarbon (NPH)

A potential hazard associated with the introduction of NPH as a pressurizing fluid during core drilling was discussed. It was noted that this would not be a problem with the initial core sample but it has potential for accumulation in the tank for subsequent samples. Introduction of NPH and its possible accumulation as a condensate on tank risers and walls was not considered a potential triggering mechanism hazard but was identified as potential additional fuel for combustion on the upper tank surfaces if ignition from other sources occurred in the tank. However, there is no NPH in Tank 101-SY at present because the tank has never been core-sampled. The panel agreed, however, that this hazard is amenable to elimination, and that NPH should not be used in the initial core drilling. The first sample segments in the crust will not require a pressurizing fluid. Other fluids are potential candidates for use as a pressurizing fluid; the panel considered an evaluation of them outside its charter except to conclude that the pressurizing fluid should be nonflammable.

The lack of any pressurizing fluid when sampling the solid crust sample segments will help preserve the integrity of the sample segments from that region.

### 4. Ammonium Nitrate ( $\text{NH}_4\text{NO}_3$ )

The formation of  $\text{NH}_4\text{NO}_3$  in the gas space above the waste was cited as a possible hazard. Evidence of the formation of small amounts of the compound was found on the filters of other tanks. It was concluded that only relatively massive quantities of this material in concentrated form on the crust would constitute a hazard. The presence of organic material, such as NPH, in this material would significantly increase the hazard. The formation of  $\text{NH}_4\text{NO}_3$  in significant amounts was considered very unlikely. (Ammonium nitrate cannot exist in highly alkaline environments.) The panel recommends that the ventilation system filter and tank exhaust duct surfaces be examined to determine if any of this material is present. The decision to not use NPH will further decrease this hazard. The panel concluded that no appreciable unknown hazard is present from  $\text{NH}_4\text{NO}_3$ .

### 5. Red Oil

The potential for "red oil", a reactive nitrated hydrocarbon which may form in the PUREX process from reactions of tributyl phosphate and uranyl nitrate, was considered. It was concluded that it was extremely unlikely that this material could exist in the highly alkaline environment of Tank 101-SY (pH 13). F. D. Fisher has authored a report which describes this topic; the report is now in the review process. The panel agreed that no significant hazard exists from a "red oil" reaction.

## 6. H<sub>2</sub> + Higher Nitrogen Oxides

A small amount of NO<sub>x</sub> was seen in the grab samples analyzed by mass spectrograph. Substantial amounts of higher nitrogen oxides are not believed likely because of their potential reactions with the organic species. F. D. Fisher provided ternary diagrams of flammability limits of hydrogen-air-nitrogen oxide mixtures for nitric oxide (NO), nitrous oxide (N<sub>2</sub>O), and various N<sub>2</sub>O-NO mixtures. The ternary diagrams show no substantive difference in lower flammability limits of the mixtures than for hydrogen in N<sub>2</sub>O or air. The panel believes that because of the small amount of higher nitrogen oxides present and the small difference in the flammable composition limits, that no concern exists from this topic.

## 7. Effects of a Pressure Pulse ("Burp") During the Core Drilling Operation

The observed pressure changes during the burp events are only a few inches of water. The panel believes that this by itself is not sufficient to create any hazard. It is theoretically possible, but believed very unlikely, that the core drilling operation itself could initiate a substantial gas release. Measurable gas releases of H<sub>2</sub> and N<sub>2</sub>O were not initiated by the air lancing operations conducted several years ago. See discussion of the next item. The panel believes that if no potential for spark is present, then no additional hazard is presented. Scheduling the core drill operation soon after a burp will reduce the potential for another sizable gas release, either coincident with core drilling or being caused by it.

## 8. Toxic Gas Releases

The panel identified ammonia (NH<sub>3</sub>), carbon monoxide (CO), nitrogen oxides, and possibly chlorine (Cl<sub>2</sub>) as potential toxic gases that could be released. Chlorine was regarded as extremely unlikely at the tank conditions. Concentrations of CO were reported as less than 0.01% in the gas released during the previous burp (remember that this gas is diluted by the approximately 370 ft<sup>3</sup>/min circulation in the tank), but over 10% in some of the gas evolved from the simulated slurry mixtures. (It must be noted that the simulated slurry was tested at laboratory scale.) Ammonia has been reported in Drager tube analyses (gas sample drawn through a cylinder where it reacts with a resin; the length of resin that changes color indicates the quantity of gas) of gas in Tank 101-SY, and a smell of ammonia has been reported in the vicinity of some of the tanks. Further investigation showed that air lancing Tank 101-SY caused indications from Drager tube analysis that ammonia increased to 700 to 2000 ppm during air lancing operations, and decreased to about 20-100 ppm which was the value before lancing. Continuing discussion raised the possibility that this gas was not ammonia but hydrazine, which would give a similar indication in the Drager tube at half the concentration (100 ppm hydrazine would read like 200 ppm ammonia).

The panel concluded that the ventilation system operating at about 370 ft<sup>3</sup>/min provides sufficient protection against release of toxic gases to the vicinity of the workers performing the core drilling. Operability of the ventilation system will be a prerequisite for conducting the core drilling operation for a number of reasons. The ventilation system is alarmed to

indicate its inoperability. If these conditions are satisfied, then there is no significant hazard from toxic gas release.

#### 9. Chain Reactions

The concern expressed by the panel is that a flame in the gas space would create temperatures sufficient to initiate the nitrate-organic reaction constituents in the dried crust (item #1). The presence of sufficient organic in the crust to create an explosive mixture cannot be ruled out at this time. However, the panel also believes that the key element in risk mitigation is the avoidance of a spark source to ignite the hydrogen-nitrous oxide mixture. If there is no spark, then there is minimal risk from any of these other considerations.

#### 10. Reactions with Hydrazine

This topic was added as a result of item #8 which raised the possibility of hydrazine (and hydroxylamine) as reaction products. These compounds have significant flammability. The panel concluded that there was no greater risk associated with a hydrazine "pocket" encountered by the drilling operation than there would be with a hydrogen pocket. The key consideration as mentioned, is the absence of an energy source (spark) to ignite the flammable gas. A large gas pocket is believed to be very unlikely in the dried crust, and a pocket in the slurry will contain enough moisture to retard ignition or reduce the tendency for flame to spread.

APPROVALS

W. F. Brehm - 5-15-90  
W. F. Brehm

R. P. Colburn  
R. P. Colburn

F. D. Fisher  
F. D. Fisher

D. L. Herting  
D. L. Herting

H. H. Van Tuijl  
H. H. Van Tuijl

J. Mishima  
J. Mishima

## APPENDIX A

### SENIOR CHEMISTS PANEL

#### WORK SCOPE:

1. Develop a list of important chemical reactions.
  - A. List all important chemical reactions that may occur in the tanks based on the knowledge of chemicals that have been added to tank 101-SY. Identify important parameters such as heats of reactions, important reaction products, flammable gas producing reactions, very reactive reaction products, unstable reaction products and important information regarding the reaction kinetics.
  - B. Identify what influence the radiation field may have had or is having in regard to the types of chemicals in the tank and the types of chemical reactions that have occurred or may occur.
  - C. Categorize the potential reactions in terms of their importance, or relative importance.
  - D. Identify what information, data or analysis are required that would help to quantify just how important the reactions are.
2. Evaluate proposed core drilling activities.
  - A. Are the chemical of which the crust is composed able to produce major chemical reactions that need to be considered and evaluated before attempting a core drill? Or, are the chemicals in the crust stable? Can an energy source (e.g. spark) initiate reactions of the crust materials? If so, what can be done to preclude and/or alleviate these reactions?
  - B. Provide recommendations regarding the proposed core drilling process in terms of what gaseous reactions need to be considered and what may be done to preclude these reactions and/or alleviate the consequences from these reactions. For example, hydrogen-oxygen reactions, hydrogen-nitrous oxide reactions, inerting, water flooding, etc.
3. Assist with chemical analysis efforts.
  - A. Identify types of samples that need to be collected and types of analysis that need to be completed. Help to clarify the relative importance of chemical reactions identified in item 1 by the reaction products that can or can not be measured.
  - B. Help with the identification and development of sample collection techniques.
  - C. Identify data that needs to be collected and analyzed in order to more clearly understand the chemical processes in the tank.

4. Provide assistance to the stabilization process.
  - A. How can the chemicals be stabilized so that they will not present an unacceptable hazard?
  - B. What methods may be considered or used to remove the wastes from the tanks that would not present an unacceptable hazard?
  - C. If stabilization is not achievable in the short term, what should be done to minimize the potential from any chemical reactions?
5. Assist with safety analysis and risk assessment efforts.
  - A. Complete Items 1, 2 and 3.
  - B. Provide further consultation regarding chemical reactions and their potential consequences as required.

## APPENDIX B

DON'T SAY IT --- Write It!

DATE: April 27, 1990

TO: W. F. Brehm N2-01  
 R. D. Colburn L4-55  
 F. D. Fisher T5-12  
 D. L. Herting T6-50  
 J. Mishima K6-03  
 H. H. Van Tuyl P7-22  
 W. H. Yunker L5-58

FROM: W. D. Leggett L5-04

Telephone: 6-4520

cc: N. W. Kirch R2-11  
 L. D. Muhlestein N1-28  
 D. A. Reynolds R2-11  
 WOL File/LB

XC: D. G. Baide R1-51 R. E. Raymond 1-6  
 M. V. Berrichoa R3-30 A. R. Schade B1-3  
 R. M. Black R1-19 M. R. Shannon B1-3  
 M. T. Bouchey R2-40 D. D. Stepnewski N1-3  
 H. F. Naughterty R2-53 J. B. Waldo N2-5  
 G. D. Johnson L5-03 D. D. Wodrich R2-2

SUBJECT: OBJECTIVES FOR SENIOR CHEMISTS PANEL

We are planning to take core samples from waste tank 101-SY in the near future (perhaps next week); we want to identify and minimize any hazards associated with this process. We would like this group of experts in chemistry to:

- 1) Examine what is known about the chemical makeup of the wastes in tank 101-SY.
- 2) List those reactions which could take place and release enough energy to be a hazard in the core sampling process.
- 3) Use the available information on the tank and chemical science to eliminate hazardous reactions from the list where you can. Carefully delineate the basis for each elimination.
- 4) Among the remaining hazardous reactions, identify those which could be eliminated by choice of core sampling procedure and equipment (e.g., water deluge of the drill bit).
- 5) Of the remaining reactions, identify those which we could test for in a clearly safe manner (e.g., lab mockup or small sample collection with special tools).
- 6) Identify any other means you think would add to the safety of the core sampling process.
- 7) Prepare to go over your conclusions with Dr. Chet Gerlecki (Hazard Research, Inc.) on Monday or Tuesday. Document your conclusions following this discussion.
- 8) (Somewhat longer term) recommend tests we should make on the core samples to resolve any remaining hazards questions.
- 9) (Longer term) provide recommended tests we should make on core samples in order to better predict the behavior of this waste and evaluate proposed engineered remedies intended to improve the safety of storing it.



APPENDIX C

MEETING ATTENDEES

Name	Organization	Attended		
		4-27	4-30	5-1
W. F. Brehm	FFTF MASF and Plant Systems Engineering	x	x	x
G. D. Fisher	Plutonium Processing Support Laboratory	x	x	x
H. H. Van Tuyl	PNL Analytical Chemistry Laboratory	x	x	x
D. A. Reynolds	Tank Farm Process Technology	x		x
D. L. Herting	Process Chemistry and Engineering Laboratories	x	x	x
R. P. Colburn	Chemical and Waste Process Applications	x	x	x
N. W. Kirck	Tank Farm Process Technology	x	x	x
L. D. Mubestein	Safety Support Systems	x	x	
J. Mishima	PNL Aerosol Science and Applied Meterology	x	x	x
W. D. Leggett	Advanced Systems Engineering	x	x	x
T. B. Powers	Safety Support Systems	x	x	
R. D. Marusich	Safety Support Systems		x	x
C. G. Jecki	Hazards Research, Inc.			x
O. S. Wang	Safety Support Systems		x	x
J. C. Biagini	Tank Farm Support Process Engineering	x		
J. B. Waldo	FFTF Engineering			x

APPENDIX D

TABLE 3.1

Organics<sup>(a)</sup> Identified in Organic Complexant Waste from Tank 107 AN

Chelating/Complexing Agents	Concentration <sup>(b)</sup>	
	mM	g/L
Citric Acid	64.39	4.61
N-(2-Hydroxyethyl)ethylenediaminetriacetic Acid (HEDTA) <sup>(c)</sup>	37.53	4.53
Ethylenediaminetetraacetic Acid (EDTA)	31.41	3.77
Methane Tricarboxylic Acid	17.37	1.48
Nitrilotriacetic Acid (NTA)	7.33	0.53
<b>Chelator Fragments</b>		
Ethylenediaminetriacetic Acid (ED3A) <sup>(d)</sup>	17.91	1.72
N-(2-Hydroxyethyl)ethylenediamine-N,N'-diacetic Acid (HEDDA) <sup>(e)</sup>	2.30	0.26
N-(ethylene)ethylenediaminetriacetic Acid (E <sub>2</sub> DTA)	2.28	0.23
N-(2-Hydroxyethyl)iminodiacetic Acid (HFIDA) <sup>(f)</sup>	2.14	0.18
N-(2-Hydroxyethyl)-N'-(methyl)ethylenediamine-N,N'-diacetic Acid (MeHEDD'A) <sup>(g)</sup>	1.83	0.20
N-(methyl)ethylenediamine-N,N'-diacetic Acid (MeEOD'A) <sup>(h)</sup>	1.02	0.08
Iminodiacetic Acid (IDA)	187.5	10.82
<b>Molecular Weight (MW) Species<sup>(i)</sup></b>		
A: MW 122	0.90	0.04
F: MW 173	0.23	0.02
J: MW 247	0.90	0.08
<b>Carboxylic Acids</b>		
Docos-13-enoic Acid	2.50	0.67
Hexanedioic Acid	2.04	0.19
Hexadecanoic Acid	2.04	0.39
Phthalic Acid	1.10	0.10
Nonanedioic Acid	0.83	0.07
Tetradecanoic Acid	0.68	0.12
Pentanedioic Acid	0.60	0.04
Octadecanoic Acid	0.54	0.11
Hydroxybutanedioic Acid	0.33	0.01
Butanedioic Acid	0.10	0.01
<b>Alkanes</b>		
nC <sub>23</sub> - nC <sub>35</sub>	7.77	2.50
<b>Phthalate Esters</b>		
Dibutylphthalate	1.24	0.23
Dioctylphthalate	0.08	0.01
Total Organic Carbon (TOC)	3870	44.00
% TOC Identified --- 75.1%		

(a) Identified as methyl esters (BF<sub>3</sub>/methanol)

(b) Quantitation based on six GC analyses with FID detection; the standard deviations are: citric acid, ± 5.7%; EDTA, ± 7.0%; HEDTA, ± 12.2%; NTA, ± 3.1%; ED3A, ± 2.6%; MeEOD'A, ± 9.1% Methane Tricarboxylic Acid, HEDDA and MeHEDD'A, ± 7.0% each; and MW species, ± 7.0% each.

(c-h) Identified by GC-MS and FT-IR as: (c) MW 288 lactone; (d) MW 244 lactam; (e) MW 230 dehydrated dimethylester; (f) MW 230 lactone; (g) MW 186 lactam; (h) and MW 173 lactone

(i) MWs assigned to unknown chelator fragments on the basis of electron impact (70 eV) GC-MS

ATTACHMENT B



From: Analytical and Process Chemistry  
Letter # : FH:90:0051  
Date : May 4, 1990  
Subject :  $\text{NaNO}_2$  Addition Into 8D-1

To : J.M. Pope.....M/S-M

I talked with Bob Ondrejcin (Savannah River) about potential hazards which might be encountered when adding 2000 lbs. of  $\text{NaNO}_2$  into tank 8D-1. We discussed the chemistry at several steps during the addition process such as:

- o Reactions during the dissolution of the solid  $\text{NaNO}_2$ .
- o Method of addition of the  $\text{NaNO}_2$  solution into 8D-1.
- o Effect of current and future temperatures of 8D-1 on nitrite ion in the tank.

The greatest hazard with  $\text{NaNO}_2$  is in storage of the crystalline material. Dissolving  $\text{NaNO}_2$  into water does not present any hazard as long as the solution is basic. The  $\Delta H_{\text{soln}}$  shows this to be an endothermic reaction. Therefore no heat will be generated in the process. However, if  $\text{NaNO}_2$  is dissolved into an acidic solution,  $\text{pH} < 4$ , then decomposition of the nitrite ion rapidly occurs. Nitrite decomposition is an exothermic reaction. This situation should be carefully avoided.

The question of the method of addition of  $\text{NaNO}_2$  into 8D-1 was addressed. Bob and I both agree there should be adequate agitation of 8D-1 during the addition of  $\text{NaNO}_2$  to prevent a temporary buildup of localized high concentrations. The density of the  $\text{NaNO}_2$  solution is greater than the liquid in 8D-1. Thus without agitation, the nitrite solution will temporarily collect at the bottom. Diffusion will eventually take place, but it is wise to avoid high concentrations of  $\text{NaNO}_2$ . If it must be added as a solid, then the same considerations should be taken into account as the case without agitation. The  $\text{NaNO}_2$  should be added slowly over as large an area as possible to prevent the possibility of localized high concentrations. In reviewing the makeup

NaNO<sub>2</sub> Addition Into 8D-1 (Cont'd.)

of 8D-1, it appears very unlikely there could be any violent chemical reactions with the nitrite since 8D-1 already has significant nitrite ion in solution and there are no organic compounds in 8D-1 for the nitrite to oxidize. If it is impossible to agitate 8D-1, then it would be preferable to spray the NaNO<sub>2</sub> solution over the entire surface of the liquid in the tank. NaNO<sub>2</sub> solution is more dense than the liquid in 8D-1, so if sprayed across the liquid surface, the NaNO<sub>2</sub> solution will diffuse rapidly into the liquid as it passes to the bottom.

Finally, we discussed the temperature effects as they pertain to the stability of nitrite ion in solution. Bob said Savannah River has a long history of evaporating high level liquid waste which contain similar levels of nitrites. The liquids are heated to 140 ° C and there has never been a problem with nitrite reactions in this process at these temperatures. The temperature of 8D-1 is much lower, ~70° C and unlikely to exceed 100° C. Savannah River waste is maintained at a basic pH.

Physical properties of NaNO<sub>2</sub> (1):

- o Decomposition begins at 320° C.
- o Solubility in water is 81.5 g/100ml @ 15° C. Solubility increases with increasing temperature.
- o  $\Delta H_{\text{soln}} = 4900 \text{ cal/mole}$

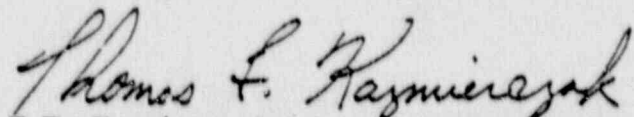
MSDS Warnings: (2)

- o Oxidizer. Avoid shock, friction, heat and flame.
- o Incompatible with cyanides, strong acids, strong reducing agents, combustible materials and organic materials.
- o Dried material may explode if exposed to heat, flame or shock.

References:

- (1) CRC Handbook of Chemistry and Physics; 67th Edition.
- (2) MSDS - J. T. Baker Chemical Company

If you should have any questions or comments please call the undersigned at extension 4987.

  
T.F. Kazmierczak, Senior Scientist  
Analytical and Process Chemistry  
West Valley Nuclear Services Co., Inc.  
Mail Stop - 56

ATTACHMENT B

From : STS Engineering  
WIN : SG:88:0049  
Date : May 19, 1988  
Subject : Hydrogen Generation in the STS Process

To : R. E. Lawrence, Jr.  
D. J. Sawyer

cc: P. Burn  
R. F. Itzo  
A. J. Howell  
R. B. Reeves  
C. G. Skillern  
L. W. Wiedemann  
MRC 1820, 0513

References: Perry's Chemical Engineers Handbook, 4th Edition

Kurath, Bray, and Holton, "Review of the West Valley Supernatant Treatment System Operational Sequence", February 1988

L. L. Burger, "Potential for Radiation Induced Corrosion in the 8D-1 Tank", January 1988

SUMMARY OF REPORT:

Radiolysis of water has been identified as a potential source of hydrogen gas production in the STS process system.

This report utilizes data on hydrogen generation given by the above-mentioned reports and postulates worst case scenarios for the accumulation of hydrogen. Utilizing very conservative assumptions based on hydrogen solubility in water, it can be safely concluded that no hydrogen gas will build up in the columns during steady state operation; and, that proper venting and dilution will prevent buildup of hydrogen gas in Tanks D-001 and 8D-3 and when there is no flow through the columns.

Almost all of the hydrogen produced by radiolysis would be produced in the ion exchange columns, where high concentrations of Cs-137 will be contained in the zeolite. The potential for hydrogen generation increases correspondingly with the degree of column loading.

The attached calculations show the potential for hydrogen production during normal processing, while recirculating water during shutdown periods, and during stagnant conditions if no recycle is occurring. Conservative assumptions are used to

determine if a problem could possibly exist. These assumptions are: 1) All energy from the Cs<sup>-137</sup> loaded on the column is contained within the column; i. e. none escapes. Thus, the theoretical amount of hydrogen generated is higher than in reality; 2) No hydrogen produced by radiolysis is assumed to recombine with oxygen to form water or otherwise "escape"; 3) The supernatant in 8D-2 is already assumed to be hydrogen saturated at 80°C due to radiolysis in 8D-2. Even making this assumption, the hydrogen in the supernatant is of such low concentration that it is negligible, and has no bearing on solubilities in the columns; 4) Column loadings of 360 KCi for the first column and 180 KCi for the second column were assumed. Actual column loadings for the first and second column are expected to be 220 KCi and 110 KCi; 5) Calculations are based on the theoretical hydrogen production rates given in the reports. It should be noted that no hydrogen has ever been detected in the off-gas from Tank 8D-2.

STEADY STATE PROCESSING:

The ion exchange columns will be at a pressure of at least four atmospheres due to flow restriction at the discharge of the postfilter by FCV-035 which controls the process flow rate. The solubility of hydrogen in the columns at these conditions will be higher than at any other point in the process, due mainly to the partial pressure of H<sub>2</sub> being high in the column compared to Tanks D-001 and 8D-3, which are sparged with air to control the hydrogen concentration to <2% in air. The hydrogen in solution while the columns are under pressure will be at ~21.4% of solubility limits at 2 gpm flow and ~7.1% at a flow rate of 6 gpm.

STORAGE IN 8D-3:

When the liquid from the postfilter enters Tank 8D-3, it drops in pressure from four atmospheres to approximately one atmosphere releasing the hydrogen in solution. The partial pressure of hydrogen in the Tank 8D-3 atmosphere will be controlled to prevent exceeding 2% H<sub>2</sub> by sparging Tank 8D-3 with an air flow of 0.115 SCFM. A flow of 0.1 cfm through the dilution air line to 8D-3 in addition to the 0.017 cfm currently flowing through the instrument bubblers would dilute the H<sub>2</sub> in Tank 8D-3 to < 2%.

STAGNANT COLUMN:

In the case of a stagnant column at one atmosphere which has been loaded with 360 KCi of cesium resulting in an H<sub>2</sub> generation rate of 2.92 l/hr., the column will reach saturation in 1.68 hours if not vented. After this time, a gas bubble will start to form. If the column is vented, the hydrogen will attempt to escape due to the partial pressure of hydrogen in vent line to 8D-1 being < 2%, versus 66.7% before vent is opened. The released hydrogen will be carried to Tank 8D-1 by a purge flow rate of 1 SCFM of air in the vent line. The vent line is a 2" line, except at the jumpers,

where it is 1-1/2" in diameter. It should be noted that per procedure, a column will not normally be left in a stagnant condition. Chilled supernatant or water will normally be flowing through the column. When fully loaded, the column will be expeditiously emptied of the cesium-loaded zeolite to preclude gas formation. In the event that flow through the Ion Exchange Columns stops, the Ion Exchange Columns will be vented immediately per operating procedure TOP 50-36.

#### SHUTDOWN WATER RECYCLE

In the case of shutdown with water recycle, the hydrogen will remain in solution in the column. The rate of hydrogen production will be 35 l/day for a column partially loaded to 180 KCl. This equates to ~1.46 liters/hr [0.05 SCFH]. This hydrogen gas formed in the columns will escape in D-001, as this tank is under a lower pressure than the columns (two atmospheres) and the partial pressure of the hydrogen in D-001 is less than in the columns. At the normal air purge rate for Tank D-001 level and density instruments of 4.5 SCFH, the hydrogen released into Tank D-001 will be diluted to ~1.14%, or 57% of the safe limit of 2%. Tank D-001 vents to 8D-1, where the hydrogen will be further diluted by normal in-leakage of approximately 100 SCFM of air.

A concern has been raised over a possible sudden release of hydrogen in Tank D-001, such as when depressurizing Tank D-001 from the normal operating pressure of two atmospheres to one atmosphere. The recycle water from the columns enters Tank D-001 near the top of the tank into the air space. This method of entry into the tank, combined with the normal turbulence in the tank caused by the instrument bubblers and continuous operation of the mixing eductor, will facilitate escape of the excess hydrogen from solution. Therefore, the solution in Tank D-001 will not contain more hydrogen than can be put into solution at two atmospheres. This says that with Tank D-001 at 80% level (operating maximum) or 1500 gallons, approximately 4.1 liters of hydrogen will be in solution. Reducing the pressure from two atmospheres to one atmosphere will release approximately 2.0 liters of hydrogen in the 5-10 minutes required to vent D-001. This 2 liters of hydrogen would dissipate in the 300 gallon (1135 liter) air space and would further be diluted in 8D-1. It should be noted that normal operating level of D-001 during water recycle is 50%, or approximately 1000 gallons, thereby reducing the amount of hydrogen released.

#### ZEOLITE STORAGE IN TANK 8D-1

The cesium-loaded zeolite from the STS Ion Exchange Columns will be temporarily stored in Tank 8D-1, resulting in a theoretical hydrogen production rate of 3100 liters per day at the end of supernatant processing. PNL has previously calculated that an air flowrate of 3.8 SCFM would be adequate to maintain the hydrogen

concentration within safe limits. The actual rate of air flow through Tank 8D-1 is on the order of 100 cfm. Again, it should be noted that no hydrogen has ever been detected in the off-gas from Tank 8D-2, which currently has all of the cesium stored in it.

HYDROGEN DETECTION:

Hydrogen detection in Tanks 8D-1 and 8D-3 can be accomplished by sampling using existing sampling methods, and analysis of the off-gas from these tanks. These analyses can provide assurance that hydrogen concentrations remain within safe limits within tanks.

There is no positive method of hydrogen detection in the STS Ion Exchange Columns. With the columns under pressure as in water recycle or steady state mode of operation, no free gas will buildup in the column, thereby making the detection of hydrogen in the columns of lesser importance.

CONCLUSIONS:

Hydrogen will be produced in the STS process in the STS Ion Exchange Columns as a result of the cesium loaded on the zeolite Ion Exchange Media. In steady state operation, all hydrogen should stay in solution in the column, escaping in the storage tank, 8D-3, where it is diluted with air. During recirculation with water, the hydrogen is diluted with air in Tank D-001. Hydrogen concentrations are maintained at safe levels at all times by dilution with air.

When a fully loaded column is taken off line, it normally will be dumped. If it cannot be dumped, it will be vented to allow any gas formed to escape into the vent system flowing to 8D-1, where in-leakage of air will dilute any hydrogen formed to well within safe limits. The proper dilution of any hydrogen formed with air can be verified by sampling of the off-gas from either Tank 8D-1 or Tank 8D-3.

Therefore, it can be stated that although hydrogen gas will theoretically be produced in the STS system, proper safeguards have been established utilizing existing equipment which will maintain the hydrogen concentration within safe limits.

*Carl F. Ross*

C. F. Ross, Senior Engineer  
STS Engineering  
West Valley Nuclear Services Co., Inc.

Approved: *D. K. Ploetz*

D. K. Ploetz, Manager

CFR:cea

Attachment

CEA1404



ATTACHMENT A - CALCULATIONS

Henry's Law  $X_A = \frac{P_A}{H_A}$  where  $H_A$  = Henry's constant  
 $P_A$  = Partial Pressure of  $H_2$  in atmosphere  
 $X_A$  = mole fraction  $H_2$  in solution

In 8D-2, based on off-gas sampling, assume  $H_2$  level in off-gas at 1%  $H_2$  at one atmosphere at 80°C.

$$X_A = \frac{0.01}{7.55 \times 10^4} = 1.32 \times 10^{-7} \text{ mol } H_2/\text{mol } H_2O$$

Water = 55.5 mol/liter

$H_2$  = 0.0889 mol/l and 2.0159 g/mol

$$H_2 \text{ in supernatant} = 1.32 \times 10^{-7} \text{ mol } H_2/\text{mol } H_2O \times \\ 55.5 \text{ mol/l } H_2O \times \\ 2.01592 \text{ g/mol} + 0.0889 \text{ g/l}$$

$$H_2 \text{ in supernatant} = 1.66 \times 10^{-4} \text{ l } H_2/\text{l } H_2O$$

1  $H_2$ /1  $H_2O$  In column at 4 atmospheres, pressure, 10°C, and assuming mole fraction  $H_2$  in gas 0.667.

$$\text{At 4 atmospheres } 4 \times 0.667 = 2.668$$

$$X_A = \frac{P_A}{H_A} = \frac{2.668}{7.42 \times 10^4} = 3.596 \times 10^{-5} \text{ mol } H_2/\text{mol } H_2O$$

$$1 \text{ } H_2/H_2O = 0.045 \text{ l } H_2/\text{l } H_2O \text{ maximum solubility}$$

Column at one atmosphere, not vented, at 20°C

$$X_A = \frac{P_A}{H_A} = \frac{0.667}{6.83 \times 10^4} = 9.76 \times 10^{-6} \text{ mol } H_2/\text{mol } H_2O$$

$$1 \text{ } H_2/\text{l } H_2O = 0.0123$$

Column at one atmosphere, vented to 8D-1, 2% H<sub>2</sub> in air.

$$X_A = \frac{P_A}{H_A} = \frac{0.02}{6.83 \times 10^4} = 2.83 \times 10^{-7} \text{ mol H}_2/\text{mol H}_2\text{O}$$

$$1 \text{ H}_2/1 \text{ H}_2\text{O} = 3.69 \times 10^{-4}$$

In 8D-3 at one atmosphere, 2% H<sub>2</sub> in air at 25°C

$$X_A = \frac{P_A}{H_A} = \frac{0.02}{7.07 \times 10^4} = 2.83 \times 10^{-7} \text{ mol H}_2/\text{mol H}_2\text{O}$$

$$\text{H}_2 = 3.5 \times 10^{-4} \text{ 1 H}_2/1 \text{ H}_2\text{O}$$

In D-001 at two atmospheres, 2% H<sub>2</sub> in air at 20°C

$$P_A = 0.2 \times \text{two atmospheres} = 0.04$$

$$X_A = \frac{P_A}{H_A} = \frac{.04}{6.83 \times 10^4} = 5.85 \times 10^{-7} \text{ mol H}_2/\text{mol H}_2\text{O}$$

$$\text{H}_2 = 7.28 \times 10^{-4} \text{ 1 H}_2/1 \text{ H}_2\text{O}$$

Hydrogen generation in columns, steady state operation.

Assume 1st column loaded to 360 KCl, 2nd column loaded to 180 KCl, just prior to shutdown.

H<sub>2</sub> generation rate 105 l/day. 72.9 ml/min.

Max. H<sub>2</sub> in solution possible = .045 l H<sub>2</sub>/l H<sub>2</sub>O

$$\begin{aligned} \text{At 2 gpm flow rate, H}_2 &= \frac{.0729 \text{ l/min.}}{2 \text{ gpm} \times 3.785 \text{ l/g}} \\ \text{H}_2 &= 0.0096 \text{ l H}_2 / \text{l H}_2\text{O} \end{aligned}$$

$$\% \text{ Solubility} = \frac{.0096}{.045} \times 100\% = 21.3\%$$

$$\begin{aligned} \text{At 6 gpm flow rate, H}_2 &= \frac{.0729 \text{ l/min.}}{6 \text{ gpm} \times 3.785 \text{ l/g}} \end{aligned}$$

$$\text{H}_2 = .0032 \text{ l/min.}$$

$$\% \text{ Solubility} = \frac{.0032}{.045} = 7.1\%$$

Hydrogen in Stagnant Column - column volume 462 gal.

Non-Vented at .0123 l H<sub>2</sub>/l H<sub>2</sub>O max. H<sub>2</sub> in solution =  
.0123 l H<sub>2</sub>/l H<sub>2</sub>O x 462 gal. x 3.785 = 21.5/l H<sub>2</sub> max.

At shutdown at 2 gpm flow rate, liquid in column will have .0096 l H<sub>2</sub>/l H<sub>2</sub>O x  
462 gal. x 3.875 l/gal = 16.79 l H<sub>2</sub> in solution

$$\begin{aligned} \text{Time to reach equilibrium} &= \frac{4.72 \text{ l capacity remaining}}{2.92 \text{ l/hr produced @ 360 KCl}} \end{aligned}$$

$$= 1.6 \text{ hours to reach equilibrium}$$

after which gas bubble will start to form.

Vented column

Total H<sub>2</sub> in solution =  $3.69 \times 10^{-4}$  l H<sub>2</sub>/l H<sub>2</sub>O x 462 gal. in column x 3.785 l/gal.

Total H<sub>2</sub> in solution = 0.645 liters H<sub>2</sub> in column.

Any H<sub>2</sub> in excess of 645 ml will effervesce to the vent system. At maximum concentration, a volume of 20.85 liters of H<sub>2</sub> will escape to the vent system.

Columns in water recycle - maximum loading of 2nd column = 180 KCl, which will generate 35 l/day H<sub>2</sub> in IX columns at 4 atmospheres, @ 2 gpm, the solution will be ~7% of saturation. At higher flow rates, the % saturation will be still lower. Thus, no free hydrogen gas will be produced in the column. However, once recycle brings Tank D-001 to the saturation level of  $7.28 \times 10^{-4}$  l H<sub>2</sub>/l H<sub>2</sub>O, the tank will release 35 l/day or 1.458 l/hr. to D-001 air space. The D-001 instrument bubblers provide an air flow of 127.4 l/hr, which will dilute this hydrogen to 1.14% H<sub>2</sub>. In addition, D-001 vents to 8D-1, where in-leakage air will further dilute the hydrogen.

Venting D-001 from two atmospheres to one atmosphere pressure.

At 80% on LI-016 D-001 (assume water, 1.0 density)

D-001 contains 1500 gallons (5678 liters)

At two atmospheres, H<sub>2</sub> solubility  $7.24 \times 10^{-4}$  l H<sub>2</sub>/l H<sub>2</sub>O

At one atmosphere, H<sub>2</sub> solubility  $3.69 \times 10^{-4}$  l H<sub>2</sub>/l H<sub>2</sub>O

Total H<sub>2</sub> in solution - two atmospheres

1 H<sub>2</sub> =  $5678 \times 7.24 \times 10^{-4}$  = 4.11 liters

Total H<sub>2</sub> in solution - one atmosphere

1 H<sub>2</sub> =  $5678 \times 3.69 \times 10^{-4}$  = 2.10 liters

H<sub>2</sub> released during venting = 2.01 liters

Assuming 300 gallons (1135 liters) air space, the H<sub>2</sub> released would add  $\frac{2.01}{1135} \times 100\% = 0.18\%$  H<sub>2</sub> to air space

1135

Since D-001 will normally have approximately 1.14% H<sub>2</sub> in the air space, adding 0.18% to this normal level would increase H<sub>2</sub> to 1.33%, well within safe limits.

ATTACHMENT B

OAK RIDGE NATIONAL LABORATORY  
OPERATED BY MARTIN MARIETTA ENERGY SYSTEMS, INC.

POST OFFICE BOX 2008  
OAK RIDGE, TENNESSEE 37831

April 19, 1988

Mr. Charlie McVay  
West Valley Nuclear Services Co., Inc.  
P. O. Box 191  
West Valley, New York 14171-0191

Dear Charlie:

As we agreed, I am summarizing the results of our organic analyses of your sample 8D-2 Decon Supernate on work order no. L3053901. I will send the results of the Curium isotopic analysis later this week when the results are available.

Initial Radiochemical Screening:

Portions of the sample were subjected to standard radiochemical screening measurements to confirm the gross alpha and beta levels and major radionuclides and determine appropriate containment. The results were as follows:

Gross alpha	1.47 E3 ± 0.04 E3	Bq/ml
Gross beta	8.01 E3 ± 0.18 E3	Bq/ml
Cs-137	1.02 E3 ± 0.004 E3	Bq/ml
Sb-125	5.32 E2 ± 0.06 E2	Bq/ml

These results are in excellent agreement with the analyses you provided with the sample.

Total Carbon and Total Organic Carbon:

These forms of carbon were estimated by catalytic oxidation and measurement of evolved carbon dioxide by ND-IR before and after acidification of the sample. Assuming that no elemental carbon is present, these steps would determine total carbon and total organic carbon (respectively). A second determination was made of total organic carbon after further acidification and vigorous shaking to ensure removal of inorganic carbon. The results were as follows:

Total Carbon	2,640 ug/ml
Total Organic Carbon	141 ug/ml
Total Organic Carbon (2nd determination)	156 ug/ml

The second determination of total organic carbon agrees with the first within experimental error ( $\pm 10\%$  [2s]), and suggests that the purging of carbonate was successful.

**Organic Compound Characterization:**

The determination of the major compounds of interest (oxalic acid, citric acid, and tartaric acid) plus any others likely to be present (e.g., alkanes) was approached with three procedures: gas chromatography (GC) of base/neutral and also derivatized acid fractions, GC of the derivatized residue from sample evaporation, and ion exclusion chromatography of diluted sample.

The first approach was the preparation and analysis of the base/neutral and acid fractions for GC analysis. The alkalinity of a 15 ml aliquot of sample was enhanced with 1 ml of 1M NaOH, and the sample was extracted 3 times with 5 ml of methylene chloride. We have found less carryover of radioactivity when extracting with methylene chloride than with diethyl ether. Severe emulsion problems were experienced, and the best form of agitation was found to be tumbling the extraction vial. The acid fraction was prepared by adjusting the pH to 4 or 5 (pH paper) with 1 N HNO<sub>3</sub> and extracting 3 times with 5 ml of methylene chloride. A lower pH would have been desirable, but bubbling and evolution of nitrogen oxides (potentially chemically reactive towards compounds in the sample) and the buffering capacity of the salts made acidification difficult. Both fractions were concentrated to 0.5 ml by nitrogen blow-down. A blank (salt solution made up of 21.1% NaNO<sub>3</sub>, 10.9% NaNO<sub>2</sub>, 2.7% Na<sub>2</sub>SO<sub>4</sub>, and 1.5% NaHCO<sub>3</sub>, pH ca. 10, to model the inorganic matrix of the 8D-2) and an aliquot of 8D-2 spiked to 100 ug/ml with oxalic, tartaric, and citric acids were similarly extracted and derivatized. Methyl esters of the acid fractions were prepared using BF<sub>3</sub>/methanol and the reagent manufacturer's instructions.

The base/neutral fractions were analyzed using GC with both 15 and 30 m Megabore (0.53 mm ID) capillary columns and flame ionization detection. No differences were observed among the samples and no peaks attributable to the 8D-2 were detected, indicating the lack of gas chromatographable compounds within the limits of sensitivity (0.1 - 0.3 ug/ml) and boiling range (ca. 69° - 380°C) of the procedure. The specific compounds calibrated and the limits of detection were,

n-C <sub>5</sub> H <sub>14</sub> through n-C <sub>23</sub> H <sub>48</sub>	< 0.1 ug/ml
Diethylbenzene	< 0.1 ug/ml
Diisobutylphenylphosphonate	< 0.3 ug/ml
Tri-n-butylphosphate	< 0.1 ug/ml

The derivatized acid fractions were analyzed using capillary column (0.32 mm ID x 30 m) GC with on-column injection and flame ionization detection. Derivatized standards of oxalic, tartaric, and citric acids, plus the C<sub>11</sub>-C<sub>18</sub> even carbon number monocarboxylic acids were run. The tartaric acid standard did not produce a GC peak. Apparently, the additional hydroxyl group did not derivatize, and left the acid too polar for GC. None of these

April 19, 1988

compounds were detected in the sample or spiked sample. The lack of recovery of the acids in the spiked sample indicates that either the extraction efficiency was poor or that other sample material which was carried over into the acid fraction interfered with the derivatization. A lower pH during extraction might improve recoveries.

The second approach was derivatization of the dried residue from the evaporation of an aliquot of 8D-2, and GC of the derivative using the same on-column injection capillary GC as for the acid fraction analysis. Aliquots of 0.5, 1.0, and 2.0 ml were dried in the bottom of a 40 ml EPA volatile organics vial under a stream of nitrogen gas at 60°C and were derivatized using  $\text{BF}_3$ /methanol. A 1.0 ml aliquot of 8D-2 was spiked to 100 ug/ml with oxalic, tartaric, and citric acids. The spiked oxalic acid was recovered at 102%, the citric acid was 26% recovered, and none of the tartaric acid was recovered (however, the derivative of the standard did not chromatograph). The GC of the sample did not reveal any compounds.

To reduce the potential interference of the salt in the derivatization of the dried residue, a 0.2 ml aliquot of 8D-2 was diluted with 1 ml of deionized water and then dried and derivatized as above. The smaller aliquot and dilution should produce less salt to interfere, and a thinner film of salt crystals which could physically shield acids from the derivatization reagents and harbor entrained water or water of hydration which would destroy the derivatization reagent. The recovery of the 100 ppm spike of oxalic acid was 185%, and citric acid was 90%. No acids were observed in the 8D-2 or the blank. The limit of detection was estimated at 10 ug/ml with a precision of ca.  $\pm$  20 to 30%.

These results indicated that, in spite of the derivatization problems caused by the salts, the oxalic and citric acids were not major species in the 8D-2, and they were not present above ca. 10 ug/ml.

The final method employed was ion exclusion chromatography. The specific target compounds were tartaric acid (its methyl ester did not elute in GC) and EDTA. An ORH-801 Organic Acids Column (30 cm x 0.65 cm) from EM Science was used for this investigation. The mobile phase was 0.1 N  $\text{H}_2\text{SO}_4$ , the column was thermostatted at 35°C, and the variable wavelength UV absorbance detector was set to 210 nm. Chromatography of standards and standards spiked into the model salt solution indicated that oxalic and citric acids and EDTA were obscured by the salts in the sample. Tartaric acid eluted as a shoulder between two large salt peaks. The only means of keeping this feature on scale with the 8D-2 sample was to dilute the sample 5:1 and adjust the baseline zero. By using these conditions and also running the 8D-2 before and after spiking with tartaric acid, it was estimated that the tartaric acid was < 60 ug/ml in the undiluted 8D-2.



Mr. Charlie McVay

-4-

April 19, 1988

In summary, the total organic compound content of the sample, 141 ug/ml, is not accounted by the oxalic acid (< 10 ug/ml), citric acid (< 10 ug/ml), or tartaric acid (< 60 ug/ml), or any base/neutral compound which is gas chromatographable and boils between ca. 69° and 380°C (< 0.1 ug/ml). Experience at the Pacific Northwest Laboratory suggests that highly polar, water-soluble compounds comprise the bulk of the total organic carbon in some nuclear waste samples. We have a lot of work ahead to determine these compounds in such high salt, alkaline, radioactive sample matrices.

I hope that placing upper limits on the concentrations of the three acids has been helpful to your grouting studies. We appreciate your providing us with this work, and hope that we can be of further help in the future as we expand our capabilities for the organic analysis of mixed wastes.

Sincerely;

*Wayne H. Griest*

Wayne H. Griest  
Organic Chemistry Section  
Analytical Chemistry Division

WHG:pmt

cc: D. A. Costanzo  
M. R. Guerin  
R. S. Ramsey  
W. D. Shults  
B. A. Tomkins

**memorandum**Idaho Operations Office  
West Valley Project Office

DATE: May 3, 1990

SUBJECT: Assessment of Potential Safety Issues at the West Valley Demonstration Project (WVDP)

TO: J. E. Solecki, Acting Assistant Manager  
for Environmental Restoration  
and Waste Management

In regard to the evaluation of potential safety issues and an assessment of hydrogen generation at the WVDP, West Valley Nuclear Services Co. Inc. (WVNS) has prepared the two letter reports <sup>for</sup> me. The letter dated April 9, 1990 evaluates the generation potential of H<sub>2</sub> in the Supernatant Treatment System (STS) process and the West Valley high level waste tanks. The letter ~~report~~ dated April 30, 1990 assesses possible environmental and safety related issues in other WVDP waste management units, namely the high level waste tanks, spent fuel storage area and the stability of the NRC-Licensed Disposal Area (NDA). The Project Office staff has had extensive discussions with WVNS in evaluating these facilities and we agree <sup>with</sup> to the evaluations. Both letter reports are provided to you for inclusion in the Idaho reply to EM-1.

In addition to the above concerns, the ever increasing number of low level waste packages which are interimly stored on site has the potential to become a future safety and environmental concern. Whereas any single waste container or family of packages are not a perceived risk, the accumulation of thousands of waste packages in numerous "tents" becomes an operational constraint. These waste containers in storages must be frequently monitored and if deterioration of the container is evident, they are overpacked at an incremental worker radiation exposure. Similarly, long term storage of the low-level waste in seven separate locations (Drum Cell, Lag Storage Building, three active tents, plus two tents under construction) will increase the safety surveillance overview required for the WVDP.

Should you have any questions, please contact E. Maestas on FTS 473-4314.

*Tom Rowland*  
for W. W. Bixby, Director  
West Valley Project Office

Attachment

cc: T. W. McIntosh, DOE-HQ

~~EM:029:90 - 0832:90:01~~

EM:am

West Valley  
Nuclear Services Company  
Incorporated

RESPONSE

DW:2892

P.O. Box 191  
West Valley, New York 14171-0191

April 09, 1990

Dr. W. W. Bixby, Director  
Mail Stop - DOE  
West Valley Project Office  
U.S. Department of Energy  
P.O. Box 191  
West Valley, New York 14171-0191

Dear Dr. Bixby:

SUBJECT: Assessment of Hydrogen Generation at the WVDP

- Reference:
- 1) Letter EM:024:90 - 0745:90:01, E. Maestas to R.E. Lawrence, "Assessment of H<sub>2</sub> Generation," dated March 30, 1990
  - 2) Letter EA:87:0067 - Draft, R.F. Gessner to S. Marchetti, "8D-1 and 8D-2 Air Circulator Rotometers," dated March 30, 1987
  - 3) Letter SG:88:0049, D.K. Floetz to R.E. Lawrence, Jr., "Hydrogen Generation in the STS Process," dated May 19, 1988
  - 4) Letter BW:88:0109, W.A. Ross to Dr. J.M. Pope, "STS Hydrogen Generation and Corrosion Potential in Tank 8D-1," dated May 16, 1988
  - 5) Letter RS:89:0046, S.J. Szalinski to Distribution, "Minutes for December 13, 1989 Radiation and Safety Committee Meeting," dated December 18, 1989

Per WVPO's request contained in Reference (1), WVNS has assessed the generation of hydrogen within waste storage tanks and process systems at the West Valley Demonstration Project (WVDP). The results of this assessment are reported in this letter.

Issues related to hydrogen generation within waste storage tanks or process systems at the WVDP have previously been raised. For example:

- o Taking air circulators out of service in HLW storage tanks 8D-1 and 8D-2 (Reference 2)
- o Hydrogen generation in the Supernatant Treatment System (STS) Ion Exchange Columns (References 3 and 4)
- o Cessation of sampling for hydrogen in the vaults of the HLW tanks 8D-1 and 8D-2 (Reference 5)

CD:90:0015

MAH1613

Based on engineering evaluations and actual process measurements, WVNS has concluded that the potential for the accumulation of hydrogen in an unsafe condition is very low. Hydrogen surveillances of the off-gasses from Purex waste tanks 8D-1 and 8D-2 and Thorex waste tanks 8D-3 and 8D-4 were conducted between 1976 and the present. All analyses indicate a hydrogen concentration below the lower detection limit (less than 1.0 vol.% as sampled). Analyses performed from 1988 to present, using a more sensitive detector, revealed hydrogen concentrations below a lower detection limit of 0.1 vol.% as sampled. The Lower Flammability Limit for hydrogen in air is 4.0 vol.%, with a Lower Detonation Limit of 18 vol.%. Normal airflow venting rates provide continuous, uninterrupted dilution to well below these limits. A back-up electrical power supply serves to maintain ventilation blower operation in the event of site power interruptions.

Similarly, normal venting and dilution in the Supernatant Treatment System assures adequate dilution of hydrogen to a safe condition. Proper safeguards, established utilizing existing ventilation equipment and controlled by operating procedures SOP 50-25, SOP 50-36 and 50-37, assure continuous dilution of any hydrogen formed. Backup calculations (see Attachment C) support the conclusion that safely diluted conditions are achieved in all operating configurations of the STS. Elsewhere in the Integrated Radwaste Treatment System, radiation intensities are far lower, resulting in much lower potentials for radiolytic generation of hydrogen in significant quantities.

WVNS has reviewed the report on generation of significant quantities of hydrogen in a HLW storage tank at Hanford. As indicated by Attachment A, there are certain differences in the characterization of these wastes which, when compared, would lead to the conclusion that the WVDP high level wastes possess a much lower hydrogen generation and accumulation potential. Although a higher level of radioactive cesium and strontium exists in the WVDP wastes, there are no impediments to the eventual escape and dilution of hydrogen produced by the radiolysis. The Hanford waste, although lower in activity, contains organic material of a quantity many orders of magnitude more than that contained in WVDP wastes, resulting in a relatively high potential for the production of hydrogen by a chemical reaction/decomposition mechanism. In addition, the reported low permeability (crust) characteristic of waste stored in the Hanford tank could possibly hinder any diffusion and dilution of hydrogen gas.

CD:90:0015

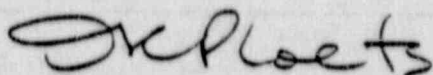
MAH1613

Dr. W.W. Bixby

-3-

After review of the details presented with the generation of significant concentrations of hydrogen in HLW storage tanks at Hanford, WVNS has concluded that dissimilarities between the wastes would indicate a very low possibility of a similar incident from occurring at West Valley.

Very truly yours,



---

D.K. Floetz, Manager  
Mail Stop - 305  
Plant Engineering  
West Valley Nuclear Services Co., Inc.

CD:90:0015

DKP:mah

Attachments:      A)    Comparison of Differences Between WVDP and Hanford HLW  
                         B)    Reference (1)  
                         C)    Reference (3)

cc: R.B. Provencher (MS-DOE) DOE/WVPO

MAH1613

ATTACHMENT A

COMPARISON OF WVDP AND HANFORD HLW

RADIOACTIVITY

HANFORD - 3 MILLION CURIES (Cs, Sr)

WVDP - 30 MILLION CURIES (Cs, Sr)

Although the greater quantity of radioactivity in WVDP HLW will contribute to a higher generation of hydrogen by radiolysis, calculations show that the airflow within Tanks 8D-1 and 8D-2 is sufficient to reduce the theoretical quantity of hydrogen generated by radiolysis to a safe concentration (Attachment C). Actual hydrogen generation rates are less than theoretical, because the presence of nitrates in the HLW suppresses the formation of hydrogen. It should be noted that hydrogen has never been detected in the off-gas from Tank 8D-3/8D-4, as well as Tanks 8D-1 and 8D-2.

ORGANIC CONTENT

HANFORD - 557,000 gallons of concentrated organic waste in a tank filled with a total of 1,070,000 gallons of HLW

WVDP - 100 ppm concentration

The presence of only trace quantities of organics in the WVDP HLW minimizes the formation of hydrogen by chemical degradation or by chemical reaction.

PHYSICAL CHARACTERISTICS

HANFORD - Tank SY-101 contains a thick, impermeable crust;  
content temperature = 60°C

WVDP - The supernatant in Tank 8D-2 is a homogeneous liquid  
content temperature = 80°C

The solubility of hydrogen in supernatant or water at these temperatures is low, so any hydrogen formed by radiolysis is quickly dispersed to the vapor space in HLW storage tanks 8D-1 and 8D-2 at West Valley, where it is then diluted with air and swept out of HLW tanks 8D-1 and 8D-2. There are no impediments, accumulations or obstructions at the liquid-vapor interface that would cause hydrogen to accumulate.



ATTACHMENT B

**Department of Energy**

Idaho Operations Office  
West Valley Project Office  
P.O. Box 191  
West Valley, NY 14171

March 30, 1990

Mr. R. A. Thomas, President  
West Valley Nuclear Services Co., Inc.  
P. O. Box 191  
West Valley, New York 14171

ATTENTION: R. E. Lawrence Jr., Plant Services Manager

SUBJECT: Assessment of H<sub>2</sub> Generation

Dear Sir:

The DOE-Idaho has requested an assessment of the potential radiolysis or chemical generation of H<sub>2</sub> gas within waste storage tanks or process systems at the West Valley Demonstration Project (WVDP). Accordingly, please prepare a letter report of the West Valley Nuclear Services Co. Inc., (WVNS) position on this subject including the feasibility of hydrogen explosion. In your reply, please include as attachments, existing technical support documentation. Your reply is requested as soon as possible, but no later than April 6, 1990. Should you have any questions, please contact me on extension 4314 or R. B. Provencher on extension 4101.

Sincerely,

A handwritten signature in cursive script that reads "E. Maestas".

E. Maestas  
West Valley Project Office

cc: J. E. Solecki, DOE-ID

EM:024:90 - 0745:90:01

EM/sl

ATTACHMENT C

From : STS Engineering  
WIN : SG:88:0049  
Date : May 19, 1988  
Subject : Hydrogen Generation in the STS Process

To : R. E. Lawrence, Jr.  
D. J. Sawyer

cc: P. Burn  
R. F. Itzo  
A. J. Howell  
R. B. Reeves  
C. G. Skillern  
L. W. Wiedemann  
MRC 1820, 0513

References: Perry's Chemical Engineers Handbook, 4th Edition

Kurath, Bray, and Holton, "Review of the West Valley Supernatant Treatment System Operational Sequence", February 1988

L. L. Burger, "Potential for Radiation Induced Corrosion in the 8D-1 Tank", January 1988

SUMMARY OF REPORT:

Radiolysis of water has been identified as a potential source of hydrogen gas production in the STS process system.

This report utilizes data on hydrogen generation given by the above-mentioned reports and postulates worst case scenarios for the accumulation of hydrogen. Utilizing very conservative assumptions based on hydrogen solubility in water, it can be safely concluded that no hydrogen gas will build up in the columns during steady state operation; and, that proper venting and dilution will prevent buildup of hydrogen gas in Tanks D-001 and 8D-3 and when there is no flow through the columns.

Almost all of the hydrogen produced by radiolysis would be produced in the ion exchange columns, where high concentrations of  $Cs^{137}$  will be contained in the zeolite. The potential for hydrogen generation increases correspondingly with the degree of column loading.

The attached calculations show the potential for hydrogen production during normal processing, while recirculating water during shutdown periods, and during stagnant conditions if no recycle is occurring. Conservative assumptions are used to



determine if a problem could possibly exist. These assumptions are: 1) All energy from the Cs<sup>-137</sup> loaded on the column is contained within the column; i. e. none escapes. Thus, the theoretical amount of hydrogen generated is higher than in reality; 2) No hydrogen produced by radiolysis is assumed to recombine with oxygen to form water or otherwise "escape"; 3) The supernatant in 8D-2 is already assumed to be hydrogen saturated at 80°C due to radiolysis in 8D-2. Even making this assumption, the hydrogen in the supernatant is of such low concentration that it is negligible, and has no bearing on solubilities in the columns; 4) Column loadings of 360 KCi for the first column and 180 KCi for the second column were assumed. Actual column loadings for the first and second column are expected to be 220 KCi and 110 KCi; 5) Calculations are based on the theoretical hydrogen production rates given in the reports. It should be noted that no hydrogen has ever been detected in the off-gas from Tank 8D-2.

STEADY STATE PROCESSING:

The ion exchange columns will be at a pressure of at least four atmospheres due to flow restriction at the discharge of the postfilter by FCV-035 which controls the process flow rate. The solubility of hydrogen in the columns at these conditions will be higher than at any other point in the process, due mainly to the partial pressure of H<sub>2</sub> being high in the column compared to Tanks D-001 and 8D-3, which are sparged with air to control the hydrogen concentration to <2% in air. The hydrogen in solution while the columns are under pressure will be at ~21.4% of solubility limits at 2 gpm flow and ~7.1% at a flow rate of 6 gpm.

STORAGE IN 8D-3:

When the liquid from the postfilter enters Tank 8D-3, it drops in pressure from four atmospheres to approximately one atmosphere releasing the hydrogen in solution. The partial pressure of hydrogen in the Tank 8D-3 atmosphere will be controlled to prevent exceeding 2% H<sub>2</sub> by sparging Tank 8D-3 with an air flow of 0.115 SCFM. A flow of 0.1 cfm through the dilution air line to 8D-3 in addition to the 0.017 cfm currently flowing through the instrument bubblers would dilute the H<sub>2</sub> in Tank 8D-3 to < 2%.

STAGNANT COLUMN:

In the case of a stagnant column at one atmosphere which has been loaded with 360 KCi of cesium resulting in an H<sub>2</sub> generation rate of 2.92 l/hr., the column will reach saturation in 1.68 hours if not vented. After this time, a gas bubble will start to form. If the column is vented, the hydrogen will attempt to escape due to the partial pressure of hydrogen in vent line to 8D-1 being < 2%, versus 66.7% before vent is opened. The released hydrogen will be carried to Tank 8D-1 by a purge flow rate of 1 SCFM of air in the vent line. The vent line is a 2" line, except at the jumpers,

where it is 1-1/2" in diameter. It should be noted that per procedure, a column will not normally be left in a stagnant condition. Chilled supernatant or water will normally be flowing through the column. When fully loaded, the column will be expeditiously emptied of the cesium-loaded zeolite to preclude gas formation. In the event that flow through the Ion Exchange Columns stops, the Ion Exchange Columns will be vented immediately per operating procedure TOP 50-36.

#### SHUTDOWN WATER RECYCLE

In the case of shutdown with water recycle, the hydrogen will remain in solution in the column. The rate of hydrogen production will be 35 l/day for a column partially loaded to 180 KCi. This equates to 1.46 liters/hr [0.05 SCFH]. This hydrogen gas formed in the columns will escape in D-001, as this tank is under a lower pressure than the columns (two atmospheres) and the partial pressure of the hydrogen in D-001 is less than in the columns. At the normal air purge rate for Tank D-001 level and density instruments of 4.5 SCFH, the hydrogen released into Tank D-001 will be diluted to 1.14%, or 57% of the safe limit of 2%. Tank D-001 vents to 8D-1, where the hydrogen will be further diluted by normal in-leakage of approximately 100 SCFM of air.

A concern has been raised over a possible sudden release of hydrogen in Tank D-001, such as when depressurizing Tank D-001 from the normal operating pressure of two atmospheres to one atmosphere. The recycle water from the columns enters Tank D-001 near the top of the tank into the air space. This method of entry into the tank, combined with the normal turbulence in the tank caused by the instrument bubblers and continuous operation of the mixing eductor, will facilitate escape of the excess hydrogen from solution. Therefore, the solution in Tank D-001 will not contain more hydrogen than can be put into solution at two atmospheres. This says that with Tank D-001 at 80% level (operating maximum) or 1500 gallons, approximately 4.1 liters of hydrogen will be in solution. Reducing the pressure from two atmospheres to one atmosphere will release approximately 2.0 liters of hydrogen in the 5-10 minutes required to vent D-001. This 2 liters of hydrogen would dissipate in the 300 gallon (1135 liter) air space and would further be diluted in 8D-1. It should be noted that normal operating level of D-001 during water recycle is 50%, or approximately 1000 gallons, thereby reducing the amount of hydrogen released.

#### ZEOLITE STORAGE IN TANK 8D-1

The cesium-loaded zeolite from the STS Ion Exchange Columns will be temporarily stored in Tank 8D-1, resulting in a theoretical hydrogen production rate of 3100 liters per day at the end of supernatant processing. PNL has previously calculated that an air flowrate of 3.8 SCFM would be adequate to maintain the hydrogen

concentration within safe limits. The actual rate of air flow through Tank 8D-1 is on the order of 100 cfm. Again, it should be noted that no hydrogen has ever been detected in the off-gas from Tank 8D-2, which currently has all of the cesium stored in it.

HYDROGEN DETECTION:

Hydrogen detection in Tanks 8D-1 and 8D-3 can be accomplished by sampling using existing sampling methods, and analysis of the off-gas from these tanks. These analyses can provide assurance that hydrogen concentrations remain within safe limits within tanks.

There is no positive method of hydrogen detection in the STS Ion Exchange Columns. With the columns under pressure as in water recycle or steady state mode of operation, no free gas will buildup in the column, thereby making the detection of hydrogen in the columns of lesser importance.

CONCLUSIONS:

Hydrogen will be produced in the STS process in the STS Ion Exchange Columns as a result of the cesium loaded on the zeolite Ion Exchange Media. In steady state operation, all hydrogen should stay in solution in the column, escaping in the storage tank, 8D-3, where it is diluted with air. During recirculation with water, the hydrogen is diluted with air in Tank D-001. Hydrogen concentrations are maintained at safe levels at all times by dilution with air.

When a fully loaded column is taken off line, it normally will be dumped. If it cannot be dumped, it will be vented to allow any gas formed to escape into the vent system flowing to 8D-1, where in-leakage of air will dilute any hydrogen formed to well within safe limits. The proper dilution of any hydrogen formed with air can be verified by sampling of the off-gas from either Tank 8D-1 or Tank 8D-3.

Therefore, it can be stated that although hydrogen gas will theoretically be produced in the STS system, proper safeguards have been established utilizing existing equipment which will maintain the hydrogen concentration within safe limits.

*Carl F. Ross*

C. F. Ross, Senior Engineer  
STS Engineering  
West Valley Nuclear Services Co., Inc.

Approved:

*D. K. Ploetz*  
D. K. Ploetz, Manager

CFR:cea

Attachment

CEA1404

ATTACHMENT A - CALCULATIONS

Henry's Law  $X_A = \frac{P_A}{H_A}$  where  $H_A$  = Henry's constant  
 $P_A$  = Partial Pressure of  $H_2$  in atmosphere  
 $X_A$  = mole fraction  $H_2$  in solution

In 8D-2, based on off-gas sampling, assume  $H_2$  level in off-gas at 1%  $H_2$  at one atmosphere at 80°C.

$$X_A = \frac{0.01}{7.55 \times 10^4} = 1.32 \times 10^{-7} \text{ mol } H_2/\text{mol } H_2O$$

Water = 55.5 mol/liter

$H_2$  = 0.0889 mol/l and 2.0159 g/mol

$$H_2 \text{ in supernatant} = 1.32 \times 10^{-7} \text{ mol } H_2/\text{mol } H_2O \times \\ 55.5 \text{ mol/l } H_2O \times \\ 2.01592 \text{ g/mol} + 0.0889 \text{ g/l}$$

$$H_2 \text{ in supernatant} = 1.66 \times 10^{-4} \text{ l } H_2/\text{l } H_2O$$

1  $H_2$ /l  $H_2O$  In column at 4 atmospheres, pressure, 10°C, and assuming mole fraction  $H_2$  in gas 0.667.

$$\text{At 4 atmospheres } 4 \times 0.667 = 2.668$$

$$X_A = \frac{P_A}{H_A} = \frac{2.668}{7.42 \times 10^4} = 3.596 \times 10^{-5} \text{ mol } H_2/\text{mol } H_2O$$

$$1 \text{ } H_2/H_2O = 0.045 \text{ l } H_2/\text{l } H_2O \text{ maximum solubility}$$

Column at one atmosphere, not vented, at 20°C

$$X_A = \frac{P_A}{H_A} = \frac{0.667}{6.83 \times 10^4} = 9.76 \times 10^{-6} \text{ mol } H_2/\text{mol } H_2O$$

$$1 \text{ } H_2/\text{l } H_2O = 0.0123$$

Column at one atmosphere, vented to 8D-1, 2% H<sub>2</sub> in air.

$$X_A = \frac{P_A}{H_A} = \frac{0.02}{6.83 \times 10^4} = 2.83 \times 10^{-7} \text{ mol H}_2/\text{mol H}_2\text{O}$$

$$1 \text{ H}_2/1 \text{ H}_2\text{O} = 3.69 \times 10^{-4}$$

In 8D-3 at one atmosphere, 2% H<sub>2</sub> in air at 25°C

$$X_A = \frac{P_A}{H_A} = \frac{0.02}{7.07 \times 10^4} = 2.83 \times 10^{-7} \text{ mol H}_2/\text{mol H}_2\text{O}$$

$$H_2 = 3.5 \times 10^{-4} \text{ 1 H}_2/1 \text{ H}_2\text{O}$$

In D-001 at two atmospheres, 2% H<sub>2</sub> in air at 20°C

$$P_A = 0.2 \times \text{two atmospheres} = 0.04$$

$$X_A = \frac{P_A}{H_A} = \frac{.04}{6.83 \times 10^4} = 5.85 \times 10^{-7} \text{ mol H}_2/\text{mol H}_2\text{O}$$

$$H_2 = 7.28 \times 10^{-4} \text{ 1 H}_2/1 \text{ H}_2\text{O}$$

Hydrogen generation in columns, steady state operation.

Assume 1st column loaded to 360 KCl, 2nd column loaded to 180 KCl, just prior to shutdown.

H<sub>2</sub> generation rate 105 l/day, 72.9 ml/min.

Max. H<sub>2</sub> in solution possible = .045 l H<sub>2</sub>/l H<sub>2</sub>O

$$\begin{aligned} \text{At 2 gpm flow rate, H}_2 &= \frac{.0729 \text{ l/min.}}{2 \text{ gpm} \times 3.785 \text{ l/g}} \\ \text{H}_2 &= 0.0096 \text{ l H}_2/\text{l H}_2\text{O} \end{aligned}$$

$$\% \text{ Solubility} = \frac{.0096}{.045} \times 100\% = 21.3\%$$

$$\begin{aligned} \text{At 6 gpm flow rate, H}_2 &= \frac{.0729 \text{ l/min.}}{6 \text{ gpm} \times 3.785 \text{ l/g}} \end{aligned}$$

$$\text{H}_2 = .0032 \text{ l/min.}$$

$$\% \text{ Solubility} = \frac{.0032}{.045} = 7.1\%$$

Hydrogen in Stagnant Column - column volume 462 gal.

Non-Vented at .0123 l H<sub>2</sub>/l H<sub>2</sub>O max. H<sub>2</sub> in solution =  
.0123 l H<sub>2</sub>/l H<sub>2</sub>O x 462 gal. x 3.785 = 21.5/l H<sub>2</sub> max.

At shutdown at 2 gpm flow rate, liquid in column will have .0096 l H<sub>2</sub>/l H<sub>2</sub>O x  
462 gal. x 3.875 l/gal = 16.79 l H<sub>2</sub> in solution

$$\begin{aligned} \text{Time to reach equilibrium} &= \frac{4.72 \text{ l capacity remaining}}{2.92 \text{ l/hr produced @ 360 KCl}} \end{aligned}$$

= 1.6 hours to reach equilibrium  
after which gas bubble will start to form.

Vented column

Total  $H_2$  in solution =  $3.69 \times 10^{-4}$  l  $H_2$ /l  $H_2O$  x 462 gal. in column x 3.785 l/gal.

Total  $H_2$  in solution = 0.645 liters  $H_2$  in column.

Any  $H_2$  in excess of 645 ml will effervesce to the vent system. At maximum concentration, a volume of 20.85 liters of  $H_2$  will escape to the vent system.

Columns in water recycle - maximum loading of 2nd column = 180 KCl, which will generate 35 l/day  $H_2$  in IX columns at 4 atmospheres, @ 2 gpm, the solution will be 7% of saturation. At higher flow rates, the % saturation will be still lower. Thus, no free hydrogen gas will be produced in the column. However, once recycle brings Tank D-001 to the saturation level of  $7.28 \times 10^{-4}$  l  $H_2$ /l  $H_2O$ , the tank will release 35 l/day or 1.458 l/hr. to D-001 air space. The D-001 instrument bubblers provide an air flow of 127.4 l/hr, which will dilute this hydrogen to 1.14%  $H_2$ . In addition, D-001 vents to 8D-1, where in-leakage air will further dilute the hydrogen.

Venting D-001 from two atmospheres to one atmosphere pressure.

At 80% on LI-016 D-001 (assume water, 1.0 density)

D-001 contains 1500 gallons (5678 liters)

At two atmospheres,  $H_2$  solubility  $7.24 \times 10^{-4}$  l  $H_2$ /l  $H_2O$

At one atmosphere,  $H_2$  solubility  $3.69 \times 10^{-4}$  l  $H_2$ /l  $H_2O$

Total  $H_2$  in solution - two atmospheres

l  $H_2$  =  $5678 \times 7.24 \times 10^{-4}$  = 4.11 liters

Total  $H_2$  in solution - one atmosphere

l  $H_2$  =  $5678 \times 3.69 \times 10^{-4}$  = 2.10 liters

$H_2$  released during venting = 2.01 liters

Assuming 300 gallons (1135 liters) air space, the H<sub>2</sub> released  
would add  $\frac{2.01}{1135} \times 100\% = 0.18\%$  H<sub>2</sub> to air space

1135

Since D-001 will normally have approximately 1.14% H<sub>2</sub> in the air space, adding  
0.18% to this normal level would increase H<sub>2</sub> to 1.33%, well within safe  
limits.