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# CHEMICAL MECHANISMS FOR GAS GENERATION IN TANK 241-SY-101*

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# CHEMICAL MECHANISMS FOR GAS GENERATION IN TANK 241-SY-101

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## INTRODUCTION

In the early 1940s, production of nuclear materials for use in weapons began at the newly established Hanford works under the Manhattan Project. Although several chemical processes were used to separate the Pu from the U and fission products, all of the wastes were stored in underground mild steel tanks ranging in size from about 190 $m^3$ to 3800 $m^3$ (50 000 gal to 1 000 000 gal). Use of mild steel required that the wastes be made alkaline before being placed in the tanks.

During the 1950s, recovery of the valuables (mainly uranium) from the tanks led to projected increases in waste volume that exceeded the available tank space. To decrease the volume of the stored waste, a ferrocyanide scavenging process was developed in which $Na_4Fe(CN)_6$ [ideal stoichiometry] was precipitated in mildly alkaline solution. This precipitate carried with it most of the $^{137}Cs$. Slight changes to the process also allowed for the precipitation of the $^{90}Sr$ and $^{60}Co$. The decontaminated solutions were then sent to soil cribs for final disposal. The solids and some liquids remained in the tanks.

As various other chemical processes were developed, the volume of the waste continued to increase. Eventually, the decision was made to transfer all liquids from the single-shell tanks used in the early years to new double-shell tanks. Although other techniques were tested for reducing the liquid volume before transfer to the double-shell tanks, the bulk of the liquid both from the then operating plants and the liquid recovered from the single-shell tanks were passed through crystallizer-evaporator units. The volume of the each double-shell tank exceeds 3800 $m^3$ and the 28 tanks contain a total volume of $2.3 \cdot 10^5$ $m^3$ of stored waste (Hanlon 1992).

The mixing of these wastes over the years has led to several safety concerns. These safety concerns fall into six categories:

1. wastes that generate flammable gasses or gas mixtures
2. wastes that contain high concentrations of ferrocyanides or tanks suspected of containing large amounts of ferrocyanides
3. wastes that contain greater than 3 wt% total organic carbon
4. wastes from which toxic or noxious vapors are suspected of emanating
5. wastes that contain high radiolytic heat
6. wastes that may contain sufficient fissile material to pose a criticality concern.

Of these categories, only the chemistry associated with the generation of flammable gasses will be discussed.

## HISTORY OF TANK 241-SY-101

Of the 28 double-shell tanks and of the 8 tanks, both single- and double-shell, that are suspected of containing flammable gas generating wastes, the waste in Tank 241-SY-101 stands out as unique and has been most studied. This tank is most notable because the episodic release of flammable gases is the most spectacular. Waste was first added to this tank in 1977 and was added during several campaigns from 1977 to 1981. The fill history has been documented (Strachan et al. 1990), and the general composition of the waste is shown in Table 1 (Herting et al. 1992).

**Table 1.** Molar Composition of Waste in Tank 241-SY-101 by Major Constituent

| Component | Bulk | Liquid |
|---|---|---|
| $NaNO_3$ | 2.2 | 2.7 |
| $NaNO_2$ | 4.0 | 3.8 |
| $NaAlO_2$ | 2.0 | 1.7 |
| $Na_2CO_3$ | 0.4 | 0.1 |
| NaOH | 2.4 | 2.3 |
| Total Organic Carbon | 2.4 | 1.2 |

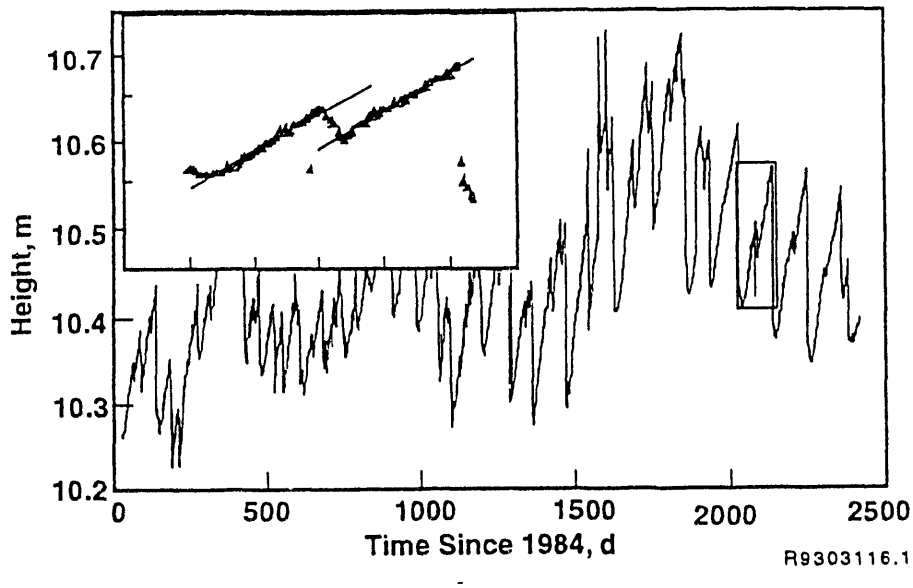


**Figure 1.** Waste Height Data From Tank 241-SY-101.

Shortly after the last waste was added to the tank, the waste volume began to increase, and a short time later the waste volume rapidly decreased. This episodic growth and release is shown in Figure 1 and continues to this day. The periodicity has, until recently, been fairly regular at 90 to 110 days between decreases. Recently, the period has lengthened to about 150 days.

Studies done in the early 1980s (Delegard 1980) without radiation revealed that the growth of the slurry was done to the generation of gases. These gases were found to consist of $H_2$, $N_2O$, $N_2$, and possibly $NH_3$. In 1990, a concerted effort was begun to study the behavior of the waste in this tank. Gases from the tank were indeed found to consist of the same gases identified by Delegard (1980). What was more disconcerting was that the concentration of $H_2$ was often found to exceed the lower flammability limit (1%) during these gas release events and on occasion to exceed 5% for a few minutes.(1) These facts combined lead to much safer operations and intensive studies to determine the chemistry and physics of gas generation and release.

Recent investigations have been summarized in several documents (Strachan and Morgan 1990, Strachan and Morgan 1991 a, b, c; Strachan 1992 a, b; Schulz and Strachan 1992; Babab et al. 1992 and others). These studies have led to the current understanding of the physical nature of the waste in the tank. From a few weeks after a gas release event until the next release event, the waste appears to consist of four layers. This understanding is depicted in Figure 2. A sludge is thought to exist at the bottom of the tank because the temperature in this region does not seem to change during a gas release event. Above the sludge is a layer of slurry approximately 4.7 m (180 in.) thick. This layer is thought to be nonconvecting because during the period between gas release events, a nearly parabolic temperature profile is developed. Above this layer is thought to lie a layer that is also about 4.7 m thick. This layer is thought to be convecting because of the nearly isothermal profile. The uppermost layer is thought to be a crust or foam-like material. In this layer the temperature decreases nearly linearly to the temperature of the dome space. Further discussion of the physics of the waste in this tank is beyond the scope of this chapter. Therefore, the remainder of the discussion will center on the chemistry of the waste in this tank.

## RESULTS FROM THE CHEMICAL MECHANISM STUDIES

As indicated above, the chemistry in this waste is under study. It is necessary to understand the mechanism by which these gases are generated because the waste will have to be treated at some time for final disposal - these wastes cannot be stored indefinitely in these steel tanks. Whatever disposal method is selected must deal with the complex chemistry that exists in these wastes so that the treatment leads to safe disposal rather than a situation that requires either constant monitoring or further treatment. Toward this end, a set of studies is being carried out at Argonne National Laboratory, Georgia Institute of Technology, Pacific Northwest Laboratory, and Westinghouse Hanford Company to determine the mechanism by which the gases are being generated from the waste in Tank 241-SY-101.

Actual mechanistic work is being carried out a Georgia Institute of Technology using simulated waste materials without radiation. The composition of this waste is based on the inorganic analyses of the actual waste (Table 1) and an educated guess about the organic constituents. This educated guess is based on process history, the

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(1) The tank head space is ventilated using a exhaust fan at 0.2 to 0.3 $m^3/s$ (400 to 600 $ft^3/min$). The volume above the waste in the tank is about 140 $m^3$ (37,000 $ft^3$).

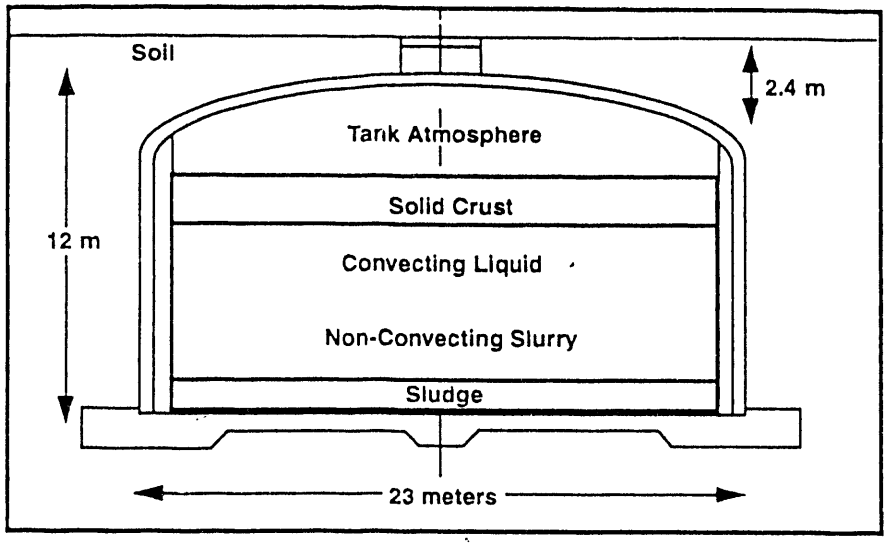


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Figure 2. Schematic of Tank 101-SY.

work by Delegard (1980 and 1987), and Lokken et al. (1986). It was found that a dilute solution of formaldehyde in strong base (Siemer in Strachan 1991) yielded hydrogen and not the typical Cannizzaro products. This led investigators to part of the puzzle. Delegard (1980) determined that the presence of aluminum, presumably as $AlO_2^-$, was necessary for the reaction to product $H_2$. Similarly, nitrite and base were also needed for the reaction. From this information and some preliminary work with $^{13}C$-labelled and $^{15}N$-labelled organic compounds, the prototypic reactions shown in Figure 3 for the thermal degradation of glycolate were proposed.

The validity of most of these reactions has been confirmed from the studies with $^{13}C$-labelled organic chemicals. The observation that only $NO_2^-$ participates in the reactions is supported by the studies with $^{15}N$-labelled $NO_2^-$ and $NO_3^-$. These react in the presence of the organics to yield $N_2O$ and $N_2$; $NH_3$ appears to be a product of the organic nitrogen, but not entirely. This information is summarized in Tables 2 and 3.

**Table 2.** Gases Generated Under Thermal Conditions

| Component | Gas |
|---|---|
| $CH_2O$ | $H_2$ |
| Glycolate | $H_2$ |
| $NO_2^-$ | $N_2O$, $N_2$ |
| $R_3N$[1] | $N_2O$, $N_2$, $NH_3$ |

[1] R = H and/or alkyl group

**Table 3.** A Summary of the Results from the Studies with $^{13}C$-Labelled Organics

| Complexant | Products |
|---|---|
| HEDTA[1] | $CH_2O$, $C_2O_4^{2-}$, EAMA, EA, $^{13,12}C$-glycine |
| HEDTA[2] | $HCO_2^-$, $CO_2$, $C_2O_4^{2-}$, EAMA, u-EDDA, IDA, s-EDDA or EDMA, $^{13}C$-glycine |
| Glycolate | $C_2O_4^{2-}$ |

1 $^{13}C$ on the B-hydroxyethylene group
2 $^{13}C$ on the B-carboxyethylene groups
HEDTA - (2-hydroxyethylene) ethylenediaminetriacetate
EAMA - ethanolaminemonacetate
EA - ethanolamine
EDDA - ethylenediaminediacetate (u- unsymmetrical, s - symmetrical)
IDA - iminodiacetate
EDMA - ethylenediaminemonoacetate

In the suggested thermal mechanism, two-carbon moieties are removed from the organic molecule and, depending on the electron rearrangement, a two- or single-carbon moiety eventually yields $H_2$. The case of glycolate is, of course, much simpler, but forms the basic understanding of the decomposition of the more complex molecules. ?

While these experiments have elucidated what may be the foundation for the reactions that take place in the actual waste, the gas compositions that result from these and other laboratory experiments, including the radiolysis experiments described below, are much different from the gas compositions that are observed in the tank (Pederson and Strachan 1993). The exact reason for this difference is uncertain at this time, but may be due to the difference between the organic composition of the waste in the tank and the compositions used in the laboratory studies. The fact that the gas composition is a sensitive function of the simulated waste composition has been documented by Bryan and Pederson (in Strachan 1992b; Schulz and Strachan 1992).

Reactions in the presence of radiation are being carried out at Argonne National Laboratory. In these studies, sensitive gas measuring devices are being used that have been developed over many years of studying radiation chemistry. These techniques are described by Meisel (in Strachan 1991). From these studies, it has been shown that the amount of gas generated from the radiolysis of water is surpassed by the amount thermal generated from the ~~radiation~~ chemistry in simulated waste solution. The direct generation of gases by radiolysis constitutes about 20% of the total gas generated during these experiments. It appears that the presence of radiation causes other reactions to occur that would not occur without the radiation. These reactions are the result of free radicals that are generated from the radiation. Although the radiation chemistry of the $OH^-/NO_3^-/NO_2^-$ system is well known (Meisel in Strachan 1992a), the contribution to the radiation chemistry by the organics is not well understood and would require a substantial investment in time to come to a good understanding.

It has been found that the $G(H_2)$(1) is independent of dose and dose rate. This is illustrated in Figure 3 for a simulated waste solution containing EDTA. For $N_2O$, the $G(N_2O)$ has a limited dependence on dose; at lower doses, the $G(N_2O)$ increases. This

(1) The "G-value" is the number of molecules generated, in this case $H_2$, per 16 aJ (100 eV) of radiation energy.

| | |
|---|---|
| (1) | $Al(OH)_4^- + NO_2^- \rightleftarrows Al(OH)_3\text{-}O\text{-}N\text{-}O^- + OH^-$ |
| (2) | $Al(OH)_3\text{-}O\text{-}N{=}O + HO\text{-}CH_2\text{-}CO_2^- \rightleftarrows Al(OH)_4^- + O{=}N\text{-}O\text{-}CH_2\text{-}CO_2^-$ |
| (3) | $O{=}N\text{-}O\text{-}CH_2\text{-}CO_2^- \rightarrow NO^- + O\text{-}CH_2 + CO_2$ |
| (4) | $O{=}N\text{-}O\text{-}CH_2\text{-}CO_2^- + OH^- \rightarrow NO^- + H\text{-}(CO)^-\text{-}CO_2 + H_2O$ |
| (5) | $2NO^- \rightleftarrows N_2O_2^{2-}$ |
| (6) | $N_2O_2^{2-} + H_2O \rightleftarrows HN_2O_2^- + OH^-$ |
| (7) | $HN_2O_2^- \rightarrow N_2O + OH^-$ |
| (8) | $N_2O + Al(OH)_3\text{-}O\text{-}N\,O^- \rightarrow N_2 + Al(OH)_3\text{-}O\text{-}NO_2$ |
| (9) | $N_2O + NO_2^- \rightarrow N_2 + NO_3^-$ |
| (10) | $CH_2{=}O + OH^- \rightleftarrows HO\text{-}CH_2\text{-}O^-$ |
| (11) | $HO\text{-}CH_2\text{-}O^- + OH^- \rightleftarrows {}^-O\text{-}CH_2\text{-}O^- + H_2O$ |
| (12) | ${}^-O\text{-}CH_2\text{-}O^- + H_2O \rightarrow H_2 + H\text{-}COO^- + OH^-$ |
| (13) | $H\text{-}(CO)\text{-}CO_2^- + OH^- \leftrightarrows {}^-O\text{-}CH(OH)\text{-}CO_2^- \leftrightarrows ({}^-O)_2\text{-}CH\text{-}CO_2^-$ |
| (14) | $({}^-O)_2\text{-}CH\text{-}CO_2^- + H_2O \rightarrow H_2 + {}^-O_2C\text{-}CO_2^- + OH^-$ |

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**Figure 3.** Proposed Mechanism of Thermal Degradation of Glycolate.

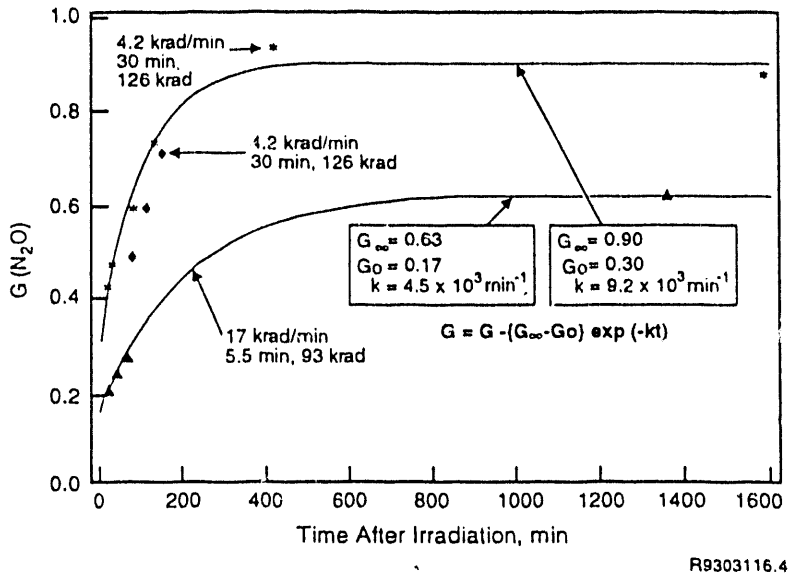
may be due to the conversion of $N_2O$ to $N_2$ and $O_2$ in the radiation field. As in the studies of the thermal generation of gases, it has been determined that the source of the $N_2O$ is $NO_2^-$ not the organic nitrogen.

The case for free radical generation is made stronger by the observation that preirradiation of the simulated waste solutions before performing a thermal gas generation experiments leads to an increase in the gas generation rate. This is summarized in Figure 4. In this experiment, solutions that had been set aside after determining the $G(H_2)$ and $G(N_2O)$ were heated ~~several weeks~~ later to determine the rate of thermal generation of gases. ~~Three solutions were studied; two had a total dose of 126 krad achieved at two dose rates and one had a dose of 93 krad. The lines drawn in this figure are the result of a least squares fit using the equation.~~

$$\cancel{G = G_\infty - (G_\infty - G_0)\exp(-kt)}$$

Additional experiments were performed and the results are shown in Table 4.

From these data it can be seen that the temperature sensitivity of the $N_2O$ production is greater than the $H_2$ production. Although the "Control" and the "Preirradiated" solutions contained both EDTA and HEDTA in equimolar concentrations, it has been shown that these reactions are essentially independent (see Meisel in Strachan 1992b). As with the results from the thermal experiments described above and those that have been performed at Pacific Northwest Laboratory and Westinghouse Hanford Company, the generation rates and the relative concentrations of the gases produced in the laboratory experiments do not match the values observed for the gases in the tank vapor space.




rate of thermal generation of $H_2$ & $N_2O$

Figure 4. Effect of Preirradiation on the ~~G ($N_2O$)~~ for the Solution shown in the footnote of Table 4 ~~with 0.17 m EDA~~.

Table 4. Results for $G(H_2)$ and $G(N_2O)$ from the Preirradiation Experiments.

| Sample | Concentration, M | $G(H_2)$ 60°C | $G(H_2)$ 30°C | Ratio | $G(N_2O)$ 60°C | $G(N_2O)$ 30°C | Ratio |
|---|---|---|---|---|---|---|---|
| EDTA | 0.085 | 0.062 | 0.043 | 1.44 | 1.10 | 0.54 | 2.04 |
| HEDTA | 0.085 | 0.054 | 0.047 | 1.15 | 0.77 | 0.54 | 1.43 |
| Control | 0.065 | 0.063 | 0.045 | 1.40 | 0.87 | 0.49 | 1.78 |
| Preirrad | 0.065 | 0.080 | 0.047 | 1.70 | 1.06 | 0.48 | 2.21 |

Note: Both the Control and the Preirradiated solutions contained 0.065 M each of EDTA and HEDTA; the total dose was 130 krad at 4.4 krad/min; the ratio is the 60°C value divided by the 30°C value; the solution used had an inorganic composition 2.12 M NaOH, 2.79 M $NaNO_3$, 2.22 M $NaNO_2$, and 1.30 M $NaAlO_2$.

## CONCLUSIONS

The experiments performed to date have elucidated large portions of the reaction mechanism for the chelator chemicals that are suspected of making up the organic content of the waste solutions in Tank 241-SY-101. These mechanisms must await confirmation through accurate organic analyses of the tank waste. These analyses are ongoing, but are complicated because of the solution complexity and the highly radioactive nature of the samples.

Based on the laboratory results and limited knowledge of the organic constituents in the waste, it appears likely that formaldehyde and glyoxalate are the key species that yield $H_2$. The other two principal gaseous species appear to originate from the inorganic chemicals, specifically $NO_2^-$. However, the presence of the organic species

is required for this reaction to proceed. The source of $NH_3$ appears to be principally from $NO_2^-$, but a significant portion appears to originate from the organic amines.

While the thermal generation of gases form the chelators seems well understood, radiation changes the reactions. In the thermal reactions, EDTA does not react very fast. However, in the presence of radiation, the reaction proceeds rapidly. Therefore, it is expected that the products in the actual waste may be different from those observed in the thermal reaction, but similarities are also expected. Radiation is not expected to change the basic mechanism by which these species decompose; however, additional products are present from the free radicals produced by radiation. Subsequent reaction of these products would be expected to follow routes similar to those shown in Figure 3.

Progress is being made in the understanding of both the physical and chemical behavior of the waste in Tank 241-SY-101. As this understanding evolves, a better approach toward the mitigation of the potential safety hazard associated with this waste can be taken.

## REFERENCES

Badad, H., Johnson, G.D., Lechelt, J.A., Reynolds, D.A., Pederson, L.R., Strachan, D.M., Meisel, D., Jonah, C., and Ashby, E.C, 1991, "Evaluation of the Generation and Release of Flammable Gases in Tank 241-SY-101," WHC-EP-0517, Westinghouse Hanford Company, Richland, Washington.

Delegard, C.H, 1980, "Laboratory Studies of Complexed Waste Slurry Volume Growth in Tank 241-SY-101," RHO-LD-124, Rockwell Hanford Operations, Richland, Washington.

Delegard, C.H, 1987, "Identities of HEDTA and Glycolate Degradation Products in Simulated Hanford High-Level Waste," RHO-RE-ST-55P, Rockwell Hanford Operations, Richland, Washington.

Hanlon, B.M, 1993, "Tank Farm Surveillance and Waste Status Summary Report for October 1992," WHC-EP-0182-55, Westinghouse Hanford Company, Richland, Washington.

Herting, D.L., Bechtold, D.B., Crawford, B.A., Welsh, T.L., and Jensen, L, 1992, "Laboratory Characterization of Samples Taken in May 1991 from Hanford Waste Tank 241-SY-101," WHC-SD-WM-DTR-024 (Revision 0), Westinghouse Hanford company, Richland, Washington.

Lokken, R.O., Scheele, R.D., Strachan, D.M., and Toste, A.P, 1986, "Complex concentrate Pretreatment FY 1986 Progress Report, PNL-7687, Pacific Northwest Laboratory, Richland, Washington.

Pederson, L.R., and Strachan, D.M, 1993, "Status and Integration of the Gas Generation Studies Performed for the Hydrogen Safety Program - FY-1992 Annual Report," PNL-8523, Pacific Northwest Laboratory, Richland, Washington.

Schulz, W.W., and Strachan, D.M, 1992, "Minutes of the Tank Waste Science Panel Meeting March 25-27, 1992," PNL-8278, Pacific Northwest Laboratory, Richland, Washington.

Strachan, D.M, 1991, "Minutes of the Tank Waste Science Panel Meeting February 7-8, 1991," PNL-7709, Pacific Northwest Laboratory, Richland, Washington.

Strachan, D.M, 1992a, "Minutes of the Tank Waste Science Panel Meeting November 11-13, 1991," PNL-8047, Pacific Northwest Laboratory, Richland, Washington.

Strachan, D.M, 1992b, "Minutes of the Tank Waste Science Panel Meeting July 9-11, 1991," PNL-8048, Pacific Northwest Laboratory, Richland, Washington.

Strachan, D.M., and Morgan, L.G, 1991a, "Minutes of the Tank Waste Science Panel Meeting September 13-14, 1990," PNL-7599, Pacific Northwest Laboratory, Richland, Washington.

Strachan, D.M., and Morgan, L.G, 1991b, "Minutes of the Tank Waste Science Panel Meeting July 20, 1990," PNL-7598, Pacific Northwest Laboratory, Richland, Washington.

Strachan, D.M., and Morgan, L.G, 1991c, "Minutes of the Tank Waste Science Panel Meeting June 26-27, 1990," PNL-7602, Pacific Northwest Laboratory, Richland, Washington.

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