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CONTENTS

1.0	INTRODUCTION	1-1
2.0	OBJECTIVE	2-1
3.0	SCOPE	3-1
4.0	TEST BACKGROUND	4-1
5.0	DESCRIPTION OF TEST	5-1
5.1	TEST ITEM	5-1
5.2	TEST CRITERIA	5-1
5.3	TEST ENVIRONMENT	5-2
5.4	CRITERIA FOR APPARATUS DESIGN	5-2
5.5	PRESTART CONDITIONS	5-3
5.6	TEST APPARATUS	5-3
5.7	SYNTHETIC GROUT FORMULATION	5-6
5.8	DATA	5-6
5.8.1	Gas Generation Rate Data	5-6
5.8.2	Gas Composition Data	5-7
5.8.3	Determination of Amount of Gas Produced	5-8
5.8.4	Key Instrument Sensitivity and Calibration	5-8
6.0	EXPECTED RESULTS	6-1
7.0	TEST PROCEDURE	7-1
8.0	SAFETY	8-1
9.0	QUALITY ASSURANCE	9-1
10.0	LABORATORY QUALITY CONTROL SAMPLES	10-1
10.1	REFERENCE SAMPLES (STANDARDS)	10-1
10.2	CALIBRATION BLANKS	10-1
11.0	PERFORMANCE AND SYSTEM AUDITS	11-1
12.0	CORRECTIVE ACTION	12-1
13.0	QUALITY ASSURANCE REPORT	13-1
14.0	DATA SHEETS	14-1
15.0	REFERENCES	15-1
	APPENDIX A WASTE SOURCE TERM FOR MAKE-UP OF SYNTHETIC WASTE	A-1
	APPENDIX B JOB SAFETY ANALYSIS	B-1

LIST OF TERMS

ANL	Argonne National Laboratory
DOE	U.S. Department of Energy
GC	Gas Chromatograph
LFL	Lower Flammability Limit
NDE	Nondestructive Examination
OSR	Operating Safety Requirements
PCL	Process Chemistry Laboratories
PNL	Pacific Northwest Laboratories
psia	lb/in ² , absolute
WHC	Westinghouse Hanford Company

GROUT GAS GENERATION TEST PLAN

1.0 INTRODUCTION

This document is to formalize the procedure provided in Section 7.0. The procedure is for gas generation experiments from grout produced by using either synthetic tank waste or actual tank material. This is the detailed procedure for the gas generation tests as referenced in Section 4.10 of WHC-SD-WM-TP-136, the *Hanford Grout Disposal Program-Campaign 102 Feed Characterization and Test Plan* (Hendrickson 1993). Section 2.0 discusses the objective of these experiments, which is to measure the rate of gas generation and to determine the gas composition. The experiments measure the pressure buildup in closed containers, from which gas samples are collected for gas analysis by either mass spectrometry or gas chromatography. The scope is provided in Section 3.0. Section 4.0 presents background for the test. Section 5.0 describes the test, with details on the test criteria, the criteria for apparatus design, the experimental apparatus and methods, the grout formulation, and the data to be generated. The expected results are discussed in Section 6.0. Section 7.0 presents one table with the detailed procedure and a second table with notes on the steps in the procedure. Sections 8.0 and 9.0 discuss safety and quality assurance issues. Sections 10.0 through 15.0 discuss (Section 10) laboratory quality control samples, (Section 11) audits, (Section 12) corrective action, (Section 13) quality assurance report, (Section 14) data sheets, and (Section 15) references.

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2.0 OBJECTIVE

These experiments are performed to measure the rate of gas generation for the various gases produced when grout, which was prepared using tank waste, is heated at 65 °C. In addition, experiments will be conducted using grout made from synthetic tank waste. These will serve as practice for the tests using radioactive grout, as well as providing a comparison with the series of experiments being done at Argonne National Laboratory (ANL). The overall objective of these experiments, as explained by Hendrickson (1993), is to provide data for evaluation of safety risks presented by gas generation in the grout vault after making grout with tank waste. The experiments will provide verification/confirmation for gas generation rates for the ANL testing, as discussed in the next section.

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3.0 SCOPE

This work is being performed as outlined in Hendrickson (1993), Section 4.10 and expanded on in the following discussion. The testing of hot grout samples for the radiolytic generation of hydrogen (H_2), nitrous oxide (N_2O), and possibly other gases is necessary because of the potential impact of these gases on the grout vault section of the Grout Facility Safety Analysis report. The gas is generated by radiolytic and chemical decomposition of water, nitrates, and organic species. The radiation-induced reactions have been observed in many Hanford Site waste tanks and in the laboratory by gamma irradiation of liquid waste simulants.

Laboratory testing on simulated grout specimens in gamma fields is planned for both Argonne National Laboratory (ANL) and Hanford. The ANL testing is designed to provide a statistically significant data set concerning the breakdown of chemical components of the grout. These tests will provide additional gas generation yield information that may be applied to a general radiochemical model for grouts.

The gamma irradiation testing at the Hanford Site on simulated grout will use more massive specimens of grout for examining gas generation rates, gas holdup, and liquid rejection mechanisms.

The testing of grout specimens that contain actual radioactive waste in the present experiments at WHC will serve to provide verification/confirmation of gas generation rates for the ANL and possibly the Hanford Site Gamma Pit testing. Comparing the results from the four radioactive grout specimens at WHC with the results at ANL (and possibly the Hanford Site) will entail statistically comparing the data means to determine if they are from the same populations. The radioactive grout testing may provide verification of the proposed gas generation Operational Safety Requirement (OSR) in the Grout Safety Analysis Report (WHC 1992g). At a minimum, the testing will provide confirmation of the ANL results, by providing a data point that can be compared with similar ANL data. The ANL data may be required to meet a grout gas generation OSR in the SAR.

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4.0 TEST BACKGROUND

Studies using synthetic mixtures for the waste in tank 241-SY-101 show that using different organic components provides gas generation at different rates, producing gaseous species in different proportions (Person 1993; Meisel 1991). The present synthetic waste formulation closely matches the tank contents, as discussed in Section 5.7. The organic species are formulated so that the breakdown products will form similar organic species to those found in tank waste, according to the current available technology at WHC and PNL. This synthetic waste formulation uses the best estimates of the mean values of synthetic waste; it represents the current state-of-the-art in waste and grout formulation.

The measurements using the radioactive grout will have the correct organic species present (i.e., they use actual tank material). Therefore these experiments should provide the correct contribution from the chemical mechanism. The contribution from radiolysis will be correct, except that it will be diminished somewhat, because of the modest size of the present experimental reactors. We estimate that about 40 percent of the energy of the ionizing radiation will escape from the grout during the experiments.* (A more accurate estimate from a Monte Carlo simulation will be included in the final report.) This loss contrasts to the small fraction of energy that will escape from the large grout vaults to be used.

The present estimates of the gas generation rate vary by more than an order of magnitude. Thus, our radioactive grout experiments should provide a better estimate of the rate, as it should be no more than about 40 percent low. A conservative rate estimate of gas production can then be established by assuming all of the gas production is from radiolysis and correcting the measured rate. A more accurate estimate of the total gas generation rate can be made by using the results of the tests at WHC and ANL to estimate the relative contribution of the radiolytic mechanism in these experiments. Then only this contribution to the rate will be corrected for the loss of ionizing radiation.

*The estimate results from the following: ^{137}Cs is the predominate source of ionizing radiation, giving off β -particles that carry 0.28 of the energy (Appendix C, Meisel, 1991), which have a range in grout that is much shorter than the minimum path length in the grout, so that essentially all of this energy is absorbed. The gamma ray, which carries 0.72 of the energy, is responsible for the energy that is lost. Using 0.18 cm^{-1} as the absorption coefficient in grout (section 3.2.4, Roblyer, 1993) with the minimum path length in the present grout sample (3.6 cm) and Beer's Law gives the fraction of gamma energy lost as 0.52, so that the fraction of the total energy lost is $0.52(0.72) = 0.38$.

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5.0 DESCRIPTION OF TEST

5.1 TEST ITEM

Experimental observations record the pressure changes when grout made with synthetic tank waste, or actual waste, is maintained at an elevated temperature in a reaction vessel. The pressure buildup data will be analyzed to determine the rate of gas generation by using the free volume in each reaction chamber. The observations of the gas pressure versus time are complemented by analyses of the gas composition at various times. Some gas analyses will be performed at the Pacific Northwest Laboratory (PNL) by mass spectrometry; other analyses will be performed at Westinghouse Hanford Company (WHC) using gas chromatography.

Four replicate experiments will be performed on the grout made with synthetic tank waste. These experiments are referred to as using nonradioactive grout, in contrast to the four replicate experiments using grout made with actual tank waste, referred to as radioactive grout.

5.2 TEST CRITERIA

In addition to the criteria in Section 4.10 of TP-136 (Hendrickson 1993), the following will apply. The tests will be considered complete after the grout samples produce sufficient gas to adequately measure the rate of gas production and the gas composition, or when sufficient time has passed that the maximum rate of gas generation is so small that it is no longer a concern.

The criterion defining an adequate measurement is based on the width of the 95 percent confidence interval for the mean gas generation rate calculated from the four grout sample results. Using the Student's t-table with 3 degrees of freedom, the 95 percent confidence interval is given by $\langle x \rangle \pm 3.182s/n^{0.5}$, where $\langle x \rangle$ is the mean, s is the standard deviation, and n is the number of determinations (4, in this case). An adequate measurement is one that will meet the following criterion.

- The gas generation rates shall be determined to be within a factor of two (i.e., $1.591s \leq 2\langle x \rangle$). If practical, the determination should be within 50 percent ($1.591s \leq 0.5\langle x \rangle$). The length of the experiment will be adjusted, depending on results during the first 2 to 3 months. The values in this criterion are based on the best judgment of the personnel who are modeling gas concentrations in the grout vault, and on what can reasonably be expected in the gas generation experiments.

The maximum time will be one such that the total gas generation would correspond to a radiolytic G value as given by

- The G value for the gas generation experiment where it is not necessary to continue the test shall be the best estimate for the maximum gas generation rate. This is 0.04 moles/hr for the grout vault, which is a G value of 0.01416 molecules/100eV. Using

the conditions assumed in Section 6.0, this G value produces a pressure buildup at a rate of 2.5×10^{-4} psi/day. See Roblyer (1993) for conversion factors.

The basis for the lower gas generation rate cutoff is the modeling in Roblyer (1993). This modeling indicates that a grout vault generating 0.4 moles/hr of gas reaches flammable levels in the leachate sump. The goal is to ensure that the hydrogen concentration never exceeds 1 percent in the sump, which is 25 percent of the Lower Flammability Limit (LFL) of hydrogen in air. To account for approximations and potential unknowns in the modeling and in the gas generation experiments, it is desirable to continue the experiments until they can ensure that the gas generation rates are an order of magnitude below that needed to achieve flammability in the leachate sump. This provides an adequate contingency for unknowns and approximations. Before terminating the experiment, in any situation, laboratory personnel shall consult with Grout Technology to determine if the experiment should be continued.

The maximum experimental run time period is estimated to be about 120 days, using the minimum G value given above and assuming that the standard deviation in the pressure measurement is the same as the accuracy specification of the gauge. The 120 days consists of an initial 30-day period that produces only a small pressure increase, followed by a 90-day period where the estimated $s = 1.1\langle x \rangle$, so that $1.591s = 1.8 \langle 2 \rangle$.

The tests will be performed by personnel from the Process Chemistry Laboratories (PCL), with additional support from other Hanford groups for analytical work, calibrations, leak testing, and apparatus assembly.

5.3 TEST ENVIRONMENT

The nonradioactive grout experiments will be located in the 222-SA Laboratory. The radioactive grout experiments will be in a hood in the 222-S Laboratory, room 1-B.

5.4 CRITERIA FOR APPARATUS DESIGN

Each apparatus should be fabricated and operated to meet the following criteria.

- The apparatus temperature should be controlled to 65 ± 5 °C in the curing chamber and during the estimated 4-month test period. The 65 °C temperature was chosen based on the heat transfer analysis in Crea (1992) Figure 3, and discussions with WHC and PNL technical formulation experts. The time period that the grout is above 65 °C, even at the worst case given in Crea, is small compared to a 30-year time of interest for gas generation concerns.
- The maximum short-term temperature of the grout in the capsule shall be less than 90 °C. The basis for this limit is that any temperature up to at least 90 °C will not appreciably harm the grout.

- All components in direct contact with the radioactive waste must withstand a gamma and beta radiation field up to 310 Rad/hr during the experiment, which corresponds to a maximum integrated exposure of 2×10^6 Rad.
- The maximum expected experimental duration is about 5 months, with a 10-month design life.
- The preferred construction material is type 304 stainless steel, with welded construction or compression fittings.
- The systems shall withstand a maximum pressure of 0.1 MPa (15 psig).

5.5 PRESTART CONDITIONS

- The grout specimens (4 radioactive and 4 nonradioactive) have been cured for 28 days at 65 °C.
- Test sample apparatus for leaks. A low leak rate system is required; each capsule for radioactive grout shall be He-leak checked after assembly for detectable leaks to 10^{-7} cc-atm/sec maximum leak rate. This leak testing should be performed by qualified personnel from the nondestructive examination (NDE) group at WHC.
- Minimize loss of water from samples.

5.6 TEST APPARATUS

Figure 5-1 diagrams the manifold used for experiments with radioactive grout to connect the four reactors through a filter to (1) the gas sample bulb (with valve R) connected through valve S, (2) two additional pressure gauges connected through valve P, (3) the vacuum pump through valve V, and (4) a port that can be connected directly to the gas chromatograph (GC). The filter (Millipore Wafergard F Mini Inline Gas Filter WGFG 01 HS1) removes 99.999999 percent of particles larger than $0.003 \mu\text{m}$. This filter keeps the gas samples free from particles that are radioactive. The two pressure gauges are from MKS Instruments, Inc. They are Type 122 with either a 1000-Torr or a 10-Torr range. The apparatus for nonradioactive grout is identical, except for not having the port for the direct connection to the GC, and not having valve L to the 10-Torr pressure gauge.

The reactors are located under the four valves shown at the bottom of Figure 5-1. Figure 5-2 shows a schematic of each reactor with its pressure gauge and valve A. Valve A is connected to valve C, which connects to the cold finger, and to valve B to the manifold (valve B is shown at the bottom of Figure 5-1). The cold finger is constructed of glass, with graduations so that the volume can be read during the distillation (see Section 5.8.3).

Figure 5-1 Manifold with Pressure Gauges (10-Torr and 1000-Torr), Sample Port with Sample Bulb, with Valves to Four Reactors, Vacuum Pump, and Gas Chromatograph.

Figure 5-2. Reactor and Cold Finger with Pressure Gauge and Valves A, B, and C.

Each reactor is a container made from stainless steel vacuum equipment assembled using a copper gasket. The pressure gauge is welded, and the other seals are compression fittings, except for an o-ring seal to the sample bulb. The lower portion of each reactor is a half-nipple with a welded bottom that forms a cylindrical vessel on a flange. The flange and tube outside and inner diameters (inches) are 4.63, 3.0, and 2.87, respectively. The half-nipples and their mating flanges are manufactured from 304 stainless steel. Only this material is in direct contact with the radioactive waste, so that no significant radiation damage is expected. Each reactor is located inside an oven made from a 4-L stainless steel beaker with a heating mat on the outside.

The oven temperature is set for 65 °C, and a temperature controller from Omega Engineering, Inc. (model BS5001T1) maintains the temperature within 2 °C of this value. On a few occasions, the temperature will be varied by about 2 °C to observe the resulting pressure change. The observed effect will be used to correct the gas pressure for temperature effects, which are primarily the result of the changes in the vapor pressure of water.

5.7 SYNTHETIC GROUT FORMULATION

The formulation is designed to match the mean concentrations of most of the nonradioactive components in the tank. The characterization of tank 105-AN waste is recorded in Welsh (1991). The 105-AN tank contents were transferred to 102-AP in 1993. Tank 105-AN characterization results were combined with the characterization results of the heel in 102-AP from the previous campaign to develop the best estimate of the tank contents. These specifications are provided in Appendix A, which is a letter specifying the synthetic waste contents. The organic species are formulated so that the breakdown products will form similar organic species to those found in tank waste, according to current knowledge at WHC and PNL.

5.8 DATA

This section describes the different parameters measured, together with considerations of how to minimize the errors involved.

5.8.1 Gas Generation Rate Data

The measured parameters are time and the amount of gas produced. The main source of error in the gas generation rate is determining the amount of gas produced. The first step in this determination is to correct the observed pressures for temperature variations. This is done by observing the change in pressure per degree change in temperature for temperature changes that occur in a short time period (e.g., changes of about 2 °C occurring within 1 to 6 hours). These changes are averaged to determine the pressure variation factor f_p . This factor is periodically checked. A new value is used when the variation is larger than three times the estimated standard deviation of the individual determinations, or if the values show a trend with time (such that including the time trend in the fit significantly reduces the apparent scatter in the observations). Once the f_p factor is determined, the observed pressure p is corrected to 65 °C using the observed temperature in Celsius T_c and

$$p_c = p + (T_c - 65) f_p.$$

This provides a first-order correction for temperature effects on the vapor pressure of water, for the temperature variation of the solubilities of ammonia and other gases, for the change in pressure of permanent gases, for any temperature effect on the free volume available to the gas, and for other temperature effects. The amount of gas produced is determined from the free volume for the gas V (measured at the start and end of the experiment, with a check each time a gas sample is taken) from

$$\Delta n = \Delta p_c V / (338.15 R),$$

where Δp_c is calculated by subtracting the p_c value at time zero and R is the gas constant. Time zero is the time when the grout first reaches the desired temperature (this will normally be taken as 65 °C, but a value in the range of 60 to 64 °C will be used if the temperature stabilizes at this value for longer than 6 hours before reaching 65 °C).

If air is found in the gas analysis (in both of the duplicate samples), the Δn value will be corrected by multiplying by the ratio $\text{Product}/(\text{Product} + \text{Air})$, where Air and Product represent their respective concentrations. This correction will be made when Air is greater than values found for residual air in sample bulbs during the calibration runs discussed in the Section 5.8.2.

In this experiment there is the potential that gas may be trapped within the grout matrix, so that it does not contribute to the pressure measured above the grout. This problem will be addressed at the end of the experiment. At that time, a cooled chamber that is attached via a heated side arm will collect the distillate (primarily water) from the heated grout. Test experiments collected a volume of distillate equal to 60 percent of the initial volume of the grout. The distillation will thus open passages into the grout interior to facilitate escape of trapped gas.

The amount of gas released during the distillation will be determined from the observed pressure changes and the measured volumes. The volumes in the reactor and the cold finger will be measured at the start and end of the distillation, together with the amount of distillate. The amount of gas present at the start and end of distillation will be computed from the volumes and the pressures (and the temperatures) at the start and finish. The difference will give the amount of gas retained within the grout, a quantity that is interesting for comparison with model calculations.

5.8.2 Gas Composition Data

The measured parameters are the different relative concentrations of the gaseous components in the gas sample, not including water vapor. The analysis will use a GC; some samples will be analyzed by mass spectrometry to ensure that all important gases are looked for by GC. The analytical instruments will be operated according to their procedures. These procedures include protocols to establish and periodically check the calibration factors, and to establish the measurement accuracy.

The main sources of error in the gas compositions for this procedure are air leakage (either the air present when attaching the sample bulb, or leakage into the sample bulb after sampling), gases remaining from the previous filling of the sample bulb, and errors in sampling the gas in the reactor. Previous experience (Person 1993) has shown that three flushes of the sample bulb with helium (fill to 800 Torr, pump to <20 Torr) are sufficient to remove gases from the previous filling, as well as air, to levels <0.06 percent.

Duplicate samples will allow detecting leaking sample valves (or operator error), as well as establishing the experimental precision of the combination of the gas sampling method and the analytical technique for each species.

Additional tests, which are not covered in this document, will be performed to measure sampling errors from effects such as separation of He and

H₂ from heavier gases during expansion through the Teflon* membrane in the filter, or pumping effects when water condenses after the hot vapor expands into the cool manifold. These tests will use calibrated gas mixtures, sometimes in the presence of hot water vapor, and collect samples for analysis. Repeated samples will also be collected, where enough samples are collected that most (ca. 90 percent) of the gas has been sampled.

The gas analysis results from the calibrated mixtures will establish the magnitude of any preferential sampling of gases of different masses, diffusion coefficients and polarity. If any sampling effect is found that is larger than the measuring precision, such an effect will be corrected by multiplication by the ratio of the true concentration to the measured concentration. These correction factors (if necessary) will be determined before any sample (other than the samples of the initial gas fillings, which are >99 percent pure He) is analyzed.

A reasonable goal for the measurement uncertainty is 10 percent of the concentration $\pm$ 0.1 percent, with larger uncertainties allowed for a few species, such as NH₃ and NO_x (but not for H₂, N₂O, oxygen, nitrogen, and argon). A statement of the uncertainty of the determinations will be included in the final report.

5.8.3 Determination of Amount of Gas Produced

This section discusses how the amount of product gas will be estimated. The product gas is calculated as the difference between the summed total concentration and sum of the helium and air concentrations.

The amount of N₂ from air is estimated by multiplying the measured concentration of Ar by an average N₂/Ar ratio. The air concentration is then the sum of this inferred N₂ concentration with the measured values for O₂ and Ar. The multiple for Ar would be 83.6 if the N₂/Ar ratio were the same as it is for pure air. However, earlier measurements of this ratio were consistently lower (Person 1993). The average ratio measured for air mixtures was 82.2, so this is used as the estimated ratio. Several of the measurements in synthetic waste found even smaller values of the ratio; the correct ratio is estimated to be between 75.7 and 83.6.

The N₂/Ar ratios less than 83.6 may result from sampling effects discussed in Section 5.8.2, from different solubilities, from different amounts of gas adsorption, or possibly from N₂ reactions. For example, argon is about twice as soluble as N₂ in pure water.

5.8.4 Key Instrument Sensitivity and Calibration

The key instruments are those that measure the pressure (especially) and temperature. The analytical instruments to analyze the gas samples are also key instruments, but their calibrations are done via their own procedures.

*Teflon is a trademark of E. E. du Pont de Nemours and Company in Wilmington, DE.

The temperature measurements are made by type K thermocouples from Omega Engineering, Inc., model KMQSS-062(G), as read by the Omega Engineering Data Logger, model OM501. The thermocouples were calibrated by comparison with a calibrated thermocouple at two temperatures, one near 0 and one near 100 °C. The data loggers were calibrated at temperatures of 25 and 65 °C using a model C-65 thermocouple calibrator from Wahl Instruments, Inc., which is traceable to the National Institute of Standards and Technology. The calibrator has been certified by the Westinghouse Instrument Standards Laboratory (certification number 702-13-55-004, expiration date 6/4/94).

Pressure measurements are made using pressure transducers from Sensotec, Inc., model TJE, with a range of 0 to 25 psia and a minimum accuracy of ± 0.025 psi. The pressure indicator is also from Sensotec, Inc., the model GM, which provides a 0 to 5 V output signal that is recorded by the data logger. The sensitivity of the indicator display is 0.01 psi. Each transducer is used with a particular indicator unit. Each pair was calibrated by the Westinghouse Standards Laboratory using standards traceable to the National Institute of Standards and Technology or nationally recognized standards (certification number 641-31-04-026, expiration date 6/15/94).

The calibration is checked by comparing pressure readings with those of the 1000-Torr manifold pressure gauge. This gauge has a sensitivity of 0.1 Torr, and an accuracy specification of $\pm 0.15\%$ of reading, after correcting the zero. The gauges were calibrated by MKS Instruments, Inc. using standards traceable to the National Institute of Standards and Technology. The zero on the 1000-Torr gauge is established by comparing readings at low pressure with those on the 10-Torr gauge. The 10-Torr gauge is a similar instrument from MKS Instruments, Inc., with an accuracy specification of ± 0.5 percent of reading, after correcting the zero. A comparison of two 10-Torr gauges established that low pressure readings (below 3 Torr) agreed within 0.05 Torr over a 2-month period, which indicates a small zero drift for these gauges.

The calibration sheets (originals, or copies) will be taped into a laboratory notebook.

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6.0 EXPECTED RESULTS

It is expected that the gas generation in radioactive grout occurs via the two mechanisms of radiolysis and chemical. The rate of hydrogen production by radiolysis is proportional to the G value and the absorbed dose rate. The previous study of the radiolysis mechanism in grout (Friedman 1985) reported the G value for the production of all gas to be 0.018 molecules/100 eV. This value is much lower than the G value for H_2 production of 0.45 molecules/100 eV in pure water and values around 0.05 molecules/100 eV found in synthetic tank waste (Meisel 1991). As the nitrite and nitrate in the waste react with radicals to reduce the $G(H_2)$ from that of pure water, we assume that the $G(H_2)$ values will lie in the range from 0.004 to 0.06 molecules/100 eV.

The chemical mechanism produces gas in the absence of ionizing radiation, via reactions that are expected to proceed more rapidly the higher the temperature. Radiolysis is assumed to produce about one-third of the H_2 in tank 241-SY-101 (Babad 1992), which leaves about 0.7 from the chemical mechanism. This would correspond to about 0.02 %Vol/day (percentage change in volume by gas formation per day). The average temperature of tank 241-SY-101 is about 55 °C, so this rate would be twice as fast at 65 °C, if the reported activation energy of 15 kcal/mole is used (Person 1993). Thus, 0.04 %Vol/day appears to be a reasonable upper limit, considering that tank 241-SY-101 is a tank with particularly rapid gas generation, and reducing the mobility of the reactants by placing them in a grout matrix should reduce the rate of chemical reactions.

In the studies of gas generation in synthetic tank waste, the fraction of H_2 in the gas has varied from a few percent to about 50 percent (Person 1993; Meisel 1991), and H_2 is estimated to constitute about one-third of the gas generated in tank 241-SY-101 (Babad 1992). Thus a reasonable expectation is that the total gas generation rate may be 2 to 5 times the rate of production of H_2 .

Using the above assumptions provides an upper limit of the chemical gas generation rate of 0.2 %Vol/day, which would correspond to about 0.1 %Vol/day when the volume of grout is used, as there is about a 50 percent dilution of the waste volume with the grout dry blend. Thus 300 mL of grout in each reactor would produce a maximum of 0.3 mL of gas per day. Assuming a free volume of 50 mL, this would produce a maximum pressure change of 0.09 psi/day for gas at a pressure of 15 psia. This number is large enough for easily monitoring the pressure change, with 30 days producing a pressure change of 2.7 psi. If we use a rate 90 times smaller as an estimate in our grout, then the same assumptions provide a pressure change of 0.001 psi/day. Such a change will be harder to measure, as it takes 25 days to increase the pressure by an amount equal to the accuracy specification of the Sensotec pressure gauges. After 30 days, the expected pressure increase is 0.03 psi, which can still be measured by GC, as this is a change of 2000 ppm.

The radiolysis contribution is estimated by using the assumptions that:

- G(total gas) is 0.018 to 0.3
- The internal dose rate is 310 Rads/hr
- The grout density is 1.52 g/mL, and, 60 percent of the ionizing radiation is absorbed in the grout.

This provides the estimate for the total rate of gas production by radiolysis of 0.00035 to 0.0059 %Vol/day. Assuming a grout volume of 300 mL, a free volume of 50 mL, and a pressure of 15 psia, provides a pressure increase of 0.00032 to 0.0053 psi/day. A 30-day period would provide a pressure change of 0.01 to 0.16 psi, changes that range from small to easily measurable. However, even 0.01 psi corresponds to a change of 640 ppm, which should be measurable on the GC, if the GC is connected to the manifold.

7.0 TEST PROCEDURE

The experimental procedure is provided in Table 1, with details of the procedure steps discussed in Table 2. Before beginning the procedure, prepare four grout samples each of radioactive and nonradioactive grout following the steps outlined in TP-136 (Hendrickson 1993), except that the grout samples will be formed into large blocks, and not ground into small particles. Water loss will be minimized during the period after the grout has cured by storing in leak-free stainless steel containers with copper gaskets.

Table 1. Test Procedure for Gas Generation by Grout

1.	Calibrate thermocouples and pressure gauges for reaction vessels.
2.	Verify that manifold leak rate is <0.1 Torr/hour.
3.	Load cured grout material into lower portions of reaction vessels. Minimize the free volume. Minimize exposure to air.
4.	Assemble reaction vessels: Cu gasket between flanges, bolt together. Close valves A.
5.	For nonradioactive grout, assemble the control- and measurement-thermocouples onto the reactor and mount reactor in oven. For both nonradioactive and radioactive grout, connect reactor to manifold.
6.	Initial flush with He. Pump to 1 psia, pressurize with He to 29 psia, and observe that system is free from large leaks. Leave pressurized for next step.
7.	Leak test the reactor. If the leak rate is too large, retighten the bolts on the Cu-seal. Repeat steps 6-7 for four reactors.
8.	For radioactive grout, assemble the control- and measurement-thermocouples onto the reactors, mount reactors in ovens, and connect to manifold.
9.	Verify that manifold leak rate is <0.1 Torr/hour.
10.	Make initial measurements of free volume in reactors at ambient temperature while replacing residual air in the reactor with helium.
11.	Measure volumes between valve A and valve B, volume of manifold (for valves S and P open and closed), and volumes of sample bulbs (see Figures 5-1 and 5-2). Heat reactors, adjusting control temperature to give 65 °C, after intermediate pauses (for 30 to 90 minutes) at 45 and 55 °C. Record pressures and temperatures, to allow estimation of vapor pressure of condensable (or soluble) species. Record pressure and temperature every hour for first 24 hours or so.
12.	Measure free volume in reactor at 65 °C. Leave He-filled at 29 psia.
13.	Collect two gas samples in bulbs (see Table 2 for details). Use care to end with He pressure from 14.5 to 20 psia inside reactor. End with nearly the same He pressure between valve A and valve B, to minimize leakage across valve A (add He as necessary to provide pressure). Record pressure and temperature every hour for first 20 to 30 hours after sample. Observe that the temperature actually controls around 65 °C. Repeat steps 12-13 for four reactors.

Table 1. Test Procedure for Gas Generation by Grout

14.	Manually observe temperature and pressure at least every 5 days. In these observations, ensure that the temperature is maintained within 1 °C of 65 °C and that the pressure and temperature are recorded every 6 hours (with a graphical record during the time between recordings). Also, record the pressure reading, together with the zero and calibration values from the Sensotec pressure gauge readouts, to allow corrections for drifts in zero and sensitivity. Two or three times every 30 days, offset the temperature by about 2 °C for 30 to 90 minutes, to measure the effect of temperature on pressure.
15.	After 30 days at temperature, or if pressure builds up above 24 psia, collect two gas samples as in step 13. Measure the amount of gas removed by observing pressures before and after expansion into the known volume of the sample bulb and manifold. This provides a check on the value of the free volume in the reactor.
16.	After sampling, measure free volume in reactor at 65 °C while replacing the gas in the reactor with helium (use two expansions from reactor, two expansions into reactor). Leave He-filled at 29 psia overnight. Then collect two gas samples as in step 13, ending with He pressure from 14.5 to 19 psia inside reactor and the same He pressure between valve A and valve B. Record pressure and temperature every hour for about 24 hours after sample.
17.	Repeat steps 15 and 16 until end of test (ca. 120 days, see Section 5.2 for criteria for end). The 30-day period between samples may be adjusted, depending upon rate of gas production. On the final collection, do not add He after expansion.
18.	Before the end of the run, attach graduated cold finger (after calibration of volume at 5 °C) to valve C. Verify that leak rate is <0.01 Torr/hour. Measure volume of cold finger (beyond valve C). Connect cooling lines to water bath.
19.	Apply heating tape to side arm (valve C and the tubing between top of oven and cold finger).
20.	Determine the voltage that must be applied to heating tape to give a temperature around 75-80 °C. Repeat steps 18 - 20 for each reactor.
21.	Repeatedly expand gas from reactor into reference volume to measure free volume in the reactor, at the same time measuring the volume of gas removed from reactor. After each expansion, close valve A and pump out gas from manifold. Reduce pressure until <0.8 psia.
23.	Turn on heater to side arm of cold finger. Adjust voltage to maintain temperature of side arm at 75-85 °C. Turn on circulating, chilled water (5 °C) to cold finger.
24.	With reactor at 65 °C, record pressure and temperature, as well as the volume of liquid in cold finger at various times.

Table 1. Test Procedure for Gas Generation by Grout

25.	When distillation has effectively stopped at 65 °C, collect two gas samples (as in step 13), observing pressures to determine quantity of gas removed. In addition, collect gas samples whenever pressure increases above 6 psia, to maintain a low pressure during distillation. Then heat reactor to 105 °C (heat side arm to 115-125 °C). Record pressure and volume until distillation effectively stops.
26.	When distillation has effectively stopped at 105 °C, collect two gas samples as in step 13. Also, collect additional samples if pressure rises above 6 psia while heating at 105 °C. Again, note volume of gas removed on sample collection.
27.	Measure free volume of reactor (valve C closed), as in step 12.
29.	Open valve C and close valve A. Measure free volume in cold finger (with water), as in step 10. Close valve C.
30.	Remove cold finger and collect two aliquots of cooled liquid for analysis for pH, SpG, ammonia, nitrite, and nitrate.
31.	Remove reactor from oven. Remove lower portion of reaction vessel and observe dehydrated grout.

Table 2. Notes for Test Procedure for Gas Generation by Grout
(Numbers Refer to Steps in Table 1).

<p>2 (also 9). Keep the manifold leak rate small enough that the pressure buildup is <0.002 psi/hour (0.1 Torr/hour), so that the pressure buildup during the measurements (which typically last <1 hour) is less than 0.002 psi, which is 20% of the resolution of the pressure gauge. With a manifold volume of 70 mL, this is $(0.002/14.7)(70/3600) = 2.6 \times 10^{-6}$ mL-atm/s.</p>
<p>3. When loading grout material into reactor, minimize the free volume, so as to increase the sensitivity of the system to pressure changes. The radioactive grout has been cured inside the reactor bottom, to minimize the free volume. Minimize exposure to air in order to avoid removing moisture from the outer surfaces.</p>
<p>6. In the pressure test, He may be absorbed into pores in the grout. Thus, the pressure may drop when there is no leak. A leak will have a constant rate of drop over a longer range of pressure.</p>
<p>7. Leak test the reactor. For nonradioactive grout: observe the pressure as a function of time to eliminate any large leak. For radioactive grout: use helium leak tester after calibration of sensitivity. Then disconnect reactor from manifold (while pressurized with He at 29 psia), place it in the test chamber, seal test chamber lid with vacuum putty material, and evacuate chamber through the helium leak tester. This will verify that the reactor and valve A are free from leaks above a measured level. This level must be no larger than 10^{-7} mL-atm/s, with a level in the 10^{-9}-10^{-8} mL-atm/s range highly desirable.</p>
<p>10. (also 11, 12, 16, 21, 27, and 29). Measure the volumes by expanding into a sample bulb with a previously calibrated volume, followed by expanding from the pressurized bulb into the unknown volume. This process also replaces air in the reactor with helium. When measuring the reactor free volume, keep the minimum pressure at a value above the vapor pressure of water (which is smaller over a solution than over pure water; a value of 0.8-1 psia (40-50 Torr) is reasonably above the vapor pressure at 25 °C and 4.1-4.2 psia (210-220 Torr) is reasonable at 65 °C. Wait until pressures equilibrate (10 minutes should be adequate for samples with grout, 30 seconds when no grout is present, but only wait 4 minutes in step 10). Do two to four expansions from the reactor, alternating with expansions into the reactor, recording the pressure readings on both the gauge on the reactor and the gauge on the manifold. Each time, pressurize with He to 850-1050 Torr (17-20 psia). Pump to 40-50, or 210-220 Torr, at 25 or 65 °C, respectively. Do not pump for longer than 1 minute at pressures within 50 Torr of the desired pressure, to minimize water vapor loss. For step 10 do two expansions, in step 11 do four, in step 12 do three, in step 16 do two, and in steps 21, 27 and 29 do four.</p>

Table 2. Notes for Test Procedure for Gas Generation by Grout
(Numbers Refer to Steps in Table 1).

11. (also 12, 16, 21, 27, and 29). Compare readings with pressure gauge on manifold, to check pressure calibration. Check zero reading on 1000-Torr gauge by comparison with low-pressure reading on 10-Torr gauge.
13a. To collect sample in bulb: open valve B, evacuate bulb and manifold (<5 Torr), three He flushes (fill to 800-1000 Torr, pump to <5 Torr). Use reactor pressure and volumes of manifold, region between valves A and B, pressure gauge region of manifold, and sample bulb volume to choose volume to open to reactor during sampling. The final pressure after collecting two samples should be 14.5 to 19 psia inside the reactor. Therefore adjust the size of the volume that the gas expands into when valve A is opened, according to the pressure available. For example, use the minimum volume when the pressure is small: close valve B before opening valve A. If the pressure is larger, expand into a larger volume: e.g., close valves P and S (with valve B open) before opening valve A, or, if a larger pressure is available, close P and open S before opening valve A. After the initial expansion, close valve A and then expand into a volume containing the sample bulb. Record the volumes used, so that the quantity of gas removed can be calculated. After closing valve S, open valve P to get a pressure reading in the manifold, if valve P was closed earlier. If P is open to the reactor during the expansion, compare pressure readings. Open valve A fully for 10 to 20 seconds during the expansion. The object is to open far enough to avoid differential collection of He through a small opening, and to not be open long enough for the development of pumping effects from the condensation of water vapor.
13b. If final pressure is outside the range from 14.5 to 19 psia, redo step 12. Close valve B at end (valve A already closed), adjusting the pressure (adding He, if necessary) within the region from valve A to valve B to a value within 0.7 psi of pressure in reactor, to minimize leakage across valve A.
16. Allow pressure to equilibrate and gases to mix before the gas sampling by waiting overnight.
18. Attach graduated cold finger (after calibration of volume at 5 °C) to valve C. Verify that leak rate is <0.03 Torr/hour for each cold finger, so that 60-hour distillation will leak <2 Torr. Measure volume of cold finger (beyond valve C) on each reactor. Procedure as in step 10, except use valve C in place of valve A, pump to <5 Torr, use four expansion cycles, and only use manifold pressure gauge (as valve A is closed).
20. Keep entire side arm (and valves B and C) warmer than reactor, so that water vapor will condense only in cold finger.
25 (also 26). Maintain a low pressure during distillation to speed the diffusion of the water vapor to the cold finger.

8.0 SAFETY

The experimental procedure involves hazards because of radioactive material (in the case of the radioactive grout tests), using pressurized gas, and the possibility of overpressurizing the reactors. These safety concerns have been addressed previously for another test that measured gas generation while heating tank waste. The Job Safety Analysis, PCL 93-01, for that test is provided in Appendix B.

In these tests, use appropriate care in handling the compressed gas (helium). Also, avoid overpressurization by monitoring the gas pressure regularly (every 5 to 7 days), and by adjusting the power level to the ovens so that the maximum temperature will not exceed 75 to 85 °C. The latter step will ensure that a temperature controller failure would only modestly increase the gas generation rate. The present experiment is safer than the test discussed in Appendix B, where the maximum temperature was higher.

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9.0 QUALITY ASSURANCE

All testing will be conducted in accordance with laboratory procedures approved by Grout Technology or their designate and as documented by this test plan. The test plan has been categorized as impact level 2Q. The design and fabrication of the test equipment is not critical. The test procedure in this experiment will be to impact level 2Q.

The final report will outline the design and fabrication of the final test apparatus, and any changes made in the apparatus during the experiment. Changes to the experiment that do not affect the scope of the plan will be allowed by laboratory personnel, and documented by red lining the procedure. Changes that affect the scope or purpose of the plan will be performed only with the written approval of Grout Technology personnel.

A controlled notebook will be maintained in accordance with WHC-CM-5-4, Section 3.6, paragraph 6. Data from each test will be entered into the notebook, including notes on the test setup, observations regarding the performance of the system during the experiments, and analytical results from the sample analyses. Much of the data will be collected using data sheets developed to organize the conduct of the experiments to record relevant parameters in the appropriate sequence. These data sheets will be taped into the notebook.

The temperature and pressure calibrations are discussed in Section 5.8.4. Calculations for calibration and data reduction will be reviewed by a second scientist.

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10.0 LABORATORY QUALITY CONTROL SAMPLES

Quality control sample requirements vary depending on the analytical techniques. In general, the laboratory control samples include the following:

10.1 REFERENCE SAMPLES (STANDARDS)

These gas samples are used to estimate the accuracy of the analytical method. Reference samples are prepared from an independent, traceable standard. One or two of these samples are required for each batch of samples analyzed within a 2-week period; one is to be analyzed before the samples, and one after if there are more than 16 samples in the batch.

10.2 CALIBRATION BLANKS

These samples are used to calibrate the analytical instruments. The preparation and usage of these samples will be performed according to the requirements of the methods.

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11.0 PERFORMANCE AND SYSTEM AUDITS

The characterization and testing of the contents of Tank 102-AP for campaign 102 is a one-time project; it has been judged that project-specific performance and system audits are not required at this time. However, the performance of the analytical methods will be checked through the use of reference, and calibration blanks, (see previous section). In addition, Quality Assurance audits and surveillances are conducted randomly to evaluate overall laboratory activities.

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12.0 CORRECTIVE ACTION

The needs for QA-related corrective actions may be identified by the formal data validation and review process or informally by personnel who are involved in the characterization and testing of the samples. Grout Technology will implement the appropriate corrective actions or transmit the needs for corrective actions to the attention of appropriate responsible organizations. These corrective actions may include assigning a qualifier to the affected data, reviewing/modifying the sampling and analytical procedures, or resampling if necessary.

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13.0 QUALITY ASSURANCE REPORT

Although the characterization and testing of the contents of Tank 102-AP for Grout Campaign 102 is a one-time project, characterization of other grout feed will be needed in the future. Thus, a report summarizing the performance of the measurement systems, the data quality, the significant QA problems and recommended solutions should be included. Grout Technology will be responsible for preparing this report which may be a standalone or as part of the final characterization report.

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14.0 DATA SHEETS

Data sheets are provided for volume measurements. The volumes are measured by using the ideal gas law with a previously measured reference volume. The expansion cycles have an expansion from the unknown volume into a total volume that includes the unknown volume and the reference volume, alternating with expansion from the reference volume into the unknown volume. One or two sheets are used to record the two to four expansion cycles. The valves listed on the data sheets are shown in Figures 5-1 and 5-2. Data sheets are provided for use when measuring the manifold volume, the manifold volume and the volume between valves A and B, the volume of a sample bulb, and the free volume in a reactor containing grout, with sheets for this determination provided for both room temperature and 65 °C.

Manifold Volume Determination from Reference Volume, Page of 2, Date:

Room Temperature _____								
Mount Reference Volume Bulb: _____								
Manifold: _____								
Measure manifold volume (ideal gas law) from known reference volume. Four expansions from manifold into reference volume, alternating with expansion into manifold. Use He; fill to 800-1050 Torr, pump to <5 Torr. Valve S always Open. See manifold diagram for valve identities.								
Valve Positions. Valves B are over reactors, always Closed. V is for vacuum, R is reference bulb valve.				Comment	Time	Target Manif. Press. (Torr)	1000-Torr Gauge Pressure	10-Torr Gauge (Only Read When on Scale)
Action	B	R	V					
Pump Out	C	O	O C			<5		
Close R	C	C	C			<5		
He Fill	C	C	C			800		
Open R	C	O	C					
Close R	C	C	C					
Pump out	C	C	O C			<5		
Open R	C	O	C					
Pump Out	C	O	O C			<5		
Close R	C	C	C			<5		
He Fill	C	C	C			800		
Open R	C	O	C					
Close R	C	C	C					
Pump out	C	C	O C			<5		
Open R	C	O	C					

Observer _____ Date _____

Measure Manifold Vol+Volume Between Valves A&B for Reactor from Ref. Volume.
 Page of 2, Date: _____

Room Temperature _____								
Mount Reference Volume Bulb: _____								
Manifold: _____								
Measure manifold volume (Valves P, S Open) plus volume between valves A and B on Reactor: _____ (Valve C Closed) versus reference volume. Four expansion cycles using He: fill to 800-1050 Torr, pump to <5 Torr.								
Valve Positions. Valve B for one reactor Open, Valve A Closed. V is for vacuum, R is reference bulb valve.				Comment	Time	Target Manif. Press. (Torr)	1000-Torr Gauge Pressure	10-Torr Gauge (Only Read When on Scale)
Action	B	R	V					
Pump Out	0	0	0 C			<5		
Close R	0	C	C			<5		
He Fill	0	C	C			800		
Open R	0	0	C					
Close R	0	C	C					
Pump out	0	C	0 C			<5		
Open R	0	0	C					
Pump Out	0	0	0 C			<5		
Close R	0	C	C			<5		
He Fill	0	C	C			800		
Open R	0	0	C					
Close R	0	C	C					
Pump out	0	C	0 C			<5		
Open R	0	0	C					

Observer _____ Date _____

Sample Bulb Volume Measurement from Manifold Volume, Page of 2, Date: _____

Room Temperature _____								
Mount Sample Volume Bulb: _____								
Manifold: _____								
Measure sample bulb volume using previously calibrated volume of manifold above valves B to reactors. Four expansion cycles with He: fill to 800-1050 Torr, pump to <5 Torr. Valve P is always Open.								
Valve Positions. Valves B are over reactors, always Closed. V is for vacuum, R is sample bulb valve.				Comment	Time	Target Manifold Pressure (Torr)	1000-Torr Gauge Pressure	10-Torr Gauge (Only Read When on Scale)
Action	B	R	V					
Pump Out	C	O	O C			<5		
Close R	C	C	C			<5		
He Fill	C	C	C			800		
Open R	C	O	C					
Close R	C	C	C					
Pump out	C	C	O C			<5		
Open R	C	O	C					
Pump Out	C	O	O C			<5		
Close R	C	C	C			<5		
He Fill	C	C	C			800		
Open R	C	O	C					
Close R	C	C	C					
Pump out	C	C	O C			<5		
Open R	C	O	C					

Observer _____ Date _____

Measure Reactor Free Volume (With Grout), Room Temperature, Date: _____

Reactor Temperature _____				Reference Volume _____				
At Low Pressure: 1000-Torr: _____				10-Torr: _____				
<p>Measure free volume in reactor with grout (valve C always Closed and valve B always Open) plus manifold volume (valves P,S always Open) from reference volume. Two expansion cycles with He: fill to 850-1050 Torr, pump to 40-50 Torr. Press calibration button on reactor pressure readout, and short sensor output for readout zero, for two runs at low and high pressures. Wait 4 minutes for partial equilibration at each pressure change.</p>								
Valve Positions. Valve A is Open. V is for vacuum, R is ref volume.				Reactor Pressure (psia)	Time	Set Man. Pres Torr	1000-Torr Gauge Press.	Comments
Action	A	R	V	4 minutes			4 minutes	
Pump Out	0	0	0 C			<50		
Close R RPCalib RP Zero	0	C	C			<50 Cal. Zero		
He Fill RPCalib RP Zero	0	C	C			900 Cal. Zero		
Open R	0	0	C					
Close R	0	C	C					
Pump out	0	C	0 C			<50		
Open R	0	0	C					
Pump Out	0	0	0 C			<50		
Close R	0	C	C			<50		
He Fill	0	C	C			900		
Open R	0	0	C					
Close R	0	C	C					
Pump Out	0	C	0 C			<50		
Open R	0	0	C					

Observer _____ Date _____

Measure Reactor Free Volume (With Grout). Page of . 65 °C Temperature.
Date:

Reactor Temperature _____				Reference Volume _____						
At Low Pressure: 1000-Torr: _____				10-Torr: _____						
<p>Measure free volume in reactor with grout (valve C always Closed and valve B always Open) plus manifold volume (valves P,S always Open) from reference volume. Three (or 2) expansion cycles with He: fill to 950-1050 Torr, pump to 210-220 Torr. Press calibration button on reactor pressure readout, and short sensor output for readout zero, for two runs at low and high pressures (at 6 minutes delay). Wait for equilibration at each pressure change, take readings at 4, 6, and 10 minutes.</p>										
Valve Positions. Valve A is Open. V is for vacuum, R is ref volume.				Reactor Pressure (psia)		Time	Set Man. Pres Torr	1000-Torr Gauge Press. (Torr)		
Action	A	R	V	6min	10min			4min	6min	10m
Pump Out	0	0	0 C				<220			
Close R RPCalib RP Zero	0	C	C				<220 Cal. Zero			
He Fill RPCalib RP Zero	0	C	C				1000 Cal. Zero			
Open R	0	0	C							
Close R	0	C	C							
Pump out	0	C	0 C				<220			
Open R	0	0	C							
Pump Out	0	0	0 C				<220			
Close R	0	C	C				<220			
He Fill	0	C	C				1000			
Open R	0	0	C							
Close R	0	C	C							
Pump out	0	C	0 C				<220			
Open R	0	0	C							

Observer _____ Date _____

15.0 REFERENCES

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APPENDIX A

WASTE SOURCE TERM FOR MAKE-UP OF SYNTHETIC WASTE

From: Grout Technology
Phone: 3-1072 R4-03
Date: December 17, 1992
Subject: WASTE SOURCE TERM FOR MAKE-UP OF SYNTHETIC WASTE

7E220-92-192

To: A. P. Hammitt T6-50

cc: S. D. Bolling T6-30
J. M. Conner R4-03
P. J. Crane H11-14
D. W. Hendrickson R4-03
C. A. Hinman H0-33
M. J. Horhota H4-16
J. W. Shade R4-03
J. A. Voogd R4-03
G. H. Weissberg R3-10
WJP:GT/File LB

The purpose of this memo is to transmit the subject composition to allow make up of synthetic waste at the 222-S Laboratory. Please review the information and contact me if there are problems or suggestions.

The attached table is modified from the draft document WHC-SD-WM-TP-136 by Doug Hendrickson, and based on the sample results from 102-AP and 106-AN, WHC-SD-TP-065. Mean concentration values for campaign 102 are used because the gas generation and liquid evolution from the grout needs to be the average of the entire vault, not the worst case. When we are working with one million gallons of grout the best estimate (mean) rates are needed. In most of the uses the 95 percent confidence interval can be calculated when the mean rates are known, which can supply limiting boundaries for proposed Safety Analysis Report Operational Safety Requirements. The 102-AP mean final values shown on the table should be the target points for make up of the synthetic waste solution, with the following exceptions:

- The organic waste addition should include only the main 4 major ingredients, EDTA, HEDTA, citric acid, and hydroxyacetic acid. The total organic of 7070 ppm should be made up of the 4 major organics in proportion. Since this difference is only 12 ppm organics, (0.17 percent) major corrections are not expected.
- Include chemicals to the waste for 102-AP final mean concentrations which are more than 100 ppm for ions Ag to S-2. The concentrations of compounds not included will not be significant when the dry materials are added to the waste to make grout. Specifically the fly ash and Attapulgate clay composition will have a significant amount of impurities in it from the combustion process and mining. The dry blend miscellaneous ion addition will dwarf that of the minor components in the waste.

A. P. Hammitt
Page 2
December 17, 1992

7E220-92-192

The mean final 102-AP compositions represent 12 percent AP-102 waste, and 88 percent AN-106 waste.

Note that the appropriate potentially hazardous metals are to be included in the waste. This was not done with the PNL pilot plant material.

Justification of the waste ingredients are given in WHC-SD-WM-TP-082, Grout Formulation Verification...Test Plan. The waste plan justification given in -082 can serve as the basis of other test plans justification as needed.

The following organizations will need this waste:

Geotechnical Eng/Paul Crane-20 gal

222-S Lab/Paul Hammitt/Argonne National Laboratory samples-.5 gal
(100 cylinders, .5 inch diameter by 6 inch long)

222-S Lab/PH and Chet Hinman/Co60 test-1 gal
(10 cylinders, 5 inch diameter by 5 inches long)

Add 10 percent for misc

TOTAL 24 gal

If there are any suggestions or changes to the recommended waste composition please contact on 373-1072.

W. J. Powell, Principal Engineer
Grout Technology

bce

Attachment.

106-AN and 102-AP Blended Composition									
			102-AP	106-AN	106-AN	106-AN 95% confidence composition	102-AP final mean	102-AP Final	102-AP Final
Component	Units	MW	Heel	Mean	SD	Comp.	see units	g/L	Mol/L
Ag	ppm	107.868	0.094729	< 3.63		3.63	3.20	3.20e-03	2.97e-05
Al	ppm	26.98154	0.947291	9590	1710	12661.16	*8429.29	8.43e+00	3.12e-01
As	ppm	74.9216	0.047365	0.072		0.072	0.07	6.90e-05	9.21e-07
B	ppm	10.81		* 32.0		31.993	28.12	2.81e-02	2.60e-03
Ba	ppm	137.33	0.473645	< 11.1		11.1	9.81	9.81e-03	7.15e-05
Be	ppm	9.01218	0.018946			0	0.00	2.29e-06	2.54e-07
Bi	ppm	208.9804	2.841872	< 145		145	f 127.79	1.28e-01	6.12e-04
Ca	ppm	40.08	0.852562	77.3	14.3	102.9828	68.05	6.80e-02	1.70e-03
Cd	ppm	112.41	0.189458	< 49.6		49.6	43.62	4.36e-02	3.88e-04
Ce	ppm	140.12		*< 5		5.0059	4.40	4.40e-03	3.14e-05
Cr	ppm	51.996	1.610394	569	95.4	740.3384	500.32	5.00e-01	9.62e-03
Cu	ppm	63.546	0.189458	< 3.75		3.75	3.32	3.32e-03	5.22e-05
Fe	ppm	55.847	1.799853	< 6.90		6.9	6.28	6.28e-03	1.12e-04
Hg	ppm	200.59	0.000379	< 0.05		0.05	0.04	4.40e-05	2.19e-07
K	ppm	39.0983	9.472908	1020	144	1278.624	f 897.68	8.98e-01	2.30e-02
La	ppm	138.9055		*< 0.4		0.41941	0.37	3.69e-04	2.65e-06
Li	ppm	6.941		*< 7.8		7.8471	6.90	6.90e-03	9.94e-04
Mg	ppm	24.305	1.326207	2.78		2.78	2.60	2.60e-03	1.07e-04

MHC-SD-MM-TP-180, Rev. 0

106-AN and 102-AP Blended Composition										
			102-AP		106-AN	106-AN	106-AN 95% confidence composition	102-AP final mean	102-AP Final	102-AP Final
Component	Units	MW	Heel		Mean	SD	Comp.	see units	g/L	Mol/L
Mn	ppm	54.938	0.094729	<	55.6		55.6	48.88	4.89e-02	8.90e-04
Mo	ppm	95.94	0.473645	<	66.6		66.6	58.60	5.86e-02	6.11e-04
Na	ppm	22.98977	11367.77		89300	10100	107439.6	79866.63	7.99e+01	3.47e+00
Nd	ppm	144.24		*<	17.6		17.588	15.46	1.55e-02	1.07e-04
Ni	ppm	58.7	0.189458	*	69.4		69.4	61.02	6.10e-02	1.04e-03
P	ppm	30.97376	5020.641		6270	772	7656.512	6118.77	6.12e+00	1.98e-01
Pb	ppm	207.2	3.789163	<	460		460	404.78	4.05e-01	1.95e-03
Pd	ppm	106.4		*<	38		37.882	33.30	3.33e-02	3.13e-04
Sb	ppm	121.75	7.578327				0	0.92	9.17e-04	7.53e-06
Se	ppm	78.96	0.047365		0.134		0.134	0.12	1.24e-04	1.56e-06
Si	ppm	28.0855	2.273498	*	50.2		50.2	44.40	4.44e-02	1.58e-03
Sn	ppm	118.69	4.736454				0	0.57	5.73e-04	4.83e-06
Ta	ppm	180.9479		*<	176		175.88	154.59	1.55e-01	8.54e-04
Ti	ppm	47.9	0.094729	<	3.51		3.51	3.10	3.10e-03	6.46e-05
U	ppm	238.029	0.208404		4		4	3.54	3.54e-03	1.49e-05
V	ppm	50.9415	0.284187				0	0.03	3.44e-05	6.75e-07
W	ppm	183.85	4.736454				0	0.57	5.73e-04	3.12e-06
Zn	ppm	65.38	4.736454	<	9.44		9.44	8.87	8.87e-03	1.36e-04

A-4

MHC-SD-WM-TP-180, Rev. 0

106-AN and 102-AP Blended Composition

			102-AP	106-AN	106-AN	106-AN 95% confidence composition	102-AP final mean	102-AP Final	102-AP Final
Component	Units	MW	Heel	Mean	SD	Comp.	see units	g/L	Mol/L
Zr	ppm	91.22	4.736454	< 27.8		27.8	25.01	2.50e-02	2.74e-04
CN-	ppm	26.0177	0.094729	6		6	5.29	5.29e-03	2.03e-04
S-2	ppm	32.06	0.947291			0	0.11	1.15e-04	3.58e-06
NH4+	M	18.0383	0.357106			0	0.04	7.80e-01	4.32e-02
NH3	M	17.0304		0.0072		0.00722238	0.01	1.08e-01	6.35e-03
CO3-2	M	60.0092	0.031261	0.350	0.065	0.46674	0.31	1.87e+01	3.11e-01
Cl-	M	35.453	0.000976	0.071	0.011	0.09111206	0.06	2.21e+00	6.23e-02
F-	M	18.9984	0.000828	< 0.0023		0.00231598	0.00	4.06e-02	2.14e-03
SO4-2	M	96.0576	0.016578	0.0268	0.0040	0.03391578	0.03	2.45e+00	2.55e-02
NO3-	M	63.0049	0.001914	1.187	0.200	1.54638131	1.04	6.58e+01	1.04e+00
NO2-	M	46.0055	0.010863	0.601	0.010	0.61896	0.53	2.44e+01	5.30e-01
PO4-3	M	94.97136	0.162934	0.1885	0.0236	0.23083843	0.19	1.76e+01	1.85e-01
OH-	M	17.0073	0.105546	0.484	0.128	0.713888	0.44	7.45e+00	4.38e-01
TOC	g/L	12.011	0.179985	3.26		3.26	2.89	2.887177	0.240378

A-5

106-AN and 102-AP Blended Composition									
Component	Units	MW	102-AP Heel	106-AN Mean	106-AN SD	106-AN Comp.	102-AP Final mean	102-AP g/L	102-AP Mol/L
2-Phenoxyethanol	ppm	138.17	0.161039	0.710		0.71	6.44e-01	6.44e-04	4.66e-06
Phoxyethoxyethanol	ppm	182.22	0.445227	0.590		0.59	5.72e-01	5.72e-04	3.14e-06
Phenoxydiethoxyethanol	ppm	226.27	0.009473	1.200		1.2	1.06e+00	1.06e-03	4.67e-06
Undecane	ppm	156.32	0.009473			0	1.15e-03	1.15e-06	7.34e-09
N Alkanes	ppm	366.71	0.97571			0	1.18e-01	1.18e-04	3.22e-07
Alicyclic Alkanes	ppm	378.72	0.161039			0	1.95e-02	1.95e-05	5.15e-08
Diethylphthalate	ppm	390.62	0.047365			0	5.73e-03	5.73e-06	1.47e-08
Benzeneacetic Acid	ppm	137.16	0.009473			0	1.15e-03	1.15e-06	8.36e-09
N,N-diethylthiourea	ppm	132.23	0.009473			0	1.15e-03	1.15e-06	8.67e-09
Butanedioic Acid (Succinic Acid)	ppm	118.09	20.36675			0	2.47e+00	2.47e-03	2.09e-05
EDTA	ppm	292.25	0.97571	1131.551		1131.551	9.95e+02	9.95e-01	3.40e-03
Citric Acid	ppm	192.14	1.951419	1859.847		1859.847	1.63e+03	1.63e+00	8.51e-03

106-AN and 102-AP Blended Composition

Component	Units	MW	102-AP Heel	106-AN Mean	106-AN SD	106-AN Comp.	102-AP Final mean	102-AP g/L	102-AP Mol/L
MeEtIC	ppm	127.14	3.410247			0	4.13e-01	4.13e-04	3.25e-06
Acetone	ppm	58.08		0.074		0.074	6.50e-02	6.50e-05	1.12e-06
Butanone, 2-	ppm	72.12		0.075		0.075	6.59e-02	6.59e-05	9.14e-07
Dichloroethene, 1,1-	ppm	96.94		< 0.011		0.011	9.67e-03	9.67e-06	9.97e-08
Trichloroethene	ppm	131.39		< 0.022		0.022	1.93e-02	1.93e-05	1.47e-07
Toluene	ppm	92.15		< 0.022		0.022	1.93e-02	1.93e-05	2.10e-07
Chlorobenzene	ppm	112.56		< 0.023		0.023	2.02e-02	2.02e-05	1.80e-07
Phenol	ppm	94.11		< 0.1		0.1	8.79e-02	8.79e-05	9.34e-07
Nitrobenzene	ppm	123.11		< 0.035		0.035	3.08e-02	3.08e-05	2.50e-07
Benzoic Acid	ppm	122.13		< 0.62		0.62	5.45e-01	5.45e-04	4.46e-06
Dinitrophenol, 2,4-	ppm	184.11		< 1.1		1.1	9.67e-01	9.67e-04	5.25e-06
Diethylphthalate	ppm	222.24		< 0.02		0.02	1.76e-02	1.76e-05	7.91e-08
Di-n-butylphthalate	ppm	278.38		< 0.38		0.38	3.34e-01	3.34e-04	1.20e-06
Butylbenzylphthalate	ppm	302.4		< 0.12		0.12	1.05e-01	1.05e-04	3.49e-07
bis(2-Ethylhexyl)phthalate	ppm	390.62		< 0.046		0.046	4.04e-02	4.04e-05	1.04e-07

A-7

106-AN and 102-AP Blended Composition									
Component	Units	MW	102-AP Heel	106-AN Mean	106-AN SD	106-AN Comp.	102-AP Final mean	102-AP g/L	102-AP Mol/L
2-Chloro cyclohexanone	ppm	132.59	<	0.37		0.37	3.25e-01	3.25e-04	2.45e-06
1,2-Dichloro cyclohexane	ppm	153.05	<	1.2		1.2	1.05e+00	1.05e-03	6.89e-06
1-Bromo-2-chl oro cyclohexane	ppm	197.5	<	1.1		1.1	9.67e-01	9.67e-04	4.90e-06
2,7-Dimethyl- 2,6-Octadiene	ppm	138.25	<	0.41		0.41	3.60e-01	3.60e-04	2.61e-06
Hydroxyacetic acid	ppm	76.052		736.156		736.156	6.47e+02	6.47e-01	8.51e-03
HEDTA	ppm	278.26		4309.533		4309.533	3.79e+03	3.79e+00	1.36e-02
Total Organic	ppm		28.5324	8045.315		8045.315	7074.917	7.074917	0.034103
Volume	gal		135650	985000		985000	1120650		
Volume	L		513480	3728550		3728550	4242030		
Volume	inches		49.327	358.182		358.182	407.509		

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APPENDIX B

JOB SAFETY ANALYSIS

JOB SAFETY ANALYSIS	Job Description	JSA Number
	Gas Generation from Tank Waste	PCL 93-01
	Component	Building/Area
	Process Chemistry Laboratories	222S 200W
Reviewed By INDUSTRIAL SAFETY AND FIRE PROTECTION	Prepared By	Date
	J. C. Person	05/26/93
Date 6-2-93	Initials <i>JCP</i>	Review Dates
SAFETY EQUIPMENT REQUIRED	TOOLS AND EQUIPMENT REQUIRED	JOB PREPARATION
HMPD, Finger Rings, Coveralls, Shoe Covers, 2 pr. Surgeons' Gloves, Radioactive Hood, Lab Eyewash and Shower, Radioactive Shielding, Tray, Hot Cell with Weighted Support for Sample for Job Step 1.	Apparatus (furnished), all-metal construction, as shown in diagram.	Leak test apparatus so that apparatus will be leak-free when assembled with Cu gasket. Check for safe appearance of electrical connections and insulation. Review RWP #S-006. Have dose rate measurement on sample material.
	HAZARDOUS MATERIALS	RELATED REQUIREMENTS
	Radioactive waste from tanks (e.g., 101-SY), which is corrosive (pH >13). Pressurized cylinder of helium (He).	Radiation Work Procedure Yes ☒ No ☐ Nuclear Safety Specification Yes ☐ No ☒
JOB STEP	HAZARD	HAZARD CONTROL AND PROTECTIVE EQUIPMENT
See attached table of safety rules for hazardous steps.	See attached.	See attached.

Safety Rules for Hazardous Steps in Test Procedure for Gas Generation Experiments (Job Step Number Refers to Step in Table 1).

Job Step	Hazard	Safety Rules and Safe Practices
1. Load waste material into lower portion of reaction vessel within hot cell. Move into hood.	Sample will read around 1.5 Rad. Spilling sample.	Seal vessel with stopper. Use weighted sample support to prevent sample tipping. Place sample in tray behind shielding.
2. Assemble reaction vessel using Cu gasket.	Dose.	Use plate nuts to speed assembly. Use shielding.
3. Place reaction vessel in oven, connect to manifold.	Dose.	Place shielding in front of oven as soon as possible.
4. Add He to test reaction vessel for leaks by observing rate of pressure decrease at pressures around 1200 Torr (8.5 psi). Same applies to addition of He in job steps 6, 7, 9, 11, 12, 14, 16, 17	Use of pressurized gas.	Adjust pressure regulator on cylinder to deliver 10 to 12 psi. Open valve to line to manifold. Slowly open valve on manifold, do not exceed 1200 Torr (8.5 psi).
13. After 30 days (or if pressure above 1150 Torr), cool to ambient. Same applies to pressure buildup in step 18.	Overpressurization of system by gas generation.	Monitor pressure and rate of increase at least every 5 days. Use two methods to limit oven temperature. See separate analysis.
14. Collect sample in bulb: open valve B, evacuate bulb and manifold, 3 He flushes, 750 Torr (14.5 psia) to <10 Torr, open bulb and valve A to sample.	Dose. Heated handle of valve A at 100°C. Use of pressurized gas.	Use secondary shielding to reduce dose while oven door is open. Use leather gloves to open valve A. Use rules in step 6 for gas handling.
22. Remove reactor from oven. Remove lower portion of reaction vessel.	Dose. Spillage.	Keep sample behind shielding when possible. Use tray under area. Keep vessel upright.
23. Prepare sample for analysis.	Dose. Spillage.	Keep sample over tray and behind shielding. Be careful transferring material into vial.

Table 1. Test Procedure for Gas Generation Experiments

1. Load waste material into lower portion of reaction vessel.
2. Assemble reaction vessel: Cu gasket between flanges, bolt together.
3. Place reaction vessel in oven, connect to manifold.
4. Add He (around 1200 Torr) for leak test of reaction vessel. Use He leak test equipment, or observe rate of pressure decrease.
5. At ambient temperature, pump out to 20 Torr.
6. Three flushes with He: fill to 800 Torr, pump to 20 Torr. Compare pressure readings with pressure gauge on vacuum system.
7. Fill with He to 140 Torr (all pressures are total pressures).
8. Heat to 75°C for 3 - 5 hrs, pump to 180 Torr.
9. Three flushes with He: fill to 800 Torr, pump to 180 Torr.
10. Cool to ambient overnight, repeat steps 5 and 6.
11. Helium fill to 140 Torr, heat to 65°C for 3 days, repeat step 10.
12. Helium fill to 650 Torr, heat to 65°C, pump to 760 Torr.
13. After 30 days (or if pressure above 1150 Torr), cool to ambient.
14. Collect sample in bulb: open valve B, evacuate bulb and manifold, three He flushes (fill to 750 Torr, pump to <10 Torr), then open valve A to sample directly from vessel. Compare pressure readings, as in step 6.
15. Repeat steps 5 and 6.
16. Helium fill to 140 Torr, heat to 100°C for 2 days, repeat step 10.
17. Helium fill to 350 Torr. Heat to 100°C. Pump/add He to give 760 Torr.
18. After 10 to 30 days (when pressure builds up, keep pressure below 1200 Torr), collect sample in bulb, as in step 14. Cool to ambient.
19. Repeat step 14.
20. Repeat steps 15 and 17.
21. Repeat steps 18 and 19.
22. Remove reactor from oven. Remove lower portion of reaction vessel.
23. Prepare sample for analysis.
24. Repeat experiment, possibly with additional degassing. If still generating gas at step 21, repeat steps 17 - 19.

Analysis of Overpressurization Danger from Gas Generation.

The sample chamber is constructed 304-stainless steel; see Fig. 1 for a diagram. An Ultra-High Vacuum (UHV) flange is welded to a tube with 0.065" walls, which is closed by welding to a flat plate that is 0.12-in. thick. The apparatus includes other UHV vacuum components, a pressure transducer, 0.25" o.d. tubing, and a Millipore Wafergard F mini inline gas filter. Only the filter is pressure tested (3000 psi). The remainder of the system must be kept below 15 psi, as it has not been qualified under WHC-CM-4-3, Industrial Safety Stds, Standard PS-4. In this standard, Section 1 defines pressure systems as those that operate at pressures more than 15 psi (1536 Torr).

The pressure transducer is calibrated to operate up to 1200 Torr (8.5 psi), and it may be damaged by pressures above 20 psi. Thus, there is no desire to operate the apparatus as a pressure vessel. This analysis is to ensure that pressures do not exceed 15 psi, and that normal operation limits the pressure to 8.5 psi or less. The analysis is for experiments to be conducted at temperatures of 65 to 100°C.

In our previous experiments using material from tank 101-SY, the rate of gas generation at 100°C was measured at values (expressed in units of mmole of gas produced per day per mole of organic carbon) around 0.3. The reported values for four individual measurements varied from 0.19 to 0.38 mmole/day/moleC, for material with 84 to 93 mmoleC present in sample volumes of 30 to 58 mL. In this analysis, the rate of pressure buildup is taken as 0.3 mmole/day/moleC.

We first calculate a base gas generation rate, assuming that 100 mmoleC is present. This rate is 0.03 mmole/day, or 0.9186 mL-atm/day at 100°C. The apparatus has a free volume of about 95 mL, so the rate of pressure rise is 0.0097 atm/day, or 7.349 Torr/day. Thus, the expected pressure increase in a 5-day period is about 37 Torr. For the limiting case where the gas generation rate was 10-times as large as expected, the pressure increase in 5 days would only be 367 Torr (7 psi).

By using the criterion that the gas will be sampled to reduce the pressure whenever the pressure exceeds 1150 Torr (7.5 psi), the maximum pressure will not exceed 15 psi after 5 days, even if the gas generation rate is 10 times the expected rate. As the experiment progresses, the observed rate of pressure buildup can be used to better predict the pressures expected. Also, the variability observed in the rate of pressure rise can be used to give more realistic estimates of the maximum pressure expected after 5 days. Thus, the pressure can be reduced sooner, if the pressure rise is more rapid, or the pressure can be monitored more often.

The rate of gas buildup will be lower at lower temperatures, so that monitoring pressures at 5-day intervals will ensure that the pressures remain low. Thus, the above analysis indicates that monitoring the pressure at 5-day intervals is conservative, allowing for a factor of 10 in the rate above the earlier result. However, it is not good practice to monitor at time intervals much longer than 5 days because of other concerns (e.g., the chart recorder paper may run out).

The pressure could increase at a rate 10 times faster if the temperature were increased to values well above 100°C. The change in rate at different

temperatures can be predicted from the activation energy. For example, the rate of gas generation in the tank and the rate observed in the laboratory at 100°C can be used to give a rough estimate of 14.4 kcal/mole for the activation energy. A more conservative estimate of the increased rate from heating comes from using the 24.5 kcal/mole activation energy reported for HEDTA in simulated tank waste. At this activation energy, the rate will increase a factor of 10 for a temperature increase to 128°C. Thus, using a second method that limits the oven temperature to a value around 120°C will thus provide a safe environment, even if the primary temperature controller were to fail in the "on" position. This second method can be achieved by adjusting the maximum power to the oven, by using another temperature controller, or by using a temperature limit switch.