

Gas Concentration Measurements in Underground Waste Storage Tanks

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Section 1: Introduction

Currently over 100 underground tanks at the Hanford facility in eastern Washington state are being used to store high-level radioactive waste. With plans for a long-term nuclear-waste repository in Nevada in place (though not yet approved), one promising use for these underground storage tanks is as a temporary waystation for waste destined for the Nevada repository. However, without a reasonable understanding of the chemical reactions going on within the tanks, transporting waste in and out of the tanks has been deemed to be unsafe.

One hazard associated with such storage mechanisms is explosion of flammable gases produced within the tank. Within many of the storage tanks is a *sludge* layer. This layer, which is a mixture of liquid and solids, contains most of the radioactive material. Radioactive decay and its associated heat can produce several flammable materials within this layer. Two components of particular concern are hydrogen (H_2) and nitrous oxide (N_2O), since they are highly volatile in the gaseous phase. Though the tanks have either forced or natural convection systems to vent these gases, the possibility of an explosion still exists.

Measurements of these gases are taken in several ways. Continuous measurements are taken in the *headspace*, which is the layer between the tank ceiling and the liquid (supernatant) or sludge layer below. (For a schematic of some general tank designs, see Fig. 1.) In tanks where a supernatant layer sits atop the sludge layer, there are often *rollovers* or *gas release events* (GREs), where a large chunk of sludge, after attaining a certain void fraction, becomes buoyant, rising through the supernatant and releasing its associated gas composition to the headspace. Such changes trigger a sensor, and thus measurements are also taken at that time.

Lastly, a *retained gas sample* (RGS) can be taken from either the supernatant or sludge layer. Such a core sample is quite expensive (roughly a million dollars per series), but can yield crucial data about the way gases are being produced in the sludge and convected through the supernatant.

Unfortunately, the measurements from these three populations do not seem to match. In particular, the ratio

$$r = \frac{[\text{N}_2\text{O}]}{[\text{H}_2]} \quad (1.1)$$

varies from population to population. r also varies from tank to tank, but this can more readily be explained in terms of the waste composition of each tank. Since H_2 is more volatile than N_2O (and since there are more sources of oxygen in the headspace), lower values of r correspond to more hazardous situations.

This variance in r is troubling, since we need to be able to explain why certain values of r are lower (and hence more dangerous) in certain areas of the tank. In this report we examine the data from three tanks. We first verify that the differences in r among

populations is significant. We then postulate several mechanisms which could explain such a difference.

Section 2: Statistical Testing

Before attempting to explain any differences in the measurements of r among populations, we must verify that the differences are statistically significant. We divide the measurements into three groups: those *steady-state* measurements taken at regular intervals in the headspace, the measurements in the headspace taken directly after a gas release event (GRE), and retained gas samples (RGS) in the two components of the core: the supernatant and the sludge.

Once we have our sample sets r_i for each region, we use a standard t -test to test if the means of the populations are different. The t -test assumes that the variables are normally distributed. However, the variances of each population may be different. (For more details on the description and use of the t -test, see [1].) Fortunately, Excel can handle this type of calculation. We can do the t -test for both r and r^{-1} ; since the variances are different in each case, we get different results.

The raw data from [2], as well as the details of the statistical calculations, are listed in Tab. 1–3. There are three tanks under consideration. Tank AW-101 has a lower sludge layer, an upper supernatant layer, and a thin layer of crust between the supernatant and the headspace (see Fig. 1). Statistically, we have a high degree of certainty that the mean r in the sludge is different from the mean r in both the steady-state and GRE samples. Since there was only one supernatant measurement, we could not perform the t -test there. From the data it seems statistically reasonable to conclude that the mean r in the steady-state and GRE are the same (or nearly so).

Tank AN-105 has the same configuration as AW-101. Here the analysis indicates that the supernatant layer does not have the same mean as any of the other samples. However, the confidence intervals for the other populations are much smaller. The closest relationship between the means is between the GRE events and the sludge.

Tank A-101 has an inverted configuration: there is a sludge layer floating on top of a supernatant layer. Due to this configuration, there are no rollovers. In this tank, there are large (greater than 95%) confidence intervals that the means of the steady-state, sludge, and supernatant measurements are all different.

One note regarding weighting: for the standard analysis, when we computed the mean associated with each sample or each region, we weighted using the percentage of H_2 in the sample. This is necessary because one must always weight according to the denominator of the ratio. However, upon later examination we found qualitatively that the amount of N_2O in each sample varied less than the amount of H_2 . Therefore, more reliable *weighted* means may be realized by calculating the mean of the weighted r_i^{-1} , rather than the weighted r_i .

Section 3: Solubility, No Adsorption

At first blush, there seem to be two possible ways for gas to transport from the sludge through the supernatant in tanks where the sludge is at the bottom. Either gas bubbles are produced which rise to the surface, or supersaturated aqueous solution is thermally convected to the surface, where it evaporates. However, when an RGS is taken, the components H_2 and N_2O are extracted in a vacuum. Hence, the measured r is some weighted average of the ratio of components in the gaseous phase and the ratio of components in the aqueous phase. Thus, the first step is to determine how these two effects contribute to the measured value of r .

At equilibrium, Henry's Law relates the concentration in various phases ([3], p. 189):

$$[\text{comp. } i(\text{aq})] = K_i RT [\text{comp. } i(\text{g})], \quad (3.1)$$

where K_i is the Henry's Law constant (usually expressed as K_H) for component i , R is the ideal gas constant, and T is the temperature. Since we use vacuum extraction to measure the components, we can measure only the total concentration of any substance. Therefore, we must establish a relationship between the concentration in the gaseous phase and the total concentration:

$$[\text{comp. } i] = [\text{comp. } i(\text{aq})]v_1 + [\text{comp. } i(\text{g})]v_g \quad (3.2a)$$

$$[\text{comp. } i] = [\text{comp. } i(\text{g})](v_g + K_i RT v_1)$$

$$[\text{comp. } i(\text{g})] = \frac{[\text{comp. } i]}{v_g + K_i RT v_1}, \quad (3.2b)$$

where v_g is the proportion of the volume of the core sample in the gas phase, and v_1 is the proportion of the volume of the core sample in the liquid phase. Here we have used (3.1).

To calculate the ratio in the gas phase, we have

$$r_g = \frac{[\text{N}_2\text{O}(\text{g})]}{[\text{H}_2(\text{g})]} = \frac{[\text{N}_2\text{O}](v_g + K_{\text{H}_2} RT v_1)}{[\text{H}_2](v_g + K_{\text{N}_2\text{O}} RT v_1)}, \quad (3.3)$$

where we have used (3.2b). Note that since we have calculated the ratio, the proportion of any other gases (such as N_2) in solution is not needed. We make an additional observation. The quantity $K_i RT$ is quite small (on the order of 10^{-3} or less). Therefore, unless v_g is very small, we see that each of the parentheses in (3.3) may be replaced by v_g , and hence r_g is approximately the measured r .

Unfortunately, in the tables in [2], volume fractions are measured as percentages of the non-gas waste, which we shall denote by w . Therefore, we see that

$$1 + w_g = \frac{V_1 + V_s + V_g}{V_1 + V_s} = \frac{V_T}{\text{non-gas waste}}, \quad (3.4)$$

where V is the volume of each phase. Using (3.4), we see that

$$v = \frac{w}{1 + w_g} \quad (3.5)$$

for any of the phases. In addition, we are not given w_1 , only w_s . To calculate w_1 , we note that

$$\begin{aligned} w_1 + w_s &= 1 \\ w_1 &= 1 - w_s. \end{aligned} \quad (3.6)$$

Fortunately, since we are taking ratios, (3.3) still holds with v replaced by w throughout. Using (3.6), we have

$$r_g = \frac{[\text{N}_2\text{O}][w_g + K_{\text{H}_2}RT(1 - w_s)]}{[\text{H}_2][w_g + K_{\text{N}_2\text{O}}RT(1 - w_s)]}. \quad (3.7)$$

To calculate the ratio in the aqueous phase, we have

$$r_{\text{aq}} = \frac{[\text{N}_2\text{O}(\text{aq})]}{[\text{H}_2(\text{aq})]} = \frac{[\text{N}_2\text{O}(\text{g})]K_{\text{N}_2\text{O}}}{[\text{H}_2(\text{g})]K_{\text{H}_2}} = \frac{K_{\text{N}_2\text{O}}r_g}{K_{\text{H}_2}}. \quad (3.8)$$

Now that we have values for the ratios of the substances in the gaseous and aqueous phases, we must calculate the ratio that actually escapes the supernatant and crust layers. This calculation is dependent in some way on the transport process within the layer. Suppose that in the sludge layer, diffusion is the dominant transport mechanism for the components in the aqueous phase. Assuming a constant source in the sludge, we have that

$$D_{\text{N}_2\text{O}} \frac{\partial^2 [\text{N}_2\text{O}(\text{aq})]}{\partial z^2} = -S_{\text{N}_2\text{O}}, \quad (3.9a)$$

$$D_{\text{H}_2} \frac{\partial^2 [\text{H}_2(\text{aq})]}{\partial z^2} = -S_{\text{H}_2}, \quad (3.9b)$$

where D is the molecular diffusion coefficient, S is the strength of the source term, and z is the distance down measured from the sludge-liquid interface. At the bottom of the tank ($z = h$), there can be no flux:

$$D_{\text{N}_2\text{O}} \frac{\partial [\text{N}_2\text{O}(\text{aq})]}{\partial z}(h) = 0, \quad (3.10a)$$

$$D_{\text{H}_2} \frac{\partial [\text{H}_2(\text{aq})]}{\partial z}(h) = 0. \quad (3.10b)$$

If we are in a steady state, the mass flux escaping through the interface must be equal to the mass flux produced, and hence we have

$$D_{\text{N}_2\text{O}} \frac{\partial [\text{N}_2\text{O}(\text{aq})]}{\partial z}(0) = S_{\text{N}_2\text{O}}h, \quad (3.11a)$$

$$D_{\text{H}_2} \frac{\partial [\text{H}_2(\text{aq})]}{\partial z}(0) = S_{\text{H}_2}h. \quad (3.11b)$$

Solving equations (3.9)–(3.11), we have

$$[\text{N}_2\text{O}(\text{aq})](z) = \frac{S_{\text{N}_2\text{O}}}{D_{\text{N}_2\text{O}}} \left(hz - \frac{z^2}{2} \right), \quad (3.12a)$$

$$[\text{H}_2(\text{aq})](z) = \frac{S_{\text{H}_2}}{D_{\text{H}_2}} \left(hz - \frac{z^2}{2} \right). \quad (3.12b)$$

Computing the ratio in the aqueous phase, we have

$$r_{\text{aq}}(z) = \frac{[\text{N}_2\text{O}(\text{aq})](z)}{[\text{H}_2(\text{aq})](z)} = \frac{S_{\text{N}_2\text{O}}}{D_{\text{N}_2\text{O}}} \frac{D_{\text{H}_2}}{S_{\text{H}_2}} = \frac{S_{\text{N}_2\text{O}} D_{\text{H}_2}}{S_{\text{H}_2} D_{\text{N}_2\text{O}}}. \quad (3.13)$$

But since we are in a steady state, we have that

$$r_{\text{h}} = \frac{S_{\text{N}_2\text{O}}}{S_{\text{H}_2}}, \quad (3.14)$$

where the h stands for the steady-state headspace measurement. Hence we have

$$r_{\text{aq}} = \frac{D_{\text{H}_2}}{D_{\text{N}_2\text{O}}} r_{\text{h}}. \quad (3.15)$$

Note that r_{aq} is independent of z . To compute the ratio in the gaseous phase, we use (3.1) to obtain

$$r_{\text{g}} = \frac{[\text{N}_2\text{O}(\text{g})]}{[\text{H}_2(\text{g})]} = \frac{K_{\text{H}_2} [\text{N}_2\text{O}(\text{aq})]}{K_{\text{N}_2\text{O}} [\text{H}_2(\text{aq})]} = \frac{D_{\text{H}_2} K_{\text{H}_2}}{D_{\text{N}_2\text{O}} K_{\text{N}_2\text{O}}} r_{\text{h}}. \quad (3.16)$$

In this model, the measured value of r in the sludge portion of the retained gas sample would be

$$\begin{aligned} r_{\text{sludge}} &= \frac{[\text{N}_2\text{O}]}{[\text{H}_2]} = \frac{[\text{N}_2\text{O}(\text{g})]v_{\text{g}} + [\text{N}_2\text{O}(\text{aq})]v_1}{[\text{H}_2(\text{g})]v_{\text{g}} + [\text{H}_2(\text{aq})]v_1} \\ &= r_{\text{aq}} \frac{w_1 + w_{\text{g}}/K_{\text{N}_2\text{O}}RT}{w_1 + w_{\text{g}}/K_{\text{H}_2}RT} = r_{\text{h}} \frac{D_{\text{H}_2}(1 - w_{\text{s}} + w_{\text{g}}/K_{\text{N}_2\text{O}}RT)}{D_{\text{N}_2\text{O}}(1 - w_{\text{s}} + w_{\text{g}}/K_{\text{H}_2}RT)}. \end{aligned} \quad (3.17)$$

From [4], p. 78, we have that

$$D_{\text{H}_2} = 5.0 \times 10^{-5} \text{ cm}^2/\text{s}, \quad (3.18)$$

where the diffusivity has been measured in water. From [5], Table 3-319, we have that the diffusivity of N_2O is given by

$$D_{\text{N}_2\text{O}} = 1.8 \times 10^{-5} \text{ cm}^2/\text{s}. \quad (3.19)$$

The value of R we obtain from [3], p. 7:

$$R = 8.2057 \times 10^{-2} \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}}. \quad (3.20)$$

The details of the calculations are listed in Tab. 4. We note that in most cases, $w_{\text{g}}/K_{\text{H}_2}RT > 1$, and hence we see that $r_{\text{sludge}} \approx r_{\text{g}}$. The values of D and K given in Tab. 4 for the two components force $r_{\text{g}} < r_{\text{h}}$, which doesn't match with our measurements. Therefore, we conclude that solubility considerations alone cannot explain the data.

Since relatively more H_2 is in the headspace than is predicted by the solubility mechanism alone, some other mechanism must be occurring simultaneously. Perhaps the components can also be adsorbed onto solids in the sludge. We consider that possibility in §4. Also, another form of transport may occur in the sludge. We consider that possibility in §5.

Section 4: Adsorption Calculations

As mentioned in the previous section, in some of the tanks the measurements of the ratio r do not match with the model where the components are only in the gaseous or aqueous phases. In particular, in tank AW-105 the ratio in the sludge is higher than in the GRE. Therefore, another mechanism must be postulated. Suppose that the components also adsorb onto the surface of the sludge. Due to the extraction process, any H_2 and N_2O stored in this way would also be added to the ratio measured in an RGS. Hence, (3.2a) must be replaced by

$$[\text{comp. } i] = [\text{comp. } i(\text{aq})]v_1 + [\text{comp. } i(\text{g})]v_g + \langle \text{comp. } i(\text{s}) \rangle a_s, \quad (4.1)$$

where $\langle \text{comp. } i(\text{s}) \rangle$ is the concentration of component i adsorbed (measured in units of moles per area, which is why we don't use brackets), and a_s is the ratio of the area of reacting surface to the total volume.

If during a GRE only components in the gaseous phase in the sludge were released into the headspace, this would imply that the ratio of the components in the gaseous phase in the sludge would be the same as that in a GRE. Therefore, in order to determine the feasibility of the adsorption mechanism, we calculate the percentage P of possible adsorption sites which would have to be occupied in order for the GRE and gaseous sludge ratios to be the same. Therefore, we must solve the following equation:

$$\begin{aligned} [\text{comp. } i] &= [\text{comp. } i(\text{aq})]v_1 + [\text{comp. } i(\text{GRE})]v_g + \langle \text{comp. } i(\text{s}) \rangle a_s \\ [\text{comp. } i] - \langle \text{comp. } i(\text{s}) \rangle a_s &= [\text{comp. } i(\text{GRE})](v_g + K_i RT v_1) \\ [\text{comp. } i(\text{GRE})] &= \frac{[\text{comp. } i] - \langle \text{comp. } i(\text{s}) \rangle a_s}{v_g + K_i RT v_1}. \end{aligned} \quad (4.2)$$

As a first approximation, we assume that the H_2 does not adsorb much at all. Therefore, computing the ratio in the gas, we have

$$\begin{aligned} r_{\text{GRE}} &= \frac{[N_2O(\text{GRE})]}{[H_2(\text{GRE})]} = \frac{([N_2O] - \langle N_2O(\text{s}) \rangle a_s)(v_g + K_{H_2} RT v_1)}{[H_2](v_g + K_{N_2O} RT v_1)} \\ &= \left(1 - \frac{\langle N_2O(\text{s}) \rangle a_s}{[N_2O]}\right) \frac{[N_2O](v_g + K_{H_2} RT v_1)}{[H_2](v_g + K_{N_2O} RT v_1)} \\ &= \left(1 - \frac{\langle N_2O(\text{s}) \rangle a_s}{[N_2O]}\right) r_g, \end{aligned} \quad (4.3)$$

where r_g is the value in (3.3) obtained using the measurements.

To estimate a_s , we assume that the absorbing surface is made up of some number of spheres N with equal radius \mathcal{R} . Then we see that

$$\begin{aligned} V_s &= \frac{4\pi N\mathcal{R}^3}{3} = (4\pi N\mathcal{R}^2)\frac{\mathcal{R}}{3}, \\ v_s &= \frac{\mathcal{R}a_s}{3}, \\ a_s &= \frac{3v_s}{\mathcal{R}} = \frac{3w_s}{\mathcal{R}(1+w_g)}. \end{aligned} \quad (4.4)$$

To calculate the percentage P of possible sites adsorbed, we take the ratio of the molar area concentration actually used $\langle N_2O(s) \rangle$ to the total molar area concentration if the surface were covered. However, this latter value is just the reciprocal of the area occupied by one mole of N_2O , which we denote by A_{N_2O} . Thus, we have

$$P = A_{N_2O}\langle N_2O(s) \rangle. \quad (4.5)$$

Substituting (4.5) and (4.4) into (4.3) and solving, we have

$$\begin{aligned} \frac{r_{GRE}}{r_g} &= \left(1 - \frac{3w_s P}{A_{N_2O}\mathcal{R}[N_2O](1+w_g)}\right) \\ P &= \frac{A_{N_2O}\mathcal{R}[N_2O](1+w_g)}{3w_s} \left(1 - \frac{r_{GRE}}{r_g}\right). \end{aligned} \quad (4.6)$$

Lastly, we calculate the area A_{N_2O} using the molar volume of N_2O , which we denote by V_{N_2O} :

$$\begin{aligned} A_{N_2O} &= N\pi\mathcal{R}_{N_2O}^2 \\ &= N\pi \left(\frac{3V_{N_2O}}{4N\pi}\right)^{2/3} \\ &= (N\pi)^{1/3} \left(\frac{3V_{N_2O}}{4}\right)^{2/3}. \end{aligned} \quad (4.7)$$

Substituting (4.7) into (4.6), we have the final expression:

$$P = \frac{\mathcal{R}[N_2O](1+w_g)(N\pi)^{1/3}V_{N_2O}^{2/3}}{3^{1/3}4^{2/3}w_s} \left(1 - \frac{r_{GRE}}{r_g}\right). \quad (4.8)$$

Clearly (4.8) is only meaningful when $r_{GRE} < r_g$.

Several points are worth noting:

1. There should be some suspicion of (3.1) in the case where there is adsorption. Not only may it be incorrect from first principles, but also it seems that when calculating K_i for our system, the experimentalists assumed no adsorption. However, this would

not be a problem if the amount in the aqueous phase is much smaller than either of the other two phases.

2. If we believe that during a GRE most of the component released is from the gaseous phase, then the considerations in (1) above shouldn't matter that much, since we are simply trying to account for the differences between the gaseous and adsorbed phases.

The detailed calculations are listed in Tab. 5. We note that we have approximately 4% adsorption in AW-101. This seems to be a reasonable proportion of sites occupied. However, in tank AN-105 we have negative adsorption. This is due to the fact that in this tank r during a GRE is slightly more than the ratio in the gaseous phase. Therefore, another mechanism must be responsible for the difference there.

Section 5: Other Transport Mechanisms

Since the adsorption model does not account for the differences in measured ratios in all tanks, we now postulate a totally different transport mechanism to account for the difference. A schematic of the process appears in Fig. 2. We consider a piece of sludge with practically no bubbles in it at all. Then

1. Since the mass flux out of the headspace must be equal to the mass flux produced, we state that the components are produced in the sludge in the same ratio as the steady-state headspace ratio. These components are produced in both the aqueous and gaseous phases. However, due to the large yield stress of the sludge, bubbles are trapped inside the sludge, rather than rising to the top.
2. As gas is produced (with ratio roughly equal to the GRE value), the void fraction of the piece of sludge increases. From [6] we know that this piece will become buoyant when the void fraction reaches approximately 0.1. At this point, the piece rises through the sludge and the supernatant to come to rest floating at the top. This constitutes a rollover or GRE.
3. Once the piece of sludge has reached the headspace, gas can easily convect through cracks in it. The bubbles escape, and the piece of sludge comes to a new equilibrium with very few bubbles in it.
4. Since little gas remains in the piece of sludge, it is no longer buoyant, and hence it returns to the bottom of the tank to begin the process anew.

Note that this theorized transport process is fundamentally different from the others, which tacitly assumed that the system was in some sort of steady state. Here we have more of a periodic structure to the system. Of course, this series of steps is idealized. In practice, the sludge would settle and it would not be the same piece which transported the gas over and over again.

We note that if a sample is taken in stage 1 (which constitutes the vast majority of the duration of the cycle due to the relatively slow production rate of the gas), the measured ratio will include components in both the gaseous and aqueous phases. Since r for the aqueous phase is usually higher than for the gaseous phase, samples with low void fractions will show higher r values than in the GRE. However, this is not a result of a higher r_g in the sludge; rather it is a consequence of the fact that both aqueous and gaseous phases are considered when measurements of r are taken.

If the above mechanism is the dominant one, we would expect to see a monotonically decreasing dependence of the measured r for RGS as a function of void fraction. However, examination of the data (even within the same core sample) shows that this is not the case. Therefore, this transport mechanism may have to be combined with adsorption or other processes to produce a more realistic picture of the dynamics within the tank.

For completeness, we hypothesize the following model for the qualitative form for the dependence in a system dominated by this mechanism. The total ratio of components

measured is

$$\begin{aligned} r_{\text{sludge}} &= \frac{[\text{N}_2\text{O}(\text{aq})]v_1 + [\text{N}_2\text{O}(\text{g})]v_g}{[\text{H}_2(\text{aq})]v_1 + [\text{H}_2(\text{g})]v_g} \\ &= \frac{[\text{N}_2\text{O}(\text{g})]}{[\text{H}_2(\text{g})]} \frac{K_{\text{N}_2\text{O}}RTw_1 + w_g}{K_{\text{H}_2}RTw_1 + w_g}. \end{aligned} \quad (5.1)$$

Suppose that the first ratio is a constant k . This is certainly an assumption that must be checked, but note that in some sense this is what we have been tacitly using in our analysis. In other words, we have tried to find ways that, no matter whether the measurements are taken in the sludge, the steady-state, or after a GRE, the ratio in the gaseous phases is always the same.

To find the value of the constant, we note that when the void fraction is 0.1, we have a gas release event. To calculate to w_g , we have

$$w_g = \frac{0.1}{1.1} = \frac{1}{11}. \quad (5.2)$$

Substituting (5.2) into (5.1), we have

$$\begin{aligned} r_{\text{GRE}} &= k \frac{K_{\text{N}_2\text{O}}RT(1 - w_s) + 1/11}{K_{\text{H}_2}RT(1 - w_s) + 1/11} \\ k &= r_{\text{GRE}} \frac{K_{\text{H}_2}RT(1 - w_s) + 1/11}{K_{\text{N}_2\text{O}}RT(1 - w_s) + 1/11}. \end{aligned} \quad (5.3)$$

Substituting (5.3) into (5.1), we have

$$r_{\text{sludge}} = r_{\text{GRE}} \frac{K_{\text{N}_2\text{O}}RT(1 - w_s) + w_g}{K_{\text{N}_2\text{O}}RT(1 - w_s) + 1/11} \frac{K_{\text{H}_2}RT(1 - w_s) + 1/11}{K_{\text{H}_2}RT(1 - w_s) + w_g}. \quad (5.4)$$

In general, $K_iRT(1 - w_s)$ will be a small number. So for w_g near $1/11$, we should have a near-asymptote at r_{GRE} . However, for smaller void fractions, both terms are of the same order and hence we should get a larger ratio since $K_{\text{N}_2\text{O}} > K_{\text{H}_2}$.

Unfortunately, the details of these calculations, which are listed in Tab. 4, do not match with the measured data. Therefore, it is reasonable to assume that other transient effects play a role. We note the following two transient effects which may act to decrease r in the headspace.

1. From our data in Tab. 4, we see that the solubility of H_2 is an order of magnitude smaller than that of N_2O , and thus a higher proportion of H_2 is in gaseous form than of N_2O . Therefore, during GREs relatively more H_2 may be released.
2. From our data in Tab. 5, we note that the diffusivity of H_2 is higher than that of N_2O . This higher diffusivity may enhance the transport of H_2 to the headspace, influencing the background measurements there. On longer timescales, however, the greater solubility of N_2O makes its diffusive transport more effective, which would tend to increase r in the headspace. Note that the latter transport would dominate in

the case where no GREs occur and the system is able to approach steady state. This is of course exactly the case in tank A-101, where the r in the headspace is higher than that of the adjoining sludge layer.

It is therefore worth quantifying the timescales for aqueous diffusion in the sludge layer. We consider $h^2/4D$ to be a rough representative timescale, where h is the depth of the sludge layer. (We use the half-width to account for the fact that gas is produced throughout the sludge.) Considering that the average sludge layer has a depth which is $O(10\text{ m})$, we obtain timescales of

$$\frac{(10^3\text{ cm})^2}{4D_{\text{H}_2}} = (10^3\text{ cm})^2 \frac{\text{s}}{4(5 \times 10^{-5}\text{ cm}^2)} = 5 \times 10^9\text{ s} = 159\text{ yr for H}_2,$$

$$\frac{(10^3\text{ cm})^2}{4D_{\text{N}_2\text{O}}} = (10^3\text{ cm})^2 \frac{\text{s}}{4(2 \times 10^{-5}\text{ cm}^2)} = 1.25 \times 10^{10}\text{ s} = 396\text{ yr for N}_2\text{O}.$$

Such figures are obviously longer than typical intervals between GREs, so transient effects are likely to be significant in the background measurements. Such comparisons are clearly rather sensitive to layer thicknesses.

Section 6: Conclusions and Further Research

In order to ensure the safe transport and storage of high-level nuclear waste, scientists must have a clear picture of the chemical and transport processes taking place within storage facilities. One hazard to be avoided is the explosion of volatile gases produced within radioactive storage tanks. Though the tanks are vented, gas mixtures of gas can still form which are susceptible to ignition.

Measurements of the ratio of N_2O to H_2 within these tanks varies quite a bit. Variations among tanks can be partially attributed to the waste composition in various tanks. Some of the variations within layers (supernatant or sludge) of the same tank may be attributed to inhomogeneities within the waste composition. Such an explanation is more feasible in the sludge, since the supernatant we consider to be thermally well-mixed.

However, variations among layers in the same tank pose vexing questions. Which reflects the “true” ratio? Which reflects the production ratio? Could components in a low (volatile) ratio in the sludge or supernatant be suddenly released to the headspace where they risk ignition? These safety questions are the ones we have attempted to answer.

Since the number of samples is so small, it is natural to attribute at least part of the variation to sampling error. However, when we tested the populations with a standard t -test (which takes into account the number of samples), we found that the differences in the means were often statistically significant.

We hypothesized several modes of transport and storage of the various components. First we examined the case where the components were either in the aqueous or gaseous phase. We examined this case when diffusion dominated in the sludge. Such calculations led to predictions which did not always match with the data gathered from the tanks. Therefore, we hypothesized that either diffusion did not dominate in the sludge, or that there were other storage mechanisms for the components.

Focusing on the latter hypothesis, we then examined the case where the components could be adsorbed onto the solid particles in the sludge. With a relatively low percentage of sites occupied, the data for one tank could be made to match with the theoretical predictions. However, for the other tanks there were still lingering questions. Thus, we hypothesized a new transport mechanism where gas is transported to the surface primarily through gas release events which do not accurately reflect the ratio of components in the sludge for most of the production cycle. However, these predictions did not fully match the data, either.

Therefore, there are still several areas left open to inquiry:

1. Neither the adsorption nor new transport theories can account for why the supernatant ratio is different from the steady-state and GRE ratios.
2. It would be a good idea to run the calculations with the data from the other two tanks listed in [2] to see how the models compare.
3. Since we examined each of the transport and storage mechanisms separately, it might be a good idea to try various combinations of them to see if they yield better results.

Nomenclature

Variables and Parameters

Units are listed in terms of length (L), mass (M), moles (N), time (T), or temperature (Θ). The equation number where a particular quantity first appears is listed.

- a_s : surface area of solid divided by total volume of waste (4.1).
- A : area occupied by one mole of adsorbed substance, units L^2 (4.5).
- D : molecular diffusivity, units L^2/T (3.9a).
- h : depth of sludge layer, units L (3.10a).
- K : Henry's Law constant, units $NT^2/(ML^2)$ (3.1).
- k : constant ratio $[N_2O(g)]/[H_2(g)]$ when doing data fitting.
- N : number of molecules per mole, value 6.02×10^{23} .
- P : proportion of adsorption sites occupied (4.5).
- \mathcal{R} : radius of solid particle in sludge, units L .
- R : ideal gas constant, value $8.2057 \times 10^{-2} \text{ L} \cdot \text{atm}/(\text{mol} \cdot \text{K})$, units $ML^2/(NT^2\Theta)$ (3.1).
- r : ratio of the concentration of N_2O to the concentration of H_2 (1.1).
- S : production rate of gas, units $N/(L^2T)$ (3.9a).
- T : temperature, units Θ (3.1).
- V : volume, units L^3 (3.4).
- v : true volume fraction (3.2a).
- w : measured volume fraction, which is the fraction of the non-gas waste (3.4).
- t : student's t statistic.
- z : distance down from top of sludge layer, units L (3.9a).

Other Notation

- aq: used to indicate the aqueous phase (3.1).
- g: used to indicate the gas phase (3.1).
- h: as a subscript, used to indicate the headspace (3.14).
- l: used to indicate the liquid phase (3.2a).
- s: used to indicate the solid phase (3.4).
- T : as a subscript, used to indicate a total (3.4).
- $\langle \rangle$: used to indicate molar surface concentration, units N/L^2 (4.1).
- $[]$: used to indicate molar volume concentration, units N/L^3 (1.1).

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Figure 1: Tank Descriptions

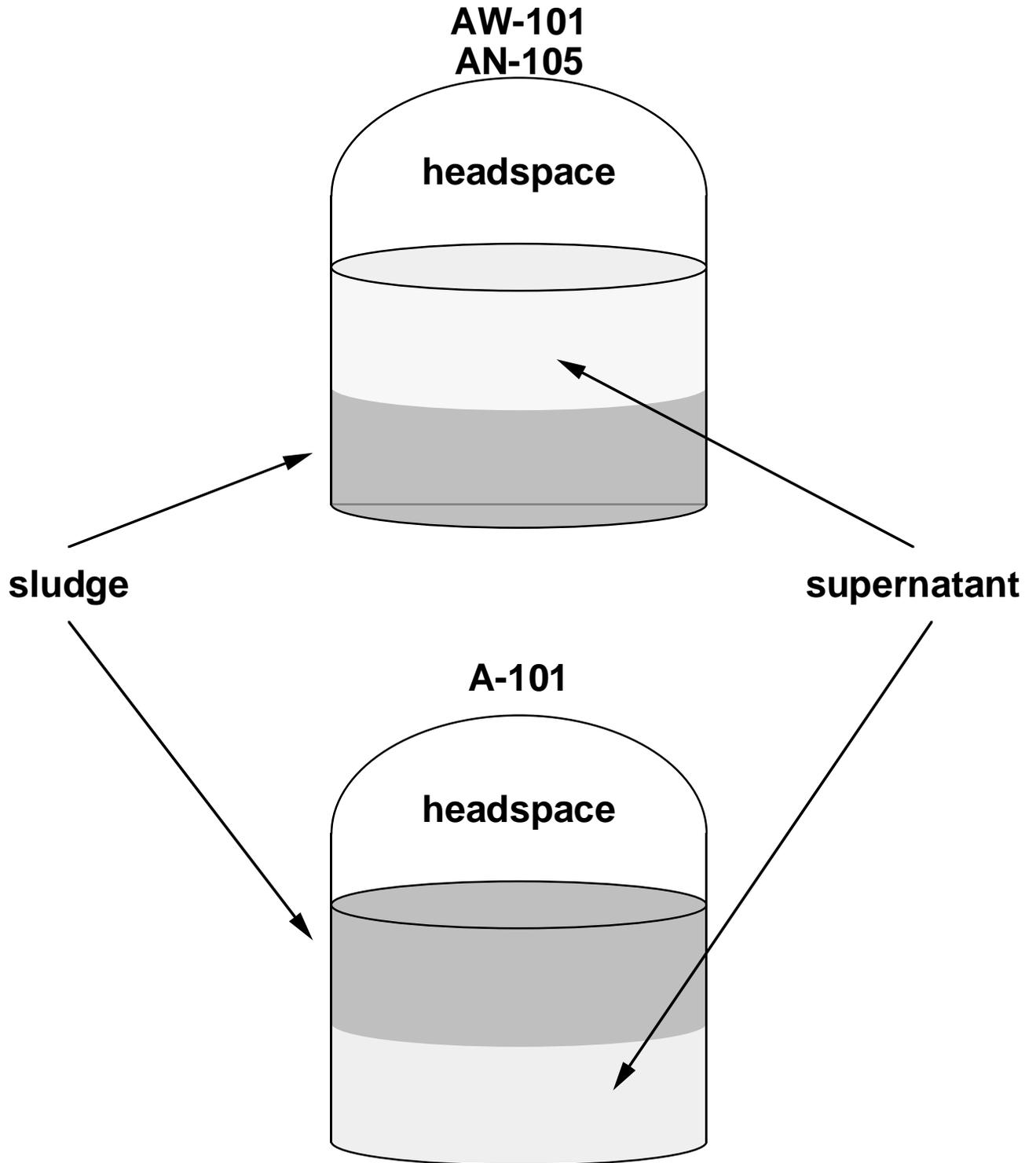
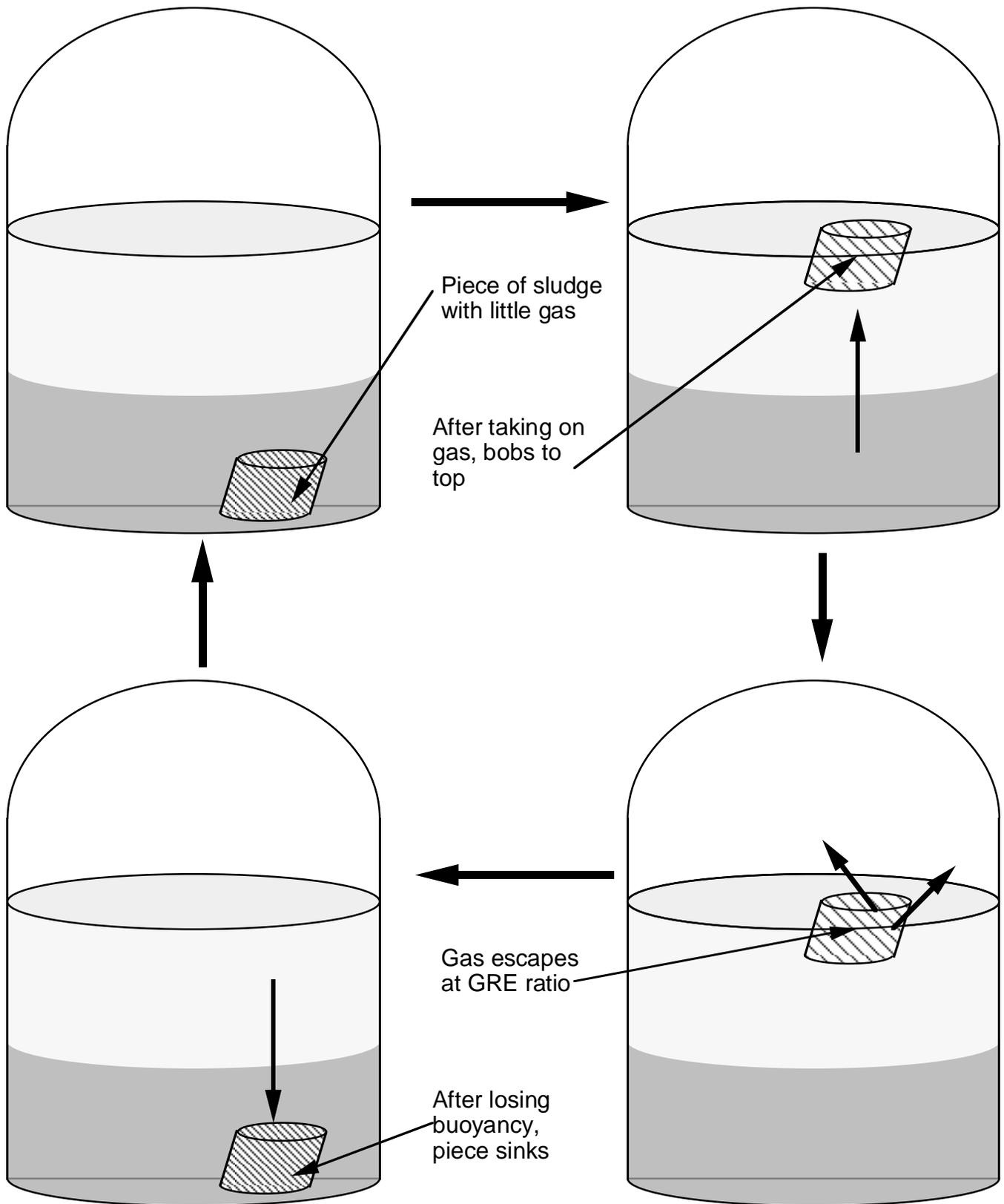


Figure 2: New Transport Cycle



AW-101 Data							
					H₂		N₂O
Area	Sample	H₂	N₂O	N₂O/H₂	weight	H₂/N₂O	weight
Steady-State		0.05	0.00	0.02	0.21	58.75	0.16
		0.05	0.00	0.02	0.21	52.22	0.18
		0.04	0.00	0.02	0.18	50.00	0.16
		0.03	0.00	0.02	0.11	43.33	0.12
		0.04	0.00	0.03	0.17	38.00	0.20
		0.02	0.00	0.03	0.07	34.00	0.10
		0.01	0.00	0.04	0.05	24.00	0.10
	Mean (weighted)	0.23	0.01	0.02		44.51	
	Mean (unweighted)			0.03		42.90	
				1/Previous Unweighted Mean		39.63	
GRE	11/30/94	0.09	0.00	0.03	0.14	30.33	0.18
	10/21/94 (d)	0.30	0.01	0.03	0.44	33.11	0.53
	8/2/95 (d)	0.29	0.01	0.02	0.42	57.00	0.29
	Mean (weighted)	0.67	0.02	0.03		39.65	
	Mean (unweighted)			0.03		40.15	
				1/Previous Unweighted Mean		37.17	
Sludge	RGS(A) 17	530	106	0.20	0.14	5.00	0.11
	RGS(A) 19	1610	220	0.14	0.42	7.32	0.22
	RGS(A) 21	1190	320	0.27	0.31	3.72	0.32
	RGS(B) 18	280	120	0.43	0.07	2.33	0.12
	RGS(B) 22	210	230	1.10	0.05	0.91	0.23
	Mean (weighted)	3820	996	0.26		3.84	
	Mean (unweighted)			0.43		3.86	
				1/Previous Unweighted Mean		2.35	
Supernatant	RGS(A)	94	11	0.12		8.55	
supernatant	RGS (A)	94	11	0.12	0.03	8.55	0.02
sludge		530	106	0.20	0.15	5.00	0.16
sludge		1610	220	0.14	0.47	7.32	0.33
sludge		1190	320	0.27	0.35	3.72	0.49
	Mean (weighted)	3424	657	0.19		5.21	
	Mean (unweighted)			0.18		6.15	
				1/Previous Unweighted Mean		5.54	
sludge	RGS (B)	280	120	0.43	0.57	2.33	0.34
sludge		210	230	1.10	0.43	0.91	0.66
	Mean (weighted)	490	350	0.71		1.40	
	Mean (unweighted)			0.76		1.62	
				1/Previous Unweighted Mean		1.31	

A-101 Data							
Area	Sample	H ₂	N ₂ O	N ₂ O/H ₂	H ₂ weight	H ₂ /N ₂ O	N ₂ O weight
Steady-State		0.04	0.01	0.14	0.03	7.36	0.03
		0.15	0.02	0.14	0.13	6.95	0.11
		0.04	0.01	0.15	0.03	6.55	0.03
		0.14	0.02	0.16	0.12	6.23	0.12
		0.14	0.02	0.16	0.13	6.17	0.13
		0.15	0.03	0.16	0.14	6.16	0.14
		0.10	0.02	0.17	0.08	5.94	0.09
		0.14	0.02	0.17	0.12	5.87	0.13
		0.13	0.02	0.17	0.11	5.73	0.12
		0.12	0.02	0.18	0.10	5.62	0.11
	Mean (weighted)	1.13	0.18	0.16		6.14	
	Mean (unweighted)			0.16		6.26	
				1/Previous Unweighted Mean		6.22	
Sludge	RGS (24)	3400	400	0.12	0.16	8.50	0.24
	RGS (24)	6230	440	0.07	0.29	14.16	0.26
	RGS (15)	5200	410	0.08	0.25	12.68	0.24
	RGS (15)	6300	450	0.07	0.30	14.00	0.26
	Mean (weighted)	21130	1700	0.08		12.43	
	Mean (unweighted)			0.08		12.34	
				1/Previous Unweighted Mean		11.82	
Super	RGS (24)	55	79	1.44	0.26	0.70	0.30
	RGS (24)	112	103	0.92	0.53	1.09	0.39
	RGS (15)	43	82	1.91	0.20	0.52	0.31
	Mean (weighted)	210	264	1.26		0.80	
		Mean (unweighted)			1.42		0.77
				1/Previous Unweighted Mean		0.70	
sludge	RGS(24)	3400	400	0.12	0.35	8.50	0.39
sludge		6230	440	0.07	0.64	14.16	0.43
supernat.		55	79	1.44	0.01	0.70	0.08
supernat.		112	103	0.92	0.01	1.09	0.10
	Mean (weighted)	9797	1022	0.10		9.59	
	Mean (unweighted)			0.64		6.11	
				1/Previous Unweighted Mean		1.57	
sludge	RGS(15)	5200	410	0.08	0.45	12.68	0.44
sludge		6300	450	0.07	0.55	14.00	0.48
supernat.		43	82	1.91	0.00	0.52	0.09
	Mean (weighted)	11543	942	0.08		12.25	
	Mean (unweighted)			0.69		9.07	
				1/Previous Unweighted Mean		1.46	

AN-105 Data								
Area	Sample	H₂	N₂O	N₂O/H₂	H₂ weight	H₂/N₂O	N₂O weight	
Headspace		0.01	0.00	0.14	0.05	7.38	0.04	
		0.02	0.00	0.14	0.20	7.10	0.17	
		0.02	0.00	0.15	0.16	6.65	0.14	
		0.01	0.00	0.17	0.06	6.00	0.06	
		0.01	0.00	0.18	0.11	5.70	0.11	
		0.01	0.00	0.19	0.09	5.32	0.10	
		0.00	0.00	0.20	0.04	5.00	0.04	
		0.00	0.00	0.20	0.04	5.00	0.04	
		0.01	0.00	0.20	0.06	4.93	0.08	
		0.01	0.00	0.20	0.09	4.90	0.11	
		0.01	0.00	0.21	0.09	4.80	0.11	
	Mean (weighted)	0.11	0.02	0.17		5.82		
	Mean (unweighted)			0.18		5.54		
				1/Previous Unweighted Mean		5.58		
GRE		0.42	0.09	0.20	0.28	4.88	0.30	
		1.07	0.20	0.19	0.72	5.35	0.70	
		Mean (weighted)	1.49	0.29	0.19		5.21	
		Mean (unweighted)			0.20		5.12	
					1/Previous Unweighted Mean		5.11	
Super	RGS(12)*	66	100	1.52	0.30	0.66	0.42	
	RGS(7)*	72	68	0.94	0.32	1.06	0.29	
	RGS(7)	84	68	0.81	0.38	1.24	0.29	
		Mean (weighted)	222	236	1.06		0.94	
		Mean (unweighted)			1.09		0.98	
				1/Previous Unweighted Mean		0.92		
*indicates from thin layer at top of sludge which behaves like supernatant								
Sludge	RGS(12)	3100	550	0.18	0.22	5.64	0.17	
	RGS(12)	6300	1230	0.20	0.45	5.12	0.38	
	RGS(12)	3460	1220	0.35	0.25	2.84	0.37	
	RGS(7)	1040	260	0.25	0.07	4.00	0.08	
		Mean (weighted)	13900	3260	0.23		4.26	
		Mean (unweighted)			0.24		4.40	
				1/Previous Unweighted Mean		4.10		

AN-105 Data							
Area	Sample	H ₂	N ₂ O	N ₂ O/H ₂	H ₂ weight	H ₂ /N ₂ O	N ₂ O weight
super*	RGS(12)	66	100	1.52	0.01	0.66	0.03
sludge		3100	550	0.18	0.24	5.64	0.18
sludge		6300	1230	0.20	0.49	5.12	0.40
sludge		3460	1220	0.35	0.27	2.84	0.39
Mean (weighted)		12926	3100	0.24		4.17	
Mean (unweighted)				0.56		3.56	
1/Previous Unweighted Mean						1.79	
super*	RGS(7)	72	68	0.94	0.06	1.06	0.17
super		84	68	0.81	0.07	1.24	0.17
sludge		1040	260	0.25	0.87	4.00	0.66
Mean (weighted)		1196	396	0.33		3.02	
Mean (unweighted)				0.67		2.10	
1/Previous Unweighted Mean						1.50	
AN-105 Calculations							
T-test		Confidence interval that means are NOT the same					
SS v. GRE (r)		73.91%		68.62%		GRE v. Sludge (r)	
SS v. GRE (1/r)		83.07%		65.42%		GRE v. Sludge (1/r)	
SS v. Sludge (r)		80.00%		94.64%		GRE v. Super (r)	
SS v. Sludge (1/r)		87.66%		99.57%		GRE v. Super 1/(r)	
SS v. Super (r)		94.81%		94.47%		Super v. Sludge (r)	
SS v. Super (1/r)		100.00%		99.07%		Super v. Sludge (1/r)	

AW-101 Sludge Calculations							
Sludge Calculations	H₂	N₂O	N₂O/H₂	w_g	w_s	w_i	KN₂O
RGS(A) 17	530	106	0.20	0.02	0.26	0.74	1.60E-04
RGS(A) 19	1610	220	0.14	0.04	0.26	0.74	1.60E-04
RGS(A) 21	1190	320	0.27	0.04	0.26	0.74	1.60E-04
RGS(B) 18	280	120	0.43	0.02	0.26	0.74	1.60E-04
RGS(B) 22	210	230	1.10	0.02	0.26	0.74	1.60E-04
	KH₂	R	T	r_{measured}	Eq. (3.17)	Eq. (6.4)	
RGS(A) 17	1.30E-05	0.082057	315.75	0.20	0.01	0.03	
RGS(A) 19	1.30E-05	0.082057	316.15	0.14	0.00	0.03	
RGS(A) 21	1.20E-05	0.082057	310.65	0.27	0.00	0.03	
RGS(B) 18	1.30E-05	0.082057	316.55	0.43	0.01	0.03	
RGS(B) 22	1.20E-05	0.082057	308.95	1.10	0.00	0.03	
AN-105 Sludge Calculations							
Sludge Calculations	H₂	N₂O	N₂O/H₂	w_g	w_s	w_i	KN₂O
RGS(12A-17)	3100	550	0.18	0.06	0.28	0.72	9.70E-04
RGS(12A-19)	6300	1230	0.20	0.11	0.28	0.72	9.70E-04
RGS(12A21)	3460	1220	0.35	0.06	0.28	0.72	9.80E-04
RGS(7B-18)	1040	260	0.25	0.02	0.28	0.72	9.70E-04
	KH₂	R	T	r_{measured}	Eq. (3.17)	Eq. (6.4)	
RGS(12A-17)	6.40E-05	0.082057	319.15	0.18	0.04	0.21	
RGS(12A-19)	6.40E-05	0.082057	319.15	0.20	0.03	0.19	
RGS(12A21)	6.10E-05	0.082057	312.15	0.35	0.03	0.21	
RGS(7B-18)	6.40E-05	0.082057	319.15	0.25	0.05	0.29	

