Modeling Large Gas Release Events from "Dry" Waste Tanks

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Section 0: Introduction

This problem was brought to the Workshop on Mathematical Problems in Industry by Dr. Mary E. Brewster of Pacific Northwest Laboratories. The basic scenario is one with which anybody interested in ecology and safety is familiar; large tanks have been filled with toxic waste, and the object is to determine whether or not they are safe.

The tanks in question number about 200 and are situated on the Hanford 'tank farms' in Washington State. A typical tank has a diameter of 75 feet, is between 37 and 50 feet deep, and has a volume of order 10^6 US gallons. The tanks are situated underground and contain high-level radioactive waste that has been generated as a byproduct of many years' plutonium production and recovery. The waste also contains components that arise from radioactive decay processes.

The tanks contain a complicated mixture of components, but for modelling purposes it is convenient to think of the constituents as 'sludge', 'saltcake' and gas. It is generally agreed that the sludge may be thought of as a shear-thickening fluid which possesses a yield stress. Many of the tanks also originally contained liquid, but most of this may now be regarded as having been pumped out. The saltcake, which consists largely of sodium nitrate, may be either dry or 'wet' (partially saturated). Some tanks are thought to contain layers of saltcake 100 inches thick, above a layer of 2 inches sludge, but in other tanks these dimensions may be reversed so that a thin layer of saltcake overlies a thick sludge layer. From a safety point of view, the main interest of the current study centres upon the hydrogen gas contained or produced in the tanks (nitrous oxide, ammonia and other potentially flammable gases are also produced, but we largely ignore these below; it should be remembered, however, that these gases may effectively decrease the lower flammability limit of hydrogen/air mixtures). The gas may be retained in solution (as ammonia), exist as bubbles in the sludge, or be present in the pores of the saltcake; the lower flammability limit for hydrogen/air mixtures is about 4 per cent, and safety limits are usually fixed at around 1 per cent.

The group working on this problem focussed their efforts upon three main questions:

(1) How much hydrogen can the dry saltcake hold ? (If the answer is relatively little, then the saltcake may be disrupted and broken up without fear of potentially dangerous gas escapes).

(2) Can important parameters be identified for the wet saltcake/sludge system that could be measured to attempt to characterize the gas retention and release ?

(3) How are bubbles released in the sludge and how do they grow ? - If the saltcake acts as a 'lid' and holds in gas, is a catastrophic release event possible, and, if so, how much gas will be released ?

All of these questions will be addressed below.

IMPORTANT NOTE 1: The team working on this problem was truly transatlantic. For this reason, no attempt has been made to standardise the units and both metric and imperial measurements appear. Conversion between the two is easy however, and great efforts have been taken to ensure that the particular units being used are clearly indicated.

IMPORTANT NOTE 2: After the meeting, the value for the yield stress of the sludge was revised by three orders of magnitude. In most of this report the 'new' value has been used, but it is recommended that the reader should check exactly which value has been used when interpreting any of the results given below.

Section 1: Motion of Bubbles in Sludge

Initially, we consider the problem of bubble generation and rise in the sludge. First we analyse the growth of a bubble in a viscous material (possibly with nonlinear rheology). This problem has been considered by Nye (1953). If the bubble is of radius R, and the sludge velocity is $u(r)$ (in spherical polar coordinates), then

$$\frac{1}{r^2}\frac{\partial}{\partial r}(r^2 u) = 0 \Rightarrow u = S/r^2, \tag{1.1}$$

assuming incompressibility of the sludge. The non-zero components of the strain-rate and stress tensors are

$$\dot{\varepsilon}_{rr} = \frac{\partial u}{\partial r}, \quad \dot{\varepsilon}_{\theta\theta} = \dot{\varepsilon}_{\phi\phi} = \frac{u}{r}, \tag{1.2}$$

$$\tau_{\theta\theta} = \tau_{\phi\phi} = -\frac{1}{2}\tau_{rr}, \tag{1.3}$$

and $\tau_{rr} < 0$ for $u > 0$ (opening). The second invariants are then $(2\tau^2 = \tau_{ij}\tau_{ij},\ 2\dot{\varepsilon}^2 = \dot{\varepsilon}_{ij}\dot{\varepsilon}_{ij})$

$$\tau = \frac{\sqrt{3}}{2}|\tau_{rr}|, \quad \dot{\varepsilon} = \sqrt{3}\frac{S}{r^3}, \tag{1.4}$$

and a momentum balance gives

$$\frac{\partial p}{\partial r} = \frac{1}{r^2}\frac{\partial}{\partial r}(r^2\tau_{rr}) + \frac{\tau_{rr}}{r} = \frac{\partial \tau_{rr}}{\partial r} - \frac{2\sqrt{3}}{r}\tau. \tag{1.5}$$

If the flow law is

$$\dot{\varepsilon} = f(\tau) \tag{1.6}$$

(this can include Bingham or Herschel-Bulkley type fluids), then

$$f(\tau) = \frac{\sqrt{3}S}{r^3}, \tag{1.7}$$

whence $f'd\tau/f = -3dr/r$, and the integral of (1.5) is

$$[p - \tau_{rr}]_R^r = \frac{2}{\sqrt{3}}\int_{\tau(R)}^{\tau(r)}\frac{\tau f'(\tau)d\tau}{f(\tau)}. \tag{1.8}$$

At $r = R$, $p - \tau_{rr} = p_b$ (bubble pressure), and if $\tau_{rr} \to 0$ as $r \to \infty$, then

$$\Delta p = \frac{2}{\sqrt{3}} \int_0^{\tau^R} \frac{\tau f'(\tau) d\tau}{f(\tau)}, \tag{1.9}$$

where $\Delta p = p_b - p_s$, p_s is sludge pressure, and τ^R is the value of τ at $r = R$. For a Bingham fluid with yield stress τ^*, the lower limit of (1.9) is τ^*.

The kinematic condition on $r = R$ implies that the bubble growth is given by

$$\frac{\dot{R}}{R} = \frac{S}{R^3} = s, \text{ say,} \tag{1.10}$$

and from (1.4),

$$\sqrt{3}s = f(\tau^R) \tag{1.11}$$

determines τ^R. Hence (1.9) and (1.11) determine s as a function of Δp.

As an example, consider a Newtonian fluid with viscosity η so that

$$f(\tau) = \frac{\tau}{2\eta}. \tag{1.12}$$

Then we find

$$\frac{\dot{R}}{R} = \frac{\Delta p}{4\eta}. \tag{1.13}$$

1.1 Bubble dynamics

Assume that a mass flux J (mass/unit area/time) of H_2 diffuses through the sludge to the bubble. If the density of the bubble is given by the perfect gas law

$$p_b = \rho R_v T / M_{H_2}, \tag{1.14}$$

where M_{H_2} is the molecular weight of H_2 (kg kg-mole^{-1}), R_v is the gas constant, T is absolute temperature, and ρ is the gas mass density (kg m^{-3}), then

$$\frac{d}{dt}(R^3 p_b) = \frac{3R_v T J R^2}{M_{H_2}}. \tag{1.15}$$

Now let us suppose that the bubble rises slowly through the sludge due to Stokes flow. If the depth below the salt-cake is z, then a Stokes buoyancy balance gives

$$\dot{z} = -\frac{2\rho_s g}{9\eta} R^2, \tag{1.16}$$

where ρ_s is the sludge density.

1.2 Reaction dynamics

In a quasi-steady state, the mass fraction of H_2 in the sludge is given by the equation

$$\nabla.[\rho_s D \nabla c] + R^* = 0, \tag{1.17}$$

where R^* is the reactive source term in units of kg H_2 (m^3 sludge)$^{-1}$ s^{-1}, and c is the mass fraction of H_2. Following Bird, Stewart and Lightfoot (1960), and using molecular weights

$$M_{NaOH} = 40, \quad M_{H_2O} = 18, \quad M_{H_2} = 2, \tag{1.18}$$

we have the following relationships. For a 40% mass fraction of H_2O in the sludge, the sludge has molecular weight

$$M = [(0.4/M_{H_2O}) + (0.6/M_{NaOH})]^{-1} = 26.9, \tag{1.19}$$

$$\rho_{H_2} = M_{H_2} c_{H_2}, \tag{1.20}$$

where ρ_{H_2} is the mass density of H_2, c_{H_2} is the molar concentration, and the total mass density $\rho \approx \rho_s$ (the sludge density), assuming $\rho_{H_2} \ll \rho_s$. Then

$$c \approx \rho_{H_2}/\rho_s, \tag{1.21}$$

the molar concentration of the sludge is

$$c_s = \rho_s/M, \tag{1.22}$$

and the mole fraction of H_2 is

$$x_{H_2} = \frac{c_{H_2}}{c_s + c_{H_2}} = \frac{c}{c + (M_{H_2}/M)}. \tag{1.23}$$

We anticipate that $c \ll M_{H_2}/M \approx .074$, then

$$x_{H_2} \approx Mc/M_{H_2}. \tag{1.24}$$

Henry's law

In equilibrium at a gas/liquid interface,

$$p_g = Hx_g, \tag{1.25}$$

where p_g is the gas pressure, x_g is the mole fraction of gas in the liquid, and $H \approx 7.75 \times 10^4$ bar (mole fraction)$^{-1}$. Therefore, using (1.24), we have to solve (1.17) with

$$c = \frac{p}{\tilde{H}}, \quad \rho_s D \frac{\partial c}{\partial r} = J \quad \text{on} \quad r = R, \tag{1.26}$$

where $p = p_b$, and

$$\tilde{H} = H(M/M_{H_2}) = 1.04 \times 10^6 \text{ bar}, \tag{1.27}$$

and we will also prescribe

$$\frac{\partial c}{\partial r} = 0 \;\; \text{on} \;\; r = r^*, \tag{1.28}$$

where $r = r^*$ is a notional catchment boundary, which is discussed further below. The solution is

$$c = \frac{R^*}{2\rho_s D}\left[R^2 - \frac{1}{3}r^2 - \frac{2}{3}\frac{R^3}{r}\right] + \frac{p}{\tilde{H}} + \frac{JR}{\rho_s D} - \frac{JR^2}{\rho_s Dr}, \tag{1.29}$$

and to satisfy (1.28),

$$JR^2 = \frac{R^* r^{*3}}{3}, \tag{1.30}$$

where we assume $r^* \gg R$.

Nucleation dynamics

The question now is, how to choose r^*. Our assumption is based on the dynamics of nucleation (see also Allemann et al. (1990), chapter 7). The concentration profile between bubbles ($\sim 2r^*$ apart) is supersaturated, and we suppose that beyond some critical supersaturated concentration, c^*, bubbles will nucleate. This suggests that we take $c \approx c^*$ at $r = r^*$, and prescribe c^* (from nucleation dynamics, which will not be considered in detail here). Using (1.29), we find (with $r^* \gg R$)

$$JR \approx \rho_s D\Delta c, \tag{1.31}$$

where Δc is the critical supersaturation ($= c^* - c|_R$).

Initial bubble size

If the sludge has a yield stress τ^* (this is ~ 6700 Pa), then a simple force balance indicates that bubbles will grow *in situ* until

$$R \sim \frac{\tau^*}{\Delta\rho g} = R_c. \tag{1.32}$$

With $\tau^* = 6700$ Pa, $\Delta\rho = 1700$ kg m^{-3}, $g = 10$ m s^{-2}, we estimate $R_c \sim 0.4$ m.

1.3 Governing equations

The equations (1.15), (1.16) and (1.13) are

$$\frac{\dot{R}}{R} = \frac{\Delta p}{4\eta}, \quad \dot{z} = -\frac{2\rho_s g}{9\eta}R^2, \quad (R^3 p)\dot{} = [3R_v T\rho_s D\Delta c/M_{H_2}]R, \tag{1.33}$$

where $\Delta p = p - p_s$, $p_s = \rho_s gz + p_{sc}$ is the sludge pressure, and p_{sc} is the salt-cake overburden pressure.

We now non-dimensionalise the equations by scaling

$$z \sim d, \quad R \sim R_c, \quad t \sim \frac{9\eta d}{2\rho_s g R_c^2}, \quad p \sim \rho_s g d, \tag{1.34}$$

where d is, for example, the sludge depth. We then find, in dimensionless variables,

$$\Delta p = p - p_s$$
$$\Delta p = \delta \dot{R}/R$$
$$p = \bar{p}_{sc} + z \tag{1.35}$$
$$\dot{z} = -R^2$$
$$(R^3 p)\dot{} = \beta R,$$

where

$$\bar{p}_{sc} = p_{sc}/\rho_s g d, \quad \delta = 8R_c^2/9d^2, \quad \beta = \frac{27 R_v T \eta D \Delta c}{2 M_{H_2} \rho_s g^2 R_c^4}. \tag{1.36}$$

We use values $R_c = 0.5$m, $\rho_s = 1.7 \times 10^3$ kg m^{-3}, $g = 9.8$ m s^{-2}, $d = 5$m, $\eta = 1$ Pa s, $R_v = 8.3 \times 10^3$ kg m^2 s^{-2} kg-mole^{-1} K^{-1}, $T = 330$ K, $D = 5.1 \times 10^{-9}$ m^2 s^{-1}, $\Delta c = 10^{-6}$, $M_{H_2} = 2$ kg kg-mole^{-1};
then

$$\delta \approx 8.89 \times 10^{-3}, \quad \beta \approx 8.87 \times 10^{-12}. \tag{1.38}$$

The initial conditions for (1.35) are

$$R = 1, \quad z = z_0, \quad \Delta p = \Delta p_0 \quad \text{at} \quad t = 0, \tag{1.39}$$

where $z_0 \sim 1$, and

$$\Delta p_0 = \frac{2\gamma}{\rho_s g d R_c}, \tag{1.40}$$

where γ is the surface energy, $\gamma \approx 0.07$ N m^{-1} (Mahoney and Trent (1995)). Hence $\Delta p_0 \approx 3.3 \times 10^{-6}$.

We see that $\Delta p \ll 1$ for $t > 0$, and R and p satisfy, to lowest order,

$$(R^3 p)\dot{} = 0, \quad \dot{p} = -R^2, \tag{1.41}$$

with solution

$$R = \left(\frac{p_0}{p}\right)^{1/3}, \tag{1.42}$$

where p_0 is the initial value of p. If we define

$$\Pi = \frac{p_{sc} + p_s g d}{p_{sc}} \tag{1.43}$$

to be the ratio of the sludge pressure at the tank base to the saltcake overburden pressure, then the maximum bubble size at the base of the saltcake is given (relative to R_c) by

$$R \approx \Pi^{1/3}. \tag{1.44}$$

The maximum bubble thickness thus increases for thinner saltcakes, and sizeable bubbles may easily be produced. If $\Pi = 10$ (5 metres sludge below 0.5 metres saltcake) then $R \approx 2.15$ (corresponding to 2.15 m). In conclusion, we find that we may expect bubbles of order (metres) size may generated by simple aggradation under the saltcake. Since this is only one or at most two orders of magnitude smaller than the tank radius, the analysis of section 5 provides a worst-case estimate of the possibility of the release of a large trapped gas bubble. We note also that, not surprisingly, the size of bubble produced depends crucially upon the order of magnitude of the yield stress in the sludge; for the resettled sludge in the notorious 'burp tank' 241-SY-101, for example, where the yield stress is only about 10 Pa, the corresponding bubble size reduces to only about 1.4 mm.

Section 2: The Dry Saltcake

In this section of the report we attempt to ascertain the amount of H_2 gas present in the (dry) saltcake portion of a cylindrically symmetric tank. The first question to ask is: what is the dominant mechanism driving the gas flow in the dry saltcake? We answer this by comparing the diffusive and convective time scales in the medium. For this, we first note that the diffusivity of H_2 in the dry saltcake is reduced by the *tortuosity* $\chi \geq 1$, which measures the relative deviation of a particle path in the porous medium from a straight line ($\chi = 1$). We assume that for the dry saltcake the tortuosity is around 10. Then we have

$$D_d \approx \frac{D_a}{\chi} = \frac{0.6 \text{ cm}^2/\text{sec}}{10} = 0.06 \text{ cm}^2/\text{sec}. \tag{2.1}$$

A typical height scale of the dry saltcake is given by

$$H_d \approx 100 \text{ in} = 250 \text{ cm}. \tag{2.2}$$

Therefore, we have the following diffusive time scale, which roughly measures the time it would take for a particle of the gas to diffuse out of the porous medium:

$$T_D = \frac{H_d^2}{D_d} = \frac{(250 \text{ cm})^2}{0.06 \text{ cm}^2/\text{sec}} = 12 \text{ days}. \tag{2.3}$$

For the convective time scale, we need to know the volumetric flux rate G of gas produced by the sludge, and the radius r of the tank. Typical values are

$$G \approx 100 \text{ ft}^3/\text{day} = 31.25 \text{ cm}^3/\text{sec}, \qquad r \approx 37.5 \text{ ft} = 1125 \text{ cm}. \tag{2.4}$$

This produces a convective velocity which we shall need often:

$$U = \frac{G}{\pi r^2} = \frac{31.25 \text{ cm}^3/\text{sec}}{\pi(1125 \text{ cm})^2} = 7.86 \times 10^{-6} \text{ cm/sec}. \tag{2.5}$$

Note the rather small size of U. So the convective time scale, which roughly measures the time it would take for a particle to traverse the medium driven only by convection, is given by

$$T_C = \frac{H_d}{U} = \frac{250 \text{ cm}}{7.86 \times 10^{-6} \text{ cm/sec}} = 1 \text{ yr}. \tag{2.6}$$

Therefore, in the dry salt cake the diffusive process dominates.

Since over four decades have passed since these tanks were first filled with waste, we assume we have a steady state equation which depends only on z, so our system reduces to the following:

$$D_d \frac{d^2 C}{dz^2} = 0, \qquad C(H_d) = 0, \tag{2.7}$$

where C is the concentration of H_2 in the gas mixture. We have assumed that at the top of the saltcake ($z = H_d$), atmospheric convection takes away any hydrogen gas that may still remain. Now at the interface with the sludge ($z = 0$), we can impose one of two conditions. First, we know that the percentage of H_2 in the gas mixture *produced in the sludge* (denoted by C_P) is approximately 0.3. However, our system is such that air from the top can also diffuse down to the boundary of the sludge, so the actual *volume fraction* may differ.

A more reasonable boundary condition is given by the flux of H_2 gas, which we can calculate. The volumetric flux of gas out of the sludge is given by the velocity of the gas at the sludge boundary, which is the gas produced divided by the area:

$$\text{flux of gas out} = \frac{G}{\pi r^2} = U.$$

The flux of hydrogen gas into the porous medium is given by the flux out multiplied by the proportion of H_2 in the mixture, which gives us a flux per area as if the entire saltcake were porous. It is not, and thus we must divide by the *porosity* ϵ of the medium ($\epsilon = 1$ if the saltcake were completely porous). Therefore, we have

$$\text{flux} = -D_d \frac{\partial C}{\partial z}(0) = \frac{C_P U}{\epsilon}. \tag{2.8}$$

Equation (2.7) tells us that the flux is constant, so we have

$$C(z) = \frac{C_P U \chi}{D_a \epsilon}(H_d - z). \tag{2.9}$$

An interesting quantity to calculate is $C(0)$, which is

$$C(0) = \frac{C_P T_D}{T_C \epsilon}. \tag{2.10}$$

Since $T_D \ll T_C$, we have that $C(0) \ll C_P$. This confirms our hypothesis that air has diffused down to the sludge layer. We shall also need the average value of C in the saltcake, which is easy to calculate since the profile is a straight line:

$$\bar{C} = \frac{C_P U \chi H_d}{2 D_a \epsilon}. \tag{2.11}$$

Two quantities we wish to know are the volume of the gas in the dry saltcake V_{d,H_2} and the volume fraction of the gas ϕ_{e,H_2} if it were released all at once into the void space. For the first, we note that we must multiply the average concentration of the gas by the porosity to get the void fraction ϕ_{d,H_2} of H_2:

$$\phi_{d,H_2} = \epsilon \bar{C} = \frac{C_P U \chi H_d}{2 D_a}. \tag{2.12}$$

Note that this calculation removes the porosity ϵ from our result. Then we get the volume by multiplying by the total volume of the saltcake:

$$V_{d,H_2} = \pi r^2 H_d \phi_{d,H_2} = \frac{C_P G \chi H_d^2}{2D_a}. \tag{2.13}$$

Lastly, to calculate ϕ_{e,H_2}, we divide by the dome space. This is not necessarily a cylinder, but the value is known:

$$\phi_{e,H_2} = \frac{V_{d,H_2}}{V_e} = \frac{C_P G \chi H_d^2}{2D_a V_e}. \tag{2.14}$$

We now calculate the values for a real tank, namely S112. The parameters are the following:

$$H_d = 110 \text{ in} = 275 \text{ cm}, \qquad G = 92 \text{ L/day} = 1.06 \text{ cm}^3/\text{sec}, \qquad \chi \approx 10,$$

$$r = 1125 \text{ cm}, \qquad C_P = 0.3, \qquad V_e/V_d = 1.6.$$

Then we have that

$$U = 2.68 \times 10^{-7} \text{ cm/sec},$$

$$\phi_{d,H_2} = \frac{(0.3)(2.68 \times 10^{-7} \text{ cm/sec})(10)(275 \text{ cm})}{2(0.6 \text{ cm}^2/\text{sec})} = 1.84 \times 10^{-4}, \tag{2.15}$$

$$V_{d,H_2} = \pi(1125 \text{ cm})^2(275 \text{ cm})(1.84 \times 10^{-4}) = 2.01 \times 10^5 \text{ cm}^3 = 7.45 \text{ ft}^3, \tag{2.16}$$

$$\phi_{e,H_2} = \phi_{d,H_2} \frac{V_d}{V_e} = \frac{1.84 \times 10^{-4}}{1.6} = 1.15 \times 10^{-4}, \tag{2.17}$$

which is far below the lower flammability limit of 0.04. If the tank is composed mostly of dry saltcake, then this calculation would lead to a preliminary conclusion that the tank is safe. However, if the tank has a relatively large amount of wet saltcake, then further calculations are needed. These calculations will be undertaken in the following sections.

Section 3: No Production
in the Wet Saltcake

Next we consider flow in the wet saltcake. From conservation of mass for the gas, we have

$$\epsilon \frac{\partial \rho_g}{\partial t} = -\frac{\partial(\rho_g v_g)}{\partial z}, \tag{3.1}$$

where ρ is the density and v the velocity of our diffusing species. As before, we want to model steady flow which only depends on z, so equation (3.1) becomes

$$\frac{d(\rho_g v_g)}{dz} = 0. \tag{3.2}$$

We assume that in the wet saltcake, the gas behaves like an incompressible fluid, so we have a constant ρ_g. Therefore, we have a constant v_g.

We consider this as flow in a porous medium; therefore the velocities in the liquid and gas phase are given by

$$v_l = -\frac{k_l}{\mu_l}\left(\frac{dp_l}{dz} + \rho_l g\right), \tag{3.3a}$$

$$v_g = -\frac{k_{gw}}{\mu_g}\left(\frac{dp_g}{dz} + \rho_g g\right), \tag{3.3b}$$

where k is the permeability of the saturated saltcake with respect to the diffusing species and μ is the viscosity and p the pressure of that species. We assume that at steady state the liquid is not moving and is simply serving to saturate the medium and coat the pores, so we have

$$\frac{dp_l}{dz} = -\rho_l g. \tag{3.4}$$

The pressures in the gas and liquid are coupled by

$$p_g - p_l = p_c = \kappa(\phi_g)\gamma, \tag{3.5}$$

where p_c is the capillary pressure, ϕ_g is the volume fraction of our gas, κ is the curvature and γ is the interfacial tension. Since our velocity is a constant, we assume that the capillary pressure is also a constant, so we may combine (3.3b)-(3.5) to yield

$$v_g = -\frac{k_{gw}}{\mu_g}\left(-\rho_l g + \rho_g g\right), \tag{3.6}$$

Now to avoid the problem of considering how large bubbles will move into small pores. we assume that the bubbles are produced at the boundary of the wet saltcake with the

sludge. However, the cross-sectional area of the pores available for transport is now given by the volume fraction of the gas $\phi_g(0)$, rather than the full porosity ϵ, as was true in the dry saltcake. Therefore, we have

$$v_g(0) = -\frac{k_{gw}g}{\mu_g}(\rho_g - \rho_l) = \frac{G}{\pi r^2 \phi_g(0)} = \frac{U}{\phi_g(0)}. \tag{3.7}$$

Since our velocity v_g is a constant, we have from (3.7) that

$$\frac{k_{gw}g}{\mu_g}(\rho_l - \rho_g) = \frac{U}{\phi_g(0)}. \tag{3.8}$$

Solving for k_{gw}, we have

$$k_{gw} = \frac{U\mu_g}{g(\rho_l - \rho_g)\phi_g(0)}. \tag{3.9}$$

Now we are going to use our expression for k_{gw} to estimate the void fraction ϕ_g of the gas with respect to the total volume of the porous medium. For a porous medium with spherical particles, we have that

$$k_g(\phi) = \frac{d_p^2}{\chi}\frac{\phi^3}{(1-\phi)^2}, \tag{3.10}$$

where d_p is the diameter of the particles in the medium. This is a form of the Kozeny-Carman equation (see, for example, Bear (1972)). However, note that since our ϕ_g is so small, the exponent of ϕ_g in the numerator will be crucial. Also, equation (3.10) is based on the assumption that there is a more or less continuous distribution of gas (which would correspond to a higher value of ϕ_g). However, this may not be the case here. These faulty assumptions may perhaps lead to errors in our estimates.

Now we examine equation (3.10) in both regions. In the wet saltcake, the void fraction consists only of the gas, since the liquid is reducing the pore size:

$$k_{gw} = \frac{d_p^2}{\chi}\frac{\phi_g^3}{(1-\phi_g)^2}. \tag{3.11a}$$

However, in the dry saltcake, there is no liquid, so the void fraction consists of the full pores. Therefore, we use the porosity:

$$k_{gd} = \frac{d_p^2}{\chi}\frac{\epsilon^3}{(1-\epsilon)^2}. \tag{3.11b}$$

Once again, the reasoning used to derive equations (3.11) is exactly analogous to that used to derive (2.8) and (3.7).

There are two ways of measuring ϕ_g. The first way is to set the two values of k_{gw} from (3.11a) and (3.8) equal to one another:

$$\frac{U\mu_g}{g(\rho_l - \rho_g)\phi_g(0)} = \frac{d_p^2}{\chi}\frac{\phi_g^3}{(1-\phi_g)^2}. \tag{3.12}$$

Therefore, we see that ϕ_g must be a constant. Solving for ϕ_g, we have

$$\frac{\phi_g^4}{(1-\phi_g)^2} = \frac{U\mu_g\chi}{gd_p^2(\rho_l - \rho_g)} = \frac{1}{K}. \tag{3.13}$$

Alternatively, we may combine equations (3.11) to yield

$$k_{gw} = k_{gd}\frac{\phi_g^3(1-\epsilon)^2}{(1-\phi_g)^2\epsilon^3}$$

$$\frac{U\mu_g}{g(\rho_l - \rho_g)\phi_g} = k_{gd}\frac{\phi_g^3(1-\epsilon)^2}{(1-\phi_g)^2\epsilon^3}$$

$$\frac{\phi_g^4}{(1-\phi_g)^2} = \frac{U\epsilon^3\mu_g}{gk_{gd}(\rho_l - \rho_g)(1-\epsilon)^2}. \tag{3.14}$$

Then if k_{gd} can be determined experimentally, equation (3.14) yields an expression for ϕ_g. In either case, we then have

$$\phi_{w,\text{H}_2} = C_P\phi_g, \tag{3.15}$$

$$V_{w,\text{H}_2} = \pi r^2 H_w\phi_{w,\text{H}_2}, \tag{3.16}$$

$$\phi_{e,\text{H}_2} = \frac{V_{w,\text{H}_2}}{V_e}. \tag{3.17}$$

Now we introduce some typical measurements to get an estimate of ϕ_g. We have the following values:

$$\chi \approx 10, \qquad d_p \approx 5\times 10^{-3}\text{ cm}, \qquad g = 981\text{ cm/sec}^2. \tag{3.18a}$$

The gas released from the sludge is approximately 40% N_2, 30% H_2, 25% NH_3, and 5% NH_3. Therefore, for μ_g and ρ_g, we use the viscosity of air, since the gas released by the sludge is similar to air, and the values shouldn't be that different. For all calculations of μ and ρ, we use a temperature of 140° F = 60° C, which is the approximate temperature of the sludge. So we have

$$\mu_g = 1.999\times 10^{-4}\text{ g/(cm·sec)}, \qquad \rho_g = 1.06\times 10^{-3}\text{ g/cm}^3, \qquad \rho_l = 9.77\times 10^{-1}\text{ g/cm}^3. \tag{3.18b}$$

We also use the value of U from (2.5).

Using (3.18) in (3.13), we have

$$\frac{\phi_g^4}{(1-\phi_g)^2} = \frac{(7.86\times 10^{-6}\text{ cm/sec})[1.999\times 10^{-4}\text{ g/(cm·sec)}](10)}{(981\text{ cm/sec}^2)(5\times 10^{-3}\text{ cm})^2(9.77\times 10^{-1} - 1.06\times 10^{-3})\text{ g/cm}^3}$$

$$= \frac{1.57\times 10^{-8}}{(2.45\times 10^{-2})(9.76\times 10^{-1})}$$

$$= 6.56\times 10^{-7}$$

$$\phi_g = 0.028. \tag{3.19}$$

To complete our work, we need the following parameters:

$$C_P = 0.3, \qquad r = 1125 \text{ cm}, \qquad H_w = 1000 \text{ cm}, \qquad V_e = 25000 \text{ ft}^3 = 6.75 \times 10^8 \text{ cm}^3.$$

Therefore, we have

$$\phi_{w,\text{H}_2} = (0.3)(0.013) = 0.0084, \tag{3.20}$$

$$V_{w,\text{H}_2} = (0.0039)\pi(1125 \text{ cm})^2(1000 \text{ cm}) = 3.35 \times 10^7 \text{ cm}^3 = 1240 \text{ ft}^3, \tag{3.21}$$

$$\phi_{e,\text{H}_2} = \frac{1.55 \times 10^7 \text{ cm}^3}{6.75 \times 10^8 \text{ cm}^3} = .050. \tag{3.22}$$

This exceeds the lower flammability limit of H_2. Therefore, we see that the situation where there is a large amount of wet saltcake and a significant volume of sludge underneath producing gas can be quite hazardous. However, it is also prudent to recall that we are modeling a highly unlikely event: that is, that all the gas in the wet saltcake could *simultaneously* be released into the dome space.

We may also use (3.18) in (3.14), yielding

$$\begin{aligned}
\frac{\phi_g^4}{(1 - \phi_g)^2} &= \frac{(7.86 \times 10^{-6} \text{ cm/sec})(0.3)^3[1.999 \times 10^{-4} \text{ g/(cm·sec)}]}{k_{gd}(981 \text{ cm/sec}^2)(9.76 \times 10^{-1} \text{ g/cm}^3)(0.7)^2} \\
&= \frac{9.04 \times 10^{-14} \text{ cm}^2}{k_{gd}}.
\end{aligned} \tag{3.23}$$

Section 4: Production in the Wet Saltcake

Next we add the complication of gas production inside the wet saltcake. We assume that some proportion α of the gas is produced inside the wet saltcake. An easy estimate to make would be to assume that the liquid in the sludge and the liquid in the wet saltcake would be equally likely to produce gas, and each would produce at a rate proportional to its volume:

$$\alpha = \frac{\text{volume of liquid in wet saltcake}}{\text{total volume of liquid}} = \frac{(\epsilon - \bar{\phi}_g)H_w}{H_s + (\epsilon - \bar{\phi}_g)H_w}. \tag{4.1}$$

Other estimates might use surface area instead of volume as the relevant measurement in the porous medium.

The volumetric flux of gas from the bottom would then be given by

$$v_g(0) = \frac{U(1-\alpha)}{\phi_g(0)}. \tag{4.2}$$

The total production rate of gas is given by the total mass of gas produced in the wet saltcake divided by the area of the saltcake:

$$\text{total production rate} = \frac{\rho_g G \alpha}{\pi r^2} = \rho_g U \alpha.$$

To get a production rate per height, we simply note that at each height, the pore density is related to the volume fraction of gas, so we have

$$\frac{\text{production rate}}{\text{height}} = \frac{\rho_g U \alpha}{H_w(\epsilon - \phi_g)}. \tag{4.3}$$

We add (4.3) to our steady-state conservation-of-mass equation (3.2) to yield

$$\frac{d(\rho_g v_g)}{dz} = \frac{\rho_g U \alpha}{H_w(\epsilon - \phi_g)}. \tag{4.4}$$

Note that our work in section 3 corresponds to the case when $\alpha = 0$.

We see that in this case our velocity will be a function of z. We can then no longer assume that our capillary pressure will be a constant. By comparison with experiments, we can give an approximate form for $\kappa(\phi_g)$:

$$\kappa(\phi_g) \approx \delta\phi_g + \text{constant}, \tag{4.5}$$

where we assume δ to be an $O(1)$ constant. Substituting (4.5) into (3.5), we have

$$p_g - p_l = p_c = \gamma[\delta\phi_g + \text{constant}],$$ (4.6)

so equation (3.6) becomes

$$v_g = -\frac{k_{gw}}{\mu_g}\left(-\rho_l g + \rho_g g + \gamma\delta\frac{d\phi_g}{dz}\right).$$ (4.7)

Substituting (4.7) in (4.4) and using the fact that we are assuming that the gas is incompressible, we have

$$\frac{d}{dz}\left\{\frac{k_{gw}}{\mu_g}\left[(\rho_l - \rho_g)g - \gamma\delta\frac{d\phi_g}{dz}\right]\right\} = \frac{U\alpha}{H_w(\epsilon - \phi_g)}.$$ (4.8)

Substituting (3.11a) in (4.8), we have

$$\frac{d_p^2}{\chi\mu_g}\frac{d}{dz}\left\{\frac{\phi_g^3}{(1-\phi_g)^2}\left[(\rho_l - \rho_g)g - \gamma\delta\frac{d\phi_g}{dz}\right]\right\} = \frac{U\alpha}{H_w(\epsilon - \phi_g)}.$$ (4.9)

Note that we have a second-order differential equation for which we have prescribed only one boundary condition. However, if we do prescribe another condition, equation (4.9) can be solved numerically for ϕ_g.

In order to simplify matters, we normalize z by letting $z = H_w y$:

$$\frac{d_p^2}{\chi\mu_g}\frac{d}{dy}\left\{\frac{\phi_g^3}{(1-\phi_g)^2}\left[(\rho_l - \rho_g)g - \frac{\gamma\delta}{H_w}\frac{d\phi_g}{dy}\right]\right\} = \frac{U\alpha}{(\epsilon - \phi_g)}, \qquad 0 \le y \le 1.$$ (4.10)

We can simplify (4.10) even further if we measure the relative magnitudes of the bracketed terms. Using values from section 3, we have that the magnitude of the first term is

$$|(\rho_g - \rho_l)g| = (9.76 \times 10^{-1}\ \text{g/cm}^3)(981\ \text{cm/sec}^2) = 957\ \text{g}\cdot\text{cm}^2/\text{sec}^2.$$ (4.11a)

Given the fact that at 60° C, $\gamma = 66.2$ g/sec^2 (Batchelor (1985)), we have that the second bracketed term is

$$\left|-\frac{\gamma\delta}{H_w}\frac{d\phi_g}{dy}\right| = O(\phi_g) \times \left|-\frac{66.2\ \text{g/sec}^2}{1000\ \text{cm}}\right| = O(\phi_g)\left(6.62 \times 10^{-2}\ \text{g}\cdot\text{cm}^2/\text{sec}^2\right).$$ (4.11b)

Therefore, even without ϕ_g being small (which it is), the second term is dominated by the first term, so we now have, to leading order,

$$\frac{d_p^2(\rho_l - \rho_g)g}{\chi\mu_g}\frac{d}{dy}\left[\frac{\phi_g^3}{(1-\phi_g)^2}\right] = \frac{U\alpha}{(\epsilon - \phi_g)}.$$ (4.12)

Note then that H_w does not appear in our equations to leading order except through the parameter α.

Since we have reduced our second-order differential equation to a first-order one by considering parameter sizes, it is then reasonable to conclude that we have a boundary layer near $y = 0$. However, In order to calculate the gas in the saltcake, we only need to calculate $\bar{\phi}_g$, which is defined as

$$\bar{\phi}_g = \int_0^1 \phi_g(y)\, dy. \tag{4.13}$$

Therefore, even if we do have a boundary layer, since we would be averaging across its negligible width, the contribution from the boundary layer to the average value $\bar{\phi}_g$ would be negligible.

Now we make another simplifying assumption. First, we note that ϕ_g is small, so we neglect it when compared with ϵ. Then (4.1) becomes

$$\alpha = \frac{\epsilon H_w}{H_s + \epsilon H_w} \tag{4.14}$$

and (4.12) becomes, subject to (4.2),

$$\frac{d_p^2(\rho_l - \rho_g)g}{\chi \mu_g} \frac{\phi_g^3}{(1 - \phi_g)^2} = \frac{U\alpha y}{\epsilon} + \frac{U(1-\alpha)}{\phi_g(0)}$$

$$\frac{\phi_g^3}{(1 - \phi_g)^2} = \frac{U\chi\mu_g}{d_p^2(\rho_l - \rho_g)g}\left[\frac{\alpha y}{\epsilon} + \frac{(1-\alpha)}{\phi_g(0)}\right]$$

$$= \frac{1}{K}\left[\frac{\alpha y}{\epsilon} + \frac{(1-\alpha)}{\phi_g(0)}\right]. \tag{4.15}$$

If $\alpha \neq 1$, then equation (4.15) may be solved algebraically for $\phi_g(0)$ and then for $\phi_g(y)$.

However, we wish to consider the case where $\alpha = 1$; that is, we assume that all the gas is produced in the wet saltcake. One way that this can happen is if the volume of sludge is much less than the volume of liquid. Then we have that $H_s \ll \epsilon H_w$. Using the values from section 3, we require that

$$H_s \ll (0.3)(1000 \text{ cm}) = 300 \text{ cm}.$$

But we have experimental data that shows that in some tanks H_s can be as low as 5 cm, so this is a reasonable assumption for some tanks. In this case, equation (4.15) becomes

$$\frac{\phi_g^3}{(1 - \phi_g)^2} = \frac{y}{K\epsilon}. \tag{4.16}$$

Note that since ϕ_g is small, ϕ_g is approximately proportional to $y^{1/3}$ for small y. Hence, we would expect our neglected interfacial tension term to produce a layer in the *derivative* of ϕ_g, which would contribute even less to our calculation of $\bar{\phi}_g$ than we originally guessed.

We could now invert (4.16) numerically to solve for ϕ_g. However, with a little trickery we can calculate $\bar{\phi}_g$ without solving the cubic. For we see that since $\phi_g(0) = 0$, we have

$$\int_0^1 \phi_g(y)\, dy = \int_0^{\phi_g(1)} [1 - y(\phi_g)]\, d\phi_g, \quad \text{where } y(\phi_g) = K\epsilon \frac{\phi_g^3}{(1 - \phi_g)^2}. \tag{4.17}$$

So we have

$$\bar{\phi}_g = \phi_g(1) - K\epsilon \int_{1-\phi_g(1)}^1 \frac{(1-u)^3}{u^2}\, du$$

$$= \phi_g(1) - K\epsilon \left\{ 3\log[1 - \phi_g(1)] + \frac{\phi_g^3(1) + 3\phi_g^2(1) - 4\phi_g(1) - 2}{2[1 - \phi_g(1)]} - 1 \right\}. \tag{4.18}$$

Now we produce numerical results using our values from section 3. Then we have that

$$K\epsilon = \frac{(5 \times 10^{-3}\text{ cm})^2(0.3)(9.76 \times 10^{-1}\text{ g/cm}^3)(981\text{ cm/sec}^2)}{(7.86 \times 10^{-6}\text{ cm/sec})(10)[1.999 \times 10^{-4}\text{ g/(cm·sec)}]}$$

$$= 4.57 \times 10^5 \tag{4.19}$$

$$\frac{\phi_g^3(1)}{[1 - \phi_g(1)]^2} = (K\epsilon)^{-1} = 2.19 \times 10^{-6}$$

$$\phi_g(1) = 0.01287 \tag{4.20}$$

$$\bar{\phi}_g = 0.01287 - (4.57 \times 10^5)(7.21 \times 10^{-9}) = 0.00958. \tag{4.21}$$

Note that since $\bar{\phi}_g \ll \epsilon$, our assumption to neglect ϕ_g when compared with ϵ is valid.

Therefore, we have

$$\phi_{w,H_2} = (0.3)(0.00958) = 2.87 \times 10^{-3}, \tag{4.22}$$

$$V_{w,H_2} = (2.87 \times 10^{-3})\pi(1125\text{ cm})^2(1000\text{ cm}) = 1.14 \times 10^7\text{ cm}^3 = 423\text{ ft}^3, \tag{4.23}$$

$$\phi_{e,H_2} = \frac{1.14 \times 10^7\text{ cm}^3}{6.75 \times 10^8\text{ cm}^3} = .017. \tag{4.24}$$

This is lower than the flammability limit of H_2, though still over the commonly accepted "danger limit" of 1% H_2. Therefore, we see that the case $\alpha = 1$ is safer than the case $\alpha = 0$, all other things being roughly equal. Therefore, we see that the magnitude of the threat is related to how small α is.

Section 5 The release of large gas bubbles

The calculations of section 1 showed that bubbles of size O(1) metres may be produced in the sludge. The possibility thus arises that there will be a build-up of gas beneath the saltcake. In a worst-case scenario, the saltcake suddenly ruptures and releases the stored gas; a model to predict the amount released in such an event clearly depends on the properties of the saltcake and the mechanisms involved in rupture.

The first mechanism that will be discussed relies on the observation that observations indicate that the saltcake is effectively 'glued' to the sides of the tank. If a gas cavity at a given pressure forms beneath a saltcake layer of a given thickness, then the saltcake will deform and eventually rupture. 'Lubrication puncturing' of the saltcake layer is then discussed.

5.1 Failure of a clamped saltcake layer

Assume that a layer of H_2 has collected beneath a saltcake that is 'stuck' to both sides of the tank. The layer is assumed to be composed of agglomerated bubbles, and has pressure $p(t)$. Gas generation causes the pressure to rise, and, since (as observed above) the diffusion and convection times in the saltcake are of the order of a number of days, the gas layer cannot escape and therefore (since the sludge is incompressible) deforms the saltcake.

To study this phenomenon, we examine the problem of the deformation of a loaded circular plate of (undeformed) radius R and height $2h$. In its undistorted position, the plate is assumed to occupy the region $\{0 \leq r \leq R, \ | z | \leq h\}$. On the assumption that the $h \ll R$, we may employ plane stress theory (see, for example, Timoshenko and Goodier (1987)). Introducing the standard Airy stress function $\psi(r, z)$, and assuming that there is no θ-dependence, we find that ψ must satisfy

$$\nabla^4 \psi = 0. \tag{5.1}$$

Denoting the components of the stress tensor by T and assuming that the r, θ and z components of displacement are given by u, v and w respectively, we note that, according to plane stress, the quantities v, $T_{r\theta}$ and $T_{\theta z}$ are zero, though in general $T_{\theta\theta}$ is not. Also, in terms of the Airy stress function, we have

$$T_{rr} = \left(\nu\nabla^2\psi - \psi_{rr}\right)_z \tag{5.2}$$

$$T_{\theta\theta} = \left(\nu\nabla^2\psi - \frac{1}{r}\psi_r\right)_z \tag{5.3}$$

$$T_{zz} = \left((2-\nu)\nabla^2\psi - \psi_{zz}\right)_z \tag{5.4}$$

$$T_{rz} = \left((1-\nu)\nabla^2\psi - \psi_{zz}\right)_r \tag{5.5}$$

$$u = -\frac{1+\nu}{E}\psi_{rz} \tag{5.6}$$

$$w = \frac{1+\nu}{E}(2(1-\nu)\nabla^2\psi - \psi_{zz}) \tag{5.7}$$

where, as usual, ν and E denote the Poisson ratio and Young modulus for the saltcake. The boundary conditions to be satisfied are $T_{rz} = T_{zz} = 0$ on $z = h$, (assuming that the top of the saltcake is stress free) whilst on $z = -h$ we have $T_{rz} = 0$, $T_{zz} = -p$. On $r = R$, the clamping gives $u = w = 0$. As posed, this is not a simple problem to solve, though it can be done in terms of complex potentials. A simpler approximate approach consists of seeking a polynomial expression for ψ. Some simple calculus shows that an appropriate expression is given by

$$\psi = A\left(16\,z^6 - 120\,z^4 r^2 + 90\,z^2 r^4 - 5\,r^6\right) + B\left(8\,z^6 - 16\,z^4 r^2 - 21\,z^2 r^4 + 3\,r^6\right) +$$

$$C\left(8\,z^4 - 24\,r^2 z^2 + 3\,r^4\right) + D\left(2\,z^3 - 3\,r^2 z\right) + F\left(r^2 z + z^3\right)$$

where the constants A, B, C, D and F are to be determined. Imposing the stress conditions on $z = \pm h$ and also insisting that the average x-displacement is zero on $r = R$, we find that

$$A = -\frac{p}{84480h^3}(11\nu + 8), \quad B = \frac{p}{2816h^3}, \quad C = -\frac{p}{256h}, \quad D = \frac{p}{60(\nu - 1)}, \quad F = \frac{p}{20(\nu - 1)}$$

and the stresses are therefore given by

$$T_{rr} = \frac{pz^3}{8h^3}(2+\nu) + \frac{\nu p}{2(\nu-1)} - \frac{3p}{32h^3}(\nu r^2 + 3r^2 + 4h^2) \tag{5.8}$$

$$T_{zz} = -\frac{p}{4h^3}(z+2h)(z-h)^2 \tag{5.9}$$

$$T_{rz} = -\frac{3rp}{8h^3}(h^2 - z^2). \tag{5.10}$$

Thus the maximum value of T_{zz} is given by $-p$ and the maximum value of T_{rz} is $-3Rp/8h$, and, since we assume that $R \gg h$, is likely to be the larger. When the value $-3Rp/8h$ exceeds the yield stress σ_y of the saltcake at some point, the saltcake will rupture and the gas will be released.

To close the model, the pressure must be related to the height of the cavity and the amount of gas contained therein. Again, some simple assumptions are used to accomplish this. Setting $z = -h$, the cavity volume V_C may be calculated by evaluating

$$V_C = 2\pi \int_0^R wr\,dr = \frac{\pi p R^2(1+\nu)}{128Eh^3(1-\nu)}[(1-\nu)^2 R^2(R^2 + 12h^2) + 8h^4(\nu^2 - 22\nu + 13)]$$

Assuming a constant temperature T_0, we know that from the perfect gas law $p(t) = \rho_g \mathcal{R} T_0$ where $\mathcal{R}$ is the gas constant and ρ_g the density of the hydrogen. The mass of gas M that will be released will therefore be given by $M = V_C \rho_g$, and thus

$$M = \frac{pV_C}{\mathcal{R} T_0} \tag{5.12}$$

where

$$p = \frac{8h\sigma_y}{3R}.$$

Thus finally

$$M = \frac{\sigma_y^2 \pi (1+\nu)}{18 \mathcal{R} T_0 E h (1-\nu)}[(1-\nu)^2 R^2 (R^2 + 12h^2) + 8h^4(\nu^2 - 22\nu + 13)]. \tag{5.13}$$

In order to get some feeling for the amounts of gas that could be released, some (wild) guesses for the relevant parameters were used in the absence of concrete data. The values $R = 10$m, $h = 1/2$m, $\nu = 3/10$, $E = 10^{10}$ Pa, $\sigma_y = 5 \times 10^9$ Pa, $\mathcal{R} = 8.3$ m^2/sec^2/K and $T_0 = 330$K gave a gas release of mass 3091 kg; to determine whether or not this is threatening, correct values would have to be used.

5.2 Lubrication puncturing of a saltcake layer

To study this mechanism, we assume that a bubble at (constant) pressure $p_b(t)$ lies in the region $y > 0$, the distance from the bottom of the bubble to the x-axis (a layer of saltcake) being denoted by $h(x,t)$. Because of the coordinate system chosen, gravity is assumed to act in the positive y-direction. The equations of motion for the flow in the region between the bubble and the saltcake are given by

$$u_t + uu_x + vu_y = -\frac{1}{\rho}p_x + \nu(u_{xx} + u_{yy})$$

$$v_t + uv_x + vv_y = -\frac{1}{\rho}p_y + \nu(v_{xx} + v_{yy})$$

$$u_x + v_y = 0.$$

The mechanism for saltcake fracture in this case is the large pressure that is produced in the thin gap between the bubble and the saltcake; denoting a typical gap width by h_0 and assuming that distances in the x-direction are characterized by L, we write $\delta = h_0/L$ and assume that a typical velocity is given by U. Non-dimensionalizing according to $u = \bar{u}$, $v = \delta U \bar{v}$, $x = L\bar{x}$, $y = \delta L \bar{y}$, $t = L\bar{t}/U$ and $p = \mu U/(L\delta^2)\bar{p}$, we find, upon dropping the bars, that the lowest order equations for the flow are

$$0 = -p_x + u_{yy}, \quad g = p_y, \quad u_x + v_y = 0.$$

For g to enter the lowest order equations, it is essential that the non-dimensional quantity (related to the Bond number)

$$\frac{\mu U}{p \rho L \delta^3}$$

is order one. These equations may now be solved, subject to the obvious conditions that $u = v = 0$ at $y = 0$, whilst at $y = h$ we have $v = h_t + u h_x$ and $u_y = 0$. To derive an extra condition for the film/bubble interface, the pressure p_f in the film may be related to $p_b(t)$ using

$$p_f - p_b = -\gamma h_{xx}$$

where γ is, as usual, the surface tension. Carrying out the standard lubrication-type integration of the continuity equation now gives the equation for $h(x,t)$ as

$$(h^3(g h_x + \gamma h_{xxx}))_x + 3 h_t = 0 \tag{5.14}$$

,

which must be solved subject to (for example) $h = h_0(x, 0)$ and $h_x = h_{xxx} = 0$ at $x = 0$. The pressure on $y = 0$ may then be determined, since it may be written in temrs of $h(x,t)$ as

$$p(x, 0, t) = p_b(t) - \gamma h_{xx} - h;$$

if this pressure exceeds a (known) critical pressure, then the slatcake punctures and the gas bubble is released. Various submodels to completely determine the shape of the bubble were discussed during the meeting, but there is clearly scope for further work here; although this model does not provide then simple estimates that the models above a re capable of, mathematically, it is probably the most interesting.

Section 6: Further Research

Other areas of research are immediately suggested by the results in sections 1-5. Most simply, the result that $\alpha = 1$ in section 4 could be relaxed. This would then allow sections 3 and 4 to be combined into one general result for all α. Different forms of the permeability law (3.10) could be used to determine their effect on our results for ϕ_{e,H_2}. If possible, a measurement of k_{gd} could be taken so we could use (3.23) to determine ϕ_g. Numerical simulations of equation (4.9) could be performed in order to see if we lost any significant qualitative structure when we made our simplifying assumptions. The bubble size calculations of section 1 seem to indicate that there is a possibility of fairly large single (rather than continuous) gas release events if large bubbles build up beneath the saltcake and produce pressures high enough to cause a rupture. Evidently there is a complicated 'trade-off' in this situation, as one might expect that a thick layer of saltcake, though less prone to rupture, could hold more large, trapped bubbles. For very thick saltcake layers, however, the sludge layer is likely to be too thin to produce much gas. Further work on the models is section 5 could therefore be undertaken to determine the most hazardous relative depths of sludge and saltcake.

A number of different models have been considered in this report, and there are clearly many ways in which the data may be interpreted. If a single recommendation had to be made based on the work carried out, however, then it is likely to be to the effect that, whilst there seem to be few scenarios in which the flammability limit is reached, there are 'worst cases' where the recognized safety limits may be exceeded and there is cause for concern.

Nomenclature

Variables and Parameters

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

C: concentration of H_2 with respect to the gas mixture., dimensionless (2.7).

c_α: molar concentration of species α, dimensionless (1.21).

d: diameter, units L (3.10).

D: diffusivity of H_2, units L^2/T (2.1).

E: Young's modulus, units ML/T^2 (5.7).

g: acceleration of gravity, units L/T^2 (3.3a).

G: total production rate of gas mixture, units L^3/T (2.4).

H: height of a layer of the tank, units L (2.2).

h: height of saltcake, units L (5.8).

k: permeability, units L^2 (3.3a).

K: dimensionless parameter (3.13), value

$$K = \frac{d_p^2(\rho_l - \rho_g)g}{U\chi\mu_g}.$$

M_α: Molecular weight of species α, units $M/M - mole$ (1.14).

p: pressure, units M/LT^2 (3.3a).

r: radius of tank, units L (2.4).

R: bubble radius, units L (1.8).

$\mathcal{R}$: universal gas constant, units $L^2/T^2/K$ (5.12).

t: independent variable measuring time, units T (3.1).

T: time scale, units T (2.3).

$T_{\alpha\beta}$: components of stress tensor, units M/LT^2 (5.2).

U: convective velocity of the system, units L/T (2.5), defined by

$$U = \frac{G}{\pi r^2}.$$

v: velocity of a fluid species, units L/T (3.1).

V: volume, units L^3 (2.13).

y: nondimensional variable measuring height (4.10).

z: independent variable measuring height, units L (2.7).

α: proportion of gas produced in the wet saltcake, dimensionless (4.1).

γ: interfacial tension, units M/T^2 (3.5).

δ: coefficient in ϕ_g-dependent capillary pressure equation (4.5)., units L^{-1}.

ϵ: porosity of the porous medium, dimensionless (2.8).

χ: tortuosity of the porous medium, dimensionless (2.1).

κ: curvature, units L^{-1} (3.5).

ϕ: volume fraction, dimensionless (2.12).

ψ: Airy stress function, (5.1).

μ: viscosity, units M/LT (3.3a).

ν: Poisson's ratio, dimensionless (5.2).

τ^*: yield stress of sludge, units M/LT^2 (1.32).

σ_y: yield stress of saltcake, units M/LT^2 (5.13).

ρ: density of constituent of the mixture, units M/L^3 (3.1).

Other Notation

a: as a subscript, used to indicate air (2.1).

c: as a subscript, used to indicate capillary pressure (3.5).

C: as a subscript, used to indicate convection (2.6).

d: as a subscript, used to indicate the dry saltcake (2.1).

D: as a subscript, used to indicate diffusion (2.3).

e: as a subscript, used to indicate the empty portion of the tank (2.14).

g: as a subscript, used to indicate gas (3.1).

H_2: as a subscript, used to indicate hydrogen gas (2.12).

l: as a subscript, used to indicate liquid (3.3a).

p: as a subscript, used to indicate the particle forming the porous medium (3.10).

P: as a subscript, used to indicate a production rate (2.8).

s: as a subscript, used to indicate the sludge (4.1).

w: as a subscript, used to indicate the wet saltcake (3.3b).

$^-$: used to indicate average values (2.11).

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