CONF-901116--7

PNL-SA--18137

DE91 005618

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August 1990

Presented at the
XIV International Symposium
on the Scientific Basis
for Nuclear Waste Management
Boston, Massachusetts
November 26-29, 1990

Work supported by
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

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WASTE STORAGE IN THE VADOSE ZONE AFFECTED BY WATER VAPOR CONDENSATION AND LEACHING

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ABSTRACT

One of the major concerns associated with waste storage in the vadose zone is that toxic materials may somehow be leached and transported by advecting water down to the water table and reach the accessible environment through either a well or discharge to a river. Consequently, care is taken to provide barriers over and around the storage sites to reduce contact between infiltrating water and the buried waste form. In some cases, it is important to consider the intrusion of water vapor as well as water in the liquid phase. Water vapor diffuses through porous material along vapor pressure gradients. A slightly lower temperature, or the presence of water-soluble components in the waste, favors water condensation resulting in leaching of the waste form and advection of water-soluble components to the water table. A simple analysis is presented that allows one to estimate the rate of vapor condensation as a function of waste composition and backfill material. An example using a waste form surrounded by concrete and gravel layers is presented. The use of thermal gradients to offset condensation effects of water-soluble components in the waste form is discussed. Thermal gradients may be controlled by design factors that alter the atmospheric energy exchange across the soil surface or that interrupt the geothermal heat field.

Contribution from the Pacific Northwest Laboratory, operated for the U.S. Department of Energy by Battelle Memorial Institute. This research was funded by the U.S. Department of Energy Office of Health and Environmental Research under Contract DE-AC06-76RLO 1830.

INTRODUCTION

Hazardous waste is often buried beneath the soil surface in the vadose zone. One of the concerns about burial in the vadose zone is that hazardous materials may leach from the disposal site down to the ground water and eventually resurface to be ingested into living biological systems. While technology for safe storage in the vadose zone continues to be developed and applied, there has been limited consideration of the potential for water-vapor condensation on buried waste, leading, in turn, to the leaching of soluble materials down toward the ground-water table.

The relative humidity of the vadose zone is invariably high. Even in arid climates, values of 99% or more are the rule. At this high humidity, a slight reduction in the equilibrium water-vapor pressure at a surface will cause condensation of water vapor if conditions on the surface are favorable for nucleation. In general, condensation on a surface may be triggered by a slight decrease in temperature or by the reduction in water-vapor pressure caused by the presence of soluble components. Consequently, when buried waste contains water-soluble components, it will invite vapor condensation, but temperatures in and around a buried waste site may be purposely manipulated so that a thermal gradient opposes vapor-pressure gradients induced by the soluble components. Thus, water may be forced to evaporate from the waste rather than condense in it. Our purpose is to bring these phenomena into perspective with regard to the performance of buried waste sites.

VAPOR CONDENSATION

Consider the generic case diagrammed in Figure 1. The waste is enclosed in a concrete vault and the vault is surrounded by a layer of gravel. A material with low permeability is used to cover the site, so that most of the precipitation will run off as surface water and the remainder will be mostly removed by evapotranspiration. The gravel layer also protects against the intrusion of water by forming a capillary break. The small pores in the vadose zone material surrounding the gravel layer act as a blotter, thus preventing water from entering the large pores formed by the gravel. The water in the vadose zone material thus slowly drains downward under the influence of gravity, rather than flowing into the gravel and wetting the concrete waste container.

While this type of design effectively controls normal liquid water movement in the unsaturated vadose zone, it does not address the possibility of water-vapor distillation. Water vapor diffusing along a vapor pressure gradient condenses on any surface with a water-vapor pressure less than the vapor pressure in the gas phase [1,2]. This, of course, assumes the surface is favorable for the nucleation of liquid-phase water, which is seldom a limitation in the vadose zone. After burial, the relative humidity of the gas phase in the surrounding vadose zone will become very near 100% (i.e., at least greater than 98%). Water vapor will then diffuse across the gravel layer and condense in the waste site until the liquid films covering surfaces in the waste and in the pores of the concrete containers reach the same equilibrium vapor pressure as that of the surrounding vadose zone. If there are significant amounts of soluble material, this may require a very long time to achieve the dilutions required for equilibrium. In any case, capillary pressures will cause the pores in the concrete to fill with water, and thus block the diffusion of water vapor through the container walls. However, if there are water-soluble compounds in the waste, they will lower the vapor pressure of water and cause distillation from the inside of the concrete container onto the soluble waste components. The gas phase in the container will slowly be displaced by a saline solution. If the pores in the waste material are larger than the pores in the concrete container, the saline solution will begin to drain through the pores in the concrete and down into

FIGURE 1. Cross section of a generic waste burial site where one (A) or more (B) layers of backfill have been used to control the intrusion of water. The labels a, b, c, D, l, and p are variables defined by the equations in the text.

the vadose zone below the waste site. If the pores in the waste form are smaller or near the same size as those in the concrete container, they will fill with water and the soluble components will diffuse into the concrete wall, eventually arriving at the concrete-gravel interface. In either case, vapor condensation will continue at this interface, forming saline droplets that flow down the walls of the concrete container, or depending on the pore-size distribution in the wall and waste form, flow through the wall's pores, evaporate, and recondense, to drip out the bottom of the container into the gravel below. The rate of leaching will be controlled by the rate of condensation at the concrete-gravel interface, which at steady state is the same as the rate of vapor diffusion across the gravel layer. The diffusive flux across the gravel layer is relatively easy to estimate.

THEORY

Consider the example diagrammed in Figure 1A. Suppose that the installation has been in place long enough for isothermal conditions to develop and for condensation to fill all the pores in the concrete retaining wall with water. Further assume the pores in the waste form are filled with water. Water-soluble components in the waste form will, therefore, be diffusing through the pores in the concrete wall toward the concrete-gravel interface. Water vapor diffusing from the moist vadose zone material will be condensing at the concrete-gravel interface and diluting the solution at the end of the concrete pores. As the vapor condenses, it will form a film of water that drains downward, and a steady-state condition develops that depends on the rate of arrival of both water vapor and diffusing solutes at the concrete-gravel interface.

The steady-state rate of diffusion, j , of solutes through the concrete wall is

$$j = B \frac{b-c}{m} \quad (1)$$

where B is the diffusion coefficient for solutes in the concrete, b is the concentration of solutes on the inside of the wall of thickness, m , and c is the concentration of solutes at the concrete wall gravel interface [2]. The steady-state flux of vapor, J , is given as

$$J = D \frac{a-p}{l} \quad (2)$$

where D is the diffusion coefficient of water vapor through the gravel, a is the vapor concentration in equilibrium with the moist vadose zone material, l is the thickness of the gravel layer, and p is the concentration of water vapor at the gravel wall interface [2].

The concentration of the solution at the gravel wall interface will be determined by mixing the arriving solute with the condensing water vapor. Therefore, when the flux of solutes is expressed as $g/(cm^2s)$ and the flux of water vapor as $g/(cm^2s)$, the concentration, c , of the surface film of water on the wall must be

$$c = \frac{j}{J} \rho \quad (3)$$

where j/J is g of solute/ g of water, and multiplied by the water's density, ρ , giving g of solute/ cm^3 of water.

The water-vapor pressure at the concrete-gravel interface is controlled by the temperature and concentration of solutes. At constant temperature, the vapor concentration in air can be approximately expressed as

$$p = a - nc \quad (4)$$

where a is the vapor concentration over pure water at atmospheric pressure and any given temperature. The constant, n , may be obtained from tables showing the effect of vapor pressure lowering due to solute concentration [3].

Note that at constant temperature the vapor concentration, a , in Eq. 2 is essentially identical to the constant, a , in Eq. 4 because the relative humidity in the vadose zone with low-soluble salt concentration is 98% to 100%. Thus, a , n , and ρ are known from handbook data. This leaves the four unknowns, c , j , J , and p in Eq. 1-4, since b , m , D , B , and l are design parameters. Solving these equations algebraically leads to

$$c = \frac{Bb}{mJ} \left(1 + \frac{B}{mJ} \right)^{-1} \quad (5)$$

where

$$J = 0.5(-n_1 + [n_1^2 - 4n_2]^{1/2}) \quad (6)$$

with

$$n_1 = Bl/m \quad (7)$$

and

$$n_2 = Dh_2Bb\rho/lm \quad (8)$$

Note that Eq. 5 gives the solution concentration as g of solute/cm³ of water. This may be changed to g solute/g solution as $c/\rho (1 + c/\rho)^{-1}$, and then to g solute/ml of solution if the density of the solution is known.

These values for c and J provide an estimate of the effect of condensation on the long-term leaching rate of solutes from the waste site. If the projected leaching rate is too high, one option is to adjust the design parameters: m , l , D , B , or b . It might also be necessary to consider the effect of more than one layer for a moisture barrier around the waste.

Consider the case diagrammed in Figure 1B, but suppose now it is made up of two distinct layers with vapor-diffusion coefficients, D and D' . For example, one layer might have large pores, while the second had smaller but hydrophobic pores. At steady state

$$J = D \frac{p' - p}{l_0} = D' \frac{a - p'}{l'} \quad (9)$$

solving for p' gives

$$p' = \left(\frac{D'a}{l} - \frac{Dp}{l} \right) / \left(\frac{D}{l} + \frac{D'}{l'} \right) \quad (10)$$

$$\text{or } p' = k_0 - k_1 p$$

where k_0 and k_1 are constants defined by Eq. 10. From Eq. 9, then

$$J = D' \left[\frac{(a + k_0) - k_1 p}{l'} \right] \quad (11)$$

which may be used in place of Eq. 2 to find values for c and J , as already noted. Obviously, this approach may be extended to include any number of layers around the waste container, so long as the water movement is dominated by vapor diffusion.

In some cases, the pores in the container walls do not fill with water, so these walls must be considered as a separate layer for analysis of vapor condensation on the waste form. Two conditions are required for the pores to remain air filled: 1) the water condensing on the waste form must drain away so rapidly that the air space in the waste form does not fill with solution, and 2) the osmotic pressure of the solution in the waste form must be greater than the capillary "air-entry" pressure of the pores in the container walls. The osmotic pressure, P , of the solution can be estimated as

$$P = (RT \ln h)/V \quad (12)$$

where V is the partial molar volume of the solution, R is the gas constant, T is the absolute temperature, and h is the relative humidity of the saturated solution. The air-entry pressure, P , for the pores in the container wall may be approximated as

$$P = 2\gamma/r \quad (13)$$

where r is the pore radius, γ is the air-solution interface surface tension, and the pores are hydrophilic, so that the solution-wetting angle is zero.

If the pores in the waste containers wall do fill with water from vapor condensation but do not make liquid contact with the solution in the waste form due to rapid drainage out of the bottom, no solutes will diffuse into the pore walls. In this case, the steady-state relative humidity at the outside of the container wall may be approximated with Eq. 12 written in the form [1]

$$h = \exp [(P - \Delta P)V/RT] \quad (14)$$

where ΔP is the pressure drop, per Darcy's law, due to liquid water flow through the pores in the container walls [1].

Equations 6-14 all assume constant temperature and water-filled pores so that the water-vapor pressure is only a function of solute concentration or capillary pressure. The temperature, of course, also affects the water-vapor pressure and so the presence of a thermal gradient may be a very important factor. When osmotic and capillary pressures have no significant effect on the water-vapor pressure, the effect of a thermal gradient on the vapor-diffusion rate from warm to cool may be described in the temperature range of 0 to 45°C as

$$J = \beta(1.56 \times 10^{-5} T^2 + 2.72 \times 10^{-3}) dT/dz \quad (15)$$

where J is in mm of liquid/hr (i.e., in the same sense that rainfall is measured), T is temperature in °C, z is distance in cm, and β is a constant that depends on the liquid water content and pore-size distribution of the material. Values of β range from less than one in dry, porous media to as much as six at intermediate water contents and decrease to zero at liquid saturation. In general, β values vary from two to three in moist, unsaturated soil [1].

Equation 12 shows that J decreases as the temperature decreases. Thus under a steady-state thermal gradient, condensation must occur in any volume

element where the relative humidity is 100%. This rate of condensation is the rate of change of vapor flux, or from Eq. 15

$$dj/dz = 3.12 \times 10^{-5} \beta T (dT/dz)^2 + \beta (1.56 \times 10^{-5} T^2 + 2.72 \times 10^{-3}) d^2T/dz^2 \quad (16)$$

It follows that where the thermal gradient is linear over a distance, z , the second derivative is zero and the vapor-condensation rate will be approximately proportional to the square of the thermal gradient.

Equations 15 and 16 are useful for making estimates of potential thermal distillation and condensation in and around buried waste sites. Thermal distillation also may move relatively large amounts of energy as latent heat, which should be accounted for in temperature simulations of buried waste sites.

DISCUSSION

Table I shows some sensitivity examples of the rates of vapor condensation on a concrete container filled with waste, as sketched in Figure 1A. The standard case assumed a NaNO_3 concentration of 5 moles/l of water (i.e., b in Figure 1A). The NaNO_3 diffusion coefficient in the concrete wall was $5 \times 10^{-8} \text{ cm}^2/\text{s}$. A 50-cm concrete wall thickness and a 1-m-thick gravel backfill layer with an effective [4] water-vapor diffusion coefficient of $0.1 \text{ cm}^2/\text{s}$ were used also. A constant temperature of 13°C was assumed, the relative humidity of the vadose zone was taken as 100% with the equilibrium relative humidity of the NaNO_3 solution as $\text{rh} = 100 - 2.5c$, with c as moles of NaNO_3/l of water. Each entry in Table I shows the effect of changing one of the design parameters.

As pointed out in the theory section, a thermal gradient also may be quite important in determining the net vapor flux. For the example given in Table I, the equilibrium relative humidity of the waste material was $100 - 2.5 \times 5 = 87.5\%$ at 13°C . If the temperature at the gravel-vadose zone interface could be lowered to 11°C , while the waste remained at 13°C , there would be no vapor-pressure gradient across the gravel backfill and, consequently, no vapor

TABLE I. Examples of Design Parameter Values on the Rate of Water-Vapor Condensation and on the Concentration of NaNO_3 at the Concrete-Gravel Interface.

Conditions	Vapor Condensation (mm/yr)	NaNO_3 Concentration (moles/l of H_2O)
Standard*	0.26	2.7
Concrete 100 cm Thick	0.21	2.2
Concrete 25 cm Thick	0.32	3.3
Vapor Diffusion $0.24 \text{ cm}^2/\text{s}$	0.47	2.0
NaNO_3 Diffusion $5 \times 10^{-7} \text{ cm}^2/\text{s}$	0.43	4.4
NaNO_3 Diffusion $5 \times 10^{-9} \text{ cm}^2/\text{s}$	0.11	1.1
Gravel 50 cm Thick	0.42	2.2
Gravel 200 cm Thick	0.23	4.7
NaNO_3 8 moles/l of H_2O in Waste	0.36	3.7
NaNO_3 3 moles/l of H_2O in Waste	0.18	1.9

* NaNO_3 diffusion $5 \times 10^{-8} \text{ cm}^2/\text{s}$, vapor diffusion $0.1 \text{ cm}^2/\text{s}$, concrete wall 50 cm thick, gravel layer 100 cm thick, and NaNO_3 5 moles/l of H_2O .

condensation on the concrete walls. If the gravel-vadose zone interface could be cooled to less than 11°C , water vapor would evaporate from the waste form and condense in the cooler vadose zone.

Thermal gradients in the vadose zone are a natural consequence of geothermal heat flow from the earth's core to the ground surface. Local thermal gradients also occur from coupling between the vadose zone and atmospheric energy fluxes. The geothermal gradient varies from area to area, but a representative value is 0.03°C/m [5]. This causes water to evaporate from the ground-water table and diffuse upward through the vadose zone, continuously condensing along the way as shown in Eq. 13. The condensed water moves downward due to gravity, slowly leaching soluble material into the ground-water aquifer. The presence of an insulating layer anywhere in the vadose zone requires a larger thermal gradient to develop that drives the given steady-state geothermal heat flux. Thus, the temperature below an insulating layer in the vadose zone becomes slightly warmer, while the temperature above the layer gets a bit cooler. This, of course, assumes the insulation layer is 5 m or more below the ground surface, which is the approximate depth of influence of the annual surface temperature variations. In any case, an insulating layer changes the horizontal thermal gradients and vapor-pressure gradients around its perimeter.

Manipulating the energy exchange between the vadose zone and the atmosphere appears to have a greater potential than manipulating the geothermal flux to maintain significant local thermal gradients in the first 10 to 30 m below the earth's surface. See for example the cross section sketched in Figure 2. Here, the waste containers are surrounded by a trench, partly backfilled with rock to create a donut-shaped system with large pores that offer low resistance to convective gas flow. In places, this coarse rock backfill extends above the land surface to form small chimneys. When the air temperature is less than the temperature of the rock, convection will occur and the vadose zone around the rock will be cooled. When the air is warmer

FIGURE 2. Cross section of a passive cooling tunnel that surrounds a waste storage site.

than the rock, stable conditions produced by the thermal inversion will reduce the exchange of heat between the atmosphere and vadose zone. The cool mass of the material in and around the trench will then provide a perpetual water-vapor sink for distillation from the waste site. This kind of passive cooling occurs in natural ice caves.

Even in relatively mild Southern Idaho, south of the 45th parallel, a natural ice cave has existed for many years. The cave was formed during a period of lava flow [6]. The ends of one lava tube later collapsed to form a cave covered with 10 to 30 m of fractured rock and only one relatively small opening. Records indicate that, in 1880, the cave was discovered filled with ice, and was later used as a commercial source of ice for the town of Shoshone. In 1930, the entrance was enlarged and a second opening was blasted through the roof. In a few years, all of the ice melted. In the 1950s, the sizes of the openings were reduced and the ice reformed, with the mass of ice now controlled at a constant amount with a specific vent size. Robinson [7], writing in a non-technical bulletin, said that ice continues to form during the summer months via the coupling between the gas pressures in the cave's rooms and the surface air-pressure fluctuations associated with variable wind speed. This coupling, he believes, leads to Joule-Thomson cooling and, thus, temperatures below freezing in the cavern. Whether or not Joule-Thomson cooling is significant, one may observe the formation of hoarfrost on some of the cave walls in July, even when the outside air temperatures are greater than 35°C.

While our discussion here has been focused on creating a thermal gradient to offset the effect of water-soluble components in the waste form, the ice-cave concept might be considered to provide continuous passive drying for waste burial sites. One could also enhance the drying by using some of the more passive solar-heating methods to warm the buried waste forms. This general concept for designing passive drying in parts of the vadose zone also may be useful for containing some spills and past releases of toxic liquid wastes in the ground.

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