Temperature and Saturation Effects on Diffusion of Carbon Dioxide through Tuff

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The United States has many nuclear power plants in operation today and the problem of high-level radioactive waste disposal is a problem of national concern. The operation of a geologic repository for the permanent disposal of radioactive waste is presently under serious consideration by the United States Government in accordance with the 1982 Nuclear Waste Policy Act. Three candidates for the site of the first geologic repository included burial sites in basalt, salt, and tuff rock formations (Annotated outline, 1987). However, when the United States Congress passed the budget reconciliation act of December 1987, all site-specific research on the design and development of a high-level nuclear waste repository was restricted to the Yucca Mountain tuff site. The repository is expected to be built sometime between 1998 and 2003 if a construction authorization is given by the Nuclear Regulatory Commission.

The Topopah Spring Member of the Paintbrush Tuff in Yucca Mountain Nevada is a prime candidate for the site of the first national high-level radioactive waste repository. Spent fuel from power reactors is currently considered to be the most significant commercial high-level nuclear waste form. According to Van Konynenburg et al. (1985), radionuclides with long half-lives will have significant remaining activities after a 300- to 1,000-year containment period. The long-lived radionuclides that could enter the vapor phase at spent-fuel storage temperatures are ^{14}C and ^{129}I.

Carbon-14 is produced in the primary cooling water of nuclear power plants. Part of the carbon-14 is released to the atmosphere, primarily as CH_4 and CO_2. Thomas and Brown (1985) have calculated the health effects that would occur if all of the carbon-14 produced in a 400-GW(e) fuel cycle operating for 100 years is released to the atmosphere. They concluded that an average of six additional deaths per year will occur because of the carbon-14 release to the atmosphere.

Scientists have been conducting research on various aspects and conditions for design and operation of a safe, high-level waste repository. One of the questions to be answered in characterizing the site is the extent of diffusion of radioactive gases, such as carbon dioxide and iodine, to the accessible environment. The objectives of this study were to measure the effect of temperature and water content on the effective diffusivity of carbon dioxide through tuff. There is no data available on the effect of saturation and temperature on gas diffusivity through volcanic rock tuff. This study provides data which may be used to estimate the amount of carbon dioxide that will diffuse through volcanic rock tuff. Since Topopah Spring Tuff samples were not made available, experiments were conducted with tuff samples from a nearby location called Rainier Mesa Ash flow from "G" tunnel. Since it would be very hard, if not impossible, to statistically sample a mountain to determine the best value of diffusivity, we worked with the samples cored from about a 30-kg "G" tunnel tuff sample.

Methods

A steady-state diffusion method was used to determine the effective diffusivity of carbon dioxide gas through "G" tunnel tuff. The steady-state method used for the counter diffusion of gases in porous solids was developed by Wicke and Kallenbach (1941) and modified by Bardakci and Gasner (1981). In applying the method, a pure gas flows past each side of a "thin" pellet of an experimental porous material which is placed in a diffusion cell. A schematic of the diffusion cell is shown in Figure 1. The counter diffusion fluxes of the two gases through the pellet are then determined by measuring the composition of the exit gas stream on each side of the diffusion cell. The pressure gradient across the pellet is maintained near zero to eliminate gaseous transport due to pressure difference. The flowchart of the steady-state diffusion measurement system is given in Figure 2.

In this study, sample cylinders (1.91 cm in diameter) were made by coring a tuff rock sample using a carbide tipped hole saw as shown in Figure 3. Sample cylinders were then sliced using a diamond wafering blade mounted in a low-speed saw to give a 0.16-cm-thick pellet. The pellet sample was then mounted

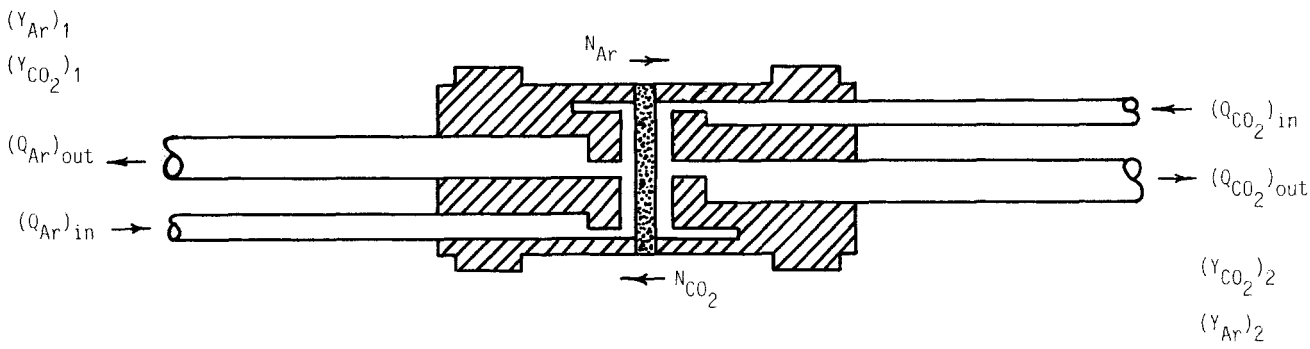

Figure 1. Single-pellet high-temperature diffusion cell.

in the diffusion cell. The diffusion cells were fabricated from 1.91-cm stainless steel rods contained inside a 1-in. (2.54-cm) NPT stainless steel coupling. Each of the two threaded end rods has gas inlet and outlet tubes. The temperature in the diffusion cell was measured on each side of the pellet using chromel-alumel thermocouples connected to a calibrated digital temperature indicator. The pellet samples were weighed and mounted between the two rods. The pellets were sealed with a nonporous Saureissen cement for high-temperature studies and lead washers for low-temperature (below 373 K) studies.

Dry gases were used for the experiments with dry pellets. The diffusion cell was mounted and placed in a tubular furnace equipped with a temperature controller. The temperature was held constant during the diffusivity measurements. Carbon dioxide gas was sent radially across one face of the pellet and argon gas across the other face. In a separate study, we determined that mass transfer resistance can be neglected when the gas flow rate is above 700 cm^3/min on each side of the pellet. Therefore, the flow rate of gases were always above 700 cm^3/min. The differential pressure across the pellet was maintained near zero by using a calibrated differential pressure cell. The critical variable is the pressure differential. The most sensitive part of the experiment was to maintain the differential pressure at zero by manually adjusting valves in each of the gas exit streams. Carbon dioxide and argon were supplied from compressed gas cylinders. Sensitive gas flowmeters were used to measure exit gas flow rates. The system pressure, the average pressure of the exit gas lines, was about 0.34 atm gauge.

The moisture content of the sample pellet was maintained nearly constant by controlling the moisture content in the inlet gas streams by bubbling the inlet gases through water placed in Erlenmeyer flasks heated with hot plates. The temperature and composition of the water vapor in the gas were monitored so that the proper amount of water vapor was introduced to the gas streams to keep the level of pellet saturation almost unchanged during the diffusivity measurement.

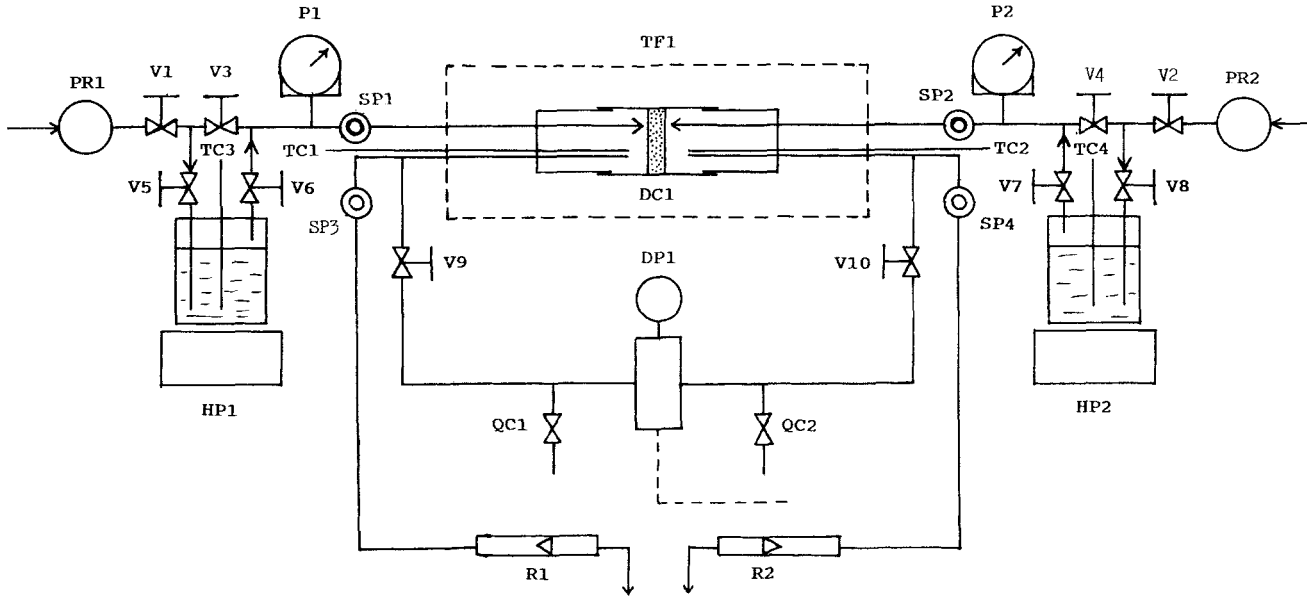

Figure 2. Steady-state diffusion measurement system.

PV = pressure regulator
V = hand valve
TC = thermocouple
TF = tubular furnace
DC = diffusion cell
SP = sampling ports, septums
HP = hot plates
QC = quick connects
R = rotameter
DP = differential pressure cell and indicator
P1, P2 = pressure gauges

Figure 3. "G" Tunnel tuff, cored sample, and diffusion cell parts.

Sampling tees with septums were placed in the inlet and outlet gas lines. Gas samples were obtained using a syringe and were injected to a computerized gas chromatograph equipped with a printer/interface. The data from the chromatograph were automatically sent to a Perkin Elmer computer which utilizes a software system to analyze the composition of the exit gas streams. Gas separation in the chromatograph was obtained using a 183-cm-long, 0.32-cm-OD stainless steel column packed with POROPAK-Q. The percent saturation of the pellets was determined gravimetrically before and after the diffusion measurements, and the average percent saturation was used.

The molar flux of carbon dioxide through the pellet was calculated from Eq. 1 using the argon side exit stream flow rate, the mole fraction of carbon dioxide, and the cross-sectional area of the pellet.

$$N_{CO_2} = \frac{4P}{RT}(Q_{Ar})(Y_{CO_2})_1/(D^2\pi) \tag{1}$$

The effective diffusivity of carbon dioxide through the samples was calculated using the diffusion cell, chromatographic data, and the following equation:

$$N_{CO_2} = -\frac{P}{RT}D_e\left[\frac{(\overline{Y_{CO_2}})_1 - (\overline{Y_{CO_2}})_2}{r}\right] \tag{2}$$

Since the arithmetic mean of carbon dioxide concentration across a pellet gives a better representation of the gas concentration on each side of the pellet, the following mole fractions were used in Eq. 2:

$$(\overline{Y_{CO_2}})_1 = \frac{0 + (Y_{CO_2})_1}{2} \tag{3}$$

$$(\overline{Y_{CO_2}})_2 = \frac{1 + (Y_{CO_2})_2}{2} \tag{4}$$

The diffusion cells are designed to eliminate the mass transfer resistance.

The data were obtained using nonradioactive carbon dioxide. The results can be adjusted to estimate the effective diffusivity of radio-active carbon dioxide by accounting for the molecular weight differences. According to Evans et al. (1961), the ratio of the effective diffusivity of carbon dioxide (with carbon-14) to effective diffusivity of carbon dioxide (with carbon-12) is equal to square root of the ratio of molecular weight of carbon dioxide (with carbon-12) to molecular weight of carbon dioxide (with carbon-14).

Results and Discussion

Although the diffusivity of carbon dioxide through the volcanic rock is very low, it was still within the sensitivity of the experimental system. The effective diffusivity for carbon dioxide through "G" tunnel tuff at 304 K was measured to be 0.0018 cm^2/s. The effective diffusivity was measured at a series of temperatures between 304 K and 802 K using another pellet made from the same coring. The results are shown in Figure 4. As expected, the effective diffusivity of carbon dioxide increases with temperature. The effective diffusivity of carbon dioxide increased from 0.0026 to 0.0076 cm^2/s over the temperature range. The experiment was repeated twice using separate samples. The results are also shown in this figure. Since tuff is a naturally occurring heterogeneous material, the pore structure and the effective diffusivity of carbon dioxide are different at each temperature for different samples. In all cases, however, the effective diffusivity increased as a function of the temperature. The following empirical equation was obtained using average values of the effective diffusivity at each temperature.

$$D_e = 0.003 - 1.032 \times 10^{-5} \times T + 1.768 \times 10^{-8} \times T^2 \tag{5}$$

The effective diffusivity of the carbon dioxide through the "G" tunnel tuff was also determined as a function of the average percent saturation from 313 K to 353 K. The results are given in Figure 5. One sample was used over the entire saturation range and at a fixed temperature to illustrate the effect of sample variability and the effect of the average percent saturation. Percent saturation is defined here as the percent moisture content rela-

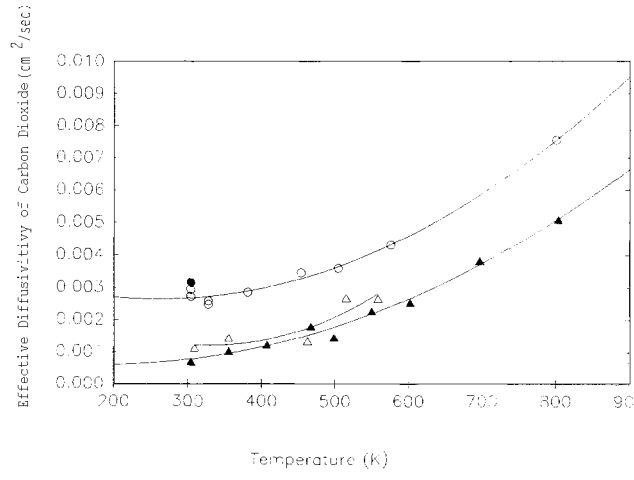

Figure 4. Effective diffusivity of carbon dioxide through Rainier Mesa Member of the Timber Mountain tuff as a function of temperature.

●, Sample #1; O, Sample #2; ▲, Sample #3; △, Sample #4

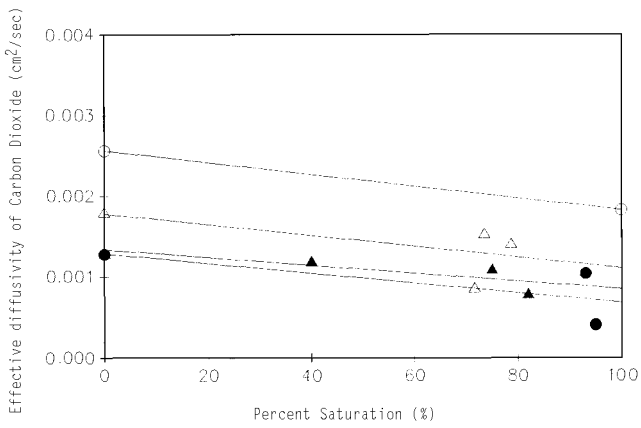

Figure 5. Effective diffusivity of carbon dioxide through Rainier Mesa Member of the Timber Mountain tuff as a function of percent saturation.

O, 313 K (Sample #5); △, 333 K (Sample #6); ▲, 343 K (Sample #7); ●, 353 K (Sample #8)

tive to the maximum moisture content for that specific pellet. The maximum moisture content ranged from 3.82 to 5.59% depending on the porosity of the sample. The average percent saturation is the same as average of the percent saturation measured before and after each experiment and has a variation of ± 15%. Since it was very difficult to maintain the average percent saturation constant, the data are somewhat scattered. However, the effective diffusivity decreased with percent saturation, and the average the slope of all the lines in Figure 5 is -7.1×10^{-6} cm^2/(second × percent saturation). If the saturation data are combined with Eq. 5, the following equation was obtained to estimate the effective diffusivity of "G" tunnel tuff as a function of temperature and the percent saturation.

$$D_e = 0.003 - 1.032 \times 10^{-5} \times T + 1.768 \times 10^{-8} \times T^2 - 7.107 \times 10^{-6}(\%\,\text{Saturation}) \quad (6)$$

This information on the diffusion of gases through tuff may provide data to determine whether the Nuclear Regulatory Commission and Environmental Protection Agency regulations can be met. There is presently no available data for the diffusivity of carbon dioxide through tuff. Since it is very difficult, if not impossible, to statistically sample a mountain, our data might not provide the best value for diffusivity through tuff. Although it might be inappropriate to use the data to design a repository in the Topopah Spring Tuff layer, they do give an estimate of the magnitude of the carbon dioxide diffusion and how the effective diffusivity changes with temperature and water content of tuff.

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Notation

a = average pore radius, cm
D = effective pellet radius, cm
d = density of the pellet, cm^3/g
D_e = effective diffusivity of carbon dioxide, cm^2/s
M = molecular weight of carbon dioxide, 44.01 g/gmol
N_{CO_2} = molar gas flux, gmol/cm^2 · s
P = absolute pressure, atm
Q_{Ar} = exit flow rate of argon, cm^3/s
R = ideal gas constant, 82.06 atm cm^3/gmol · K
r = pellet thickness, cm
T = absolute temperature, K
$(Y_{CO_2})_1$ = exit mole fraction of carbon dioxide (argon rich stream)
$(\overline{Y_{CO_2}})_1$ = average mole fraction of carbon dioxide in argon side of the diffusion cell
$(\overline{Y_{CO_2}})_2$ = average mole fraction of carbon dioxide in the carbon dioxide side of the diffusion cell

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