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TEMPERATURE AND SATURATION EFFECTS ON DIFFUSION OF CARBON DIOXIDE THROUGH TOPOPAH SPRING TUFF.
Part I

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ABSTRACT

The effective diffusivities of carbon dioxide through lower non-lithophysal zone of the Topopah Spring Tuff (outcrop sample of the proposed nuclear repository site layer) and USW H-6 test well samples of the Topopah Spring Tuff (proposed repository layer) were determined using a steady state diffusion method. The effective diffusivity of carbon dioxide through the non-lithophysal zone tuff increased with temperature and decreased as the moisture content increased. The following correlation was obtained to estimate the effective diffusivity of carbon dioxide through the non-lithophysal zone tuff as a function of temperature and percent saturation.

$$D_e = -1.1578 \times 10^{-4} + 2.9885 \times 10^{-6}\, T + 5.3104 \times 10^{-9}\, T^2 - 5.0739 \times 10^{-6}\ (\%\ \text{saturation})$$

The effective diffusivity of carbon dioxide through the USW H-6 test well sample of the Topopah Spring Tuff, which was taken at a depth of 338 m, also increased with temperature. For this repository layer, the effective diffusivity of carbon dioxide was 0.00093 $\text{cm}^2\ \text{s}^{-1}$ at 312 K. The following correlation was obtained to estimate the effective diffusivity of carbon dioxide through the proposed repository layer as a function of temperature and percent saturation.

$$D_e = 9.1242 \times 10^{-4} - 3.5180 \times 10^{-6}\, T + 1.2168 \times 10^{-8}\, T^2 - 5.0739 \times 10^{-6}\ (\%\ \text{saturation})$$

INTRODUCTION

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

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sites in basalt, salt, and tuff rock formations [1]. 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. [2], radionuclides with long half-lives will have significant remaining activities after a 300–1000 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 [3] 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 were released to the atmosphere. They concluded that an average of six additional deaths per year would 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 Topopah Spring Tuff. There is no data available on the effect of saturation and temperature on gas diffusivity through volcanic rock tuff except the study by Bardakci et al. [4,5] on ‘G’ Tunnel tuff. Bardakci et al. [4] found the following equation to estimate the effective diffusivity of carbon dioxide through ‘G’ Tunnel tuff as a function of temperature and saturation.

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

The samples studied were cored from a 60 kg large rock sample of lower non-lithophysal zone of the Topopah Spring Tuff. This rock is an outcrop sample and taken from the extension of the proposed repository site layer. This rock was from Busted Butte location which is 4 miles distant from the repository site and located at the south of the Yucca Mountain. The properties of outcrop samples from this location are given by Nimick and Schwartz [6].

Only one single Topopah Spring Tuff sample of the proposed repository site layer which had a diameter of 2.54 cm and the thickness of 0.222 cm, could be obtained. The sample was taken from the USW H-6 test well between 338.08 m and 338.24 m below the earth surface. Bish and Vaniman [7] report the mineralogical composition of a core sample taken from USW H-6. Between depths of 333.0 m and 344.1 m, the USW H-6 test well consisted of 20.5 ± 5 wt.% quartz, 10.5 ± 5 wt.% cristobalite, 1 wt.% mica, and 68 ± 10% alkali feldspar. Craig et al. [8] reported the geohydrologic data for the test well USW H-6. Daily et al. [9] reported some of the properties of the samples from the same well.

This study provides data which may be used to estimate the amount of carbon dioxide that will diffuse through the lower non-lithophysal zone of the Topopah Spring tuff (proposed repository layer). Since it would be very hard, if not impossible, to statistically sample a mountain, this data might not provide the best value for gas diffusivities through tuff.

EXPERIMENTAL

A steady state diffusion method was used to determine the effective diffusivity of carbon dioxide gas through both tuff samples. The steady state method used for the counter-diffusion of gases in porous solids was developed by Wicke and Kallenbach [10] and modified by Bardakci and Gasner [11]. 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 Bardakci diffusion cell described by Bardakci and Gasner [11] and Bardakci et al. [4,5]. A schematic of the Bardakci diffusion cell is shown in Fig. 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

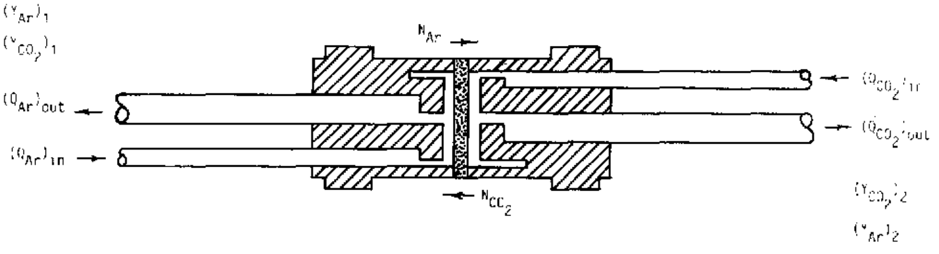

Fig. 1. Schematic of the Bardakci diffusion cell for high temperature gaseous diffusion measurements.

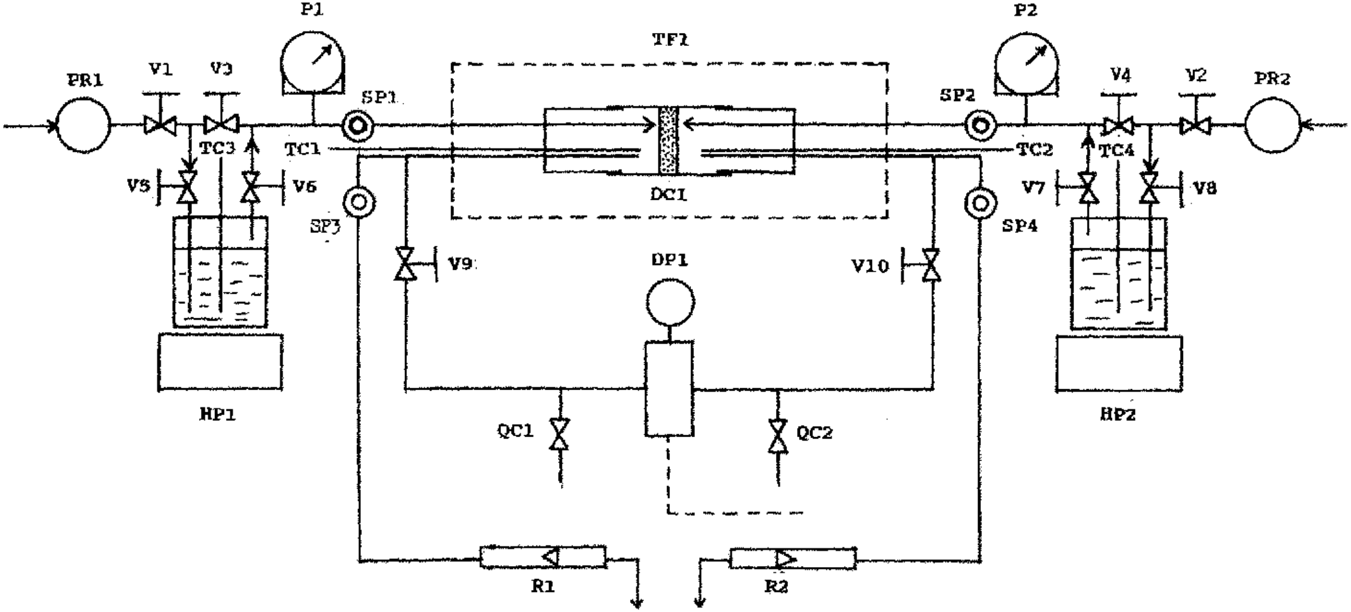

Fig. 2. Flowchart for the steady state diffusion measurement system. PR, pressure regulator; V, hand valve; TC, thermocouple; TF, tubular furnace; DC, diffusion cell; SP, sampling port, septums; HP, hot plates; QC, quick connects; R, rotameter; DP, differential pressure cell and indicator; P1 and P2, pressure gauges.

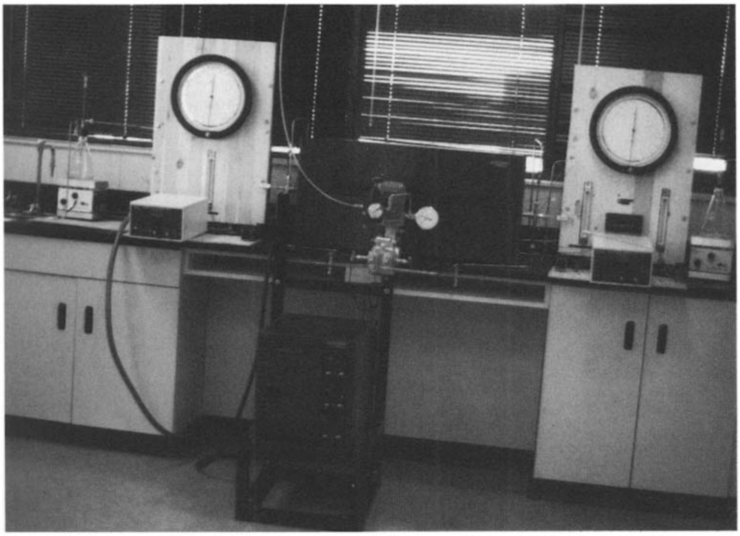

Fig. 3. General view of the diffusion measurement system.

flowchart and the overall view of the steady state diffusion measurement system are given in Figs. 2 and 3 respectively.

In this study, sample cylinders (1.91 cm in diameter) were made by coring the tuff rock sample using a diamond tipped hole saw. The picture of sample rock from lower in the non-lithophysal zone of Topopah Spring tuff is given in Fig. 4. 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 in the diffusion cell. The diffusion cells were fabricated from 1.91 cm stainless steel rods contained inside a 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 non-porous 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^{-1} on each side of the pellet. Therefore, the flow rate of gases was always above 700 cm^3 min^{-1}. 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

Fig. 4. Rock sample from the lower non-lithophysal zone of the Topopah Spring Tuff.

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.

Sampling tees with septa were placed in the inlet and outlet gas lines. Gas samples were obtained using a syringe and were injected into a computerized gas chromatograph equipped with a printer/interface. The data from the chromatograph was automatically sent to a Perkin–Elmer computer running software to analyze the composition of the exit gas streams. Gas separation in the chromatograph was obtained using a 183 cm long, and 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 eqn. (1) using the argon side exit stream flow rate, the concentration 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 and chromatographic data and the equation

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

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 eqn. 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 were designed to eliminate the mass transfer resistance.

The data were obtained using non-radioactive carbon dioxide. The results can be adjusted to estimate the effective diffusivity of radionuclide carbon dioxide by accounting for the molecular weight differences. According to Evans et al. [12], the ratio of the effective diffusivity of carbon dioxide with carbon-14 to the effective diffusivity of carbon dioxide with carbon-12 is equal to the square root of the ratio of the molecular weight of carbon dioxide with carbon-12 to the 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 is still within the sensitivity of the experimental system. For the non-lithophysal zone of the Topopah Spring Tuff, results show that the effective diffusivity of carbon dioxide is 0.00148 $cm^2\ s^{-1}$ at 298 K and 0.00115 $cm^2\ s^{-1}$ at 303 K for the first and second samples respectively. As expected, the effective diffusivity of carbon dioxide through the non-lithophysal zone tuff increased with temperature as shown in Fig. 5. In Fig. 5, each run represents the experiments done with separate pellets cut from the same rock samples. The sample #1 had a porosity of 0.144. The second sample had a porosity of 0.140. The mean pore radius values of 51.1 nm and 20.1 nm were obtained for the samples #1 and #2 respectively using an AUTOSCAN60 mercury porosimeter (Quantachrome Corporation, NY).

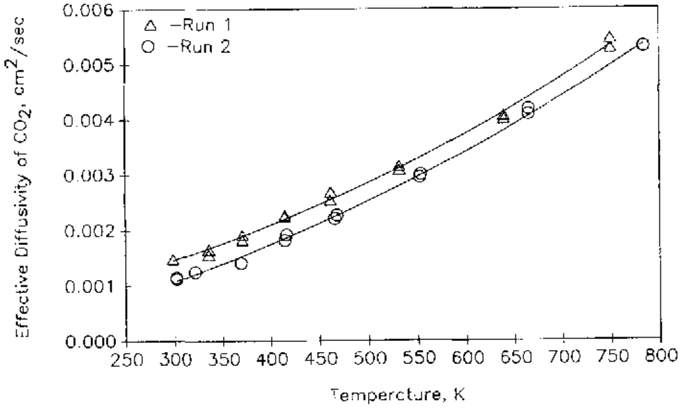

Fig. 5. Effective diffusivity of carbon dioxide through the lower non-lithophysal zone of the Topopah Spring Tuff.

Since the sample #1 had a higher porosity and larger mean pore radius, the effective diffusivity values for that sample is slightly higher. The specific surface areas of the sample #1 and sample #2 are 0.87 and 0.83 $m^2\ g^{-1}$ respectively. For the dry non-lithophysal zone samples the following empirical correlation was obtained to estimate the effective diffusivity of carbon dioxide as a function temperature and percent saturation.

$$D_e = -1.1578 \times 10^{-4} + 2.9885 \times 10^{-6}\, T + 5.3104 \times 10^{-9}\, T^2 \tag{5}$$

The experiments were carried out with two separate samples as a function of the average percent saturation. The average percent saturation is 100 times the ratio of the average moisture content during the experiment to the maximum moisture content of that specific sample. 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. The average percent saturation is the average of percent saturation before and after each experiment and varied plus or minus 15% saturation. The effective diffusivity of carbon dioxide decreased as the moisture content of the lower non-lithophysal zone tuff increased as shown in Fig. 6, in which only one sample was used during the runs carried out at 302 K, and another sample was used during the runs at 344 K. The slope of the lines for the first and the second samples are -5.0370×10^{-6} and $-5.1108 \times 10^{-6}\ cm^2\ s^{-1}$ $(\%\ saturation)^{-1}$ respectively. The average slope of both lines in Fig. 5 is $-5.0739 \times 10^{-6}\ cm^2\ s^{-1}\ (\%\ saturation)^{-1}$. When the saturation data were combined with eqn. (5), the following equation was obtained to estimate the effective diffusivity of carbon dioxide as a function of temperature and percent saturation.

$$D_e = -1.1578 \times 10^{-4} + 2.9885 \times 10^{-6}\, T + 5.3104 \times 10^{-9}\, T^2 - 5.0739 \times 10^{-6} \times (\%\ saturation) \tag{6}$$

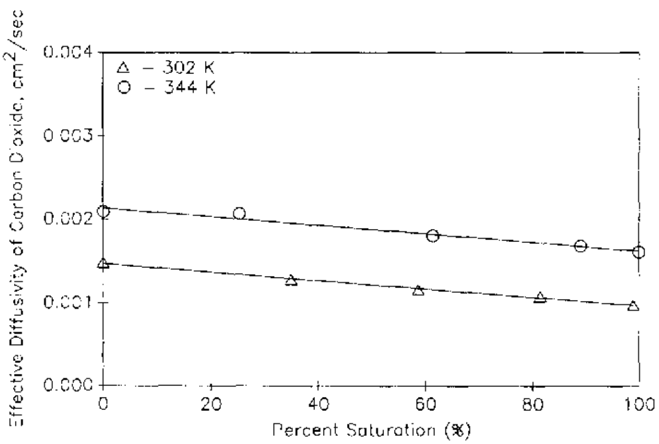

Fig. 6. Effective diffusivity of carbon dioxide through the lower non-lithophysal zone of the Topopah Spring Tuff as a function of percent saturation.

The effective diffusivity of carbon dioxide through the USW H-6 test well sample of the Topopah Spring Tuff (proposed repository site layer) also increased with temperature, as shown in Fig. 7. For the repository layer the effective diffusivity of carbon dioxide was 0.00093 $cm^2\ s^{-1}$ at 312 K. The porosity of this sample was 0.137, which is lower than the porosity of the non-lithophysal zone tuff. The specific surface area was higher (0.910 $m^2\ g^{-1}$) and the mean pore radius was lower (4.4 nm). The following empirical correlation was obtained to estimate the effective diffusivity of carbon dioxide through the proposed repository layer as a function of temperature. Since the effective diffusivities of outcrop samples are close to those of USW H-6 test well samples, one can assume that the slope of the effective diffusivity of carbon dioxide vs. percent saturation lines is the same for both

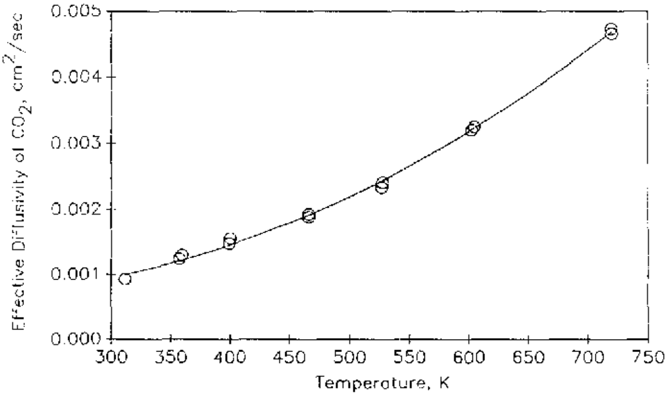

Fig. 7. Effective diffusivity of carbon dioxide through the USW H-6 test well sample of the Topopah Spring Tuff.

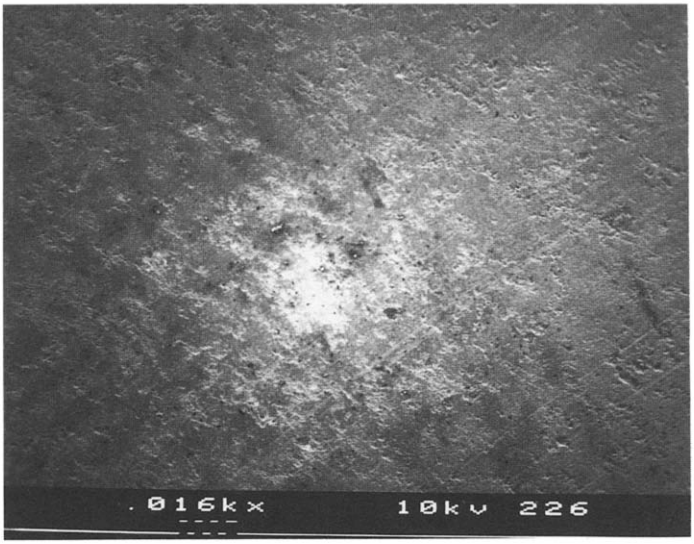

Fig. 8. SEM micrographs the lower non-lithophysal zone of the Topopah Spring Tuff at an original magnification of 16×.

non-lithophysal zone tuff and USW H-6 test well tuff samples. Therefore the following empirical correlation was obtained to estimate the effective diffusivity of carbon dioxide through the proposed repository layer as a function

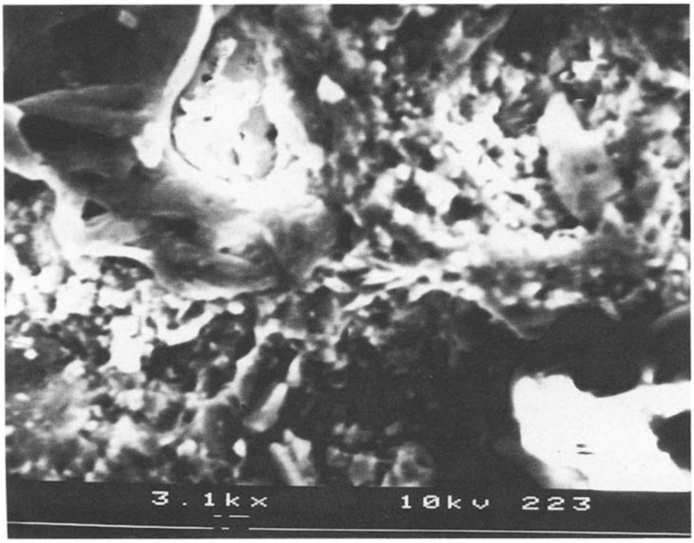

Fig. 9. SEM micrographs the lower non-lithophysal zone of the Topopah Spring Tuff at an original magnification of 3100×.

Fig. 10. SEM micrograph of the USW H-6 test well sample of the Topopah Spring Tuff at an original magnification of 44×.

of temperature and percent saturation.

$$D_e = 9.1242 \times 10^{-4} - 3.5180 \times 10^{-6}\, T + 1.2168 \times 10^{-8}\, T^2 - 5.07390 \times 10^{-6} \times (\%\ \text{saturation}) \qquad (7)$$

The scanning electron microscope (SEM) micrographs of the non-lithophysal zone of the Topopah Spring Tuff are given in Figs. 8 and 9. The SEM

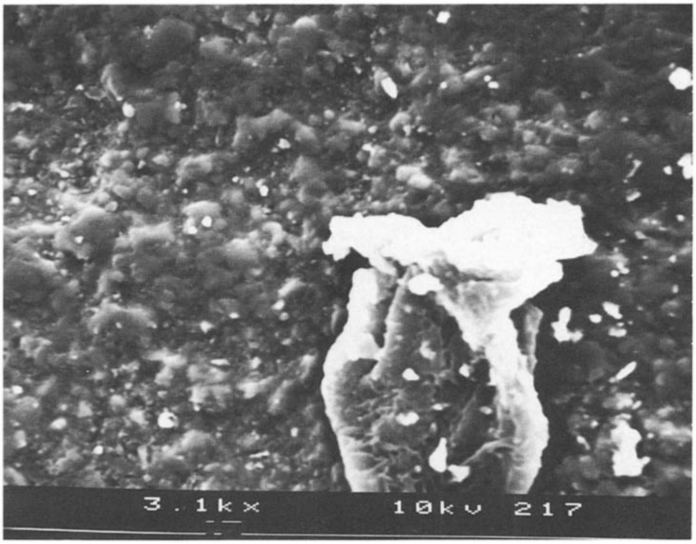

Fig. 11. SEM micrograph of the USW H-6 test well sample of the Topopah Spring Tuff at an original magnification of 3100×.

micrographs of USW H-6 sample are given in Figs. 10 and 11. As can be seen, the non-lithophysal zone has pore openings; however, it is very hard to see the pores in the USW H-6 sample.

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. Since it is very hard, 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 this data to design a repository in the Topopah Spring Tuff layer, our data 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.

CONCLUSIONS

The following conclusions can be drawn from this study.

1. The effective diffusivity of carbon dioxide through all the tuff samples investigated increased with temperature.
2. The effective diffusivity of carbon dioxide decreased as the moisture content of the lower non-lithophysal zone tuff increased.
3. The following empirical correlation was obtained to estimate the effective diffusivity of carbon dioxide through the lower non-lithophysal zone of the Topopah Spring Tuff as a function of temperature and the percent saturation.

$$D_e = -1.1578 \times 10^{-4} + 2.9885 \times 10^{-6}\, T + 5.3104 \times 10^{-9}\, T^2 - 5.0739 \times 10^{-6}(\%\ \text{saturation})$$

4. The following empirical correlation was obtained to estimate the effective diffusivity of carbon dioxide through the proposed repository site tuff, namely Topopah Spring Tuff, as a function of temperature and percent saturation.

$$D_e = 9.1242 \times 10^{-4} - 3.5180 \times 10^{-6}\, T + 1.2168 \times 10^{-8}\, T^2 - 5.0739 \times 10^{-6}(\%\ \text{saturation})$$

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NOMENCLATURE

D = effective pellet diameter, cm
D_e = effective diffusivity of carbon dioxide, $\mathrm{cm^2\ s^{-1}}$
M = molecular weight of carbon dioxide, 44.01 g $\mathrm{(g\ mol)^{-1}}$
N_{CO_2} = molar gas flux, g mol $\mathrm{(cm^2\ s)^{-1}}$
P = absolute pressure, atm
Q_{Ar} = exit flow rate of argon, $\mathrm{cm^3\ s^{-1}}$
Δr = pellet thickness, cm
R = ideal gas constant, 82.06 atm. $\mathrm{cm^3\ (g\ mol\ K)^{-1}}$
T = absolute temperature, K
$(Y_{CO_2})_1$ = mole fraction of carbon dioxide in the exit of argon 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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