



Diffusion of chloride-36 and carbon-14 in a backfill barrier composed of 75% basalt and 25% bentonite by Craig G Rieger

A thesis submitted in partial fulfillment of requirements for the degree of Master of Science in Chemical Engineering
Montana State University
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Abstract:

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The diffusion of chloride was found to increase with increasing temperature.

Increasing the bulk density of the diffusion medium inhibited the movement of chloride and reduced the diffusion coefficient.

A one-dimensional model that was solved using the assumption of linear sorption of the tracer described the diffusion of chloride well.

The effective diffusion coefficient of chloride is larger for experimental systems in which the tracer is initially present in the diffusive medium compared with when it is initially present in a solution adjacent to the medium.

The diffusion coefficients of carbon-14 were not measurable because it formed a precipitate or sorbing complex with calcium and/or magnesium.

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Craig G Rieger

A thesis submitted in partial fulfillment of
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of
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Bozeman, Montana

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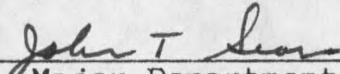
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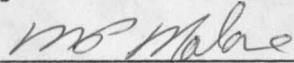
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ABSTRACT

Effective diffusion coefficients were measured for chloride-36 at ambient temperature ($\sim 20^{\circ}\text{C}$), 60°C , and 90°C in a water-saturated 75%/25% basalt-bentonite mixture. Three separate tests for each of the given temperatures were run at two bulk densities of the medium, i.e., $1.6\text{g}/\text{cm}^3 \pm .1\text{g}/\text{cm}^3$ and $1.8\text{g}/\text{cm}^3 \pm .1\text{g}/\text{cm}^3$. The same tests were run for carbon-14, but the data could not be analyzed to find diffusion coefficients.

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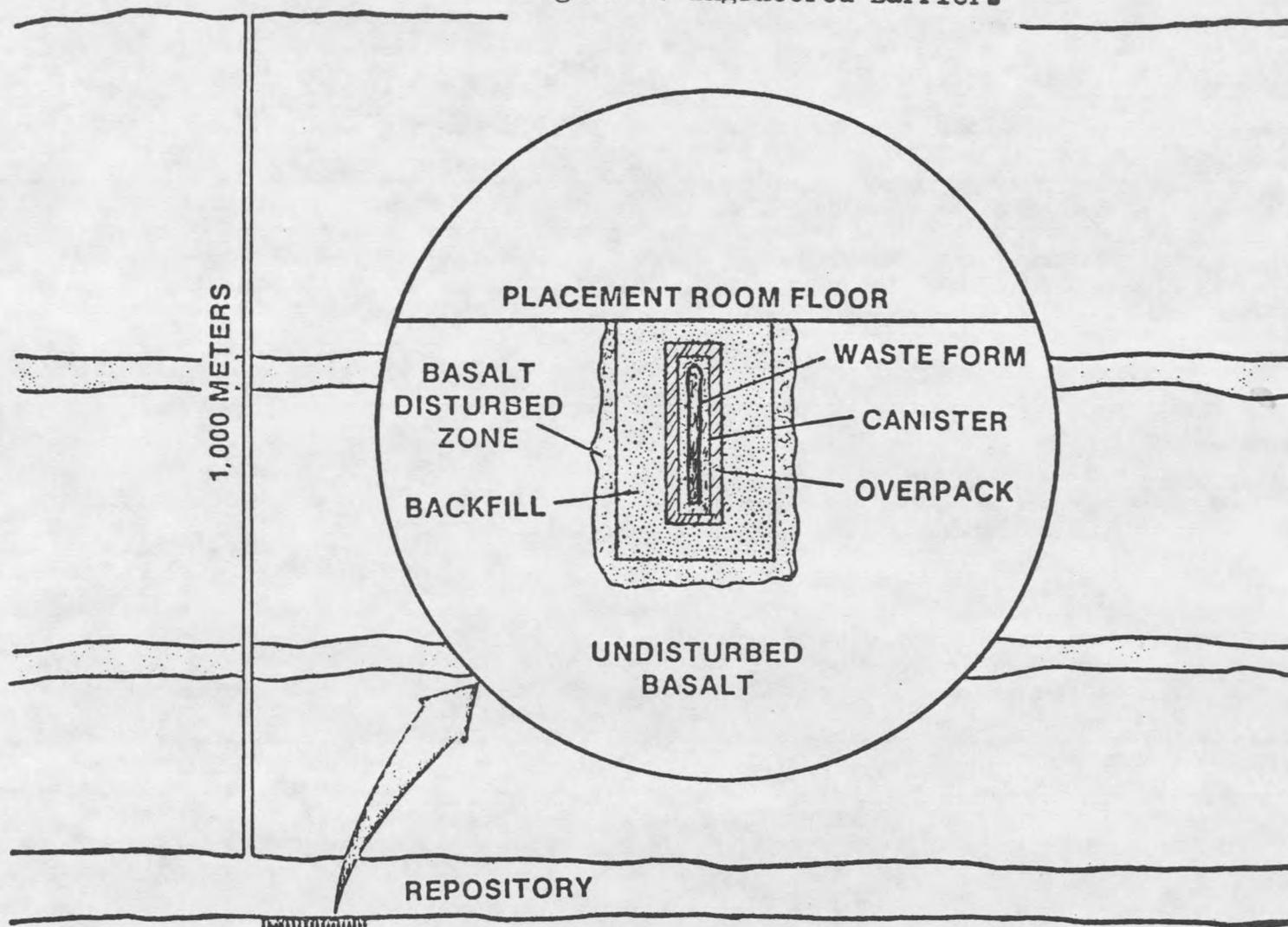
The diffusion coefficients of carbon-14 were not measurable because it formed a precipitate or sorbing complex with calcium and/or magnesium.

INTRODUCTION

In 1951, electricity was first generated using nuclear fuel in the United States (1). Since then, nuclear power has become an important alternate source of energy in this country. Consequently, the safe disposal of radioactive waste produced from atomic reactors and defense work is an important national problem (2). One of the most attractive disposal alternatives is to deposit the wastes in deep, stable geologic formations, i.e., salt, tuff, basalt (2). Basalt and tuff are both volcanic formations, the latter being derived from ash and is consequently more porous. Both natural and engineered barriers will be used to impede the movement of radionuclides into the biosphere from these repositories (3). This generalized concept is diagramed in Figure 1 for engineered barriers in basalt (3). Each barrier is designed in accordance with the specific waste form chosen to be buried and also with respect to the geologic environment that controls the stability of the repository (3).

In this investigation the backfill barrier will be the medium of interest. The backfill barrier is a continuous layer that surrounds the waste container, filling all the void between the overpack and the host rock

Figure 1. Engineered Barriers



(4). To be an effective backfill barrier, a substance must have the capacity to sorb radionuclides diffusing from the waste material (4). Just as important, the backfill material should have a low permeability, adequate thermal conductivity for heat transfer, and be resistant to fracture (4). In this way, the backfill can act as an inhibitor of radionuclide migration in the event of canister leaks, etc. In this work the barrier will be composed of 75% crushed basalt and 25% sodium bentonite clay. This mixture is a candidate for use in the basalt repositories proposed for the Hanford nuclear waste disposal area (5).

Certain standards of repository performance have been set by the Environmental Protection Agency (EPA) and the Nuclear Regulatory Commission (NRC) (6). The repository must be shown to satisfy these requirements before it can be licensed (6). Therefore, a study must be undertaken to obtain data on the performance of the repository. One of the first steps in this study is the measurement of effective diffusion coefficients for the various radionuclides through the proposed backfill barrier (5). A range of experimental conditions which effect reaction conditions and chemical transport properties in the area of the repository must be included in the study (6). In this

work, temperature and bulk density have been chosen as the main variables, because of the significant effects they have on the diffusion of the radionuclides. The tracers will be chloride-36 and carbon-14, diffusing through a water-saturated backfill. Although both radionuclides are used in anion form, each may exhibit different types of behavior in the clay (7,8). Therefore, the properties of the backfill are an important factor in how the tracers diffuse.

THE BACKFILL

The starting raw bentonite used in the testing was mainly a sodium bentonite clay, as mentioned earlier. The remaining portions included components such as quartz, feldspars, and smaller amounts of other impurities (5).

Basalt is a low-permeable, magmatic rock that is prevalent in the geologic formations of the proposed repositories on the Hanford area. Its permeability is on the same order of magnitude as bentonite, i.e., 10^{-9} - 10^{-15} m/s (9,10). This material will be used in the barrier in the form of small, granular particles (less than 16 mesh), facilitating compaction of the mixture. Therefore, because of the small size and low permeability of the basalt particles in the backfill, it is not considered to be a

medium through which diffusion occurs. The bentonite acts as a continuous medium for diffusion, and reduces the pore volume throughout the compacted backfill(6). It does this by adsorbing water and swelling to fill the voids in the crushed basalt(7).

RELATED WORK

Several factors, besides those already mentioned, also influence the diffusion of radionuclides through a porous solid. Temperature is one such factor that was varied in this work. A general trend of how temperature affects the diffusion coefficient is known. Relyea(11) states that diffusion increases with temperature, due to the increase in the kinetic energy of the particles.

Eriksen et al. have run diffusion tests on bentonite, using chloride-36 and iodide-131 as tracers, in both breakthrough and concentration profile tests (12). In these experiments two temperatures were used (25°C , 70°C), and air-dry bentonite was compacted before water uptake (and saturation) occurred. They found considerable resistance to the diffusion of chloride-36 and iodide-131, most likely caused by interactions with the clay-water system. The smaller interparticle and intralamellar voids seemed to inhibit the diffusion of water through the bentonite. The

larger intralamellar and interparticle voids were therefore assumed to be the main passages of the anions.

In Kissel's et al. (13) investigation of chloride movement through Houston Black swelling clay, they too found that the larger (connected) soil pores are often important pathways for Cl^- movement. Even though Cl^- can move quickly through these pores, there was some resistance to the Cl^- movement due to interactions of the clay structure and the negative charge of the anions. Movement of anions in this system may also be different than in compacted clays, where there will be reductions in the size and differences in the shape of the voids and pores(14). Therefore, the interactions between the radioactive anions and the clay/water system may be different for compacted and uncompact clay. For example, Lai et al. (15), like Kissel et al. (13) found that the negative charge of the clay seemed to have been a factor in anion diffusion. Repulsive forces that are created were found to reduce the mobility of the anion. Compaction of the clay further reduces the cross-sectional area available for diffusion and by doing this creates a larger repulsive force of the clay on the anion.

Dutt and Low(16) postulated that not only are anions repulsed by the negative clay layers, but they also have

difficulty entering the clay from an adjacent solution. Eriksen et al. (12) used a test where the initial concentration of the tracer was present in the fluid adjacent to the clay. The radionuclide would then diffuse into the clay as well as through it. Comparing with Hamid's (17) results, Eriksen et al.'s values for the diffusion coefficient of iodide were one to two orders of magnitude smaller. In Hamid's work (17), he measured the diffusion coefficient within clay soil for iodide. Therefore, the postulate of Dutt and Low must have some validity.

In Dutt and Low's (16) work they also compared the diffusion of alkali chlorides with that of heavy water (D_2O). They found very little difference between the size of the values except that the diffusion coefficient for the heavy water was larger. This is because the electrical interactions of the clay with the ions reduced the mobilities of the ions (16).

The retention of iodine in various substances was studied by B. Allard et al. (19). A significant amount of iodine was found to be sorbed by montmorillonite, especially in the presence of chloride. Hamid (17) also found iodide to be sorbed onto clay soil. Consequently, Hamid (17) found the diffusion coefficient for I-ions to be lower than that for Cl-ions. This implies that Cl^- ,

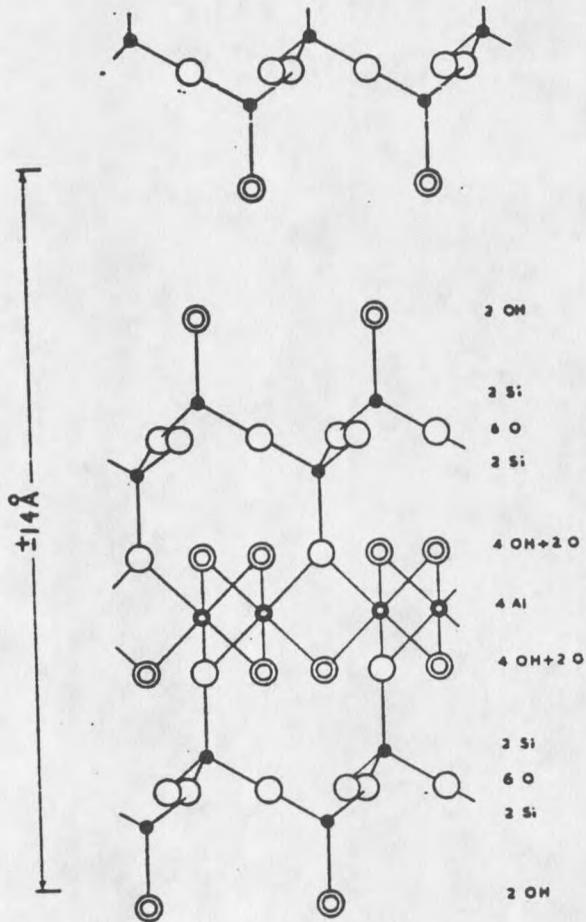
although also an anion, is less likely to be sorbed by a clay than I^- . Because they are both halogens, the properties of the ions should be similar (19). The iodide ion is much larger though, and the electrostatic interactions of the clay layers with the ion may be greater and consequently a difference in sorption properties results.

Other studies have been performed on the movement of radionuclides in compacted bentonite (12,15,20). Many radionuclides, which exist as cations under repository conditions are sorbed by the clay due to cation-exchange processes. Movement of the cations can be assumed to be through the interlamellar as well as the intralamellar space, unlike anions (12).

CLAY MINEROLOGY

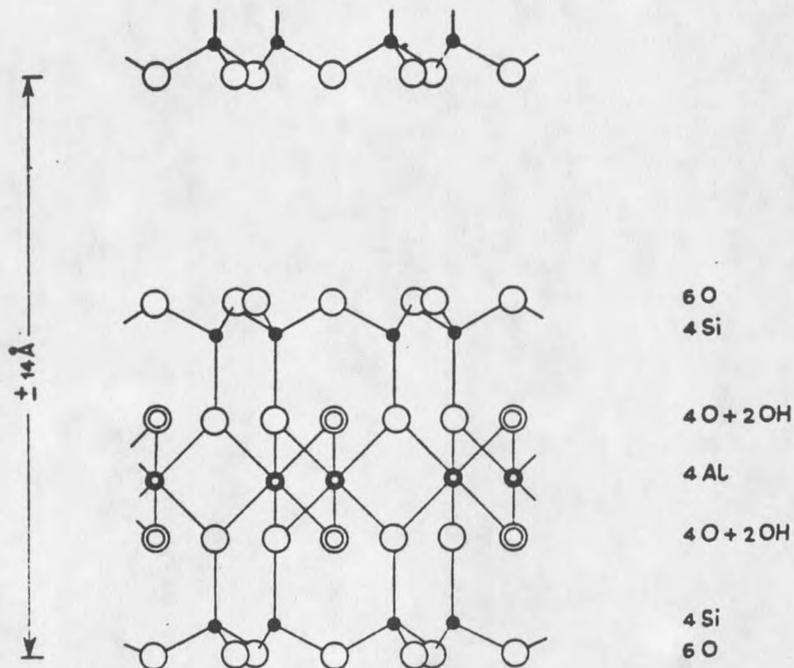
Two idealized lattice structures for montmorillonite, the major component of bentonite rock are depicted in Figures 2 and 3 (8). These structures depict the clay as neutral, although montmorillonite is known to have a negative charge (7). This charge is created because the composition of the clay platelet can vary due to isomorphous substitution of the trivalent Al with Mg, Fe, Cr, Zn and other atoms (7). That is, aluminum, with its

Figure 2. A Proposed Structure For Montmorillonite



THE PROPOSED STRUCTURES FOR MONTMORILLONITE (IDEALISED)

Figure 3. A Second Proposed Structure For Montmorillonite



THE PROPOSED STRUCTURES FOR MONTMORILLONITE (IDEALISED)

higher positive valence is replaced by elements of a lower valence. The tetravalent Si itself will occasionally be replaced by Al in the structure (7).

The layer structures are weakly bonded to each other with van der Waals forces (7). The water will penetrate these layers and form hydrogen bonds with the oxygen-containing clay platelet surfaces (7). The resulting interlamellar swelling can add up to four monomolecular layers of water between the layers of clay (7). Depending on how little the pressure is that is put on the clay, repulsion of like-charged clay layers can cause the uptake of more water (7). If the water causes the plates to separate by more than 10\AA , which is more than three times the size of the tracers used in this investigation, a second stage of swelling occurs (7). This type of swelling will cause the bentonite clay to expand to much larger volumes and disperse into a finely divided suspension (7).

Because the crystal layers carry a net negative charge, this charge is compensated for by cations adhering to the surface of the layers (7). When water is present, these cations will tend to diffuse away from the surface due to a lower concentration in the bulk solution (7). The resulting double layer thickness then contains cations that are readily exchangeable (7). Diffusing cations therefore

may have movement hindered due to sorption on the clay (7). Anions, on the other hand, will be repelled by the negative clay layers and remain in the bulk water of the intralamellar space (7).

The double layer can be varied in size by the amount of electrolyte present (21). In this way, electrolyte concentration can cause swelling of the clay and a reduction of its porosity (21). Consequently, the resulting double layer will be decreased in width and the pores will become more clogged with increasing ion concentration (7,21). For monovalent counter-ion concentrations varying from 0.01-100mmol/dm³, the approximate double layer thickness varies from 1000 down to 10 \AA (7). For divalent counter-ions in the same concentration range, the thickness varies from 500-5 \AA (7). The pH of the clay solution is also known to affect the double layer, especially at the edges where aluminum ions are exposed (7). The edge has a tendency to become positive at low pH (7). This will give the clay an ability to sorb anions, albeit small amounts compared to the net negative charge of the clay (7,22).

CHLORIDE-36

Radiotracers have found increasing importance in the study of water movement through porous media (23). In this

investigation, chloride-36 has been chosen as a tracer of water diffusion through the backfill. This tracer was chosen due to the tendency of the chloride to diffuse through the pore water with little chance of being sorbed onto the clay (24).

There are some differences between the movement of water and chloride through a clay because of the influences of the negative potential in the pore volume (7). Rolfe and Aylmore (25) reported that diffusion can at least partially compensate for these differences, which would be more noticeable at higher flow rates through the clay. This suggests that chloride movement in the clay is much like that of water at low pressures. Therefore, the chloride-36 tracer should describe the transport of water through the bentonite with some accuracy. Tritium, in the form of heavy water, should even be better at describing the water transport in the clay, but the differences between it and Cl^- should also be small (16).

CARBON-14

Carbon-14 (half-life: 5730 yrs.) in radioactive waste is a potential long-term biological hazard (26). In the form of carbonate, which is the tracer used in this work, it can react with Ca^{++} or Mg^{++} in the groundwater to form a

weak complex or precipitate (27). Consequently, sorption of the complex or precipitate on the bentonite can occur (26). The formation of the magnesium or calcium complexes and precipitates depend on the temperature, pH, Eh, and concentrations of the ionic species in the groundwater (26,28). Carbon-14 may react with hydrogen and form other species as well, such as carbonic acid and HCO_3^- ion (26). There is also a chance that the carbonic acid will react to form CO_2 and water, depending on where the equilibrium lies (28).

Allard et al. (26) investigated the possibility of carbon-14 sorption using various geologic media, including sodium montmorillonite and also a bentonite/quartz (10/90) mix. Using several contact times (3days-6mos.), they found that while there was no sorption on sodium montmorillonite, there was some on the bentonite/quartz mix. They explained this by pointing out that the bentonite used contained calcium, which gave a higher concentration of calcium ion in the liquid. It is therefore possible that there is no carbonate sorption on the bentonite if it is a sodium clay. However, to determine the actual importance of carbonate sorption, the effects of other variables will have to be established ,e.g., calcium concentration.

Besides the information already given, ^{14}C -carbonate tracer is expected to have the same anion interactions with the clay as chloride-36, possibly more pronounced because of the larger negative charge of the carbonate. However, the actual role that the different size and shape may have on the diffusion of the two radionuclides is uncertain. Carbonate is expected to have a smaller diffusivity than chloride because of its larger size (11), i.e., about 2.81\AA and 1.81\AA , respectively (29,30). Also, it is known that calcium carbonate can cause variations in the swelling behavior of clay (31), which may affect its diffusion properties.

RESEARCH OBJECTIVE

The objective of this research was to measure effective diffusion coefficients for chloride-36 and carbon-14 through a compacted 75/25 basalt/Na-bentonite mixture. The tests will be performed at three different temperatures, i.e., 20, 60, and 90°C , and two bulk densities, i.e., 1.6 and 1.8g/cm^3 . From the data, a relationship between the effective diffusion coefficient and the two variables is to be determined. The experimental results should also develop a better understanding of the mechanism of anion movement through swelling clays.

EXPERIMENTAL

MATERIALS

The basalt used was taken from the Columbia Basin area in the state of Washington. The rock was originally picked from outcroppings near the Hanford area. This specific basalt was chosen due to its availability in the underlying formations of the proposed radioactive waste repository on the Hanford site. Only those samples that did not appear to be weathered, i.e., yellowed or eroded, had been chosen. The rock was then crushed to smaller sizes before it was available for use in this investigation.

The rock was further crushed in a shadow box. The relative amounts of each appropriate mesh size are given in Table 1.

Table 1. *Relative Amounts of Sized Basalt Used

**Mesh	-16+60	-60+120	-120+230	-230+325	-325+400	-400
Amount(g)	1558	120	174	58	30	60
Total of All Mesh=2000g						

*- These amounts are relative because 4000g were prepared and then this amount was split in half with a riffle splitter

**- - means that it passes through this mesh size
+ means that it will not pass through this mesh size

A technician determined the grain density of the basalt mixture to be 2.89g/cm^3 using a air equilibration pycnometer. The procedure involves putting a known amount of sample in a vial with water (32). The necessary parameters such as water density are known.

The sodium bentonite used was mined in Wyoming. The specific location is unknown. The bentonite came in a fine powdered form and contained small amounts of impurities such as quartz and feldspars (5). The bentonite was chosen due to its ability to swell and fill voids in rock, but also due to its low permeability and retardation properties (7). The grain density of the bentonite was determined to be 2.69g/cm^3 by R.A. Carlson, a fellow worker (33).

A 666.7g portion of bentonite was stirred in with the basalt mixture to form a 75/25 mix of basalt to bentonite. The resulting blend was split four times with a riffle splitter for mixing purposes, and then split into eight portions, archived, and stored.

To obtain portions small enough for the individual tests, the larger containers were mixed as before and then split down into 8-18g individual portions. During this procedure, the portion that was to be split was mixed thoroughly before each splitting. It was found that this method would appear to give a more accurate splitting of

the material. Once enough small portions were made, e.g., there were two for each test, the samples were archived and stored.

The moisture content of the basalt/bentonite mixture was determined to be 1.5% in March of 1984. The moisture content was redetermined in July of 1984 and was found to be 2.7%. The procedure for determining the moisture contents was ASTM D2216-80. The method involved the drying of a backfill sample for approximately 1 day in a GCA/Precision Scientific heated vacuum dessicator set at $110^{\circ}\text{C} \pm 5^{\circ}\text{C}$. The first moisture content measurement on the backfill used a drying oven, as called for in the procedure, instead of a heated vacuum dessicator. The other measurement of the moisture content of the backfill used the dessicator because it kept the atmosphere thoroughly dry around the drying sample. For other moisture content readings of the test cores, the samples (1-2.5g slices of the core) were possibly contaminated with a tracer. To safely contain the radioactivity, the heated vacuum dessicator could conveniently be put in a hood whereas an oven could not.

EXPERIMENTAL PROCEDURE

A piece of equipment called a diffusion cell was fabricated by craftsmen for this investigation. The cell contains two half cells, depicted in Figure 4b. There is a surrounding cylinder with screw caps on the outside. The total cell as it appears on the outside is pictured in Figure 4a.

The half cells were to be packed similarly in most respects for each cell, i.e., backfill composition, bulk density, except that one half cell contained a tracer while the other did not. For diffusion to occur, one of the half cells containing the tracer was put in contact with the other half cell containing only the saturated backfill mixture.

Two bulk densities, 1.6g/cm^3 and 1.8g/cm^3 were used in this investigation, although for the carbon-14 tests only 1.6g/cm^3 was used. To produce test cores that were of the right bulk density, a certain amount of a synthetic groundwater was put with the air-dry backfill samples and mixed. The amount of water to be used was given by the following equations (34):

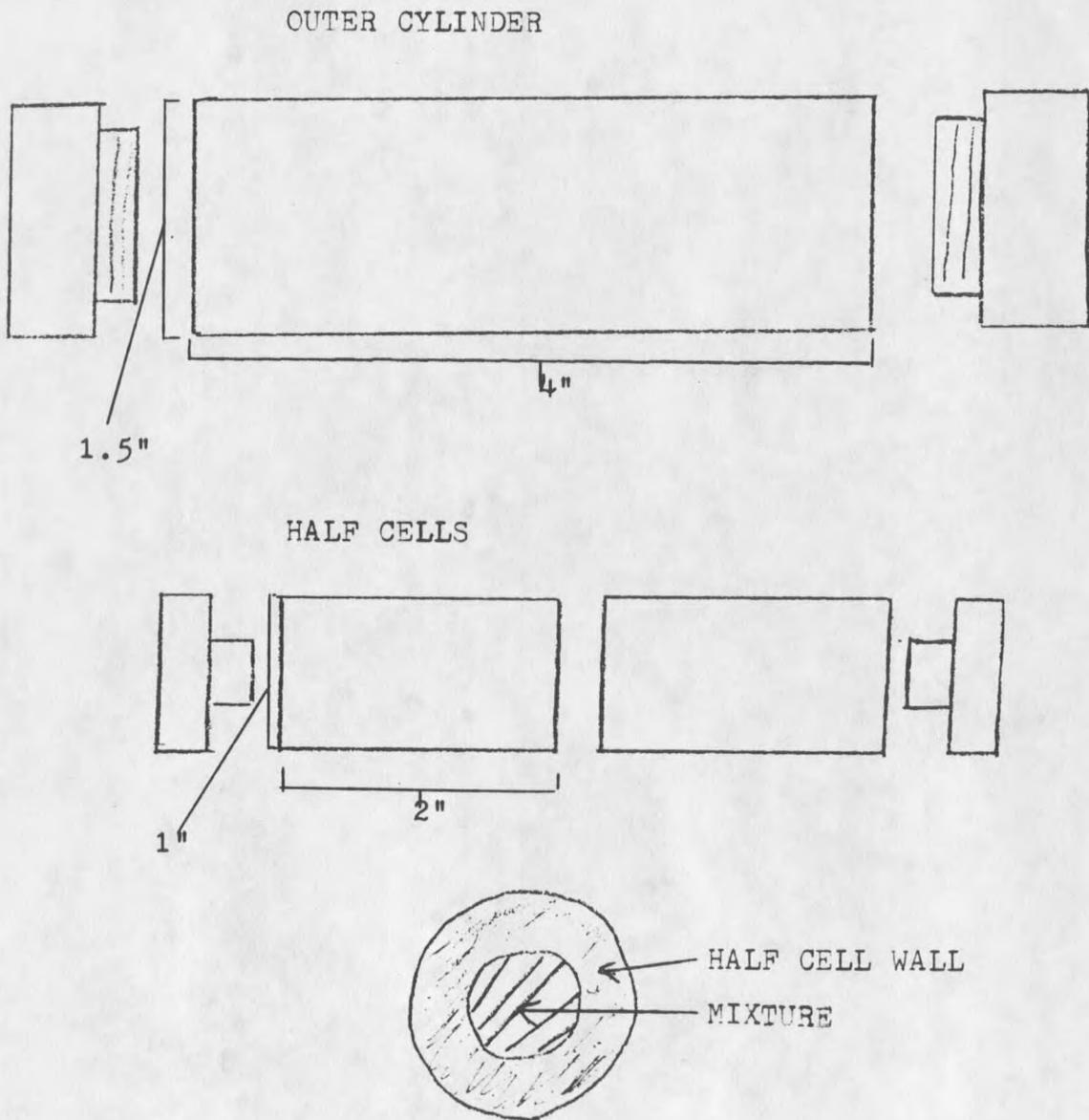
Amount of Air-dried Backfill:

$$X = (BD)(V_h)(1+W)$$

Total Porosity of Backfill-water Mixture:

$$P_t = 1 - [X] \left[\frac{F_1}{PD_1} + \frac{F_2}{PD_2} \right] / [V_h(1+W)]$$

Figure 4. Diffusion Cell Parts



Amount of Water To Be Added To Dry Backfill:

$$Y_w = (P_t)(PW)(V_h) - (W)(X)$$

X=amount of air-dried backfill (g)

BD=specified bulk density (g/cm^3)

V_h =volume of half cell ($\sim 5.3\text{cm}^3$)

W=moisture content of backfill

P_t =total porosity of the resulting backfill-water mixture

F_i =weight fraction of the i th component in the backfill
(75% basalt/25% bentonite)

PD_i =grain density of the i th component in the backfill

PW=density of water ($1\text{g}/\text{cm}^3$)

Y_w =amount of water (g) needed to be added to air-dry backfill sample to get specified bulk density

Since two mixtures were prepared for each test cell, each water amount was measured separately. For the untagged mixture, i.e., without the tracer, the synthetic groundwater was measured out on a scale ($\pm 0.001\text{g}$) and set aside. For the tagged mixture, a $20\mu\text{l}$ spike was added to the measured water amount for the chloride-36 tests and a $40\mu\text{l}$ for the carbon-14 tests. Two $20\mu\text{l}$ samples were then taken from the tagged mixture to be counted for an initial concentration determination. Also, 15ml of instagel (containing a phosphor) were added to each sample for purposes of counting on the Packard (Tri-carb 4000 series) scintillation machine.

The water samples, tagged and untagged, were added to the two backfill samples and stirred thoroughly. (Note: The mixtures were stirred again after an hour.) The sample

containers containing the mixtures were then put in a humidity chamber (dessicator filled with water) for equilibration overnight. The teflon parts of the diffusion cell were put under water overnight to insure total saturation of the parts. The next day the total weight of the parts ($\pm 0.01g$) was determined.

The half cells were packed starting with the untagged mixture. First, small amounts of the mixture were spooned into the half cell. Second, the mixture was packed down with a stainless steel rod until saturation was reached, or rather until the material glistened. This process was continued until the half cell was filled to about 1/16" above the top. The packed material was then levelled with a straight-edged blade. This procedure was repeated for the tagged mixture.

Once both half cells were packed, a teflon disk was placed between the half cells as they were brought together. This unit was then loaded into the surrounding cylinder. The diffusion cell was then reweighed in order to determine the amount of material packed in the cell. The cell was equilibrated after weighing for as long as deemed necessary to reach uniformity of concentration in the tagged half cell. For chloride-36 this period was only one day because it is a fast moving tracer.

After the time for equilibration had passed, the teflon disk was removed from between the half cells to allow diffusion of the tracer. During this period, the diffusion cell was placed in a humidity chamber controlled at one of the three temperatures (ambient~20,60,90°C). For the 60°C environment a New Brunswick Controlled Environment Incubator Shaker was used. For the 90°C environment a Blue M Stabil-therm oven was used. The diffusion was allowed to continue until the tracer went a sufficient amount into the untagged portion of the diffusion cell but not to the end. In order to determine a correct amount of time, some extra trials had to be used.

After the diffusion time had expired, the diffusion cell was removed from the given humidity chamber. Approximate diffusion times were as follows: 1) They were about five hours for the ambient tests; 2) about 3 hours for the 60°C tests, and 3) about 2 hours for the 90°C tests. For the 60°C and 90°C tests the cells were put in an ice bath for five minutes first, and then the cells would be frozen in liquid nitrogen for five minutes (35). The inner clay core was extruded using the machine depicted in Figure 5. First, the outer shell was removed. Then, using the can pictured on the left of Figure 5, the inner (backfill) core was extruded.

