AN APPARATUS FOR MEASUREMENT
OF RADIONUCLIDE TRANSPORT RATES IN ROCK CORES

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Abstract

An apparatus and procedure for the study of radionuclide transport in intact rock cores are presented in this report. This equipment more closely simulates natural conditions of radionuclide transport than do crushed rock columns. The apparatus and the procedure from rock core preparation through data analysis are described. The retardation factors measured are the ratio of the transport rate of a non-retarded radionuclide, such as ^3H , to the transport rate of a retarded radionuclide. Sample results from a study of the transport of $^{95\text{m}}\text{Tc}$ and ^{85}Sr in brine through a sandstone core are included.

Introduction

The relative transport rates for radionuclides released into groundwater are important in the consideration of a specific rock type for a nuclear waste repository. A variety of laboratory sorption techniques exist which use crushed rock in both static batch tests and dynamic column tests. The main advantage of the core sorption method is that the geometrical and geochemical characteristics of the rock are preserved. In crushed rock columns however, the geometrical changes are substantial, and the geochemical changes produced in crushing the surface depend on the homogeneity of the rock. The core sorption apparatus and technique developed at LLNL simulate the flow of radionuclides through intact rock cores. The apparatus was designed to approximate naturally occurring conditions. Confining pressure is applied to the core to simulate the rock's overburden pressure. The low solution flow rate is similar to the flow rate of groundwater expected in a repository. The retardation rates obtained from this system can therefore be used to predict the behavior of radionuclides in field studies. Our aim in this paper is to give a description and general discussion of the apparatus and its use for our colleagues working on radionuclide sorption and transport. This work has been supported by the Office of Nuclear Waste Isolation under the auspices of the Battelle Pacific Northwest Laboratories.

Equipment Design

Our rock core sorption studies resemble liquid chromatography (LC) experiments in that solution is passed through the core, a radioactive tracer is injected, effluent samples are collected, and the activities of the radionuclides in the effluent samples are determined. Equipment and

techniques developed for LC were used in the design of the core sorption apparatus. The design was also influenced by the work of Lakner (1) and Hearg (2). Equipment specifications for the core sorption apparatus are given in Table 1. A schematic of the apparatus is shown in Figure 1.

Table 1. Equipment Specifications

Pump--Altex Model 100
available flow rates--0.01 to 9.99 mls/min
available fluid pressures--0 to 10,000 psi
operating fluid pressures--0 to 5,000 psi
Spike Injection Valve--Altex Model 210
available sample loops--20 μ l, 50 μ l, 250 μ l, 500 μ l
acceptable fluid pressures--0 to 6,000 psi
Pressure Transducers
Altex Model SP70A
Range--0 to 15,000 psi
Doric Transducer Indicators Model 420
Hydraulic Pump
SC Hydraulic Engineering Model 50-100-25 pump
available pressure range--0 to 40,000 psi
operating pressure range--0 to 7,000 psi
Fraction Collector--SMI Series 1205
γ -ray Detection System
3" x 3" NaI(Tl) crystal--Harshaw 12SW12-W3, well-type
efficiency--9,600 cps/ μ Ci for ^{60}Co
resolution--8%
Canberra 30 Multichannel Analyzer
Hewlett Packard 5055 Printer
β^- Detection System
Packard Tri-Carb Liquid Scintillation Spectrometer Model 3320
Insta-Gel Scintillator
Operating Temperature--room temperature ($\sim 23^\circ\text{C}$)
Sample dimensions
length--25.4 mm
diameter--26 mm

A commercially available solution metering system pumps the transport solution through the rock core at a constant flow rate. Confining pressure is

Figure 1: SCHEMATIC OF CORE SORPTION APPARATUS

applied to the jacketed rock core to simulate the natural overburden pressure on an in situ sample. Pressure transducers measure the solution pressures on the inlet and outlet sides of the rock core. A spike injection loop holds a known volume of radioactive tracer until the valve is turned and the tracer is introduced into the flow path. On the outlet side of the core, a throttle valve regulates the flow rate. This regulation is accomplished by opening or closing the throttle to vary the size of the flow path. A carousel-type fraction collector holds polyethylene sample tubes. The samples are collected for a set time interval. The γ -ray emitting radionuclides are determined in our laboratory using a NaI(Tl) well-type detector with a multi-channel analyzer. The α^- emitting radionuclides are determined in LLNL's α^- counting facility.

Figure 2 shows the sample assembly in detail. Since previous experience has shown that stainless steel is less likely to sorb radionuclides than brass, the parts of the apparatus which come in contact with the transport solution are made of stainless steel. The gland nut, back-up rings, sleeves, O-rings, and crescent rings are used to hold the sample in place and to prevent leaks when the confining pressure is applied. The cartridge, gland nut, back-up ring, and sleeve are made of brass. An SC Hydraulic Engineering Corp. Model 10-500-25 air-operated oil pump applies the confining pressure to the Halthane jacket which surrounds the core and end fittings.

Before the rock core is placed in the sample assembly, the jacket is molded around the core and end fittings. Lakner used Scotchcast 221 for the jacketing material; however, it takes 72 hours to cure and has an easily damaged surface. We have substituted a polyurethane adhesive polymer developed at Lawrence Livermore National Laboratory, Halthane 73-18 (3), for the Scotchcast. Halthane 73-18 cures overnight to a sturdy jacket tightly bonded to the core. Stainless steel end fittings (Figure 2) are placed at

Figure 2: SAMPLE ASSEMBLY

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each end of the rock core. Teflon gaskets are placed between the core and end fittings to cushion the end of the core and improve the fit between the core and end fitting. This assembly is placed into the mold (Figure 3). A Teflon mold is used for easy release of the mold from the cured Halthane jacket. Figure 3 and 4 show the mold, jacketed core, and end fittings. The jacketing process is described in the procedure section of this report.

As noted in Table 1 the solution metering system (pump) and spike injection valve are commercial LC equipment. The Altex Model 100 dual piston positive displacement pump has pulsation damping features. The pump delivers solution at a constant flow rate or at a constant pressure, but normally operates in the constant flow rate mode. The spike injection valve is an Altex Model 210 high pressure valve. Spike loops of 500 μ l and 250 μ l were utilized to deliver the activity of tracers desired into the transport solution flow path.

To determine hydrological properties, such as the hydraulic conductivity of the rock core, the solution pressure gradient along the core must be known. Altex Model SP70A pressure transducers measure the solution pressure on the inlet and outlet side of the cores with Doric Model 420 transducer indicators to display the pressure.

In order to achieve lower flow rates and, therefore, longer residence times of the spike in the core, a throttle valve is placed after the outlet pressure transducer. A 100-increment vernier marks the setting on the throttle valve, and the change in dead volume with change in throttle valve setting was measured.

Effluent fractions are collected in pre-weighed 12 x 75 mm polypropylene tubes with caps. A Scientific Manufacturing Industries Fraction Collector (Series 1205) is used to collect the effluent on timed intervals. The

Figure 3: STAINLESS STEEL END FITTINGS AND ROCK CORE IN TFE TEFLON MOLD

Figure 4: ASSEMBLED MOLD AND HALTHANE 73-18 JACKETED SAMPLE AND END FITTINGS

carrousel of the collector has a capacity for 150 tubes which fit into the well of the NaI(Tl) crystal for γ counting.

The radionuclide concentrations in the effluent fractions are determined by γ and liquid scintillation counting. Gamma emitters are counted in a NaI(Tl) well-type detector. The detector is a Marshaw 3" x 3" well-type crystal (Model 12SW12-W3) with a resolution of 3% and a peak efficiency of 9600 cps/ μ Ci for ^{60}Co . A Canberra 30 1024-channel analyzer is used for data collection and display. A NaI(Tl) detector was chosen instead of a Ge(Li) detector because, with the limited number of γ -rays to be detected, the greater efficiency of the NaI(Tl) was more important than the higher resolution of a Ge(Li) system.

Tritium is determined by liquid scintillation counting. The sample is vacuum distilled to remove brine salts and interfering radionuclides. Duplicate samples are mixed with Insta-Gel scintillator and counted in a Packard Tri-Carb Liquid Scintillation Spectrometer (Model 3320). This spectrometer is specially designed to be very sensitive for low energy β^- emitters, such as tritium.

Procedure

A core sorption run involves:

- 1) Preparing the rock core and mounting it in the core sorption apparatus,
- 2) Saturating the rock core with the transport solution,
- 3) Injecting the radionuclide spike into the flow path and
- 4) Collecting the eluted solution using the sample collector.

The post run analyses include fraction weighing, fraction counting, core slicing, core slice counting, system rinsing and rinse counting. The data are computer analyzed.

Cylindrical rock cores used in the apparatus are drilled out of a larger sample. The ends of the core are ground to make a 26 mm diameter x 25.4 mm long core. The core is dried overnight under vacuum at 35°C. The core and end fittings (Figure 3) are jacketed in Halthane 73-18, which is prepared by mixing the prepolymer and curing agent and degassing for 20-25 minutes. The Halthane is injected into the Teflon mold (Figures 3 and 4) from the bottom to eliminate air bubbles in the jacket. Following an overnight cure at room temperature, the jacketed sample is carefully removed from the mold (Figure 4). The confining pressure cartridge and sample are assembled as in Figure 2.

To saturate the core, the transport solution is pulled into the jacketed core using a vacuum. Prior to attaching the sample assembly to the pump, spike injection valve, pressure transducers, and throttle valve, the spike injection valve is loaded with the radionuclide tracer and the sample assembly fittings are filled with transport solution to prevent air bubbles from entering the saturated core. Once the sample assembly is in place the confining pressure is applied to the core via the SC oil pump. The transport solution is pumped through the core to equilibrate the core and solution.

Confining, inlet and outlet pressures, pump flow rate settings, and sampling intervals are recorded at the start and throughout the run. A sampling interval is chosen to give good time resolution of the data and to collect sufficient solution for γ and β^- counting. When the core and transport solution have equilibrated and at least five effluent samples have been collected, the radionuclide tracer is injected. Effluent activity levels are monitored by γ counting as the run proceeds. When the activity levels approach background, the sampling interval is lengthened.

The run is ended when the activity levels are at background, or a few counts above. The time, sample number, confining, and inlet and outlet

pressures are recorded. The supply pump is disconnected and filtered compressed air is passed through the core to expel the remaining solution. The effluent samples are capped, weighed, and γ -counted.

The sample cartridge is disconnected from the rest of the apparatus and disassembled. The Halthane jacket is carefully removed from the core and end fittings. The solution outlet face of the core is marked. To determine the axial distribution of the radionuclides retained by the core, the core is first potted in a mixture of 10:1 EPON 815:TETA. EPON 815 is a modified epoxy resin from Shell Chemical Co. and TETA is tetraethylene tetraamine. The potted core is sectioned perpendicular to the cylindrical axis using a Buehler ISOMET 11-1180 Low Speed Saw with a diamond wafering blade. To minimize the transfer of radioactivity between slices, sectioning proceeds from the outlet toward the inlet end, and the cutting fluid is discarded after each section. The sections are γ -counted for 10^5 seconds on Ge(Li) detectors since the geometry of the well-type NaI(Tl) detectors is not suitable for counting the core slices.

To remove any radioactive residue the disassembled system pieces are rinsed with approximately five ml of 6 M HNO_3 . The rinse liquids are weighed and counted.

Prior to jacketing the core in Halthane the static pore volume of the rock core is determined. The core is placed under vacuum for at least 18 hours. The core is saturated with degassed, deionized water. The core is repeatedly weighed until a constant weight is achieved. The volume of water

taken up by the core is used as the static pore volume. The dynamic dead volume of the system is measured by passing a radionuclide tracer spike through the system using a reference sample of dense alumina with a bore of $5.8 \times 10^{-3} \text{ cm}^3$ through its center. The dead volume is 1.817 cm^3 when measured from the leading edge of the spike in the effluent. When measured from the peak of the spike in the effluent it is 2.704 cm^3 . A static dead volume of 1.34 cm^3 resulted from physically measuring the system volume. This geometric value differs by 1% from the value taken at the leading edge. *This is as expected. The increase in the dead volume from the leading edge measurement to the peak position measurement is due to the volume of the spike used and the system dispersion.* This dead volume information can be used as a starting point for fitting equation 1 to the experimental data for each radionuclide.

Data Analysis

A single radionuclide migration run generates a large amount of data:

- o Spike data
 - radionuclide concentrations, spike volume and time of injection
- o Effluent sample data
 - sample numbers, weights, count times, count output, sampling times and intervals
- o Core data
 - dimensions, pore volume and section activities
- o Residual activity from the system clean-up.

To reduce the effluent sample data, a computer program, REDU, was developed by Glenn Hage and H. C. Weed at LLNL. REDU performs three main functions. It calculates the volume, flow rate, sampling times, and radionuclide activity for each sample. It graphs the tabulated results versus time, sample number, and volume. It graphs theoretical equations along with the experimental data as a function of cumulative volume.

Sample collection times are interpolated for each sample number from a few input times. Sample volumes are calculated from sample weights. These data produce a flow rate for each sample and cumulative volume passed through the core. For each radionuclide the activity calculations use counter efficiency, decay corrections, and background values to determine the integrated activity (A), normalized activity (A/A_0), concentration (C), and normalized concentration (C/C_0). A_0 and C_0 represent the initial spike activities and concentrations, respectively.

The data are graphically presented with plots of flow rate versus time, activity versus time for each radionuclide, and A/A_0 and C/C_0 versus time and cumulative volume for each radionuclide. REDU contains a curve plotting subroutine which plots a theoretical transport equation along with experimental data by adjusting parameters such as the dispersion coefficient and reference volume. The paper of Weed et al (4) discusses the equations used for these curves.

Example of Experimental Results

The core sorption apparatus and experimental procedure were used to study radionuclide migration in sandstone cores from the St. Peter, Berea, Kayenta and San Felipe Formations. The transport solution was a synthetic Waste Isolation Pilot Plant brine (WIPP Brine B). The NaCl concentration in WIPP Brine B is approximately 4M.

Figure 5 displays the experimental results for a Kayenta sandstone. This is an example of a study of radionuclide transport in sandstones by Weed et al. (4). The radionuclide spike contained ^3H , ^{95m}Tc , and ^{85}Sr . The vertical arrow indicates the point of spike injection. The delay between the spike injection and the leading edge of the ^3H peak is due to dead volume effects in the system.

The continuous curve in Figure 5 was plotted using values calculated from Equation (1).

$$C/C_0 = \frac{B}{\sqrt{DN'}} \exp \left[-\frac{Lv}{4D} \frac{(1 - N')^2}{N'} \right] \quad (1)$$

$$B = \frac{V_{\text{spike}}}{V_{\text{pore}}} \sqrt{\frac{Lv}{4\pi}} \quad (2)$$

V_{spike} = volume of radionuclide spike (cm^3)

V_{pore} = static pore volume (cm^3)

L = sample length (cm)

v = pore velocity (cm/sec) (assumed constant)

D = dispersion coefficient (cm^2/sec)

t' = time for unretarded flow (sec)

t = time for retarded flow (sec)

$N' = vt'/L$

$N = vt/L$

The retardation factor, R , is

$$R = \frac{N}{N'} = \frac{t}{t'}$$

Retardation factors of 1.0 for ^{95m}Tc and 1.2 for ^{85}Sr were determined from the calculations. The estimated error is 20%. The paper of Weed et al (4) elaborates on this work and the calculations for R .

Figure 5: C/C_0 vs. N for Kayenta Sandstone.

^3H (+), ^{95m}Tc (O), ^{85}Sr (X).

(Weed et al, ref. 4)

Summary

The apparatus described was designed to study radionuclide transport rates through rock cores. The design was simplified by the use of commercial liquid chromatography equipment. Special end pieces and a confining pressure vessel are used with a Halthane 73-18 jacket to pressurize the core simulating the overburden pressure and to confine fluid flow path to the rock core. The mold and procedure for jacketing the core in Halthane 73-18 are described.

The radionuclide activity is measured by γ -counting in a NaI(Tl) well-type detector system. For ^3H determinations the samples are vacuum distilled, mixed with a scintillant and counted on a Packard Tri-Carb liquid scintillation detector.

The data are computer analyzed by a program REDU and a theoretical model is fitted to the data. Example data from a study of ^3H , $^{95\text{m}}\text{Tc}$ and ^{85}Sr transport in WIPP brine through a Kayenta sandstone core are shown. Further data obtained with this apparatus are discussed in reference 4.

Retardation factors obtained from experiments using this apparatus are valuable in the consideration of a specific rock type for a nuclear waste repository. By approximating naturally occurring conditions the migration of the radionuclides in these experiments should give retardation values which will compare favorably to field radionuclide migration studies. Radionuclide migration through fractured granite is now being studied using this apparatus.

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