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THE DISTRIBUTION OF PLUTONIUM IN A ROCK CONTAINMENT ENVIRONMENT

by

S. Fried, A. M. Friedman, and R. Weeber

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# The Distribution of Plutonium in a Rock Containment Environment<sup>+</sup>

S. FRIED, A. M. FRIEDMAN<sup>\*</sup> AND R. WEEBER<sup>\*\*</sup>

Chemistry Division

Argonne National Laboratory, Argonne, Illinois 60439

## INTRODUCTION

The increasing amounts of radioactive waste material accumulating from reactor operations makes the disposal and safekeeping of this material of vital importance. This is especially true for those nuclides of long half life.

Regardless of the technical details of a particular disposal method it is obvious that in a "depository" the ultimate secondary container must be some rock stratum.

It is necessary not only to consider the rock strata as barriers but also as possible conduits for ground waters and as providing for the dispersal of radionuclides and their ultimate incorporation into the biosphere. With this in mind studies

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<sup>+</sup>Work performed under the auspices of the U. S. Atomic Energy Commission.

<sup>\*</sup>and College of Environmental and Applied Sciences, Governor's State University, Park Forest, Illinois 60466.

<sup>\*\*</sup>Thesis Parts Student, Governor's State University, Park Forest, Illinois.

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have been undertaken to determine the behavior of long-lived radionuclides, particularly Pu and Am ( $T_{\frac{1}{2}}$  24,000y and 450 y) in rock strata.

The present paper presents some of the results obtained on the migration and absorption of Pu in certain rocks.

#### EXPERIMENTAL

The experiments were of two types. In the first set, studies were made of migration of solutions of Pu through cores of Niagara limestone and basalts. A high pressure chromatographic absorption apparatus was constructed and is shown diagrammatically in Figure 1. The function of the piston is to exert pressure on the solution while isolating it from the pressurizing gas.

At the start of an experiment a small amount of  $^{238}\text{Pu}(\text{NO}_3)_4$  tracer in neutral aqueous solution was placed on the surface of the disk of stone and allowed to dry at room temperature. Successive increments of  $\text{H}_2\text{O}$  were then forced through the limestone disk and the depth of penetration of the Pu tracer was measured by the X-ray absorption technique.

This technique depends upon the fact that the three uranium L X-rays, which accompany 25% of all  $^{238}\text{Pu}$  decays are of slightly differing energies and therefore have different absorption coefficients in the limestone. Figure 2 shows the spectrum of these L X-rays observed through several samples of wet limestone. These were thin measured slices of the limestone which were interposed as absorbers between a source of  $^{238}\text{Pu}$  radiation

and the detector. As is easily seen the ratio of the intensities of the  $L_1/L_2$  X-rays decreases with the thickness of the stone, similarly the  $L_3/L_2$  ratio increases with thickness. It is a simple matter to calibrate the change in these ratios as a function of thickness (penetration), since the X ray intensity ratios change logarithmically with thickness. In the time interval after each increment of  $H_2O$  had passed through the sample, the L X-ray spectrum was measured through the surface of the stone and the average depth of penetration of Pu tracer was determined by comparing the measured  $L_1/L_2$ , and  $L_3/L_2$  ratios to the calibration curve.

The results of these experiments yielded a migration coefficient,  $m = 30 \pm 10$  micrometers/meter ( $\mu/m$ ) of water flow for the limestone and  $61 \pm 8 \mu/m$  for the basalts. Where  $m$  is the average distance traveled by the Pu atoms for every meter traveled by the  $H_2O$  molecules.

The second set of experiments consisted of measurements of the surface absorption coefficient of Pu on the stones. In these experiments disks of the stone were immersed in solutions of  $.00004 M \text{ } ^{238}\text{Pu}(\text{NO}_3)_4$ . Small aliquots (.05%) of the solutions were removed, dried on Ta planchets and then placed in an internal alpha proportional counter. When the counting rate of samples taken at 12 hour intervals had become constant this was regarded as evidence of the attainment of equilibrium.

We will define an absorption constant as:

$$k = (\text{activity of Pu/ml of solution}) / (\text{activity of Pu/cm}^2 \text{ of stone})$$

It was found that the value of  $k$  for pure solutions of  $\text{Pu}(\text{NO}_3)_4$  at .00004 M was  $.10 \pm .02$  for limestone and  $.07 \pm .02$  for basalts. In order to observe the effect on this absorption constant of other ions the value of  $k$  was measured for solutions containing  $\text{NaCl}$ ,  $\text{CaCl}_2$ ,  $\text{LaCl}_3$  and  $\text{ZrCl}_4$  at various molarities. Figures 3, 4, and 5 illustrate the variation in  $k$  as a function of the concentration of these salts for the limestones and basalts used.

#### Computer Model and Experimental Results with Fissure

The computer model, MARGIE, is a simplified variation of a calculation we have used for predicting multiorder buildup of isotopes in reactors. It traces the distribution of Pu activity over many small increments of the face of a fissure or leak during the addition and washing cycles. The only input needed for the program is the surface absorption coefficient, dimension of the fissure, and volume of solution in which the Pu is added or with which it is eluted.

Figure 6 is an example of the output of the program for a typical calculation. 10 ml of solution containing the activity was presumed to be introduced into\* the top of the fissure and allowed to flow through, this was then presumed to be followed by 20 ml of water wash. The curves represent the distribution of the activity on the face of the rock after the wash period; it is calculated for three systems with three different absorption coefficients,  $k = .04$ ,  $.066$  and  $.133$ . In Figure 6,  $d$  is the distance along the rock face in the direction of flow

expressed in millimeters, and  $f$  is the fraction of the original activity absorbed per 0.25 mm strip across the fissure. As is expected the higher the value of  $k$  the further and more rapidly the activity moves. It should be remembered that  $k$  is defined as (Activity of Pu/ml of solution)/(Activity of Pu/cm<sup>2</sup> of rock).

To test this model of the relationship of the surface absorption coefficient to the migration rate through the fissure we constructed a model fissure. This was done by sealing a smooth slab cut from a basalt core to the face of a teflon block that had a .0127 cm depression milled down its face. This then formed a fissure that was .0127 x 1 x 4 cm in size. <sup>238</sup>Pu tracer was dissolved in 10 ml of water and allowed to flow through this fissure at a rate of 3 ml per day. This was then followed by 20 ml of water wash. After this the slab of rock was removed, dried, and the surface was scanned by a scanning alpha counter with a spatial resolution of 0.25 mm. Figure 7 is a plot of the activity observed in these .25 mm strips. The left hand peak at .20 inches (5.8 mm) from the top of the fissure corresponds to the calculated position of a peak of activity with  $k = .04$  which is close to the value for our solutions. The second peak at 1.7 inches (43 mm) from the top corresponds to a peak of activity with  $k = .35$ . Since the solutions were composed of pure water and tracer this was an unexpected result.

Our present feeling is that this more rapidly moving peak, if found to be reproducible, is composed of a chemical form of plutonium which does not absorb strongly, perhaps a (Pu)<sub>n</sub> polymer;

and that the flow through the fissure is so fast (1.71 m/day of water flow) that it does not have time to reach equilibrium. We are now working on a method to identify the chemical form of the plutonium in this peak.

The migration of the plutonium through a fissure of this size, a .0127 cm crack, is much more rapid than through the small pores of the stone. Instead of 60 microns/meter of water flow as found in part 2 even the slowly moving peak ( $k = .04$ ) moves 217 microns/meter of water flow and the rapidly moving peak moves over 2000 microns/meter of water flow. These rates depend on the (volume/surface area) ratio of the fissure and will be larger for larger fissures. This also implies an average pore diameter of 30-60 microns for the sample of rock used in the measurements of part 2, if the migration is through interconnecting pores.

#### SUMMARY

The results of these studies indicate that our basic assumption of the intercorrelation of the migration coefficients and surface absorption coefficients to the migration through fissures is verified. However, they also point out that a great deal of effort must be spent studying the effects of other solute species, the chemical nature of the plutonium itself and the kinetics of the absorption process before any understanding of the macroscopic characteristics of the transport of plutonium can be reached.

3/26/74/ljc

## FIGURE CAPTIONS

- Figure 1. Schematic diagram of the high pressure chromatographic column. The apparatus was constructed of stainless steel.
- Figure 2. L X-ray spectra of the  $^{238}\text{Pu}$  source using 9, 990  $\mu\text{m}$ , and 1727  $\mu\text{m}$  thick limestone absorbers between the source and detector. In all cases the spectra were normalized to the same number of counts in the  $L_2$  X-ray peak.
- Figure 3. Surface absorption coefficients of .00004 M  $\text{Pu}(\text{NO}_3)_4$  solutions on limestone as a function of the concentration of other salts, i.e.  $\text{ZrCl}_4$ ,  $\text{LaCl}_3$ ,  $\text{CaCl}_2$ , or  $\text{NaCl}$ .
- Figure 4. Behavior of the absorption coefficient of Pu as a function of the concentration of other salts for dense basalt cores.
- Figure 5. Behavior of the absorption coefficient of Pu for porous basalt cores.
- Figure 6. Calculated distribution of Pu on surface of fissure.
- Figure 7. Measured distribution of Pu on surface of fissure.



# APPARATUS FOR FORCING WATER THROUGH SAMPLES OF SOLID ROCK

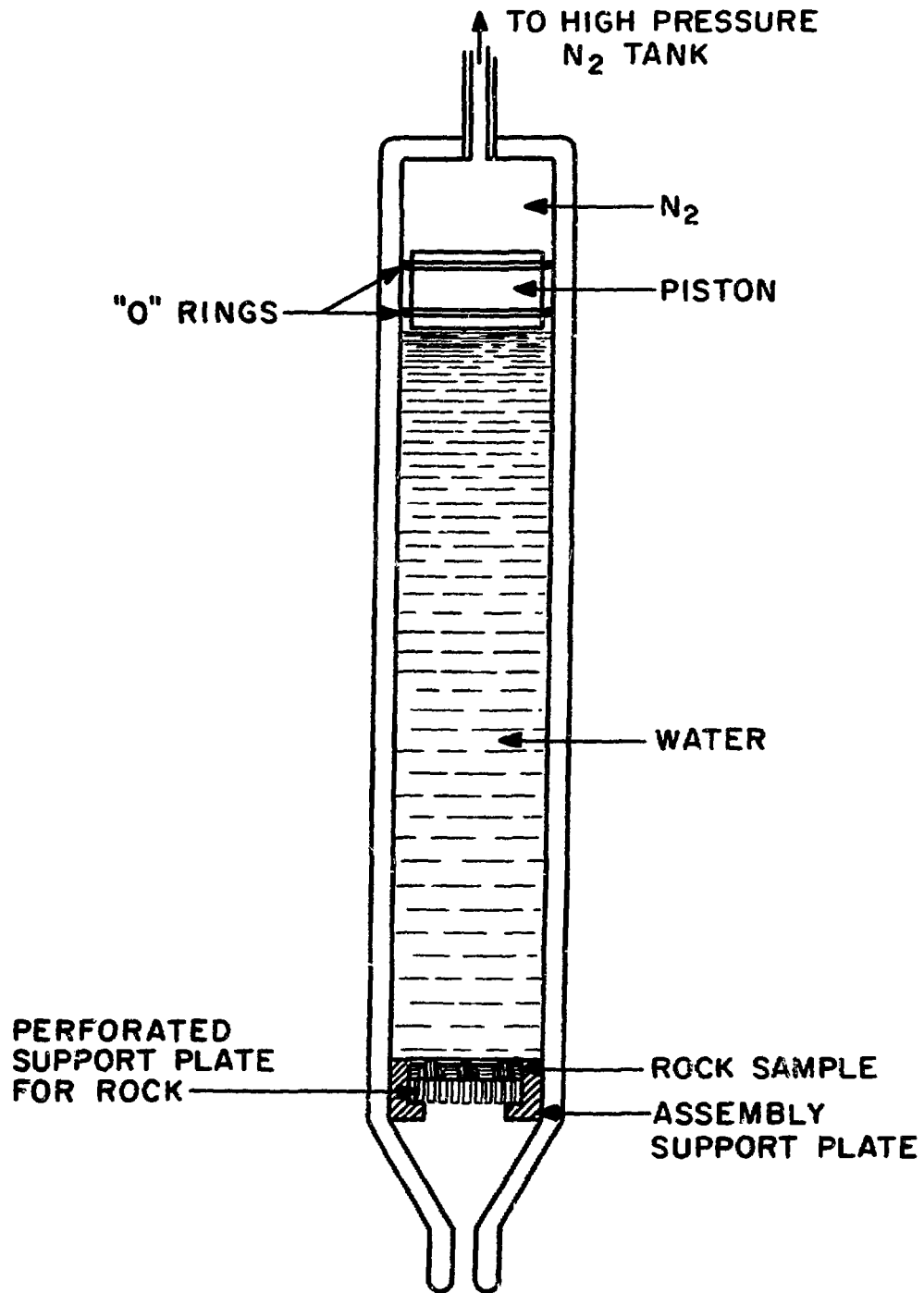


FIGURE 1

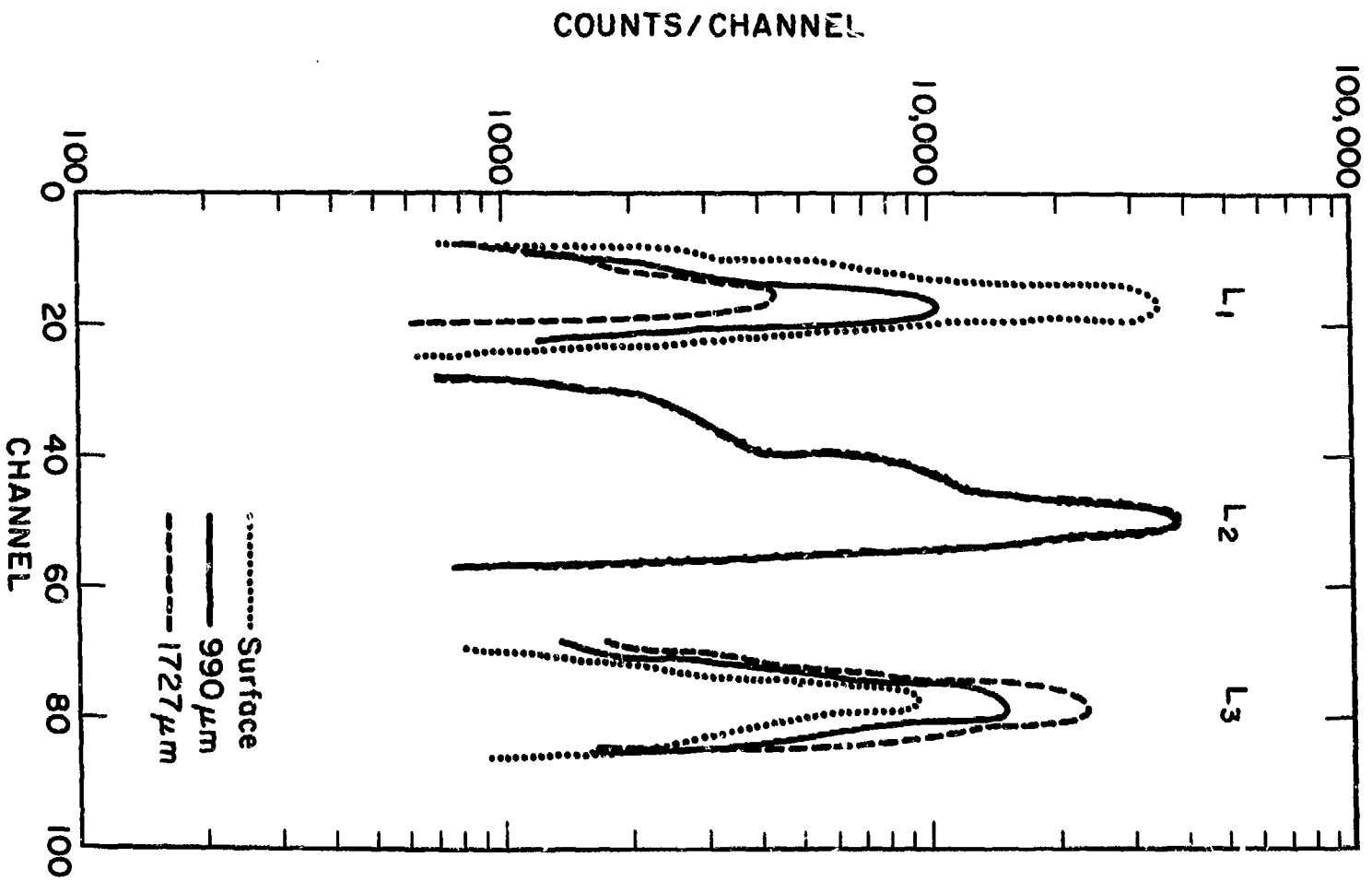


FIGURE 2

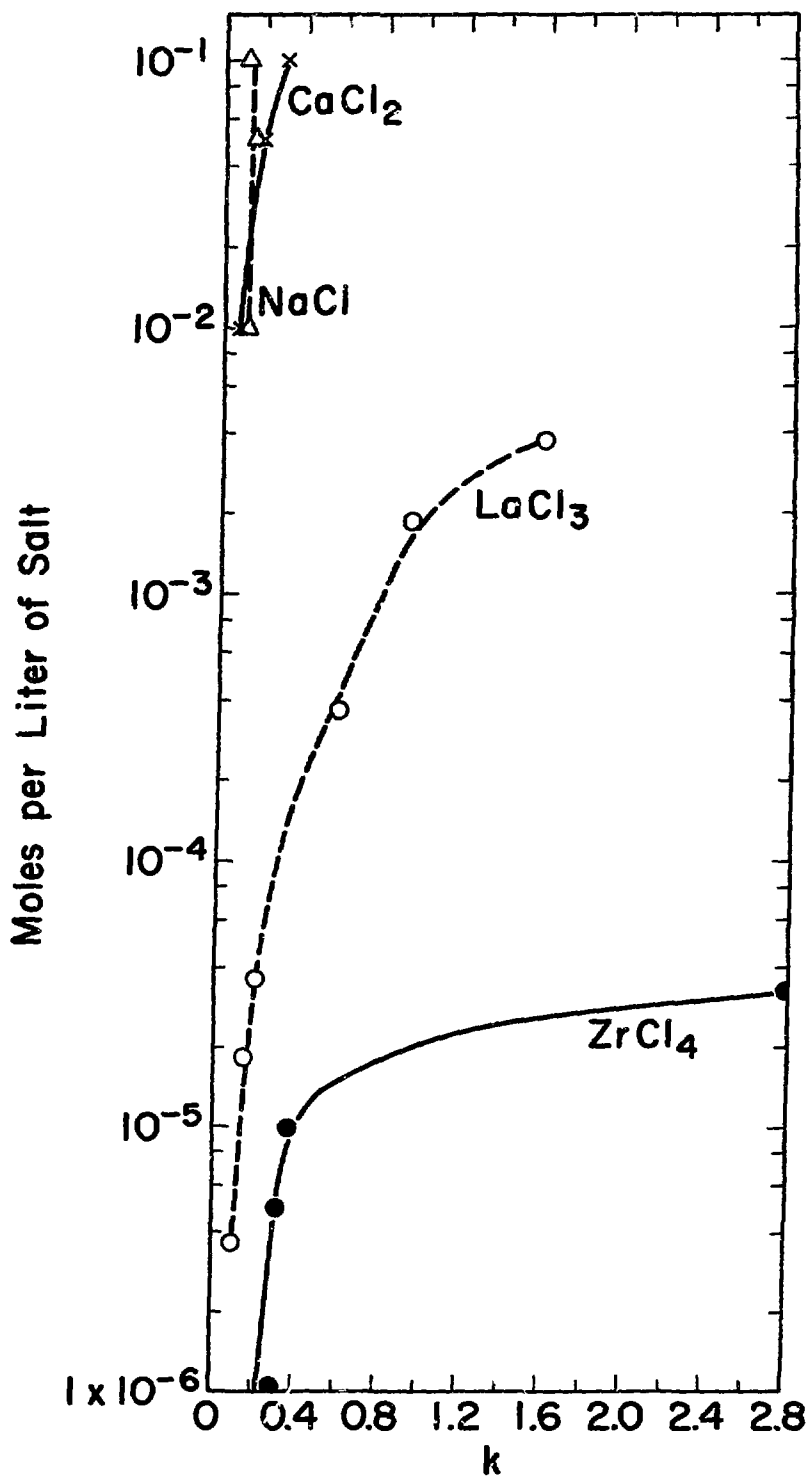


FIGURE 3

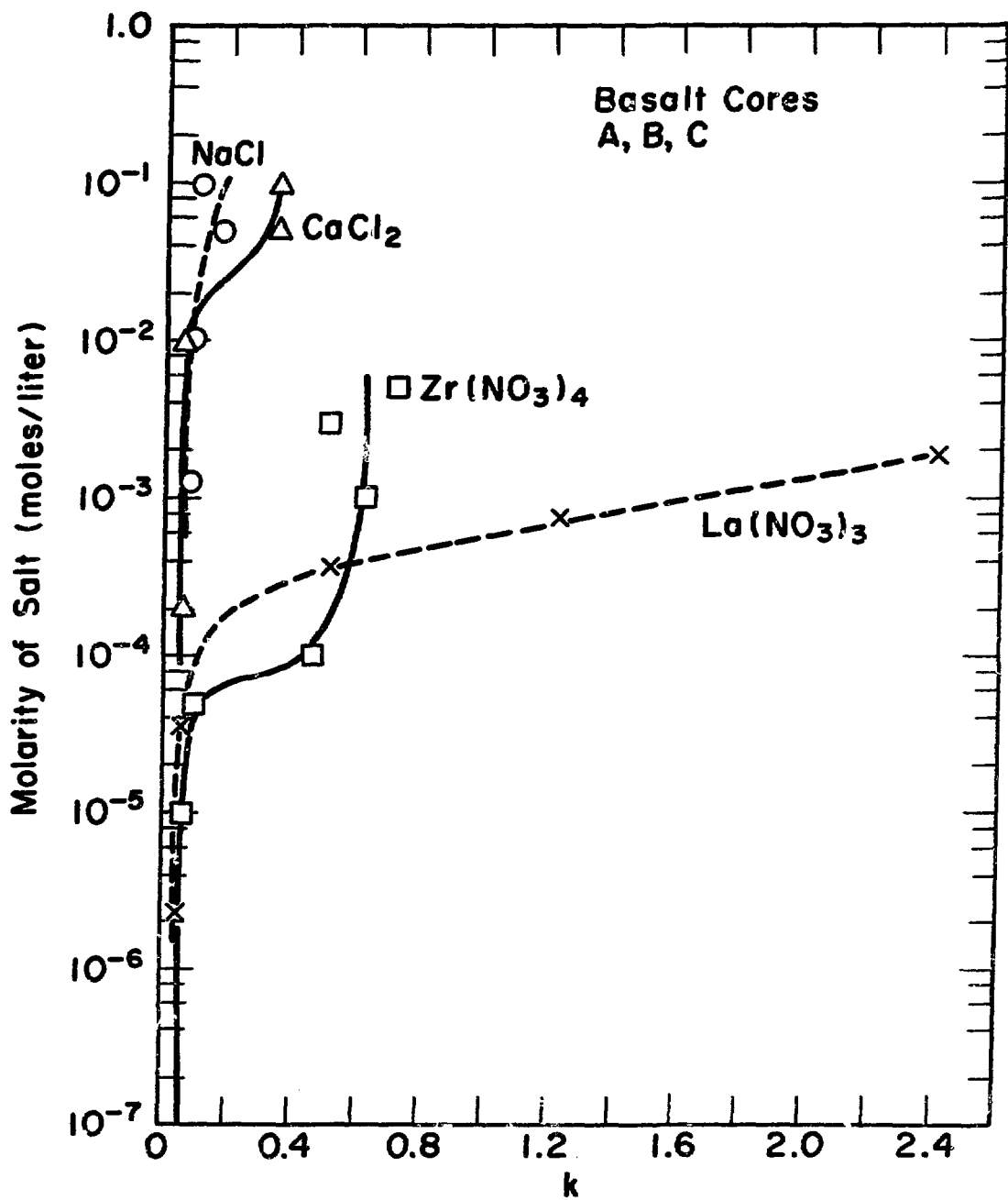


FIGURE 4

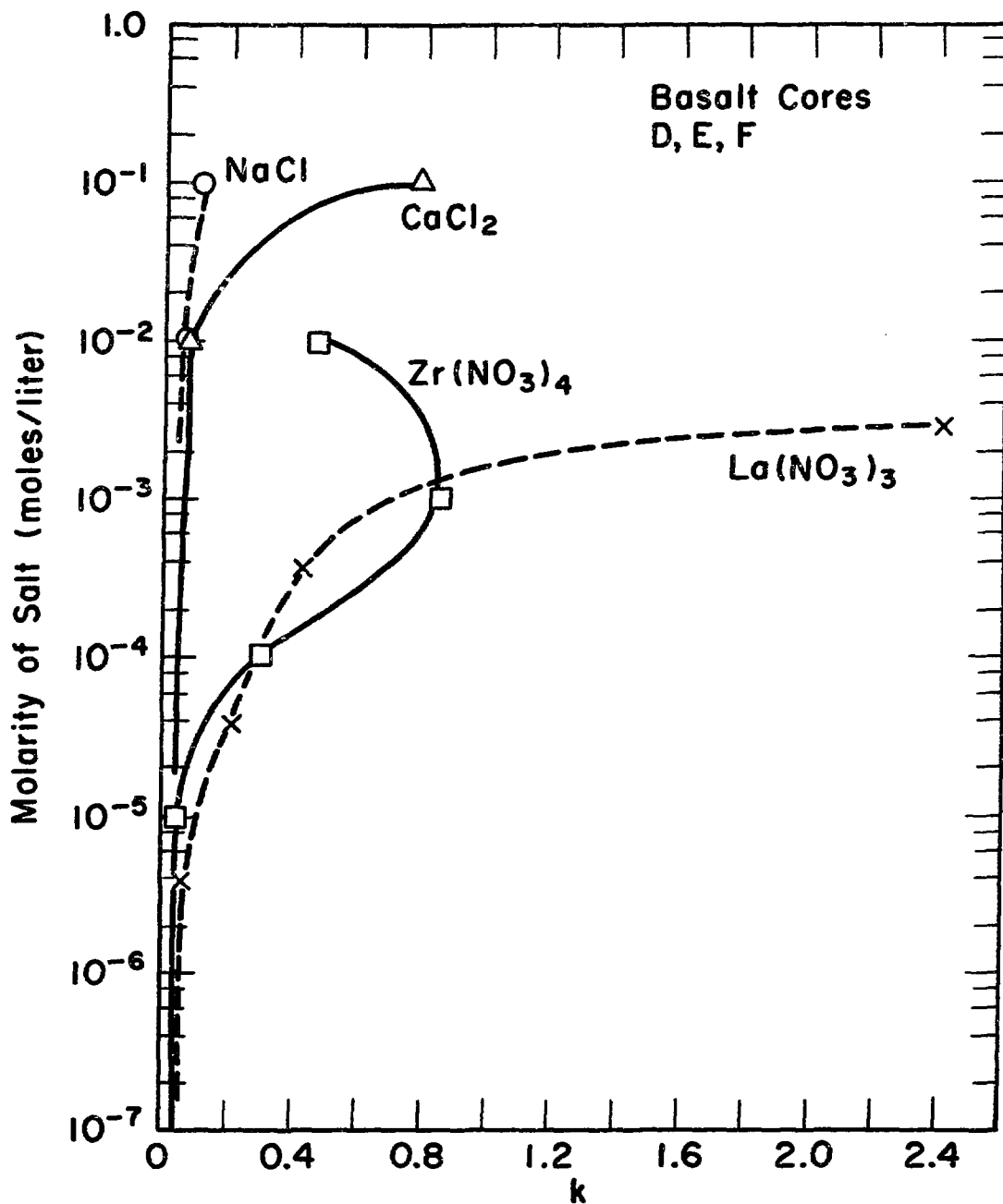


FIGURE 5

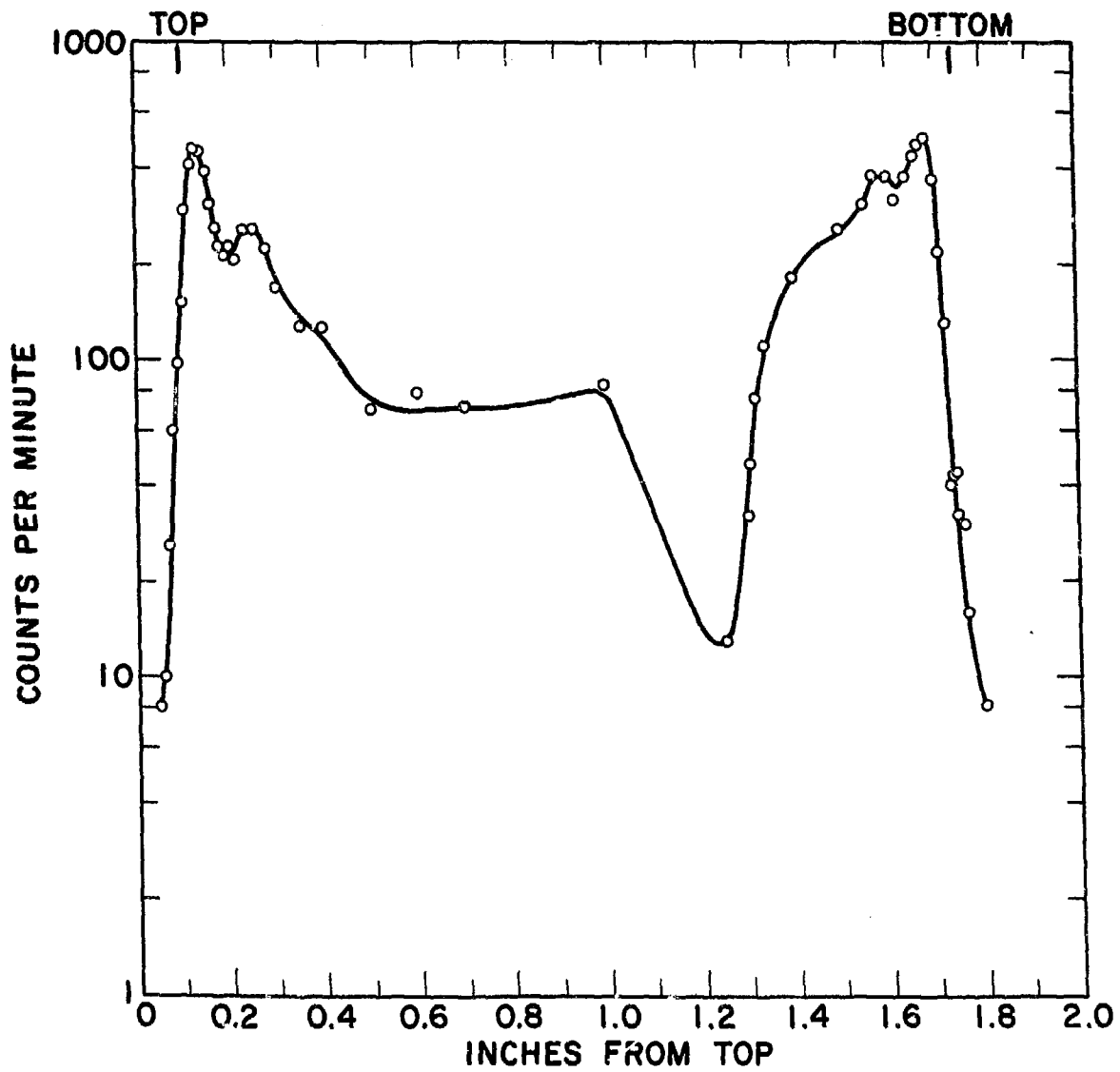


FIGURE 6

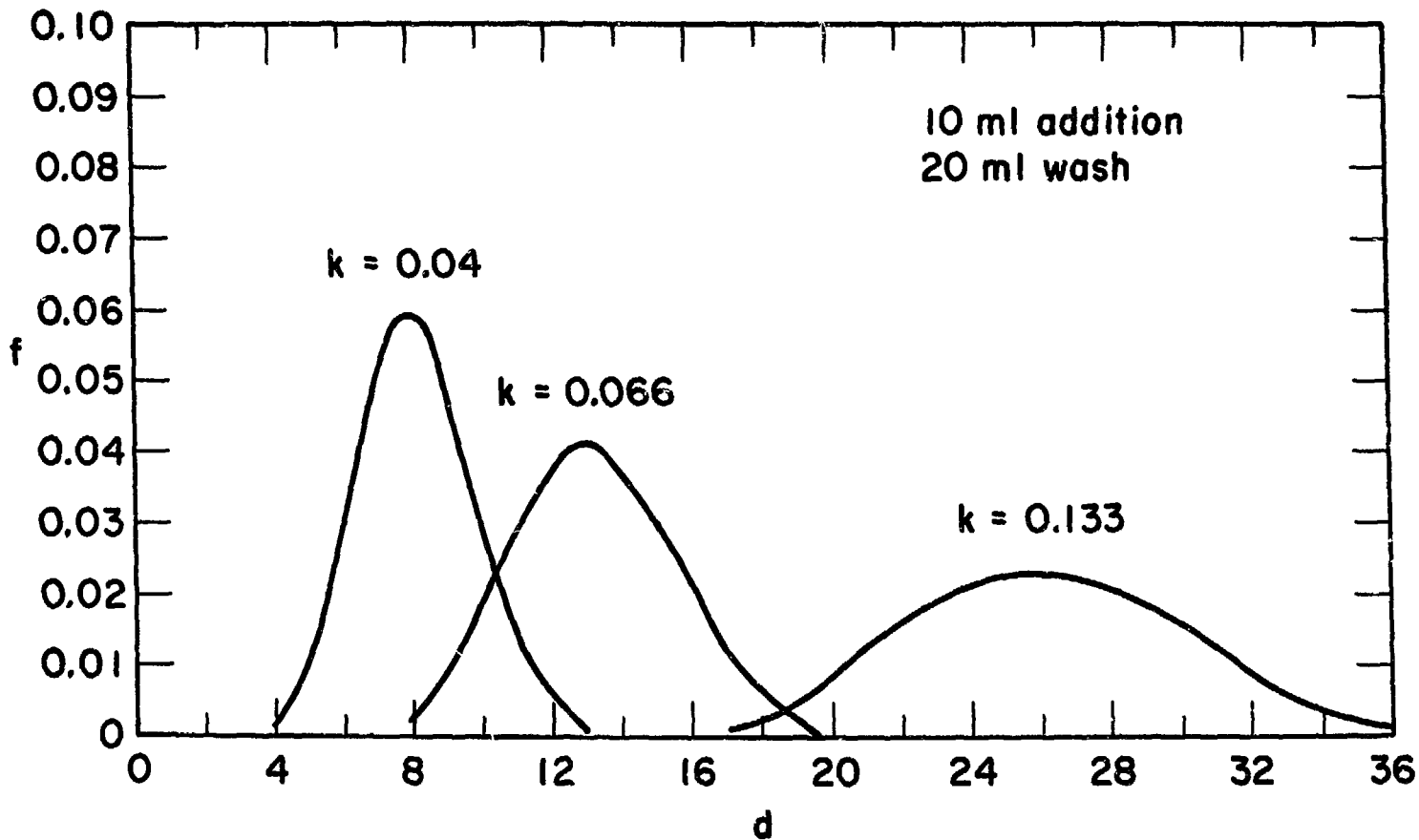


FIGURE 7