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FRACTIONATION OF STABLE CHLORINE ISOTOPES DURING TRANSPORT THROUGH SEMIPERMEABLE MEMBRANES

by

Darcy Jo Campbell

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1985

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SIGNED: Darcy J. Campbell

APPROVAL BY THESIS DIRECTOR

This thesis has been approved on the date shown below:

S. N. Davis

S. N. DAVIS
Professor of Hydrology
and Water Resources

2/27/85
Date

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TABLE OF CONTENTS

Page

LIST OF ILLUSTRATIONS vii

LIST OF TABLES ix

ABSTRACT x

1. INTRODUCTION 1

2. LITERATURE REVIEW 4

Previous Geological Membrane Research 5
  Ion Filtration Studies 5
  Studies Related to Isotope Fractionation by Geological Membranes 17
Previous Synthetic Membrane Research 24
  Ion-Filtration Studies 26
  Studies Related to Isotope Fractionation by Synthetic Membranes 27
Summary of Previous Research 29

3. EXPERIMENTAL PROCEDURE AND RESULTS 31

Forced-Flow Experiment 31
  Equipment 31
  Sampling 33
Diffusion Experiments 33
  Equipment 36
  Sampling 41
  Description of Specific Experiments 42
Sample Analysis 43
Results 47
  Forced-Flow Experiment 47
  Diffusion Experiments 50

4. INTERPRETATION OF RESULTS 52

General Trends 52
  Forced-Flow Experiment 52
  Diffusion Experiments 54

TABLE OF CONTENTS--Continued

Page

Conceptual Models 69
  Adsorption 69
  Simple Diffusion 70
  Back Diffusion 70
  Ion Pairing 71
Discussion of Mathematical Models 73
  Forced-Flow Experiment 73
  Diffusion Experiments 81

5. CONCLUSIONS 84

Improvements in Present Research 85
Further Research 86
  Laboratory Studies 86
  Field Studies 87
  Biomedical Research 89

APPENDIX A: SYNTHETIC MEMBRANE INFORMATION 90

APPENDIX B: METHODOLOGY AND RESULTS OF ADSORPTION TESTS . . . 92

APPENDIX C: CALCULATIONS OF FRACTIONATION PREDICTED BY THE PHILLIPS-BENTLEY MODEL FOR THE FORCED FLOW EXPERIMENT 95

REFERENCES 98

LIST OF ILLUSTRATIONS

Figure Page

1. Anion Exclusion 6
2. Reverse Osmosis 9
3. Forced-Flow Apparatus 32
4. Examples of Membrane Structure Types 38
5. Diffusion Cell 1 39
6. Diffusion Cell 2 40
7. $\Delta\delta^{37}$Cl Values of Effluent from Forced-Flow Experiment . . . 48
8. Ion-Filtration Efficiency (IFE) and Isotope Fractionation with Time: Forced-Flow Experiment 53
9. Effect of Pore Size on $\Delta\delta^{37}$Cl 55
10. Effect of Pore Size on Ion-Filtration Efficiency (IFE) . . . 56
11. Effect of Cation-Exchange Capacity on $\Delta\delta^{37}$Cl 58
12. Effect of Cation-Exchange Capacity on Ion-Filtration Efficiency (IFE) 60
13. Ion-Filtration Efficiency vs. Isotope Fractionation with Variable Cation Exchange Capacity (CEC) 61
14. Effect of Concentration on $\Delta\delta^{37}$Cl 62
15. Effect of Concentration on Ion-Filtration Efficiency (IFE) 63
16. Ion-Filtration Efficiency vs. Isotope Fractionation with Variable Concentration 64
17. Effect of Stirring on $\Delta\delta^{37}$Cl 65

LIST OF ILLUSTRATIONS--*Continued*

Figure Page

18. Effect of Stirring on Ion-Filtration Efficiency (IFE) . . . 67

19. Ion-Filtration Efficiency vs. Isotope Fractionation with Variable Stirring 68

LIST OF TABLES

Table Page

1. Forced-Flow Test: Isotope Fractionation Values 34

2. Summary of Synthetic Membrane Properties 37

3. Diffusion Tests: Isotope Fractionation Values 44

4. Forced-Flow Experiment: Ion-Filtration Efficiency 49

5. Diffusion Experiments: Ion-Filtration Efficiency 51

6. Chlorine Isotope Fractionation Predicted by Phillips-Bentley Model for Forced-Flow Experiment 82

ABSTRACT

The stable isotope ratio of chlorine is a potential hydrogeochemical tool. A recently-developed technique allows detection of differences in the isotope ratio of water samples. Measured variations cover a range of 3.0 ± 0.12 per mil. In deep aquifer brines, enrichment in ^{37}Cl seems to increase with increasing chloride concentration. Two types of experiments were performed, short-term (9-20 days) and long-term (five months), in an effort to produce fractionation in the laboratory. The short-term experiments involved isothermal diffusion of chloride across six synthetic, semipermeable, cation-exchange membranes. Variables in the experiments were cation-exchange capacity, pore size, concentration, and stirring. The long-term experiment involved the forced flow of a sodium chloride solution through a bentonite membrane. Both types of experiments produced over 1.2 ± 0.12 per mil fractionation, with isotopically heavier effluent solutions. Fractionation appears to increase with increasing cation-exchange capacity. Conceptual and mathematical models are presented.

CHAPTER 1

INTRODUCTION

The stable isotope ratio of chlorine, $^{37}Cl/^{35}Cl$, has recently been suggested as a potential hydrological and geochemical tool (Kaufmann et al., 1984; DeSaulniers et al., 1984). The ratio may be useful as a means of obtaining information concerning the direction and velocity of ground-water flow, chlorine geochemistry and sources of chloride in the subsurface, and the mechanisms contributing to the formation of brines in deep sedimentary basins. To date, only a small number of ground-water samples from various aquifers have been tested for the ratio, and knowledge of chlorine isotope ratios found in nature is limited. However, the measured variations of $\delta^{37}Cl$ in ground-water samples cover a range of 3.0 ± 0.24 per mil, from -1.3 to +1.7 per mil (Kaufmann, 1984).[1] This information indicates that the isotope ratio may be useful as a hydrologic tracer, as are the stable isotope ratios of sulfur, oxygen, hydrogen, carbon, and nitrogen. Fractionation (a change in the δ value) of various isotopes has been observed in conjunction with ion filtration in deep sedimentary basins. Kaufmann et al. (1984) suggested that the passage of ground water through clay or shale layers may fractionate the stable chlorine isotopes. Analysis

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[1] $\delta^{37}Cl$ = [(Rsample - Rstandard)/ Rstandard] x 1000, where R = $^{37}Cl/^{35}Cl$, and the standard is SMOC (Standard Mean Ocean Clorine).

of deep aquifer brine samples indicates both enrichment and depletion in ^{37}Cl (Hoering and Parker, 1961 and Kaufmann et al., 1985).

Several interesting questions are raised by these observations:

1) What are the mechanisms causing chlorine fractionation in aquifers? How are the electrostatic, chemical and mechanical forces involved interacting to produce a change in the ratio?

2) Can chlorine fractionation be produced in the laboratory by building model systems which simulate flow through a clay layer in a sedimentary aquifer?

3) If fractionation can be produced, can the results of laboratory experiments be applied to field systems?

4) Finally, is ion filtration by clay or shale layers in an aquifer correlated with chlorine isotope fractionation?

These questions are the motivation for the research described in this report.

Two types of experiments were performed in an effort to produce fractionation in the laboratory; short-term (9- to 20-day) diffusion tests and a long-term (five-month) forced-flow test. The short-term experiments involved isothermal diffusion of chloride through a synthetic, semipermeable membrane contained in a diffusion cell. The synthetic membranes were cation exchangers, chosen to simulate a clay layer in the subsurface. The diffusion cells consisted of two reservoirs separated by the membrane. The lower (influent) reservoir contained a sodium chloride solution, and the upper reservior held a solution of sodium nitrate of equal molarity (to minimize osmotic effects).

This apparatus simulates a sedimentary system where clay or shale layers separate waters with different chloride concentrations. Six membranes, varying in cation-exchange capacity and pore size, were used in a series of 16 experiments. Other variables in the experiments were concentration of the influent solution and stirring in the influent reservoir.

The long-term experiment involved the forced flow of a sodium chloride solution through a clay membrane. Both the diffusion and the forced-flow experiments produced significant fractionation, and in all cases resulted in an isotopically heavier effluent solution. The magnitude of the fractionation varied from +0.01 to +1.7 per mil, ±0.12 per mil, and appears to generally increase with increasing cation-exchange capacity.

CHAPTER 2

LITERATURE REVIEW

The purpose of this chapter is to acquaint the reader with some of the research regarding geologic membranes and synthetic membranes. The relationship of both types of membranes with respect to ion filtration and isotope fractionation is reviewed. First, a definition of "membrane" is necessary. As defined by the prominent membrane researcher, Karl Sollner (1944),

> A physico-chemical membrane is a phase or structure interposed between two phases or compartments which obstructs or completely prevents gross mass movement between the latter, but permits passage, with varying degrees of restriction, of one or several species of particles . . . between the two adjacent phases or compartments . . . and which, thereby acting as a physico-chemical machine, transforms with varying degrees of efficiency (according to its own nature and the nature and composition of the two adjacent phases or compartments) the free energy of the adjacent phases or compartments, or energy applied from the outside to the latter, into other forms of energy.

The passage of material across the membrane may be caused by various forces, including gradients of concentration, pressure, and electrical potential. Semipermeable membranes are membranes which allow passage of some species (e.g., water), while restricting passage of other species (e.g., ions). Some examples are synthetic membranes used in medical research and industrial applications for dialysis, ultrafiltration, and reverse osmosis. Semipermeable biological membranes occur universally in plants and animals, regulating the exchange of materials within the organism.

Previous Geological Membrane Research

Examples of geological membranes include zeolites, soils, some argillaceous rocks (Young and Low, 1965), glacial till (Wood, 1976), fractured tuff (Walter, 1982) and clays and shales. In this section, the primary emphasis is on clay and shale membranes. Both ion filtration and isotope fractionation studies are reviewed.

Ion Filtration Studies

The phenomenon of ion filtration is generally explained in terms of anion exclusion. Membranes can exclude components on the basis of size and/or electrical restrictions. Geological materials such as sandstone usually have pore sizes larger than the largest hydrated radii of ions found in ground water (Marine and Fritz, 1981), but compacted clays and shales have been shown to exclude ions (Figure 1). Double layer thicknesses are comparable to pore sizes in clay-rich rocks, and overlap of the double layers is believed to be the cause of anion exclusion.

Russell (1933) was perhaps the first to suggest that clays and shales may act as semipermeable membranes. In 1947, DeSitter postulated that brines may form in isolated basins because confining layers act as semipermeable membranes which allow water, but not salts, to pass. Marshal (1949) discussed the electrochemical properties of mineral membranes. He studied crystals of cation-exchange minerals and

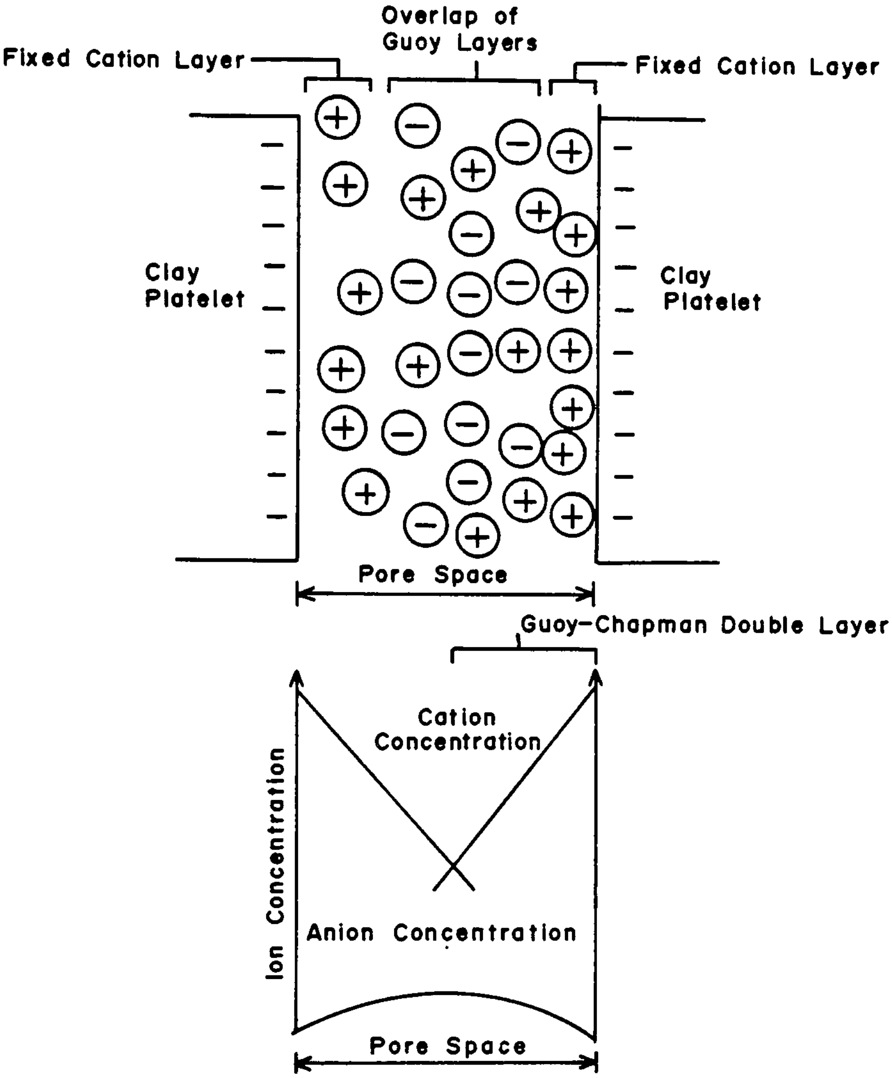


Figure 1. Anion Exclusion.

Clay minerals have negative surface charges due to broken bonds and isomorphous substitution of monovalent for divalent cations in the mineral lattice. The cations in an electrolyte solution are attracted to the clay surface. As the pore is compacted, the double layers overlap, lowering the concentration of the anions in the pore solution, leading to anion exclusion (also called Donnan exclusion).

montmorillonite clays, and used the Teorell (1937) and Meyer and Sievers (1936) theory (for porous, charged materials), and Donnan membrane equilibrium to successfully predict the behavior of ions passing through the mineral membranes. The Teorell-Meyer-Sievers (TMS) theory and Donnan membrane equilibrium will be discussed in Chapter 4. Marshal suggested that plugs of colloidal electrolytes in a gel form could be used in place of clay membranes to study the thermodynamics of flow through membranes.

Wyllie (1948 and 1955) measured the electrical potential developed across shale as a result of concentration differences of the solutions separated by the shale. He suggested that ion filtration by compacted shales could explain the high salt concentration of formation waters in sedimentary rocks. McKelvey, Spiegler and Wyllie (1957) noted that clays may have properties in common with synthetic membranes. They showed that certain synthetic ion-exchange membranes restrict the flow of dissolved salts, and they stated that a similar effect might be obtained with clay minerals, due to similarities in properties between the two. This process of salt filtration "could be responsible not only for the concentration of brines within the subsurface but also for separation of various salts" (McKelvey, Spiegler and Wyllie, 1957).

Shortly after this, Berry and Hanshaw (1960) demonstrated that osmosis can operate in geological environments when clays separate waters of different salt concentrations, indicating that clays can act as semipermeable membranes. In 1962, McKelvey and Milne presented experimental evidence showing that flow of salts through compacted bentonite and shale can cause salt filtration. A sodium chloride solution was forced through each of these materials under a differential pressure of 5,000-10,000 pounds per square inch (psi). A maximum influent to effluent concentration ratio of eight was observed, and they noted that the ratio decreased with increasing influent concentration, with increasing porosity, and with increasing input pressures. The authors theorized that the amount of salt filtration was related to the ion-exchange properties of the membrane, and that bentonite, with a large surface area and high cation-exchange capacity, was the most favorable clay for experimentation.

Next, Bredehoeft et al. (1963) presented a mathematical model predicting the distribution of ions in a geologic basin. They suggested that in artesian basins, water enters the aquifer in recharge areas, and flows upward slowly through confining layers (see Figure 2). If a clay layer does restrict the flow of ions (which are in the recharge water or the formation water), the concentration of ions in the lower layers would increase, as theorized by DeSitter (1947). This is the pattern observed in nature. Brine concentrations in natural aquifers may exceed 200,000 mg/1, and Na^+ and Cl^- are the primary constituents. These brines usually occur: 1) in deep formations, grading to fresh water near the surface; 2) near saline surface water bodies which communicate with ground water; 3) close to evaporite deposits; 4) in sediments containing trapped sea water; and 5) in formations containing fluids which have migrated from these sources.

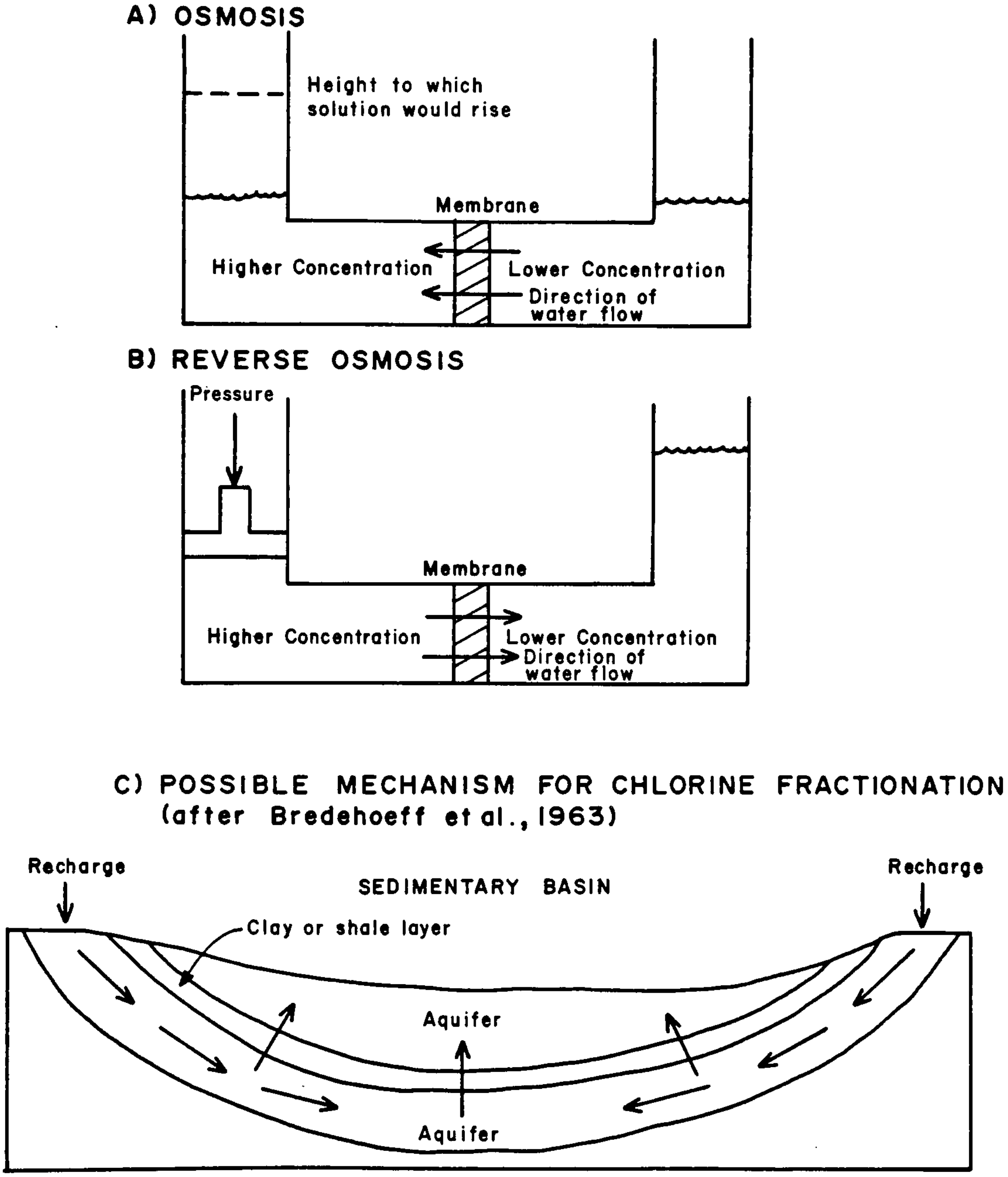


Figure 2. Reverse Osmosis.

Bredehoeft et al. (1963) noted that a satisfactory explanation had not been presented for the formation of brines in the first category. In order to simplify their model, diffusion was neglected, and only convective flow was considered. They also assumed that osmotic effects due to concentration differences would be very small, if the difference in concentration of solutions separated by a clay layer was small. The model predicted concentrations that were in close agreement with brine concentrations in the Illinois Basin.

Kemper (1961) and Kemper and Maasland (1964) developed an equation describing the effect of salt and water diffusion (due to osmosis) on salt filtering. They forced 0.01 M (molar) NaCl solutions through sodium- and calcium-bentonite clay plugs. The plugs were compacted under a pressure of 48 bars (700 psi) and the differential pressure was 10-17 bars (145-250 psi). Both viscous (convective) and diffusive transport of water and salt through the clay were modeled. Viscous flow is proportional to the pressure gradient, and is caused both by forced flow and by salt concentration differences which cause osmotic pressure differences. Diffusive flow is due to concentration differences and was modeled using Fick's first law. The experiments indicated that increasing pressure differentials and decreasing pore size caused increased salt filtraton. This pressure dependence is opposite in sign to that obtained by McKelvey and Milne (1962), but the pressures used by Kemper and Maasland were much lower. The authors reasoned that larger pores, corresponding to lower pressure, would allow faster viscous flow. If viscous flow is much larger in magnitude than diffusive flow, then salt filtering efficiencies would increase. However, they also stated that larger pores reduce the degree of negative adsorption and increase the effective diffusivity of salt through the membrane, which would decrease filtration efficiency. They noted that the latter effect is usually larger than the former, which is consistent with their experimental results. An electrolyte restriction coefficient (σ) was used by the authors, which depends on membrane properties and the concentration gradient. The magnitude of σ increases as concentration and pore size decrease. The authors mention that ultrafiltration (herein defined as filtration by size) may be possible for a small portion of the salt filtration observed in compacted clays.

Mokady and Low (1966) presented a method to measure the diffusion coefficients of Na^+ and Cl^- in clay-water slurry systems. They observed a decreased diffusion coefficient with increasing salt and clay concentrations. For the bentonite used, the diffusion coefficient of Cl^- ranged from 4.0 - 10.0 x 10^{-6} cm^2/sec, while the free-water diffusion coefficient of Cl^- is 2 x $10^{-5} cm^2/sec$. The percentage of clay in the system ranged from 10% to 20%, and NaCl concentration varied from 0.05-0.40 M.

In 1968, Mokady and Low performed diffusion experiments using a cell packed with Na-bentonite. They allowed 0.05 M and 0.0001 M NaCl to diffuse through the clay for ten months, and determined the diffusion coefficients of Na^+, Cl^-, and water. The diffusion coefficient of Cl^- was 3.0 - 6.0 x 10^{-6} cm^2/sec. The free water diffusion coefficients were determined in another diffusion cell, by measuring the flux of the radioisotopes, ^{36}Cl and ^{22}Na. The free water coefficient for Cl^- was 1.97 x 10^{-5} cm^2/sec. The purpose of the experiments was to investigate the mechanism by which water moves through a charged, porous system. Specifically, does the water in a clay system move by diffusion or by viscous flow, in response to a concentration gradient? They concluded that, in their experiments, the water moves by viscous or quasi-viscous flow. However, a similar analysis by the same authors showed that the Na^+ and Cl^- move primarily by diffusion. For any of the components, they state that the driving force for flow is the partial molar free energy gradient. The authors reported that the diffusion coefficients measured seemed to be markedly influenced by proximity to clay surfaces and by ultrafiltration.

By 1968, geological field evidence for ion filtration was being presented. Chemical and pressure anomalies were shown to cover part of the San Juan Basin, New Mexico (Berry, 1960), and these anomalies were best explained by the osmotic and salt-filtering properties of clays. Berry and Hanshaw (1960) suggested that chemical and pressure anomalies were also present near Alberta, Canada and in parts of the San Joaquin Valley, California. Bredehoeft et al. (1963) proposed that the Illinois Basin brines were caused by salt filtration by clay membranes. Graf et al. (1966) indicated that the geochemistry of brines of the Michigan Basin could be a result of ion filtration by shale membranes.

Van Everdingen (1968) noted the similarity between the membrane behavior of clays and shales and the behavior of synthetic (cellulose acetate) membranes used in reverse osmosis. In the desalination literature, the selectivity of synthetic membranes regarding ion flow was explained by differences in the size of the hydrated radius of various ions. After reviewing clay membrane research, he stated that the selectivity sequence for natural membranes is also highly dependent on the size of the hydrated ionic radius. His model of the transport of salts and water through porous, semipermeable membranes is as follows:

1) Water is transported by molecular diffusion and by convection (due to a hydraulic gradient).
2) Ion transport is caused by:
    a) sorption and diffusion in the membrane matrix (governed by the concentration gradient);
    b) pressure-biased activated diffusion of ions in near-molecular-size pores in the membrane, which is caused by both the concentration and the hydraulic gradients; and
    c) hydrodynamic flow of salt through the larger pores, caused by the hydraulic gradient.

Van Everdingen proposed that a and b above are highly dependent upon the hydrated ionic radius. He also concluded that ion filtration should decrease with a lower compaction pressure and a higher hydraulic gradient, because more and larger pores would be opened.

Berry (1969) also discussed shales and clays as semipermeable membranes. He predicted the relative passage rates of dissolved species, and the effects of temperature, pressure, and chemical concentration of the influent solution on the efficiency of the membrane. According to Berry (1969), the relative passage rate of chemical species through a shale should depend on a number of factors, including the activity of the influent solution, relative dissociation of the species, non-ionic adsorption, relative adsorption of divalent versus monovalent cations at cation-exchange sites, and the relative influence of mass effects on transport rates. Berry noted that dissociation phenomena are probably most important in determining species passage rates through shale membranes, as was first indicated by White (1965). Berry predicted that an increase in temperature would decrease membrane filtration efficiency, because increased temperature might decrease dissociation, reduce the ion-exchange capacity of the membrane, and possibly reverse the ion selectivity sequence of Eisenman (1962).

Kharaka and Berry (1973) performed laboratory measurements to investigate the questions presented by Berry (1969). They used four different clays and a shale membrane, placed in a filtration apparatus. High differential pressures of 41-275 bars (600-4,000 psi) and high compaction pressures of 138-655 bars (2,000-9,500 psi) were used. Temperature of the influent solution varied from 20-70 degrees Celsius (°C). The authors were the first to use multi-component influent solutions, which are much more similar to natural solutions than the NaCl solutions used by most other investigators. The measured filtration efficiencies increased with increasing ion-exchange capacity, with decreasing concentration of the influent solution, and with increasing compaction pressure. Efficiency decreased slightly at higher temperatures for solutions with the same ionic concentration. The authors proposed that ion flow through membrane pores would be governed by concentration of the influent and pore solutions, velocity of water flow (due to the hydraulic gradient), and electrical interactions of the ion with the "streaming" potential (induced by forced flow through the membrane). Kharaka and Berry used the membrane model of Teorell, Meyer, and Sievers (TMS model) to describe their system. The TMS equation had been used with geological membranes in the past by Walton (1958), Berry (1959), and Hanshaw (1962). This model does not account for any of the following; diffusion into and out of the membrane, ion pairing or complexing between ions in solution, and interactions (such as adsorption) between the species and the clay particles. The TMS equation was not successful in predicting the effluent concentration values obtained in Kharaka and Berry's experiments. The discrepancy was believed to be due to the use of free solution mobilities for the ions, rather than membrane mobilities. The authors reasoned that the decrease in membrane efficiency at higher temperatures is partly due to a higher degree of ionic association at higher temperatures. A problem they noted with their experimental conditions was that pressure gradients in field situations are often 10^{-5} to 10^{-6} times lower than those used in the laboratory. Therefore, membrane efficiencies in the subsurface should be greater than those measured in the laboratory, because higher pressures (faster flow rates) decrease efficiency.

Hanshaw and Coplen (1973) developed a theory explaining how and to what extent ion filtration occurs. The model is an application of the TMS theory and Donnan membrane equilibuium. They obtained reasonable agreement between theoretical and laboratory results. Laboratory experiments consisted of forcing 0.01 N (normal) solutions through montmorillonite discs. Compaction pressure was 330 bars (4,800 psi) and differential pressure was 100 bars (1,450 psi). Hanshaw and Coplen's model of ion filtration is based on the idea that ion exclusion by clay membranes depends on the ion-exchange capacity, or excess negative charge on the aluminosilicate framework of the clay. The charged pores retard anion flow, as shown in Figure 1. The degree of anion exclusion is pressure dependent because pressure affects the electrical environment of the clay pores.

Marine and Fritz (1981) presented a model to quantify anomalous hydraulic heads in a buried Triassic basin in South Carolina. They stated that osmotically-induced hydraulic pressure is primarily dependent upon concentration differences across the membrane, type of ions, type of clay, and pore size. The model utilizes non-equilibrium thermodynamics to evaluate phenomenological friction coefficients in membrane systems, and the approach is based on the equations of biophysical researchers Katchalsky and Curran (1965). The theoretical treatment showed that, for porosities less than 10% (which includes most shales), membrane filtration efficiency approaches 100% for moderate concentration gradients. They also demonstrated that in the buried Triassic basin, anomalous hydraulic heads are best explained by osmosis through illite-rich membranes which are 30-300 m thick.

Graf (1982) stated that overpressuring is adequate to overcome chemical osmosis and cause reverse osmosis. Some demonstrated overpressuring mechanisms in sedimentary sequences are rapid deposition of fine-grained sediments and dehydration of gypsum. Other probable mechanisms are the conversion of smectite to illite, tectonic compression, and aqua-thermal pressuring. Graf also noted that strong evidence exists for the formation of brines by membrane concentration of sea water solutes. The evidence includes the similarity of hydrogen isotope values (δD) for pore fluid water and local meteoric water, and the need for large sources of Mg^{++} and Cl^- in basins which seem to be evaporite-free.

This review of the body of knowledge regarding the behavior of geological membranes indicates that ion filtration is not well understood; as mentioned previously, the theory of ion filtration as a mechanism which produces subsurface brines is still controversial. However, equations based on general membrane theory have been applied to geological membranes with some success (e.g., Bredehoeft et al., 1963, Kharaka and Berry, 1973, and Hanshaw and Coplen, 1973).

Studies Related to Isotope Fractionation by Geological Membranes

In the following section, some of the research regarding isotope fractionation, as related to ion filtration, is reviewed. Both field and laboratory studies have been performed.

One of the first field studies of the isotopic composition of subsurface basins was conducted by Clayton et al. (1966). They analyzed δD (δ Deuterium) and $\delta^{18}O$ (δ^{18}Oxygen) for 95 oil-field brines from the Illinois, Michigan and Alberta Basins, and from the Gulf Coast. The δD values for each basin indicated that the brines are not simple marine evaporite deposits, nor could they have originated from a well-mixed oceanic reservoir, even though the rocks appear to be marine. Clayton et al. suggested that the original water was lost by flushing and that present formation water was relatively modern meteoric water.

The processes which might alter the D/H (deuterium/hydrogen) ratios within a basin were presented by Clayton as: climatic variation; isotopic exchange between water and hydrocarbons, hydrogen sulfide, and other minerals; evaporation; and diffusion. Using the same data, Graf et al. (1965) discussed the possibility of isotope fractionation by flow through shale membranes. They predicted that the effluent on the low pressure side should be isotopically lighter. The evidence for isotope fractionation during ion filtration included the prediction of the direction of vertical fluid movement between pairs of nearby sampling points. The direction indicated by isotope values (using an ion filtration model) agreed with the available hydrological data. The authors also proposed that some very high deuterium values might be due to extremely slow flow rates, allowing significant diffusional mixing on the influent side of the shale membrane. These samples were from areas with little ground-water recharge.

Laboratory experimentation resulted from this growing body of field evidence. Coplen and Hanshaw (1973) hypothesized that fractionation of isotopes in ground water by flow through fine, compacted sediments is a common occurence in nature. They performed forced-flow experiments, measuring isotopic differences between influent and effluent reservoirs. Their results were consistent with the model used by Graf (1965) for the interpretation of field data. Distilled water and a 0.01 N (Normal) NaCl solution were forced through Na-montmorillonite plugs, with a compaction pressure of 330 bars (4,800 psi) and a differential hydraulic pressure of 100 bars (1,450 psi). For the distilled water experiments, the effluent was depleted in deuterium and oxygen-18 by 2.5 per mil and 0.8 per mil, respectively. Increasing fractionation with increasing salt concentration was not detected, for NaCl solutions up to 0.01 N.

Clay was used for the experiments because the authors reasoned that, for natural materials, the largest isotope fractionation would occur in fine-grained materials with high ion-exchange capacities. Coplen and Hanshaw stated that this reasoning applies if the mechanisms causing fractionation are adsorption and molecular diffusion, which should be most important in materials of very small particle size. The apparatus used in their work was the same as that used by Hanshaw and Coplen (1973). A model developed by Coplen (1970), based on the Rayleigh distillation equation, was applied to these data and yielded good results. Coplen and Hanshaw concluded that ion filtration is a mechanism which might cause isotope fractionation, due to a hydration sphere effect. They did not observe such an effect, possibly due to the low salt concentration of their solutions. Coplen and Hanshaw state that hydrogen isotope fractionation during salt filtration operates because each of the ions is surrounded by a sphere of water molecules, and that the hydrogen isotope composition varies between coordinated and non-coordinated water. If a solution undergoes salt filtration, coordinated and non-coordinated water could be separated, causing isotope fractionation. Some of the mechanisms believed to be causing fractionation in their experiments were adsorption and molecular diffusion. They acknowledged that the pressure gradient used (270 bars/cm or 3900 psi/cm) was greater than any reasonable field values, and that any isotope fractionation observed in their experiments was probably a minimum effect. Fractionation would become more efficient at lower flow rates if adsorption was the mechanism causing the fractionation.

Benzel and Graf (1984) studied the effect of clay membrane thickness and fabric orientation on the efficiency of ion filtration and oxygen isotope fractionation. The smectite membrane thickness ranged from 0.5 cm to 2.0 cm, and the membranes were compacted under a pressure of 345 bars (5,000 psi). The differential pressure varied from 69 to 138 bars (1,000-2,000 psi), and the solution forced through the clay was 0.79 M in NaCl and 0.079 M in $CaCl_2$. The well-oriented clay cakes (membranes), with porosities of 50% less than those of the random cakes, were twice as efficient at filtering ions. Ion filtration efficiencies for the well-oriented membranes ranged from 50-68%. Membrane thickness seemed to have no effect on filtration efficiency. The oxygen isotope ratios obtained from this study appeared to be independent of the solution concentration, and no relationship between isotope fractionation and clay fabric or cake thickness was observed. The effluent solutions were both enriched and depleted in ^{18}O in these experiments.

Using the same apparatus, Haydon and Graf (1984, in press) investigated the temperature dependence of smectite membrane behavior regarding ion-filtration and oxygen isotope-fractionation efficiencies. Compaction pressures were 3,450-6,900 bars (5,000-10,000 psi), and differential pressure was 1,380 bars (2,000 psi). Temperatures ranged from 20°C to 180°C, and the concentration of the injected brine was 5.0 M in NaCl and 0.45 M in $CaCl_2$. The clay cakes had a random orientation and were one to two centimeters thick. The results indicated that the increased compaction pressure led to a doubling of filtration efficiency for Ca^{++} and increased the filtration efficiency for Na^+ by 60%. Increasing the temperature in these experiments also increased the efficiencies observed. The authors stated that, for the series of tests performed, the results were due to an interaction between changes in viscosity, hydrated radius of the cation, the streaming potential, and compaction pressure. The oxygen isotope ratio increased very slightly in the effluent solution for experiments at 140°C and 180°C, but decreased at 20°C. Increasing temperature caused the effluent to be heavy with respect to oxygen isotopes. Coplen and Hanshaw (1973) also found that ^{16}O is favored at 20°C. It was not possible to determine if this reversal was due to temperature or other effects.

Demir (1984) conducted additional experiments with this apparatus, studying the electrokinetic and chemical aspects of ion filtration. Operating conditions included a compaction pressure of 3,450 bars (5,000psi), a differential pressure of 1,380 bars (2,000 psi), and a temperature of 20°C. A NaCl solution (approximately 1.1 M) and a

$NaCl$-$CaCl_2$ solution (0.92 M in NaCl and 0.075 M in $CaCl_2$) were used in different experiments. The clay plugs were 0.3-0.5 cm thick, with various fabric orientations. Salt filtering efficiencies of 27%-48% were observed, with Na^+ transported preferentially. The change in the oxygen isotope ratio ranged from -0.25 per mil to -0.63 per mil for the effluent.

Phillips and Bentley (1984) noted that isotope fractionation has been observed during ion filtration, but that the mechanisms causing fractionation have not been determined. They stated that the importance of fractionation of stable isotopes during ion filtration is related to their use in groundwater dating, as tracers of subsurface chemistry, and in determining paleoclimatic conditions at the time of recharge. In order to use isotopes (e.g., oxygen, hydrogen, sulfur, or chlorine) for these purposes, the mechanisms fractionating the isotopes must be understood and, if possible, quantified. The authors combined a membrane filtration equation based on Donnan membrane equilibrium and TMS theory (after Hanshaw and Coplen, 1973), the Rayleigh distillation equation, and Staverman's reflection coefficient (as redefined by Marine and Fritz, 1973, using non-equilibrium thermodynamics) to obtain an equation predicting the hydrogen isotope ratio of the residual (influent) solution after ion filtration. The experimental deuterium data of Coplen and Hanshaw (1973) match the values predicted by the model very well. The authors also presented an equation to determine the isotope composition of a chloride solution after forced flow through a typical clay membrane, which predicted that the effluent should be isotopically heavier than the influent solution. The mathematical model will be presented in Chapter 4.

Kaufmann et al. (1984) improved a chlorine isotope ratio measurement procedure which permits the detection of $\delta^{37}Cl$ with a precision of ±0.12 per mil. A number of ground water samples were analyzed, which showed $\delta^{37}Cl$ variations of up to 3.0 per mil with respect to Standard Mean Ocean Chloride (SMOC). Samples from salt deposits and saline geothermal springs were generally enriched in comparison with the standard (seawater). Some ground-water samples were enriched while others were depleted in ^{37}Cl, with respect to SMOC. In general, saline ground water was isotopically heavier with increasing depth in an aquifer, as indicated by oil field brines from Texas and Louisiana. Total chlorine concentration of the brines was highly correlated with the chlorine isotope ratio, within each aquifer. Kaufmann et al. suggested that possible mechanisms for fractionation are precipitation and dissolution of evaporites and diffusion of chloride. They proposed that a counter-current system can exist in an aquifer, causing chlorine fractionation. When water is forced to flow through a clay or shale membrane, two forces are working in opposition: the hydraulic gradient and the concentration gradient (if present) cause ions to approach an electostatic field. The net electrical field, caused by the negative charge on the clay mineral surfaces and by the streaming potential, acts in a direction opposite to that of the hydraulic and concentration gradients. This theory predicts an isotopically lighter solution with increasing distance along the flow path. Desaulier et al. (1984)

showed that chloride in clay pore water becomes enriched in ^{37}Cl with depth, and this distribution can be described by a diffusion equation. The chloride diffused through a glacio-lacustrine clay bed in Ontario, Canada.

Previous Synthetic Membrane Research

After a brief introduction, synthetic membrane studies related to ion filtration and isotope fractionation are reviewed.

Historical developments in the physical chemistry of synthetic membranes are presented in this section. In the 1860's, Traube developed "semipermeable" copper ferrocyanide membranes to measure the osmotic pressure of sucrose solutions. These measurements were later used by Van't Hoff (1887) and Raoult (1884) to derive the classical theory of solutions. Parchment was used in the 1920's in the sugar and dye industries to remove salts and other impurities by dialysis. Karl Sollner, the "dean of American membranologists", made great contributions to membrane research while working with Freundlich on membrane dialysis, electrodialysis and ultrafiltration (Hwang and Kammermeyer, 1975). Sollner studied the electromotive forces involved in synthetic semipermeable membranes, and was highly influenced by Donnan's (1911) famous paper on membrane equilibrium theory. In 1932, Sollner developed a theory of the mechanism of anomalous osmosis (osmosis due to varying sizes of adjacent pores), and verified the theory experimentally with the help of Freundlich, Nernst, and Planck. He was the first to show that an exhaustive quantitative treatment of the electrochemical membrane system is possible. Later, when synthetic perm-selective membranes were developed, his theory was again verified. According to Sollner, Bethe and Toropoff conceived of the basis of today's highly-developed theory of the electrochemistry of porous membranes. This basic concept is the correlation of the electrokinetic charge of the membranes and their electromotive properties, electrolytic permeabilities, and polarization behavior. Sollner summarized the electrical interactions during ion filtration as follows (from Hwang and Kammermeyer, 1975):

> Those charges (e.g., anionic groups) which are fixed to the pore wall, and which form the immovable part of the electrical double layer at the membrane-matrix-solution interface, cannot participate in the movement of ions across the membrane either by thermal motion (diffusion) or under the influence of an electric current. Their counterions (e.g., cations), however, which are dissociated off into the pore water, are freely movable and can move under the influence of a concentration or potential gradient.

Michaelis (1927) experimented with collodion membranes (the first nitrocellulose membranes, composed of cotton or wood pulp), which were extremely ion-selective. Then Teorell (1935, 1937) and Meyer and Sievers (1936) proposed the fixed-charge theory of ionic membranes, which is the quantified basis of modern electrochemical membrane research.

Sollner (1944) also used collodion membranes to investigate the mechanism of ion restriction. It was known at this time that by impregnating collodion membranes with either proteins or alkaloids, the membrane could be transformed from electronegative (cation-permeable, as are clays and shales) to electropositive (anion-permeable). By examining the ash content of the membranes which behave differently, he found that a higher amount of anionic impurities correlated with improved cation permeability. The impurities were acidic nitrocellulose molecules (carrying carboxyl groups) which are part of the natural cellulose fiber. Sollner's model of these membranes required that the impurities form an essential part of the membrane structure. The charge density of the structural elements (e.g., anionic groups) determine the electrochemical activity of the membrane. Sollner suggested that when an electrolyte solution comes in contact with a cation-permeable membrane, the cations which are originally adsorbed onto the fixed anionic groups are replaced with cations in the solution. He thus concluded that the base-exchange capacity at the pore surfaces of a membrane determines its electrochemical activity.

Ion-Filtration Studies

Extensive theoretical and applied research may be found in the literature, regarding the use of synthetic membranes for various ion-filtration applications, including desalinization, filtering in food industries, biomedical uses, separation of uranium isotopes, water pollution analysis, etc. Some fields of study are membrane filtraton (Brock, 1983; Hwang and Kammermeyer, 1975), ultrafiltration (Cooper, 1979), desalinization (Turbak, 1981; Sourirajan, 1977), ion-exchange membranes (Flett, 1983), and perfluorinated membranes (Eisenberg and Yeager, 1982). The development of mathematical models is much more common in these fields than in geological membrane research. The interested reader is referred to the citations above for various approaches to ion-filtration theory.

Studies Related to Isotope Fractionation by Synthetic Membranes

Aston (1920) was probably the first to use a porous membrane for the purpose of isotope separation. He concentrated neon isotopes by gaseous diffusion through a porous clay tube. Uranium isotopes have been concentrated by gaseous diffusion through porous barriers.

Dressner and Kraus (1962) investigated the possibility of using ion-exchange materials for desalination by reverse osmosis. The theoretical study used a solution of the Poisson-Boltzmann equation for cylindrical micropores and for a regular lattice of charged rods. The Boltzmann equation relates spatial charge variations in the ion-exchange material to electrical potential, and the Poisson equation gives the relationship of electrical potential to ionic concentration. The Poisson-Boltzmann equation assumes that: ions are point charges; there is no interaction between ions or selective adsorption of ions by the surface; the solvent is a structureless continuum with a dielectric constant equal to that of the equilibrium solution; and there are no edge effects on the ion-exchange surface. The equation obtained by Dressner and Kraus gives anticipated salt rejection as a function of effective pore radius. Also incorporated in the equations are valence of the ion, temperature, solution density, the local fixed charge distribution, and the dielectric constant of the solution and the ion-exchange material. Dressner and Kraus concluded that porous ion-exchange materials would be useful only for filtering solutions with low original salinity.

A recent investigation of isotope fractionation due to diffusion through semipermeable cellulose membranes was conducted by Thau-Alexandrowicz (1978). He traced the movement of water by performing a series of experiments involving diffusion across membranes of various pore sizes and chemical compositions. Tritium and ^{18}O were used to investigate the structure of water in membrane pores. The diffusion cells consisted of two Plexiglas half-cells which clamped together, and the solutions in both compartments were homogenized by use of magnetic stir bars. The author found that, for large pore sizes (0.8 μm), the self-diffusion ratio of tritium relative to that of ^{18}O (T/O) was nearly equal to that for protium relative to ^{16}O in bulk water. An increase in the self-diffusion ratio with a decrease in pore size was attributed to increased structure at the water-membrane boundary. Calcium chloride, which acts as a structure promoter by causing the formation of a thicker and more rigid double layer, was added to the influent solution in some experiments. The presence of $CaCl_2$ also increased the T/O diffusion ratio, as compared to bulk water self-diffusion coefficients. The results indicated that T/O may present a means to detect changes in the state of water in membranes and solutions, although no conclusion could be drawn on the nature of the changes at that time. It was not possible to test the effect of varying chemical composition of the membrane on the T/O ratio, as no two membranes with the same structure but varying chemistry were available. However, the author expected that the presence of varying functional groups (e.g., carboxyl or sulfonate groups) on the membrane would yield different T/O values.

Summary of Previous Research

This chapter has provided the reader with a summary of research regarding geological and synthetic membranes. After this review, it may be concluded that a variety of interpretations of the mechanisms involved in ion filtration and isotope fractionation with semipermeable membranes exists.

The process of ion filtration seems to be similar in both geological and synthetic membranes, as described below.

> Geological Membranes. Anion exclusion whereby the concentration of the anions in the pore solution is lower than their concentration in the external solution, is responsible for the membrane properties of clays and shales (Kharaka and Berry, 1973);

and

> Synthetic Membranes. When a charged microporous body is in equilibrium with an external electrolyte solution, the co-ions (i,e., ions whose charge has the same sign as that of the fixed charge) are repelled from, and the counter-ions attracted to the membrane surface, setting up an electrical double layer at the membrane-solution interface. In this double layer, the ionic concentrations and the electrical potential are highly non-uniform; in particular, the average co-ion concentration in the microporous solid is less than that in the feed solution (Sourirajan, 1975).

Preferential ion filtration was explained in terms of ion "concentration in the pore solution, electrostatic interactions with clay and electrokinetic effects due to the streaming potential, and moblilty effects" due to convective and diffusive flow (Kharaka and Berry, 1973). This led to selectivity sequences dependent upon the degree of complex formation, ionic charge, and hydrated radii of the dissolved species.

Isotope fractionation by semipermeable membranes may be due to diffusion and electrostatic interactions with clays (Hanshaw and Coplen, 1973). Borrowing from ion-filtration research, additional mechanisms may include electrokinetic, mobility, and concentration effects. Selectivity of isotopes might then be dependent upon: relative mass, ionic charge, and hydrated radii of the two isotopes; the rate of flow of solution through the membrane; the electrostatic charge on the clay; pore size; and the propensity of the isotopes for ion pairing or complexing.

The purpose of the experiments described in the following chapter is to investigate the effect of changes in influent concentration, membrane pore size, electrostatic charge on the membrane, and amount of stirring in the influent reservoir on chlorine isotope fractionation and on chloride filtration. The ionic charges and the hydrated radii of the stable chlorine isotopes are assumed to be identical.

CHAPTER 3

EXPERIMENTAL PROCEDURE AND RESULTS

As mentioned previously, two types of experiments were performed in this study in an effort to produce isotope fractionation in the laboratory. The long-term (five-month) forced-flow experiment and the 16 short-term (one- to three-week) diffusion experiments were designed to aid in the analysis of the mechanisms involved in fractionation.

Forced-Flow Experiment

Equipment

The experimental apparatus is shown in Figure 3. A 0.26 M solution of NaCl was forced through a Na-bentonite plug under a hydraulic pressure of 15.5 bars (225 psi). The injection solution was prepared with four-times-distilled water and NaCl from Fischer Scientific (S-271, Lot 71S162), as were the influent solutions used in all of the experiments. The δ^{37}Cl of the influent solution was measured as 0.04 ± 0.12 per mil, relative to SMOC. The clay plug was prepared with the influent solution so that the clay would be saturated with the same chloride when the test began. The Na-bentonite was obtained from American Colloidal (CS/Granular). The moisture content of the plug was 25%, and the compaction pressure used in plug preparation was 5.9 bars (86 psi), conforming to ASTM Standard D698, 1980.

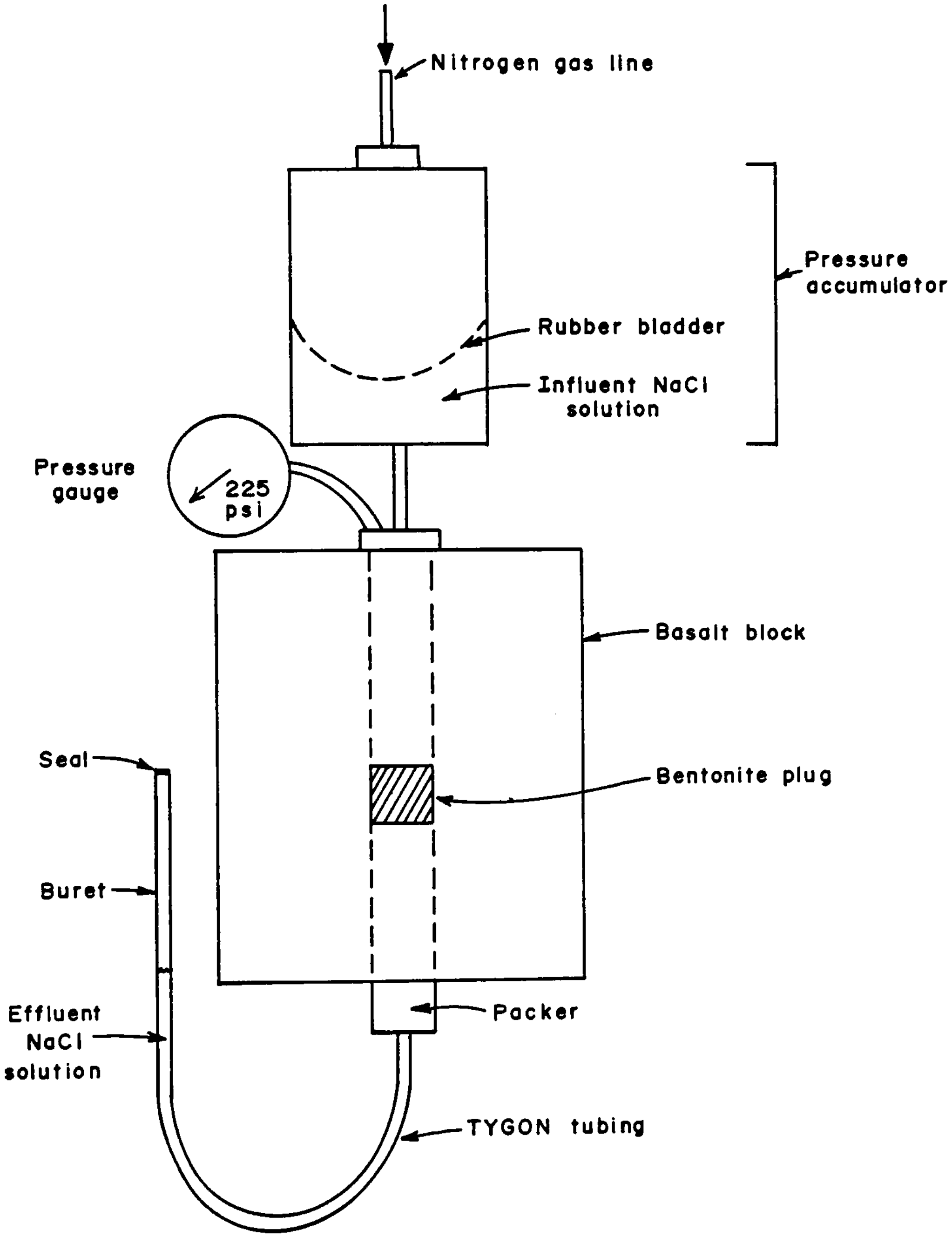


Figure 3. Forced-Flow Apparatus.

The clay plug (2.5 cm in diameter, 2.5 cm in length) was placed in a basalt container which was 15 cm in diameter and 25 cm in length, with a hole (2.5 cm in diameter) drilled through the middle. A packer, which allowed free flow of water, was inserted in the effluent end to hold the clay in place. The packer was attached to tubing leading to a buret, which allowed the flow rate to be measured. The sample collection section was airtight to prevent evaporation. Finally, the apparatus was attached to a pressure accumulator (EMG Accumulators, Inc., Port Huron, MI) which held approximately one liter of injection solution. The influent reservoir was not stirred. A rubber bladder was connected to a nitrogen gas line, which provided the regulated pressure. A flow of approximately 0.4 ml per day was obtained, indicating a tight seal between the clay and the basalt.

Sampling

Samples were collected approximately monthly with a sterile syringe. The samples were analyzed for $\delta^{37}Cl$ by the technique described in a subsequent section of this chapter. Results of isotopic analyses are presented in Table 1.

Diffusion Experiments

The short-term experiments were designed to detect the effect of cation-exchange capacity, pore size, concentration and stirring on the ability of the synthetic membranes to separate ^{37}Cl and ^{35}Cl. The synthetic membranes have several properties in common with compacted clays. They are available with cation-exchange capacities ranging from

Table 1

Forced-Flow Test: Isotope Fractionation Values

Date of Sampling	Time (days)	δ^{37}Cl of Influent Solution* (o/oo) ±0.12	δ^{37}Cl of Effluent Solution (o/oo) ±0.12	$\Delta\delta^{37}$Cl = δ_{EFF} - δ_{INF} (o/oo) ±0.12
5/02/84	29	0.04**	+1.70	+1.66
5/30/84	57	0.04	+1.60	+1.56
6/18/84	76	0.04	+1.51	+1.47
7/23/84	111	0.04	+0.51	+0.47

* Values are given with respect to SMOC.
**Average of 4 values.

zero to approximately 100 milliequivalents per 100 grams (meq/100g), which corresponds to the range found in natural clays. As perm-selective membranes, the selectivity sequence for cations is similar to that for clays. The membranes are a fixed matrix of cation-exchange sites in a stable film form (Cooper, 1979). By adjustments in the ion-exchange groups (carboxylic and sulfonic groups) attached to the basic structure (cellulose nitrate, cellulose acetate, or perfluorinated polymer) of the membrane, various ion-selectivity sequences can be achieved (Flett, 1983). Like clays, these negatively-charged synthetic membranes reject divalent anions more effectively than monovalent anions. Also, like clays, synthetic membrane ion-filtration efficiency increases with decreasing influent concentration, decreasing pore size, and decreasing applied pressure. The membranes are available with pore sizes ranging from approximately 0.015 μm to > 10 μm (micrometers). Haydon (1983) calculated pore diameters for compacted montmorillonite ranging from 6 to 37 Å for a compaction pressure of 5,000 psi, and 6 to 31 Å for a compaction pressure of 10,000 psi ($1Å = 1 \times 10^{-4}$ μm). Due to the similarity in physical properties between the clay and synthetic membranes (pore size and magnitude of cation-exchange capacity), and the similarity of behavior in their ion-filtering properties, the synthetic membranes were used to simulate compacted clay membranes. These membranes allow much better control over pore size and cation-exchange capacity than do natural clay plugs. The synthetic membranes are also much thinner than clay plugs, allowing diffusion to proceed at a faster rate. Other advantages of the synthetics are their durability and the ease of obtaining a tight seal in the diffusion cells using these membranes.

Initially, a synthetic membrane was tested to determine whether diffusion through the membrane could fractionate chlorine. After finding that the clay and synthetic experiments yielded δ^{37}Cl values with the same sign and roughly the same magnitude as the clay, a series of experiments were planned.

Equipment

Influent solutions were prepared as described previously, and 0.2 M or 2.0 M concentrations were used. The influent solutions had a δ^{37}Cl value of 0.04 ± 0.12 per mil. The membranes used are described in Table 2, and more details are provided in Appendix A. Pore size ranged from 0.015 μm to > 10 μm. Figure 4 shows a photomicrograph of three membrane types. Cation-exchange capacity ranged from 0 to 100 milliequivalents per 100 grams (meq/100g).

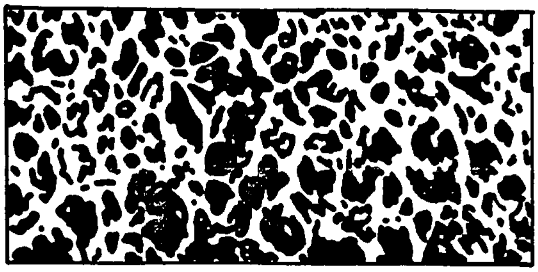
Diffusion cells 1 and 2, illustrated in Figures 5 and 6, respectively, are similar to those used by Thau-Alexandrowicz (1978), with each cell consisting of two Plexiglas half-cells. Cell 1 was designed by the author and cell 2 was designed by Walter (1982). A membrane separated the reservoirs, and clamps and O-rings sealed the apparatus. A sodium chloride solution placed in the lower reservoir was allowed to diffuse across the membrane. Osmotic effects were minimized by partially filling the upper reservoir with an equal molality solution of sodium nitrate.

Table 2

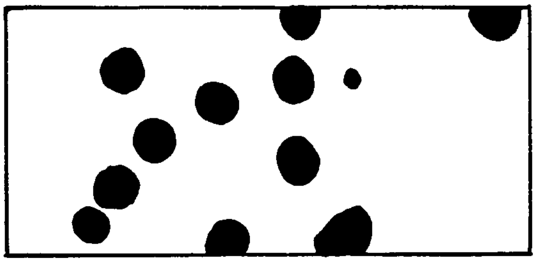
Summary of Synthetic Membrane Properties

Membrane	Approximate* Cation-Exchange Capacity (meq/100g)	Approximate Pore Size (μm)	Description of Chemistry	Supplier
A	10	5-10	cellulose nitrate with carboxy methyl groups	Micro Filtration Systems
B	10	0.5	styrene divinyl benzene with sulfonic acid groups	Gelman Sciences, Inc.
C	0	0.015	polycarbonate	Nucleopore Corp.
D	0	0.40	polycarbonate	Nucleopore Corp.
E	0	0.45	cellulose nitrate	Micro Filtration Systems
F	100	>10	perfluorinated polymer with carboxylic and sulfonic films (Nafion)	E. I. DuPont de Nemours and Co., Inc.

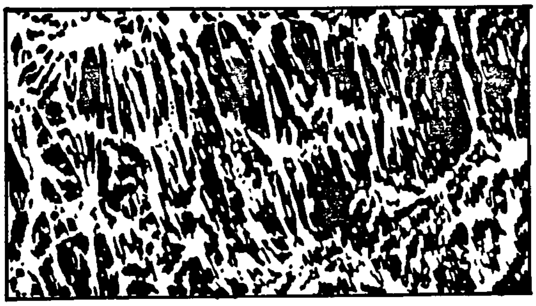
*Cation-exchange capacities and pore sizes are generally listed in the respective catalogues, but technical representatives for the suppliers stated that the values listed are approximate, average values. Estimates of variability in these parameters were not available.



Cellulose Acetate
(x 2500, approximately)



Polycarbonate by Nucleopore
(x 2500, approximately)



Nafion by duPont
(x 1000, pore size 0.5μm)

Figure 4. Examples of Membrane Structure Types.

Sources: Brock (1983) and MFS catalog (1983), scanning electron micrographs.

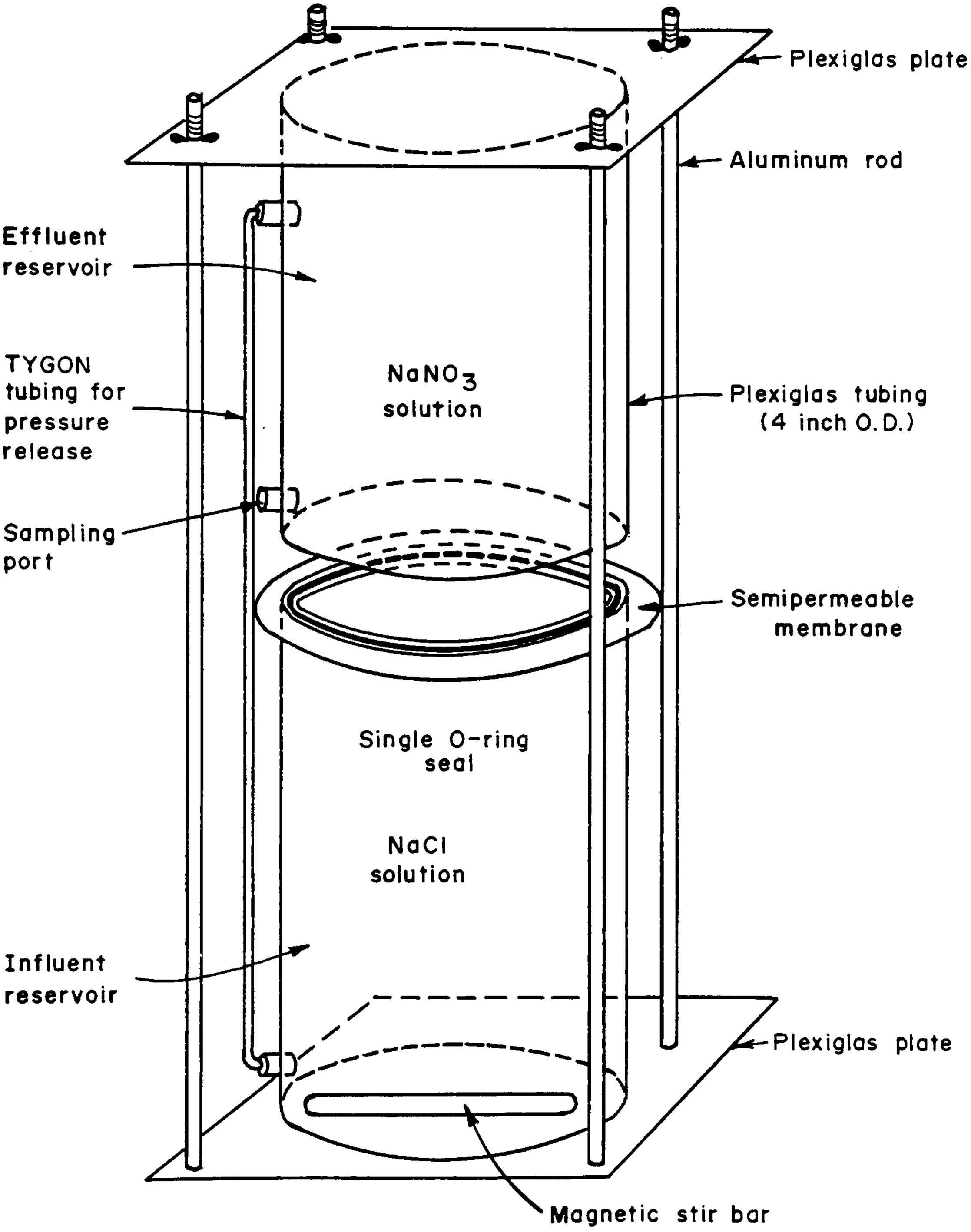


Figure 5. Diffusion Cell 1.

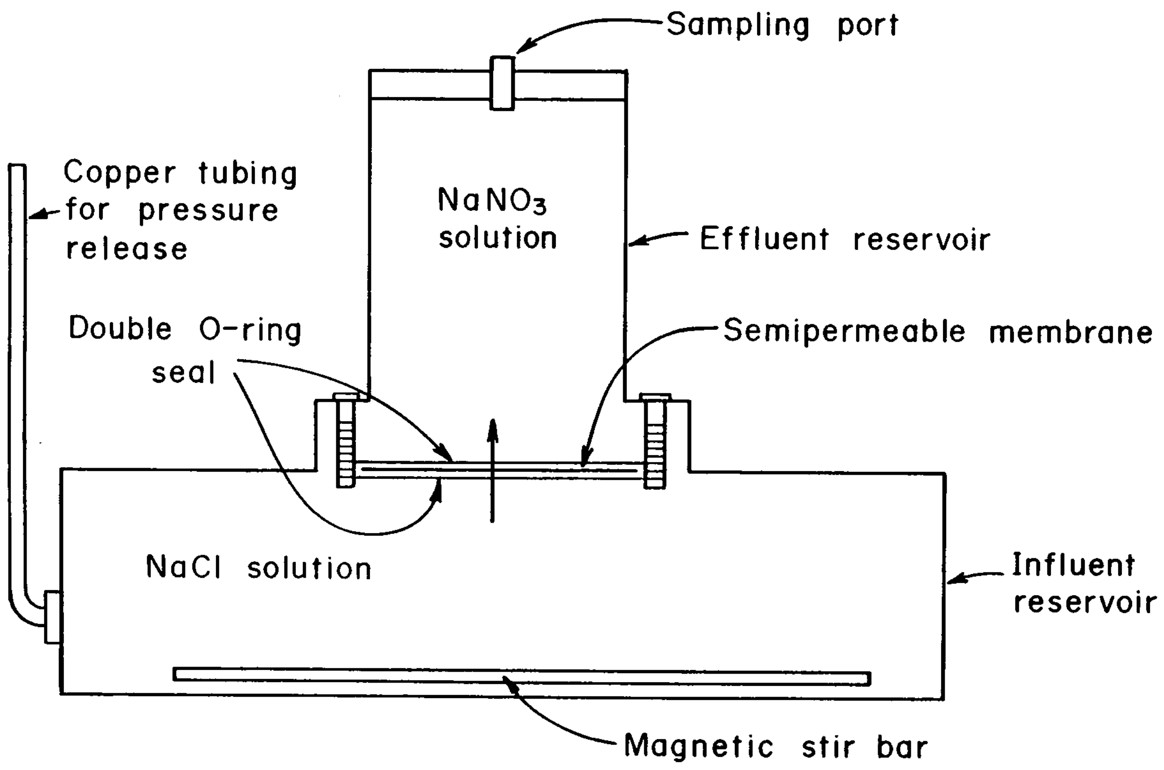


Figure 6. Diffusion Cell 2.

A stir bar in the lower reservoir kept the influent reservoir well-mixed. The cell rested on a stir plate and slow stirring was continuous for the length of the experiment, with short (less than 8-hour) breaks to prevent overheating. The diffusion cell was placed in a constant temperature water bath, maintained at 21 ± 3°C by a Haake brand heater/circulator. This was necessary to eliminate thermal diffusion effects. Thermal diffusion is one method which has been used to separate chlorine isotopes in solution (Rutherford, 1973).

Sampling

Samples were collected from the influent and the effluent reservoirs, after a 9- to 20-day period. This length of time was necessary to obtain enough sample (approximately 15 mg of NaCl) for isotope analysis. A syringe and tubing were used to draw off the effluent samples, which were placed in Nalgene sample containers. A portion of the original influent solution was saved, and parts of these samples were analyzed in order to determine fractionation values.

Precautions were taken to prevent contamination of samples. Between experiments, the cells were washed well, soaked in a dilute nitric acid bath, and rinsed with four-times-distilled water. All syringes and tubing were treated in a similar manner. Hands were washed well to avoid introducing additional NaCl into the diffusion cells or into the samples to be analyzed.

Description of Specific Experiments

The diffusion cell experiments tested the effect of several factors on the membranes' chlorine isotope fractionation efficiencies. The variables considered were the influent NaCl concentration (0.2 M or 2.0 M), membrane pore size (ranging from 0.015 μm to > 10 μm), the cation-exchange capacity of the membrane (0-100 meq/100g), and stirring. Another purpose of the experiments was to determine if these variables affect ion-filtration efficiency and isotope-fractionation efficiency in the same manner.

Some of the factors which have been shown to affect ion filtration are pore size, concentration of the influent solution, and cation-exchange capacity. The anion exclusion ability of a compacted clay is a direct function of its pore size distribution, if other parameters are held constant (Demir, 1984). Pore size should affect mobility through the membrane due to both electrostatic and electrokinetic interactions between the ion and the clay. Higher concentration tends to decrease ion-filtration efficiency because the membrane contains a higher concentration of cations and anions and hence is less effective at anion exclusion. Concentration also affects the degree of ion pairing. The cation-exchange capacity seems to correlate with the anion-exclusion properties of clays, as cation exchange is one method by which clays obtain negative charges. Membranes of high ion-exchange capacity should theoretically be most effective at salt rejection (Dressner and Kraus, 1963). Stirring was tested to determine if the buildup of structured water next to the membrane slows down diffusion, and to see if homogeneity of the lower reservoir affects the results.

Table 3 summarizes the 16 experiments performed in this study. The pairs of experiments which tested the effect of pore size are 1 and 2, 3 and 4, 5 and 6, 7 and 9, and 8 and 10. Experiments designed to give an indication of the effect of cation-exchange capacity on chlorine isotope fractionation were 4 and 11, 5 and 13, 1 and 12, 1 and 9, and 3 and 10. Tests 1 and 3, 2 and 4, 7 and 8, 9 and 10, and 11 and 12 yielded an indication of the concentration effect. The stirring factor was investigated in pairs 1 and 6, 2 and 5, and 12 and 13. Three repeat experiments (14, 15 and 16) were performed to check the reproducibility of the experimental method.

Sample Analysis

The samples were analyzed by mass spectrometry of methyl chloride ions (CH_3Cl^+), according to the method described by Taylor and Grimsrud (1969). The steps involved are the following:

1) Precipitation of silver chloride. A portion (1 to 10 ml, depending on expected concentration) of the sample was placed in a beaker which had been cleaned with nitric acid. Chloride-free water (four-times-distilled) was added to the beaker to increase volume to 50 ml. The pH was decreased to 2 by addition of dilute nitric acid (prepared with chloride-free water). The ionic strength of the solution was adjusted to approximately 0.4 by addition of 50 ml of 0.8 M potassium nitrate (prepared with chloride-free water). The solution was heated nearly to its boiling point, and an excess of 0.1 M $AgNO_3$

Table 3

Diffusion Tests: Isotope Fractionation Values

Experiment Number	Time (days)	Concentration (moles/l)	Negative Charge (meq/100g)	Pore Size (μm)	Stirring*	Cell #	$\Delta\delta^{37}Cl = \delta_{EFF} - \delta_{INF}$ (per mil, W.R.T. SMOC) **
1	16	0.2	10	0.5	*	2	+0.21 ± 0.12
							+0.25 ± 0.12
							+0.23 ± 0.12 avg
2	20	0.2	10	5-10	+	1	+0.22 ± 0.12
3	14	2.0	10	0.5	+	2	+0.84 ± 0.12
							+0.86 ± 0.12
							+0.85 ± 0.12 avg
4	14	2.0	10	5-10	+	1	+0.05 ± 0.12
5	13	0.2	10	5-10	-	1	+0.05 ± 0.12
6	13	0.2	10	0.5	-	2	+0.01 ± 0.12
7	9	0.2	0	0.015	+	1	+0.36 ± 0.12
8	11	2.0	0	0.015	+	2	+0.58 ± 0.12
9	16	0.2	0	0.4	+	1	+1.36 ± 0.20
							+1.16 ± 0.12
							+1.26 ± 0.20 avg
10	18	2.0	0	0.45	+	2	+0.66 ± 0.12
							+0.32 ± 0.12
							+0.49 ± 0.12 avg
11	10	2.0	100	>10	+	2	+1.22 ± 0.12
12	11	0.2	100	>10	+	1	+0.94 ± 0.12
13	10	0.2	100	>10	-	1	+1.14 ± 0.20
14†	10	2.0	0	0.015	+	2	+0.76 ± 0.20
15†	16	2.0	10	5-10	+	1	+1.06 ± 0.20
16†	16	0.2	10	5-10	-	2	+0.60 ± 0.12

* A + indicates stirring, a - indicates no stirring.

**δ_{INF} = 0.04 ± 0.12 $^{o}/oo$ and is the average of four determinations of $\delta^{37}Cl$ for influent solutions (+0.11, +0.03, +0.00, and +0.03).

† Repeat experiment. 14 is a duplicate of 8, 15 a duplicate of 4, and 16 a duplicate of 5.

was added to precipitate all the chloride as AgCl. The precipitate was then filtered on Millipore 0.45 μm filters and dried in the oven at 80°C for 12 hours.

2) Reaction of AgCl with methyl iodide. The AgCl was scraped from the filter paper, and placed in sample containers. Care was taken to clean the scraping tool and hands between samples. The precipitate was powdered and the homogenized, 50 mg sample was placed in a Pyrex reaction vessel, which led to a vacuum line. An excess of methyl iodide (CH_3I) was distilled into the reaction vessel and frozen onto the AgCl by immersing the lower part of the vessel into liquid nitrogen. The vessel was then evacuated of all gas, cut with a propane-oxygen torch, and sealed. It was then placed in an oven at 100°C for 48 hours. In the oven, AgCl reacted with CH_3I to produce AgI and CH_3Cl (methyl chloride).

3) Transfer. The reaction vessel was again attached to a vacuum line, and a steel bellows was used to break the tube. The gas was then frozen into a vessel designed to attach to the gas chromatograph.

4) Separation of CH_3Cl from CH_3I. The CH_3Cl and excess CH_3I were swept from the vessel into a preparative gas chromatograph (Hewlett Packard No. 775). Conditions included a five-foot column packed with Poropak Q, a temperature of 100°C, and a helium flow rate of 100 ml/min. The CH_3Cl emerged within three minutes. The temperature was then increased to 120°C and the CH_3I emerged after eight minutes. Yields were occasionally measured to ensure that all the chlorine was recovered.

5) Transfer. The gas was transferred on the vacuum line to a vessel compatible with the mass spectrometer (V G Micromass 602C).

6) Measurement of $\delta^{37}Cl$ (Taken from Kaufmann, 1984). The mass spectrometer measured the isotope ratio of CH_3Cl gas (CH_3-$^{37}Cl^+$/ CH_3-$^{35}Cl^+$). During sample measurements, the collector slit width masked all but the m/e = 52 peak for the minor beam and m/e = 51 + 50 peaks for the major beam. In calculating isotope ratios, the 50 and 52 peaks are of interest. Variation in the 51 peak does not affect the measurement results significantly, as determined by monitoring the 51/(50 + 49) ratio. The mass spectrometer compared sample and reference gases to a precision of 0.03 per mil. Results are calculated as the per mil difference in the ratio of the sample gas (x) from a commercially produced reference gas (r) with the following equation:

$$\delta_{x-r} = \left[\frac{(52/50+51)x - (52/50+51)r}{(52/50+51)r} - 1 \right] x\ 1000$$

The mean isotope difference of the standard (Standard Mean Ocean Chloride) from the reference gas is +2.82 per mil with a standard deviation of ± 0.06. Results with respect to SMOC are calculated with the following equation:

$$\delta_{x-smoc} = \delta_{x-r} + \delta_{r-smoc} + \frac{(\delta_{r-smoc})(\delta_{x-r})}{1000}$$

The total analytical standard deviation, determined from more than 20 replicates of the laboratory standard NaCl over a one-year period, is ±

0.12 per mil; this deviation is used as the precision for the measurement technique. Variations of $^{13}C/^{12}C$ and D/H are minimized by using the same batch of methyl iodide and repeated standardization. Fragmentation patterns should be the same for equally pure sample and reference methyl chloride on a given day's run, and have not been found to vary significantly with filament changes. Frequent monitoring of the constancy of the 51/(49+50) difference between reference and sample ensures the validity of the data.

Results

Forced-Flow Experiment

The amount of ^{37}Cl transported preferentially through the clay seems to decrease with time, as indicated in Table 1 and Figure 7. The concentrations of influent and effluent solutions were also measured, by gravimetric analysis after precipitation of AgCl. This parameter was measured in order to determine ion-filtration efficiencies of the membranes and to compare them with isotope-fractionation efficiencies. Ion filtration efficiency (in %) is defined as $(M_t - M_m/M_t) \times 100\%$, where M_t is the theoretical mass of chloride which would flow through a non-reactive membrane in a given time by convection and diffusion, and M_m is the mass flux of chloride which was measured. Membrane efficiency is a measure of the relative amount of chloride retained in the influent reservoir. Calculations and results are given in Table 4.

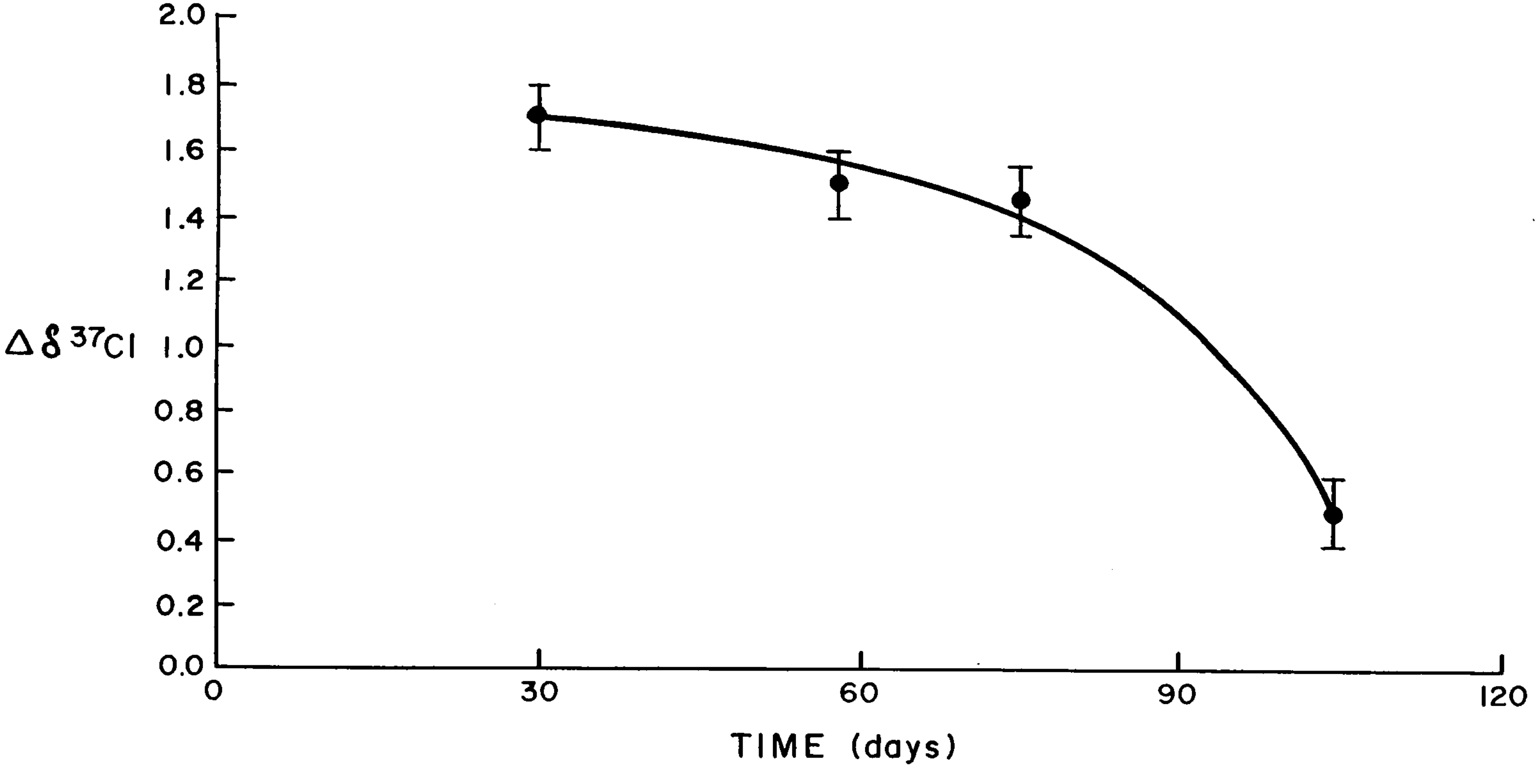


Figure 7. $\Delta\delta^{37}Cl$ Values of Effluent from Forced-Flow Experiment.

$\Delta\delta^{37}Cl = \delta^{37}Cl_{EFFLUENT} - \delta^{37}Cl_{INFLUENT}$.

Table 4

Forced-Flow Experiment: Ion-Filtration Efficiency

Date of Sampling	Theoretical Mass of Cl^- in Effluent (mg)	Volume of Effluent (l)	Concentration of Cl^- in Influent (mg/l)	Time (days)	Measured Mass of Cl^- in Effluent (mg)	Ion-Filtration Efficiency(±2%) $= (\frac{M_T - M_M}{M_T}) \times 100\%$
5/02/84	99.3	0.010	9103	29	59.4	40.2
5/30/84	101.5	0.011	9148	28	56.4	44.4
6/18/84	59.4	0.006	9206	19	34.6	41.7
7/23/84	141.1	0.015	9239	35	80.2	43.2

Theoretical mass was calculated using the following equation (Freeze and Cherry, 1979):

$$\frac{M_T/V_E}{M_I/V_I} = \frac{1}{2}\left[\operatorname{erfc}\left(\frac{x-\bar{v}t}{2\sqrt{Dt}}\right) + \exp\left(\frac{\bar{v}x}{D}\right)\operatorname{erfc}\left(\frac{x+\bar{v}t}{2\sqrt{Dt}}\right)\right]$$

where M_T = mass of chloride in effluent (theoretical)
M_M = mass of chloride in effluent (measured)
V_E = volume of effluent
M_I = mass of chloride in influent (measured)
V_I = volume of influent

$x = 2.5$ cm
$\bar{v} = Q/nA = 0.40$ cm/day $= 4.57 \times 10^{-6}$ cm/sec
t = time (in seconds)
$D = 1.484 \times 10^{-5}$ cm^2/sec (Weast, 1970)

Diffusion Experiments

Isotope analyses were presented in Table 3. The concentrations of influent and effluent solutions were also measured for these experiments and ion-filtration efficiencies are given in Table 5. Efficiency is defined as in the previous section, but in this case the theoretical mass is that which is predicted by the following solution of the diffusion equation (Crank, 1976):

$$C(x,t) = C_0[\mathrm{erfc}\,\frac{x}{2\sqrt{Dt}}]$$

Terms in the equation are defined in Tables 4 and 5. Results of all experiments are discussed in the following chapter.

Table 5

Diffusion Experiments: Ion-Filtration Efficiency

Experiment	Theoretical Mass of Cl^- in Effluent (mg)	Volume of Effluent (l)	Concentration of Cl^- in Influent (mg/l)		Time (days)	Diffusion Coefficient (x 10^{-5} cm^2/sec)	X (cm)	Measured Mass of Cl^- in Effluent (mg)	Ion-Filtration Efficiency (±2%) $= (\frac{M_T - M_M}{M_T}) \times 100\%$
			M^*	A^{**}					
1	190	0.027	6,904	7,039	16	1.483	0.01	265	0.0(leakage)
2	1,318	0.191	6,904	7,039	20	1.483	0.01	937	28.9
3	1,726	0.025	69,040	70,390	14	1.484	0.01	1,408	18.4
4	13,118	0.190	69,040	70,390	14	1.484	0.01	8,706	33.6
5	1,408	0.200		7,039	13	1.483	0.01	1,232	12.5
6	186	0.028	6,758	7,039	13	1.483	0.01	153	17.9
7	1,263	0.183	6,904	7,039	9	1.483	0.01	1,064	15.8
8	1,864	0.027	69,040	70,390	11	1.484	0.01	1,625	14.5
9	1,584	0.225		7,039	16	1.483	0.01	1,130	28.7
10	1,161	0.017		70,390	18	1.484	0.01	1,033	11.0
11	1,535	0.022		70,390	10	1.484	0.04	341	77.8
12	1,711	0.243		7,039	11	1.483	0.04	235	86.3
13	1,936	0.275		7,039	10	1.483	0.04	1,321	31.8
14	2,252	0.032		70,390	10	1.484	0.01	1,981	12.0
15	14,080	0.200		70,390	16	1.484	0.01	9,774	30.6
16	204	0.029		7,039	16	1.483	0.01	180	11.8

* M is measured concentration.
**A is assumed concentration.

Theoretical mass was calculated using the following equation: $\frac{M_T}{V_E}(x,t) = \frac{M_I}{V_I}\left[\mathrm{erfc}\left(\frac{x}{2\sqrt{Dt}}\right)\right]$

where x = thickness of membrane (estimated), D = diffusion coefficient of chloride (Weast, 1970), and other variables are as defined in Table 4.

CHAPTER 4

INTERPRETATION OF RESULTS

General Trends

Forced-Flow Experiment

The amount of isotope fractionation decreased with time. One possible explanation is a Rayleigh-type process; as the $^{37}Cl/^{35}Cl$ ratio in the influent reservoir decreases, the $^{37}Cl/^{35}Cl$ ratio of the chloride passing through should also decrease. This would apply only if the influent reservoir was not well-mixed. In fact, the "infinite" reservoir (0.75 l capacity) fed a stream of solution through a thin tube, and there was no stirring or circulation of the solution next to the membrane. The $^{37}Cl/^{35}Cl$ ratio in the solution next to the membrane could have changed during the 5-month experiment.

Ion-filtration efficiency appears to remain constant with time. Ion-filtration theory predicts that as influent concentration increases with time, ion-filtration efficiency should decrease. However, the chloride concentration of the influent reservoir changed from approximately 9100 mg/l to 9340 mg/l during the 5-month experiment (see Appendix B). This increase of only 3% might not be large enough to affect ion-infiltration efficiency. Values of ion-filtration efficiency and isotope fractionation with time are given in Figure 8. With so few data and with the uncertainties in the chloride and isotope

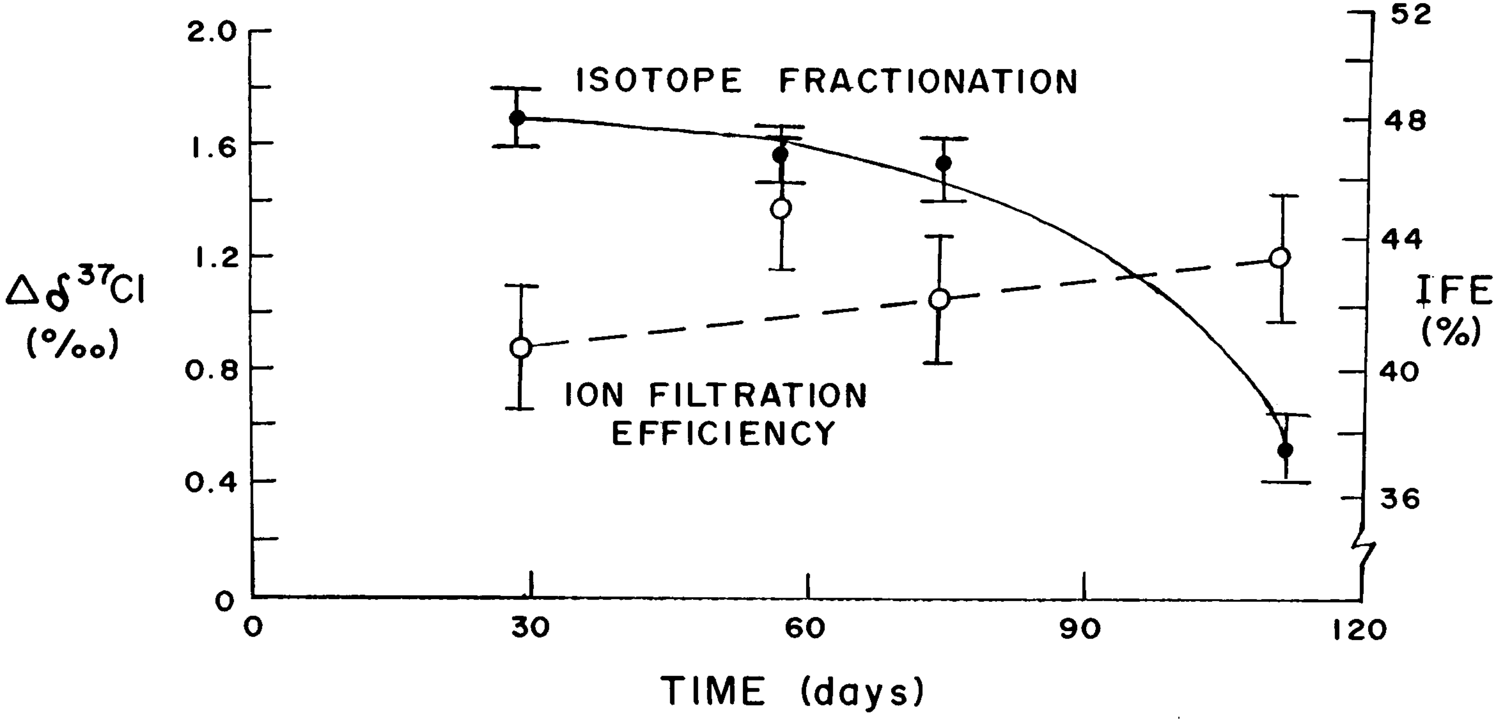


Figure 8. Ion-Filtration Efficiency (IFE) and Isotope Fractionation with Time: Forced-Flow Experiment.

measurements, no correlation between isotope fractionation and ion-filtration efficiency can be shown.

Diffusion Experiments

Pore Size. The results of experiments performed to test isotope fractionation dependency on pore size are plotted in Figure 9. The number of the experiment is printed near each point. Pore size, in the range tested, appears to have no consistent effect on isotope fractionation. Results from experiments 15 and 16 were substituted for the results from experiments 4 and 5. Leakage was suspected in experiments 4 and 5, so they were run again, and the second set of experiments (15 and 16) produced fractionation while experiments 4 and 5 did not. The membrane used in experiments 4, 5, 15 and 16 has relatively large pores and therefore high permeability. Any movement (bumping) of the apparatus during the experiments could have caused flow from the lower to upper reservoir. Experiments 6 and 16 are identical to experiments 1 and 2, respectively, except that the former were not stirred.

Next, the ion-filtration efficiency versus pore size is plotted for each pair of experiments, in Figure 10. Theory predicts an increase in ion-filtration efficiency with a decrease in pore size. The slope of the line varies from slightly positive to slightly negative, within the error of measurement of ion-filtraton efficiencies (approximately ± 2%). From these data I conclude that no consistent relationship between pore size and ion-filtration efficiency is observed. Experiment 1 shows the effect of leakage or a large error in concentration measurement, because the ion-filtration efficiency was

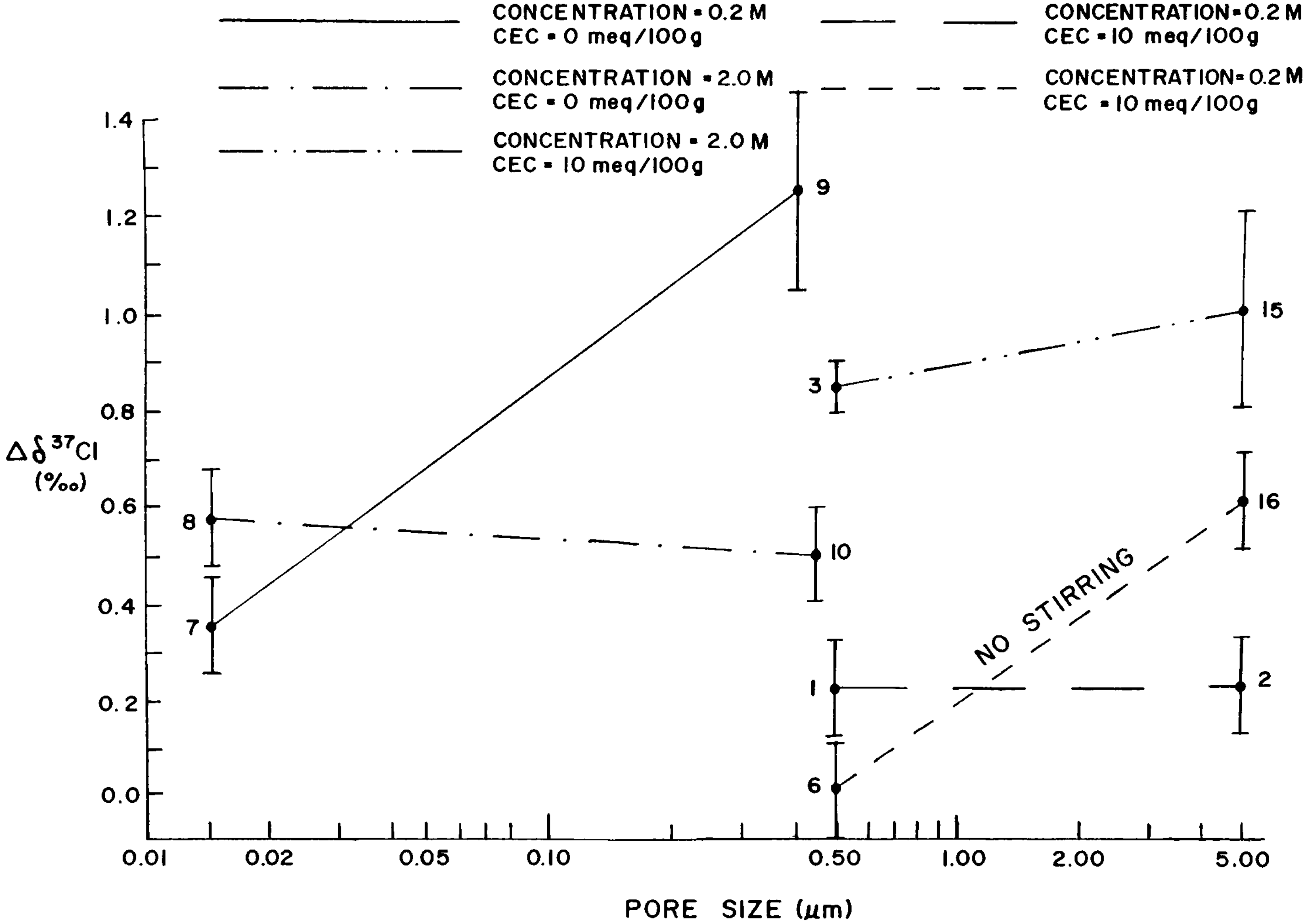


Figure 9. Effect of Pore Size on $\Delta\delta^{37}Cl$.

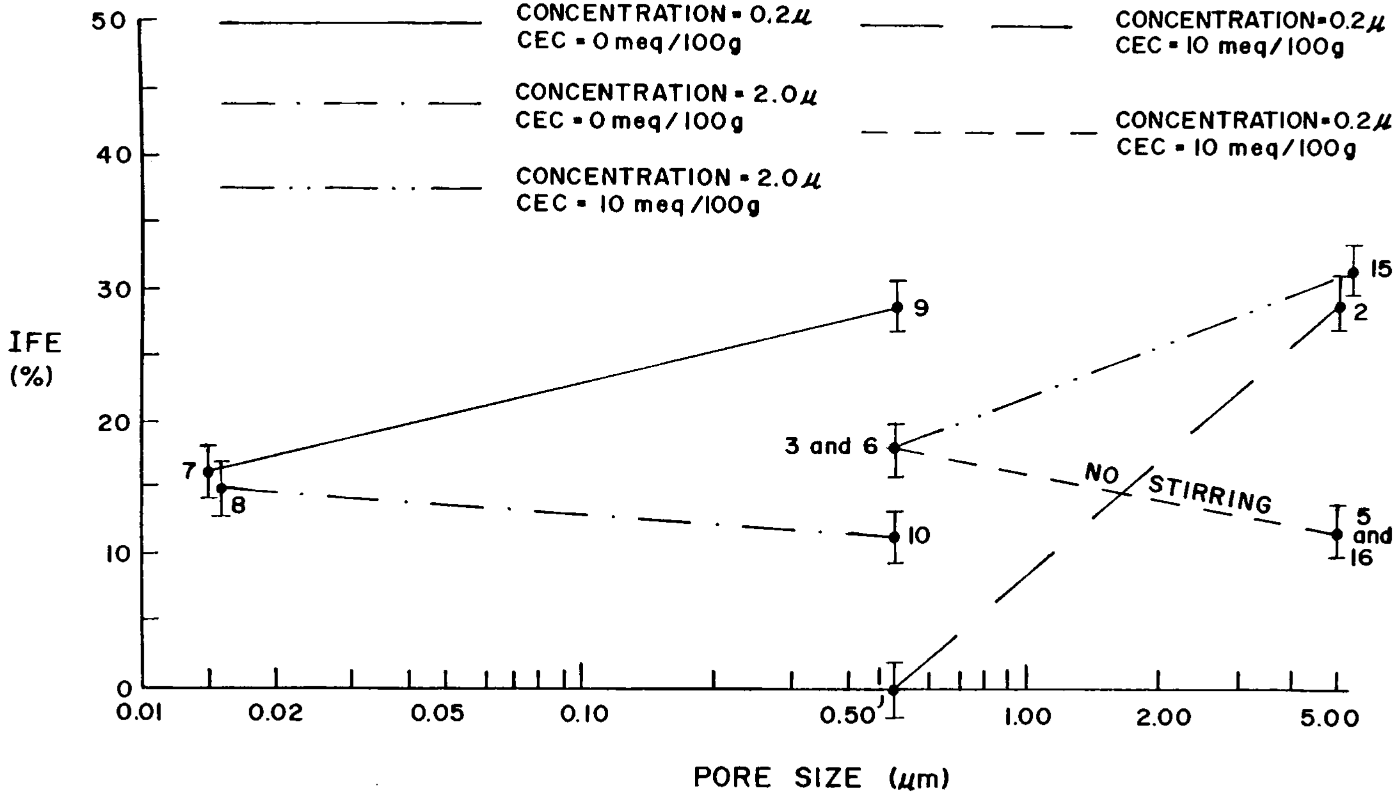


Figure 10. Effect of Pore Size on Ion-Filtration Efficiency (IFE).

0%. No relationship between ion-filtration efficiency and isotope-fractionation is apparent from a comparison of Figure 9 with Figure 10.

The pore sizes may have been too large to cause an effect in the experiments. As mentioned in Chapter 3, the smallest pore size (0.015 µm) of the membranes used was about one order of magnitude larger than the pore size of a compacted clay.

Cation-Exchange Capacity. Figure 11 presents the cation-exchange capacity versus δ^{37}Cl plots for the relevant experiments. Recall that results from experiment 1 are suspected to be incorrect. A positive correlation may exist between cation-exchange capacity and isotope fractionation. However, due to the scarcity of data, no statistical analysis is possible. Cation-exchange capacity appears to have a greater effect on the δ^{37}Cl value than any of the other variables in the experiments. After drawing this conclusion, it may seem unusual that a membrane with a cation-exchange capacity of zero would cause isotope fractionation (e.g., experiments 9 and 10). The membranes used in these experiments, like most microporous cellulose nitrate, cellulose acetate, or polycarbonate filters, carries an electrostatic charge. The magnitude of the charge, when the membrane is in contact with an electrolyte solution, could not be estimated by the manufacturers. These "neutral" membranes are used to separate electrolytes, and are capable of ion filtration without being cation-exchange membranes. It therefore seems reasonable that the membranes could also cause chlorine isotope fractionation.

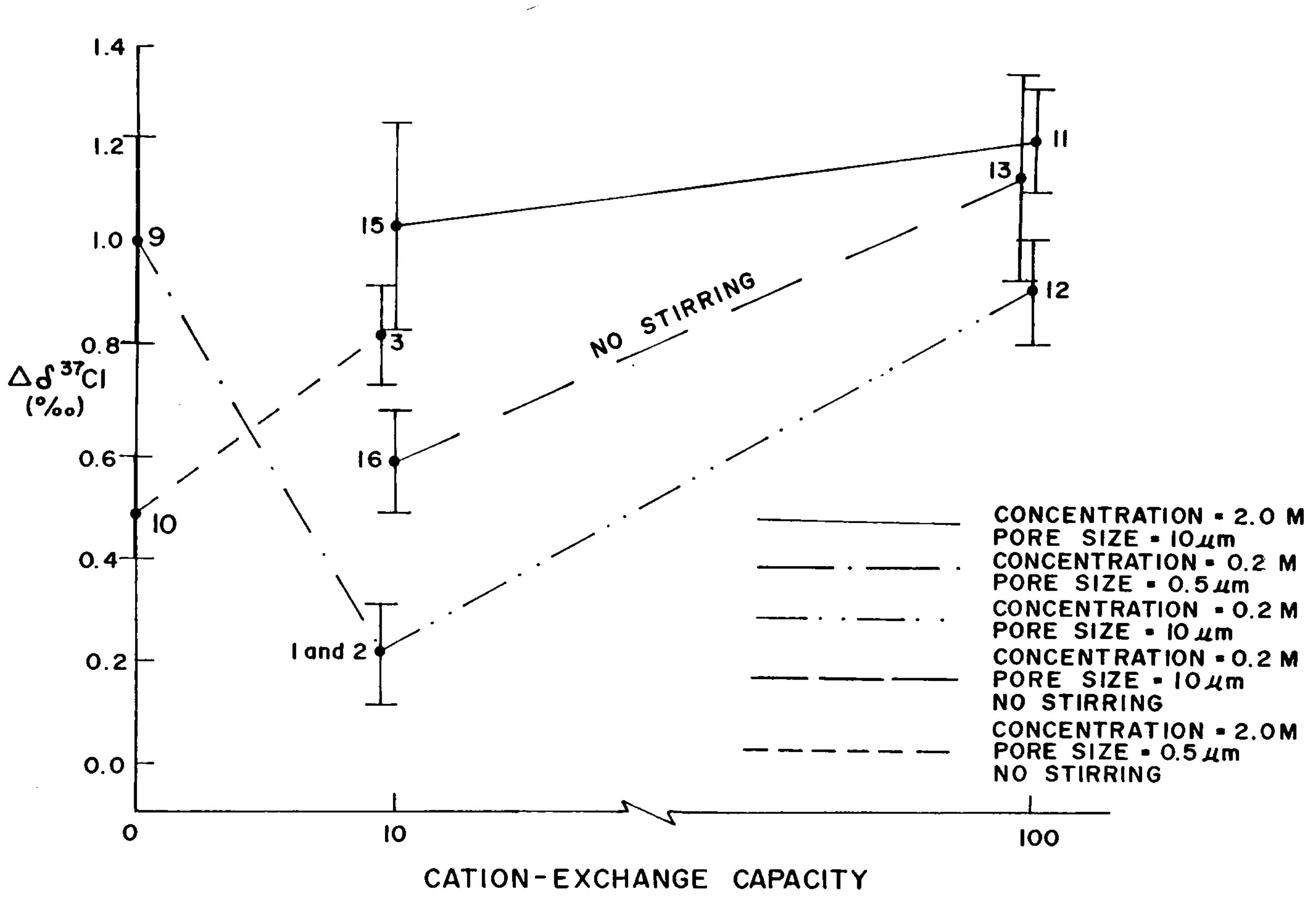


Figure 11. Effect of Cation-Exchange Capacity on $\Delta\delta^{37}Cl$.

Figure 12 illustrates the relationship between ion-filtration efficiency and cation-exchange capacity. Again, experiment 1 results are in error. A positive correlation seems to be in evidence, which would be predicted by ion-filtration theory (e.g., Marine and Fritz, 1981). A graph of $\delta^{37}Cl$ versus ion-filtration efficiency (IFE) for these experiments is shown in Figure 13, and reveals a positive linear relationship between isotope fractionation and ion-filtration efficiency. The experiment number and the corresponding cation-exchange capacity are printed near each data point.

Concentration. An increase in concentration causes both increasing and decreasing isotope fractionation, for the concentration range of 0.2 to 2.0 molar (Figure 14). Recall that results from experiment 1 are suspected to be incorrect. Experimental pair 7/8 shows no fractionation within the precision of measurement (± 0.12).

Ion-filtration efficiency versus concentration is given in Figure 15. A flat or slightly negative slope is illustrated (neglecting experiment 1 results). Diffusion and ion-filtration theory predict a negative slope. No consistent correlation between ion-filtration efficiency and isotope fractionation can be seen in Figure 16.

Stirring. Investigation of the effects of stirring was a peripheral part of the project; however, stirring may decrease isotope fractionation in one set of experiments (16/2), as seen in Figure 17. The other sets of experiments show no effect within the measurement precision of ± 0.12 per mil. One possible effect of stirring is that

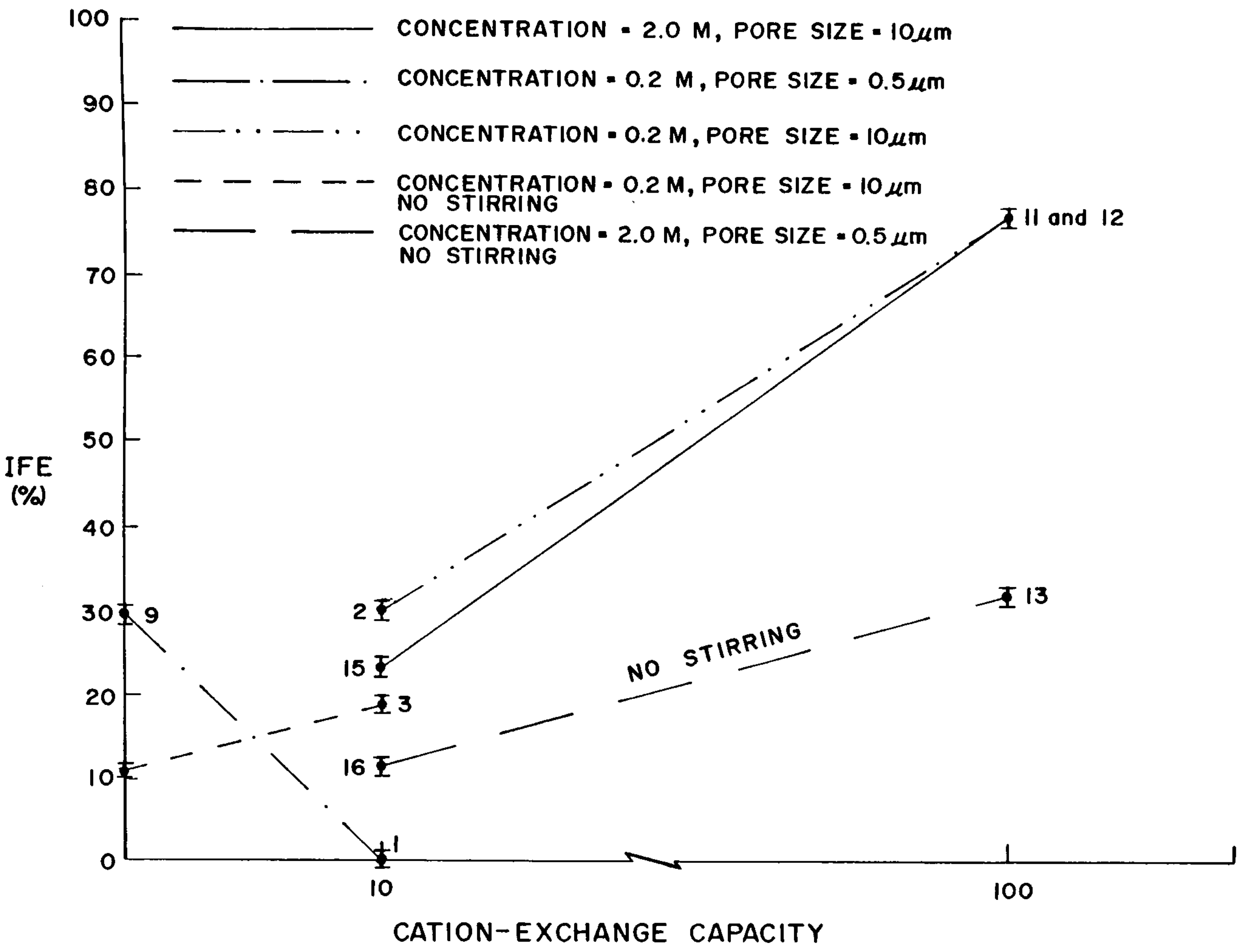


Figure 12. Effect of Cation Exchange Capacity on Ion-Filtration Efficiency (IFE).

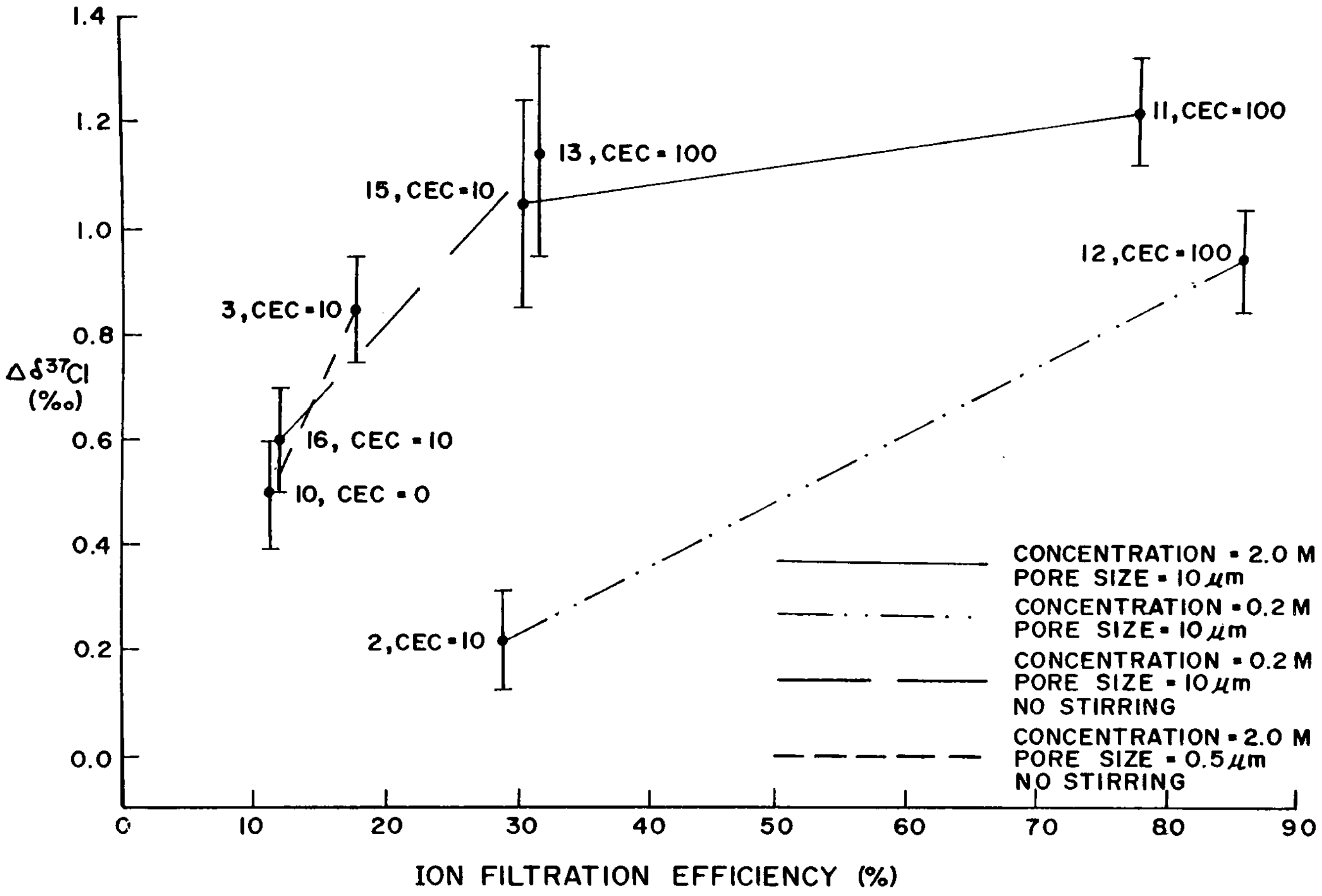


Figure 13. Ion-Filtration Efficiency vs. Isotope Fractionation with Variable Cation Exchange Capacity (CEC).

CEC is given in meq/100 g. Each point has an experiment number and CEC value printed next to it. Precision for ion filtration efficiency is ±2%.

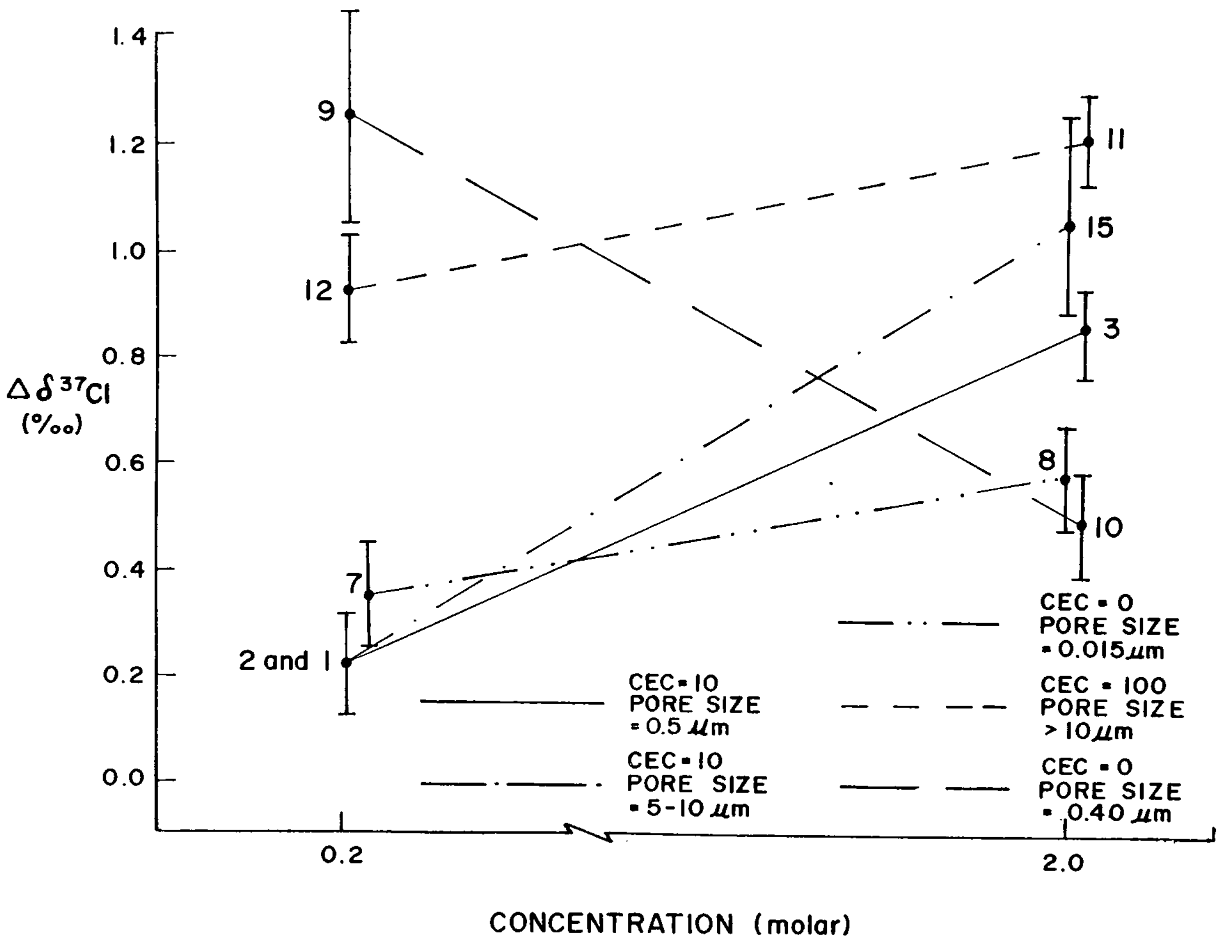


Figure 14. Effect of Concentration on $\Delta\delta^{37}Cl$.

Cation-exchange capacity (CEC) is expressed in meq/100 g.

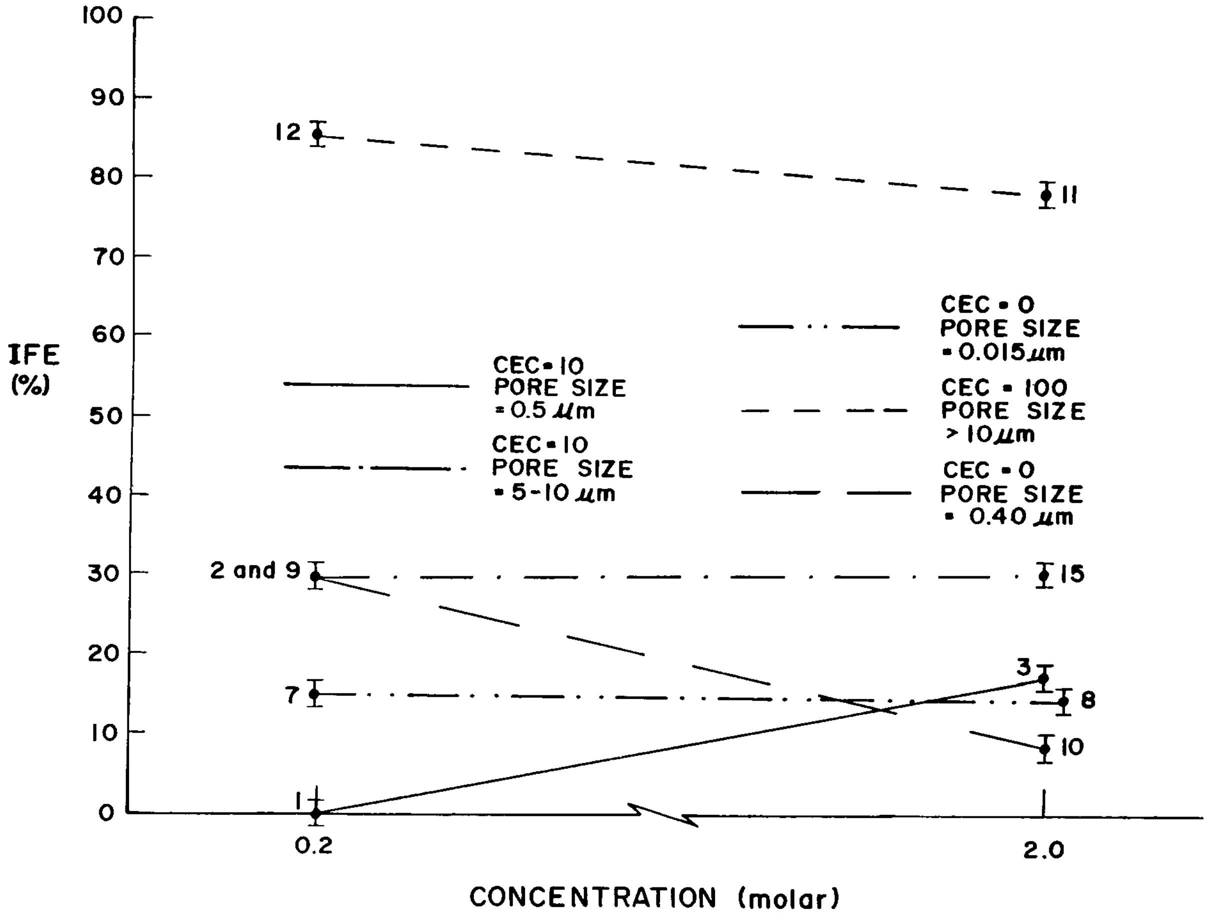


Figure 15. Effect of Concentration on Ion-Filtration Efficiency (IFE).

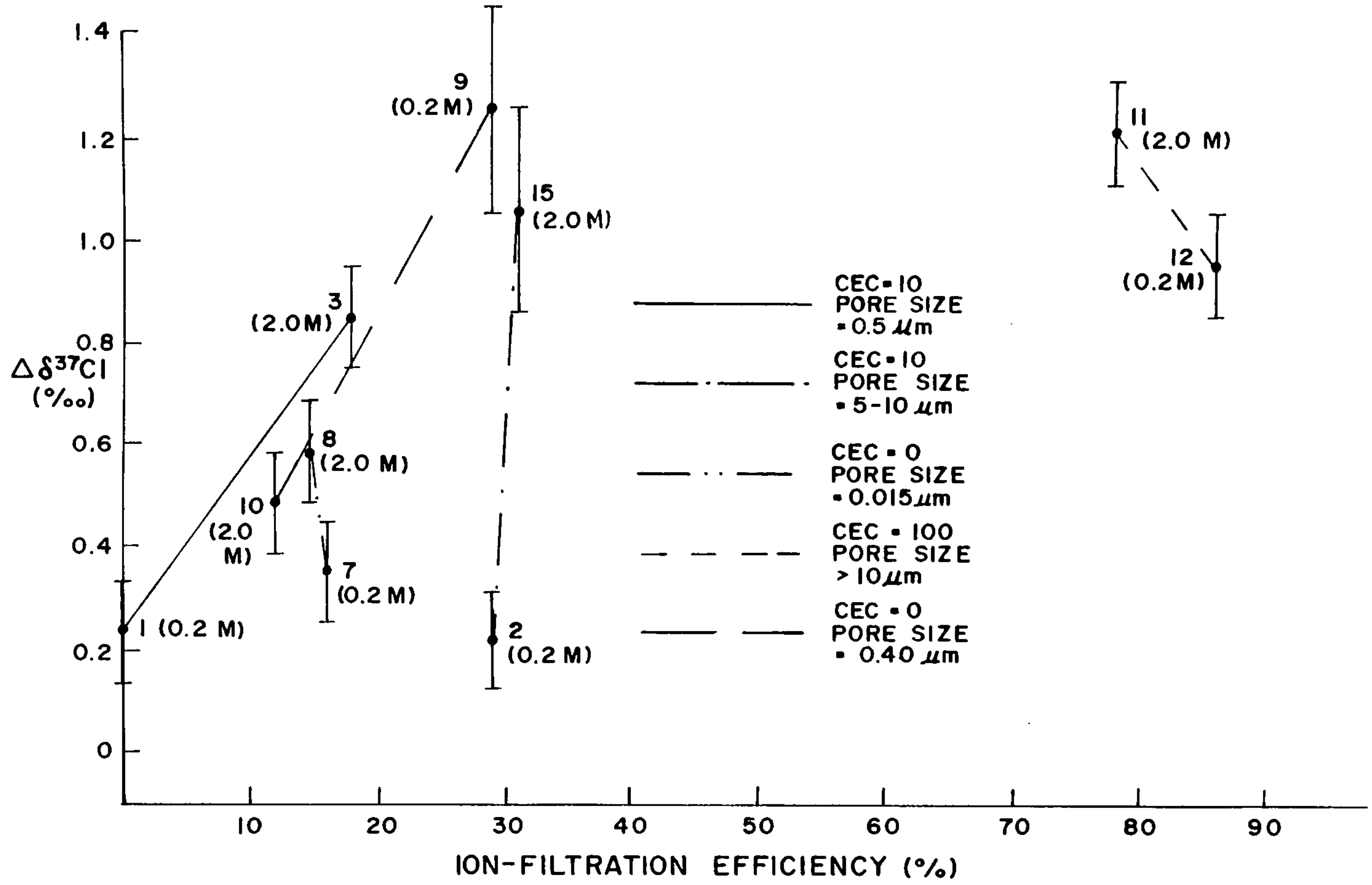


Figure 16. Ion-Filtration Efficiency vs. Isotope Fractionation with Variable Concentration.

Precision for ion filtration efficiency is ±2%.

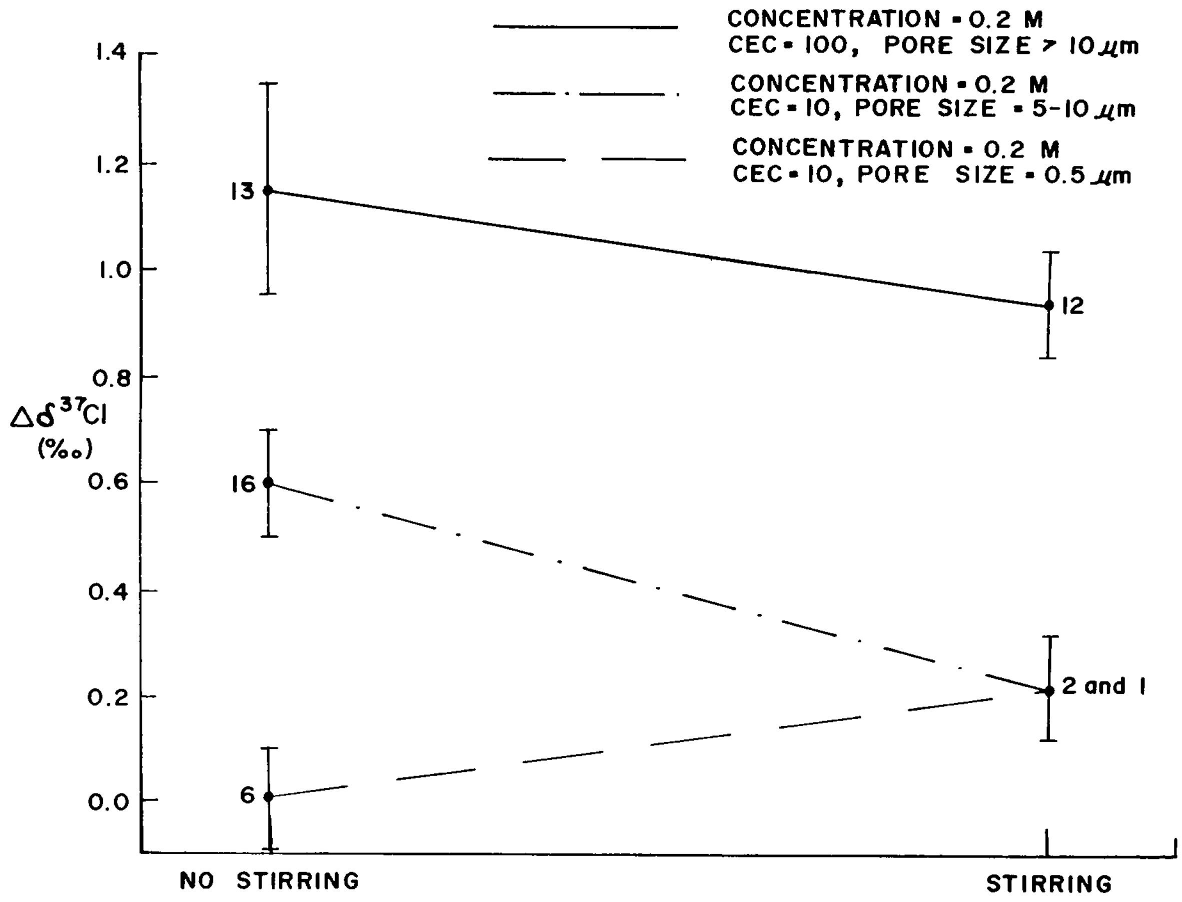


Figure 17. Effect of Stirring on $\Delta\delta^{37}Cl$.

Cation-exchange capacity (CEC) is given in meq/100 g.

in an unstirred solution, the chlorine isotope ratio may become more negative in the influent reservoir next to the membrane, as the heavier isotope passes through preferentially. Then the lighter isotope would have a relatively higher concentration next to the membrane than the heavier isotope, and the lighter isotope would therefore be more likely to pass through the membrane. With stirring, fresh solution should continually pass by the membrane, depletion of the heavier chloride would not occur, and fractionation of the chlorine isotopes would increase. Stirring might also affect fractionation by partially destroying the structured water next to the membrane. Stirring seems to slightly decrease fractionation in the large-pore experiment, which could occur if stirring causes convective flow across the membrane.

Error may be introduced by stirring in two ways. First, if the speed and duration of stirring are not identical in all experiments, fractionation results could be affected. Uniformity was attempted for all experiments. Secondly, if stirring was too vigorous it could cause convective flow across the membrane. However, the measured flux of chloride across the membrane was smaller than that expected for diffusive flow without a membrane present, so it seems likely that the stirring did not induce convective flow.

Ion-filtration efficiency increased with stirring, as predicted by ion-filtration theory (Figure 18). The results shown in Figure 19 indicate no consistent correlation between ion-filtration efficiency and isotope fractionation for this parameter. The ion-filtration

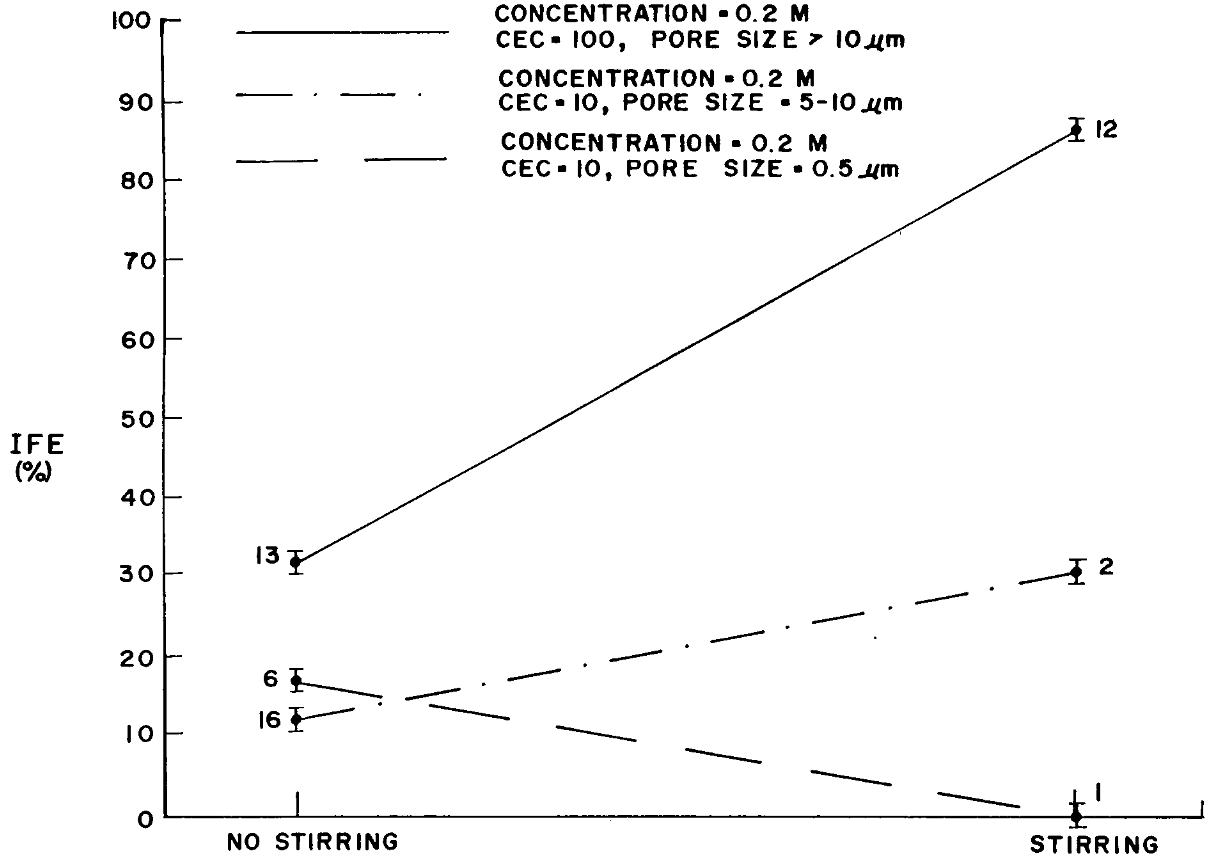


Figure 18. Effect of Stirring on Ion-Filtration Efficiency (IFE).

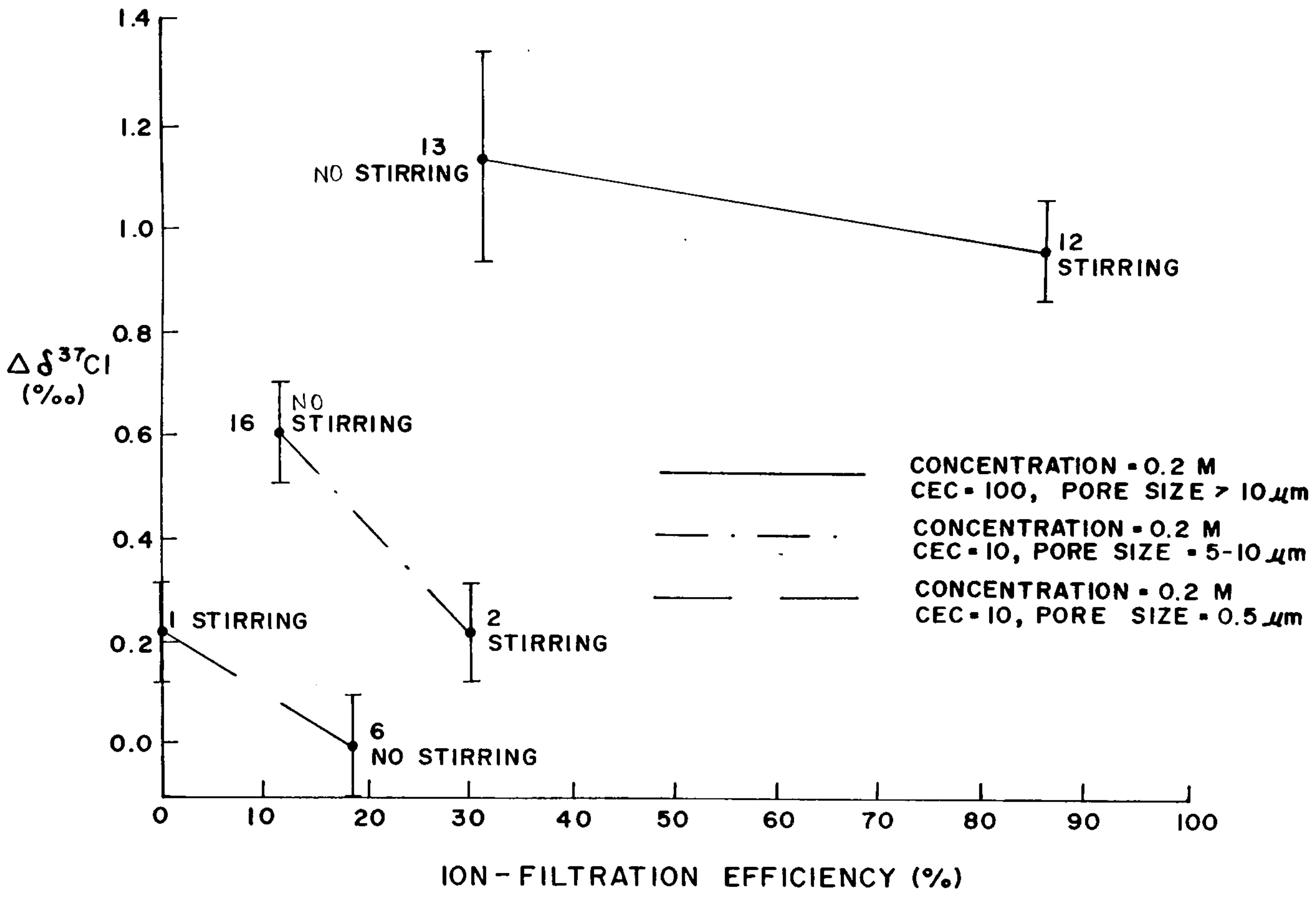


Figure 19. Ion-Filtration Efficiency vs. Isotope Fractionation with Variable Stirring.

efficiency for experiment 1 is believed to be incorrect, as mentioned previously.

Conceptual Models

Four different conceptual models were considered in trying to understand the membrane-electrolyte system. In general, the models are not mutually exclusive. A combination of the mechanisms described in the various models (e.g., adsorption and diffusion) is probably responsible for the observed behavior.

Adsorption

This model assumes that some type of preferential adsorption or anion exchange is responsible for isotope fractionation in the experiments. Because most clays have a much higher cation-exchange capacity than anion-exchange capacity (a ratio of approximately 10 to 1), anion-exchange or adsorption is not a likely mechanism. However, Coplen and Hanshaw (1973) stated that fractionation of hydrogen and oxygen isotopes during flow through semipermeable membranes was due to adsorption. For this reason, adsorption was considered a possible (though unlikely) mechanism for chlorine fractionation in the experiments. The $^{37}Cl^-$ could be preferentially adsorbed onto the membrane surface, thus allowing it to diffuse through the membrane faster due to easier access to the surface. Another idea is that $^{35}Cl^-$ is preferentially adsorbed within the membrane, allowing the $^{37}Cl^-$ to flow through faster.

In order to test this hypothesis, I performed adsorption tests on the clay and Nafion membranes (Appendix B) using a technique described by Mokady and Low (1966). The results indicated that adsorption did not influence isotope fractionation.

Simple Diffusion

Diffusion of chlorine isotopes in a counter-current system has been used as a separation technique (Madorsky and Strauss, 1947). When planning experiments which might fractionate chlorine isotopes, it seemed reasonable to predict that the lighter isotope would diffuse preferentially through the membranes, due to its lighter mass and corresponding higher mobility. This did not prove to be the case, so this hypothesis was rejected.

Back Diffusion

This model was proposed by Phillips and Bentley (1984), and involves the following physical system: as $^{35}Cl^-$ and $^{37}Cl^-$ flow toward a negatively-charged surface, they experience a force of repulsion due to the electrical field at the surface. The slightly greater mass allows the heavier isotope to reach a closer approach to the surface relative to the lighter isotope, due to the greater inertia of the heavier isotope. Conversely, the lighter isotope is more mobile and can diffuse away from the negatively-charged surface more effectively. Back diffusion leads to a higher concentration of $^{37}Cl^-$ in the vicinity of the membrane surface than in the bulk influent solution; the

$^{37}Cl/^{35}Cl$ ratio in the effluent solution reflects this increase in $^{37}Cl^-$ concentration.

Ion Pairing

The hypothesis of ion pairing was conceived of during the course of experimentation (Long and Kaufmann, 1984), although White (1965) and Berry (1969) stated that dissociation phenomena are probably the most important mechanisms determining species passage rates through shale membranes. The model predicts that $^{37}Cl^-$ forms the uncharged ion pair $Na^{37}Cl^o$ more readily than $^{35}Cl^-$ forms the pair $Na^{35}Cl^o$. If the zero point energy for a $Na^{37}Cl^o$ bond is lower than that for a $Na^{35}Cl^o$ bond, the heavier isotope would be more stable as a $NaCl^o$ ion pair. The heavy pair would flow through the negatively-charged membrane more efficiently than $^{35}Cl^-$ ions and more often than $Na^{35}Cl^o$.

The importance of ion pairing in flow of electrolytes through membranes was described by Cussler (1984). "Imagine that a 1-1 electrolyte is diffusing from one aqueous solution across a membrane into another. If the dielectric constant of the membrane is low, any diffusing ions will tend to associate, forming ion pairs of no net charge." The flux then varies with the square of the concentration difference across the membrane. When the concentrations of the solutions are low, the solute will be ionic, but when C_0 is zero and the other solution is highly concentrated, ion pairs will be paramount and flux will vary with the square of the concentration.

In order to estimate the chlorine isotope ratio of a $NaCl^o$ ion pair, the following assumptions must be made. Assume that ion pairing alone is responsible for the observed fractionation. Suppose that the heavy pair forms preferentially and that the two pairs pass through the membrane in an identical manner, and also assume that the $^{37}Cl^-$ and $^{35}Cl^-$ behave identically in their passage through the charged barrier. The reaction responsible for the fractionation can then be written as:

$$Na^{35}Cl^o + {}^{37}Cl^- = Na^{37}Cl^o + {}^{35}Cl^-$$

and

$$\alpha = K_{eq} = \frac{[Na^{37}Cl^o]\ [^{35}Cl^-]}{[Na^{35}Cl^o]\ [^{37}Cl^-]}$$

or

$$\alpha = \frac{(37/35)NaCl^o}{(37/35)Cl^-}$$

To determine the fractionation expected in the $NaCl^o$ ion pair, values must be substituted for α and $(37/35)Cl^-$. For the clay experiment performed in this study, α is approximately 1.0015. According to Johnson and Pytkowicz (1978), the amount of free chloride in sea water (with an ionic strength of 0.72 M and a pH of 8.1) is 83.2%, and the amount of NaCl pairs is 11.5%. If about 80% of the chloride is free, and the $^{37}Cl/^{35}Cl$ ratio for the influent solution is 0.3240 (sea water ratio), then the value of $(37/35)Cl^-$ will be very near 0.3240. The isotope ratio in the $NaCl^o$ ion pair would then be:

$$(37/35)NaCl^o = (0.3240) \times (1.0015) = 0.3245$$

If preferential ion pairing is the mechanism causing fractionation, then the value of (37/35)$NaCl^0$ would have to be larger than 0.3245, because some of the dissociated chlorine probably does cross the membrane. The fractionation due to ion pairing would be partially cancelled by the passage of free chloride (with a ratio of $^{37}Cl/^{35}Cl$ = 0.3240) into the effluent side.

To test the ion pairing explanation for chlorine isotope fractionation, laboratory tests might be performed to see if chlorine has an affinity for preferential pairing of one of the isotopes. Direct laboratory measurement of chlorine isotope fractionation during ion pairing is probably not currently possible.

Discussion of Mathematical Models

Forced-Flow Experiment

The results of the forced-flow experiment were shown in Figure 5. In order to find an appropriate mathematical model to describe the system, it is useful to review pertinent reverse-osmosis theory.

Reverse osmosis is the process of pressurized flow of a solution through a semipermeable membrane. The effluent is enriched in one or more constituents and a high concentration of other constituents is left on the influent side. The mechanism of reverse osmosis is not fully understood, and the parameters controlling the rate, selectivity, etc., are a topic of debate (Sourirajan, 1977). Sourirajan, who developed the first membranes used in industrial desalination, summarized the following theoretical approaches to reverse-osmosis theory. These approaches were developed for neutral membranes, not for ion-exchange membranes.

1. Preferential sorption/capillary flow. This theory postulates that reverse osmosis is governed by membrane surface phenomena. It assumes that the membrane surface is microporous and heterogeneous, and states that the chemical nature of the surface, and the number and size of pores control reverse osmosis. There is no necessary correlation between the size of the critical pore diameter and sizes of solute and solvent molecules. Separation is due both to pore size and membrane chemistry, so the pore diameter may be several times larger than the solute molecules and the molecules can still be filtered. "The magnitude of solute and solvent flux is determined by the magnitude of preferential adsorption, effective thickness of the membrane, the size, number and distribution of pores on the membrane, and operating pressure, temperature and flow conditions" (Sourirajan, 1977).

One application of this theory is the equation developed by Glueckauf (1965). He used the approach that ions are repelled when they are near a material of low dielectric constant, while water is preferentially adsorbed. The dielectric constant is a measure of the amount of induced electric dipole moment of the molecules in a substance, due to the presence of an external electrical field. Water has a very high dielectric constant compared to that of synthetic membrane materials. The equation expresses ion repulsion during reverse osmosis as a function of pore radius, ionic radius, ionic charge, solution concentration, and dielectric constants of the solution in the pore and of the membrane material.

Another application of the basic preferential sorption/capillary flow theory was developed by Bean (1972). He looked at diffusion through pores and the electrostatic force causing ions to avoid regions of low dielectric constant. He developed an equation describing solute separation as a function of dielectric constants of the membrane and pore solution, pore radius, viscosity of pore solution, diffusivity of the solute in water, ionic charge, and operating temperature and pressure. Both the Glueckauf and Bean equations predict that solute separation increases as dissociation of the solute increases.

2. Solution-Diffusion Mechanism. Lonsdale (1970) assumes that the membrane surface is non-porous and homogeneous (i.e., a "perfect" membrane), and that the solute and solvent dissolve in the membrane and permeate through it.

3. Partition Coefficient Approach. Anderson and Heyde (1973) model reverse osmosis by defining the partition coefficient of the solute between water and cellulose acetate.

4. Free Energy Approach. Eisenman (1962) used the relative free energy of interaction between water and membrane sites to explain the selectivity of membranes with respect to different ions. Matsura et al. (1975) developed a variable, the free energy parameter for ions, which was related to the solute transport parameter as determined by reverse osmosis experiments. The parameter describes the free energy change involved in the repulsion of ions at the membrane interface.

Variables in the equation are the valence, electronic charge, and crystallographic radius of the ion, and the dielectric constant of the solvent.

The mathematical models described above apply to neutral membranes. When the membrane surface has a fixed charge (as do clay and synthetic cation-exchange membranes), additional separation is expected (Sourirajan, 1977). Some of the charged-membrane models are those proposed by Kemper and Maasland (1964) and Dressner and Kraus (1962), and were briefly described in Chapter 2.

All of the approaches described above have one thing in common: none has a parameter which can be used sucessfully to describe isotope flow for either the forced-flow or diffusion experiments performed in this study. Gluekauf uses ionic radius as a variable, but the difference in the ionic radii of the two isotopes is so small that his model predicts no separation by reverse osmosis. Bean's model incorporates diffusivity, but his equation predicts no fractionation when used with the forced-flow and diffusion test results from this study. The equation is not sensitive enough to diffusivity of the two isotopes, as the diffusion coefficients are so similar. Lonsdale's "perfect" membrane, which is non-porous and homogeneous, has little in common with the membranes used in this study. The free energy approach is interesting, but is not developed for isotope application. For both the free energy and the partition coefficient approaches, numerous careful experiments would have to be performed in order to obtain thermodynamic and adsorption data.

Biophysical Models. Ion transport through membranes is of great concern in biophysical research, and isotopes are used as tracers in flow across biological membranes. However, it appears that isotopes have generally been assumed to behave identically in flow through membranes, in order to simplify the models (Tosteson, 1978). Stochastic transport of ions through membranes (Mackey, 1975 and Frehland, 1982) can be described using a variety of mathematical models. One of the simplest is Teorell-Meyer-Sievers theory, described in the next section.

Phillips-Bentley Model. A mathematical model that attempts to describe the variable flow of isotopes through membranes is proposed by Phillips and Bentley (1984). Their theory incorporates five concepts: Donnan membrane equilibrium, the Teorell-Meyer-Siever theory, Staverman's reflection coefficient, the Rayleigh equation, and non-equilibrium thermodynamics. These concepts are described below.

1) Donnan membrane equilibrium. This relationship requires that the product of ion activities in the solutions outside the membrane equals the product of ion activities in the membrane pore solution. Assuming concentrations are equal to activities (true only at infinite dilution),

$$C_s^2 = C_c C_a = \frac{\overline{C}_c \overline{C}_a}{n^2}$$

where C_s = concentration of solute in the membrane

C_c = concentration of cations in the external solution

C_a = concentration of anions in the external solution

$\overline{C}_c$ = concentration of cations in membrane pores

$\overline{C}_a$ = concentration of anions in membrane pores

n = porosity of the membrane

The equation above is required by Donnan (also called Gibbs-Donnan) equilibrium. For details on the thermodynamically-derived Donnan potential arising at the interface of a membrane and electrolyte solution, see Schultz (1980) or a physical chemistry text.

2) <u>Teorell-Meyer-Siever theory</u>. The Teorell-Meyer-Siever theory is a model for the diffusion potential across a charged membrane, and it incorporates Donnan equilibrium equations. As expressed by Hanshaw (1962), for a univalent salt,

$$C_s = \overline{C}_a = -1/2\ x + 1/2\ (x^2 + 4C_s{}^2n^2)^{1/2}$$

where x = total fixed negative charge on clay per kilogram of pore solution (eq/kg), and other variables are as defined in the previous equation. The equation states that charges are balanced within the membrane.

3) <u>Staverman's reflection coefficient</u>. Staverman (1952) defined this term as:

$$\sigma = \frac{\Delta P}{\Delta \pi}$$

where ΔP = measured osmotic pressure across the membrane, and

$\Delta\pi$ = the theoretical osmotic pressure across the membrane.

The term sigma is zero at equilibrium, when net flux is zero. Sigma is non-zero for non-ideal membranes. This term is a measure of the membrane's ability to discriminate between the solute and solvent.

4) Non-equilibrium thermodynamics. Phillips and Bentley used the equations derived by Katchalsky and Curran (1965) and Marine and Fritz (1981). The equations state that the thermodynamic forces acting on a membrane are counterbalanced by the sum of the mechanical frictional forces (R_i) acting on the solution components within the membrane. Incorporating the reflection coefficient into the thermodynamic framework,

$$\sigma = 1 - \frac{(R_w + 1)\dfrac{\bar{C}_a}{C_a}}{\left[[R_w[\dfrac{\bar{C}_a}{\bar{C}_c}] + 1] + R_{wm}[R_m[\dfrac{\bar{C}_a}{\bar{C}_c}] + 1] \right] n}$$

where R_w = ratio of friction coefficients between cation and the water to that between the anion and water (= 1.63)

R_{wm} = ratio of friction coefficients between the anion and the membrane to that between the anion and water. R_{wm} ranges from 0 to 1 depending on the degree of compaction of the membrane.

For low concentrations, this reduces to:

$$\sigma \cong 1 - \left[\frac{(R_w+1)m}{nx(R_{wm}+1)} \right]$$

where m = chloride concentration in influent solution after filtration.

5) Rayleigh equation. Isotope fractionation can be modeled by means of the Rayleigh distillation equation:

$$\frac{dN_2}{dN_1} = \alpha \frac{X_1}{X_2}$$

where N_1 and N_2 are the number of atoms of two isotopic species, X_1 and X_2 are their mole fractions, and α is the isotope fractionation factor. Use of this equation assumes that the isotope reaction is carried out in such a way that the products are isolated from the reactants immediately after formation.

Phillips-Bentley Equation. For anions in a membrane filtration system, isotope fractionation in the residual reservoir (per mil) is given as (Phillips and Bentley, 1984):

$$\delta_r - \delta_o = 10^3 \left\{ \left(\frac{m}{m_o}\right)^{\frac{U_h - U_L}{U_L}} - 1 \right\}$$

where δ_r = $\delta^{37}Cl$ after filtration (influent reservoir)

δ_o = $\delta^{37}Cl$ before filtration (influent)

m = Cl^- concentration after filtration (influent)

m_o = Cl^- concentration before filtration (influent)

U_h = ionic mobility of heavy isotope

U_L = ionic mobility of light isotope

$\left(\frac{U_h-U_L}{U_L}\right)$ = -0.0017 (Konstantinov and Bakulin, 1965).

The term $[(U_h-U_l)/U_l]$ is equal to α, the fractionation factor for the process. It is interesting that the $\Delta\delta^{36}$Cl value of the first effluent from the clay experiment was +1.70 per mil, which is equal to negative α. This simplified form of the Phillips-Bentley equation holds for M or M_0 between approximately 0.005 Molal and 1 M, for cation exhange capacities between 20 and 100, for a porosity of 40% and R_{wm} = 0.1. The equation was used to determine the expected δ^{37}Cl values of effluent solutions in the clay experiment. Appendix C presents the calculations. Because the equation gives results in terms of the residual influent solution, and my results were obtained from the effluent solution, some transformations were made. The values predicted by the equation agreed fairly well with measured values (Table 6). Although the predicted δ^{37}Cl values do not decrease with time, they are within the correct order of magnitude.

A full derivation of the above equation can be obtained from Phillips and Bentley (1984).

Diffusion Experiments

An equation which correctly predicts the chlorine isotope separation found in the diffusion experiments was not available. According to the results from the experiments, isotope fractionation efficiency

Table 6

Chlorine Isotope Fractionation Predicted by Phillips-Bentley Model: Forced-Flow Experiment

Predicted $\Delta\delta^{37}Cl$ ($^{o}/oo$)	Measured $\Delta\delta^{37}Cl$ (±0.12 $^{o}/oo$)	Date of Sampling	Time (days)
+3.09	+1.66	5/02/84	29
+3.70	+1.56	5/30/84	28
+3.09	+1.47	6/18/84	19
+3.70	+0.47	7/23/84	35

seems to be directly proportional to cation-exchange capacity of the membrane.

CHAPTER 5

CONCLUSIONS

The experiments have shown that fractionation of chlorine isotopes can be produced in the laboratory, by both diffusive and convective transport through semipermeable membranes, and that isotopically heavy effluent solutions generally result from this flux.

The isotope fractionation results from the laboratory experiments disagree in sign with the few available data from aquifer studies where chlorine fractionation is thought to be due to diffusion (DeSaulniers et al., 1984 and Kaufmann et al., 1985). The laboratory data indicate a positive correlation between cation-exchange capacity and chlorine isotope fractionation. No consistent relationship between pore size, concentration, or stirring and isotope fractionation was observed, within the ranges tested. Ion-filtration efficiency appears to be positively correlated with cation-exchange capacity and stirring.

Ion-filtration efficiency and chlorine isotope fractionation appear to be correlated only with regard to variable cation-exchange capacity in these experiments.

The laboratory tests in this study have a number of limitations. The extrapolation of results of filtration tests on synthetic membranes to clay membranes may not be valid. Also, results from the clay experiment may not apply to the field because conditions of pressure and temperature, concentration gradients, and membrane compaction pressures were not those found in the deep subsurface. A further qualifier on the results is the fact that the analytical procedure is very new, and the technique was modified and improved during the course of the project. The safest conclusions to be drawn are that some trends seem to exist, within the experimental error of ± 0.12 per mil. At least one of the variables tested (cation-exchange capacity) appears to affect fractionation. The few experiments performed obviously do not show which mechanisms are involved in the process of isotope fractionation, but they do offer some evidence suggesting that cation-exchange capacity should be considered an important variable when modeling chlorine isotope fractionation due to flow through membranes.

Two possible mechanisms responsible for chlorine isotope fractionation in the experiments are "back diffusion" and ion pairing. The back diffusion model predicts the clay experiment results reasonably well. The ion pairing hypothesis is theoretically pleasing, but is currently difficult to test.

Improvements in Present Research

If similar studies are attempted in the future, duplicate experiments should be performed for a significant number of the experiments, and two or even three replicate samples should be analyzed for every experiment (reprecipitated each time). This was attempted in my experiments, but was not possible due to restrictions in equipment and time. The analysis is extremely time-consuming and expensive and is presently performed only at the Laboratory of Isotope Geochemistry at the University of Arizona. Repeat experiments were performed for three of the 13 experiments. Results would be statistically meaningful if more experiments could be performed, and the confidence in the precision of the experimental procedure would be increased by performing more duplicate experiments and analyzing more replicate samples.

Further Research

Laboratory Studies

If future field evidence suggests that isotopically heavy effluent solutions result from flow through clay or shale membranes, the following laboratory research ideas are suggested.

Clay Membranes Tests. One obvious choice is to study the diffusion of chloride and other isotopes (S, D, O, T) across clays and to see if isotope fractionation occurs. The sulfate anion might be expected to be subject to "back diffusion" or ion pairing while H and O probably would not. Another interesting possibility is to conduct several forced-flow experiments, simultaneously looking at the response of the isotopes of chlorine, sulfur, oxygen, hydrogen, etc. If several sets of equipment were available, the effect of varying membrane compaction pressures (i.e., pore size) could be tested. A higher compaction pressure would be more realistic in modeling deep subsurface systems. Variations in differential pressure and in temperature could also be tested. Different clays could be used (montmorillonite, kaolinite, and mixtures) to test the effect of varying cation-exchange capacity on isotope fractionation efficiency in clay membranes. Another idea is modification of the influent solution; addition of

Ca^{++} would be a logical choice. This solution could be changed to a multi-component brine, as understanding of the ion-filtration system becomes more sophisticated.

Synthetic Membrane Tests. After working with the synthetic membranes, I found that their chemistry, structure, and behavior are not as well understood or documented as I had hoped. In some cases, details on chemistry and structure are trade secrets and not available. There may be a place for synthetic membrane research with isotopes, however, since these membranes may be simpler to understand and to modify than clay membranes.

If time were available, it would be interesting to run the diffusion tests longer, in order to see if any kinetic effects were observed. Forced-flow experiments could be performed with the synthetics membranes, if the proper apparatus could be found or constructed. This type of experiment (reverse osmosis) would probably model nature more closely than the simple diffusion tests. Membranes with smaller pore sizes (less than 0.015 μm) could be tested if they become available.

Field Studies

The $^{37}Cl/^{35}Cl$ ratio suggests significant possibilities in hydrogeological investigations, as present data suggest that the ratio is altered exclusively by precipitation/dissolution of evaporites, by geothermal activity, by diffusion, and possibly by flow through semi-permeable membranes (Kaufmann, 1984). An interesting field study would be the investigation of a closed basin with well-documented geology and geochemistry. If a number of fairly close, deep wells were available, the variation of $\delta^{37}Cl$ with depth and with chloride content could be measured. This could be done for a homogeneous sandy aquifer, and for an aquifer with one or more clay or shale aquitards (an ion-filtration system). This study could include the measurement of S, D, O, T, and ^{14}C, as well as major ions and other geochemical parameters. The age of the water at various depths could give some information on the degree of mixing in the aquifer, and whether the chloride values are reliable. Sampling would have to be done very carefully, preferably with packed-off intervals. In order to use $\delta^{37}Cl$ as a hydrogeochemical tool, this type of basic study is necessary. A field investigation of this nature might yield information about the validity of membrane filtration as a means of fractionating chlorine isotopes in the field.

One application of the chlorine isotope ratio is determination of brine sources in the subsurface. Anomalous chloride concentrations have often puzzled hydrologists. By using the isotopic signature of chloride, it may be possible to determine whether the chloride is due to trapped sea water, a halite bed, ion filtration, etc. However, basic information regarding chlorine isotope ratios in various substances is not yet available.

Another possible application of the stable chlorine isotope ratio is identification of pollution sources. Chlorine is ubiquitous in many types of wastes (e.g., landfill leachate, organochlorine pesticides, and solvents such as trichloroethylene).

Biomedical Research

Researchers in the biophysical and biomedical fields might be interested in using the stable isotope ratio of chlorine as a tracer for numerous applications (e.g., plant and animal membrane studies). Because chloride is such a mobile and relatively harmless ion, it could prove to be an extremely valuable tool in this field.

APPENDIX A

SYNTHETIC MEMBRANE INFORMATION

Synthetic Membrane Information

Membrane	Ordering Information	Supplier
A	MFS, CM 30 x 30	Micro Filtration Systems 6800 Sierra Court Dublin, CA 94568 (415) 828-6010
B	Gelman, SA6404, #60880	Gelman Sciences, Inc. 600 S. Wagner Road Ann Arbor, Michigan 48106 (800) 521-1520
C	Lot 86A9B25	Nucleopore Corp. 7035 Commerce Circle Pleasanton, CA 94556 (415) 462-2230
D	#119907	Nucleopore Corp.
E	MFS, A04SA090C	Micro Filtration Systems
F	Nafion N-901	E. I. Du Pont de NeMours & Co., Inc. Polymer Products Department Nafion Products Section Wilmington, DE 19898 (800) 441-9494

APPENDIX B

METHODOLOGY AND RESULTS OF ADSORPTION TESTS

Clay Adsorption Test

This procedure is similar to that used by Mokady and Low (1966).

1) Twenty grams of the bentonite used to prepare the clay membrane was combined with 1 liter of 15,000 mg/l NaCl in a beaker. The mixture was stirred continuously for 24 hours.

2) The mixture was centrifuged (13,000 RPM for 15 minutes) and the liquid poured off.

3) The clay was suspended in chloride-free water (4-times-distilled) and stirred for 24 hours. The mixture was then centrifuged and the liquid saved.

4) Steps 2 and 3 were repeated and the second liquid was also saved.

5) Neither of the liquid samples had enough chloride in solution to precipitate AgCl.

Synthetic Membrane Adsorption Test

1) A strip of Nafion cation-exchange membrane (100 meq/100 g) weighing 4.3 grams was first soaked in 5% NaOH for 5 hours. This is a pretreatment step necessary before using the membrane. The membrane was then rinsed gently three times with chloride-free water from a squeeze-bottle.

2) The membrane was placed in a solution of 15,000 mg/l NaCl for 24 hours, with continous stirring.

3) The membrane was rinsed three times with chloride-free water, as in Step 1.

4) Finally, the membrane was placed in chloride-free water for 24 hours with constant stirring, to remove adsorbed chloride.

5) The liquid from Step 4 did not contain enough chloride to precipitate AgCl.

APPENDIX C

CALCULATIONS OF FRACTIONATION PREDICTED BY THE PHILLIPS-BENTLEY MODEL FOR THE FORCED FLOW EXPERIMENT

Fractionation Predicted by Phillips-Bentley Model: Forced Flow Experiment.

Fractionation predicted for the influent solution has been converted to predicted fractionation in the effluent solution in this table.

Calculations	Units	Date of Sampling			
		5/02/84	5/30/84	6/18/84	7/23/84
$\Delta^{37}Cl$ predicted by equation for influent solution $= \delta_R - \delta_{OR} = [\frac{M}{M_o}^{-0.0017} - 1]\ 1000$	o/oo	-8.3831×10^{-3}	-1.0558×10^{-2}	-6.0829×10^{-3}	-1.7755×10^{-2}
M = influent concentration at time of sampling $= \frac{M_o V_o - M_E V_E}{V_o - V_E}$	mg/l	9,149	9,206	9,239	9,336
M_o = influent solution concentration at beginning of test	mg/l	9,103	9,149	9,206	9,239
V_o = volume of influent reservoir	l	0.750	0.740	0.633	0.618
V_E = volume of effluent reservoir	l	0.01	0.011	0.006	0.005
M_E = effluent concentration	mg/l	5,713	5,246	5,770	5,347
A = mass of total chloride in effluent	mg	57.130	57.710	34.620	80.210

Fractionation Predicted by Phillips-Bentley Model -- continued

Calculations	Units	Date of Sampling 5/02/84	5/30/84	6/18/84	7/23/84
B = mass of ^{37}Cl added to effluent = $M(V_o-V_E)\Delta\delta^{37}$Cl	mg	0.0568	0.0709	0.0352	0.0997
C = A-B = total mass of ^{35}Cl in effluent	mg	57.073	57.635	34.585	80.105
D = total mass due to ^{37}Cl excluding B = (A-B)(0.3240)	mg	18.492	18.674	11.206	25.954
D + B = total mass of ^{37}Cl in effluent	"	18.549	18.745	11.241	26.054
E = $\frac{D + B}{C}$ = ratio of masses of ^{37}Cl and ^{35}Cl in effluent		0.3250	0.3252	0.3250	0.3252
$\delta_{EFF} = (\frac{E}{0.3240} - 1)\ 1000$	o/oo	+3.09	+3.70	+3.09	+3.70
Measured δ_{EFF}	o/oo	+1.66	+1.56	+1.47	+0.47

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