

ZEOLITE MOLECULAR SIEVES

STRUCTURE, CHEMISTRY, AND USE

DONALD W. BRECK

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PREFACE

Long winded writers I abhor,
And glib, prolific chatters:
Give me the ones who tear and gnaw
their hair and pens to tatters:
who find their writing such a chore
they write what only matters.

— From "Grooks" by Piet Hein

Several years ago, I undertook the preparation of the manuscript for this book confident that zeolite science had attained a reasonable level of maturity and that the time had come for publication of an appropriate monograph. Today, with file boxes filled with obsolete manuscripts, I am much wiser. Each chapter has been subjected to several revisions and the manuscript size has increased to the point of becoming unwieldy. However, I believe that most of the important developments published and available by the end of 1972 are included. As author, I have had to use my judgment, hopefully objectively, as to the subject matter.

In order to be comprehensive, much of the detailed information on structure, synthesis, ion exchange, and adsorption has been summarized in tables. Appropriate illustrations and photographs are used. Chapter 2 includes a collection of stereophotographs of all of the basic zeolite framework structures. Most readers will find a stereoviewer desirable. A considerable amount of previously unpublished information obtained by my associates at Union Carbide Corporation during the last 25 years is included in the book.

The reader will quickly observe by a perusal of the Table of Contents that the important subject of zeolite catalysis has been deliberately omitted. This was a decision we had to make due to size and time limitations. We hope to prepare a second volume which will be concerned with zeolite catalysis and certain other areas of interest to the user of zeolites.

In the preparation of this volume, I have relied very heavily on friends and colleagues. I especially want to thank Professor J. V. Smith for his comments and review of Chapters 1, 2, and 3. He also supplied many of the models illustrated in Chapter 2. I wish to thank Ms. E. M. Flanigen and Mr. R. L. Mays for their critical review of the manuscript.

I especially want to thank my editor, Ms. N. L. Marcus, for her perserverance. The work would have been impossible without her help. I want to thank Dr. W. H. Flank for proofreading the entire manuscript and for his constructive comments. Finally, I wish to thank Union Carbide Corporation for their support and encouragement.

D. W. Breck
July, 1973

TABLE OF CONTENTS

Preface		
Chapter One	INTRODUCTION	1
A.	<i>Molecular sieve technology</i>	1
B.	<i>The scope of the book</i>	2
C.	<i>Types of adsorbents</i>	3
D.	<i>Types of molecular sieves</i>	4
E.	<i>Early observations</i>	10
F.	<i>Classification and nomenclature</i>	19
Chapter Two	STRUCTURE OF ZEOLITES	29
A.	<i>Introduction</i>	29
B.	<i>Review of silicate structures</i>	29
C.	<i>Classification of zeolite structures</i>	45
D.	<i>Theoretical zeolite structures</i>	47
E.	<i>Internal channel structure in zeolites</i>	59
F.	<i>Framework density</i>	62
G.	<i>Aperture sizes in dehydrated zeolites</i>	64
H.	<i>Zeolites of group 1</i>	67
I.	<i>Zeolites of group 2</i>	77
J.	<i>Zeolites of group 3</i>	83
K.	<i>Zeolites of group 4</i>	92
L.	<i>Zeolites of group 5</i>	117
M.	<i>Zeolites of group 6</i>	122
N.	<i>Zeolites of group 7</i>	128
O.	<i>Other zeolites</i>	132
P.	<i>Tables of zeolite structural data</i>	133
Chapter Three	MINERAL ZEOLITES	186
A.	<i>Types of occurrences</i>	187
B.	<i>Igneous zeolites</i>	189
C.	<i>Sedimentary zeolites</i>	192
D.	<i>Origin of zeolite minerals</i>	200
E.	<i>Physical properties</i>	205
F.	<i>Glossary of terms</i>	207
G.	<i>Tables of mineral zeolite data</i>	209

H.	<i>Salt occlusion or imbibition</i>	585
I.	<i>Ion exchange in fused salts</i>	587
J.	<i>Zeolite ion exchange applications</i>	588
Chapter Eight	ADSORPTION BY DEHYDRATED ZEOLITE CRYSTALS	593
A.	<i>Equilibrium adsorption of gases and vapors on dehydrated zeolites</i>	596
B.	<i>The application of isotherm equations to zeolite adsorption</i>	628
C.	<i>The molecular sieve effect</i>	633
D.	<i>Heat of adsorption</i>	645
E.	<i>Character of the adsorbed phase in zeolites</i>	660
F.	<i>Specificity of adsorption selectivity effects</i>	664
G.	<i>Adsorption kinetics and diffusion</i>	671
H.	<i>Adsorption equilibria for binary mixtures on zeolites</i>	689
I.	<i>Adsorption separation of mixtures</i>	699
Chapter Nine	MANUFACTURE AND PROPERTIES OF COMMERCIAL MOLECULAR SIEVE ADSORBENTS	725
A.	<i>Manufacturing processes</i>	725
B.	<i>Pelletization of synthetic zeolite powders</i>	742
C.	<i>Properties of commercial molecular sieves</i>	746
Appendix		756
Index		761

INTRODUCTION

Rarely in our technological society does the discovery of a new class of inorganic materials result in such a wide scientific interest and kaleidoscopic development of applications as has happened with the zeolite molecular sieves. From the first industrial research efforts in 1948 at Union Carbide Corporation until the end of 1972, over 7,000 papers and 2,000 United States patents have been published dealing with zeolite science and technology. The extent of international scientific and commercial interest in the zeolite molecular sieves was evidenced by several large conferences. In the USSR, the Second All-Union Conference on Zeolites sponsored by the USSR Academy of Sciences was held in Leningrad in 1964; a total of 81 papers were presented covering the science and application of zeolites. An international conference on molecular sieves organized by R. M. Barrer and sponsored by the Society of Chemical Industry in Great Britain was held in London in April 1967; 31 papers were presented to the 200 scientists from over 18 countries. The Second International Conference, chaired by E. M. Flanigen and L. B. Sand, was held in the United States in September 1970; the published proceedings included 77 papers (1).

The Third International Conference held in Switzerland in September 1973 was organized under the chairmanship of W. M. Meier.

A. MOLECULAR SIEVE TECHNOLOGY

The properties and uses of zeolites are being explored in many scientific disciplines: modern inorganic and organic chemistry, physical chemistry, colloid chemistry, biochemistry, mineralogy, geology, surface chemistry, oceanography, crystallography, catalysis, and in all

2 INTRODUCTION

types of chemical engineering process technology. The wide variety of applications includes separation and recovery of normal paraffin hydrocarbons, catalysis of hydrocarbon reactions, drying of refrigerants, separation of air components, carrying catalysts in the curing of plastics and rubber, recovering radioactive ions from radioactive waste solutions, removing carbon dioxide and sulfur compounds from natural gas, cryopumping, sampling air at high altitudes, solubilizing enzymes, separating hydrogen isotopes, and removal of atmospheric pollutants such as sulfur dioxide.

Cracking catalysts containing crystalline zeolite molecular sieves were first used in 1962 (2,3) and at present close to 95% of the installed capacity, which is in excess of 4 million barrels of oil per day, employs zeolite catalysts (4). Annual savings of greater than \$250 million in operating expenses and several hundred million more in capital investment have been reported.

The first experimental observations of the adsorption of gases on zeolites and their behavior as molecular sieves were conducted on zeolite minerals. The first definitive experiments on the separation of mixtures using the dehydrated zeolite mineral chabazite as a molecular sieve were performed by Barrer in 1945 (5). He classified zeolites into three groups based upon their ability to adsorb or exclude molecular species of different sizes. The classification defined the approximate intrachannel dimensions.

In 1948, the first industrial research efforts by Milton and his associates at Union Carbide Corporation resulted in the synthesis and the manufacture of synthetic zeolite molecular sieves which had never existed as minerals (6). This controlled synthesis was a key research achievement.

B. THE SCOPE OF THE BOOK

Although review articles and conference proceedings cover various aspects of the science and application of zeolite molecular sieves, a researcher or engineer is still at a loss to readily obtain specific information about zeolite molecular sieves and their use. It is this void that we hope to fill with this book.

There are two main purposes in preparing this book: It is an introduction to the subject of zeolite molecular sieves for the newcomer to the field, and a reference for additional information and background.

Details on structure, properties, characterization, synthesis, chemistry (including ion exchange, adsorption) and commercial materials are included.

Each chapter is followed by a bibliography of the pertinent published literature including patents. There are many examples in zeolite science where an issued patent is either a primary reference or the only source of essential technical information.

The industrial application of zeolite molecular sieves is a separate subject in itself. Engineering procedures and the design of processes are not covered in detail in this book.

C. TYPES OF ADSORBENTS

Commercial adsorbents which exhibit ultraporosity and which are generally used for the separation of gas and vapor mixtures include the activated carbons, activated clays, inorganic gels such as silica gel and activated alumina, and the crystalline aluminosilicate zeolites.

Activated carbons, activated alumina, and silica gel do not possess an ordered crystal structure and consequently the pores are nonuniform. The distribution of the pore diameters within the adsorbent particles may be narrow (20 to 50 Å) or it may range widely (20 to several thousand Å) as is the case for some activated carbons. Hence, all molecular species, with the possible exception of high molecular weight polymeric materials, may enter the pores. Zeolite molecular sieves have pores of uniform size (3 Å to 10 Å) which are uniquely determined by the unit structure of the crystal. These pores will completely exclude molecules which are larger than their diameter.

The pore size distribution for a zeolite molecular sieve, a typical silica gel, and activated carbon are illustrated schematically in Fig. 1.1.

The term "molecular sieve" was originated by J. W. McBain to define porous solid materials which exhibit the property of acting as sieves on a molecular scale (7).

At present, the most important molecular sieve effects are shown by the dehydrated crystalline zeolites. These materials all have a high internal surface area available for adsorption due to the channels or pores which uniformly penetrate the entire volume of the solid. The external surface of the adsorbent particles contributes only a small amount of the total available surface area.

4 INTRODUCTION

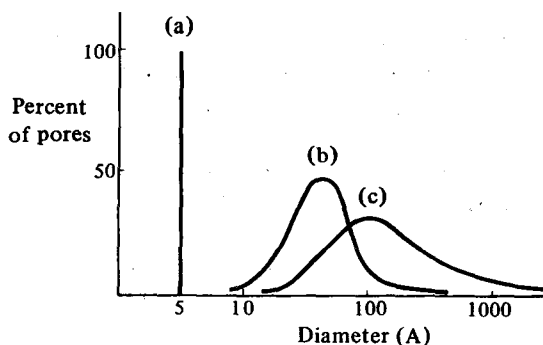


Figure 1.1 Distribution of pore sizes in microporous adsorbents. (a) Dehydrated zeolite, e.g., type A; (b) typical silica gel; (c) activated carbon.

external surface of the adsorbent particles contributes only a small amount of the total available surface area.

The zeolites selectively adsorb or reject different molecules. Molecular sieve action may be total or partial. If total, the diffusion of one species into the solid may be wholly prevented while the diffusion of a second species occurs; if partial, the components of a binary mixture diffuse into the solid at different rates depending upon the conditions.

In some cases, the *activated* diffusion of the species in the solid is of particular interest. As the size of the diffusing molecule approaches the size of the pores in the zeolite, the interaction energy between the species and the aperture increases in importance. If the aperture is sufficiently small relative to the size of the diffusing species, the repulsive interaction becomes dominant and the diffusing species needs a specific activation energy to pass through the aperture (see Chapter 8).

Although zeolite molecular sieves are today being used in diverse applications such as catalysis and ion exchange, the term "molecular sieve" is still retained although it does not completely imply this wide sphere of application. Stereospecific catalytic and ion-sieve behavior are well known.

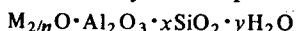
D. TYPES OF MOLECULAR SIEVES

Crystalline Zeolites

Zeolites are crystalline, hydrated aluminosilicates of group I and group

II elements,* in particular, sodium, potassium, magnesium, calcium, strontium, and barium. Structurally the zeolites are "framework" aluminosilicates which are based on an infinitely extending three-dimensional network of AlO_4 and SiO_4 tetrahedra linked to each other by sharing all of the oxygens.

Zeolites may be represented by the empirical formula



In this oxide formula, x is generally equal to or greater than 2 since AlO_4 tetrahedra are joined only to SiO_4 tetrahedra, n is the cation valence. The framework contains channels and interconnected voids which are occupied by the cation and water molecules. The cations are quite mobile and may usually be exchanged, to varying degrees, by other cations. Intracrystalline "zeolitic" water in many zeolites is removed continuously and reversibly. In many other zeolites, mineral and synthetic, cation exchange or dehydration may produce structural changes in the framework. Ammonium and alkylammonium cations may be incorporated in synthetic zeolites, e.g., NH_4 , CH_3NH_3 , $(\text{CH}_3)_2\text{NH}_2$, $(\text{CH}_3)_3\text{NH}$, and $(\text{CH}_3)_4\text{N}$. In some synthetic zeolites, aluminum cations may be substituted by gallium ions and silicon ions by germanium or phosphorus ions. The latter necessitates a modification of the structural formula.

The structural formula of a zeolite is best expressed for the crystallographic unit cell as: $\text{M}_{x/n}[(\text{AlO}_2)_x(\text{SiO}_2)_y] \cdot w\text{H}_2\text{O}$ where M is the cation of valence n , w is the number of water molecules and the ratio y/x usually has values of 1 - 5 depending upon the structure.† The sum $(x + y)$ is the total number of tetrahedra in the unit cell. The portion with [] represents the framework composition.

Although there are 34 species of zeolite minerals and about 100 types of synthetic zeolites, only a few have practical significance at the present time. Many of the zeolites, after dehydration, are permeated by very small channel systems which are not interpenetrating and which may contain serious diffusion blocks. In other cases dehydration irreversibly disturbs the framework structure and the positions of metal cations, so that the structure partially collapses and dehydration is not completely reversible. To be used as a molecular sieve, the structure of the zeolite after complete dehydration must remain intact.

*As formed in nature or synthesized. Higher polyvalent ions, e.g., rare earths, are readily introduced by cation exchange.

† Occlusion of AlO_2^- species within the zeolite structure may lower the ratio below 1.

6 INTRODUCTION

Molecular sieve action has been reported for other solids, crystalline and noncrystalline. These include coal, special active carbons, porous glass, microporous beryllium oxide powders, and layer silicates modified by exchange with organic cations.

Coal

As a result of adsorption studies, several coals were found to have pore diameters approaching molecular sizes (8). A comparison of the relative adsorption of *n*-butane and isobutane indicated that certain coals had pores with openings between 4.9 and 5.6 Å in diameter at 0° C and about 4 Å at 145° C. The adsorption capacity, however, was low and the rate of adsorption very slow.

A typical anthracite has a pore volume of 0.07 cc/g and 0.10 cc/cc coal. An anthracite coal which was activated by heating in carbon dioxide exhibited selective adsorption behavior toward *n*-butane (9). Monolayer volumes in the raw devolatilized and activated anthracites are shown in Table 1.1. The activated anthracite has a capacity of about 130 cc of *n*-butane/g and 50 cc of isobutane/g. A selectivity for *n*-butane similar to that observed in crystalline zeolites is indicated.

Table 1.1 Monolayer Volumes for Hydrocarbons on Raw and Activated Anthracite (9)

Material	V_m (cc/g)/(STP)	
	Raw	Activated
<i>n</i> -C ₄ H ₁₀	12.6	134
<i>iso</i> -C ₄ H ₁₀	8.6	54.5
<i>neo</i> -C ₅ H ₁₂	2.3	15.5

Oxides

The controlled thermal decomposition of beryllium hydroxide *in vacuo* produces BeO consisting of porous aggregates of 30 Å crystallites (10). Only 20% of the internal pore volume is available to adsorption by carbon tetrachloride and 50% by nitrogen. It was concluded that there are pores which are less than 6 Å and others less than 3 Å. The micropore size depends upon whether the hydroxide is decomposed *in vacuo* or in the presence of water vapor. The range of pore sizes is 6 - 20 Å if the decomposition occurs in water vapor where the pore

size increases at relatively low temperatures (500°C) due to crystal growth.

Glasses

Leaching alkali silicate glasses with acids results in porous adsorbents which are reported to exhibit molecular sieve-type adsorption toward small molecules (11). In general, the glasses consist of three components: an alkali such as sodium or potassium, another oxide such as B_2O_3 or Al_2O_3 , and silica. The porosity of the resulting solid depends upon the conditions of leaching and the composition. Results show that the adsorption pore volume is much lower than that in the zeolites and generally in the range of 0.01 to 0.04 cc/g as measured by water adsorption. Porous glass with uniform pore sizes of 3 - 10 Å has been reported. Small variations in the composition of the glass significantly change the behavior toward water adsorption. Porous glass molecular sieves have been reported to be more stable in acid media than crystalline zeolites. However, the fact that the porosity is produced by acid leaching of the glass and that the pore size distribution is controlled by the degree of acid leaching contradicts the argument of acid stability. It is known, moreover, that some of the zeolites are quite stable toward acid conditions. (See Chap. 6).

Recently, silica gels with pore radii of about 4 Å have been reported; silica gel commonly has pore size distributions which range from 10 to several hundred Å (12). The silica was prepared by the evaporation of a water solution of normal silicic acid at 0°C. The adsorptive properties varied with the pH of the preparation and mean pore radii were 7 - 9 Å (Table 1.2). Type I adsorption isotherms were observed and larger molecules such as benzene and CCl_4 exhibited the lowest adsorption. These silica gels, however, were found to be unstable when treated with water; the pore system collapsed.

Table 1.2 Adsorptive Properties of Silica Samples (12)

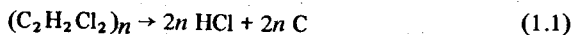
Sample	pH	SA(m ² /g)	V(cc/g)	r(Å)
1	0.97	742	0.345	9.3
2	0.94	429	0.184	8.6
3	1.87	255	0.090	7.1
4	1.67	322	0.122	7.6

SA = specific surface area, V = pore volume, r = mean pore radius.

8 INTRODUCTION

Carbon

Present methods for the preparation of carbon adsorbents with small, narrow pore size distributions are largely empirical (13, 14, 15). In general the method has involved the controlled pyrolysis of polymers such as polyvinylchloride $(C_2H_2Cl_2)_n$ and Saran (a copolymer of 80 - 90% polyvinylidene chloride with various amounts of polyvinyl chloride and plasticizer). The pyrolysis results in the loss of HCl as indicated by Eq. 1.1.



This leaves essentially pure carbon which is 25 wt% of the starting polymer (Fig. 1.2). At present little is known about the relationship between the original polymer structure in terms of the size and shape of the polymer units and the resulting pore size and shape of the microporous carbon. Originally it was thought that the resulting carbon might have a uniform pore size that was related to the initial regular polymer structure. Most of the studies have been confined to the Saran type of polymers since thermoplastic polymers do not yield good cokes upon carbonization. It is believed that the mechanism of the release of HCl during carbonization involves several steps. More than half of the HCl is lost at temperatures below 200° C; further liberation requires higher temperatures with the process being complete at 600° C. The first step is the loss of one HCl molecule per pair of carbon atoms which leads to the formation of the carbonized chain. Crosslinking then occurs followed by the elimination of another HCl.

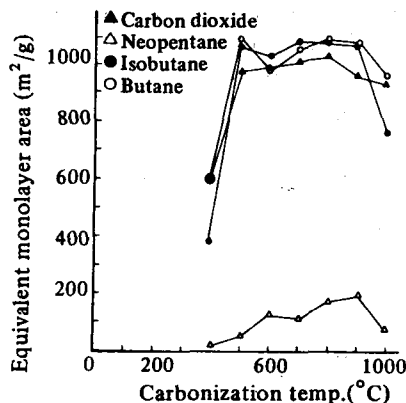
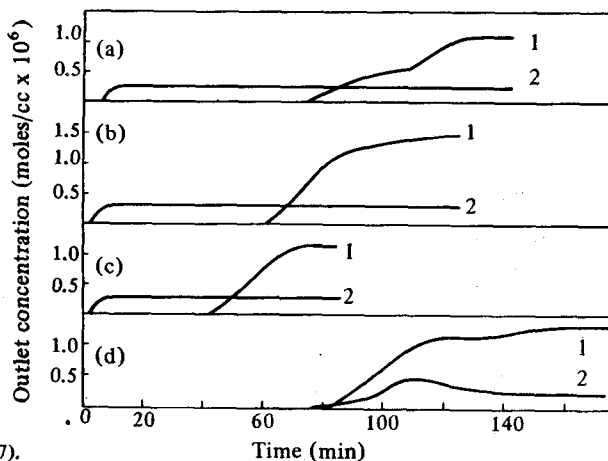


Figure 1.2 Surface area of Saran carbons heated to different carbonization temperatures (15).

The molecular sieve properties of the resulting carbons were determined by measuring the adsorption of nitrogen, carbon dioxide, *n*-butane, isobutane, and neopentane. The minimum cross-sectional diameter of these molecules (see Chapter 6) suggests their use as probes for determining the pore size. Typical results (Fig. 1.2) for a Saran-428 carbon show that except for neopentane, adsorption reached a maximum with carbonization temperatures in the range of 500 - 800°C. The very high surface areas, $\sim 1000 \text{ m}^2/\text{g}$, for butane and isobutane, as opposed to the low surface area for neopentane are noteworthy. The ability of this carbon to separate isobutane and neopentane is apparent. In addition the adsorption of benzene and cyclohexane on a Saran-derived carbon was found to be about ten times as great as the adsorption of neopentane. This indicates that the pores in Saran-derived carbons are slit-like in shape; straight-chain hydrocarbons and flat molecules are preferentially adsorbed but the adsorption of a large spherical molecule such as neopentane is slow. Fig. 1.3 compares the separation ability of two Saran-derived carbon molecular sieves with zeolite 5A and a typical activated carbon. The separation of *n*-heptane from a mixture with isooctane (2, 2, 4-trimethylpentane) by a carbon molecular sieve and zeolite 5A are shown. The carbon sieves are concluded to have slit-shaped pore constrictions ranging in size between 4.5 and 5.7 Å in thickness which connect cavities of about 12 Å in thickness. The adsorption capacities may be comparable to those of the zeolites. At present, commercial products based upon

Figure 1.3 Dynamic adsorption of *n*-heptane (1) and 2,2,4-trimethylpentane (2). (a) and (b) molecular sieve carbons; (c) molecular sieve zeolite type 5A; (d) commercial activated carbon (57).



carbons derived from polymers are not available.

Alkali Graphite Intercalation Compounds

Intercalation compounds of graphite and alkali metals adsorb small gas molecules (16). The compounds of composition $C_{24}M$ (where $M = K, Rb, Cs$) adsorb the gases H_2 , D_2 , N_2 , CH_4 , Ar to different degrees depending on the size of the intercalated atom. Adsorption isotherms of type I are exhibited by $C_{24}Rb$ for D_2 at 113°K. The compound $C_{24}K$ has an adsorption capacity for H_2 of 144 cc/g but does not adsorb N_2 at -196°C. The mole ratio is 2.1 $H_2/C_{24}K$.

As the size of the alkali atom increases, the size of the interlayer pores increases. Thus $C_{24}Cs$ adsorbs both H_2 and N_2 as well as CH_4 . In the latter case, a type III isotherm was observed. This is associated with swelling of the interlayer compound in the c-direction perpendicular to the carbon atom layers.

Selective adsorption of D_2 from a D_2 -argon mixture by $C_{24}K$ was observed at 77°K. D_2 was nearly completely adsorbed while argon adsorption was negligible. Separation of a D_2 - N_2 mixture was incomplete and substantial adsorption of N_2 occurred.

Table 1.3 Adsorptive Capacity of Alkali Graphites (63°K to 196°K)(16)

Compound	Adsorbate (molecules adsorbed gas/ atoms of alkali)			
	H_2, D_2	N_2	Ar	CH_4
$C_{24}K$	2.1	none	none	none
$C_{24}Rb$	2.05	1.0	1.2	0.9
$C_{24}Cs$	2.00	1.3	1.4	1.2

He and Ne were not adsorbed.

E. EARLY OBSERVATIONS

Zeolites were first recognized by Cronstedt (17) as a new group of minerals consisting of hydrated aluminosilicates of the alkali and alkaline earths with his discovery of stilbite in 1756. Because the mineral exhibited intumescence when heated in a blowpipe flame, he called the mineral a zeolite which comes from two Greek words meaning "to boil" and "a stone." Studies of zeolite minerals have taken place over the last two centuries. The most recently discovered zeolite mineral is garronite (1962) (18).

Ion Exchange by Soil Minerals

The misuse of the term "zeolite" to include all inorganic ion-exchange materials originated in the earliest studies of the phenomenon of ion exchange in soils. In 1845, H. S. Thompson (19) conducted experiments which showed that certain soils have the power of "decomposing" and retaining ammonium salts. When a solution of ammonium sulfate was filtered through the soil, the filtrate contained calcium sulfate and the ammonium salt was retained in the soil. Later J. T. Way (20) showed that the hydrated silicates in the soil produced this phenomenon. He was able to show that only the ammonium or the potassium was exchanged for the calcium in the soil. Subsequently Way prepared an artificial base exchanger consisting of a sodium aluminosilicate. Several years later H. Eichhorn published a paper on the action of dilute salt solutions on silicates (21), showing that the base exchange principle discovered by Way is reversible. He studied the quantitative behavior of the zeolite minerals, chabazite and natrolite, in contact with dilute salt solutions and found that sodium and calcium could reversibly replace each other in the zeolite.

The Permutites

The accepted term for synthetic aluminosilicates which are crystallographically amorphous and are prepared for their ion exchange properties is "permutite." This term should always be employed when referring to synthetic amorphous aluminosilicate cation exchange materials. A complete summary of the literature covering the preparation of permutite materials and their application up to 1930 is given by Shreve (22).

The chemical composition of most permutites is represented by an empirical formula in terms of the oxides: $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$ in which x often has a value of 5 - 6.* The chemical composition must be shown in terms of the oxide ratios since they are noncrystalline, gel-like solids. A structural formula, as is used for the crystalline zeolites, is not possible.

The first usable synthetic cation exchangers were made by a fusion method (23). However, this method had several inherent disadvantages.

* Examples are Culligan zeolite: $0.9 \text{ Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 5.5 \text{ SiO}_2 \cdot 19 \text{ H}_2\text{O}$ and Super Nalcolite: $0.7 \text{ Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6.1 \text{ SiO}_2 \cdot 15 \text{ H}_2\text{O}$.