GAS-SORPTIVE PROPERTIES
OF THE
ZEOLITE MORDENITE

Interim Report to:

Division of Research and Development
Department of Transportation and
Public Facilities
State of Alaska

Research Project 80-1
Geology/Geophysics Program
University of Alaska
Fairbanks, Alaska

Daniel B. Hawkins

September 1, 1980

Purpose:

The goal toward which these studies are directed is the application of zeolites to alternative modes of energy production. The properties of zeolites are such that they serve as gas sorbents and gas-separating materials. Thus, zeolites can be used for the production of oxygen by separation from air, for natural gas storage and hydrogen encapsulation. The natural zeolite mordenite occurring in a large deposit in Alaska has excellent properties which make it attractive for these purposes.

The immediate objectives of this study are to determine the oxygen-nitrogen separation capacity of Alaska mordenite in various ion-exchanged forms; to determine the hydrogen sorption capacity of the mordenite; to modify the mordenite to the zeolite faujasite, a zeolite having widespread industrial use.

Status:

Work began on this project in September 1979. The project funding level was $6,500.00.

Progress of the project has been frustratingly slow because of slow delivery of equipment, instrument failures and finally loss of the graduate student who was working on the project. In spite of this, valuable progress has been made and I am encouraged that the project can be brought to a successful conclusion.

Accomplishments:

1. Clinoptilolite (obtained from the Anaconda Company) and Alaska mordenite have been ground, sieved, and converted to sodium-, calcium-, potassium- and strontium-exchanged forms.

2. Alaska mordenite has been successfully converted to faujasite following Robson's (1977) procedure involving boiling the zeolite in sodium hydroxide. The conditions of the conversion have been investigated.

This is an exciting result that could extend and enhance the properties of mordenite.

3. A hydrogen generator has been installed and is functional.

4. A McBain-type gas balance has been purchased and is now being reinstalled. The balance was not received until March and when first used the system failed under vacuum. It has since been repaired and is being assembled as a component of a gas train. Figure 1, from Hayhurst, shows the configuration of the gas train and balance. All components are now available and the train will be assembled within two weeks depending upon the availability of the Inst. of Marine Science glassblower.

5. A continued literature review has revealed several articles having a direct bearing on the project.

6. As a result of a proposal written using this study as a base, funds are now pending through the University of Alaska to support a complimentary study in the use of zeolites in alternative energy production.

Discussion:

Although I have no data of my own as yet on the gas-sorptive properties of Alaska mordenite, recent work by Hayhurst (see attached letter and data) indicates that the Alaska mordenite has twice the nitrogen-sorption capacity of the zeolites presently being used industrially for this purpose. Oxygen is currently produced from air by the pressure-swing absorption cycle (see Fig. 2). Quantities up to 25-30 tons per day are produced more economically than by the liquifaction process. The enhanced nitrogen-sorption capacity of the Alaska mordenite should make it especially useful in such a system.

The ability to produce large quantities of oxygen over mordenite has a direct bearing on the production of energy by hydrogen devices.

According to Roger Billings of the Billings Energy Corporation, whom we visited in December, the most likely source of hydrogen on a large scale will be through coal gasification, a process in which oxygen is required. The combination of oxygen generation by Alaska mordenite and hydrogen production from Alaska coal may ultimately be an important contribution to the supply of energy for Alaska.

Hydrogen produced from coal is contaminated with water, carbon dioxide, carbon monoxide, sulfur dioxide, methane and nitrogen. At present, impure hydrogen containing as little as 0.5% and up to 40% by volume of these impurities is being purified over synthetic zeolites of the faujasite type (Breck, 1974, p. 711, Barrer, 1979, p. 14). Again, it seems that either mordenite or more likely faujasite produced from the mordenite may be useful in "sweetening" the hydrogen produced by steam reforming.

Finally, there is the possibility of storage of hydrogen on zeolites rather than on metal hydrides. I am no further in evaluating this possibility now than I was at the outset of this work. I have, however, a much clearer idea how to proceed and of what the equipment needs are and which zeolites are likely to be the best hydrogen-storage devices. First, it is clear that if zeolites are to be useful alternatives to metal hydrides, the zeolites must be loaded with hydrogen at high pressure. I lack the equipment to study this encapsulation but may obtain the equipment through another grant. Several features of gas encapsulation are shown in Fig. 2, namely that gases must be encapsulated at high pressures and that the encapsulation is affected by the particular ion saturating the exchange sites. Previous work (Breck, 1974, Fraenkel and Shabtai, 1977) have used the synthetic zeolite type A. I don't think that this is the optimum zeolite for hydrogen encapsulation. Table 1 (Barrer, 1979, p. 15) shows a classification of zeolites based on their molecular-sieve behavior. Mordenite is in the Type 5 category, which is characterized by the ability to separate the small gases, e.g. H_2 from larger molecules such as Kr. Type A has large diameter pores and is incapable of this separation. This should mean that mordenite, particularly natural, small-port, mordenite may be much more hydrogen retentive than Type A. This remains to be seen.

A zeolite loaded with hydrogen is not much use if the hydrogen cannot be easily removed. I think that mild heating under vacuum will remove the hydrogen but I have no data to support this. A process (Japan patent 7,726,234) recently made public (CA 1978, 617824) may bear on this problem. In this process a zeolite loaded with nitrogen was completely desorbed in two minutes in a glow-discharge field operating at 500v, 0.5A, under a pressure of 0.1 Torr. This suggests to me that novel treatment perhaps involving RF heating or ultrasonics may enhance desorption.

Work Remaining:

Most of the fundamental data gathering remains to be done. As soon as the gas train is connected, the sorption capacities of O_2, N_2 and H_2 on the different forms of mordenite and faujasite derived therefrom will be determined. This will require until at least January 1, 1981, and will be done by me inasmuch as the student assigned to the project has left. Without additional high-pressure equipment, it will be impossible to study hydrogen encapsulation. A completion report will be submitted at that time.

This brings up the question of related studies. Funding by the Alaska Legislature of various alternative energy programs in the University of Alaska has changed the perspective of this work. A question that should be resolved is what aspect of such studies should the University fund and what should be funded by the Dept. of Transportation? I suggest that the basic, scientific studies be funded by the University and the engineering studies funded by the D.O.T. This may not work well in all instances but would be a useful delimiter for studies such as mine.

Under the University of Alaska funds, I apparently have sufficient funds to purchase the requisite high-pressure equipment and other instruments necessary to evaluate the properties of zeolites. I am submitting a request now for the purchase of this equipment. I intend to continue this project with University funding and obtain the necessary gas-sorption data. If the results of these studies are favorable, I will then submit a proposal to D.O.T. in cooperation with engineers such as John Zarling or Ron Johnson to study engineering aspects of this work. Your comments and guidance in this matter will be much appreciated.

References

Breck, D.W. (1974), Zeolite molecular sieves: structure, chemistry and use. Wiley-Interscience.

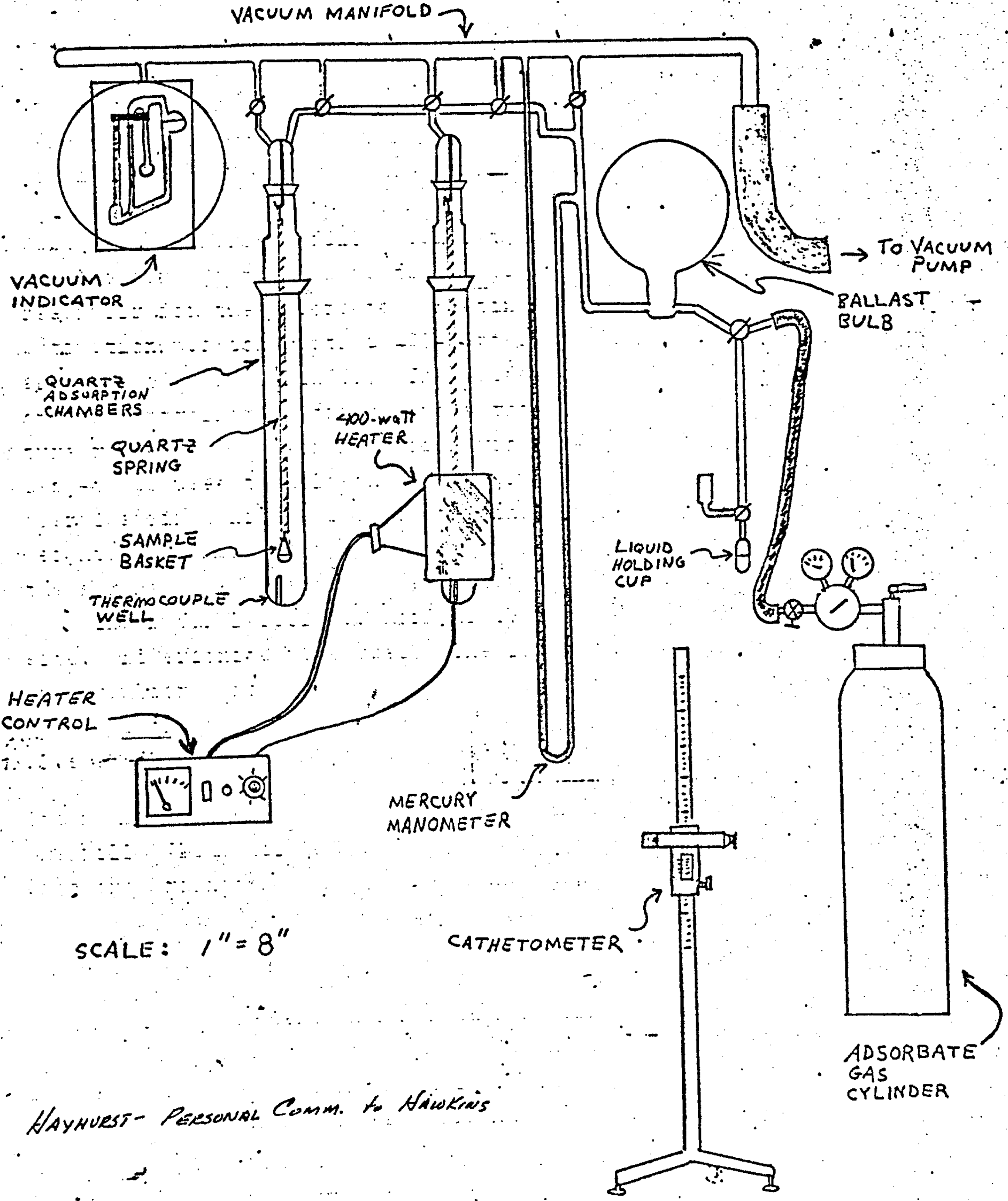
Barrer, R.M. (1978), Zeolites and clay minerals as sorbents and molecular sieves. Academic Press.

Fraenkel, D. and Shabtai, J. (1977), Sorption of hydrogen on Cs-A type zeolites. Jour. Amer. Chem. Soc. 99, p. 7074.

Robson, H.E., Riley, K.I., and Maness, D.D. (1977), Synthesis of faujasite by recrystallization of high-silica zeolites. In Molecular Sieves-II, Ed. James R. Katzer, Am. Chem. Soc. Symposium Series 40, p. 235-243.

FIGURE 4

QUARTZ Spring ADSORPTION BALANCE



SCALE: 1" = 8"

HAYHURST- PERSONAL COMM. to HAWKINS

CLEVELAND STATE UNIVERSITY
CLEVELAND, OHIO 44115

FENN COLLEGE OF ENGINEERING
CHEMICAL ENGINEERING DEPARTMENT

(216) 687-2569

October 23, 1979

Professor Daniel B. Hawkins
Department of Geology
University of Alaska
Fairbanks, Alaska 99701

Dear Dan:

I have continued to examine the adsorptive properties of the Alaskan mordenite samples you supplied. The most interesting property of these samples are their high affinity for nitrogen. We have generated N_2-isotherms for your mordenite as well as many other zeolite varieties including both synthetic and natural and we've concluded that the Alaskan mordenite has a much higher capacity than any of the samples tested, including the CaA-zeolite, used industrially (almost a factor of two).

Our most recent effort has been to construct a high-pressure adsorption apparatus capable of measuring the adsorption isotherms at pressures from ambient up to 10,000 psi. This experimental confirguration will require a rather large zeolite samples (about 10 pounds) in order to achieve a reasonable degree of sensitivity. I would like to look at the high pressure adsorption capacity for the Alaskan mordenite sample and would like to obtain a rather large mordenite sample from you if you have that quantity of material that you can spare.

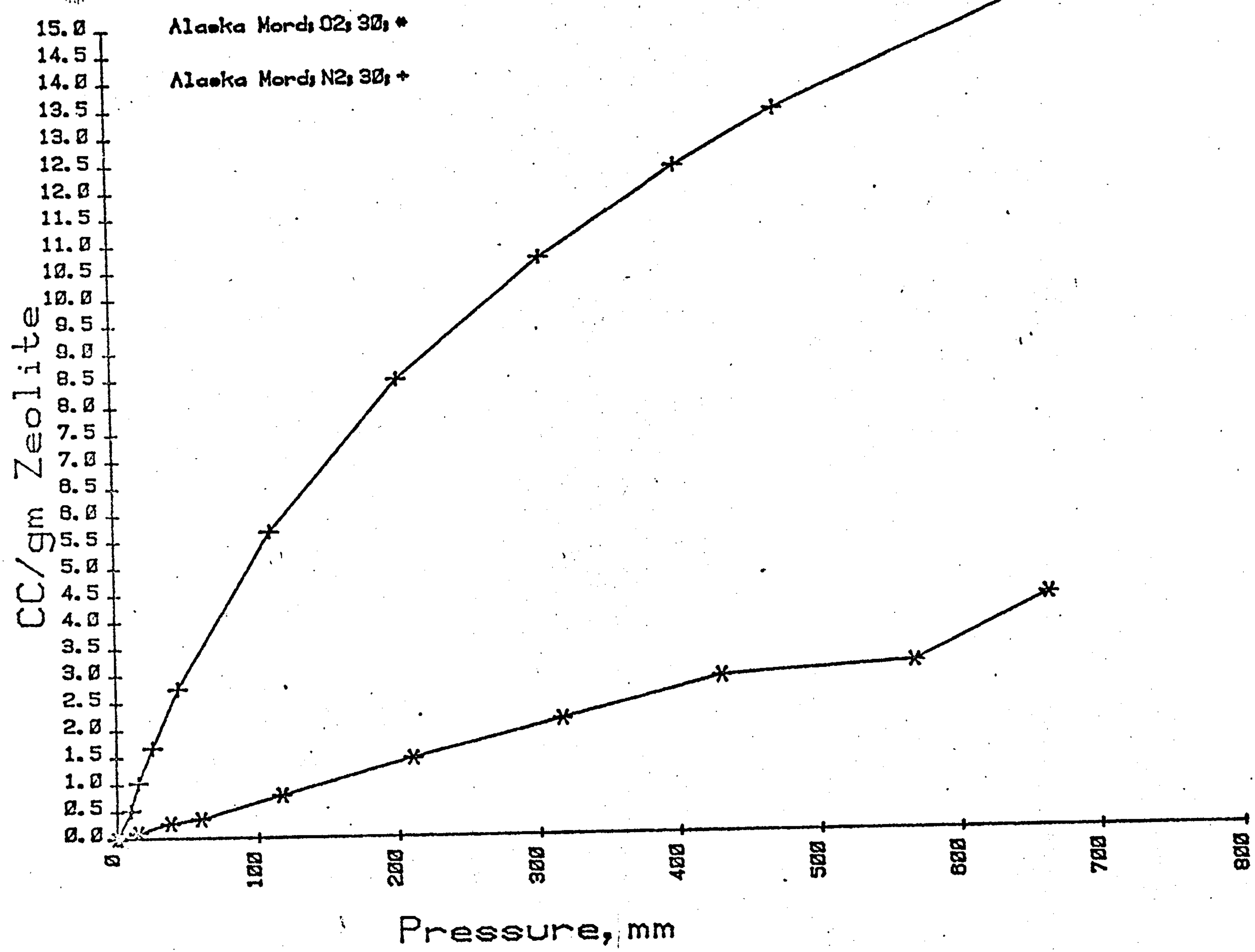
I've submitted two papers to the Naples conference with the hopes of getting at least one of them accepted. It appears that there is about twice the number of papers submitted that can be accomodated in the conference volume so it looks like it will be a good conference at least from a technical content viewpoint. I was thinking that if you were going to Naples for the conference via the lower 48 that you (and your wife, of course) might stop in Cleveland for a day or so as my guest and see our research facilities.

Looking forward to hearing from and seeing you.

Sincerely,

D. T. Hayhurst
Assistant Professor

DTH/MS


Alaska Mord; O2; 30; *
Alaska Mord; N2; 30; +
CC/gm Zeolite
15.0
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1.5
1.0
0.5
0.0
0
100
200
300
400
500
600
700
800
Pressure, mm

"LINDOX" PSA OXYGEN GENERATING SYSTEM

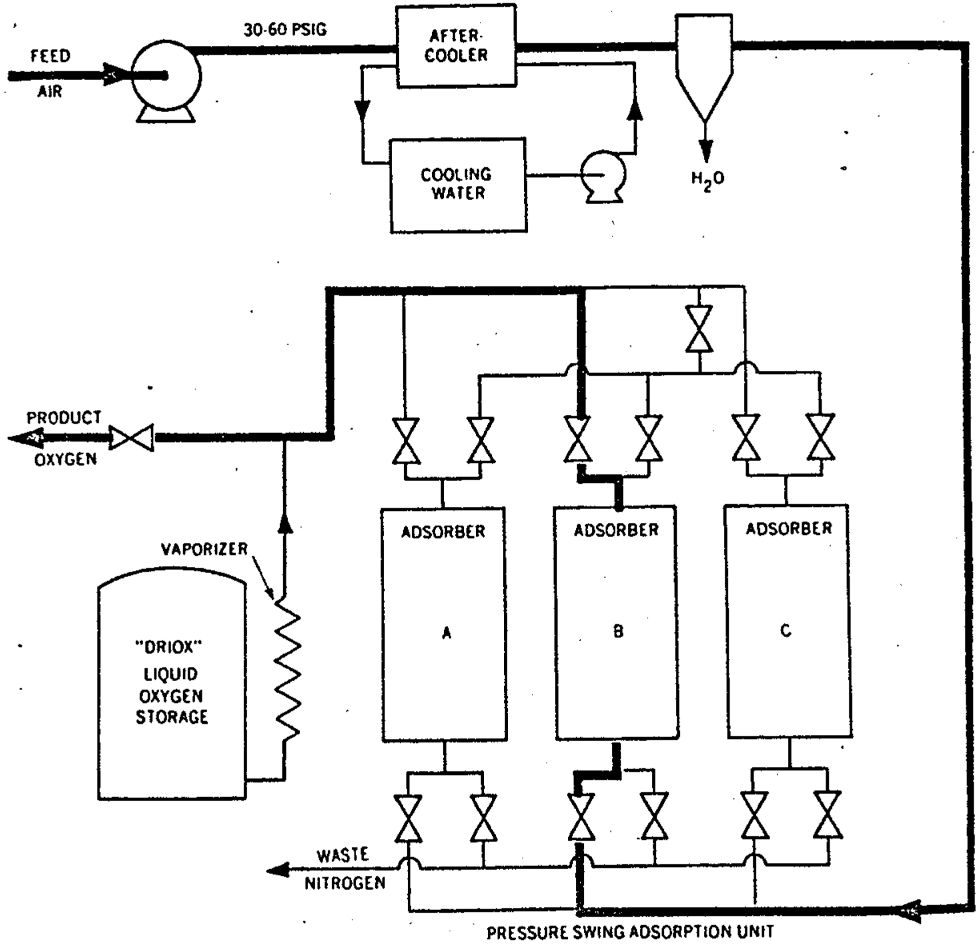

Figure 8.49 Flow diagram of the "LINDOX" PSA oxygen generating system. During the adsorption step, feed air flows through one of the adsorber vessels until the adsorbent is partially loaded. The feed is then switched to another adsorber and the first adsorber is regenerated in three steps: (1) depressurization to atmospheric pressure; (2) purging with product oxygen; and (3) the adsorber is repressurized to the adsorption pressure. In this diagram, feed air is passing through adsorber "B."

FROM BRECK, D.W. (1974)

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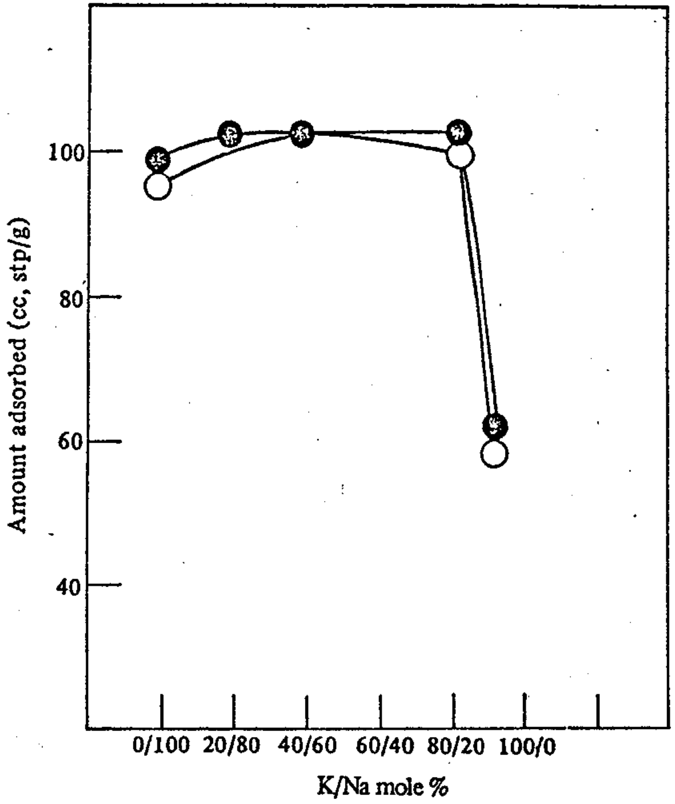


Figure 8.9 Encapsulation of krypton in zeolite A at 350°C and 62,500 psi. The particular cation composition, 40% potassium exchange, is optimum for the maximum storage capacity and stability over a long period of time. Argon and methane also encapsulate in the 40% potassium A (50).

The dark circles represent a sample shortly after encapsulation and the open circles are a sample measured 30 days after encapsulation.

TABLE 2

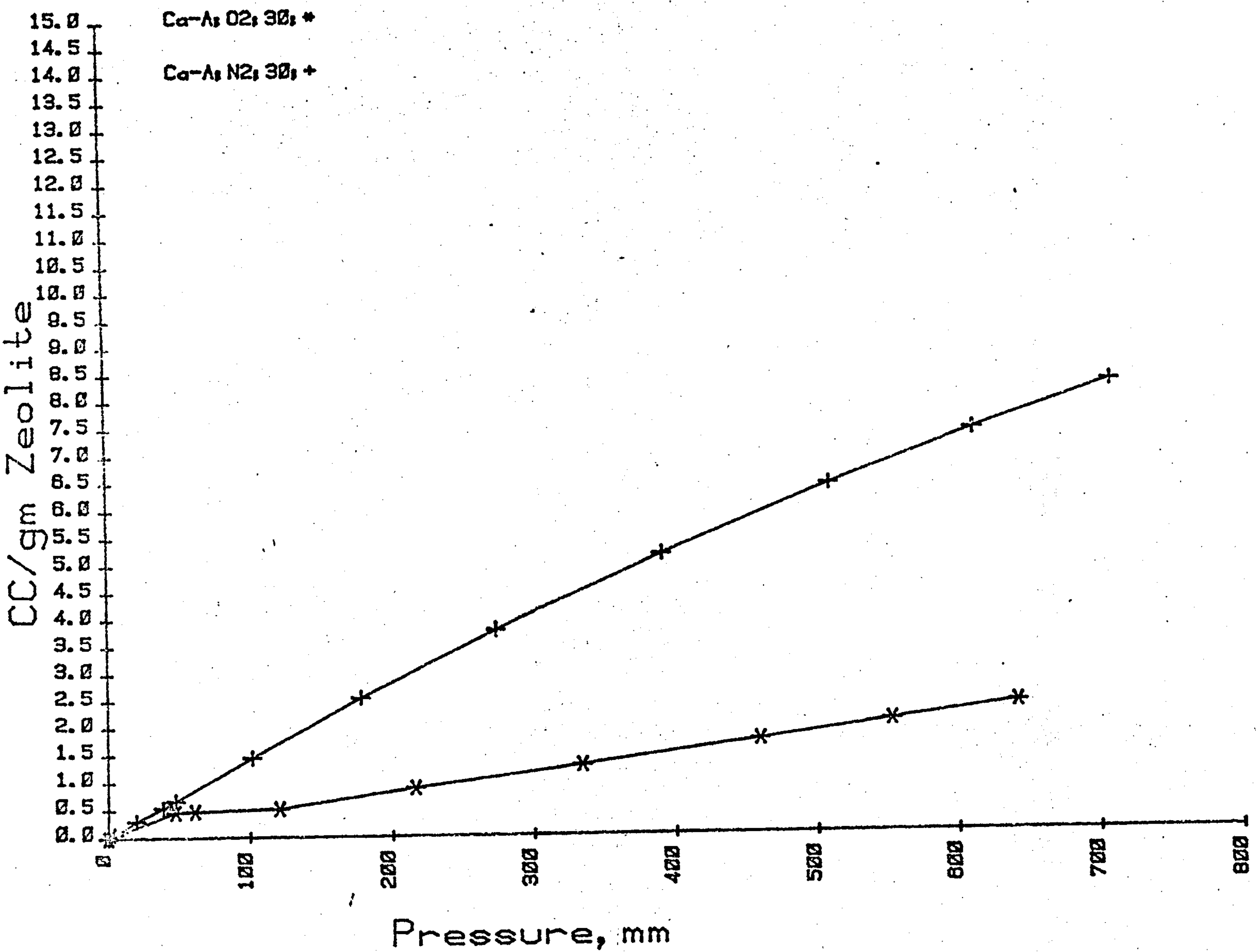
Classification of some molecular sieves

Molecular size increasing⟶

Type 5	He, Ne, Ar, CO H_2, O_2, N_2, NH_3, H_2O				Size limit for Ca- and Ba-mordenites and levynite about here (≈3·8Å)
Type 4	Kr,Xe CH_4 C_2H_6 CH_3OH CH_3CN CH_3NH_2 CH_3Cl CH_3Br CO_2 C_2H_2 CS_2				Size limit for Na-mordenite and Linde sieve 4A about here (≈4·0Å)
Type 3	C_3H_8 n-C_4H_{10} n-C_7H_{16} n-$C_{14}H_{30}$ etc. C_2H_5Cl C_2H_5Br C_2H_5OH $C_2H_5NH_2$ CH_2Cl_2 CH_2Br_2 CHF_2Cl CHF_3 $(CH_3)_2NH$ CH_3I B_2H_6	C_2F_6 CF_2Cl_2* CF_3Cl $CHFCl_2$			Size limit for Ca-rich chabazite, Linde sieve 5A, Ba-zeolite and gmelinite about here (≈4·9Å)
Type 2	SF_6 iso-C_4H_{10} iso-C_5H_{12} iso-C_8H_{18} etc. $CHCl_3$ $CHBr_3$ CHI_3 $(CH_3)_2CHOH$ $(CH_3)_2CHCl$ n-C_3F_8 n-C_4F_{10} n-C_7F_{16} B_5H_9	$(CH_3)_3N$ $(C_2H_5)_3N$ $C(CH_3)_4$ $C(CH_3)_3Cl$ $C(CH_3)_3Br$ $C(CH_3)_3OH$ CCl_4 CBr_4 $C_2F_2Cl_4$	C_6H_6 $C_6H_5CH_3$ $C_6H_4(CH_3)_2$ Cyclopentane Cyclohexane Thiophen Furan Pyridine Dioxane $B_{10}H_{14}$	Naphthalene Quinoline, 6-decyl-1, 2, 3, 4-tetrahydronaphthalene, 2-butyl-1-hexyl indan $C_6F_{11}CF_3$	Size limit for Linde sieve 10X about here
Type 1	1, 3, 5-triethyl benzene 1, 2, 3, 4, 5, 6, 7, 8, 13, 14, 15, 16-decahydrochrysene				Size limit for Linde sieve 13X about here (≈10Å)
	$(n$-$C_3F_9)_3N$				

* Freon-type molecules provide interesting border-line cases and can differentiate between certain of the zeolites grouped as Type 3. Simple ketones and esters are also border-line cases.

FROM BARRER, R.M. (1978)


Ca-A; O2; 30; *
Ca-A; N2; 30; +
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CC/gm Zeolite
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400
500
600
700
800
Pressure, mm