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Zeolite Encapsulation of H₂

S. Cooper*

J. F. Lakner

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*University of Michigan student employed at LLNL for the summer (1981).

LAWRENCE LIVERMORE LABORATORY
University of California • Livermore, California • 94550

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ZEOLITE ENCAPSULATION OF H_2

ABSTRACT

Experiments with H_2 have shown that it is possible to encapsulate gases in the structure of certain molecular sieves. This method may offer a better means of temporarily storing and disposing of tritium over some others presently in use. The method may also prove safer, and may enable isotope separation, and removal of ^3He . Initial experiments were performed with H_2 to screen potential candidates for use with tritium.

INTRODUCTION

The separation of tritium from gas streams and its safe and economic storage are the focus of ongoing scientific study. Presently, tritium is stored in the form of hydrides or in gas cylinders. Each method has drawbacks, such as high costs, low efficiency, or safety problems. An alternative may be the use of zeolites (molecular sieves) for storing tritium. Storage of $H_2^{1,2}$ and Kr^3 in zeolites has been demonstrated.

Additionally, the zeolites could possibly be used to separate ^3He from tritium (it is hoped that the ^3He would be released, leaving the tritium in the sieve). The question of whether these zeolites could be used to separate tritium from D_2 or H_2 has to be determined (their kinetic diameters may be equal, making separation impossible).

The tritium could be encapsulated in the zeolites as a means of immobilizing it for disposal or simply as a temporary storage medium from which the tritium could be recovered for use in the future.

ZEOLITES

Zeolites ("molecular sieves") are crystalline, hydrated aluminosilicate compounds. There are some 100 synthetic and some 34 naturally occurring zeolites, which have extremely uniform pore openings. The pore diameters, in sizes 3 to 10 Å, vary 1 Å or less for each diameter. This precise structuring contrasts with the widely random pore sizes of adsorbents like silica gel (100 to 200 Å) and activated charcoal (20 to >10,000 Å).

Molecular sieves have a three-dimensional interconnecting network structure of SiO_4 and AlO_4 tetrahedra.⁴⁻⁷ The tetrahedra are formed by four oxygen atoms surrounding a Si or Al atom. This structure permits an orderly sharing arrangement, allowing tetrahedra to build uniformly in four directions. Each oxygen atom has a -2 charge; each Si has a +4 charge and each Al atom has a +3 charge. The trivalency of Al causes the AlO_4 tetrahedron to be negatively charged, requiring an additional cation to balance the framework electrically. Thus, the structure may have Na, K, or Ca cations in the network. These charge-balancing cations can undergo reversible replacement reactions with other cations in aqueous solution.

In the molecular-sieve framework, up to half the quadrivalent Si atoms can be replaced by trivalent Al atoms. By controlling the ratios of the starting materials, it is possible to produce molecular sieves containing different ratios of Si to Al ions and different crystal structures containing various cations.

In type-A zeolites⁴ the tetrahedra are grouped to form an array of truncated octahedra with a SiO_4 or AlO_4 tetrahedron at each point (Fig. 1). This is known as a sodalite cage. The free diameter of the cage is about 6.6 Å; the windows of the cage are 2.2 Å in diameter. For detailed structure analysis, see Refs. 4, 5, and 6.

If sodalite cages are stacked in simple cubic forms, a network of cavities or "α cages" about 11.4 Å in diameter emerges, which is accessible through 4.2-Å-diameter openings. Eight oxygen ions surround the openings, which are partially blocked by exchangeable cations. Furthermore, there are crystallographic sites in many zeolites besides those at gates that can be occupied by cations.⁸

Figure 1. The truncated octahedron (a) and (b) the array of truncated octahedra in the framework of zeolite A (by permission of J. Wiley & Sons, from: Zeolite Molecular Sieves, D. W. Breck, 1974).

The Na form of the type-A zeolite can be represented by the formula

The number of water molecules in the structure X can be as high as 27, which is equivalent to 28.5 wt% water.

The water of hydration that fills the cavities during crystallization of a zeolite is bound loosely and can be removed by heating leaving voids that are refillable with other fluids. A zeolite can be used to selectively adsorb only those molecules that can enter the pores while excluding molecules whose larger diameters prohibit them from passing through the pores. However, the function of the zeolite as a molecular sieve is not enough by itself for encapsulation to occur. There must also be a mechanism by which the zeolite retains a gas after selectively adsorbing it.

ENCAPSULATION

Pore size can be adjusted to allow selective adsorption, if a zeolite is selected that has an appropriate cage aperture and that introduces appropriately sized cations into the structure by ion exchange. Under steady temperature and pressure conditions, fluid molecules with small enough diameters can then readily pass through the gates of the framework, filling the α - and β -cage cavities.

For the molecular sieve to encapsulate a molecule, the cation gate must first allow passage of the intruding molecules (in this case H_2) into the α and β cages, and then prohibit passage of the same molecules out of the cages. This seemingly impossible procedure can be accomplished using high pressures and temperatures. The cation size is selected so that the apertures to the cages are smaller at room temperature and pressure than the molecules to be encapsulated. But as the temperature and pressure are increased, two things occur: 1) the kinetic energy of the fluid molecules is increased, effectively reducing the potential at the gate; and 2) the cations become more mobile because of their increase in energy, effectively increasing the size of the cation gate. The combination of these two effects can be likened to the opening of a gate, thereby allowing H_2 or other gas molecules under pressure to fill the void spaces. The temperature of the system is lowered (quenched) while a high rate of pressure is maintained. This reverses the above occurrences and allows encapsulation. When the pressure is reduced, the H_2 molecules no longer have the energy to overcome the gate potential.

The encapsulate can be released by raising the temperature to the level at which encapsulation occurred; some of the H_2 may desorb at lower temperatures than this.⁹

In August 1979, LLNL confirmed the technical feasibility of H_2 encapsulation in a type-4A synthetic zeolite.² A maximum of $71\text{-cm}^3 H_2/\text{g}$ zeolite was encapsulated at high temperature (420°C) and under high pressure ($20,000\text{ psig } H_2$).

From May through August 1981, other zeolites and related substances were screened and selected for their potential suitability to this application. The technical feasibility of H_2 encapsulation was evaluated for the following zeolites:

- Zeolon-400, (synthetic clinoptilolite zeolite)
- Natural chabazite zeolite

- Zeolon-500, (synthetic chabazite/erionite zeolite)
- Unleached synthetic sodalite zeolite
- Sodalite
- Feldspathoids, cancrinite
- Linde type-3A zeolite
- Vycor "thirsty glass"
- Davison 3A

The above were chosen for various reasons outlined in their respective sections of this report. Each displays a channel geometry and dimensions consistent with this application when such characteristics are known (including adequate pore opening dimensions and void volume). Pore opening dimensions are given as kinetic diameters, which are cross-sectional diameters of hydrated pore openings. By using this diameter, elliptical and circular openings can be compared.

Throughout the paper, the term adsorption is used because, according to Breck, "It best describes the interaction between a molecule and a surface, whether it is the external surface or the internal convoluted surface of a dehydrated microporous zeolite crystal."⁴

ION EXCHANGE

Type-4A zeolite contains Na^+ cations, which are too small to allow retention of hydrogen. Hydrogen is such a small molecule (variously reported as having a kinetic diameter of 2.4 or 2.89 Å) that it is unhindered by the Na gate. Once H_2 has entered the structure, it may leak out just as readily. Therefore, to promote H_2 encapsulation, the Na ion must be replaced with a larger cation. The Cs ion was chosen for the ion exchange because of its large radius ($r = 1.67 \text{ Å}$).¹⁰ Fraenkel and Shabtai also used Cs.¹ In the case of chabazite, substantial pore openings in addition to ion exchange are reduced by the occlusion of salt. Rb was also used.

Other ions with radii between those of Na and Cs are being considered for further H_2 encapsulation experiments. These include the alkaline and rare earths, which are listed partially in Table 1.

The highest degree to which Cs can replace Na is between 62% and 65%.^{4,12} It is not enough merely to exchange the Na cation for that of Cs. Another consideration is that the exchange of Cs for Na reduces the void

Table 1. Partial listing of cations that can be used for ion exchange and their radii.¹¹

Ion	Radius Å (calculated)
Na ⁺	0.95
K ⁺	1.33
Rb ⁺	1.48
Tl ⁺	1.40 ^a
Ba ⁺	1.53
Ba ⁺²	1.35
NH ₄ ⁺	1.42
La ⁺	1.39
La ⁺³	1.15
Sr ⁺²	1.13
Sm ⁺³	1.04 ^a
Cs ⁺¹	1.69 ^a

^a Periodic table.

volume of the zeolite, also reducing the diffusion rate of H₂ molecules. These two factors reduce H₂ storage capacity. On the other hand, if the degree of exchange is not enough, the retention ability of the zeolite is greatly diminished.

Because exchange by any cation is a function of its concentration in the solution, we chose to vary the concentrations of the salt solutions. Exchanges of univalent cations for other univalent cations are more easily accomplished than exchanges of univalent cations for divalent cations and vice versa. Uni-univalent exchanges may frequently reach equilibrium in 10 h. To achieve 90% exchange, for example, ion exchange would have to be performed for roughly 1/10 the time required for the exchange to reach equilibrium. Uni-divalent exchanges are more temperature-dependent and can take from four days to three weeks to reach equilibrium.

Zeolite ion exchange capacities can vary for many other reasons, including differences in chemical composition, binding agents, water content, and the occurrence of nonstoichiometric adsorption.¹³

John Masselli of the Davison Washington Research Center, Columbia, MD, contributed the following information on ion exchange of zeolites.

- Because type-4A (Na^+ form) is not acid-stable, ion exchange must be done at a pH of 7 to 7.5.
- It is very difficult to get Cs^+ into the Ca^{++} form of zeolite. Ca^{++} is the more stable.
- A Pauli high-charge cation sticks in the zeolite structure very well (better than a monovalent cation), and is difficult to dislodge.
- The less the ionic charge on a cation, the easier it is to dislodge that cation.
- Trivalent ions are almost impossible to dislodge from the structure.

To determine the effect of cation exchange on H_2 encapsulation, we prepared 10-g zeolite samples with different ratios of Cs to Na . Each sample was prepared in a reflux column with a continuously agitated solution of CsCl in deionized water at 80°C. We controlled the degree of exchange by varying either the concentration of the CsCl solution or the length of time samples were exposed to the solution. Concentrations ranging from 3 to 35 g CsCl/ml water were used. Standard atomic absorption methods determined the percent of cation exchange.

After exchange, the suspended particles were filtered off and the samples were washed with hot distilled H_2O until all traces of entrained salts were removed. The samples were then air dried, and then dehydrated, oxidized and activated at temperature.

Zeolite samples (about 1 g) were dissolved in a solution consisting of 15 ml of concentrated (49%) HF and 10 ml of concentrated nitric acid. This solution was heated to 80°C on a hot plate and left to digest the zeolite for a few hours. When most of the zeolite had apparently dissolved, the solution was fumed off, and a whitish residue remained. The process was repeated with a fresh solution of HF and nitric acid to ensure complete digestion of the sample. The residue was picked up with 5 ml of HCL and diluted with water to the amount needed for the atomic absorption analysis.

The analysis gave Na and Cs in grams. From these two values, the number of atoms of each was calculated. From this, the percentage of Cs cations was determined (we call this quantity the percentage of Cs exchange).

Figure 2. Pressure vessel assembly for T_2 zeolite experiments.

Figure 3. Components for T_2 molecular sieve work.

APPARATUS AND PROCEDURE

The apparatus and procedure have been described in Refs. 14 and 15. The apparatus for tritium work is shown in Figs. 2 and 3.

RESULTS AND DISCUSSION

Due to time limitations, we had chosen to restrict ourselves to a single pressure and temperature excepting our experiments on clinoptilolite, Zeolon 500, and type-4A zeolite. This section begins with a summary of results and is followed in the appendices by a detailed discussion of each zeolite.

Table 2 represents the final results for encapsulation of H_2 in 11 materials.

Table 2. Results of screening tests for H₂ encapsulation in various materials.

Zeolite	Ion exchange (%)	Temp. (°C)	Pressure H ₂ (psig)	Encapsulation (cm ³) H ₂ /g zeolite (STP) by desorption ^a
Clinoptilolite Cs, exchange	53.93	350	10,000	1.17
Chabazite, natural	0	450	15,000	9.98 ^b
Chabazite, natural, Cs exchange	42.46	450	15,000	2.98
Zeolon 500 synthetic chabazite-erionite (Norton)	0	450	15,000	2.20
Zeolon 500 synthetic chabazite-erionite (Norton)	35.28	450	15,000	2.29
Davison synthetic type-3A	0	450	15,000	12.28
Davison synthetic type-3A Rb exchange	13.5	450	15,000	39.0
Cancrinite	0	450	15,000	3.31
Sodalite synthesis, unleached	0	450	15,000	32.38
Vycor "thirsty glass" (Corning)	0	450	15,000	1.67
Type-4A Cs exchange (Linde)	43.18	420	15,000	47.8 ^c
	43.18	420	20,000	71

^a The adsorbed values were usually higher for the zeolite than the desorbed values except in the case of Linde 4A where they were about equal. The discrepancies are probably due to the release of gas that did not remain trapped at 1 atm in the pore system.

^b May include a substantial amount of adsorbed H₂ or other gases.

^c Ref. 2.

The best candidate presently for T₂ work is the Cs-exchanged Linde 4A zeolite. It has a capacity of 47.8 cm³/g zeolite when prepared under pressures of 15,000 psig H₂ at 420°C. Davison type 3A, Rb exchanged, is the second best candidate, with a capacity of 39.0 cm³/g zeolite, under 15,000 psig and at 450°C encapsulation temperature. Unleached sodalite is the third best candidate. These values are the maxima for a series of ion exchanged samples for this pressure and temperature.

Care must be taken in interchanging the zeolites (e.g., 4A vs 3A) of different companies.

The synthetic zeolite, Davison 3A,⁷ differs from the Linde 4A. Davison 3A has a simple cubic structure of sodalite β cages while Linde has both α and β cages of the sodalite structure. Linde 4A has only the Na cation. Davison contains both Na and K ions. The K ion causes a reduction in pore size to 3 Å. The Rb exchanges showed some increase in capacity. Exchanging this zeolite with Cs may show an increase over the unexchanged 3A.

If clinoptilolite were to be used, additional pretreatment would be needed (probably with acid to increase the adsorptive capacity).⁴

The equilibrium of gas with chabazite was slow. Exposing chabazite to H_2 pressures for a longer time may increase its capacity.¹⁶

There is the potential of exchanging the unleached sodalite with K^+ ions and encapsulating a greater amount of H_2 . Using leached sodalite may also increase the capacity. Experiments with K-85 by Exxon Nuclear substantiates this idea.³

We were surprised that cancrinite did not encapsulate more H_2 . Experiments with neon (2.75-Å diameter vs 2.89 Å for H_2) by Barrer and Vaughn¹⁷ showed that 7 cm³ Ne/g zeolite were trapped.

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APPENDICES

APPENDIX A

CLINOPTILOLITE

The adsorption or encapsulation of H_2 by the mineral clinoptilolite has not been investigated to date.

CHARACTERIZATION

For our experiments, we obtained a synthetic clinoptilolite Zeolon-400, from the Norton Company. They provided 1/16-in. diameter pellets containing 5% alumina binder. The pellets were reduced to 1/4 in. in length.

A sample was dehydrated at 480°C for 16 h. Analysis after this treatment showed this zeolite to be 8.0% H_2O by weight.

Clinoptilolite is a very silaceous zeolite, which indicates thermal stability.

The structure of clinoptilolite is largely unknown so that no statement can be made concerning its channel dimensions except that their diameter is greater than that of Cs^{+1} (Ref. 18). The kinetic diameters of the pore openings are 3.5 Å. Its void volume of 0.34 cm^3/cm^3 zeolite is of average magnitude.⁴

Standard atomic absorption analysis was used to determine that the K to Na ratio for Z-400 is 3.88:1. The unit cell formula for Z-400 may be

Clinoptilolite may be isostructural with heulandite, which has been shown to adsorb small-size molecular gases.⁴ However, clinoptilolite is thermally stable whereas heulandite changes structurally during dehydration at a temperature greater than 130°C.

ION EXCHANGE

Ten-gram samples of clinoptilolite were refluxed with 150 cm^3 of CsCl solutions for 1 h at 80° ±2°C. The solution concentrations were

0.2 (0.197); 0.4; 1.0; 3.0; and 2.0 g CsCl/150 cm³ H₂O .

The samples were washed with distilled water to release any entrained salt and then dehydrated, oxidized, and activated at 480°C for 16 h. At this temperature, clinoptilolite begins to lose its rehydration ability.¹⁹

D. G. Howery and H. L. Thomas²⁰ have determined that all sites originally occupied by Na⁺ ions in a Na-form of clinoptilolite are readily accessible to Cs⁺. This implies a large Cs⁺ capacity and rapid approach to equilibrium. Ames¹⁸ has found that the more closely a cation approaches Cs⁺ in size, the more selective clinoptilolite becomes for that cation. The size of Cs⁺ simulates the size of Na⁺ + H₂O. In addition to size, cation charge is important. The structural H₂O of clinoptilolite is not as firmly bonded to the aluminosilicate framework. A low field strength cation such as Cs⁺ is relatively free to migrate and to more readily become fixed on an exchange site under these circumstances.¹⁸

In Z-400, Na⁺ + Cs⁺, and K⁺ + Cs⁺ both occur, but K⁺ + Cs⁺ occurs to a lesser extent. Ames¹³ has determined that the thermodynamic equilibrium constant for the K⁺ + Cs⁺ is less favorable in a sample of Hector clinoptilolite. The majority of zeolites prefer K⁺ to Na⁺ cations. K⁺ is usually present to a lesser extent on the exchanges sites.¹³ Ames has also shown that Na⁺ will exchange with K⁺ in the solution. The Na + Cs equilibrium constant is 47.6 at 25°C.

Our experiments have achieved 60% Cs exchange. The limiting capacity of clinoptilolite for Cs⁺ has not been determined to date, but would appear to be in this range (see Fig. A-1). Barrer has also reported a steric hindrance to complete exchange of Cs in clinoptilolite. This arises because the intracrystalline pore space is insufficient to contain the number of large Cs ions that would be needed to fully neutralize the anionic framework charge.²¹

H₂ ENCAPSULATION

The initial H₂ encapsulation experiments were performed at 350°C and 10,000 psig H₂. Experiments with other zeolites were performed at 450°C and 15,000 psig H₂.

Many of the Cs-exchanged clinoptilolite samples tested showed low adsorption values (Fig. A-2), and a conflicting result for 59.53%. The first

Figure A-1. Norton Zeolon-400 (synthetic clinoptilolite); ion exchange.

Figure A-2. Norton Zeolon-400 (synthetic clinoptilolite); H₂ adsorbed (cm³) vs Cs content.

four samples were not desorbed. One sample with 59.53% Cs was desorbed of 1.17 cm³ H₂/g zeolite.

Barrer found that original clinoptilolite crystals are not permeable to N₂, another small gas molecule.²² He showed that adsorptive capacity for N₂ increases with acid treatment of the zeolite. The exchange of Na⁺ by H₃O⁺ followed by outgassing rendered the intracrystalline volume of the crystals permeable to the gas. Outgassing removed structural water and most of the water from hydration of the proton. The protons then offered little obstruction to N₂ diffusion into the crystals.

Breck⁴ also reported experiments on the adsorption of Kr and CO₂ by clinoptilolite. Although the original clinoptilolite did not adsorb Kr, acid-treated clinoptilolite adsorbed both CO₂ and Kr readily.⁴ Acid treatment would also result in hydrolysis of Al-O-Si bonds.²² With increased hydrolysis of these bonds, the zeolite remains initially crystalline before eventually disintegrating into colloidal silica and aluminum salts.

If clinoptilolite is to be examined further as a potential H₂ encapsulating medium, some type of additional treatment must be developed to prepare it.

APPENDIX B

ZEOLITE CHABAZITE

The zeolite chabazite has been found to be an excellent adsorber of $\text{H}_2^{23,16}$ in tests performed to confirm its H_2 encapsulation ability.

STRUCTURE

The average observed composition of natural chabazite is²⁴

The actual number of Na, K, and Ca atoms on chabazite must be related to the Al:Si ratio by the charge relation $(\text{Na} + \text{K}) + 2\text{Ca} = \text{Al}$.²⁴

Sets of two six-membered rings of tetrahedra are linked to form ditrigonal prisms, which are themselves linked by four-membered rings in a pattern analogous to the close-packing of spheres.²⁴ The resulting framework contains large elliptical cavities entered through six apertures formed from 8-rings. Each of the six apertures are shared between two cavities. Cavities are 6 to 7 Å in diameter and about 10 Å long. Their apertures are about 3 to 4 Å in diameter. Hydrated and chlorinated forms of chabazite contain circular apertures; dehydrated chabazite contains elliptical apertures as a result of structure changes to be described later. The apertures to the ditrigonal prisms are 1.3 Å.

In 2/3 of the unit cells, one Ca atom occurs at the center of the ditrigonal prisms, and one is attached to the inside surface of the cavity. However, in the other 1/3 of the cells, there is a Ca atom at the center of each of the 6-rings.²⁴ In chabazite, the five nearest neighbors of each Ca ion are water molecules.⁴ The water molecules are not linked to the framework directly and the Ca ions are isolated by them. The framework does not collapse during dehydration, but the Ca ions in the cavities move to other sites. This changes the apertures of the 6-rings. Also, the apertures may become blocked by the Ca ions.²⁴

There are no structural data on the positions of the other cations in chabazite.

ION EXCHANGE

Both natural chabazite and the Zeolon-500 synthetic chabazite and erionite mix, were exchanged with Cs^+ . The affinity sequence of chabazite is $\text{Cs}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$.²¹

Three methods are suggested by the literature to accomplish the uni-divalent exchange $\text{Ca}^{+2} + \text{Cs}^+$. Due to time limitations, the methods chosen were percolation at less than 100°C ²³ for 2 h for Zeolon-500, and hydrothermal exchange (Fig. B-1) at 151°C for four days in an autoclave²⁵ for the more structurally stable natural chabazite.

The uni-univalent exchange $\text{Na}^+ + \text{Cs}^+$ is fairly easy to accomplish in chabazite (up to 84%). (See Ref. 21 regarding exchange isotherms in chabazite.)

The prisms with openings of $1.3 \text{ \AA}$ are not available to the Cs ions, but the Cs ions can readily invade other parts of the crystals.²¹ The 6-ring apertures would be available, but the ions would have to lie displaced away from the ring to the center of the cavity. Four Cs cations could be accommodated per unit cell--two at the 6-rings while the other two attach themselves to the internal surface of the cavity or occupy 8-rings (which form the aperture between the cavities). We believe that the Cs would block the 8-ring apertures.²⁴

Furthermore, steric effects arise that may prevent complete uni-divalent exchange when there is insufficient intracrystalline pore space to contain the number of large ions that would be needed to fully neutralize the anionic

Figure B-1. Natural chabazite; hydrothermal method of ion exchange.

framework charge.²¹ J. V. Smith reports that Hoss and Roy found deficiencies of cations when ion exchange was carried out with pH below 7.²⁴

Barrer found that chabazite gives evidence of intracrystalline salt occlusion and exchange.²⁵ This observation agreed with the open channels of chabazite as determined from its molecular sieve properties.²⁵ The large Cs^+ ions cluster in the intracrystalline cavities where they must, for lack of space, displace increasing amounts of water.²¹ Three water molecules are now associated with the Cs^+ ion.

NATURAL CHABAZITE

CHARACTERIZATION

Natural chabazite was tested for H_2 encapsulation ability. A sample of natural chabazite from Goble, OR, was obtained from Ward's Scientific Establishment. The white crystals were isolated from the matrix and crushed to between 18 and 20 mesh. A heavy-liquid separation was attempted prior to hand-picking the crystals to 95% purity.

Thermogravimetric analysis showed the sample to be 16.8% water by weight. The chabazite was dehydrated, activated, and outgassed at 440°C for 20 h under a high vacuum.

ION EXCHANGE

Ten-gram samples of natural chabazite were exchanged with Cs^+ . The ion exchange was carried out hydrothermally in autoclaves at 150°C for three days (Fig. B-1). Due to time limitations, the refluxing period was reduced from recommended four ("exchange considerable")²³ days to three days. The solution concentrations were

0.3, 3.66, 1.0, 1.5, 2.0 g $\text{CsCl}/150 \text{ cm}^3$ water .

The samples were washed with distilled water to release most of the entrained salts.

As a result of exchange, a maximum of 64.78% Cs was obtained. Figure B-1 shows that exchange using the hydrothermal method is not limiting since it

could be used in an attempt to reach the published rates of 70% to 80% exchange.

Throughout the exchange, the vapor pressure in the sample was measured and found to be normal (50 to 60 psig).

In most instances, the color of the natural chabazite changed from white to tan. Inductively coupled plasma atomic emission analysis has shown that the sample of chabazite from Goble, OR contains microquantities of Fe, which may have been oxidized during the exchange.

H₂ ENCAPSULATION

Our results confirm the literature stating that chabazite adsorbs H₂ (Fig. B-2). However, exchanged varieties of both natural chabazite and Zeolon-500 encapsulated only 1 to 2 cm³ of H₂/g zeolite, at most (Fig. B-3). Unexchanged chabazite encapsulated 10 cm³ H₂/g zeolite.

The unexchanged variety of natural chabazite appeared to encapsulate 9.98 cm³ H₂/g zeolite. This value must be reproduced before it can reliably represent the true encapsulation of an unexchanged sample of natural chabazite. Prior to desorption of H₂, a vacuum of 100 μm was created to remove any excess gas left in the sample vessel in the void above the zeolite after the overpressure had been reduced to atmospheric pressure. However, in this instance, problems were encountered with the pressure equipment that necessitated the removal of the sample after dehydration and outgassing.

Figure B-2. Natural chabazite; H₂ adsorbed (cm³)/g zeolite vs Cs content at 450°C and 15000 psig.

Figure B-3. Natural chabazite; H₂ desorbed (cm³)/g zeolite vs Cs content.

Chabazite has been shown to adsorb other gases, such as CO_2 , SO_2 , and N_2 , readily from air, which may have occurred with this sample.

Emmett and DeWitt¹⁶ have found that gas equilibrium with chabazite is slow, showing that diffusion through the crystal takes place slowly. Our volume checks of chabazite using He gas would also seem to confirm this slow diffusion.

All of our results show natural chabazite to have little potential as an H_2 encapsulating medium, using these reaction conditions. However, exposing the chabazite to H_2 for longer periods of time may increase its capacity for H_2 encapsulation.

APPENDIX C

ZEOLON-500

CHARACTERIZATION

Zeolon-500, a synthetic chabazite and erionite mix, was obtained from the Norton Company in pellet form to be used for our H₂ encapsulation tests. The length of the pellets was reduced to about 1/4-in. X-ray diffraction analysis performed at LLNL determined that the chabazite present has the unit cell formula:

The erionite present has the unit cell formula:

Chabazite is the major component in Z-500.

Analysis after thermal treatment at 350°C for 16 h under vacuum showed Z-500 to be 14.4% water by weight. Zeolon-500 is not stable to aqueous treatment at a temperature greater than 60° to 70°C.

ION EXCHANGE

Ten-gram samples were refluxed with 100 cm³ of CsCl solutions for two h at 50° ± 2°C. The solution concentrations were

0.5; 1.0; 1.5; 2.0; and 2.5 g CsCl/100 cm³ water .

The samples were washed with distilled water to release most of the entrained salt. They were then dried in air at 500°C for 16 h. As a result of exchange, a maximum composition of 53.69% Cs was achieved (Fig. C-1). The graphic representation shows limiting exchange in the range of 50% to 60%. This was slightly less exchange than achieved using a hydrothermal method with the natural chabazite.

Figure C-1. Zeolon-500 (chabazite/erionite); ion exchange percolation method $\text{Na}^+ \rightarrow \text{Cs}^+$.

H₂ ENCAPSULATION

Both the unexchanged Zeolon-500 and the Cs-exchanged Zeolon-500 were loaded with 15,000 psig H₂ for 15 min at 450°C before being quenched to room temperature while under pressure. Samples were desorbed of H₂ for an accurate measurement of the encapsulated gas.

Our results confirm information in the literature that chabazite adsorbs H₂ (cf. Figs. C-2 and C-3). However, the unexchanged and exchanged varieties of Zeolon-500 encapsulated only 1 to 2 cm³ of H₂/g of zeolite at most.

Emmett and DeWitt¹⁶ have found that gas equilibrium is slow with chabazite, showing that diffusion through the crystals is also slow. Our volume checks of chabazite using He gas would also seem to confirm this slow diffusion.

Prior to desorption of the H₂, a vacuum of ~100 μm was created to remove any excess gas left in the void above the zeolite in the sample vessel after the overpressure had been reduced to atmospheric pressure. In the time required to create this vacuum (about 3 to 10 min) much of the H₂ adsorbed by Z-500 could probably have been desorbed at room temperature (Figs. C-4 and C-5).

All our results show Z-500 to have little potential as an H₂ encapsulating medium using these reaction conditions.

Figure C-2. Zeolon-500 (chabazite/erionite); H₂ adsorbed (cm³) vs Cs content; 10,000 psi, 350°C.

Figure C-4. Zeolon-500 (chabazite/erionite); H₂ desorbed (cm³) vs Cs content; 10,000 psi, 350°C.

Figure C-3. Zeolon-500 (chabazite/erionite); H₂ adsorbed (cm³) vs Cs content; 15,000 psi, 450°C.

Figure C-5. Zeolon-500 (chabazite/erionite); H₂ desorbed (cm³) vs Cs content; 15,000 psi, 450°C.

SODALITE

The four main groups of aluminosilicate framework structures are feldspars, feldspathoids, zeolites, and quartz.

Typical feldspathoids are sodalite and cancrinite. The cubic sodalite structure is formed by stacking sodalite cages in eightfold coordination.¹⁷ The sodalite cage is a truncated octahedron formed from the shared oxygen atoms by the Al-SiO_4 tetrahedra. The octahedron has eight 6-ring and six 4-ring faces. A given central cage (called the β cage) shares each of its 6-ring faces with one of eight other such cages. This arrangement fills all space without creating additional cages. Each sodalite cage is hollow with a free diameter of 6.6 Å, and access to these cages is through the 6-ring faces of 2.3-Å free diameter. In an ideal sodalite free of any occluded salt or alkali, six of the eight 6-ring faces in any cage are occupied by Na^+ ions.

Naturally occurring sodalite contains interstitial NaCl. Its typical oxide formula is $3(\text{Na}_2\text{O}, \text{Al}_2\text{O}_3, 2\text{SiO}_2)2\text{NaCl}$.²⁶ Synthetic analogs of sodalite normally contain interstitial NaOH and/or water molecules, referred to as "basic" sodalite or sodalite hydrates. The unit cell composition of an ideal sodalite hydrate $\text{Na}_6[(\text{AlO}_2)_6(\text{SiO}_2)_6]8\text{H}_2\text{O}$ becomes $\text{Na}_6[(\text{AlO}_2)_6(\text{SiO}_2)_6] \times \text{NaOH}, (8 - 2x)\text{H}_2\text{O}$ since each NaOH replaces two water molecules.¹ Because water is present, these synthetic analogs fall within the category of zeolite. Barrer and White²⁶ report that Barth has found the NaOH to be reactive and hence present in the sodalite as Na^+ and OH^- ions rather than NaOH. The position of the Na^+ ions will be similar to the position of the structural Na^+ ions, i.e., near the 6-rings.³

A sample of synthetic, unleached, powdered sodalite produced by Grace Co. was obtained from Exxon Nuclear Idaho Co. The Na/Al ratio was 1.26:1.

The sample was dehydrated, activated, and outgassed under vacuum at 500°C for 16 h. Analysis after this thermal treatment showed the sample to be 12.6% by weight H_2O .

The sample was heated to 450°C and exposed to 15,000 psig of H_2 for 15 min before being quenched to room temperature while under pressure.

Sodalite adsorbed $72.90 \text{ cm}^3 \text{ H}_2/\text{g zeolite}$ and encapsulated $32.38 \text{ cm}^3 \text{ H}_2/\text{g zeolite}$.

Exxon Nuclear Idaho Co. exchanged this type of unleached sodalite with K^+ , which has substantially reduced leakage of Kr from sodalite. An exchanged form of sodalite may encapsulate a greater amount of H_2 .

Figures D-1 and D-2 are plots of the fraction of H_2 desorbed (Q_t/Q_∞) vs $\sqrt{\text{time}}$ (h) and the fraction desorbed vs temperature in sodalite (cf. Ref. 17 for this type of plot). A histogram of the aliquot "Q" (g) vs temperature is shown in Fig. D-3. The aliquots of gases were taken at equal time intervals rather than at equal temperature intervals. The histogram shows:

- Sodalite is sensitive to desorption of H_2 from 110° to 130°C and from 200° to 240°C .
- Sodalite experiences steady desorption from 240° to 550°C .
- Sodalite is desorbed very little after 550°C .

The graph of the fraction desorbed vs temperature shows that 90% of the H_2 has been desorbed at 350°C .

Figure D-1. Desorption kinetics from sodalite where Q_t and Q_∞ are the amounts of gas released after times t , and ∞ , respectively.¹⁷ Temperature was rapidly raised from 20° to 569°C , then held constant at $555^\circ \pm 5^\circ\text{C}$ for ~ 5 h.

Figure D-2. Sodalite [Q_t/Q_∞ vs T (°C)].

Figure D-3. Size of aliquot (Q) in 10^{-5} g vs temperature (°C).

APPENDIX E

CANCRINITE

Cancrinite is also a member of the feldspathoid group of aluminosilicate framework structures.

The cancrinite structure differs from the sodalite structure in terms of the stacking sequence of the identical layers of linked 6-rings.¹⁷ This stacking sequence leads to a system of nonintersecting channels circumscribed by 12-rings with free diameters of 6.3 Å. Large cage-like units consisting of 18 tetrahedra with an internal diameter of 5 Å are the result. Smaller channels also exist within the tetrahedra. Cations are present in both the small and large channels.

Naturally occurring cancrinite can contain interstitial Na_2SO_4 , Na_2CO_3 , or NaCl . Its typical oxide formula is $3(\text{Na}_2\text{O}, \text{Al}_2\text{O}_3, 2\text{SiO}_2)\text{Na}_2\text{CO}_3$.³ Synthetic analogs of cancrinite also normally contain reactive NaOH and/or water molecules (referred to as "basic" cancrinite or cancrinite hydrates). Since water is present, its synthetic analogs also fall within the zeolitic category. The large anions, e.g., SO_4^{2-} and Cl^- are found in the large channels in natural cancrinite.

Barrer has theorized that a perfect cancrinite free of entrained salt or alkali would be expected to be a relatively open molecular sieve rather than an encapsulating agent.¹⁷ However, stacking faults in which an occasional layer sequence interrupts another layer sequence will block the wide channels by introducing 6-rings of 2.3 Å in diameter. During synthesis, some silicate anions can be entrained in the wide channels, thereby blocking them. The Na^+ ions located along the wide channels also restrict them somewhat. Barrer and Vaughan¹⁷ have found that the Na^+ ions associated with the 6-rings even prevent entry of He into the small cavities. Their calculations confirm that only the wide channels are available for encapsulation.

Barrer and Vaughan¹⁷ have trapped as much as 7 cm³ of Ne/g synthetic cancrinite hydrate at high temperature and under moderate pressure. The kinetic diameter of Ne is 2.75 Å. Similarly, the kinetic diameter of H_2 is 2.89 Å.⁴

Our initial experiment involved a sample of natural cancrinite obtained from Wards Scientific Establishment. Aggregates of cancrinite were isolated from a matrix including natural sodalite, nepheline, feldspar, vermiculite, and montmorillonite.

The sample was dehydrated, activated, and outgassed under vacuum at 500°C for 16 h. The color of the sample changed from orange-pink to light pink. Analysis after thermal treatment showed a weight loss of 3.14%.

Our results show that natural cancrinite encapsulated $3.31 \text{ cm}^3 \text{ H}_2/\text{g}$ sample. (It had been loaded for 15 min at 450°C with 15,000 psig H_2 before being quenched to room temperature while under pressure.)

Cancrinite hydrates and basic cancrinite could also be synthesized and tested for H_2 encapsulation potential. Cancrinite can also be ion-exchanged.

APPENDIX F

DAVISON 3A

CHARACTERIZATION

We investigated the H_2 encapsulation potential of the synthetic zeolite 3A. This zeolite is produced by Davison Chemical, a division of W. R. Grace Co., and distributed by Schoofs, Inc. of Moraga, CA.

First, we obtained size 8- to 12-mesh spherical beads with effective pore sizes of 3 Å.

Both Linde and Davison Chemical produce synthetic zeolite. The synthetic zeolite 3A produced by Davison differs substantially from the Linde synthetic zeolite 4A in the following ways:

1. Davison 3A has only a simple cubic structure of sodalite β cages while Linde 4A has both the α and β cages of the sodalite structure.
2. Linde 4A has only Na cations; the Davison 3A has been synthesized to contain both Na and K cations. The K cation, being larger, causes a reduction in the effective pore size to about 3 Å.

The typical oxide formula given by the manufacturer is

The sample was dehydrated, activated, and outgassed at 500°C for 16 h. Analysis after this treatment shows this zeolite to be 2.2% H_2O by weight.

ION EXCHANGE

The manufacturer informs us that the pore openings are approximately 3 Å. This includes allowances for the cations located at the openings. The presence of K^+ may reduce the affinity of H_2 for this zeolite as well as reduce the void volume.

The diameter of the K^+ ion is 2.66 Å.¹⁰ Rb^+ , with a diameter of 2.94 Å, was chosen to replace the Na^+ and/or K^+ ions.

Ten-gram samples of 3A were refluxed with 150 ml of RbCl solution for 1 h at $80^{\circ} \pm 2^{\circ}\text{C}$. The solution concentrations were

0.5; 1.0; 2.0; 2.5; 3.0; and 3.5 g RbCl/150 cm³ H₂O .

The samples were washed with distilled H₂O to release any entrained salt. The filtrates were exposed to AgNO₃ as a check for the chloride ion.

As a result of exchange, a maximum composition of 27% Rb was achieved (27% of all potentially exchangeable cations were Rb). The graphic representation of Fig. F-1 shows limiting exchange in the range of 25%-30%.

H₂ ENCAPSULATION

Samples were exposed to 15,000 psig of H₂ for 15 min at 450°C before being quenched to room temperature while still under pressure. The results were

	H ₂ /g zeolite adsorbed (cm ³)	H ₂ /g zeolite desorbed (cm ³)
Davison synthetic 3A (no exchange)	75.32	12.28
Davison synthetic 3A (6.62% Rb)	78.36	12.63
(13.5% Rb)	--	39.0

A vacuum of 100 μm was created over 3 min in the sample vessel prior to desorption to evacuate the void above the zeolite. Some of the H₂ adsorbed by 3A could be removed by this vacuum at room temperature.

Desorption kinetics of the H₂ encapsulated in these samples are represented in Fig. F-2.

Figure F-1. Davison 3A H₂ desorbed (cm³) vs Rb content.

Figure F-2. Davison 3A ion exchange.

APPENDIX G

VYCOK GLASS

Vycor glass is a Corning product. Its cloudiness is due to organics that can be removed in an oxygen atmosphere. Leaching of components results when the glass is handled with the fingers. Therefore, the glass is best preserved under water.

Vycor glass (weighing 21.22 g) was crushed to 32-mesh size, placed in an autoclave, and heated under vacuum at 575°C for 16 h (at 600°C for 14 h, 0.1- μ m vacuum, pores may close prematurely). There was a loss in weight of 1.489 g (Vycor glass is 7.02% water by weight).

The Vycor glass was outgassed with the vacuum while being raised to a temperature of 450°C. The sample was then pressurized with H₂ to 15,000 psig, and quenched to ambient temperature while maintaining pressure. The amount of H₂ adsorbed by the glass was 9.61 cm³. The amount of H₂ desorbed was 1.67 cm³ H₂/g Vycor.

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