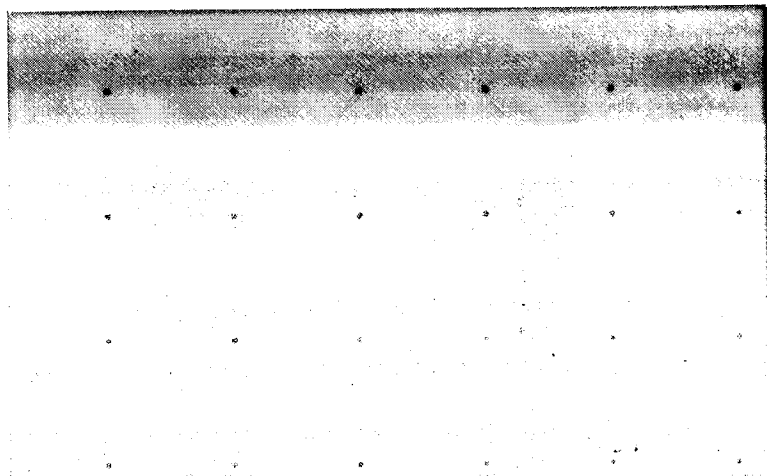


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An Interactive Qualifying Project Report
submitted to the Faculty of the
WORCESTER POLYTECHNIC INSTITUTE
in partial fulfillment of the requirements for the
Degree of Bachelor of Science

PRELIMINARY MARKET ANALYSIS FOR
LARGE ZEOLITE CRYSTALS

19 October 1987

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ABSTRACT

Zeolite crystals are used in the manufacture of countless products today, which utilize their properties of absorption, ion exchange and catalysis. It has been determined that zeolites grown in space could be much larger in size than any of those currently available on Earth. The objective of this IQP was to identify and examine some of the potential uses for these new, larger crystals. Of the several industries examined, the medical and nuclear industries offer the greatest potential.

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I. INTRODUCTION

The promise of space has opened up a countless number of new frontiers. Microgravity, low vibration platforms, and an almost perfect vacuum have caused scientists for decades to wonder how these unique properties of space can be applied to making products which would improve the quality of life on Earth.

Experimentation in space has been steadily increasing since the beginning of the United States' space program in the 1950s. With the advent of the Space Transport System, or Space Shuttle, more experiments are being carried out at greatly reduced cost. And with the coming of a permanent space station in the 1990s, space based manufacturing will also become a reality.

Today, zeolite crystals are used in the manufacture of a variety of numbers of products used in the United States, such as gasoline, and plastics. Their importance is undisputed. Recently, research conducted in the Chemical Engineering Department at Worcester Polytechnic Institute in Massachusetts has indicated that it would be possible to grow significantly larger zeolite crystals in the microgravity of space. WPI is also a member of the Clarkson Consortium, an association of colleges performing research for the purpose of growing various kinds of crystals in space. The National Air and Space Administration (NASA) has agreed to have an experimental crystal growth chamber, also designed at WPI, fly on the next Shuttle mission, currently scheduled for February of 1988.

The prospect of having zeolites which are much larger than

any of those which could be grown on Earth opens the door to many potential new applications which were not previously possible with smaller crystals.

The objective of this IQP was to identify possible areas of use for large zeolites. We identified those industries which we felt had applications to which large zeolites may be suited. We then tried to determine if zeolites could be introduced to the application and what, if any, advantages would they offer as compared to the existing way of doing things. The objective was not to examine all of the potential new uses of large zeolites - this would have been an impossible task, since many new uses might not be apparent until the large crystals are actually developed. Nor was the objective to justify the attempt to grow large zeolites in space - that has already been accomplished.

The Interactive Qualifying Project (IQP) is an essential part of the WPI Plan. It is required that all students complete an IQP, which relates science and technology to social needs and issues, to broaden their awareness of the importance of social/technological interactions. We felt materials processing in space was a topic which fully met this requirement. Upon narrowing this topic down, we felt a preliminary market study for space grown zeolites would also benefit the students and faculty working on large zeolites, in addition to meeting our own degree requirements.

This report will reveal our efforts and frustrations in identifying and investigating potential markets for large zeolites crystals. In the Background Section, some of the

technical highlights of zeolites are discussed, as well as why space based manufacture is thought to provide a solution to the problem of growing large crystals. The Background Section also discusses the current markets for small synthetic and natural zeolites. In the Methodology Section, there is a discussion of market studies and more specifically, how we did one for this IQP. The Results and Analysis Section includes the markets we examined, and the conclusions we came to concerning them. Finally, our Conclusions Section contains a summary of our thoughts on the large zeolites and this IQP.

II. BACKGROUND

2.1 Technical Aspects of Zeolites

Zeolite minerals are a type of porous or "hollow" crystal. Porous crystals (porous on a molecular scale), like all crystals are orderly, three dimensional arrays of atoms, ions or molecules. The porous nature of the crystals results in one, two and three dimensional channels, cavities and windows formed by the specific arrangement of atoms into a framework [1]. As an analogy, a building can be thought of as a framework (walls, ceilings, ...) surrounding the channels, cavities, and windows (halls, rooms, doors).

Although there are spaces between the atoms of the zeolite crystal, they are too small to readily allow the entrance of even the smallest molecules or atoms, such as water, oxygen, or carbon dioxide (these elements can diffuse slowly into the crystal). The class of crystal zeolites is unique in admitting and retaining both small and somewhat larger molecules [2].

Some other types of porous crystals include crystalline porosiles, porous aluminum phosphates, expanded clay minerals, and clathrates. These all exhibit molecular shape and size selectivity and (to different degrees) crystalline stability from the presence of guest molecules [1]. Zeolites can trap certain molecules as a sieve does. They can also bind up and selectively release specific molecules by adsorption or ion exchange [3].

In 1756 the Swedish mineralogist A.F. Cronstedt noticed that certain minerals appeared to swell and boil upon heating. He appropriately named these minerals zeolites meaning 'boiling

stones' (from the Greek; zein 'to boil' and lithos, 'stone') [4]. The bubbling he observed was from the release of water from the crystal.

There are 37 natural zeolite minerals known to exist today. The natural zeolites, including faujasite, chabazite, mordenite, and clinoptilolite, occur in various geological environments in the Earth's crust [2].

The framework of a zeolite crystal is composed of silicon, aluminum, and oxygen atoms. These three elements are combined into SiO_4 and AlO_4 tetrahedra, each tetrahedron consisting of four oxygen atoms surrounding a central silicon or aluminum atom (see Figure 2.1). Each oxygen atom is shared by two adjacent tetrahedra. Aluminum tetrahedra do not connect in series with themselves. These primary units join into secondary building units (SBU) (see Figure 2.2). It is a characteristic of zeolites to be composed of polyhedral, cage like structures (also formed of SBUs). The secondary units and polyhedra combine to form the zeolite frameworks. The ring like structures of the secondary units form the cavities and 'windows' of the porous crystals. Four typical zeolite structures are shown in Figure 2.3 [2,3,4].

The framework cavities contain alkali and alkaline metals such as lithium, sodium, potassium, calcium, and water molecules. The replacement of the silicon ions (Si^{+4}) by aluminum ions (Al^{+3}) gives rise to a net negative charge on the zeolite framework. The residual charge due to the AlO_4 tetrahedra is compensated by the presence of the metal cations. Each sodium or lithium ion can

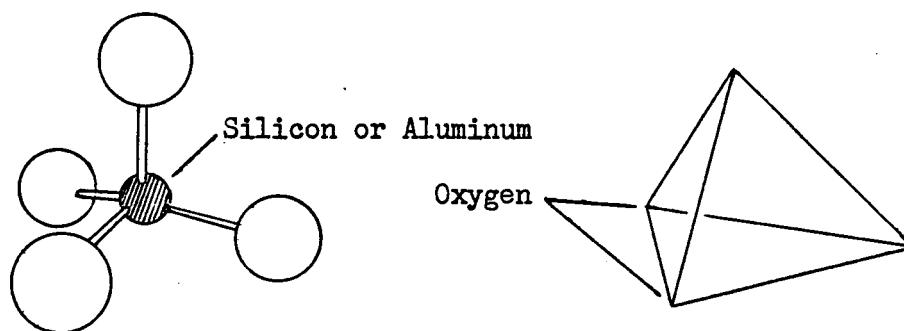


FIGURE 2.1: Representations of the SiO_4 or AlO_4 tetrahedron. Each tetrahedron consists of four oxygen atoms surrounding a central silicon or aluminum atom.

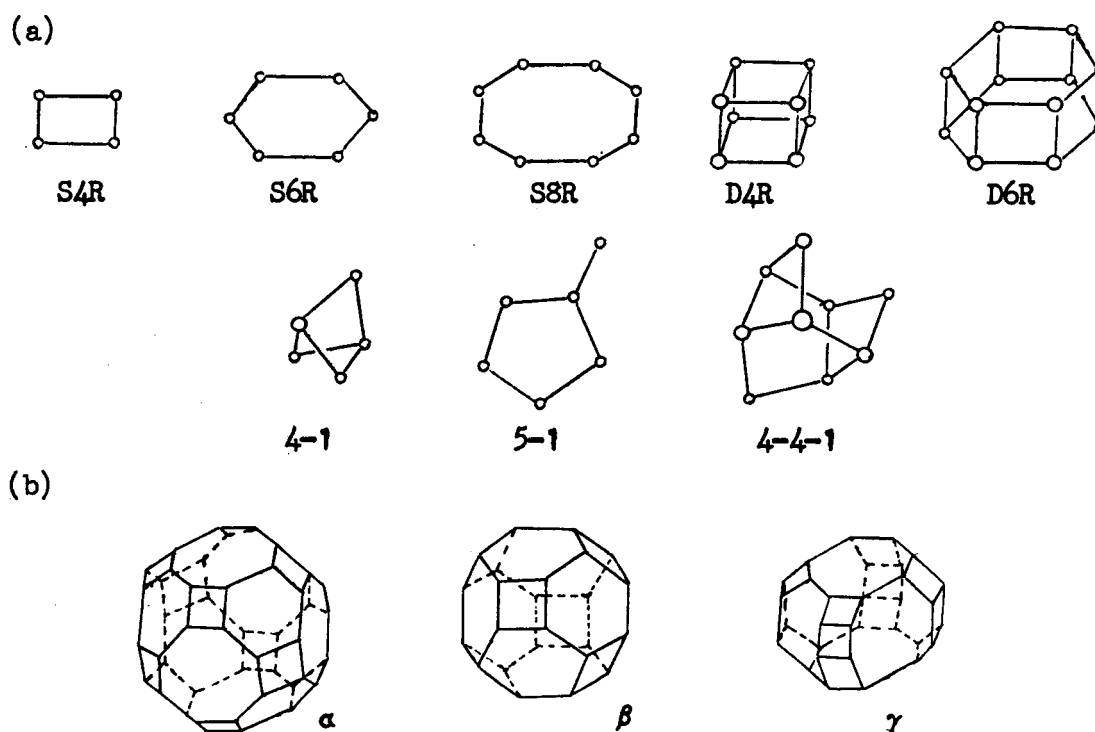
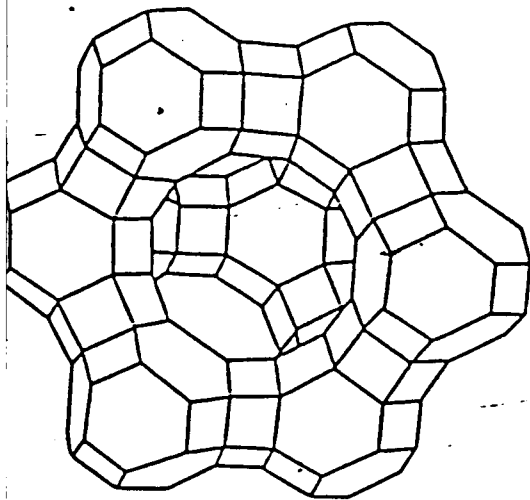
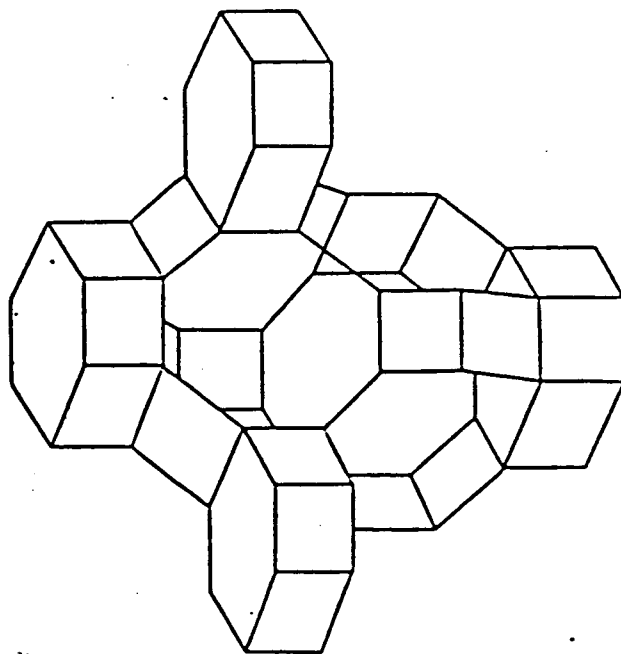


FIGURE 2.2: (a) Secondary building units of the zeolite frameworks: S4R or single four-ring; S6R or single six-ring; S8R or single eight-ring; D4R or double four-ring; D6R or double six-ring; complex 4-1 or T_5O_{10} unit; complex 5-1 or T_8O_{16} unit; complex 4-4-1 or $\text{T}_{10}\text{O}_{20}$ unit. (b) Geometrical representations of some polyhedra zeolite frameworks; α or truncated cubo-octahedron; β or truncated octahedron; and γ or 18-hedron; Each circle in (a) or corner in (b) represents the center of a tetrahedron.

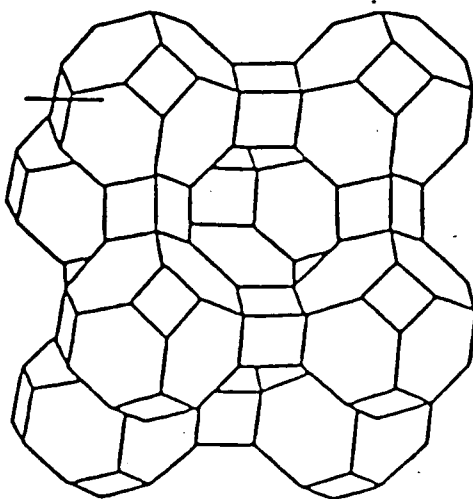
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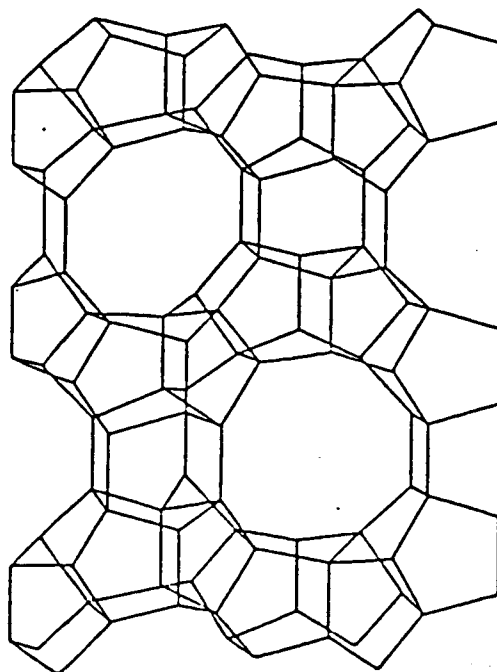
FAUJASITE



CHABAZITE



ZEOLITE A



PENTASIL LAYER

Figure 2.3: Structures of several zeolite crystals. The Si and Al atoms occur at the line intersections and oxygen atoms at the middle of the line segments. Cations and water molecules are not shown.

(Courtesy of Prof. A. G. Dixon, Worcester Polytechnic Institute.)

balance one aluminum atom (AlO₄ tetrahedron); each calcium ion can balance two aluminums. These cations are only loosely bonded to the zeolite structure and there is considerable free space to move in the large cavities. The water molecules are adsorbed on the inner surfaces of the channels of the framework. An important property of most zeolites is their ability to maintain crystal structure upon losing intracrystalline water [2,4,5].

These unique structural properties give the zeolites their desirable qualities, namely crystalline ion exchange, reversible dehydration, absorption molecular sieving, and uses as catalysts. The porous structure allows them to selectively separate, according to the size and shape of molecules, desired or undesired substances from each other. There is considerable variation in the size of these cavities, both within a given species and from one type of crystal species to the next. The molecular size pores range in size from about 2.5 to 10 angstroms in diameter (1 angstrom = 10⁻¹⁰ meters). Some of the zeolites have a porosity of nearly fifty percent of the total crystal volume [5].

Zeolites are among the most abundant of mineral species, being found in major deposits on every continent [6]. They occur in igneous, metamorphic and sedimentary rocks. Most of the large natural zeolite crystals come from filled cavities and fractures of igneous rocks, especially basalt, a common volcanic rock [4]. Volcanic ash serves as a source of silica and alumina which along with alkaline surface waters causes alterations in the basalt. Sedimentary zeolites occur as very small crystals, from 5 to 10

microns in size. These deposits are often huge and workable (suitable for mining). Zeolites are particularly abundant in saline alkaline lakes. Most sedimentary deposits consist of several types of zeolites, but virtually pure beds of single zeolite species have been found in the western United States desert areas. Other deposits are found in Japan, Italy, Cuba, Bulgaria, New Zealand, Nova Scotia, Korea, Mexico, and Germany. Analcime and clinoptilolite are among the most common type of sedimentary zeolite. Table 2.1 lists some representative natural zeolites and their properties. Table 2.2 lists natural zeolite mineral occurrences. Table 2.3 lists some synthetic zeolites and their properties [6,7].

Naturally occurring zeolites tend to be less than perfect. They tend to have structural errors and impurities. This has led scientists to develop synthetic versions of zeolites. In this way they can better control the conditions under which the zeolites form, allowing more specific and consistent chemical properties for use. The increasing present uses for zeolites and the future potential uses have prompted the demand for large amounts of pure, perfect crystals. Excellent results have been obtained in producing synthetic zeolites. Many of the natural zeolites can be produced synthetically, but new and unique crystal structures can also be produced. Synthetic zeolites (also called permutites) such as Zeolites A, X, Y, and ZSM-5 are extremely valuable since they can serve in specific applications not suited to other zeolites. The synthetic zeolites allowing the engineering of a crystal with the desired specific properties. There are, however,

TABLE 2.1

Zeolites									
name formula	colour	lustre	Mohs hardness	specific gravity	habit or form	cleavage	refractive indices	crystal system space group	remarks
analtime $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$	colourless, white, gray, pink	vitreous	5-5½	2.2-2.3	transparent to nearly opaque, brittle, well-formed crystals; radiating aggregates	very poor cleavage	$n = 1.479-1.493$	isometric Ia3d	classified as a zeolite because of its exchange and dehydration properties and as a feldspathoid because of its structure
brewsterite (Sr, Ba, Ca)Al ₂ Si ₆ O ₁₆ · 5H ₂ O	white; yellow, gray		5	2.5	prismatic crystals	platy cleavage	$\alpha = 1.510$ $\beta = 1.512$ $\gamma = 1.523$	monoclinic	
chabazite (Ca, Na ₂)Al ₂ Si ₄ O ₁₂ · 6H ₂ O	white, flesh-red	vitreous	4½	2.0-2.1	brittle, transparent or translucent, single, cube-like rhombohedrons	poor cleavage	$n = 1.470-1.494$	hexagonal R3m	
clinoptilolite (Na, K) ₄ CaAl ₆ Si ₃₀ O ₇₂ · 24H ₂ O	variable, but usually colour- less or white	vitreous	3½-4	2.1	transparent, brittle, coffin-shaped crystals	one perfect cleavage	$\alpha = 1.476-1.488$ $\gamma = 1.479-1.489$	monoclinic I 2/m	
dachiardite (K ₂ , Na ₂ , Ca) ₂ Al ₂ Si ₁₉ O ₄₈ · 18H ₂ O	colourless		4-4½	2.2	prismatic twinned crystals	one platy cleavage	$\alpha = 1.491$ $\beta = 1.496$ $\gamma = 1.499$	monoclinic	
edingtonite BaAl ₂ Si ₃ O ₁₀ · 3H ₂ O	colourless, white, pink, brown	vitreous	4-4½	2.7-2.8	pyramidal crystals; massive	two cleav- ages	$\alpha = 1.541$ $\beta = 1.553$ $\gamma = 1.557$	tetragonal P4 ₂ m	pyroelectric
epistilbite CaAl ₂ Si ₆ O ₁₆ · 5H ₂ O	colourless, white, pale pink	vitreous	4	2.2	sheaflike aggregates	one very good cleavage	$\alpha = 1.485-1.505$ $\beta = 1.497-1.515$ $\gamma = 1.497-1.519$	monoclinic	piezoelectric
erionite (Na ₂ , K ₂ , Ca) ₄ Al ₉ Si ₂₇ O ₇₂ · 27H ₂ O	white			2.0-2.1	woollike fibres; radiating crystal groups		$\alpha = 1.488-1.472$ $\epsilon = 1.473-1.478$	hexagonal P ₆ mc	
faujasite (Na ₂ , Ca) _{1.75} Al _{1.5} Si _{8.5} O ₂₄ · 18H ₂ O	colourless; yellowish		5	1.9	transparent or opaque rounded octahedrons	one distinct cleavage	$n = 1.471-1.480$	isometric Fd3m	has the most open structure of all the zeolites
ferrierite (Na, K) ₄ Mg ₂ Al ₆ Si ₁₀ O ₇₂ (OH) ₂ · 18H ₂ O	colourless, white	vitreous to pearly	3	2.2	radiating groups of bladed crystals	one perfect cleavage	$\alpha = 1.478$ $\beta = 1.479$ $\gamma = 1.482$	orthorhombic	
gishmondite CaAl ₂ Si ₂ O ₈ · 4H ₂ O	colourless or white, bluish, grayish, reddish		4½	2.2-2.3	bipyramidal crystals	one distinct cleavage	$\alpha = 1.531-1.538$ $\beta = 1.539-1.543$ $\gamma = 1.548$	orthorhombic Cmmm or Ccca	
gmelinite (Na ₂ , Ca)Al ₂ Si ₄ O ₁₂ · 8H ₂ O	colourless, white; yellow- ish, greenish, reddish-white	vitreous	4½	2.1	well-formed crystals	one good cleavage	$\epsilon = 1.474-1.480$ $\omega = 1.476-1.494$	hexagonal	
gonnardite Na ₂ CaAl ₄ Si ₆ O ₂₀ · 5H ₂ O	colourless, white, pink, brown	vitreous	5	2.3	spherules		$\alpha = 1.497-1.508$ $\gamma = 1.499-1.508$	orthorhombic	
harmotome BaAl ₂ Si ₆ O ₁₆ · 6H ₂ O	white to gray, yellow, red, brown	vitreous	4½	2.4-2.5	crosslike penetration; twinned crystals	one distinct cleavage	$\alpha = 1.503-1.508$ $\beta = 1.505-1.509$ $\gamma = 1.508-1.514$	monoclinic p2 ₁ m	
heulandite (Ca, Na ₂) ₄ Al ₉ Si ₂₈ O ₇₂ · 24H ₂ O	white to red, gray, brown	vitreous to pearly	3½-4	2.1-2.2	transparent, brittle, coffin-shaped crystals	one perfect cleavage	$\alpha = 1.491-1.505$ $\beta = 1.493-1.503$ $\gamma = 1.500-1.512$	monoclinic I 2/m	
laumontite CaAl ₂ Si ₄ O ₁₂ · 4H ₂ O	white to yellow or gray; some- times red	vitreous	3-4	2.2-2.3	prismatic crystals	two good cleavages	$\alpha = 1.502-1.514$ $\beta = 1.512-1.522$ $\gamma = 1.514-1.525$	monoclinic C2 or Cm	
levynite CaAl ₂ Si ₄ O ₁₂ · 6H ₂ O	colourless, white, grayish, reddish, yellowish	vitreous	4-4½	2.1	rhombohedral crystals		$\epsilon = 1.491-1.500$ $\omega = 1.498-1.505$	hexagonal R3m	
mesolite Na ₂ Ca ₂ Al ₆ Si ₉ O ₃₀ · 8H ₂ O	colourless to white; yellow, gray, pink, red	vitreous to pearly	5	2.3	needlelike crystal masses; almost in- variably twinned crystals	one perfect cleavage	$\alpha = 1.505-1.507$ $\beta = 1.505-1.507$ $\gamma = 1.508-1.508$	monoclinic C2	chemically inter- mediate between natrolite and scolecite;
mordenite (Na ₂ , K ₂ , Ca)Al ₂ Si ₁₀ O ₂₄ · 7H ₂ O	colourless, white; red, brown, yellow	vitreous	3-4	2.1-2.2	minute, transparent, brittle, coffin-shaped crystals; rosettes	one perfect, one good cleavage	$\alpha = 1.472-1.483$ $\beta = 1.475-1.485$ $\gamma = 1.477-1.487$	orthorhombic Cmcm or Cmc2	
natrolite Na ₄ Al ₄ Si ₆ O ₂₀ · 4H ₂ O	colourless, white, gray, yellow, red, pink	vitreous to pearly	5	2.2-2.3	slender, prismatic crystals; fibrous radiating aggre- gates	one perfect cleavage	$\alpha = 1.473-1.483$ $\beta = 1.476-1.486$ $\gamma = 1.485-1.496$	orthorhombic Fdd2	pyroelectric
phillipsite (K ₂ , Na ₂ , Ca) ₃ Al ₆ Si ₁₀ O ₃₂ · 12H ₂ O	colourless, white, pink, yellow, gray	vitreous	4-4½	2.2	brittle crystals, usually penetration twins	two distinct cleavages	$\alpha = 1.483-1.504$ $\beta = 1.484-1.509$ $\gamma = 1.488-1.514$	monoclinic P2 ₁ m or P2 ₁	
scolecite Ca ₂ Al ₄ Si ₆ O ₂₀ · 6H ₂ O	colourless to white; gray, pink, red, yellow	vitreous to silky	5	2.2-2.3	slender prismatic crystals, frequently twinned; radiating crystal masses; fibrous massive	one nearly perfect cleavage	$\alpha = 1.507-1.513$ $\beta = 1.518-1.520$ $\gamma = 1.517-1.521$	monoclinic Cc	
stilbite (Ca, Na ₂ , K ₂) ₄ Al ₉ Si ₂₈ O ₇₂ · 28H ₂ O	white; yellow, red, brown	vitreous	3½-4	2.1-2.2	sheaflike crystal aggregates; cross- like penetration twins	one very good cleavage	$\alpha = 1.484-1.500$ $\beta = 1.492-1.507$ $\gamma = 1.494-1.513$	monoclinic C2/m	
thomsonite NaCa ₂ Al ₅ Si ₅ O ₂₀ · 6H ₂ O	colourless, white; pink, brown	vitreous to pearly	5-5½	2.1-2.4	radiating spherical concretions; compact massive; columnar	one perfect, one good cleavage	$\alpha = 1.497-1.530$ $\beta = 1.513-1.533$ $\gamma = 1.518-1.544$	orthorhombic Pnma	pyroelectric
wairakite CaAl ₂ Si ₄ O ₁₂ · 2H ₂ O	colourless to white	vitreous	5½-8	2.3	usually twinned		$\alpha = 1.498$ $\gamma = 1.502$	monoclinic	
yugawaralite CaAl ₂ Si ₆ O ₁₆ · 4H ₂ O				2.2			$n = 1.495-1.504$	monoclinic	

TABLE 2.2

Occurrences of natural zeolite minerals

Name	Typical Occurrence in Igneous Rocks	Occurrence in Sedimentary Rocks
Analcime	Ireland, New Jersey, etc.	Western U.S., deep sea floor
Brewsterite	Scotland	
Chabazite	Nova Scotia, Ireland, etc.	Arizona, Nevada, Italy
Clinoptilolite	Wyoming	Western U.S., deep sea floor
Dachiardite	Elba	
Edingtonite	Scotland	
Epistilbite	Iceland	
Erionite	Rare; Oregon	Nevada, Oregon
Faujasite	Rare; Germany	
Ferrierite	Rare; British Columbia	Utah
Gismondite	Rare; Italy	
Gmelinite	Nova Scotia	
Gonnardite	France, Italy	
Harmotome	Scotland	
Heulandite	Iceland	New Zealand
Laumontite	Nova Scotia, Faroe Islands	New Zealand, U.S.S.R., Calif.
Levynite	Iceland	
Mesolite	Nova Scotia	
Mordenite	Nova Scotia	U.S.S.R., Japan, Western U.S.
Natrolite	Ireland, New Jersey	
Phillipsite	Ireland, Sicily	Western U.S., Africa, Sea floor
Scolecite	Iceland, Colorado	
Stillbite	Iceland, Ireland, Scotland	
Thomsonite	Scotland, Colorado	
Yugawaralite	Japan	

(D.W. Breck, Recent Advances in Zeolite Science, 1970)

Table 2.3 Structural Characteristics

of Synthetic Zeolites*

Zeolite	Structure		Ideal Unit Cell Symmetry	Building Units ^b				Water Void Volume ^c	T/ 1000 ^d
	Type/Group			S-R	D-R	Pore Opening	Polyhedra		
A N-A X Y	A/faujasite		Cubic, $Pm\bar{3}m$ (pseudo)	4,6,8	D-4	S-8, planar	T.O.	0.47	12.8
	Faujasite/faujasite		Cubic, $Fd\bar{3}m$	4,6	D-6	S-12, nonplanar	T.O.	0.51	12.4
	Sodalite/chabazite		Cubic, $P\bar{4}3n$	4,6	—	—	T.O.	0.50	12.8
								0.33 ^d	17.2
Hydroxy Sodalite (HS)	ZK-5/faujasite		Cubic, $Im\bar{3}m$	4,6,8	D-6	S-8, planar	—	0.44	14.7
	B(Pl)/phillipsite		Cubic, $Im\bar{3}m$	4,8	D-4	S-8, nonplanar	—	0.41	15.8
	Q/chabazite		Hex, $P6/mmm$	4,6,8	D-12	D-12, planar	Gmel.	0.38	16.7
	Gmelinite/chabazite		Hex, $P6_3/mmc$	4,6,8	D-6	S-12, nonplanar	Gmel.	0.44	14.6
ZK-5 B(Pl) Q S R G D	Chabazite/chabazite		Trigonal, $R\bar{3}m$	4,6,8	D-6	S-8, nonplanar	—	0.47	14.6
	Offretite-erionite/chabazite		Offr.: Hex., $P\bar{6}m\bar{2}$	4,6,8	D-6	S-12, nonplanar	Cancr., Gmel.	0.40	15.7
	L/chabazite		Erion: Hex., $P6_3/mmc$	4,6,8	D-6	S-8, nonplanar	Cancr.	0.32	16.3
	Cancrinite/chabazite		Hex., $P6/mmm$	4,6	—	S-12, planar	Cancr.	0.21 ^d	16.7 ^d
Hydroxy cancrinite W	Phillipsite-harmotome/ phillipsite		Hex., $P6_3$	4,8	—	S-12, nonplanar	Cancr.	0.31	15.8
	Mordenite/mordenite		Ortho., $B2mb$	4,8	—	S-8, nonplanar	—	0.28	17.2
	Analcime/analime		Ortho., $Cmcm$	4,5,8	—	S-12, nonplanar	—	0.18	18.6
			Cubic, $Ia\bar{3}d$	4,6	—	—	—		
Zeolon C									

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a number of quantitative and theoretical aspects of zeolites not yet fully understood.

Zeolites are produced under conditions of low temperature and pressure. The typical approach used in making synthetic zeolites starts with very reactive compounds including freshly prepared aluminosilicate gels, sodium aluminate, and sodium silicate. The starting materials are placed in a high pH solution, obtained by using alkali metal hydroxides and or organic bases. The solution is then appropriately enclosed, heated and pressurized. The crystals form and settle from the solution. Many of the synthetic zeolites are formed at temperatures ranging from room temperature to the boiling point of water, and with no more pressure than that generated by the reaction itself (autogenous). The formation of the zeolites is influenced by such factors as: the nature of the starting materials, homogeneity or heterogeneity of the mixture, pH of the mixture, seeding, temperature and pressure of the mixture, and reaction time (typically hours to days). As a result of the high degree of variability in forming zeolites, both natural and synthetic zeolites have a wide range of chemical composition, including variation in water, cation, and Al/Si ratios. The ease with which zeolites can be made makes them an ideal product for large scale manufacturing [8,9].

2.2 Current Uses of Zeolites

Since Cronstedt's discovery more than two centuries ago of the zeolite mineral stilbite, these crystals have only recently been commercially used to large extent [6]. Originally, the early investigations of zeolite properties were performed on rare mineral specimens collected from cavities of basaltic rocks (a common volcanic rock). In the 1800's, the ion exchange abilities of the minerals were discovered. These cations could be exchanged with other cations, with preferential exchange depending on the zeolite specie and the intrastructural variations (such as the Si/Al ratio). This led to the use of zeolites in softening hard water; that is exchanging calcium and magnesium of hard water with sodium ions from the zeolite. Heating zeolites to drive out intracrystalline water made 'dry' or active zeolites which then had enormous adsorption properties. These active zeolites can be used as drying agents (water adsorbers) [2].

Researchers of the early 1900's, recognizing the value of zeolites as ion exchangers, sought to prepare synthetic zeolites, since the natural minerals were not found in significant amounts. Reports in the late nineteenth century recorded occurrence of zeolites in sedimentary tuffs (compacted volcanic ash) and marine deposits. Discovery of deposits have increased since then, especially since World War II [2,5]. These deposits consist of very small crystals (compared with the basaltic zeolite samples) homogeneously distributed throughout the rock. Although the variety of sedimentary zeolites is limited (about five major types), a typical deposit can yield millions of tons annually.

With the advent of synthesizing zeolites in large quantities and discovery of workable natural zeolite deposits, significant progress was made in zeolite research. Various uses continue to be developed for the crystals today in the areas of synthesis, structure, ion exchange, catalysis, diffusion and adsorption.

There are specific fields of application in which synthetic zeolites have no alternative (interchangeable) natural zeolite, owing to their strict uniformity of composition, efficiency, performance quality, characteristics, size and operation of plants, and economic costs. In general, large scale, less sophisticated utilizations are reserved for natural zeolites. Application of natural zeolites (as with synthetic) requires careful examination of original rock deposit in terms of zeolite type and constancy of composition. Regenerability of a zeolite product is also important in considering which specie (natural or synthetic, type ...) can be most economically utilized [9].

It is difficult to accurately judge the present commercial usage of zeolites (natural or synthetic). According to a 1980 investigation carried out in Italy, the production of natural zeolites reached 300,000 tons per year, most of this production belonging to Europe and Japan. The greatest usages were in the building and paper industries [9]. Clarke (also 1980) noted use of some 150,000 tons annually in the building industry (mostly as components of blended cements) and 480,000 t/a in paper making industries (as a substitute for kaolin clay which is used as a paper filler or coating) [6]. The United States produces less natural zeolites due to extensive synthetic product research.

Table 2.4 gives some utilizations of natural zeolites (1984) [9].

Most of the uses of zeolites come under one of three categories (there are no exact categories), namely; ion exchange, sorption, and catalysis. Some uses of zeolites in these categories are given below.

Sorption: Simple heating of zeolites will cause loss of water, in this dry or activated state the crystals will readily readsorb water. These activated zeolites are used as anti-fog agents for double and triple glazed windows (dries the air space inside glazed or insulated glass units), as air driers in truck air-activated braking systems, and in natural gas pipelines or industrial gas processes, including removing water from ethylene, hydrogen, ethanol, alcohol, and CO₂ streams [2]. Activated zeolites will also adsorb other molecules sufficiently small to enter the pores. Materials having this size selective adsorption are called molecular sieves. Molecules larger than the nominal pore diameter are excluded from adsorption.

With appropriate modifications, the natural zeolite clinoptilolite proves especially useful as a desiccant (since clinoptilolite is one of the more common types), removing water from air, refrigerants, organic liquids (xylene, transformer oil), and in adsorbing SO₂ and CO₂ from gas streams [6]. In the case of refrigeration, clinoptilolite proves to have comparable chemical stability (after mechanical and chemical treatment), adsorption, mechanical properties, and is less expensive than any synthetic adsorbent [10].

Some sorption properties of natural and synthetic zeolites

are given in Table 2.5.

Ion Exchange: In this area, zeolites compete with resin ion exchangers. Only where resins are unsuitable have zeolites found application. Zeolites are used in four main areas as ion exchangers.

As mentioned earlier, zeolites are used to soften water, making them particularly useful in detergents where they partially replace environmentally undesirable tri polyphosphate. Synthetic zeolites fare better in water softening than natural zeolites, since the synthetic crystals have higher ion exchange capacities. In the treatment of waste, zeolites are used in removal of ammonia and ammonium from municipal, industrial, and aquacultural (fish ponds) waste waters. Natural zeolites, clinoptilolite and phillipsite, have high selectivity for the NH_4^+ ion. Again the synthetic zeolites (Linde F and W) may replace the natural materials, though good results (especially in large scale use) have been obtained with the natural zeolites. Zeolites also find agricultural use in retaining fertilizer, pesticide, and soil nutrients for extended periods of time. Finally, there is widespread application of zeolites to the removal of radioactive isotopes from radioactive waste. In 1980-82 Union Carbide used a mixture of natural (chabazite) and synthetic (Zeolite A) to treat the contaminated waters at Three Mile Island [5,6,11,].

Catalysis: A catalyst is a substance that modifies and or increases the rate of a chemical reaction without being consumed or changed in the process. With zeolites, reactants enter into the porous structure and react with the internal surface of the

TABLE 2.4.

Picture of the present world utilization of natural zeolites

(Approximate consumption values in ton/year)

	Japan	USA	Europe
<u>Building industry</u>	8,000	*	140,000
(zeolitic tuffs)			
<u>Industry/Agriculture</u>			
Insulation/protection	1-2,000	*	*
Paper filler	57,000		
Soil conditioner	10,000	*	*
Additions to diets	5-6,000	*	*
Chelating agent (NH_4)	2.5-5,000	*	*
fish cultural systems			
Deodorizing animal excr.	200	*	*
Chelating agent (NH_4)	*	2-3,000	*
municipal waste waters			
Chelating agent (metal ions,	*	*	*
radionuclides, etc.)			
O_2 air enrichment	*		
Natural gas cleaning	*	*	
Exhausted gas (SO_2) treatment		*	
Energy storage	*	*	*
Gas and water adsorption, (world)	15,000		

(*) utilization verified but data unavailable.

(R. Sersale, Natural Zeolites: Processing, Present and Possible Applications)

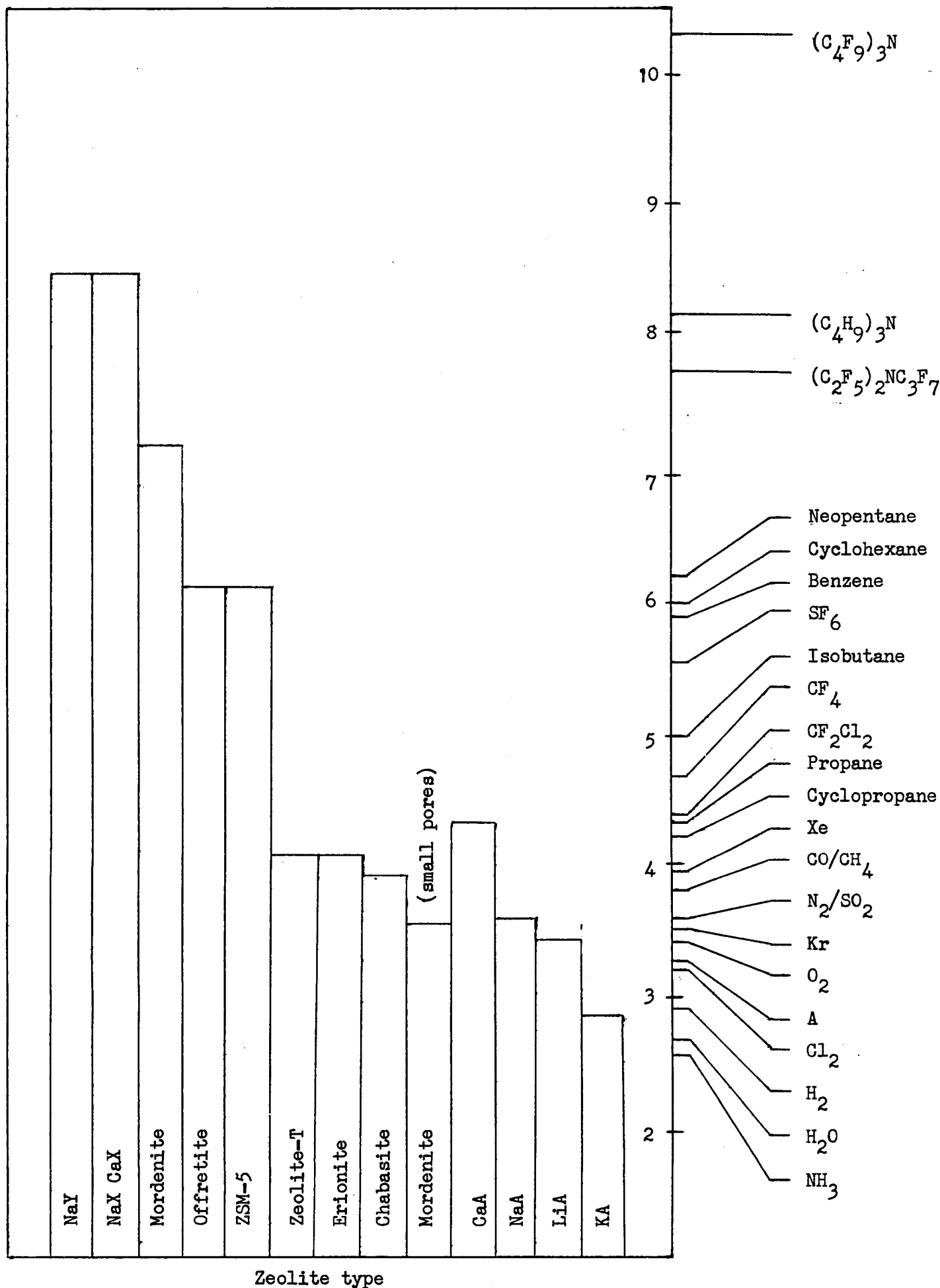


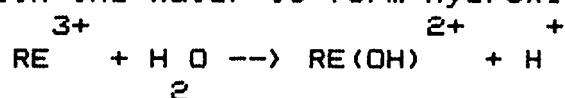
TABLE 2.5: Sorption in zeolites. Molecular sieving.

(J. Dwyer, "Zeolite structure, Composition and Catalysis", Chem. and Ind., 2 April 84)

crystal (although some reactions can occur on the external surface). For zeolite catalysts to be practical, reactants must be able to invade the crystals and products of the reactions must be able to leave. Typical one micron size zeolite crystals have a ratio of external surface to internal surface area of approximately 0.5 percent [12].

As the reactants must enter the zeolite crystal interior, the adsorption and diffusion properties of the crystal are extremely important in relation to catalysis. Both the size and shape of the oxygen windows can influence the entrance of reactants. The arrangement and types of cations in the crystal also have significant effects with respect to interior access. The ion exchange abilities of zeolites often allow a 'fine tuning' of the window size (in zeolite A a Na^+ ion can be sited in the center of the 8-ring window while higher valence cations are not) [2,12].

Perhaps the most important uses of zeolites as catalysts is in the field of petroleum processing, in particular, the cracking of gas oil to gasoline. The term cracking refers to breaking down of the large, bulky molecules into smaller molecules. Essentially all of the gasoline made worldwide by catalytic cracking depends on some form of zeolite Y. In these Y zeolites, rare earth ions RE^{3+} are exchanged for the normal cations (sodium). These rare earth ions react with the water to form hydroxides and protons



During the process the protons (H^+) react with the hydrocarbon

molecules of the gas oil to form carbonium ions. These ions then split further but return the protons to the zeolite in the process. So, the rare earth hydroxides and the protons are regenerated, producing no effective change to the zeolite [2].

Other catalytic processes include converting toluene to benzene and para-xylene (both somewhat more useful than toluene itself), and converting methanol to gasoline. Both the above processes use a form of ZSM-5 synthetic zeolite. In New Zealand, natural gas is converted to synthesis gas (mixture of hydrogen and carbon monoxide) and then to methanol. Coal can also be treated similarly [2]. The conversion of ethanol to hydrocarbons, the alkylation of benzene, and the synthesis of amines from alcohols, ethers or olefins represent other areas of interest. Table 2.6 lists some of the most commonly used natural and synthetic zeolites in catalysis [12].

Table 2.6

Properties of Common Zeolites Used as Catalysts

Zeolite name	Window. Peripheral O - atoms	Free dimensions, with out cations (A)	Dimension- ality of pore system	Types of cavity and size (A)
Linde A	8	4.1	3	Sodalite (6.6), 26 hedron (11.4)
Erionite	8	3.6 x 5.2	3	23 hedron (6.3 x 13)
ZSM-11	10	5.4 x 5.6	3	
ZSM-5	10	5.4 x 5.6 5.1 x 5.5	3	
Mordenite	12	6.7 x 7.0 2.9 x 5.7	2	
Linde X,Y	12	7.4	3	Sodalite (6.6), 26 hedron (11.8)

2.3 Customer and Manufacturer Generated Innovations

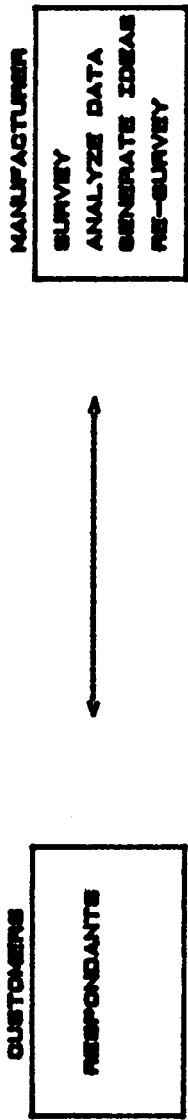
In both consumer and industrial markets today, there are two basic methods by which manufacturers get ideas which they turn into new products. The first is a manufacturer-active process, where the onus is on the manufacturer to find the ideas. The other is a customer-active process where the manufacturer gets new products ideas from customers.

The manufacturer-active process has been very successful in the consumer product marketplace. In this process (see Figure 2.4a), the manufacturer surveys potential customers to determine their needs. Based on this data, ideas for new products are generated. The customers are later surveyed again to determine if these new products would meet their needs. Manufacturers use a variety of techniques to determine customers' needs, from phone surveys to free trial usage of a new product. These feedback techniques are very important because quite often the manufacturer who can better and more quickly determine the needs and wants of his customers, can gain control of a large portion of the market.

The other way new products and innovations can come into being is as a result of customer generated ideas and requests (see Figure 2.4b). With this customer-active process, the manufacturer does not go out and look for new ideas, but merely accepts customers' ideas and problems and decides which ones have the potential to become successful new products. In addition to supplying ideas, sometimes customers also supply part of the data as to how ideas can be implemented. This approach has also

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A. MANUFACTURER-ACTIVE PROCESS



B. CUSTOMER-ACTIVE PROCESS



FIGURE 2.4

enjoyed success in the consumer marketplace. An example of this is the Pillsbury Bake-Off. Pillsbury uses this annual contest for publicity as well as for new product ideas, having derived one of its current cake lines directly from a Bake-Off winner [13].

But the industrial marketplace is different from the consumer marketplace. Eric Von Hippel has compiled data from several other studies concerning the origins of companies' successful products [13]. In one study, 62 percent of the successfully implemented projects of a R&D group concerned with plant processes were "initiated in response to direct customer request." [14] In another example, 80 percent of the new instruments manufactured by scientific instrument companies were a result of users developing ideas for manufacturers [12]. However, Von Hippel's study also revealed that certain products such as plastic additives and engineering polymers were not developed as a result of user requests or user supplied ideas. His hypothesis is that in these and similar industries, the manufacturer is very well acquainted with the needs and desires of the customer and therefore does not need to wait for a specific customer request before beginning development. He argues that in the computer business, the manufacturers know that users want more speed and computations per dollar, so they do not have to wait for a user to ask for a faster computer before developing one. Similarly, in the plastic additives business, manufacturers know customers want plastics which will degrade more slowly in sunlight, so they develop these additives without waiting for a specific request. Common sense seems to support

this hypothesis.

In industries where "he who comes out with the better product first, wins" is a fact of life, it would be suicide to wait for a customer request to start development on a new product if it is known what customers will want it.

Von Hippel's data indicates that a product has a greater chance for success if it was generated in response to a customer's idea or request for a solution to a problem, or at least if it is known that the product will fill a well established and defined need of a customer.

2.4 Industrial Marketing

Industrial or business markets exist in all the steps in the production chain from the extraction of raw materials up to, but not including wholesale and retail transactions, which are consumer activities (see Table 2.7) [15]. The primary distinction between consumer and industry is in their motives for buying. For example, public consumers purchase products to satisfy a personal or household need, while industrial consumers buy products to make other products, operate a business, or provide some form of public service [16]. The nature of a market induces the use of value analysis, which thereby increases the use of standardization and buying by technical specifications. The setting of standards is the process of obtaining an agreement on quality, design and composition for a material, component or machine and is therefore used in most all purchases [15].

The demand for industrial goods is derived from the demand for (1) consumer goods, (2) products needed by governmental agencies, and (3) goods used by nonbusiness, nongovernmental organizations [16]. Of these three the first is the most important as can be proven by past influences on the industrial market by consumer markets and shifts in social trends. Since the demand for industrial products fluctuates so widely, it is desirable to establish a broader base of customers, or more uses per product, in order to reduce the vulnerability to business swings when the customer base is too narrow.

Industrial purchasing is influenced by many factors such as

Stages in the Production Chain

STAGE 1
Raw Materials
Extraction

STAGE 2
Material
Processing

STAGE 3
Manufacturing
of Parts and
Subassembly

STAGE 4
Final Assembly

STAGE 5
Distribution
and Aftermarket

CONSUMPTION
Wholesale
and Retail Sale
to Household
Consumers

Table 2.7

product quality, cost, post-sale service, efficiency, seller reliability, terms of sale, ease and speed of delivery, and variety. "Industrial products are bought only to help the user manufacture, distribute, or sell more effectively so that it can improve its economical and competitive position." [15] Thus, industrial buyers require much more specific cost and performance information about the products they purchase. Technology is therefore important since purchasing costs include (1) initial purchase cost - amount customer pays up front, list or quoted price of product, charges for financing, freight, insurance, installation, technical assistance at startup, warranty and/or service, (2) installation and startup costs - including space alterations, connections to power sources, facilities for ensuring proper temperature and ventilating conditions, and arrangements for handling noise, waste materials, scrap and so on, and (3) operating costs - which include costs of utilizing a particular product or system, most standard accounting charges such as labor, material, power, maintenance and repair, depreciation and interest charges on the purchased item or inventory [15].

In a market study it is necessary to examine the competitors that provide a product which performs a similar function or functions. Such a competitor may not supply an exact product or one made of the same material, but if in the customer's eyes the competitive product fulfills the same function, it is very much a competitive product and therefore one to analyze. An analysis of competitors is an analysis of businesses that compete for the

same customer's sales dollars [15]. "This competitive assessment entails a knowledge of who present and potential competitors are; an analysis of how well each competitor meets the requirements of a segment; and an analysis of competitors plans and likely reactions." [15]

This previously mentioned competitive assessment may not be as direct as it appears, for companies within the same industry may have very different cost structures, which can be due to a number of factors. These include (1) the age and condition of the physical plant; (2) the effectiveness and efficiency of their machines; (3) the productivity of their labor forces; (4) the degree of forward or backward integration (which implies the use of technology or a move back to basics); and (5) size and market share [15]. Thus the study of competitor economics employs many research tools.

It is often thought that how competitive a firm is in the marketplace depends on the cost and productivity of its work force and manufacturing process. Thus the need for efficient technologies arises. This trend of thinking is especially true in mature industries where one must be a lower-cost producer to be an effective competitor [15].

Even though the preceding comments may hold true, before a supplier can compete in any industrial product or market situation, it must possess at least certain capabilities. These factors vary by market, but often include having a minimum level of quality, proven manufacturing capability, technical ability, service capability, and possibly an extensive distributor network [15].

The final stages of the production cycle include pricing. Once the product is designed to meet or excel the operating specifications and therefore enhance the economics of a particular set of customers, pricing strategies can be developed. For example, cost analysis tends to cause the producer to price to what the market will bear, rather than using a cost-plus approach that might be below the customer's value-in-use and willingness to pay. However, if the competitive products are not as cost effective, competitive prices will not be as relevant [15].

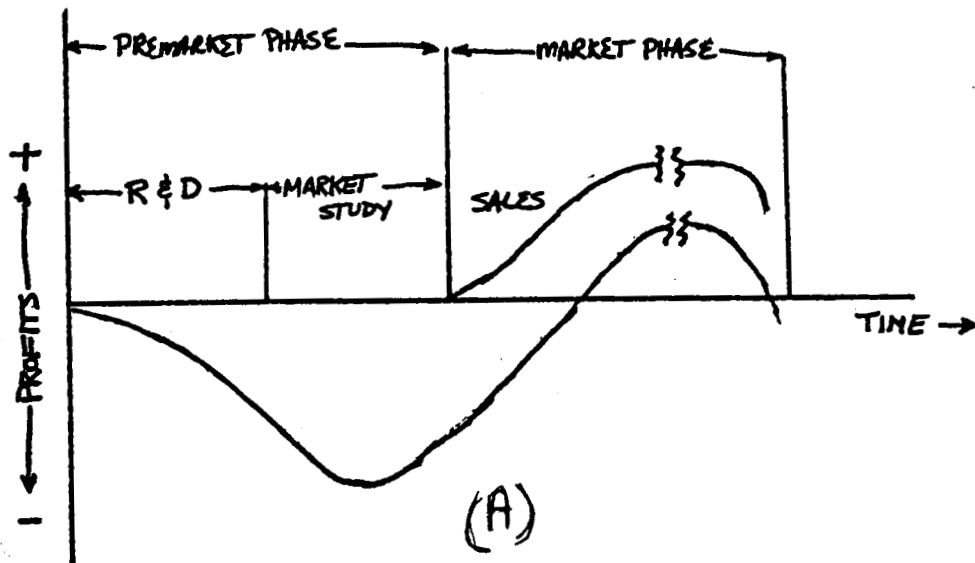
2.5 Product Life Cycle

"Every product goes through a cycle from birth, into an initial growth stage, into a relatively stable period, and finally into a declining stage that eventually ends in the death of the product." [17] (see Figure 2.5c). In the early stages of such a cycle, consumer acceptance is low, and therefore sales are low. It is during this initial stage that management makes the most decisions concerning production.

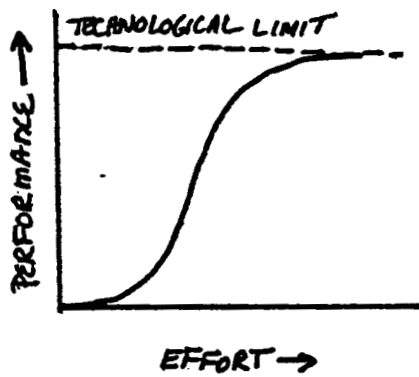
The next stage is the growth stage, in which the product has reached a growing number of customers. During this stage, design tailoring usually occurs. The following stage consists of the maturity of the product. During this stage sales are stable and grow at the rate of the economy. Competition plays a major role in this stage, as pressure exists to decrease prices. During the mature stage, new innovations or markets should be developed in order to achieve the maximum life of the product before it reaches the decline stage. During the decline stage, sales because of new technologies are introduced which can better accomplish the same job [17]. Figure 2.5a shows an expanded product life cycle which includes both the market and premarket phases, while figure 2.5c shows the simple view of the product life cycle.

Figure 2.5b shows the technology development cycle. In its early stages progress is limited by lack of ideas. As the ideas progress the curve becomes exponential until growth becomes linear. At this point progress is concerned with meeting the needs of the ideas with greatest potential. This is the period

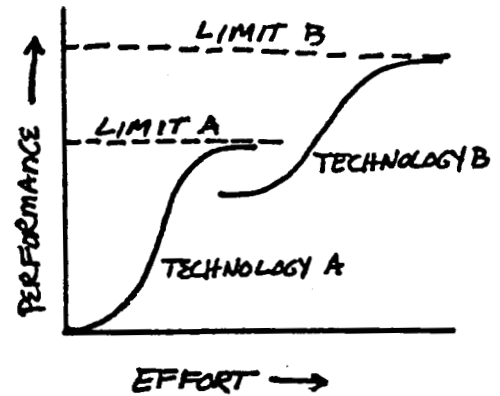
EXPANDED PRODUCT LIFE CYCLE



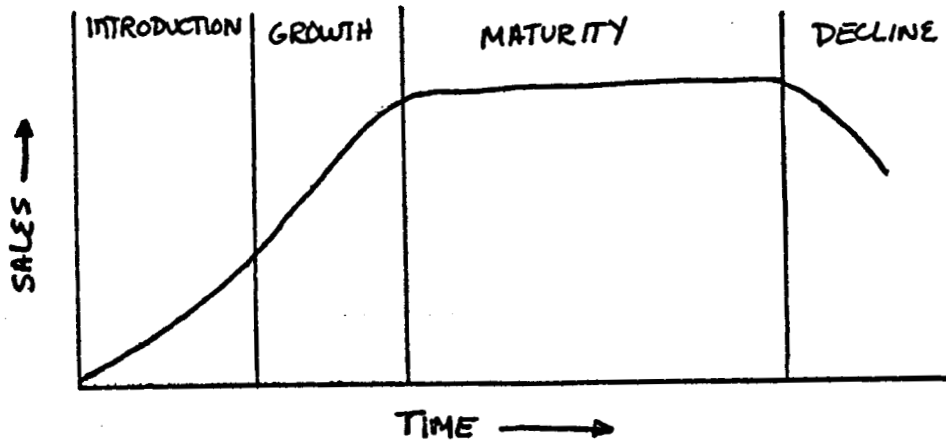
SIMPLE TECHNOLOGY DEVELOPMENT CYCLE



TRANSFER FROM ONE TECHNOLOGY GROWTH CURVE TO A NEW ONE



PRODUCT LIFE CYCLE



(C)

FIGURE 2.5

of commercial exploration as market analysis and manufacturing develop in an unsettled field.

As progress continues, technologies eventually expire and improvements become difficult. "Now the market tends to become more stabilized, manufacturing methods become fixed in place, and more capital is expended to reduce the cost of manufacturing. The business becomes capital-intensive; the emphasis is on production know-how and financial expertise rather than scientific and technological expertise." [17] The graph thus approaches its natural or social limit asymptotically. Finally, it can be seen that the success of a technology-based company depends on realizing when the technology which governs the company begins to mature, and using research and development to emphasize other uprising technologies. Figure 2.5d shows the nature of this technology transfer.

III. METHODOLOGY

To understand the steps taken to secure a market study of large space-grown zeolites, the methodology we employed should be discussed . It was first necessary in our research to assume that these large zeolites could indeed be produced readily. The products were treated as industrial goods rather than consumer goods, based on the proposed uses. Lastly, it was necessary to gather information on both present and proposed future technology in the areas of the potential available markets, in order that a comparison could be achieved. These individual steps shall now be explained.

The information concerning the properties, costs and expectations of the space-grown zeolites were supplied by WPI faculty, and existing literature. As previously stated, it was necessary to assume that (1) the large crystals could be grown and that (2) these large crystals would maintain the existing properties of zeolites today. The proposed costs of the crystals include growth on space shuttle flights as well as growth on a space station laboratory.

The competitive product information which was needed was gathered through a person-to-person contact system. Telephone calls were made and letters sent out to various officials, representatives, and scientific personnel in order to obtain the various technologies, costs and requirements of the procedures in question. Much information was also acquired through catalogues, pamphlets, and brochures which were obtained through such

contacts. Finally, it was necessary to acquire as much information as possible in any one particular area, in order that a true cost comparison could be achieved.

Based on the available information, proposed markets were discovered in which the new crystals could possibly prove beneficial. Decisions were made concerning the possibility of a market impact based on economic and cost factors. These decisions were influenced by such factors as the present economy and industrial trends which were assumed to remain relatively constant. Finally, it can be inferred that this report cannot be a true market study as it is often defined, due to the lack of information regarding the nature and cost of the zeolite process including its material, space, ventilation, and power requirements. Therefore, our analysis should be considered a suggested incentive for further in-depth research into the markets for space-grown zeolites which this paper finds suitable.

IV. RESULTS AND ANALYSIS

4.1 The Cost of Large Zeolite Crystals

As the zeolite growth process is simple, requiring no exotic chemicals or procedures, the major cost of producing large zeolite crystals in space, as with other materials, is the cost of launching the materials and equipment into orbit. Initially, large zeolites could be manufactured in small scale on the Space Shuttle. But, in the long run, large scale production of the crystals would be carried out most economically in an orbiting space station. A space station can offer both more time and area for a manufacturing operation than the shuttle. In either case, if the raw materials are to come from Earth, the cost of lifting the materials to orbit via the shuttle still exists.

From information given by Dr. B. Stone, an estimate of the cost of large zeolites can be given. In 1982 dollars a fully dedicated shuttle launch (the entire cargo bay) costs 74 million dollars or approximately 87 million dollars in 1989 dollars. Since the shuttle accident no exact figures can be given. The maximum load of the shuttle is some 65,000 lbm (29,484 kg). The ratio of maximum load to maximum cost gives a rough estimate of the cost per pound of zeolite;

$$\$87,000,000/65,000 \text{ lbm} = \$1,340/\text{lbm} = \$2,951/\text{kg}.$$

It is unlikely that a fully dedicated launch would be available at convenience or necessary. In the case of a shared use of the shuttle there are two cases to consider in pricing. With respect

to a given payload a weight load factor and a length load factor can be calculated. The weight load factor is the ratio of the weight of the payload in question to the maximum load of the shuttle (65,000 lbm);

$$\text{Weight Load Factor} = W \text{ (lbm)} / 65,000 \text{ lbm.}$$

The length load factor is the ratio of the length of the payload to the total length of the cargo bay (60 ft);

$$\text{Length Load Factor} = L \text{ (ft)} / 60 \text{ ft.}$$

The width of the load is taken into account by the weight and length ($W/L = \text{Area}$). The larger of these two factors (WLF. or LLF.) determines the price charge factor. Since the average shuttle launch has only a 3/4 full payload, this is included in the general pricing;

$$\text{Price Charge Factor} = \text{Load Factor (WLF. or LLF.)} / .75$$

Finally the charge factor is multiplied by the total shuttle flight cost;

$$\text{Cost of Load} = \text{Price Charge Factor} \times \$87,000,000.$$

Since no specific process for growing zeolites (as they have not yet been grown) can be pinpointed, no exact prices can be given for the crystals.

In general, it will cost approximately \$3,300 per kilogram of material produced (information given by Prof. A. Sacco). This figure is what NASA expects any type of commercial materials

processing in the shuttle to cost.

Beyond the costs of transporting the materials, the materials must also be processed. This additional cost consists of power consumption, cost of container, equipment, and control systems for the device. An average figure for the processing is \$1,300 per kilogram. So this gives a total cost of \$4,600 per kilogram.

Load Cost	Processing Cost	Total Cost
\$3,300/kg	+ \$1,300/kg	= \$4,600/kg.

If large zeolites can be made, it is believed they will be useful in the form of thin membranes. These membranes would be cleaved from a large crystal. There is a possibility these membranes would be structurally weak, however, composite membranes offer a solution to this. A sample calculation can be made to estimate the cost of one of these membranes. First, the cost will vary depending on the type of zeolite produced, since this will change the amounts of raw materials used (silicon, aluminum, oxygen, and cations). It can be assumed that the cost of the raw materials is negligible compared to the total cost.

Assume a 25 centimeter cube of a zeolite will be cleaved into 10,000 layers (10,000 membranes). The average density of zeolites is on the order of 2,200 kg/m³. Therefore the mass of the cube is given by;

$$25 \text{ cm} \times (1 \text{ m}/100 \text{ cm})^3 \times 2,200 \text{ kg/m}^3 = 34.4 \text{ kg}.$$

Multiply this by the average cost per kilogram (above);

$$34.4 \text{ kg} \times \$4,600/\text{kg} = \$158,125.$$

Divide by the number of layers (10,000);

$$\$158,125/10,000 \text{ membranes} = \$15.81/\text{membrane}.$$

Since no competitive product exists (membrane wise) it is difficult to say whether this is a high or low price. Certainly in a very specific application where only a zeolite membrane could be used this is not an unattractive price.

In the long run, larger scale production of the crystals would reduce the price. An especially attractive idea is that of using raw materials mined from the Moon.

The large zeolites could also be used in the pellet (bead) form now used for small zeolites. Essentially a large zeolite would be crushed to appropriate sized particles. These particles would offer substantially higher efficiency and lower pressures (as in a columnar separation process). It is not likely that large zeolites would be competitive in this area (especially large scale industrial uses) but perhaps in more specific, scientific applications (calibration of equipment, small scale specific uses with chemicals).

4.2 Nuclear Waste

Low level radioactive waste material has become a major source of controversy. This waste is produced by various sources such as the medical field, industry, government, and commercial nuclear power plants. These institutions differ not only in the types of wastes produced, but also in the amounts produced and the types of processing methods employed. In this section, the different forms of wastes will be explored as well as their associated treatment methods in order that a comparison can be made with processes utilizing zeolites. This section will be broken up by waste classification and its various producers.

4.2.1 Radioactive Waste

One of the proposed uses for space-grown zeolites is for the handling and storage of low level radioactive waste. At this time, the different forms of waste should be characterized. "Spent fuel consists of irradiated fuel discharged from a commercial reactor or spent fuels from test or research reactors." [20] These fuels are either government or commercially owned and are usually stored in pools at reactor sites and other locations. High level wastes are highly radioactive material resulting from the reprocessing of spent nuclear fuel and contains fission products which result in the release of large amounts of decay energy. The waste consists mainly of the liquid wastes remaining from the recovery of uranium and plutonium in a fuel reprocessing system and may also be in the form of sludge, calcine, or other such products into which these liquid wastes are converted to facilitate their handling and storage [20].

Transuranic (TRU) wastes are "radioactive wastes which
-9
contain more than 100 nCi/g (Curies \times 10 per gram) of alpha-emitting isotopes with atomic numbers greater than 92 and half-lives greater than 20 years." [20] These wastes result mainly from fuel reprocessing and from the fabrication of plutonium weapons and plutonium-bearing reactor fuel.

Low level waste is radioactive waste not classified as mill tailing (earthen residues), high level waste, transuranic waste, spent fuel, or by-product material. It is material contaminated with small, but potentially hazardous, levels of radioactivity.

They usually appear in the form of dry trash, paper, plastics, glass, clothing, and discarded equipment to wet sludges and aqueous, organic liquids [21]. The radiation level from this waste may be high enough to require some shielding for handling and transport.

There are basically three forms of low level waste: liquid, wet solids, and dry solids. Liquid low level wastes are fluids contaminated with radioactive particles in relatively low concentrations, such as less than one percent by volume. Forms of liquid include chemical regenerative solutions, decontamination solutions, contaminated oils, and liquid-scintillation. Wet solids are considered to be moderately thick slurries containing at least 10 percent solids by volume. It includes evaporator bottoms, spent ion-exchange media, filter precoat material, and expanded filter cartridges. Finally, dry solids consist of three main types of waste forms including trash, contaminated material, plant equipment and irradiated hardware [21]. See Tables 4.1 a-e for associated low level waste volumes. Based on these definitions the processing applications for zeolites would fall under the liquid and wet solid waste categories, since dry solids are usually just compacted.

The waste management procedure depends on the physical and chemical characteristics of the waste, its radionuclide content, half-life of the radioactive atoms, specific activity, as well as on regulations governing packaging, transportation, and disposal of the waste (see Figure 4.1). Tables 4.2 and 4.3 show the relative importance of waste characteristics as a function of

waste form, and the various technologies associated with waste forms.

LOW LEVEL RADIOACTIVE WASTE

FACT SHEETORIGINAL PAGE IS
OF POOR QUALITYLLW VOLUMES, 1986 - BY INTERSTATE COMPACTS
NUMBER'S IN THOUSANDS OF CUBIC FEET

NORTHEAST		CENTRAL STATES		ROCKY MOUNTAIN		UNALIGNED	
Connecticut	56.7	Arkansas	6.0	Colorado	1.4	Rhode Island	.2
New Jersey	37.9	Louisiana	20.1	Nevada	0.0	Vermont	13.7
	94.9	Nebraska	21.8	New Mexico	0.0	New Hampshire	1.0
		Oklahoma	50.6	Wyoming	0.0	Massachusetts	66.7
			101.0		1.4	New York	119.3
APPALACIAN		CENTRAL MIDWEST		WESTERN II		Maine	6.6
Pennsylvania	191.2	Illinois	211.9	South Dakota	0.0	Texas	.6
West Virginia	0.0	Kentucky	2.9	Arizona	3.0	North Dakota	0.0
Maryland	12.9		214.8		3.0	California	92.5
Delaware	1.1					District of Columbia	.2
	205.2						300.8
SOUTHEAST		MIDWEST		NORTHWEST		TOTAL	
Georgia	50.5	Wisconsin	5.4	Idaho	0.0	1,671,100 cubic feet	
Florida	31.5	Indiana	0.0	Washington	53.3		
Tennessee	63.7	Iowa	9.5	Oregon	98.5		
Alabama	51.3	Ohio	17.8	Utah	3.7		
North Carolina	79.7	Michigan	41.5	Alaska	0.0		
South Carolina	113.6	Minnesota	26.7	Hawaii	2.7		
Mississippi	14.1	Missouri	12.2	Montana	.8		
Virginia	73.7		113.2		158.9		
	478.1						

*NOTE: These figures were projected using the first nine months figures of 1986 for the three facilities.

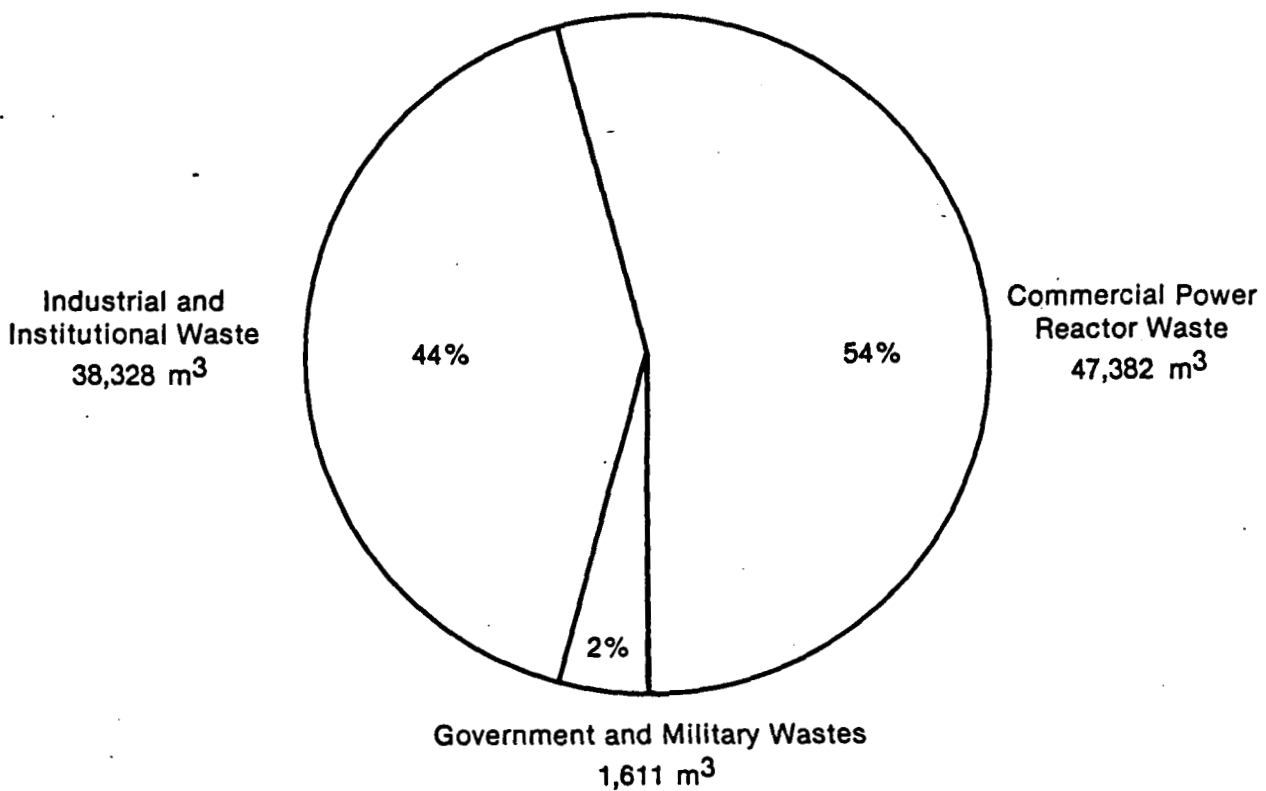
STATE COMPARISONS FOR 1979, 1983 & 1986

1979	1983	1986
1. New York	1. Pennsylvania	1. Illinois
2. South Carolina	2. Illinois	2. Pennsylvania
3. Pennsylvania	3. New York	3. New York
4. Illinois	4. South Carolina	4. South Carolina
5. North Carolina	*5. Massachusetts	5. Oregon
*6. Massachusetts	6. Virginia	6. California
7. California	7. North Carolina	7. North Carolina
8. Virginia	8. Tennessee	8. Virginia
9. Connecticut	9. Alabama	*9. Massachusetts
10. Alabama	10. California	10. Tennessee

Table 4.1a

LOW-LEVEL WASTE VOLUMES

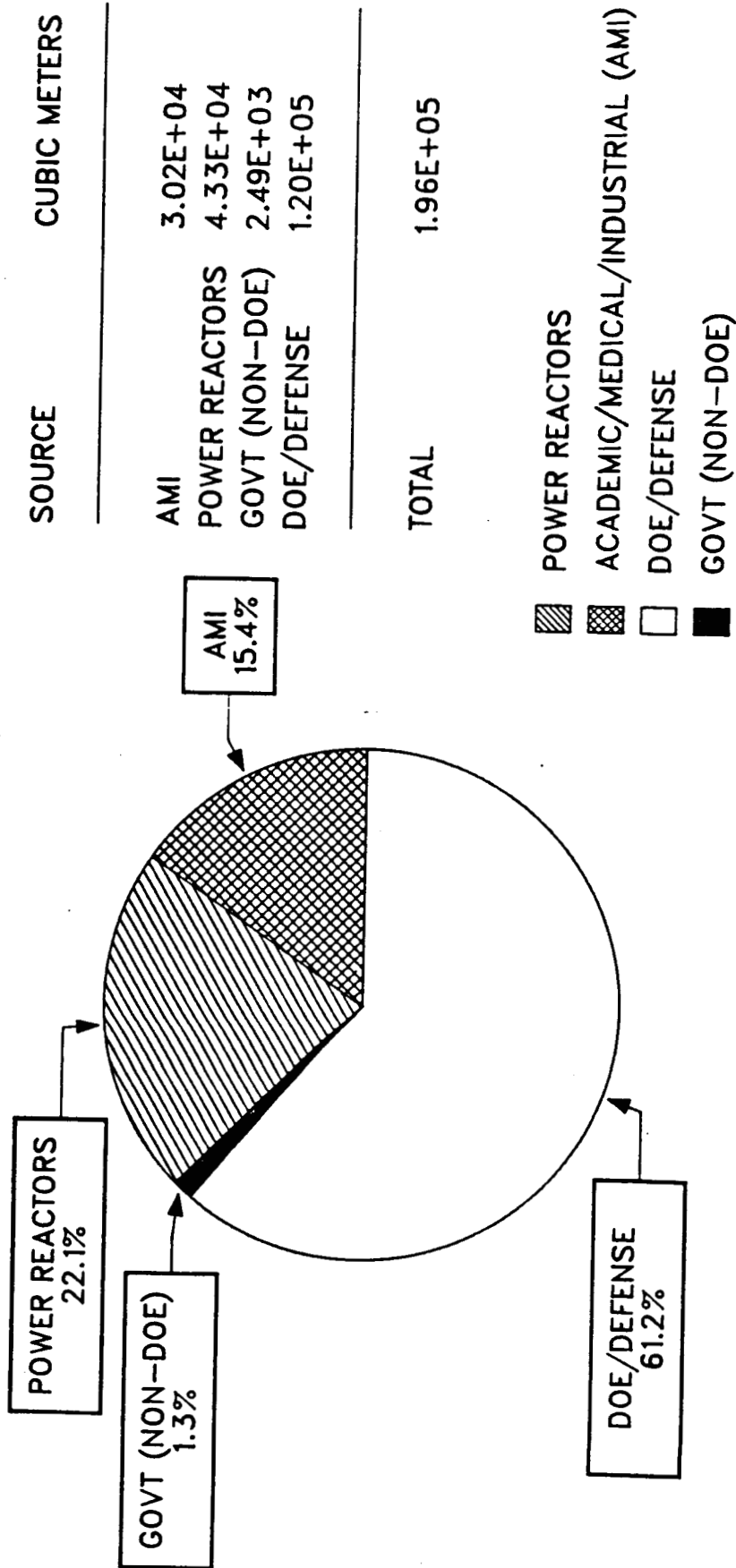
Institutional and industrial low-level wastes are generated in all 50 states, the District of Columbia, Puerto Rico, and the Virgin Islands. In 25 states, low-level wastes are produced at commercial power reactors. The volume of wastes from the various sources transported to commercial burial sites in 1981 is illustrated in Figure 1. Table 4 shows the volumes of low-level waste disposed of in 1980 and 1981 at commercial burial sites.



INEL 3 0466

Sources of low-level waste, by generator category for 1981.

Table 4.1b



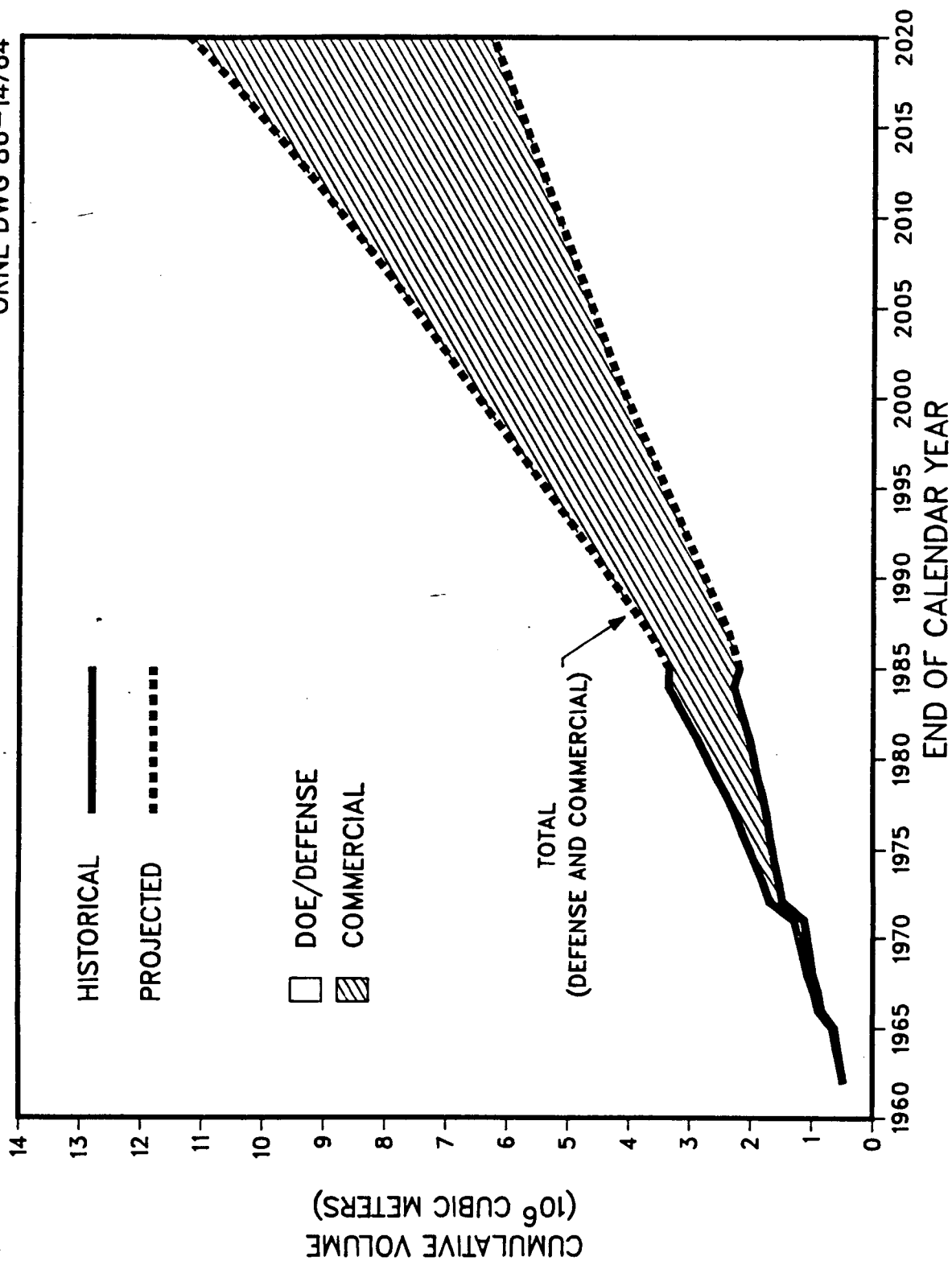
Volume of LLW buried in 1985.

Table 4.1c

Low Level Waste in the United States

Sector	Volume Cubic ft	%	Radioactivity Curies	%
Nuclear Power Plants	1,527,700	57	582,500	78
Academic/Medical	78,600	3	900	0.1
Industrial	986,600	37	158,300	21
Governmental	87,900	3	7,400	1
Total	2,680,800		1,468,000	
Governmental				
US Department of Energy	2,764,800		1,468,000	

Table 4.1d



Historical and projected cumulative volume of LLW.

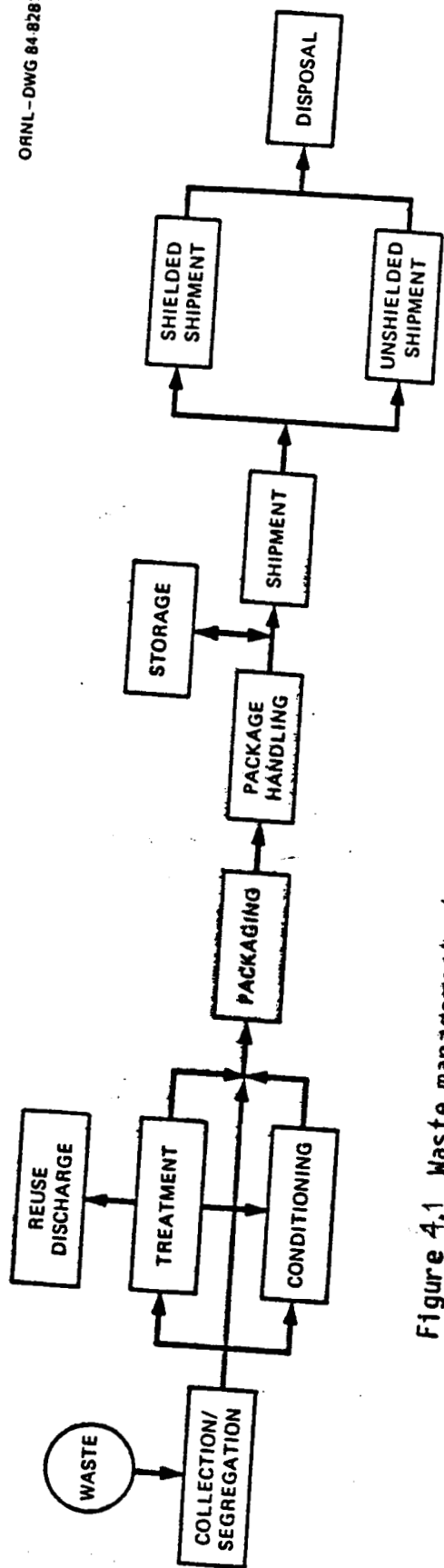


Figure 4.1 Waste management steps for low-level radioactive waste (LLW).

TABLE 4.2 RELATIVE IMPORTANCE OF WASTE CHARACTERISTICS AS A FUNCTION OF WASTE FORM

Parameter	Waste Form		
	Liquids	Wet Solids	Dry Solids
Generation rate	Major	Major	Major
Specific activity	Major	Major	Major
Radionuclide content	Major	Major	Major
Solids content	Major	Major	--
Oxidizability	--	Major	Major
Free-water content	Minor	Major	--
Multiple liquid phases	Major	--	--
Major chemical content	Major	--	Minor
Organic species	Major	Minor	--
Ionic species	Major	--	--
Viscosity	Minor	Minor	--
pH	Minor	--	--
Bulk density	Minor	Minor	Minor
Shredability	--	--	Major
Combustibility	--	Minor	Major

TABLE 4.3 MATRIX OF TREATMENT/CONDITIONING TECHNOLOGIES AND WASTE FORMS

Type of Technology	Waste Form		
	Liquids	Wet Solids	Dry Solids
Transfer Technologies			
Decontamination	--	--	X
Filtration	X	X	--
Ion exchange	X	--	--
Chemical regeneration	--	X	--
Ultrafiltration	X	--	--
Reverse osmosis	X	--	--
Concentration Technologies			
Evaporation	X	--	--
Distillation	X	--	--
Crystallization	X	--	--
Flocculation	X	--	--
Precipitation	X	--	--
Sedimentation	X	X	--
Centrifugation	X	X	--
Drying	--	X	--
Dewatering	--	X	--
Dehydration	--	X	--
Compaction	--	--	X
Baling	--	--	X
Shredding	--	--	X
Integrated systems	X	X	--
Transformation Technologies			
Incineration	X	X	X
Calcination	X	X	--
Conditioning Technologies			
High-integrity containers	--	X	X
Solidification	X	X	X
Absorption	X	X	--

Conditioning and treatment of the waste refers to the processes which transform these radioactive products into suitable forms for transportation and burial. The waste processing techniques used today are usually chosen because they are cost effective or satisfy regulatory requirements. Some examples of treatment/conditioning processes for liquid waste are defined for reference.

Transfer technology refers to the removal of radioactivity from waste streams and its transfer to another medium. These processes include filtration, ion-exchange, and membrane processes such as osmosis and ultrafiltration. Filtration is the process of separating undissolved or suspended particulate solids in a liquid stream from the liquid media by forcing it through a porous body. "Factors which should be considered in the selection of a filter include: (a) degree of filtration required; (b) the chemical compatibility of the filter medium with the liquid being processed; (c) the concentration and particle-size distribution of the solids to be removed; and (d) the volume, flow rate, temperature, and pressure of the liquid waste." [21] In general, filtration should be used when the volume of the liquid is above $38 \text{ m}^3/\text{year}$ and suspended solids content is above 2 to 3 percent.

Ion-exchange processes consist of selective removal of particles from liquids onto an exchange medium (resin). "The mechanism of ion-exchange consists of a reversible interchange of ions of the same sign between an electrolyte solution and a solid phase." [21] Types of ion-exchange methods include cation and anion

exchangers as well as mixed or separate-bed ion exchangers (demineralizers) combining the use of both cation and anion media. Filtration is often a pretreatment with this process which works best with low suspended solid content and temperatures below 60 C.

Membrane separation treatments include reverse osmosis and ultrafiltration. These processes have been used highly with nonradioactive products and have provided favorable results on tests with low level wastes. They provide the advantage of (1) no need for mechanical filter aids; (2) minimization of the requirements for chemical regeneration or disposal of expensive resins; and (3) preconcentration of the wastes without the need of major process equipment with large auxiliary heat supplies [21].

Concentration technologies are used to reduce waste volume by concentrating the radioactive species without removing them from the original waste form. The types of concentration technologies often used for liquids include evaporation, distillation, crystallization, flocculation, precipitation, sedimentation, centrifugation, and integrated systems. Evaporation can be applied to a variety of liquid wastes to concentrate relatively nonvolatile radioactive atoms from solutions with high solid content. However, due to high energy costs, evaporation is considered economically unfavorable for large volumes of liquid, over $3800 \text{ m}^3/\text{y}$ [21].

Distillation and crystallization are test-proven techniques which have not been used extensively. These processes involve removal of dissolved material from liquid waste, usually by

evaporation near atmospheric pressures. "Crystallization induces nucleation of particles of dissolved materials either by thermal activation or by seeding with ultrafine nuclei." [21] Flocculation, sedimentation, and centrifugation are processes which can be used to remove suspended solids from liquid waste with the help of such things as interaction agents and gravity. These processes are more commonly found at large Department of Energy (DOE) facilities where they experience specific limited use.

The final concentration procedure involves integrated systems which combine volume reduction through evaporation with volume increase through absorption. Based on such things as the binding material of the absorbent, this system would have to be evaluated on plant and waste basis [21].

Transformation technologies are similar to concentration technologies in principal, however, concentration is achieved by changing the physical form of the waste. The major method of this area is incineration which involves thermal decomposition of organic liquids at moderate temperatures. The resultant waste is usually of a solid form with decreased volume, but it may require some conditioning [21].

A final category of technology is that of conditioning, which involves solidification of the liquid or the use of absorbents to transform the waste into a suitable form for transportation and disposal.

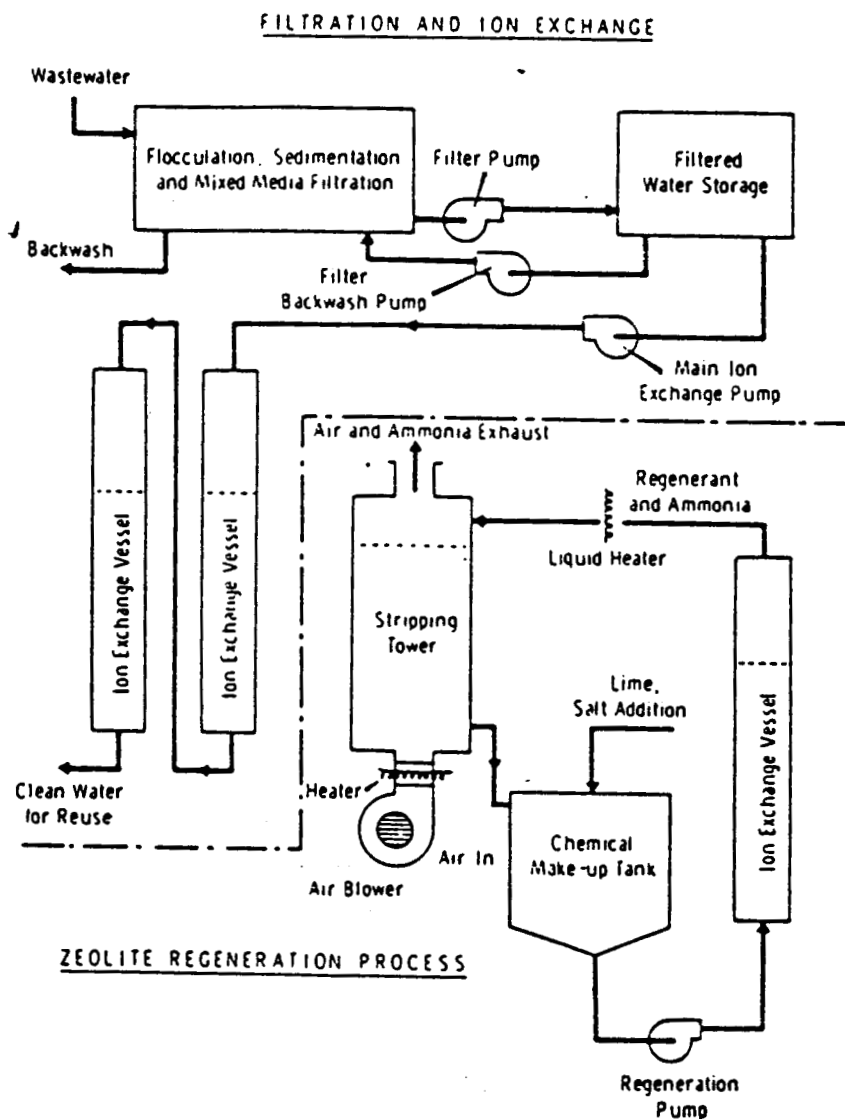
Solidification systems are those that achieve the immobilization of liquid waste within an inert matrix. These systems usually chemically encapsulate the liquid within an inert matrix. Absorbents are used to store the liquid within a porous material, from which the liquid could be extracted. [21]

Conditioning will never result in reduced total management cost because it adds steps and operations, yet does nothing to decrease waste volume. For this reason conditioning is not as extensively used at nuclear fuel-cycle and government facilities as in industrial and institutional facilities due to the smaller amount of liquid waste produced annually by the latter (1 m³).

Before looking at the various possible uses for zeolites in waste treatment, it is necessary to understand some of the regulations which govern the transportation and disposal of low level waste. These regulations are determined by the various organizations including The Department of Transportation, The Nuclear Regulatory Commission, the particular states in which transportation routes occur, The Department of Energy, and the particular disposal site operators. For example, the main regulations concerning the conditioning of waste which relate to zeolites include that liquids must either be solidified or packaged with materials capable of absorbing twice the liquid volume, and that wastes must contain less than one percent of the volume as free liquid. The next sections will discuss the major sources which produce such waste, namely institutional, industrial, commercial (nuclear), and governmental sources.

4.2.2 Use of Zeolites in Nuclear Waste Treatment

It is now necessary to describe the way in which these large zeolites would be used. First, the zeolitic material would cost approximately \$4600 per kilogram. This cost would cover both space-shot and processing costs. These products would follow a filtration/ion-exchange method of operation similar to the ion-exchange process now used (see Figure 4.2). The "channels" of the zeolite crystals would be highly selective and able to be controlled in order to remove the radioactive atoms existent in the contaminated solution. These crystal beds would most likely be highly efficient, due to the lack of binding material existent in the present pelletized zeolitic material. The resulting crystals would be processed by either some type of small scale solidification or absorption, or if the crystals were extremely dry as somewhat suspected, they could be directly packed for burial. This small quantity of zeolitic material would contain a great concentration of radioactivity and would thus have to be disposed of accordingly.



Flow chart of wastewater treatment process using clinoptilolite ion-exchange processes.

Figure 4.2

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4.2.3 Institutional

Hospitals, universities, and research centers are three major contributors to institutional waste. This waste is produced through such sources as nuclear medicine, bioresearch, and other research in physics, inorganic chemistry, materials analysis, and geology. The liquid waste produced from such activity commonly occur in the forms of liquid-scintillation waste - organic fluids, usually toluene, contained in a plastic or glass vial; organic liquids - organic laboratory solvents including alcohols, aldehydes, and organic acids; aqueous liquids - radionuclides suspended in a water solution; and biological wastes. Hardly any wet solids are produced [22].

Most institutional facilities handle the problems of radioactive waste in two ways. First, many of the smaller research facilities produce wastes with radionuclides that have relatively small half-lives. For these institutions the process of holding for decay is prevalent. This process involves storage of the particular waste in drums for a period of time equal to ten half-lives of the material. For example, Technetium-99m which has a half-life of 6.05 hours, can be held for 60.5 hours and then considered to be legally nonradioactive for disposal purposes. Other such radionuclides include Iodine-125, Iodine-123, Gallium-67, as well as many others (see Table 4.4).

The second method for the processing of liquid waste for long half-life or for facilities without the room or ability for decay is through the use of commercial waste-handling firms

TABLE 4.4 PRIMARY RADIONUCLIDES FOUND IN INSTITUTIONAL WASTES^a

Radionuclide	Half-Life	Predominant Waste Types	Used in/with Patients	Dominance in Waste Shipped (%)	Primary Wastestream	Type of Radiation
Calcium-45	165 days	Research fluids	--	--	Bioresearch	Beta
Carbon-14	5,730 years	Research fluids	--	3	Bioresearch	Beta
Cesium-137	30 years	--	Radiation therapy	--		Beta, gamma
Chromium-51	27.8 days	Research fluids	--	2	Bioresearch Medical	Gamma
Gallium-67	77.9 hours	Syringes	Yes	--	Medical	Gamma
Hydrogen-3 (Tritium)	12.3 years	Research fluids	--	75	Bioresearch 65% Other research 35%	Beta
Indium-111	2.8 days	Bottles/syringes	Yes	--	Medical	Gamma
Iodine-123	13.3 hours	Containers/syringes	Yes	--	Medical	Gamma
Iodine-125	60.2 days	Clinical and research fluids	Tests outside body	11	Medical 40% Bioresearch 59%	Gamma
Iodine-131	805 days	Bottles/syringes	Yes	--	Medical	Beta, gamma

TABLE 4.4 (continued)

<u>Radionuclide</u>	<u>Half-Life</u>	<u>Predominant Waste Types</u>	<u>Used in/with Patients</u>	<u>Dominance in Waste Shipped (%)</u>	<u>Primary Wastestream</u>	<u>Type of Radiation</u>
Molybdenum-99	66.7 hours	Depleted sources	--	--	Medical	Beta, gamma
Phosphorus-32	14.28 days	Bottles/syringes/research fluids	Yes	5	Bioresearch Medical	Beta
Rubidium-86	18.66 days	Research fluids	--	--	Bioresearch	Beta, gamma
Selenium-75	120.4 days	Bottles/syringes	Yes	--	Medical	Gamma
Sulfur-35	87.9 days	Research fluids	--	3	Bioresearch	Beta
Technetium-99m	6.05 hours	Depleted sources	--	--	Medical	Gamma
Xenon-133	5.27 days	Bottles/collectors	Yes	--	Medical	Beta, gamma
Ytterbium-169	37.8 days	Bottles/syringes	Yes	--	Medical 58% Other research 42%	Beta

a. Source: Institutional Radioactive Wastes, NUREG/CR-0028, June 1979.

(brokers). Waste brokers collect the waste from various institutions, store it for a period of time, and then make bulk shipments to disposal facilities. These brokers may either pick up the bulk waste and use their own equipment to process the waste at their facility, or provide the institutions with the necessary material to process the waste themselves, and then pick up the resulting compound. Table 4.5 displays some of the major brokers along with their processing methods and handling charges.

The processing of the various waste is different depending on its particular type. For scintillation and certain other organic liquids, incineration is the primary method of treatment. Of the remaining liquid wastes which are handled, of which Tritium (Hydrogen-3), Carbon-14, Phosphorus-32, and Iodine-125 are the principal radionuclides present, absorption or solidification are used. The differences in prices and procedure of the particular brokers interviewed, can be explained somewhat by location of particular organization, including particular state and distance to burial site, and personal preference of the brokers choice of material and processing technique. Table 4.6 gives a list of cost variables associated with a typical industry. Components A-R summarize basic operations. Some typical costs for materials are listed as well as some additional cost considerations.

In the processing of the liquid waste, only about ten to fifteen gallons of radioactive liquid exists in the 55 gallon drum, due to the regulations regarding the liquid waste. This is in comparison to the amount of absorption or solidification

material in the 55 gallon drum which usually ranges in the amount of three or four to one with respect to conditioning material to liquid waste. Thus the prices in Table 4.5 increase dramatically when the criterion of money to actual radioactive material is considered.

Table 4.5
Processing brokers and their prices

ADCO.....Chicago

- * scintillation (organic) - incinerated
- * use of both absorbent and solidification material
- amount needed 2:1 requirement
- speedy dry (clay) 100 lb. 150 lb. water /
200 lb. material
- diatomaceous earth 80 lb. in between
- perlite 40 lb. 150 lb. water /
100 lb. material
- * 15 gallons of radioactive liquid per 55 gallon drum
- * approx. cost \$25-26 per gallon of waste

NDL Organization.....New York

- * use absorbent (speedy dry)
- * process
 - (1) 10 gallon liquid in 30 gallon drum (4 cu.ft.)
and rest absorbent
 - (2) Insert (1) into 55 gallon drum (7.5 cu.ft.) and
fill void with absorbent
- * total amount of absorbent approx. 6-7 cubic feet
- * use 1.5-2 4cu.ft. bags approx. \$9.64 each

Teladine Isotopes.....New Jersey

- * use of stabilization media and absorption (pearlite)
- * approx. cost - \$500 per 55 gallon drum
- * price dependent on content and mass quantity

Radiation Service Organization (RSO).....Maryland

- * use of *portland cement
- * costs - \$522 for 55 gallon drum
\$400 for 30 gallon drum

Examples of in-house using

Harvard University

- * use of speedy dry as absorbent and then shipped out
commercially
- * absorbent to liquid approx. 3 or 4 : 1
- * radionuclides- I-125
P-32
Cromium-51
Sulfer-35
- * cost approx. \$350 per 30 gallon barrel (cost covers speedy
dry, transportation, and disposal)

MIT

- * solidify by concrete and plaster of *paris
- * material cost approx. \$5.00 per 5 gallon drum
- * radionuclides- Carbon-14
 Sulfer-35
 Hydrogen-3
- * processing-
 3 or 4 5 gallon pails in a 55 gallon drum
 or
 15-20 1 gallon jugs in 55 gallon drum
- * liquid to conditioning material in drum is 1:2
- * cost- \$400-450 per 55 gallon drum (price includes total processing)

Table 4.6
Components of cost

Collection at lab

- A. Plastic container
- B. 55 gallon bag
- C. Computer card
- D. Array sample
- E. 7 liters of absorbent/ 3 liters waste
- F. Plastic bag drum liner
- G. 30 gallon drum
- H. More absorbent to fill 30/ 50 void
- I. Plastic bag for 55 gallon drum
- J. 55 gallon drum
- K. Nut- bolt- wire
- L. Man power
 - * load
 - * array
 - * supply area
 - * data
 - * identification of drum
 - * wipe test survey
 - * transport out
 - * total time
- M. Load on truck
- N. Prepare truck papers
- O. Survey truck
- P. Transport cost
- Q. Burial cost
- R. Surcharge

Record into inventory for future

Basic Costs

Transportation varies/ area

Drums approx. \$60-80 total (includes bags, bolts, paint etc.)

Filler approx. \$2-4.50/ bag

Manpower- 1 man 20K/yr.

Additional Considerations

Surcharges on burial: \$10 per cubic foot till 1/88 than more

Are there burial charges for Isotope quantity? \$/ci.

As mentioned previously, liquid waste contains less than one percent dissolved particles in the solution. However, it appears that not all this material is radioactive. Since the actual volume concentration of the radionuclides in the liquid are not specified by law, this figure is virtually unknown or cared about. This concentration is instead measured in curies which is a measure of radioactivity. Yet, it is this volume or mass concentration of the radioactive atoms which is needed in order to calculate the feasibility of implementing a zeolitic process in order to handle the waste problem. It would indicate that if the radionuclide concentrations existed near one percent, no type of ion-exchange process would be economically feasible due to operation costs, labor costs, and material costs. However, if this figure was considerably less, as suggested by the nuclear power liquid waste, any type of ion-exchange process could be feasible, with zeolites as a possible prime candidate (see Figure 4.3).

The handling of institutional liquid waste as it is done today is geared on the process of conditioning technology. Evaporation, ion-exchange, and filtration processes are generally not used due to reasons such as lack of room, increased initial costs, inability to procure a license, and inability to provide proper ventilation. The zeolite based process would have to be able to meet the capabilities of these technologies, while not requiring special regulations and operating conditions which could hinder its use. However, as previously indicated, zeolites would be used as an ion-exchange medium, and thus it most

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COST VS. CONCENTRATION CURVE

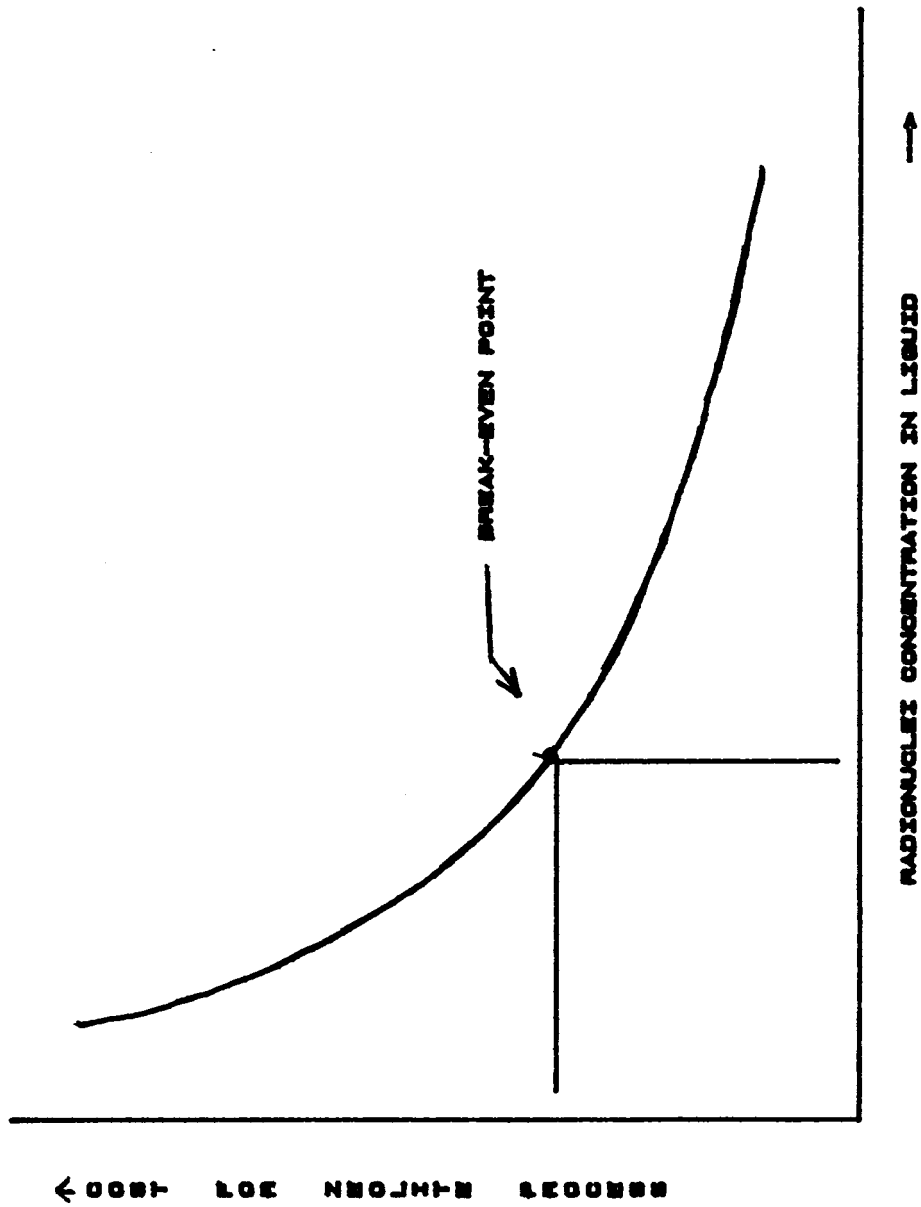


FIGURE 4.3

probably would not find its use in such a situation without the means of effective technology, and change in certain regulations. Thus, the theory that for radioactive liquid the technology that yields the highest packaging efficiency is usually the most cost effective and therefore employed, would not truly apply to institutional wastes.

4.2.4 Industry

The chief contributors of low level waste from the industrial sector are manufactures of radiopharmaceuticals for hospitals and universities, as well as manufactures of consumer products, gauges, or other special instruments that use radioactive materials. "The industry of radiopharmaceuticals includes companies that produce nuclides as raw materials for other pharmaceutical companies, as well as secondary companies that produce radiopharmaceuticals through radioactive tagging and labeling processes." [22]

The waste produced in the industrial field is similar to that in the institutional phase in that it is comprised mostly of liquid and dry solid components, with H-3 and C-14 the chief components in the radioactive liquid. Both components are termed "soft energies", with the tritium resulting mainly from the purification of exhaust air. The waste processing methods are also very similar to institutional methods with most organic wastes incinerated, wastes with short half-lives allowed to decay, and the remaining liquid usually absorbed or solidified and packaged for transportation and disposal. For example, one such major industry used a cat litter material for absorption and concrete for solidification.

As far as available prices for processing, this information was not procured due to the competitive nature of the business. However, by consulting marketing personnel at WPI, it was estimated to expect a 100 percent overhead fee applied to the prices which were available through the institutional handling.

In this way one can expect the price of handling to decrease by half, still rendering a chance for zeolites to drastically cut the existing costs. Here again, however, lies the problems of undocumented concentrations of radionuclides and existing regulations regarding the use of ion-exchange processes. It would be possible to assume that industry would be capable of handling the need for the requirements of space, proper ventilating conditions, and costs. For these reasons, the future of large zeolites is unpredictable in industry.

4.2.5 Commercial Nuclear Power Plants

Most low level waste from fuel-fabrication plants is trash material, including clothing, filters, wastepaper, and discarded equipment. The radioactive liquid produced is either the direct result of fabrication or from use as a cleaner. It is usually processed by a combination of filters and ion-exchange methods. The wet solids produced are either direct results of the fuel fabrication or secondary products produced by the treatments of the liquid waste and appearing in the form of ion-exchange resins and filter sludges (see Tables 4.7 and 4.8).

The liquids produced are generally treated by filter, ion-exchange processes as discussed above and in the beginning pages of the section. Typical filters used are cartridge filters, edge filters, and precoat filters. Cartridge and edge filters are similar in construction with the cartridge filters being disposable, while the edge filters being reusable. The precoat filters consist of porous vertical tubes called septa on which filter medium is deposited. After the filter is used, it is cleaned and then precoat again. Most treatment techniques previously discussed for liquids are applicable for wet solids. Generally, when high water content exists, physical/ mechanical concentration techniques are used, whereas when free-water content is low, conditioning is frequently more cost effective [20].

Nuclear power plants provide perhaps the largest area for the growth of large zeolite crystals. As previously mentioned, zeolites have already

Low Level Waste From a Power Reactor

Type	Volume (Cubic Ft)	Radioactivity (Curies)	Treatment
Spent Resins	11,000	1,900	Dewatered by centrifuge
Concentrated Liquids	2,000	1	Solidified in container
Filter Sludge	0	0	-
Cartridge Filters	0	0	-
Trash	26,000	10	Compacted by hydraulic press
Non-Fuel Core Comp.	0	0	-
Total	39,000	1,911	

Containers	Number	Description
Strong, Tight Packages	240	3 100-ft metal boxes
55 Gallon Drums	275	Specially made steel barrels
Liners	0	-
High Integrity Containers	1500	55 gallon high impact plastic containers
Total	2015	

Shipments	Number	Description
Flatbed Truck	20	Exclusive cargo of strong, tight packages
Type A Package	100	Protection against normal traffic conditions
Type B Package	5	Safegaurds against severe accidents
Total	125	

Classification	Per Cent	Description
Class A	90	Processed to essentially dry solid
Class B	10	Stabilized to retain size and shape
Class C	0	-

Table 4.7

TABLE 4.8 TYPICAL LWR WET SOLID WASTES AND CHARACTERISTICS

Reactor Type	Waste Description	Annual Volume (m ³)	Gross Specific Activity (Ci/m ³)	Major Nuclide
BWR A ^a	Dewatered powdered resin and ion-exchange resin	255	7.1	Cr-51, Co-60, and Zn-65
BWR B ^b	Spent resins, concentrates and filter sludges	269	7.1	Co-60 and Cs-137
BWR C ^c	Spent resins and concentrates	368	2.5	Mn-54 and Co-60
PWR D ^d	Resins, sludges, and evaporator bottoms	65	2.1	Co-57 and Co-60
PWR E ^e	Solidified concentrates	283	3.5	Co-58, Co-60 and Cs-134
	Dewatered resins	142	--	Cs-137
	Solidified resins	340	--	
	Filter cartridges	17	--	
PWR F ^f	Spent resins	9	0.10	Mn-54, Co-58, Co-60 and Cs-137
	Solidified concentrates	283	0.18	Cs-137, Cs-134
	Filter cartridges	71	1.06	Co-58 and Co-60

a. Typical 1000-MWe unit (6 years old)

b. Typical 800-MWe unit (10 years old)

c. Typical 800-MWe unit (5 years old)

d. Westinghouse 800-MWe unit (2 years old)

e. Babcock & Wilcox 800-MWe unit (6 years old)

f. Babcock & Wilcox 900-MWe unit (6 years old)

been used in the cleanup of radioactive liquid. It is estimated that the larger crystals would not create intercrystal diffusion limitations due to the lack of pelletizers. This poses the possibility of cleaving semi-permeable membranes which would be highly selective. The large zeolites would possess the capability of greater absorption due to the lack of binding material, as well as the possibility of establishing a large scale ion-bed process.

Zeolites would be in direct competition with the exchange resins used today. These resins range in price from about \$100 per cu.ft. for average resins to greater than \$200 per cu.ft. for very good resins. These resins are carefully monitored. One such method for monitoring includes recording conductivity before and after processing. When a resin bed reaches a certain level on the measuring device, it is either packed with absorbents as with cheaper resins, or cleaned and/or regenerated for further use. Methods for this required measurement include recording conductivity before and after processing. One popular method for washing the resins involves ultrasonic cleaners, in which an ultrasonic field is created, which separates the waste and resin beads due to differences in densities. These beds may be cleaned once per week on the average. Regeneration involves a chemical process which returns the capacity of the beads. For example, after washing resins which have been depleted to 50 percent of their original capacity, they return to use with the same 50 percent capacity, whereas regeneration could increase the capacity to possibly 80 percent. Thus the resins would lose 20

percent capacity after each regeneration from its original state. An example of regeneration frequency could be about every five to six months.

Zeolites offer many benefits when compared to resins. Since they can be as much as 50 percent hollow, zeolites can hold much more waste per volume of exchange bed material than resins. This is also enhanced by the fact that zeolites are more selective than resins. Thus in processing a waste stream which contains radionuclides with typical concentrations in the parts per billion range, and various added chemicals which comprise most of the volume in a bed, zeolites would be more efficient at separating the various materials and holding them.

A second benefit of zeolites is that resins degenerate under the presence of radioactivity. Thus their efficiency decreases with time as well as only being able to regenerate them to a percentage of their original capacity. However, zeolites are not effected by the radioactivity, and will thus keep their high efficiency even under high radioactive concentrations and long periods of exposure. Because of this property, they are 100 percent regenerative. There are still other examples of zeolitic benefits such as being able to run at higher temperatures as compared to resins, thus allowing for higher processing rates (see Table 4.9).

As mentioned in the other sections there is a need for the concentrations of the nuclei present in the waste, such as Sr-90, Cs-137, Co-60, Mn-54, (see Table 4.10), as well as the concentrations present in the various added chemicals. A typical

TABLE 4.9
Comparison of resins and zeolites

Property	Resin	Zeolite
Chemical nature	Organic co-polymer	Aluminosilicate crystals
Structure	Amorphous	Crystalline
Porosity	Disperse, about 10nm	Specific, less than 1nm
Particle size	Variable, up to several mm	0.1-50um*
Ion sitings	Non-specific	Clearly defined sets of sites
Thermal stability	Low	Usually high
Solution stability	High	Usually low
Radiation stability	Usually low	High
Mechanical strength	Variable	Usually high
Attrition resistance	High	Variable
Cost	High	Usually low

TABLE 4.10 PRINCIPAL RADIONUCLIDES FOUND IN REACTOR LOW-LEVEL WASTES

<u>Radionuclide</u>	<u>Half-Life</u>	<u>Type of Radiation Emitted</u>
Barium-140	12.8 days	Beta, gamma
Cerium-141	32.5 days	Beta, gamma
Cesium-134	2.05 years	Beta, gamma
Cesium-137	30.0 years	Beta, gamma
Cesium-136	13.7 days	Beta, gamma
Chromium-51	27.8 days	Gamma
Cobalt-58	71.3 days	Beta, gamma
Cobalt-60	5.26 years	Beta, gamma
Iron-59	45.6 days	Beta, gamma
Manganese-54	303.0 days	Gamma
Zinc-65	245.0 days	Beta, gamma
Zirconium-95	65.5 days	Beta, gamma

Source: Taken from The 1979 State-by-State Assessment of Low-Level
Radioactive Wastes Shipped to Commercial Burial Grounds, NUS-3440,
Revision 1, November 1980.

cost for processing and burial of reactor waste would be about \$50,000 based on the use of a 6 ft. high by 6 ft. diameter fiberglass high integrity container (160 cu. ft.) with a 200 cubic foot outside liner (cost based on liner's dimensions). However this cost does not convey the information needed to compare the efficiencies of the two systems. A typical filter/ion-exchange process may involve efficiencies of 80-90 percent for the filter and about 90-95 percent for ion-exchange. Zeolite processes are expected to at least meet, but most likely surpass these values while possessing many benefits, some of which discussed. Thus the zeolitic benefits would have to compensate for the higher cost for materials and further research would have to go into creating an effective zeolitic process.

4.2.6 Government Facilities

Low level waste is generated through government research and defense programs. The Department of Energy, which conducts research in nuclear energy, reactor safety, and waste treatment techniques, produces vast types of low level waste. Waste is also produced through the fabrication of nuclear weapons and fuel for nuclear ships and submarines [22].

The methods for processing this waste consists of virtually all of the methods described in the first section along with others not listed. All government waste is buried at government waste sites and handled by government facilities. In this way a true cost of procedure can never be attained due to the noncompetitive nature of the system.

As in the reactor waste, the future use of large zeolites is highly possible. This is due to the many similarities existing between the reactor and governmental waste. It therefore can be assumed that if large zeolites tend to be effective in either government or reactor technology, it will also be effective in the other.

4.2.7 Low level Waste-Conclusion

As seen in each of the previous subsections, the question of possible use of large space grown zeolites in the various areas of radioactive waste is not a clear answer. More information is required before these decisions can be made. For example, as stated, the volume or mass concentrations of the nuclides and chemicals are needed in each case. It seems that in order to find this information, independent tests will have to be run since the information is not required by law and therefore not readily available. Also, the effectiveness of the large zeolites will have to be proven, as well as research provided for the production of such processes. Large zeolites offer the possibility of volume reduction through a highly selective, more packing efficient material. However, this information will never be known until an actual large crystal is tested.

Another problem to consider is that of volume. While such places as industry may produce enough waste as a whole to favor the use of zeolites, when this volume is broken down by the number of industries actually contributing to this amount, the same opinions may or may not hold true.

A final piece of information which should be considered, is that due to new regulations, each state is now required to bury its own nuclear waste, or set up a regional pact with a few of its surrounding states to designate a burial site. Violations to this law induces surcharges placed on waste still shipped to out of state grounds. For example, in January 1987 the surcharge placed on the burial of the waste was \$10 per cubic foot. This

number is designated to rise in the following years and reach \$40 per cubic foot by the year 1990 [23]. These charges will not be directly paid by the states rather they will be passed on to the research facilities which produce these wastes. Thus as a recent comment by an official from NELRAD (a consortium of New England low level waste producers) suggests, facilities will now have to set aside enough extra money to cover these costs, thereby hurting such institutions as medical and industrial.

The estimated cost of setting up a waste site was twenty million dollars in 1985 [23]. Since more of these sites will now be demanded by regulations, it will also be possible for the states to provide efficient means for waste processing. In this way, zeolites and its associated processes would be in direct competition with resins and their associated processes. Thus zeolites would not have to compete as a new process which has to be far superior and cost efficient to replace an already existent process, yet as a new process which would be in direct competition with other processing for the ability to be employed.

4.2.8 High Level Waste

There is an ongoing effort to select a suitable treatment for the high level waste produced in the United States and most other countries which have nuclear power capability. The most promising option is that of solidification of the liquid, package into carbon or stainless steel containers, and then burial in deep, stable ecological strata, on land or under the deep ocean. The major consideration is that the wastes should be prevented from returning to man's environment at least until their activity has decayed to safe levels [24]. In most countries, including the United States, these wastes are being stored in containers until these decisions are made. However, in France, processes involving solidification of the wastes in glass form and burial have been implemented.

The proposed use of glass for solidification tends to be the most accepted option. Solidification immobilizes nuclear waste by embedding nearly all by-products into a single, inert form. There exists a few processes by which glass conversion is used. They can be broken up into broad groups depending on the number of stages in the cycle. One group exists of one-stage processes in which the liquid waste together with glass forming materials are continuously fed into a heated stainless steel vessel in which the mixture fuses to a homogeneous glass. Another group consists of two stage processes, in which the liquid is first dried and then mixed with glass powder into a glass-making furnace [25].

Glass has been chosen due to the ability of the high level

nuclear wastes to combine well with the standard ingredients used in glass making. Vitrified waste glasses, such as Pyrex, are very stable and have good resistance to heat, chemical action, radiation, and mechanical stress [26]. These glasses have been shown to be highly resistant to leaching of their radioactive content by ground-water. However, there has been a considerable amount of work done on the development of other solids, such as artificial rocks, in which to incorporate the high level waste. These products have also been shown to possess high leaching resistance.

Zeolites exist as one of the possible choices for material in disposal of high level waste. It has already been used today to help store high level waste due to its ability to hold its reactants for long periods of time [6]. Zeolites, could be used in two distinct ways. The first could be the direct conversion of liquid to solid waste through the use of the crystals, and then encapsulated in tanks for disposal. The second is as a pretreatment to the glass process. Since zeolites possess the ability to mix well with glass, they could be used to convert the liquid waste to solid zeolitic form, and then processed into glass. However, due to the depth of research needed, the future of large zeolites in disposal of high level waste is uncertain.

4.3.1 Leather Tanning Industries

In the leather tanning industry, filtration and separation processes are required to clean up waste waters produced. We contacted several leather tanneries in New England to determine the current costs and procedures involved with current waste water treatment procedures. As we expected, several tanneries refused to discuss this information. A few, however, did supply us with helpful information.

The cost of waste water treatment depends on many variables including plant size and geographic location, but an average estimate on the day to day operation seems to be about \$40 for a plant with a daily output of 14,000 square feet of leather. This indicates that the primary costs of the water treatment is not in operations, but rather in the initial plant setup. To setup a typical waste water treatment plant today costs in the area of \$750,000. Therefore, in order for a large zeolite process to be cost effective, it would have to significantly reduce the cost of a processing plant. While this might be possible, it would require an in depth study of the clean up processes and current plant setups to determine this for sure. We suspect, however, that given the low costs of current daily operation, as well as the relatively low cost of plant setup, a large zeolite setup would probably not be cost effective.

4.3.2 Battery Manufacturers

As with leather tanneries, battery manufacturers must also clean up waste waters. Duracell supplied us with some very helpful information. Plant size, what kinds of batteries are made, and the changing EPA requirements are only a few of the variables which would determine the cost of waste water clean-up. An average battery plant might produce 10 to 20,000 gallons of waste water per day, and it typically costs around \$100,000 per year to operate the plant. A wide variety of chemicals must be removed from the water including zinc, mercury, manganese and lubricants. Current processes for water purification include fairly simple and inexpensive ones such as gravity separation, but as the EPA standards become more rigid, Duracell will need to look into more complicated and expensive procedures, such as ultrafiltration. Currently, an ultrafiltration setup costs in the neighborhood of \$200,000. Here a zeolite process might be introduced in an attempt to achieve a high order of filtration at a lower cost. However, Duracell did mention that a fairly large portion of clean up costs were devoted to sludge removal and disposal, which would also be required in a zeolite process.

4.4 Medical/Pharmaceutical Uses of Zeolites

Zeolites could prove useful in the medical field in both separation and catalysis processes. For separation, major considerations are the size of the particles (molecules) in question and any specific constraints (such as a high pH environment) of the process incorporating the zeolites.

Most of the general separations in gas and fluid preparation involve comparatively large sized particles. Particulate matter is often present in industrial grade chemicals purchased by medical centers. In addition, particles may be incidentally introduced into a preparation (such as bits of rubber from a stopper). In preparation of an intravenous nutrition solution, consisting of amino acid, dextroses, fat emulsion, electrolytes and additives, particulate matter is easily removed by a 0.5 micron filter (about 5 to 1,000 times too big for zeolites). Sterility is ensured by a second filtering with a 0.2 micron filter. Sterilization is also performed with infrared, ultraviolet, or gamma ray radiation, and autoclaving. Filtration is the preferred method when there is question of destroying or deactivating medicines such as antibiotics and biological solutions. Bacteria and mycoplasmas are typically 1 to 5 microns in size while rickettsias vary from 0.3 to 0.5 microns in size. Viruses, the smallest agents of infestation, are from 0.02 to 0.4 microns. Since zeolites average pore size ranges from 2 to 10 angstroms (0.002 to 0.01 microns), they cannot be used to efficiently separate these microbes. Clearly, other methods would do as well as zeolites and likely at lower cost. Although

the microbes cannot be trapped by the zeolites, a zeolite membrane could be used separate and purify a fluid (blood, for example). Unfortunately, many of the components of the fluid itself may also be excluded by the membrane.

Dialysis is a process where purification of a blood is done by a simple filter when kidney function is impaired. Blood is taken from the patient and passed through a filter (the dialyzer), then returned to the patient. The filter consists of a coil of fibers (typically made of cupra-ammonium) inside a container. Blood is passed under pressure through one side of the dialyzer and an equalizing fluid (the dialysate) is passed through the other. As the blood passes through the dialyzer, impurities are adsorbed by the fibers. Unfortunately, many of the necessary blood chemicals are also filtered. These blood chemicals are maintained at correct levels by the dialysate. Large zeolite membranes may offer a simplification of this process. The zeolite membranes could be engineered to filter blood impurities with significantly less loss of necessary blood chemicals. Currently, large volumes of blood are removed from the patient and sent through the dialyzer under high pressure. This allows for faster purification (four to eight hours at a time, rather than continuous dialysis). The greater pressure across the fibers increases the rate of adsorption. The greater efficiency of zeolite membranes would allow filtration with significantly less pressure. This would reduce the volume of blood necessary to remove from the patient per period of time, and corrections of chemical blood levels could be done on a much

smaller scale. In addition, the patient's own cardiovascular system would supply sufficient pressure to run the process. With the use of large zeolite membranes, significant reductions in size and cost of dialysis equipment could be realized.

Zeolites have already proved effective in separating blood impurities. Zeolites also offer the considerable advantage of constant regenerability compared with current dialyzers (a dialyzer is typically used 6 to 7 times and then discarded). The possibility of a portable, zeolite-based, dialysis machine exists. However, there remains the question of the precise monitoring of the blood (monitoring the air in the blood and electrolyte levels). These monitoring devices represent an appreciable portion of the cost and size of the present dialysis machinery. Overall, large zeolites represent an excellent commercial option in the area of dialysis and filtration [27,28].

4.5 The Space Program and Zeolites

Students and faculty at WPI have already developed an experimental zeolite growth chamber to fly on the Space Shuttle flight planned for February 1988. The chamber consists of an insulated, closed container of water with reactive chemicals in it, which is heated by battery supplied power.

The simplicity of growing zeolite crystals have made them a perfect candidate for space based manufacturing. The plans for a permanent space station will provide facilities where long term microgravity research and large scale manufacturing of large zeolite crystals can be conducted. To mass produce large zeolites, however, a much larger scale process would be required. Before such a process can be implemented, America's space program will have to mature further.

At the very least, a permanent space station would have to house the reaction vessels, so they would not have to be repeatedly flown into and out of orbit. Also, it isn't certain that costly shuttle flights could continue without a space station in orbit. So, if the US Space Program is to continue, a space station must be in its near future.

It has been suggested that all the raw materials needed to manufacture the large zeolites could be mined from the Moon [29]. These materials could then be used to manufacture zeolites on the Moon or transported to an orbiting or stationary materials processing station. This would greatly reduce the cost of transporting the materials to the reactor. Since the surface gravity of the Moon is approximately 1/6 that of the Earth, much

less energy would be needed to lift materials from the surface.

It is also a good question whether large zeolite crystals can be produced on the lunar surface; a combination of lower gravity and increased viscosity of the reactant mixture may be sufficient to allow larger crystal growth.

Transportation of materials to and from space represents the greatest percentage cost of producing zeolites in space. Materials sent from the Moon would not require cargo hauling space crafts. Prepared packages of materials could be launched from the lunar surface off magnetic rails and 'caught' in space by large conical Kevlar bags [30].

Under mild hydrothermal conditions, zeolites can be easily synthesized from a variety of starting materials, especially volcanic glass. Glass is a major constituent of the lunar surface, and is similar in chemical composition to the volcanic glasses found on Earth. Since true lunar soil samples are limited in quantity and availability, 'analog' lunar glasses have been used to test this possibility on Earth. Hydrothermal alteration of these glasses has successfully produced a number of zeolites. Few problems are anticipated in developing procedures to produce and engineer any of the major zeolite types. Several zeolite types have been made on Earth by using similar glasses to those found on the Moon's surface, including clinoptilolite, phillipsite, and mordenite. The alteration of the glasses depends on: 1) temperature, 2) chemical composition and pH of the solution, 3) chemical composition of the starting material, and 4) the existence of an open or closed system during the alteration

process. A variety of solutions would be used to act as solvents of the glass during the synthesis procedure. Assorted carbonates and hydroxides (K_2CO_3 , Na_2CO_3 , $NaOH$, $Ca(OH)_2$) would be included in the solutions. The majority of the additional substances are also present in the lunar soil or will be byproducts of Moon based metal production [29].

There are several strong potential uses for for zeolites in space and on the Moon. Any type of isolated base requires recycling of both air and waste. Zeolites are already used on Earth for large scale sewage treatment, and would prove especially useful in a closed environment. The ease of making, wide range of properties, and regenerability of zeolites makes them ideal for any closed environment. Zeolites can be engineered to selectively filter harmful, toxic or unwanted gases from both sewage and air, including SO_2 , CO_2 , and N_2 . An atmosphere regeneration device can be made by choosing the appropriate combination of zeolites. Large zeolites membranes offer a higher efficiency of separation with less overall space being used, an important consideration in limited area space or lunar bases. A separate system could be used to provide a different atmosphere more appropriate for plant growth. Fertilizers could be provided by released ammonium from sewage treatment.

Aside from space uses of zeolites there remains the problem of returning them to Earth. Presumably this cost would be minor compared to the cost of getting materials. The estimated cost of transport and processing costs is \$4600 per kilogram.

These suggestions are very long term at best. If the

American people do not show an interest in continuing the space program, at least to the point of establishing a permanent space station, the future of any space based manufacturing ventures is in doubt. International cooperation with European nations will reduce the United States' economic burden of developing materials processing in space. The Space Shuttle would be used to transport the European Space Station to orbit. This will allow an earlier start and an incentive to process zeolites in space.

4.6 Large Zeolites as Competition for Small Zeolites

Small zeolites are quite popular as cracking catalysts as well as in other roles. We wondered if, perhaps, large zeolites might be more effective in this important aspect of the chemical industry.

Large zeolites would have greater selectivity due to longer diffusion paths and could also have increase efficiency over small pelletized zeolites due to the absence of binder material.

The way small zeolites work as cracking catalysts are as follows. Microspheres of amorphous silica-alumina have small channels (around 10 microns) leading into them. Along these channels are zeolite crystallites with pore sizes on the order of a few angstroms. Material diffuses into these channels and the molecules enter the zeolite cavities where a reaction takes place. The new material then diffuses back out.

It appears that if the crystal size is significantly increased, it would take much longer for the material to diffuse into the center of the crystal. In fact, it is possible that the inside may not be used at all as reactions would occur on the outside surface of the crystal and activated diffusion in the microspheres of the zeolite would effectively prevent access to the center of the zeolite crystal.

A similar problem exists with adsorption - with a much larger zeolite, it might take a very long time for the material to be absorbed to diffuse into the center of the crystal. If time is not important, than large zeolites could be used. But if time is important, it might be more effective, in some cases, to use

many small zeolites, which would have more easily accessible surface area.

V. SUMMARY AND CONCLUSIONS

Based on the markets we investigated, it is our conclusion that the areas with the greatest potential for large zeolite crystals is that of the nuclear and medical industries (see Summary Table). Nuclear waste cleanup is a problem that cannot be ignored. With growing pressures on states to dispose of their own waste, rather than ship it out, we feel that the use of large zeolites will be a competitive technology. Large zeolites also offer the medical industry several advantages, especially in the areas of chemical preparation and dialysis.

Some of the other industries we examined, such as leather tanning and battery manufacturing could probably employ zeolite processes, but initial indications suggest that it probably would not be cost effective.

We do feel that the research being conducted on the present scale into the manufacture of large zeolites is useful. It is probable that in the process of attempting to develop large crystals in space, much will be learned about zeolites and how they form. This knowledge may be put to use on Earth to develop larger, or better zeolites without the expense of a space based process. Also, it is possible that, upon attempting to grow zeolites in space, other unforeseen properties of space grown zeolites may become apparent, as well as new structures and chemical compositions. These findings may lead to new applications for space grown zeolites.

Large zeolite crystals are not being developed in response to

a customer initiated request or idea. Large zeolites are being developed along the line of reasoning that "there must be some problem this product will solve," rather than "there must be some product which will solve this problem." This does not mean that it will not be successful, but it does mean that extensive market studies and projections must be done on an ongoing basis to ensure success, because it is well known that having a good, innovative product does not guarantee having a successful one.

Summary Table of
Possible Applications

APPLICATIONS	ADVANTAGES	DISADVANTAGES	RECOMMENDATIONS
Low Level Nuclear Waste Cleanup	Volume Reduction Increased Effic. Regenerability	Cost and Operating Limitations	Deserves looking into, especially in light of new legislation.
Battery/ Leather Tanning Water Cleanup	Better Filter Resolution	Cost of New Plant/Process	Cost overrides advantages at this time.
Dialysis/ Medical Industry	Smaller Size Lower Pressures Regenerability Possibility of Portable Dialysis Machine	Minor	Merits serious Consideration

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