Sodium Silicates and Sodium Aluminosilicates

G.C. SCHWEIKER, Philadelphia Quartz Company, PQ Research & Development Center, Lafayette Hill, Pennsylvania, USA

ABSTRACT

A highlight summary of the chemistry and commercial manufacturing processes involved in making sodium silicates and sodium aluminosilicates (zeolites) is presented. Some relative and current raw material costs and energy needs, and overall qualitative economic comparisons of the various processes are discussed. Estimated world market consumption of both silicates and zeolites, by geographical areas and by major applications, is reviewed. Market volume projections into the near future are ventured on a worldwide basis, indicating substantial growth. Capacity to supply silicates in North America to 1983 is presently in place, but most other geographical areas of the world will require increased manufacturing capabilities to keep in balance with the projected market growth. It is suggested that zeolite production in the world will increase over fivefold by 1981, due principally to the expected rapid growth of its use in detergent formulations.

SODIUM SILICATES

Early History of Commercialization

The innovative early work of Von Fuchs in Munich, starting about 1818, is generally considered to be the base for the commercial development of the family of materials called soluble silicates (1,2). Industrial development concerning manufacturing processes and uses proceeded at an accelerating pace in Germany, France, Great Britain, the U.S., and other countries during the following half century. For example, Kuhlmann had established the manufacture of soluble silicates in France by about 1841 (3). In Great Britain, Walcker (4), Sheridan (5), Dunn (6), and Gossage (7) described methods of production and uses in silicated soaps in the years 1828-1854. In the U.S., a book on "Soap and Candles," (8) with a chapter describing the preparation of silicates, and a statement of detergent value imparted by them, was published in 1847; and a number of companies began to manufacture soluble silicates in the 1860s in larger volumes as U.S. markets grew, and improvements, such as

described by Elkinton (9) in furnace beds and continuous operations, were developed.

Chemistry, Manufacturing Processes, Comparative Economics

Although many improvements and variations in the manufacturing processes and overall economics have been made, and are still being made (10), the basic chemistry involved in the production of soluble silicates, known and described by the mid-19th century, remains the same today. Figure 1 outlines the simple chemical reations of the principal processes of commercial significance. Most of the sodium silicate products manufactured in the world today start with sand and sodium carbonate, which is heated in a furnace or other apparatus to about 1,100-1,200 C, as illustrated in equation 1. This same reaction can be made to occur, essentially in the solid state, for sodium metasilicate products, by heating to about 650-850 C, for example, in a rotary kiln (11) or fluidized bed (12). During the reaction, carbon dioxide is liberated as a gas, and the raw materials are converted into sodium silicate of a given ratio, which is dependent on the relative amounts of the starting materials used. The term "ratio" is discussed later. Equation 2 illustrates another process which, some years ago, had considerable commercial impact in many countries. Sand and sodium sulfate, together with a reducing agent, primarily carbon in the form of finely divided coal, are the raw materials in this reaction (2). Oxides of sulfur and carbon are by-products. This process can be used when Na_2CO_3 is unavailable or too expensive.

In the pressure reaction (equation 3), the starting materials are silica flour and alkali hydroxide. The materials are heated to about 130-180 C under pressure, to about 1200 kPa. An important limitation to the large-scale commercial utility of this process is that only lower ratio products − below about 2.5 − can be produced economically.

The relative cost of carbonate vs. hydroxide plays a major part in determining overall economics of the furnace or kiln vs. autoclave processes. Today, in a typical East Coast U.S. plant, Na_2CO_3 is about 0.7 as expensive as NaOH on an active Na_2O basis. On the other hand, energy
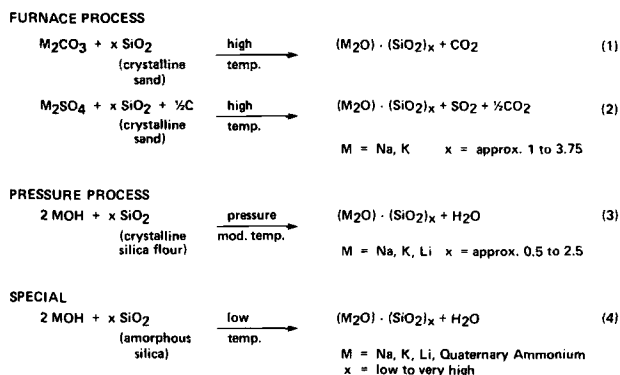
FURNACE PROCESS

$$M_2CO_3 + x\ SiO_2 \xrightarrow[\text{temp.}]{\text{high}} (M_2O) \cdot (SiO_2)_x + CO_2 \qquad (1)$$
(crystalline sand)

$$M_2SO_4 + x\ SiO_2 + \tfrac{1}{2}C \xrightarrow[\text{temp.}]{\text{high}} (M_2O) \cdot (SiO_2)_x + SO_2 + \tfrac{1}{2}CO_2 \qquad (2)$$
(crystalline sand)

M = Na, K   x = approx. 1 to 3.75

PRESSURE PROCESS

$$2\ MOH + x\ SiO_2 \xrightarrow[\text{mod. temp.}]{\text{pressure}} (M_2O) \cdot (SiO_2)_x + H_2O \qquad (3)$$
(crystalline silica flour)

M = Na, K, Li   x = approx. 0.5 to 2.5

SPECIAL

$$2\ MOH + x\ SiO_2 \xrightarrow[\text{temp.}]{\text{low}} (M_2O) \cdot (SiO_2)_x + H_2O \qquad (4)$$
(amorphous silica)

M = Na, K, Li, Quaternary Ammonium
x = low to very high

FIG. 1. Chemistry of commercial soluble silicate manufacture.

$$\text{Ratio} = \frac{x}{y} = \frac{\text{weight of silica } (SiO_2)}{\text{weight of alkali } (M_2O)}$$
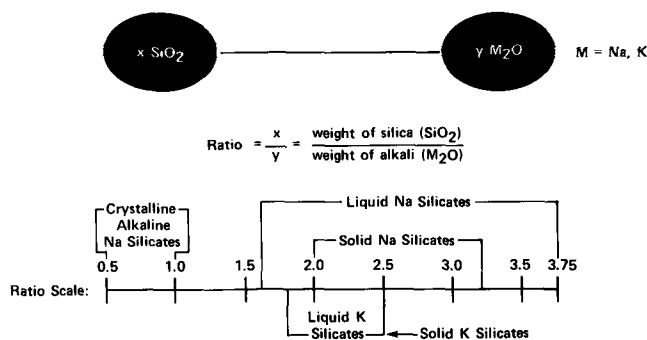
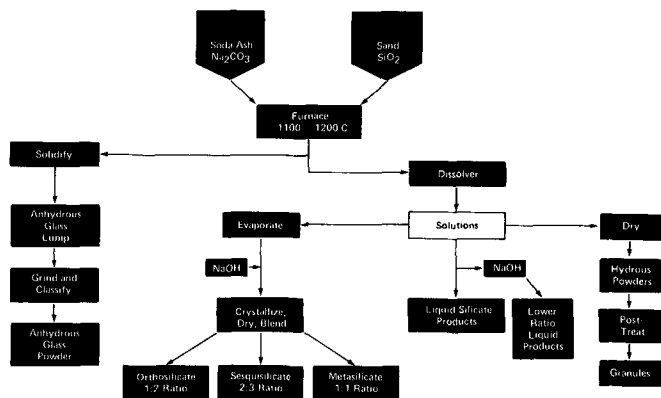FIG. 2. Silica to alkali ratio in commercial silicates of interest in detergents.

FIG. 3. Furnace process for manufacture of sodium silicate products.

requirements for a 2.4 ratio silicate made in an autoclave are only 0.3 of the cost of the same ratio silicate made in a furnace, neglecting the energy used in grinding sand to silica flour. This difference in energy cost is likely to become even more significant in the future, although there is still room for considerable energy efficiency improvements in the furnace process. At the present time, up to three times the theoretical energy is being consumed, depending on furnace production rates, in many typical open-hearth furnace plants. Versatility of product ratios and economies of scale and operation still favor the furnace as opposed to other processes, except for special lower volume requirements in certain locations, or for special products.

Equation 4 in Figure 1 illustrates essentially the same chemistry as involved in the pressure reaction, except that specialty silicates, such as quaternary ammonium silicates, can be simply made; and the limit of 2.5 does not apply to the ratio of the silicate products made in the process, when the much more expensive amorphous forms of silica are used as one of the starting raw materials in place of crystalline sand. Temperatures can range from ambient to 100 C in this process (2,13).

The most important factors determining which process is used to manufacture silicate products in volume, in any

specific location in the world, are the availability, cost, and purity of the starting raw materials; i.e., sodium vs. potassium carbonate, alkali sulfate vs. carbonate vs. hydroxide, and crystalline sand vs. amorphous silica, as well as the kind and purity of the silicate product desired. It appears that for the near future, overall production economics will continue to favor the furnace route, as a general rule, for large-volume silicate manufacture.

Silicate Product Ratios

Commercial silicate products span a wide range of silica to alkali ratio, as shown in Figure 2. In the case of sodium silicate products, weight and mole ratios are very close because Na_2O has a molecular weight of 62 and silica of 60. Weight ratios are used here. The products cover silica to alkali ratios in the range of 0.5 to 3.75 silica to 1 alkali. Above a ratio of 1, the commercial silicate products are amorphous materials. Crystalline orthosilicates, sesquisilicates, and metasilicates cover the discrete ratios of 0.5, 0.67, and 1.0, respectively. These products are known in the industry as "alkaline" silicates because of the relatively high percentage of Na_2O, which tends to make the products alkaline in nature. The higher ratio silicates are known as "siliceous" because of the relatively greater amount of SiO_2. As one would expect, solutions of the alkaline silicates have a much higher pH than the siliceous products. The range of pH covered by commercial silicate solutions is from about 10 to 14.

Furnace Process

Figure 3 illustrates a typical schematic process for the furnace method of manufacturing sodium silicate products. After the Na_2CO_3 and sand are completely reacted to form molten silicate, the melt is solidified by cooling and sold in the form of anhydrous glass lumps, or ground and classified to anhydrous glass powders. When the glass is dissolved in water, it forms the many kinds of liquid silicate products which cover a wide range of ratios and solids concentration. The more alkaline solutions are readily crystallized, dried, or blended into the meta-, sesqui-, and orthosilicate products, usually by adding NaOH to obtain the proper

TABLE I

Uses of Sodium Silicates [a]

User	% of U.S. market
I. Silica Source	37%
1. Silicate-based pigments	20%
2. Cracking catalysts	10%
3. Silica gels	3%
4. Silica sols	1%
5. Zeolites	1%
6. Titania pigments	1%
7. Calcium silicate	1%
II. Detergent Applications	30%
1. Household laundry powders	17%
2. Industrial/Institutional laundry supplies	6%
3. Household dishwashing powders	3%
4. Metal cleaning compounds	2%
5. Institutional dishwashing	2%
III. Other	33%
1. Adhesives	4%
2. Cements	4%
3. Roofing granules	3%
4. Ore flotation	2%
5. Water treatment	2%
6. Textile bleaching	1%
7. Foundry binder	1%
8. Welding rods	1%
9. Miscellaneous	15%

[a]Source: PQ Estimates.

TABLE II

Estimated World Production Capacities, Markets,
and Demand Projections for Sodium Silicates[a]
(Thousand MT, Anhydrous Basis)

World region	1975 Capacity	1975 Market	1983 Market projection
North America	1200	752	1040
Latin America	237	177	320
Western Europe	1000	846	1475
Eastern Europe	178	169	290
U.S.S.R.	200	188	300
Middle East	15	35	95
Far East	500	460	800
(Excludes India, China)			
Africa	34	54	210
Total	3364	2681	4530

[a]Source: PQ Estimates.

TABLE III

Functions of Sodium Silicates in Detergents

1. Alkalinity and Buffering — sustains pH ranges from 9.5 and above
2. Emulsification — oily and greasy soils
3. Neutralization or Saponification — acidic soils
4. Deflocculation — particulate soils
5. Soil Suspension — prevents redeposition
6. Corrosion Inhibition — protects metals and overglaze on china
7. Hard Water Control Aid — reduces multivalent ion activity
8. Surface Active Agent — moderate interfacial tension reduction
   in oil-water systems
9. Processing Aid — granule binder

ratio. These products are made in anhydrous and hydrated forms. Solutions are specially dried (such as by spray or drum drying, and including specialized post-treatment techniques) to produce hydrous powders and granules, which cover a wide range of particle sizes, densities, and physical forms. Additionally, NaOH may be used to make lower ratio liquid products from the solutions, depending on the glass ratio made in the furnace.

Competing Applications, Markets, Projections

Important uses of sodium silicates, including a subclassification of detergent applications, and the percentage of the U.S. market they consume, are shown in Table I. The three largest single uses in the U.S. are in detergents, silicate-based pigments, and catalysts. The group of detergent applications amounts to about 30% of the total U.S. consumption. The end-use distribution given in Table I for the U.S. market is similar in other industrialized, relatively highly developed countries around the world. In certain other geographical areas, the dominant uses for silicates are primarily in other markets, such as paper, textile, and building applications.

An estimate of world markets and production capacities for sodium silicates, by geographical area, along with market projections for 1983, are illustrated in Table II. While sufficient capacity is presently in place for the expected overall average market growth of 4-5% per year in North America, this is not the case for other geographical areas, particularly in Europe, Latin America, the Near to Far East, and Africa, where growth rates, on the average, are expected to be much higher.

Detergency Functions

Specific detergency builder and other helpful functions performed by sodium silicates are listed in Table III. While many of these helpful properties of silicates have long been known (2), they continue to play important functional roles in modern built detergent formulations. In fact, one property that is becoming increasingly important for zero phosphate products is the ability of silicates to control

TABLE IV

Raw Materials Cost to Produce One
MT Of Zeolite NaA (Anhydrous Basis)
(U.S. $)

Raw material	Sodium silicate process	Clay process
Sodium silicate[a]	110.8	--
Alumina trihydrate[b]	76.2	--
Sodium hydroxide[c]	26.0	53.1
Calcined kaolin[d]	--	127.9
Total	213	181

[a]Sodium silicate (3.2 ratio) — 28.7% SiO_2, 8.9% Na_2O @ $76
8.9% Na_2O @ $76/MT.
[b]White alumina trihydrate — 65% Al_2O_3 @ $139/MT.
[c]Sodium hydroxide — 50% NaOH @ $92/MT.
[d]Calcined clay @ $160/MT.

harmful hard water ions, particularly magnesium (14). A magnesium ion control agent is especially critical in detergents which contain only zeolite NaA as the hardness control agent, since zeolite NaA is relatively ineffective for magnesium, even though it is very effective for calcium ion exchange and control (15,16).

SODIUM ALUMINOSILICATES

Early History of Commercialization

Aluminosilicates have been known in nature and described as early as 1756, when a Swedish mineralogist, Baron Cronstedt, designated certain natural minerals as zeolites (17). An early patent for the synthesis of sodium aluminosilicates from hydrous silica and sodium aluminate was issued to Gans, in Germany, in 1906 (18). Most early commercial processes to manufacture amorphous sodium aluminosilicate gels (at that time also called zeolites) appear to be variations or improvements over the process described, for example, by Boehringer and Gessler in the U.S. (19), and by DeBrunn in Britain (20), whose patents issued in 1913. This process used sodium silicate and sodium aluminate as the starting raw materials. In a similar early commercial process to make "Doucil," (a sodium aluminosilicate gel that was used as an ion exchange material for water softening in the U.S.) at one of Philadelphia Quartz Company's plants starting in the 1930s, the gel was dried to about 50% water content, broken up into hard angular granules, leached, and wet screened to about 0.4 to 2.5mm (21).

The work at Linde Division of Union Carbide Company in the 1950s on the manufacture and utilization, as well as chemical understanding of the synthetic, crystalline aluminosilicates is generally considered to be the base for the first commercialization of this important family of synthetic chemical products (22-26); Now, only the crystalline aluminosilicates are referred to as zeolites, or alternatively, molecular sieves.

SILICATE PROCESS

$$2\ NaOH\ +\ Al_2O_3 \cdot 3\ H_2O\ \xrightarrow[\text{temp.}]{\text{moderate}}\ \underset{\text{Sodium Aluminate}}{2\ NaAl\ (OH)_4} \quad (5)$$

$$12\ NaAl\ (OH)_4\ +\ 4\ (Na_2O) \cdot (SiO_2)_3 + 7\ H_2O\ \xrightarrow[\text{temp.}]{\text{moderate}}\ \underset{\text{Zeolite NaA}}{Na_{12}\ [(AlO_2)\ (SiO_2)]\ 12 \cdot 27\ H_2O + 8\ NaOH} \quad (6)$$

CLAY PROCESS

$$\underset{\text{Kaolin}}{2\ Al_2Si_2O_5\ (OH)_4}\ \xrightarrow[\text{calcine}]{500 - 600\ C}\ \underset{\text{Metakaolin}}{2\ Al_2Si_2O_7\ +\ 4\ H_2O} \quad (7)$$

$$\underset{\text{Metakaolin}}{21\ H_2O\ +\ 6\ Al_2Si_2O_7\ +\ 12\ NaOH}\ \xrightarrow[\text{temp.}]{\text{moderate}}\ \underset{\text{Zeolite NaA}}{Na_{12}[(AlO_2)\ (SiO_2)]\ 12 \cdot 27\ H_2O} \quad (8)$$
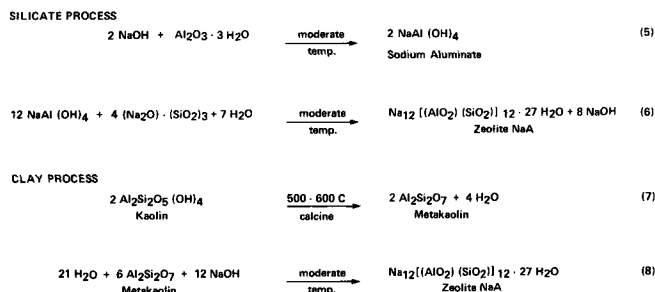
FIG. 4. Chemistry of commercial zeolite NaA manufacture.

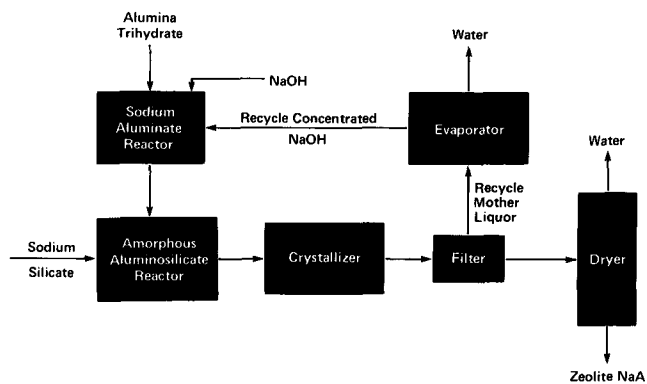FIG. 5. Process for manufacture of zeolite NaA using sodium silicate and alumina trihydrate.

FIG. 6. Process for manufacture of zeolite NaA using kaolin clay and sodium hydroxide.

These materials have a three-dimensional framework structure in which silicon and aluminum atoms are tetrahedrally coordinated to oxygen atoms (27). The framework structure enfolds cavities containing water molecules and cations that are capable of undergoing desorption and cation exchange. The presence of aluminum atoms in the framework results in negative charges — one unit of negative charge for each aluminum atom. The charges are neutralized by exchangeable cations that are in the cavities within the zeolite structure.

Chemistry, Manufacturing Processes, Comparative Economics

The chemistry of the two major manufacturing methods for making zeolite NaA is illustrated in Figure 4. One method (22-26) uses sodium silicate and sodium aluminate, which is made from alumina trihydrate and NaOH, as shown in equations 5 and 6. The other method (28-31) uses a kaolin type of clay which is calcined, and NaOH, as shown in equations 7 and 8.

Silicate Process

A schematic flow diagram for the silicate process is shown in Figure 5. In a recently described continuous process (32) for making zeolite NaA from alumina trihydrate and sodium silicate (Fig. 5), sodium aluminate is first made from alumina trihydrate and NaOH. In practice, an excess of NaOH is used to prepare a stable concentrated sodium aluminate solution. When this solution is mixed with aqueous sodium silicate, the amorphous product that forms is mixed well. When this is heated to 77-110 C, zeolite NaA crystallizes from the reaction mixture in 1 to 8 hrs. The crystals are separated from the mother liquor, and the wet filter cake product is dried. The mother liquor contains NaOH, which is concentrated by evaporation and recycled to make more sodium aluminate. Sources of silica other than liquid sodium silicate can be used in this reaction; for example, any amorphous silica may be used, but only at a major economic disadvantage.
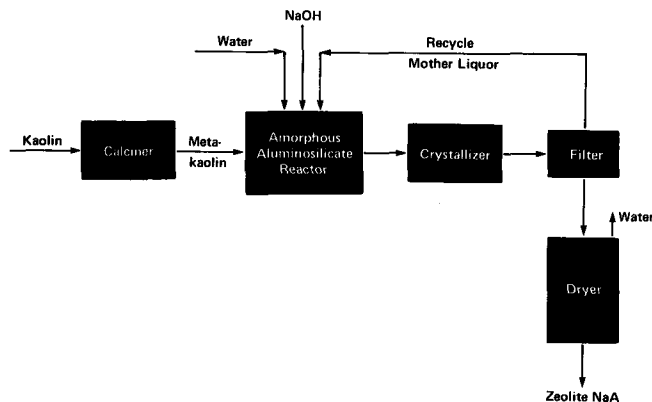
Clay Process

The process for making zeolite NaA from clay and NaOH (28,29) is outlined in Figure 6. It is always necessary to calcine the kaolin type of clay at about 500-600 C, in order to convert it to a more reactive form, called metakaolin. Metakaolin is amorphous to X-rays and no longer has the kaolin crystal structure. If the clay is not calcined, hydroxy-sodalite crystallizes during the process. Digestion of the calcined clay with aqueous NaOH results in the formation of an amorphous sodium aluminosilicate, from which zeolite NaA is crystallized in a few hours at 90-110 C. the rest of the process is similar to that previously described for the sodium silicate process, when the excess NaOH required in the clay process is recovered.

The raw materials cost of using liquid sodium silicate and alumina trihydrate is compared to that using calcined kaolin and NaOH in Table IV. The raw materials cost for the clay process can be as much as 15% lower than the raw materials cost for the sodium silicate process. Offsetting this difference in raw materials cost for most zeolite uses, however, is the cost required to remove iron and other impurities from the clay. For detergent-grade zeolites, a clay purification process must be installed, and additional capital, energy, raw materials, and manufacturing costs must be computed for each particular case.

An advantage of the clay process lies not in making more economical detergent-grade zeolites, but in making shaped zeolites for certain adsorbent applications. For example, clay can be extruded, pelletized or otherwise agglomerated, and then treated with NaOH to convert most of the clay into zeolite. The resulting product retains its original shaped structure and has good mechanical strength (27).

Competing Applications, Markets, Projections

The major applications of zeolites are in ion exchange, catalysis, and adsorption, as shown in Table V. The recent development of zeolite NaA in commercial built detergents (15,16) will undoubtedly prove to be the largest single use for zeolites in the very near future. In the U.S., the potential consumption of zeolite NaA for this purpose could grow to 225-325 thousand MT/yr, and in Europe, the potential consumption could be approximately the same. It is possible that worldwide use of zeolites in detergents could result in the consumption of 540 thousand MT or more of zeolite NaA per year, by 1981, as shown in Table VI.

The most important catalysis use of zeolites is in catalytic cracking to produce gasoline. More than 98% of gasoline produced by catalytic cracking in the U.S. utilizes synthetic zeolites X or Y. Zeolites X or Y differ chemically from A, in having higher ratios of silicon to aluminum, than the 1:1 ratio of zeolite A. Pore sizes of zeolites X and Y are approximately 8Å, twice as large as the approximate pore size of 4Å peculiar to zeolite A, and the rate, capacity, and selec-

TABLE V

Major Zeolite Uses

Ion exchange	Catalysis	Adsorption
Detergent builder	Catalytic cracking	Air drying
Water treating	Hydrocracking	Natural gas drying
	Paraffin isomerization	Hydrogen purification
	Zylene isomerization	Hydrocarbon desulfurization
	Shape selective cracking	Normal paraffin-isoparaffin
	Alkylation	separation
	Lubrication oil dewaxing	Liquid hydrocarbon drying
	Conversion of methanol	Drying of synthesis gas
	to gasoline	Drying of alcohols
		Oxygen-nitrogen separation
		Hydrogen sulfide removal

TABLE VI

Estimated Current World Markets and Projections for Zeolites[a]
(Thousand MT, Anhydrous Basis)

World region	1975	1977	1979	1981
North America				
Detergents	--	27	90	225
Catalysts	20	23	28	35
Adsorbents	11	14	16	20
Total	31	64	134	280
Latin America				
Detergents	--	--	?	?
Catalysts	3	3	4	5
Adsorbents	7	9	10	13
Total	10	12	14	18
Europe				
Detergents	--	27	90	225
Catalysts	3	4	4	5
Adsorbents	5	7	9	11
Total	8	38	103	241
Near to Far East				
Detergents	--	--	29	90
Catalysts	3	5	6	8
Adsorbents	8	11	14	18
Total	11	16	14	18
World total	60	130	300	655

[a]Source: PQ Estimates.

tivity of ion exchange are significantly different for each type of zeolite (27).

The first large-scale commercial use of zeolites was for the adsorptive separation of mixtures. In this category are drying of air, natural gas, other gases, as well as liquids, desulfurization of various petroleum-derived feeds, and separation of normal from isoparaffins (Table V). There are at least 100 commercial processes that employ zeolites to make sorptive separations (27). For most of these sorption applications, zeolite A is used.

In Table VI, estimated current world markets and market demands to 1981 for zeolites in North America, Latin America, Europe, and the Near to Far East are projected. It is clear that the volume use of zeolite NaA as a builder in detergents will dwarf all other applications now known for zeolites. The impact of pricing changes, as zeolite NaA becomes an inexpensive bulk commodity in economic competition with phosphates, on other zeolites now used for catalysts and adsorbents is difficult to predict. A plant de-

signed and used to make tens of thousands of MT of zeolite NaA per year is probably too large to make less than thousands of MT of other zeolites most economically. It is equally clear, at this time, that the chemical industry is rapidly positioning itself to manufacture the over fivefold total volume increase of zeolites needed to satisfy 1981 projected requirements.

ACKNOWLEDGMENTS

REFERENCES

1. Von Fuchs, J., Dinglers Polytech. J. 17:465 (1825).
2. Vail, J., "Soluble Silicates," Vol. I and II: ACS Monograph 116, Reinhold, New York, NY, 1952.
3. DeHaen-Cartanjen, "Die Wasserglas," Wasserglas - Fabrik (1856).
4. Walcker, A., Q. J. Sci. (London) 3:371 (1828).
5. Sheridan, J., British Pat. 6,894 (1835).
6. Dunn, A., British Pat. 7,283 (1837).
7. Gossage, W., British Pat. 762 (1854).
8. Morfit, C., "Soap and Candles," Carey and Hart, Philadelphia, PA, 1847, p. 234.
9. Elkinton, T., U.S. Pat. 39,135 (1863).
10. Felip Sugranes, J., Belgium Pat. 824,420 (1975).
11. Curll, D., U.S. Pat. 2,239,880 (1941).
12. DeLiedekerke, M., German Offen. 2,519,265 (1975).
13. Merrill, R., U.S. Pat. 2,689,245 (1954).
14. Falcone, J., and T. Campbell, Unpublished results, Philadelphia Quartz Company Laboratories.
15. Schwuger, M., and H. Smolka, Colloid Polym. Sci. 254:1062 (1976).
16. Savitsky, A., HAPPI 14:52 (1977).
17. Breck, D., J. Chem. Educ. 41:678 (1964).
18. Gans, German Pat. 174,097 (1906).
19. Boehringer and Gessler, U.S. Pat. 1,050,204 (1913).
20. DeBrunn, British Pat. 15,090 (1913).
21. Wheaton, H., U.S. Pat. 1,586,764 (1926).
22. Milton, R., U.S. Pat. 2,882,243 (1959).
23. Sensel, E., U.S. Pat. 2,841,471 (1958).
24. Estes, J., U.S. Pat. 2,847,280 (1958).
25. Weber, H., U.S. Pat. 3,058,805 (1962).
26. Michael, M., and D. Paper, U.S. Pat. 3,433,588 (1969).
27. Breck, D., "Zeolite Molecular Sieves," John Wiley and Sons, New York, NY, 1974.
28. Sensel, E., U.S. Pat. 3,009,776 (1961).
29. Maher, P., U.S. Pat. 3,185,544 (1965).
30. Maher, P., and E. Nealon, U.S. Pat. 3,205,037 (1965).
31. Veda, T., Sato, and Y. Nakamura, U.S. Pat. 3,535,975 (1970).
32. Williams, L., R. Mays, and J. Wagner, Belgium Pat. 844,473 (1977).