MOLECULAR SIEVE ZEOLITES: AN INDUSTRIAL RESEARCH SUCCESS STORY

The discovery and development of zeolites and molecular sieves depended on many factors, not least of which was management's commitment to support long-range innovative discovery research with no guarantee of commercial success.

Edith M. Flanigen

OVERVIEW: *Inspired by "superb" high school and college teachers who made chemistry "exciting," Edith Flanigen joined the Tonawanda, New York Research Laboratory of Union Carbide's Linde Air Products Division in 1952. There, in "a nearly idyllic atmosphere for creative scientific research," she embarked on a life-long career in the discovery, development and commercialization of zeolites and molecular sieves. Ultimately, she and her colleagues—"scientists of the highest quality, led and motivated by directors and leaders who were focused on discovery and innovation, expected it, and rewarded it"—developed a new generation of molecular sieves. Among the ingredients of her success: an environment that fosters innovation and top management commitment, support, willingness to take risks, and patience to allow a major discovery time to find its place in the commercial world.*

KEY CONCEPTS: *discovery research, team innovation, enlightened management, technical leadership, industrial success.*

My field is in silicate chemistry and materials, specifically in zeolite molecular sieves, a class of industrial materials used widely throughout the petroleum refining, petrochemical and chemical industries.

The roots of molecular sieves go back to 1756, when a Swedish mineralogist by the name of Cronstedt first discovered intriguing crystals in nature that seemed to froth or boil when heated in a blowpipe flame. Cronstedt called this new mineral a "zeolite," derived from the Greek words, "zeo" meaning "to boil" and "lithos" meaning "a stone."

In the decades that followed, a number of mineralogists and chemists studied and described the properties of various zeolite minerals, including their remarkable sieve-like ability to separate molecules on the basis of size. This sieving property led McBain in the early 1930s to coin the term "molecular sieve," and more significantly, enticed the first giant of molecular sieve science, Professor Richard M. Barrer of Imperial College, London, to begin a lifetime of pioneering research in zeolite science in the mid 1930s. Of key importance were Barrer's descriptions in the 1940s of gas separations with zeolite minerals that had commercial potential—descriptions that set the stage for Union Carbide's later role in synthetic zeolite discovery.

An Idyllic Research Atmosphere

I shall turn now to the Tonawanda, New York research laboratory of the Linde Air Products Division of Union Carbide Corporation in the late 1940s. The Tonawanda Laboratory presented a nearly idyllic atmosphere for creative scientific research. The scientists were of the highest quality, led and motivated by directors and leaders who were focused on discovery and innovation, expected it and rewarded it. More than a half dozen successful new businesses were spawned for Union Carbide from a decade of pioneering research at the Tonawanda Laboratory.

Enter Bob Milton, a young physical chemist, there only two years when management challenged him to seek new methods of separating air into oxygen and nitrogen, the

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major products of Linde. Milton was drawn to Barrer's pioneering reports on adsorption separations with zeolite minerals. However, since zeolite minerals were rare and unavailable in practical quantities, he shifted focus in mid-1949 to an exploratory program to synthesize zeolites in the laboratory. By year end, he had discovered a new and practical method to make several novel synthetic zeolites, including two that were to gain commercial prominence, called zeolites A and X.

In 1952, Milton was joined by a young inorganic chemist, Don Breck, who continued the discovery and study of more synthetic zeolites including one called zeolite Y, which was destined to become one of the cornerstones of the petroleum refining industry.

By 1954, largely through the championship of Bob Milton, Linde had announced it was entering the business of manufacturing and selling molecular sieve zeolites as a new class of industrial adsorbents, and in 1959 as hydrocarbon conversion catalysts—a remarkable example of discovery to commercialization of a new business venture in just five years.

When I joined the research staff at Tonawanda in 1952, my sister Joan, also a chemist, had already been there a year. Two years later, my sister Jane, another chemist, also joined the Tonawanda research staff.

I remember that the head of the personnel department was intrigued by the fact that three sisters were all chemists and all working at the Tonawanda laboratory at one time! He used to give us banks of psychological tests, thinking he would find some strange trait that turned us all into chemists. We could have told him that it was probably due to a superb high school chemistry teacher at Holy Angels Academy, Sr. St. Mary, who made chemistry exciting, and an equally superb chemistry teacher at D'Youville College, Dorothea Fitzgerald, Ph.D., who built on that excitement.

My two sisters left after short careers at Linde to marry and raise families. In 1956, I had the opportunity to join the molecular sieve synthesis group working with Don Breck and leaped at the chance. Thus my career in the zeolite synthesis area began and through the late 1950s I was successful in discovering or developing several new zeolite materials. During that early period, I developed the chemistry to scale up and facilitate the successful manufacture of zeolite Y that remains today the mainstay of the petroleum refining industry. I benefited greatly in my early career by being mentored by the pioneers Don Breck and Bob Milton.

Other Organizations Join In

During the 1950s and '60s, the gospel of molecular sieves spread and the business prospered. The Linde researchers were joined by an increasing number of disciples from many other organizations, notably Mobil Oil, Esso Research and Engineering, and W. R. Grace. A close-knit community of molecular sieve scientists grew and multiplied. I was now a senior scientist heading up Linde's molecular sieve synthesis research group in Tarrytown, New York, where the Linde Research Laboratory was relocated in 1969. We, like others, were actively working in the area of high silica zeolites, a new class of molecular sieves discovered by Mobil Oil Researchers in the 1960s, typified by zeolite ZSM-5

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Union Carbide's contribution to the area was the discovery of the first pure silica molecular sieve, silicalite, by my research group. However, Linde's molecular sieve business management (and we) would have preferred that Linde, not Mobil, had discovered the intensely-studied high-silica zeolite materials. Luckily, we were given an opportunity to redeem ourselves. In the late 1970s, Tudor Thomas, then vice president and general manager of Union Carbide's molecular sieve business, presented us with a challenge: discover the next generation of molecular sieve materials. Thomas assured us that if we made a breakthrough discovery with many new materials, Carbide would find useful and profitable applications for them.

We first set up a team consisting originally of myself, Brent Lok and Steve Wilson. Both men were recent members of the synthesis research group and just a few years out of graduate school; they were neophytes in molecular sieve synthesis and materials. We spent nearly six months studying, thinking and reading the literature and ultimately decided on a strategy to find this next unknown generation.

Up until this time, all of the natural and synthetic zeolites were based on the oxides of aluminum and silicon. Our strategy was to view the entire periodic table of the elements as the potential scope for the new compositions and structures. We ranked the elements and picked the oxides of aluminum and phosphorus as our first choices. Lok and Wilson went into the laboratory dividing the synthetic approaches. We met at least once a week to review the results of the experiments and decide on the next steps: I, the experienced guru with all the preconceived ideas, and Lok and Wilson the neophytes, the independent thinkers, unwilling to give in to my mindsets.

Hitting the Jackpot

After more than two months without success, we decided to try synthesis conditions well out of the mainstream of all previous molecular sieve synthesis. With that unconventional approach we hit the jackpot! A newly hired chemist, Celeste Messina, and others joined the team. In less than six months, more than a dozen structures were discovered. We called this family of materials "ALPO" after the chemical symbols for aluminum, phosphorus and oxygen.

Meanwhile, a seasoned synthesis researcher, Tom Cannan, added the element silicon and so "SAPO" was born. Steve Wilson added several metal elements and they also worked! And so "MEAPO" was born.

We quickly realized the great significance of our discovery and the urgency for developing it to its fullest.

By 1984 our group, now much larger, had incorporated 13 different elements into the ALPO framework, and had discovered more than 200 compositions and more than two dozen structures. We called the new generation aluminophosphate-based molecular sieves. By 1985, more than 30 patents had been filed. This new generation of molecular sieves is generally recognized as a landmark discovery in molecular sieve and inorganic chemistry. The discovery was a result of the innovative work of a group of bright, talented and hardworking individuals who collaborated as a team to achieve a challenging and exciting goal.

With our cupboards full with new materials, as promised, Union Carbide developed a business strategy to fully

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exploit the discovery. UOP, a company owned by Allied-Signal Corporation, was a world leader in application and process technology, serving the petroleum and petrochemical industry worldwide. Both Carbide and Allied-Signal saw the opportunity to wed the Carbide molecular sieve materials with the UOP processes. They formed a joint venture company in 1988 and a new UOP was born.

I am happy to say that that business strategy is also working. UOP has ready begun to reap the commercial fruit of the ALPOs with several processes under commercial development. A major one is a process to produce a light olefin from stranded natural gas, the methanol-to-olefins process to produce ethylene/propylene using a SAPO-based catalyst.

The discovery of the aluminophosphate-based generation laid the groundwork for an explosion in the discovery of new compositions and structures of molecular sieves from the 1980s through the 2000s. More than two dozen elements have been incorporated into crystalline microporous oxide frameworks. More

The Most Glamorous Exploratory Research Project

Zeolites are crystalline metal aluminosilicates that contain channels and cavities inside the crystal that are accessed by pores the size of molecules. Today they are generally described as microporous crystalline solids. More than several dozen different aluminosilicate zeolite structures are known. Bob Milton's synthesis technique, still in use today, involves the crystallization of amorphous alkali aluminosilicate gels in water at relatively mild temperatures and pressures, a technique called hydrothermal crystallization.

It was this recognized expertise in hydrothermal crystallization that led to an exciting and glamorous exploratory program we undertook in the early 1960s, along with our work in the zeolite synthesis area. At that time, there was much research ongoing in solid-state masers. The maser, an acronym for Microwave Amplification by Stimulated Emission of Radiation, was invented in 1953 as a means of amplifying radio waves into a coherent electromagnetic signal. Emerald was predicted to be the optimum crystal for this application.

The U.S. Office of Naval Research approached us to develop a hydrothermal technique for growing large single crystals of synthetic emerald for potential maser application. Norb Mumbach and I, and several others in the group, teamed up and were ultimately successful in growing gorgeous synthetic emeralds. As fate would have it, by then the masers were generally superceded by lasers, solid-state materials where ruby was the crystal of choice. Thus the industrial demand for synthetic emeralds in masers never materialized. However, Linde, capitalizing on the discovery, added emeralds to its existing star sapphire gemstone product line. For over a decade, the synthetic emeralds were manufactured and sold by Linde in a line of jewelry called the "Quintessa Collection." This exploratory project was surely our most glamorous one.—**E.M.F.**

than 100 unique structures of zeolites and molecular sieves are known, yet only some 15 structure types have been commercialized, mainly in catalytic applications.

Since their initial discovery at Tonawanda in the late 1940s and early '50s, molecular sieves have grown to over a $2 billion industry worldwide and have generated a massive scientific and technical literature. It is estimated that some 10,000 chemists and engineers are working in the field today. (In 2001, the global consumption of molecular sieves was estimated at over 3.2 billion pounds.)

Benefits to Humankind

Molecular sieves are used as adsorbents, catalysts and ion exchange materials throughout the chemical industry. Here are some of the ways they benefit you and the rest of humankind.

Molecular sieves dry and purify the natural gas that heats your home (and may run your industry). They keep the refrigerants in your refrigerators and in your automobile air conditioners from freezing. Every gallon of gasoline you put in your car is made with Breck's zeolite Y catalyst. Diesel and aircraft jet engine fuels are made with the same zeolite catalyst.

Zeolites are used as ion exchangers to clean up nuclear wastes. They were crucial to the successful cleanup of the Three Mile Island and Chernobyl nuclear upsets. More than 2.5 billion pounds of Milton's zeolite A are produced annually to take the place of the environmentally suspect phosphates in laundry detergents.

Molecular sieves are used in the dual-pane insulated windows in your home to save energy and prevent fogging, and in portable medical oxygen units to produce oxygen for emphysema patients. Recently they were introduced in a new application based on their ability to adsorb odors, and are being marketed in personal care products. Perhaps the most intriguing new application is in clotting blood. A zeolite package was contained in every military person's medical kit in Iraq and Afghanistan. The zeolite is applied to large open wounds and almost instantly stops the bleeding.

Ingredients of Success

What were the ingredients for the exceptional success of Milton's discovery of the synthetic zeolites and the molecular sieve business, and of the birth of the new generation of ALPOs? I suggest that there were many common to both:

- A commitment on the part of management to support long-range innovative discovery research with no guarantee of commercial success.
- A willingness to take that risk and to assign significant resources to back up that commitment.
- Patience to allow major discoveries to find their place in the commercial world.

How do we influence the great minds of tomorrow to embrace science, technology and innovation?

- Creating an environment and culture that fostered innovation and that attracted the best scientists and challenged them to their very limits.
- Allowing them freedom to dream, and trusting that they would succeed.
- Recognizing and rewarding them when they did succeed.

And what about the researchers: the Miltons, the Brecks, the team that discovered the new generations? They were creative minds, stretched and emboldened by excellence in their educational training; dreamers, visionaries, free spirits; at home with concepts; thinkers with uncanny chemical intuition; persistent, almost stubborn in their resolve; with a child-like impetus to play—and with just a little bit of luck!

But the greatest blessings of my career have been the people I had the honor to work with. Over the period of years with Union Carbide and UOP, I had the opportunity to work closely with some several dozens of people—people with the characteristics I just described. They each brought their unique talents, skills and personality to the task at hand—and a million-dollar bonus! They were all loving and caring human beings. And that combination, joined together in a vibrant community known as "The Discovery Group," with different people at different times, carried me on their shoulders and brought me to where I am.

But despite my euphoria with the past, I have some concerns for the future. The growth, prosperity and quality of life we enjoy in the United States and globally in the developed countries has largely been based on technological innovation. Where and how will the corporate and business culture I have described here come from? Where and how will the next generation of innovators like those I described come from? How do we encourage and influence the great minds of tomorrow to embrace science, technology and innovation? I leave those questions for the leaders in research and development and technological innovation to answer. ⦿