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TECHNICAL BULLETIN

ZEOLITE A VERSATILE AIR POLLUTANT ADSORBER

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ZEOLITE A VERSATILE AIR POLLUTANT ADSORBER

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ZEOLITE, A VERSATILE AIR POLLUTANT ADSORBER

July 8, 1998

THE PURPOSES OF THIS PAPER

The purposes of this paper are to make you familiar with zeolite, what it can contribute to control of air pollution -- particularly control of Volatile Organic Compounds (VOC) -- and what to expect in the future.

WHAT IS ZEOLITE?

Zeolite is a rock composed of aluminum, silicon, and oxygen. It occurs naturally in several regions of the world where prehistoric volcanic activity has happened near water, or the water has been present for millennia since the eruption. In 1756, the Swedish mineralogist Baron Axel Fredrick Cronstedt discovered zeolite. One account has his dog digging up the stone and him naming it zeolite from a word which means “dog” in Swedish. In another account, he found that when the zeolite (it was actually Stilbite) was heated it gave off steam. Zeolite means “boiling stone” in Greek. Since I do not know either Swedish or Greek, you will have to judge whether either or both of these stories are correct. We do know for sure that zeolite was discovered.

Zeolite has a natural porosity because it has a crystal structure with windows, cages, and supercages. The natural zeolites are limited in their window size (“pore size”) and are all hydrophilic (having an affinity for water). Some synthetic zeolites are similar to an absorbent carbon, since both can be considered hydrophobic (having an affinity for organics, with lack of or a decreased affinity for water), and can adsorb organic vapors with molecules smaller than their “pore size.” With both carbon and zeolite you can adsorb water and organic molecules; however, that for which it has affinity will displace the other molecules. Zeolite has a uniform “pore size” which leads to it being referred to as a “molecular sieve,” while carbons appear to have pores leading to smaller pores leading to still smaller pores *ad infinitum*.

“Absorbent carbon”, which is actually an adsorber, also has an affinity for water at some sites, which decreases its capacity to adsorb organic molecules from streams containing water molecules. This can be either true or false for zeolite depending on the type of zeolite that you select. Generally, the higher the silicon to aluminum ratio, the more hydrophobic the zeolite. Hydrophobic zeolite must be synthesized, for it does not occur in nature. Therefore, the race to synthesize zeolite with specific abilities is on!

WHY DO WE SYNTHESIZE ZEOLITE?

Synthesis is important because it allows scientists and engineers to (1) predict the properties of the zeolite, (2) make a zeolite with a larger “pore size,” and (3) make hydrophobic zeolite. Early attempts to synthesize zeolite simulated volcanic conditions. Hydrophilic zeolite was finally synthesized in 1949 by Milton, Breck, and others under hydrothermal conditions (i.e., below 100 °C.). In 1985, Bibby and Dale reported the synthesis of a pure silica zeolite. Others have synthesized a wide range of hydrophilic and hydrophobic zeolites.



Zeolite-like crystal structures have even been created by substituting other elements for either the aluminum or the silicon in the synthesis, but the zeolite that we will discuss here is purely an aluminosilicate.

There have been 40 natural zeolites discovered; 118 zeolites have been cataloged by the Structure Committee of the International Zeolite Association; more than 600 zeolites have been identified, and, if you were to include zeolite-like crystal structures using other elements, the number would be increasing daily. One zeolite is not exactly like any other.

The structure of a zeolite crystal is based on a tetrahedron formed by four oxygen atoms joined to a silicon atom by its four valence electrons. These tetrahedrons are joined at the oxygen “corners” to make crystals. When aluminum is present while the crystals form, the silicon is replaced by aluminum atoms which have only three valence electrons. The remaining valence electron is usually provided by either hydrogen or sodium because they are commonly found in the hydrating water. This distorts the tetrahedron and makes an “acid site” for exchange of other ions. This also makes the structure hydrophilic. If the zeolite is formed in a mix that contains an organic cation (i.e., a cation having a carbon backbone), the structure can be formed around the organic cation, using it as a template. This has led to silicon-rich hydrophobic zeolites with large enough “pore size” (or window size) to admit all but the largest petroleum molecules.

The crystal structure of a zeolite consists of windows, cages, and supercages. The windows are how the molecules reach the cages and supercages to be adsorbed or catalyzed. The cages are the smaller cells in the crystal structure. The supercages are cells in the crystal structure that are larger than cages and may even contain cages. Figure 1 shows the structure of Y zeolite as seen by red light.

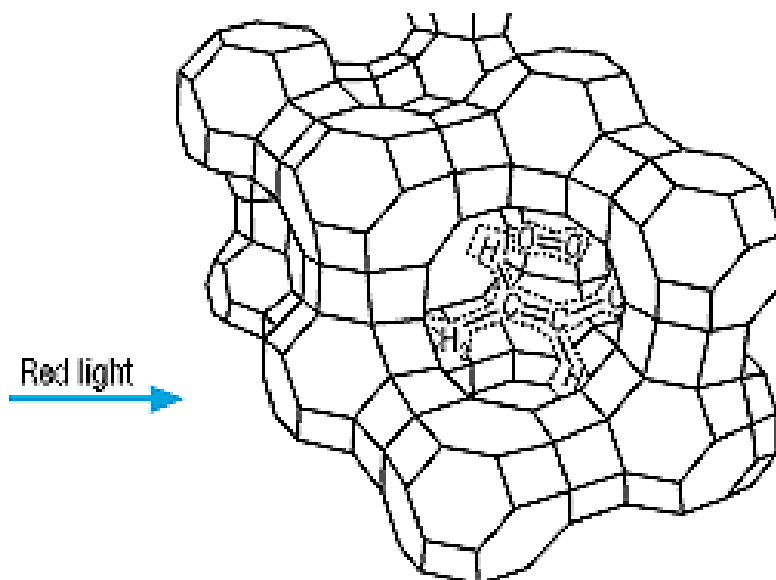


Figure 1 -- Y Zeolite Crystal Structure - Showing Windows, Cages, and Supercages

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Activation of a zeolite consists of heating or evacuating the zeolite to desorb the hydrating water or other material from the adsorption area, just as with carbon.

The cost of hydrophobic zeolites ranges from \$6.50 to \$40.00 per pound, according to PQ Corporation. Compare this with \$1.40 to \$2.00 per pound for carbon adsorbents, according to Calgon Carbon. Generally, a minimum of a ton of zeolite is needed for concentration of VOC, and this can handle up to 8,000 cfm. However, the cost of either carbon or zeolite is only a small part of the total cost of the adsorber or concentrator.

WHAT ARE THE IMPORTANT CHARACTERISTICS OF ZEOLITE?

1. Zeolite is capable of selective ion exchange.
2. Zeolite can adsorb molecules on its large internal area, provided they can pass through the windows. Zeolite and carbon are both the same in this respect, just differing in the adsorption area that can be reached by a given molecule passing through their “pores.”
3. Zeolite can be a solid acid catalyst. It can function as a strong acid (though it remains solid) when the hydration has substituted a hydrogen for the additional valence electron, or isoelectronic exchange with the aluminum occurs.
4. Zeolite can be used as a molecular sieve because it has a uniform window (or pore) size.
5. Zeolite is metastable; i.e., it is stable as long as it is at a suitable temperature and pH. Within this range, it is unaffected by wide swings in temperature, pressure, and ionizing radiation.

Natural zeolite exists as a natural rock, and these can reach boulder size. However, synthesized zeolite crystals are always less than a millimeter in size -- because the crystals grow slowly, and we usually want the zeolite in this century or millennium. These small grains can rapidly transport the adsorbed molecule to the adsorption area. Air flow through a bed of zeolite powder creates a large pressure drop. Granular zeolites have now been developed in which grains are bonded together to create larger air flow channels, and hence have lower resistance to air flow.

HOW CAN ZEOLITE BE USED TO CONTROL AIR POLLUTION?

Hydrophobic zeolite can be made by controlling the silicon to aluminum ratio or by dealuminizing a zeolite. Different types of zeolite have windows from 0.3 to 3.0 nanometers (3 to 30 Angstroms), but any one type has a nominally fixed window size. Changing the Si/Al ratio can affect the size of the window. Exchanging ions can also affect the size of the window.

Hydrophobic zeolite is currently used to concentrate VOC before destruction. These concentrators are shown schematically in Figure 2. They are essentially temperature-swing adsorbents with the bed mounted on a rotor which gets regenerated on each rotation (two to five

times per hour). The air-vapor flow from one vendor is axial through sectors in the rotor. Another vendor's design has the air-vapor flow move radially inward through segments located along the outside of the rotor.

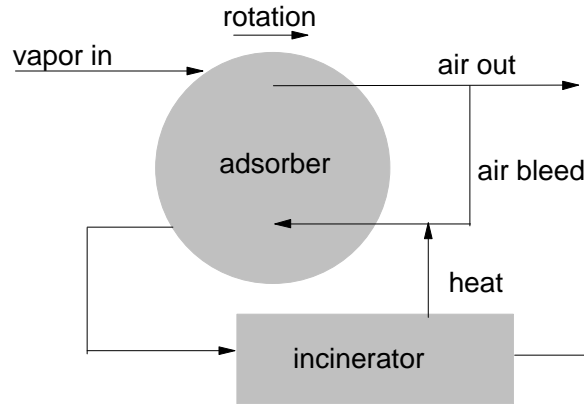


Figure 2. V O C Concentrator

The size and cost of an incinerator are related to air flow, and the air flow from the concentrator to the incinerator is reduced by about 90%. The major cost savings comes from reducing the flow of air through the incinerator, which reduces the heat needed to raise the temperature of the air flow.

Because of this, the concentration of the VOC is also increased by a factor of approximately ten, as is the heating value of the VOC. The concentrator is thus used to both reduce the size and cost of the incinerator that is used to destroy the VOC, and to reduce the amount of fuel that must be added to safely obtain the full destructive efficiency of the incinerator.

The VOC level after concentration must remain below one-fourth of the Lower Explosive Limit (LEL) for safety; therefore, the input to the concentrator should be no more than about 500 parts per million (ppm). Commonly, the inlet concentration is only a few hundred ppm. Thus, the concentrator should be used for VOC concentrations between the levels that are economical for the fixed bed adsorber and the condenser.

If an incinerator is used at such VOC levels without concentration, a lot of fuel must be added because the heating value of the VOC is so small before concentration. By concentrating the VOC, the heating value is increased and less fuel must be added. The total cost of destroying VOC is in the range of \$1,000 to \$3,000 per ton, according to Munters ZEOL. The higher total costs are for the more dilute concentrations.

Hydrophobic zeolites can be very efficient at adsorbing and desorbing VOC, as shown by the paper "Sorption and Diffusion of VOC on Hydrophobic Zeolites" Paper 83f, 1996 Annual

Meeting, American Institute of Chemical Engineers. Zeolites can be used over a wider temperature range than carbon, and are generally superior to carbon as an adsorber.

Gasoline engines emit VOC in their exhaust when they are cold. Hydrophobic zeolite is used in the catalytic converter to adsorb this VOC from the cold engine exhaust. When the engine warms up, and the hot exhaust gas desorbs the VOC from the zeolite, the zeolite then catalyzes the oxidation of the VOC. The zeolite is not altered by the 1,000 °F temperatures that are reached.

Diesel engines have an entirely different problem. They emit NO_x which can be catalytically reduced to nitrogen and oxygen (as in clean air) by a cerium-exchanged zeolite using either urea or ammonia as a reducing agent.

Separation of carbon dioxide from flue gas was investigated in Korea (Industrial Engineering Chemical Research, 1995, 34, pp. 591-598). The authors found that zeolite 13X was superior to an “absorbent carbon” in a pressure swing adsorption system. Since carbon dioxide is a greenhouse gas associated with global warming, this could be very important in reducing such emissions.

Chabazite, another zeolite, has been used as a molecular sieve to remove sulfur dioxide from flue gas. Sulfur oxides are also a product of processing some ores. Sulfur oxides are constituents of acid rain. Reducing the emissions of them could have a profoundly beneficial effect on the environment.

Clintoptilolite (a natural zeolite) can remove ammonia from wastewater. It has been used to control ammonia from urine in both “kitty litter” and horse stables. It is also used to adsorb VOC that cause odors from mildew, foot fungus, and carpets. It regenerates in sunlight and clean air. It is noteworthy that zeolite can even be used to catalyze oxidation of hydrocarbons in the presence of light. However, it can be very selective in these reactions according to CHEMTECH, 1996, 26(6), 24-30 American Chemical Society.

DOES ZEOLITE HAVE USE OUTSIDE OF CONTROLLING AIR POLLUTION?

In a word, YES. In treatment of radioactive wastes, zeolite is used to remove radioactive cesium and strontium from wastewater. Since zeolite is impervious to even high doses of radiation, it is used to exchange and trap these ions. It is capable of removing radioactive strontium at a concentration of 1 microgram per liter while sodium is present at 150,000 times that concentration. The zeolite is in powder or sand-size grains which are then used as a filler in concrete. The concrete is then cast in drums for disposal. This method of disposal is deemed impervious to salt water leaching, and the radioactive waste can be disposed of either in a landfill or by ocean dumping.

Zeolite has been used in water softening. Passing hard water through a bed of zeolite to

exchange the calcium and magnesium ions prevents them from forming insoluble soaps which we see as “soap scum.” The zeolite can be regenerated by passing salt brine through it. The chlorides of the exchanged ions are water-soluble and therefore disposal is easy. Because natural zeolites are attacked by acidic tap water, more resistant materials are now used, although hydrophilic zeolite was used for decades.

Akin to water softeners, and not subject to such attack because they are used only once, are “builders” in detergents. Zeolite is used as a “builder” and replaces most of the sodium tripolyphosphate which was formerly used and found to be environmentally harmful. Here again the zeolite removes calcium and magnesium ions from the water. Seven hundred million tons of zeolite per year are used this way. Powdered zeolite has no harmful effect on the environment beyond sometimes being a nuisance dust.

The use of zeolite catalysts in “catalytic crackers” in oil refineries was dependent upon discovery of a large window zeolite that was hydrophobic. Charles J. Plank and Edward J. Rosinski invented such a zeolite and its synthesis. Zeolite catalysts now reduce our consumption of petroleum imports by \$8 to \$16 billion dollars per year. Added to that savings is the reduced carbon dioxide emissions from reduced energy requirements of refineries.

Researchers at the University of the West Indies are seeking to use zeolite to make gasoline from ethanol. New Zealand already uses zeolite as a catalyst to make a large percentage of its motor fuel from methanol, because they lack petroleum reserves.

Zeolite is used as a dryer for compressed air. It acts as a desiccant to adsorb moisture. It can hold up to one-fourth of its weight in water without an appreciable rise in vapor pressure.

Zeolite is also used in refrigerators to dry out the refrigerant. This prevents the formation of ice crystals which could clog the flow passages and valves.

Slow release fertilizers use zeolite to control their release to the soil. Urea is converted to ammonia by soil bacteria. Clinoptilolite adsorbs the ammonia, and prevents the soil bacteria from converting it to nitrate. Subsequent slow leaching of the ammonia allows this nitrification to occur over a period of months. Otherwise, the surge of nitrates would wash out of the soil and pollute both groundwater and streams.

Zeolite is used to separate nitrogen from oxygen in air. The small difference in size between a nitrogen molecule and an oxygen molecule, along with polarization and a suitable zeolite, allows oxygen to be adsorbed selectively from air. The nitrogen is vented, and the oxygen is then desorbed. This is used to generate oxygen for aircraft crews, industrial processes, and aquariums.

Zeolites have been synthesized as a membrane, which allows their use as a molecular sieve. Molecular sieves let molecules through for which they have affinity, and that are smaller than their pore (window) size. This property is being used for chemical transducers in mixtures where

the molecular species are known. If a known diameter of molecule passes through and causes any response from the transducer, that response can be calibrated to the concentration of the known molecular species. Thus, we now have transducers that sense chemical concentration without the need for chemical reaction.

Similarly, the University of Greenwich in London, England has developed a zeolite which is used as a molecular sieve that will allow passage of water molecules -- but will not allow passage of VOC. This is a hydrophilic zeolite, for this is in the form of a thin membrane which must allow water molecules to adsorb/desorb and thus pass through. They can grow this zeolite with a pore size of 0.42 nanometers. They use it as a molecular sieve to remove the water from specimens without any loss of the VOC.

WHAT SHOULD WE EXPECT IN THE FUTURE?

Now that zeolite can be formed into granules which will allow free airflow, we should see zeolite replace carbon in fixed bed adsorbers in the U. S. This has already occurred in Europe. There is a reason for this to happen. Carbon (or metals in or on it) catalyze oxidation of VOC, and this has caused carbon bed fires. This would not necessarily occur in a zeolite bed, and even if a bed fire does occur, only the VOC would burn. The zeolite also has a non-linear adsorption isotherm, which increases adsorption at lower concentrations of VOC. This allows a removal efficiency of 99% for zeolite where carbon would have a 95% efficiency. Carbon has the efficiency advantage only at higher concentrations. Zeolite also regenerates more completely than carbon.

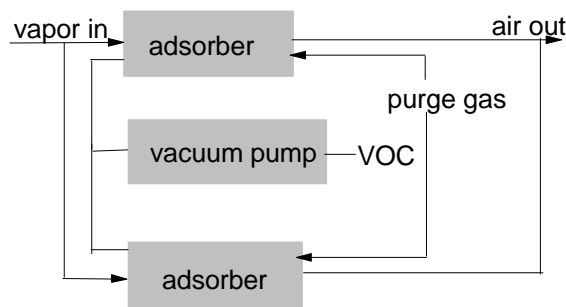


Figure 3. Vacuum Regeneration Adsorber

Catalysis also happens when a monomer, such as styrene, is adsorbed on carbon and desorbed by steam. This leaves a "heel" of polymerized monomer on the carbon in a thermal-swing steam regenerated system. Using a zeolite vacuum regenerated bed (as in Figure 3) could extend the life of the bed, recover the styrene, and perhaps make the use of zeolite economically attractive.

When zeolite becomes more commonly used in fixed bed adsorbers in the United States, we can expect that selective adsorption based on molecular diameter will be used. This would be made possible by cascading adsorbers of different zeolites, as in Figure 4. Each adsorber in the cascade would adsorb a range of molecular diameters. By selecting the zeolite based upon type and pore size, each VOC could be recovered with purity at least comparable to a commercial grade -- if only one VOC were recovered per cascade in the adsorber. Thus, the recovered VOC could provide a return on investment to help pay for the operation of the adsorber system. We understand that some VOC are changed to a different isomer by the catalytic action of some zeolites. If that is the case with your VOC, then the plant can either sell the isomer, use the new isomer instead of the old one, or change the type of zeolite which is used.

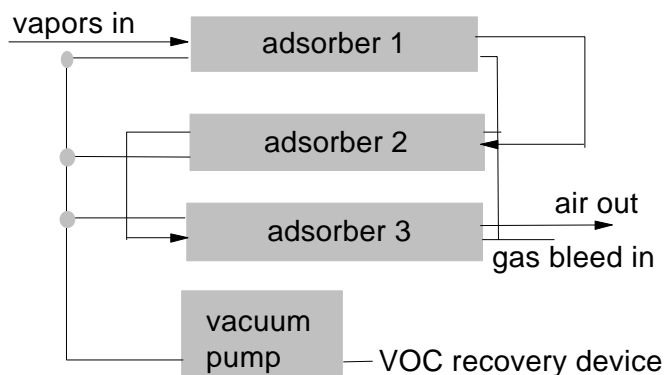


Figure 4. Cascade Vacuum Separation

WHAT ELSE DO WE NEED TO KNOW?

We need to know (1) what the effective window size is for different zeolites with different exchange atoms, and (2) what the effective molecular diameter is for each VOC. Having this knowledge, we can list the VOC that can pass through the windows and reach the adsorption area. We also need to know the critical temperature and pressure for catalyzing reaction for each VOC with each zeolite (as well as for types of carbon). The critical temperature and pressure may actually be curves, with one value for polymerization, and another for oxidation. Using these types of information, we can design the adsorber system to either avoid or use these reactions.

Some of this data is already available on the Internet and in libraries. However, it is frequently not in a form usable to persons who would design such systems. For example, available crystallographic pore sizes are actually different from the effective window sizes for VOC molecules. The information needs to be made more widely available in an appropriate form for engineers to use.

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