ZEOL ROTOR CONCENTRATORS
CONTROL VOLATILE ORGANIC COMPOUNDS
WITH HYDROPHOBIC ZEOLITES

Interesting Process
Small Conc. Metals Recovery
Munters Zeol Rotor Concentrators remove Volatile Organic Compounds (VOC) from difficult high volume air streams with relatively low inlet concentrations.

Zeol Rotor Concentrators use a proprietary adsorbent, hydrophobic zeolite, impregnated on a Munters HoneyCombe® wheel to remove VOC from process air streams. The concentrated solvents are then exhausted in a small stream, which is suitable for solvent recovery or incineration.

The unique properties of the hydrophobic zeolite permit applications which, until now, have been either too difficult or expensive to attempt. Munters zeolite has excellent adsorption capacity at very low concentrations, and can be regenerated at very high temperatures, if necessary. The hydrophobic zeolite does not adsorb water and can function efficiently at high relative humidities.

Because of these unique properties, VOC abatement systems using hydrophobic zeolite can handle difficult solvents, such as ketones and alcohols, reactive polymerizing solvents, as well as materials with high boiling points. Zeolite also can concentrate most common organic hydrocarbons, such as toluene and xylene, paraffinic and naphthenic solvents, acetates, esters, as well as many others.

THE LEADER IN ROTOR TECHNOLOGY

The heart of a Munters Zeol Rotor Concentrator is the HoneyCombe® wheel, which carries the hydrophobic zeolite adsorbent.

For more than 30 years Munters has been the leader in the manufacture and application of HoneyCombe® wheel structures in process applications.

With the combination of this expertise and hydrophobic zeolite, Munters Zeol offers VOC abatement systems in factory assembled standard sizes. Manufactured and tested at the Munters plant in Amesbury, Massachusetts, Zeol Rotor Concentrators can be shipped fully assembled, and installed on site at minimum cost. Several modules can be combined to increase capacity to meet the needs of the largest industrial plant.

ADVANTAGES OF ZEOL ROTOR CONCENTRATORS

- High efficiency at low inlet concentrations.
- Cost-effective in high volume, low capacity applications.
- Non-flammable, high temperature resistant.
- Durable Munters rotor construction provides years of service.
- Inert, non-catalytic zeolite handles reactive flammable solvents.
- Manufactured in the USA.
MUNTERS HYDROPHOBIC ZEOLITES

Starting with basic research in 1974, Munters Zeol has developed a number of hydrophobic zeolites for removal of volatile organic compounds from air or gas streams. These hydrophobic zeolites are inorganic silicates with large internal pore surfaces in well-defined crystalline structures. Munters Zeol has developed a proprietary process to manufacture zeolites with specific pore sizes and adsorption properties.

ZEOLITES WON’T BURN

Munters hydrophobic zeolites are inorganic, non flammable, and resistant to temperatures up to 1800 degrees F. Chemically, the zeolites are almost pure SiO2. They do not behave as catalysts or promote oxidation reactions.

ZEOLITE’S NARROW PORE SIZE DISTRIBUTION CREATES EFFICIENCY

Munters zeolites have very high adsorption capacity at low VOC concentrations. The graph below shows how hydrophobic zeolites have greater adsorbive capacities than carbon at low concentrations.

Producing zeolites with narrow pore size distribution also eliminates blockage of the pores by large molecules. For this reason, the working capacity of Munters zeolites is a larger proportion of its equilibrium capacity than other adsorbents.

ZEOLITES ADSORB LITTLE WATER

Munters hydrophobic zeolites adsorb very little water, even at high relative humidities. This leaves most of the pore surface available to adsorb VOC even at relative humidities greater than 80%RH. The graph below shows how activated carbon begins to adsorb water rapidly at approximately 50%RH.

EVALUATING ADSORBENTS

When evaluating adsorbents for your application, consider the advantages offered by Munters zeolites:

- Very economical for high volume, low concentration applications
- Inert, non flammable
- High capacity at low concentration
- Efficient at high relative humidity
- Resistant to acid
- Do not promote chemical reactions
- Clearly defined pore structure
- Not blocked by large molecules
- Suitable for reactive or polymerizing solvents

The hydrophobic zeolite adsorbent material is very costly to manufacture on a pound for pound basis. Consequently, it is not a suitable replacement where fixed-bed activated carbon plants offer economical and sensible solutions.
MUNTERS ZEOL "Z-BLOCK" AND FIXED BED SYSTEMS

Munters Zeol fixed bed and "Z-Block" systems are used where special conditions do not allow the use of continuous rotor concentrators.

Typical applications include the destruction of plastic fumes and smoke from hot lamination of polyethylene to paper in converting plants, destruction of styrene and other polymerizing monomers in the manufacture of fibre reinforced plastics, reaction molding or another process emitting reactive or high boiling solvents.

"Z-Block" systems allow the hydrophobic zeolite to be used in a relatively inexpensive plant design, where continuous destruction of the recovered VOC is not economical.

Fixed bed plants with zeolite in pellet form are used where high temperature pyrolysis, up to 1800 degrees F, is required to destroy the VOC.

Z-Block process flow sheet.

Fixed bed recovery plant detail.
MUNTERS ZEOL ROTOR CONCENTRATOR

Shown is a typical configuration of a Munters Zeol Rotor Concentrator. Process air containing VOC enters at intake "A" and passes through one or more filters to remove dust or other particulates.

If the VOC concentration varies greatly, it may be necessary to include a zeolite "smoothing" filter to remove "peaks and valleys" in the inlet flow concentration.

The process air passes through rotor, where VOC are adsorbed and removed from the air stream. The clean air is discharged to the atmosphere.

In a separate rotor sector, hot air or inert gas is passed through the rotor in the opposite direction to the process flow. The hot air removes the VOC from the rotor, preparing the rotor for further adsorption. The small "desorbate" stream contains all the VOC, which can be recovered or destroyed in an incinerator, which supplies the desorption heat.

<table>
<thead>
<tr>
<th>PLANT</th>
<th>NOMINAL CFM</th>
<th>HEIGHT</th>
<th>WIDTH</th>
<th>LENGTH</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO 1500</td>
<td>6,000</td>
<td>7' 0&quot;</td>
<td>7' 0&quot;</td>
<td>8' 0&quot; - 24' 0&quot;</td>
</tr>
<tr>
<td>CO 2400</td>
<td>15,000</td>
<td>9' 0&quot;</td>
<td>9' 0&quot;</td>
<td>9' 0&quot; - 25' 0&quot;</td>
</tr>
<tr>
<td>CO 2900</td>
<td>22,000</td>
<td>11' 0&quot;</td>
<td>11' 0&quot;</td>
<td>11' 0&quot; - 26' 0&quot;</td>
</tr>
<tr>
<td>CO 3500</td>
<td>33,000</td>
<td>12' 6&quot;</td>
<td>12' 6&quot;</td>
<td>11' 0&quot; - 27' 0&quot;</td>
</tr>
</tbody>
</table>

All standard sizes are fully assembled and shippable within the USA and Canada.

Systems for capacities larger than these standard sizes will be made up from multiple standard units or custom fabricated to suit individual applications.
**MUNTERS ZEOL INSTALLATIONS**

- Rotor Concentrator installation in major automotive spray painting operation.
- Fixed Bed plant for destruction of polyethylene smoke.

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In the late 1970's and early 1980's, a couple of learned professors at the University of Lund, Sweden were doing basic research into zeolite chemistry. Their purpose was to find a way to remove radioactive Cesium from the cooling water in Sweden's nuclear power plants.

The end result was a new adsorbent, hydrophobic zeolite which, in contrast to all other known natural and synthetic zeolites, does not adsorb water, and can therefore be used to adsorb organic vapors instead.

The hydrophobic zeolites are manufactured exclusively for Munters Zeol by Tosoh Zeol KK in Japan, a joint venture between Tosoh Chemical Company and Munters Zeol.

The hydrophobic zeolite is produced in pellet form for use in fixed bed applications, and as a powder, which is impregnated on Munters HoneyComb® rotor structures for Zeol Rotor Concentrators.

Although there are other adsorbents, which are used for recovery of Volatile Organic Compounds, commonly referred to as VOCs, the hydrophobic zeolite has some physical and chemical properties not available in any other existing adsorbents.

These properties are:

- Uniform pore structure
- Hydrophobicity
- Inorganic
- Synthetically produced.

Uniform Pore Structure:

The hydrophobic zeolite consists of a three dimensional network of internal pores, formed by sharing of oxygen atoms by silicon atoms. Although the chemical formula of each individual molecule is SiO₂, the sharing of the oxygens produces a net formula of SiO₂⁻.

The silicate molecules are arranged in characteristic tetrahedra, forming rings of specific number of molecules, thus forming pores of a specific size. A zeolite with 12 tetrahedra in the ring forms pores of approximately 8 Ångström.

Hydrophobicity:

Most air streams containing VOC's also contain moisture in the form of water vapor. Often the water content of the stream is much greater than the VOC content. Most adsorbents also adsorb water to varying degrees. Activated carbon, for example, has a characteristic water adsorption curve. Up to about 50% relative humidity, not much water is adsorbed, but at higher humidities, the water adsorption increases rapidly, and interferes with adsorption of organics by competing for the active sites.
Hydrophobic zeolite does not adsorb any appreciable amount of water and will function normally in relative humidities as high as 80%.

**Inorganic:**
Hydrophobic zeolite is a synthetically produced inorganic crystal, and does not depend on a naturally developed pore system. The pore size and structure is controlled chemically and can be manipulated to produce specific characteristics for particular applications.

The inorganic crystals are very stable, do not react with organics, do not have any catalytic properties, are resistant to both heat and strong acids, and cannot burn. These properties allow the use of high temperature and pressure, and permits use with reactive solvents, as well as allowing desorption at temperatures where carbon would burn.

**Synthetically produced:**
The hydrophobic zeolite is produced synthetically from readily available raw materials. It does not rely on naturally occurring pore structures, and can therefore be manufactured to suit specific applications.

Unfortunately, this manufacturing process is neither easy nor inexpensive. As a result, hydrophobic zeolites cannot compete with activated carbon on a pound to pound basis.

**New Opportunities for VOC Control**
Despite the high cost per pound of adsorbent, Munters Hydrophobic Zeolite offers some new opportunities for economical control of volatile organics.

The hydrophobic zeolite can be impregnated on a rotor honeycomb structure similar to that used for dehumidification and built by Munters for over 30 years. These "Zeol Rotor Concentrators" can be manufactured economically for airflows larger than about 20,000 cfm, and produce a concentrate which can be recovered or incinerated economically.

The adsorption characteristics of the hydrophobic zeolite are such that it can handle difficult applications, such as:

- Alcohols (except methanol)
- Ketones
- High boiling solvents
- Reactive monomers, such as styrene and methyl methacrylate
- Plastiziers and plastic breakdown vapors.
- "Normal" solvents in low concentrations.

The following are examples of existing, proven applications, and of applications which are in the development stage:

**SPRAY PAINTING APPLICATIONS**
Spray painting is a major source of VOC emissions. The cost of removing organic solvents from spray booth exhaust is both difficult and costly. The air volumes are typically quite large, up to 1 million cfm in a large auto plant, and the concentrations are low. As water is often used to remove paint particles from the air stream, the relative humidity is often 95% or higher.

Fixed bed activated carbon plants, Recuperative incinerators, Regenerative incinerators, and Carbon rotor concentrators have all been used for this application. Most require a lot of space, are heavy and costly to install, or require extensive preconditioning and safety equipment to function.

Zeol Rotor Concentrators, followed by a small thermal incinerator are simple to install, and offer operational, safety and cost advantages.
The following data were collected by BCP, Inc. Lake Saint Louis MO in evaluating VOC abatement options for painting rail cars.

### Annual Operating Cost

30,000 cfm Spray Booth Exhaust

- Thermal: 0.3
- Recuperative: 0.8
- Catalytic: 0.2
- Regenerative: 0.4

### Installed Cost

30,000 cfm Spray Booth Exhaust

- Thermal: 1.4
- Recuperative: 1.2
- Catalytic: 1.0
- Regenerative: 0.8

The Options do not include recovery, as the VOC mixtures vary constantly, and have no value as recovered solvents. Carbon rotors were excluded due to the presence of both very low and very high boiling solvents, reactive solvents, and location of the plants in high humidity areas such as the southeastern USA.

The graphs clearly show that of the control technologies evaluated, the lowest capital cost thermal incinerator also was the most costly to operate by far. Of the remaining options, the Zeol Rotor Concentrator followed by thermal or catalytic incineration was both the lowest capital cost and the lowest operating cost.

In a similar study, conducted by ABB Flakt Alpha Division, Environmental Systems Group, Madison Heights, MI for a major US auto manufacturer, a comparison was made of the cost of various options in abating a typical 130,000 cfm exhaust from a car body spray painting line.

<table>
<thead>
<tr>
<th>Automotive Spray Paint Line</th>
<th>Installed VOC Abatement Costs</th>
</tr>
</thead>
<tbody>
<tr>
<td>130,000 cfm</td>
<td>AT.1</td>
</tr>
<tr>
<td>Space Required</td>
<td>11,000 sq ft</td>
</tr>
<tr>
<td>Installed Cost (milions)</td>
<td>$6.4 million</td>
</tr>
<tr>
<td>Operating Cost (milions)</td>
<td>$48/kcfm</td>
</tr>
</tbody>
</table>

- **Alternate 1**: Wet electrostatic Precipitator, Dehumidification, Sacrificial Carbon Bed, Activated Carbon Rotor, Regenerative Incinerator
- **Alternate 2**: Dry Cassette Filter, Dehumidification, Sacrificial Carbon Bed, Activated Carbon Rotor, Regenerative Incinerator
- **Alternate 3**: Dry Cassette Filter, Dehumidification, Sacrificial Carbon Bed, Multi-Element Activated Carbon Rotor, Regenerative Incinerator
- **Alternate 4**: Dry Cassette Filter, Zeolite Flattening Filter, Zeol Rotor Concentrator, Regenerative Incinerator

The study considered various possible combinations of filtration and VOC destruction. Of all the systems, a combination of dry particulate filtration, Zeol Rotor concentrator and a thermal incinerator resulted in the lowest overall cost, and at the same time taking less space and requiring less space than the alternates.

In both of the above examples, a minimum of 95% VOC removal was required.

### POLYETHYLENE EXTRUSION

A European innovator and designer of liquid packaging systems, TetraPak laminate extruded polyethylene film to paperboard for their milk and juice cartons.

The hot polyethylene emits an acrid blue smoke, which contains volatile organics, plasticizer, and break-down products from the polyethylene itself.

The smoke is passed through a fixed bed of hydrophobic pellets, where the organics are adsorbed. Desorption takes place in two stages, using a combination of inert gas and air. The initial desorption of the volatile materials is done at 360 F, and the final removal of the plastic materials is done by passing air through the bed at 850 F. The
plastics oxidize in the bed, clearing the pores for another adsorption cycle after cooling.

The oldest plant of this type has been in operation for more than two years, and has gone through hundreds of cycles without any deterioration of the zeolite material.

The high temperature desorption/pyrolysis of the plastics is only possible in zeolite, which will withstand up to 1800 F without physical or chemical changes.

**STYRENE**

Styrene monomer is released from a number of industrial processes. Fiberglass lay-up, RIM molding of plastics are a couple of examples. The styrene is usually present in low concentrations as plants have to be well ventilated to protect workers from exposure. The styrene is quite reactive, it polymerizes readily, particularly in the presence of catalytic impurities as contained in activated carbon.

Although no plants have been built to date, zeolite offers possibilities for adsorbing styrene in low concentrations at reasonable cost, and if necessary, the polymers can be desorbed at high temperature, reactivating the zeolite within the plant itself.

**ROOM AIR PURIFICATION**

Rotogravure printing plants have been operating activated carbon recovery plants for decades. Current technology has improved recovery rates and energy costs over the last decade to a high state. However, recent lowering of the 8 hour exposure limit for toluene from 200 ppm to 100 ppm, with a potential lowering to the European standard of 50 ppm in future can pose a problem for many printers and converters.

Existing recovery plants are expensive to expand, and were specifically designed to handle high concentrations. The additional ventilation from folder enclosures and "floor-sweeps" required to lower the pressroom concentration can be handled at much lower cost in a Zeol Rotor Concentrator, and the concentrated "Desorbate" can be sent to the existing recovery plant.

**PLANT EXPANSIONS**

Many existing recovery plants are limited by air flow rather than solvent load. As the cost of a new recovery plant is often more than twice as expensive than a rotor concentrator installation, Zeol rotor concentrators are an economical alternative.

As an additional benefit, recovery plant economics often improve with increasing concentrations, so preconcentrating the VOC stream before the recovery plant can improve the overall economics of the system.

**SUMMARY**

Although hydrophobic zeolites will never replace activated carbon as a bulk adsorbent, its special properties offer new opportunities for cleaning a number of difficult VOC streams economically.

To date, Munters Zeol have installed or contracted for more than 25 rotor installations and five fixed bed plants. Some of these have been in continuous operation for over two years with excellent process results and reliability.

New applications and uses of hydrophobic zeolite are continually being developed. The bulk of this development is directed towards efficient and cost effective removal of VOC from industrial processes.
Hydrophobic Zeolites for VOC Abatement
By Lars Filth, PhD.

Hydrophobic zeolites are used to adsorb and remove volatile organic compounds (VOC) from industrial airstreams, eliminating contamination of the surrounding environment.

The atomic structure and composition of zeolites can be chosen to form pores of a specific diameter, so the material can selectively adsorb organic molecules with dimensions which are smaller than the pore sizes. In a recent development, zeolites can be made so they repel rather than attract water vapor. This avoids filling the pores with water, increasing their capacity for adsorbing organic vapors.

These properties and other unique attributes make hydrophobic zeolites very useful for certain VOC abatement applications where activated carbon has limitations.

Zeolites
Natural zeolites are crystals found in rock formations. They occur in volcanic rock, and in the sedimentary formations of ancient sea beds. Different types are often mixed together, and zeolites are also found in mixtures with other minerals such as feldspar. There are about 40 natural zeolites, each with a different chemical composition and crystalline structure.

Silicate research has allowed the manufacture of synthetic equivalents of many of the natural zeolites, and also led to development of entirely new synthetic forms. As a result, there are approximately 70 known zeolite structures. A few of these are produced in quantity because they are used industrially—primarily as catalysts in the petroleum industry, and for use in ion exchange applications.

Zeolite Structure
Zeolites are hydrated alkali-aluminosilicates. A typical composition is:

\[ \text{NaAlSiO}_4 \cdot 2\text{H}_2\text{O} \]

This crystalline structure of a zeolite can be considered two parts with different properties—the fundamental structural skeleton and the loosely attached atoms. In the zeolite above, the structural skeleton is AlSiO, which forms groups of tetrahedra, each of which has either an aluminum or silicon atom in the center and oxygen atoms in the four corners. These tetrahedra are connected to each other—they connect at the corners where they share an oxygen atom.

All the chemical bonds in this three-dimensional structure are covalent and strong. This structure is solid, but also very open, with spaces of uniform diameter. The shapes and sizes of these spaces are determined by the types of atoms in the zeolite. As the tetrahedra begin to form larger clusters, channels form at angles to the basic pores so the material presents the appearance of a ceramic sponge.

Alkali metal ions and water molecules are contained within this structure, occupying the voids and channels. These molecules and ions are loosely bound to the structural skeleton, and can be removed without affecting the strength of the basic framework.

Material Properties
Zeolites have properties which make them well-suited to a variety of separation operations.

Water Adsorption
When a zeolite is heated to between 100 and 300 Celsius, the water contained in the pores is driven off in the form of gas, as described in this reaction formula:

\[ \text{NaAlSiO}_4 \cdot 2\text{H}_2\text{O} + \text{energy} \rightarrow \text{NaAlSiO}_4 = 2\text{H}_2\text{O} \]

In this reaction, the zeolite has been activated. If the zeolite is allowed to cool to room temperature in normal ambient air, it will adsorb water from the air returning the material to the original formula. This reaction takes place very quickly even when the air is comparatively dry, making zeolite a very effective dehumidifying agent.

This dehydrating property is used in applications such as triple glazed windows, where a small amount of zeolite is included between the glass panes to trap water vapor, eliminating internal condensation during cold weather.

Ion Exchange Properties
When water containing soluble salts is passed over zeolites, metal ions in the water can be exchanged for different metal ions loosely bound to the zeolite structure.
An example of zeolite ion exchange includes:

\[ \text{NaAlSiO}_2 \cdot 2\text{H}_2\text{O} + \text{Cs}^- \rightarrow \text{CsAlSiO}_2 \cdot 2\text{H}_2\text{O} + \text{Na}^- \]

The formula shows that soluble cesium ions travel into the pores of the zeolite and change places with the sodium ions, which transfer to the water. An ion exchange has taken place. These reactions are used in many different applications. This specific reaction, for example, is used to clean waste water containing radioactive cesium.

In a more common example, a zeolite can selectively adsorb calcium ions to "soften" water. Calcium dissolved in the water is removed from the liquid, changing places with sodium ions from the zeolite. In many countries, laundry detergents contain this type of zeolite, which have the same beneficial effect on detergent performance as phosphates. Zeolite softening agents are considered more environmentally sound than phosphates, as they do not provide nutrients which would allow an excessive number of micro organisms to grow in lakes and streams.

Catalysis
A variation of the use of zeolites' ion exchange properties is to exchange catalytically active ions onto the zeolite, and then reduce the ions to their metallic form. In this process, the zeolite is an effective catalyst. Such processes are commonly used for cracking petroleum, increasing the refining yield of gasoline per barrel of crude oil.

Hydrophobic Properties
Recent developments in processing technology have made it possible to modify the atomic structure of many zeolites so they become hydrophobic—they repel water vapor rather than attract it.

The silicate molecules which make up the basic skeleton of the zeolite do not attract water. The water is attracted to the metal ions which are loosely attached to the basic silicate skeleton. Aluminum atoms in the zeolite structure have a negative charge, which is balanced by a positively-charged alkali metal ion in the zeolite pores. This alkali metal ion—often lithium, calcium or sodium—attracts water molecules.

To reduce this propensity for water adsorption, it is necessary to reduce the number of negative ions in the pores. This can be done by removing the aluminum from the zeolite, replacing it with silicon. An ideal hydrophobic zeolite would be pure SiO₂. About 20 of the 70 known zeolites can be converted to the hydrophobic form.

When the pores in the structure are not filled with water, they can attract and hold organic molecules. Research and development of industrial processes to create and utilize hydrophobic zeolites led to the formation of the company which is now Munters Zeol.

Use of Hydrophobic Zeolites
The size of the pores in each zeolite structure determines which molecules the material can adsorb. The pore sizes depend on the number of SiO₂ tetrahedra in the basic structure. The elements of this structure are rings—which can consist of 6, 8, 10, or 12 tetrahedra as shown in this graphic.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>2.6</td>
</tr>
<tr>
<td>Water</td>
<td>2.7</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>3.3</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>3.3</td>
</tr>
<tr>
<td>Oxygen</td>
<td>3.4</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>3.6</td>
</tr>
<tr>
<td>Ethylene Oxide</td>
<td>3.6</td>
</tr>
<tr>
<td>Methane</td>
<td>3.8</td>
</tr>
<tr>
<td>Butylacetate</td>
<td>4.3</td>
</tr>
<tr>
<td>Butanol</td>
<td>4.3</td>
</tr>
<tr>
<td>Acetone</td>
<td>4.3</td>
</tr>
<tr>
<td>MEK</td>
<td>4.3</td>
</tr>
<tr>
<td>Vinyl Chloride</td>
<td>4.3</td>
</tr>
<tr>
<td>Ethanol</td>
<td>4.3</td>
</tr>
<tr>
<td>Propane</td>
<td>4.3</td>
</tr>
<tr>
<td>n-Butane</td>
<td>4.3</td>
</tr>
<tr>
<td>MILK</td>
<td>4.4</td>
</tr>
<tr>
<td>Propylene</td>
<td>4.5</td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td>5.3</td>
</tr>
<tr>
<td>Benzene</td>
<td>5.9</td>
</tr>
<tr>
<td>Xylene</td>
<td>5.9</td>
</tr>
<tr>
<td>Phenol</td>
<td>5.9</td>
</tr>
<tr>
<td>Toluene</td>
<td>5.9</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>5.9</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>6.0</td>
</tr>
<tr>
<td>Styrene</td>
<td>6.0</td>
</tr>
<tr>
<td>Triethylamine</td>
<td>7.8</td>
</tr>
</tbody>
</table>

This table shows the diameter of some common chemical compounds:

The indicated pore diameters are approximate. The rings are more or less oval in shape rather than perfectly circular. The hydrophobic zeolites can adsorb organic molecules which are up to about 8 Ångström in diameter. Larger molecules are not adsorbed, and will therefore bypass a zeolite filter. A bed of zeolites functions like a reverse filter, or molecular sieve. The material captures the smaller molecules which fit into its pores, the larger molecules stay in the air, bypassing the zeolite.
Molecules in the list on the preceding page all fit into pores of various types of hydrophobic zeolites. Substances larger than 8 Ångström are very rare in commercial solvents, and unusual in industrial processes.

The polarity of the organic molecule also influences the adsorption reaction. The smaller dipolar moment the molecule has, the better it adsorbs on the zeolite. Compounds which have low solubility in water, such as toluene, benzene, xylene and styrene, adsorb very well. In contrast, substances which are highly water soluble—such as alcohols—adsorb less well on all hydrophobic adsorbents, including zeolites. Certain alcohols are exceptions to this general rule and are adsorbed more readily by zeolites than by carbon.

**Adsorptive Properties**
This graph shows the pore size distribution of Munters Zeol hydrophobic zeolite compared to a typical activated carbon used for recovery of volatile organics.

![Pore size distribution graph](image)

The pores in a zeolite are essentially all the same size. Carbon has a wide variety of pore sizes.

The range of pore sizes in the zeolite is determined by its strictly regular crystalline structure. All pores are essentially the same size. Carbon, in contrast, has a broad range of pore sizes and a larger pore volume per unit weight. This means carbon can adsorb a wide variety of different-sized compounds. However, in many circumstances this lack of selectivity is a disadvantage.

For example, most industrial air streams contain large, heavy molecules as contaminants. These "high boilers" will not adsorb on zeolite to any degree. The narrow pore size of the zeolite does not allow the large molecules to enter the zeolite structure.

In carbon and other adsorbents with a broad range of pore sizes, there are always enough pores large enough to fit high boiling compounds. The heavy molecules adsorb onto the material, blocking smaller pores from further adsorption.

Initially, activated carbon has a much higher adsorptive capacity than hydrophobic zeolite. However, "high boilers" gradually build up and reduce its capacity. Designers of activated carbon recovery systems compensate for this reduction in capacity by using extra adsorbent. This extra mass reduces the operating efficiency of the plant. Hydrophobic zeolite has a very narrow range of pore sizes, so it cannot be clogged with large molecules.

Additionally, adsorption forces are strongest in a pore which is exactly the size of the adsorbed molecule. Molecules adsorbed in closely-fitted pores are difficult to remove from the adsorbent. Zeolites can be selected with pores large enough to avoid binding the target molecules too strongly in smaller pores. This minimizes the energy needed to desorb the vapors from the zeolite surface.

**Reactive Solvents**
Certain solvents are either chemically very active or are monomers, which will polymerize on the adsorbent. Styrene is used in fibre reinforced polyester manufacture, where it is released to the air during the lay-up procedure. On the surface of the adsorbent, the monomer styrene can polymerize to form polystyrene. This material has a high boiling point as well as a large molecule size, making it impossible to desorb without using very high temperatures. Zeolite is the only hydrophobic adsorbent which can withstand such high temperatures. Inorganic crystalline zeolite is not damaged by temperatures up to 1800°F, whereas carbon will ignite and burn at much lower temperatures.

Some types of reactive solvents—in particular certain ketones—are a serious safety risk in activated carbon plants. Both MEK and cyclohexanone are well known for reacting exothermically, producing reaction by-products which damage the carbon.

These reactions are partly caused by the catalytic effects of impurities in the carbon. Hydrophobic zeolite does not contain catalytically active materials, and therefore does not promote the reactions. If such reactions do take place, zeolites can be desorbed at high temperature to remove the by-products, since the adsorbent will not burn.
Hydrophobic Zeolites for VOC Abatement

Adsorption Isotherms
These curves show the difference between the adsorption behavior of activated carbon and hydrophobic zeolite for p-xylene, a common solvent:

The illustration shows that although the activated carbon has a much higher total capacity, zeolite has a greater capacity than carbon at lower solvent concentrations.

This is of particular importance in VOC abatement applications requiring a high percentage removal rate from low-concentration inlet streams. The unique properties of hydrophobic zeolite make it feasible to remove low concentration volatile organics at relatively low capital and operating costs.

Water Adsorption
Typical VOC streams contain water in vapor form. Exhaust air relative humidity can vary from 30 to 95% RH in spray painting applications. It is important to consider the effect of this water on the adsorbent.

This graph shows the relationship between relative humidity and water adsorption on hydrophobic zeolite and on a typical activated carbon.

The zeolite does not adsorb any appreciable amount of water until the relative humidity is above 90%—whereas the carbon has adsorbed enough water at around 60% to interfere with adsorption of volatile organics.

Desorption
After adsorbing volatile organics, the adsorbent becomes saturated. It must be regenerated—desorbed—before more organics can be adsorbed. While pressure-swing cycles are common in compressed-air dehumidification applications, organics are best removed from zeolites by heating the saturated material.

Desorption is accomplished by flushing the zeolite with a hot stream of air or any inert gas. As the zeolite can withstand very high desorption temperatures, inert gas is used when high boilers must be removed, or when high concentrations of volatile solvents must be desorbed. Using hot inert gas also avoids the addition of atmospheric water vapor to the desorbate stream, and allows higher desorption temperatures than are feasible with low-pressure steam.

Hot air is used in rotary concentrators, where desorbate concentrations are below the flammable limit.

Depending on the application, the desorbate can be condensed for recovery or used as fuel in an incinerator for destruction. Where other types of VOC abatement equipment have been previously installed, they can be used to process the highly concentrated desorbate from a hydrophobic zeolite plant.

Munters Zeol
Munters Zeol produces VOC abatement systems based on hydrophobic zeolite technology. Munters has been the world leader in HoneyCombe® sorption rotor design for over 30 years. Zeol systems include:

- Skid-mounted rotary concentrators from 1,000 to 125,000 cfm capacity
- Fixed-bed zeolite adsorption plants for difficult adsorption applications
- Z-Block adsorption systems for small-capacity, difficult adsorption problems

This paper was originally published in Swedish by Dr. Lars Fälth in 1987. Jesper Granvaldt translated the text.

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