MOLECULAR SIEVES

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A subsidiary of the Arkema Group, CECA is a world player in specialty chemicals.

CECA has been manufacturing, developing and marketing adsorbents for more than 80 years and Molecular Sieves for more than 40 years.

Our company in brief:

• CECA focuses on improving its customers' performance, creating and developing adsorbents, chemical intermediates and additives.

• CECA operates an extensive manufacturing base and two research centers in France (GRL and CRRA) as well as industrial pilot plants in Honfleur, dedicated to customer service innovation.

• Facilities are ISO-certified, follow a program of good manufacturing practices, and are equipped with statistical process control tools.

• CECA offers technical services that are recognized around the world and an extensive range of products dedicated to the oil & gas markets.
Molecular Sieves
Siliporite®

Siliporite® Molecular Sieves are synthetic zeolites or metal aluminosilicates, with a porous tri-dimensional crystallized network and regular pore sizes. Based on the pore size, they are called 3, 4, 5 or 10 Å although the real pore opening is somewhat inferior to these values.

A highly active adsorbent is obtained through “activation” at high temperature. Activation aims to desorb the zeolitic water contained in the adsorbent to maximize working adsorption capacity.

The combination of a uniform porous structure, with a high adsorption capacity, enables the selective adsorption of the target molecules.

“Molecular Sieves” are so called because of their ability to screen molecules at the molecular scale. Molecular Sieves differ from other adsorbents such as Silica Gel or Activated Alumina, which have a very wide pore size distribution. See figure 1.

Figure 1: Pore diameter (Å)

Siliporite® 4 Å is the basic molecular sieve obtained by synthesis of type LTA zeolite. See figure 2. Siliporite® 3 Å is obtained by replacing part of the sodium cations of the 4 Å molecular sieve with potassium cations. Siliporite® 5 Å is obtained by replacing part of the sodium cations with calcium cations on the 4 Å. Siliporite® 10 Å is the basic molecular sieve obtained by synthesis of type FAU zeolite. See figure 3.

Figure 2: LTA - type

Figure 3: FAU - type

The different types of Molecular Sieves

- Siliporite® 4 Å is the basic molecular sieve obtained by synthesis of type LTA zeolite. See figure 2.
- Siliporite® 3 Å is obtained by replacing part of the sodium cations of the 4 Å molecular sieve with potassium cations.
- Siliporite® 5 Å is obtained by replacing part of the sodium cations with calcium cations on the 4 Å.
- Siliporite® 10 Å is the basic molecular sieve obtained by synthesis of type FAU zeolite. See figure 3.
ADSORPTION ON MOLECULAR SIEVES

Adsorption is a surface phenomenon whereby a molecule, contained in a fluid (gas or liquid), attaches itself on the surface of a solid. Adsorbents possess high porosity with internal surface area in the order of several hundred m²/gr. Zeolitic Molecular Sieves are adsorbents with well defined pore sizes and limits to adsorption selectivity. Figure 4 shows the water adsorption iso-therms for different adsorbents.

Figure 4: Water adsorption isotherms at 25°C

Molecular Sieves differ from other adsorbents in the shape of their isotherms which show a high adsorption capacity for relatively low concentrations of the adsorbate (adsorbed product). At the same time, the adsorption capacity of molecular sieves decrease with temperature increase also much slower than others adsorbents. See figure 5.

Figure 5: Water adsorption isobar (water partial pressure 10 torr)

The adsorption of different molecules by Molecular Sieves is affected by the following parameters:

1. Zeolite type.
2. Effective pore diameter.
5. Polarity of molecule.
6. Concentration or partial pressure of the adsorbate.
7. Operating temperature.
The critical diameter of some common species is shown on Table 1. It gives entry potential for a particular molecule to pass through the opening of the pores and penetrate into the crystalline structure in order to be adsorbed on the active surface.

### Table 1: Critical diameter of different molecules

<table>
<thead>
<tr>
<th>MOLECULES</th>
<th>Critical diameter in Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Helium</td>
<td>2.0</td>
</tr>
<tr>
<td>Hydrogen, Acetylene</td>
<td>2.4</td>
</tr>
<tr>
<td>Water, O₂, C, Monoxide and Dioxide</td>
<td>2.8</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>3.0</td>
</tr>
<tr>
<td>Ammonia, Hydrogen Sulphide</td>
<td>3.6</td>
</tr>
<tr>
<td>Argon</td>
<td>3.8</td>
</tr>
<tr>
<td>Methane</td>
<td>4.0</td>
</tr>
<tr>
<td>Ethylene, Ethylene monoxide</td>
<td>4.2</td>
</tr>
<tr>
<td>Ethane, Methanol, Ethanol</td>
<td>4.4</td>
</tr>
<tr>
<td>Methyl-mercaptan</td>
<td>4.5</td>
</tr>
<tr>
<td>Propane, nC₄ to nC₂₂</td>
<td>4.9</td>
</tr>
<tr>
<td>Propynene</td>
<td>5.0</td>
</tr>
<tr>
<td>Ethyl-RH, Butene 1, Butene 2 trans</td>
<td>5.1</td>
</tr>
<tr>
<td>Difluochloromethane (R 22)</td>
<td>5.3</td>
</tr>
<tr>
<td>Iso C₂₂</td>
<td>5.6</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>6.1</td>
</tr>
<tr>
<td>Toluene, Paraxylene</td>
<td>6.7</td>
</tr>
<tr>
<td>Benzene</td>
<td>6.8</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>6.9</td>
</tr>
<tr>
<td>Metalxylene</td>
<td>7.1</td>
</tr>
<tr>
<td>Tri-ethylamine</td>
<td>8.4</td>
</tr>
</tbody>
</table>

This is essentially due to 3 simultaneous actions:

- Elasticity of the adsorbate molecule,
- Mobility of the cations,
- Vibration of the molecular sieve crystal link.

On the other hand, at very low temperature, molecules with a critical size smaller than the diameter of the pores, are not adsorbed (e.g. N₂ at -195°C on a 4 Å molecular sieve).

The possibility of adsorption depends not only on the dimension and the shape of the molecules (linear, branched, ring...) but also on their polarity (Table 2).

### Table 2: Polarity scale for different molecules

<table>
<thead>
<tr>
<th>ADSORPTION INCREASING</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
</tr>
<tr>
<td>NH₃</td>
</tr>
<tr>
<td>CH₃OH, Alcohol, Aldehydes</td>
</tr>
<tr>
<td>Ketones</td>
</tr>
<tr>
<td>SO₂</td>
</tr>
<tr>
<td>Alkynes</td>
</tr>
<tr>
<td>Alkenes</td>
</tr>
<tr>
<td>CO₂</td>
</tr>
<tr>
<td>Alkanes</td>
</tr>
<tr>
<td>CH</td>
</tr>
<tr>
<td>CO</td>
</tr>
</tbody>
</table>

If there is no steric hindrance and the molecular size fits within the pore size, then the most polar molecules are adsorbed first.
INDUSTRIAL DYNAMIC ADSORPTION

In dynamic adsorption, the granular bed of adsorbent in an adsorption column (or adsorber) sees the vector fluid (gas or liquid) containing the molecules to be separated, percolated through it.

Mass transfer zone (MTZ)

The adsorbent layer (height = h) in which transfer of the molecules to be adsorbed, from the vector fluid to the adsorbent, is called the Mass Transfer Zone (MTZ). The concentration of the adsorbate, from the inlet to the outlet of the MTZ varies from the initial concentration \( C_0 \) in the vector fluid to the desired concentration \( C_s \) after treatment. See figure 6.

Above the MTZ, the adsorbent is saturated, and in adsorption equilibrium with \( C_0 \). Below it, fresh or regenerated adsorbent is free of impurities.

The length of the mass transfer zone mainly depends on:

- the adsorbate adsorption kinetic
- the fluid vector characteristics
- the fluid superficial velocity
- the type, the shape and the size distribution, of the molecular sieve
- the \( C_0 \) and \( C_s \) concentrations

The adsorption front steadily moves within the adsorbent bed, from the inlet towards the outlet, during a period called ‘Adsorption Time’. After this period, the expected purification is no longer ensured. It is then necessary to regenerate the adsorbent by desorbing the adsorbate. The velocity of the adsorption front is a function of the useful load of the adsorbate and of the adsorbate flow rate.

Figure 6: Mass Transfer Zone (MTZ)
PARAMETERS INFLUENCING ADSORPTION

Temperature

Adsorption capacity decreases as the temperature increases.
Adsorption is an exothermic process. The heat released can decrease the effective adsorption capacity.
Molecular Sieves, however, are much less affected by this phenomenon than the other adsorbents. See figure 5.

Concentration of the adsorbate

The adsorption capacity increases with the adsorbate concentration.
However, at low concentration, Molecular Sieves have a special characteristic of adsorbing much more than the other adsorbents.
This property is often the main criteria for choosing a particular molecular sieve.

Vector of the adsorbate (liquid or gaseous phase)

The vector phase containing the adsorbate influences the length of the MTZ. In the liquid phase, the mobility of the target molecules is very low.
The diffusion speed – and thus the adsorption kinetics – are sharply inferior to those found in a gaseous phase.
Therefore the flow velocity must be appreciably lower for a liquid than for a gas.

Pressure

An increase in the total pressure of the system builds up the adsorbate partial pressure, this is reflected in an increase of adsorption capacity.

Impurities

Some organic molecules present in the fluid to be treated, or in the regeneration gas (olefins, aromatics, amine, etc...) can be poisonous for Molecular Sieves.
The adsorbed and accumulated impurities can reduce the efficiency and the performance of the adsorbent.

With the specific assistance of your CECA representative, certain grades can be selected in order to reduce coadsorption of undesirable impurities and extend the lifetime of molecular sieves.

CECA engineers can help you make an appropriate selection among the many specialized products within the CECA portfolio.

REGENERATION OF MOLECULAR SIEVES

At the equilibrium stage, the phenomenon of adsorption is characterized by a saturated state.
The saturated molecular sieve can no longer adsorb.
However, the adsorption is reversible. The adsorbed substances can be desorbed or eliminated from the adsorbent by shifting the adsorption equilibrium and modifying the operating conditions, either by increasing the temperature of the adsorbent, or by decreasing the partial pressure of the adsorbate, or, less commonly, by eluting with another adsorbate.
The saturated molecular sieve recovers its adsorption capacity after desorption: this is called "regeneration".
The dynamic adsorption process is a cyclic one, with adsorption and regeneration steps, necessarily discontinuous. A continuous process is possible by shifting the cycle phases on a minimum of two adsorbers set up in parallel.
**Thermal regeneration**

Thermal regeneration is a widely used method. In most cases, the adsorbent bed is brought to a higher temperature by a hot gas stream. The desired performance, water content of the purge gas, nature of the adsorbate, and the impurities coadsorbed, define the reactivation temperature – in most cases, regeneration is carried out between 200 - 300°C (390 - 570°F).

For a given regeneration temperature, the water content of the regenerating gas will affect performance of the regenerated molecular sieve.

The heat needed to suitably regenerate takes into account:
- heat needed to heat the bed to the desired temperature,
- heat needed to heat the adsorber (this depends on the type of insulation, external or internal),
- heat needed to heat and desorb the adsorbate mass retained in the bed,
- loss of heat through the walls of the column and the supporting grids.

Organic molecules (olefins, aromatics, heavy paraffins...), present in the fluid to be treated, can be coadsorbed during the adsorption phase. In order to prevent or to minimise risks of coking during thermal regeneration, a purge with an inert gas is carried out. Another process is to gradually increase the temperature of the adsorbent bed until it reaches the required temperature. This helps to rid the bed of organics during the lower end of the temperature ramp.

The heating phase must be followed by a cooling stage in order to bring the temperature back to its initial level, in readiness for the next adsorption cycle.

**Regeneration by variation of Pressure (pressure swing)**

Regeneration by pressure swing is based on the fact that a reduction in the partial pressure of the adsorbate, corresponds to a decrease of the adsorption capacity at equilibrium.

Regeneration, with no external heat, is undertaken by purging the vessel to be regenerated, with a part of the expanded treated gas. In fact, the energy needed for the desorption is taken from the system with recovery of the major part of the adsorption heat. For this reason, in this regeneration process the cycles are very short, lasting only a few minutes.

**Regeneration by displacement or elution**

Regeneration by elution is seldom used. It is usually employed only when the above mentioned methods cannot be applied (high risk of polymerisation, coking).

The molecules to be desorbed are eluted by other molecules which are more easily adsorbed and which are easily desorbed thermally, without damaging the sieves.

**Organic molecules (olefins, aromatics, heavy paraffins...),** present in the fluid to be treated, can be coadsorbed during the adsorption phase. In order to prevent or to minimise risks of coking during thermal regeneration, a purge with an inert gas is carried out. Another process is to gradually increase the temperature of the adsorbent bed until it reaches the required temperature. This helps to rid the bed of organics during the lower end of the temperature ramp. The heating phase must be followed by a cooling stage in order to bring the temperature back to its initial level, in readiness for the next adsorption cycle.

**Figure 7: Residual water content of Siliporite® based on thermal regeneration conditions**
MANUFACTURING OF MOLECULAR SIEVES

CECA’s modern Siliporite® Molecular Sieves plants are located in Honfleur, France and in Inowroclaw, Poland. Equipped with the most advanced technologies, each plant produces a wide range of high quality products that are well adapted to market needs.

Quality Control

The quality of Siliporite® is permanently controlled by our specialized laboratories, which carry out systematic controls on the production lines and specific studies for all applications. See figure 8.

Figure 8: Manufacturing process for the production of activated zeolite Molecular Sieves

Systematic controls

• Grain size distribution analysis
• Crushing and attrition strength
• Bulk density, loss of ignition
• Ion exchange rate
• Adsorption equilibrium capacity at 25°C:
  • For water at 10 and 50% of saturated partial pressure
  • For benzene at 50% of saturated partial pressure
Specific Controls

• Adsorption capacity in well defined thermodynamic conditions, of:
  - Nitrogen
  - N Butane
  - CO₂
  - Toluene
  - Methanol, H₂S etc...
• Adsorption kinetics
• Thermal stability, etc...
# PRODUCTS FOR ALL APPLICATIONS

Molecular Sieves can be used in static applications (product is not regenerated), or in dynamic applications (product is regenerated when it becomes saturated).

CECA proposes Molecular Sieves for:

## Static applications
- Building industry: insulating glass and polyurethane (PU) formulation
- Plastics and coatings: polymers for packaging, etc...
- Automotive and refrigeration systems

## Industrial gases
- Air separation unit (oxygen plants)
- Hydrogen purification

## Oil & Gas Applications

<table>
<thead>
<tr>
<th>MARKET/TYPE</th>
<th>SILIPORITE®</th>
<th>MAIN FEATURES AND APPLICATIONS</th>
<th>SHAPE</th>
<th>SIZE</th>
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</thead>
<tbody>
<tr>
<td>3A NATURAL GAS AND LIQUIDS DRYING</td>
<td>NK30</td>
<td>Standard selective dehydration</td>
<td>beads &amp; pellets</td>
<td>1/8” &amp; 1/16”</td>
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<tr>
<td>4A</td>
<td>NK30COS</td>
<td>Selective dehydration with COS minimizing specific feature</td>
<td>beads</td>
<td>1/16”</td>
</tr>
<tr>
<td>4A</td>
<td>Optisieve 3</td>
<td>High density beads for selective dehydration and compact beds</td>
<td>beads</td>
<td>1/8” &amp; 1/16”</td>
</tr>
<tr>
<td>5A INDUSTRIAL GASES</td>
<td>H2S SDT</td>
<td>Selective dehydration of pure H2S or H2S/CO2 mixtures</td>
<td>beads &amp; pellets</td>
<td>1/16”</td>
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<tr>
<td>4A</td>
<td>NK10</td>
<td>Standard dehydration with high hydrothermal resistance</td>
<td>beads &amp; pellets</td>
<td>1/16”</td>
</tr>
<tr>
<td>5A</td>
<td>SRA</td>
<td>Amine resistant grade specially fitted for LNG and NGL processes</td>
<td>beads &amp; pellets</td>
<td>1/8” &amp; 1/16”</td>
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<tr>
<td>5A</td>
<td>Optisieve 4</td>
<td>Amine resistant grade with high density and compact beds</td>
<td>beads</td>
<td>1/8” &amp; 1/16”</td>
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<td>3A OIL &amp; GAS APPLICATIONS</td>
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<td>NK10DC</td>
<td>Dehydration and CO2 removal from natural gas stream</td>
<td>beads &amp; pellets</td>
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<td>3A</td>
<td>NK20C</td>
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<tr>
<td>13X</td>
<td>G5</td>
<td>Dehydration and sweetening (incl. C3+SH and CO2 removal)</td>
<td>beads &amp; pellets</td>
<td>1/8” &amp; 1/16”</td>
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<td>3A CRACKED GAS AND OLEFIN PURIFICATION</td>
<td>OPX-R</td>
<td>Dehydration - Resistant coke minimizing product</td>
<td>beads &amp; pellets trilob pellets</td>
<td>1/8” &amp; 1/16”</td>
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<td>OPX-T</td>
<td>Dehydration - Pressure drop minimization</td>
<td>beads</td>
<td>1/4”</td>
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<tr>
<td>3A</td>
<td>OPX-K</td>
<td>Dehydration - High kinetics formulation</td>
<td>pellets</td>
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<td>OPX-M</td>
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<td>Alumina</td>
<td>SCOS &amp; OXY30</td>
<td>Various purifications (oxygenates and sulfurs)</td>
<td>beads</td>
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<td>3A REFINING SOLUTIONS</td>
<td>NK30COS</td>
<td>C3/C4* and C6+ cuts drying; Fuel Gas drying</td>
<td>beads &amp; pellets</td>
<td>1/8” &amp; 1/16”</td>
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<tr>
<td>4A</td>
<td>NK10</td>
<td>H2 make-up drying; LPG drying; C3/C4 drying; BTX drying</td>
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<tr>
<td>4A</td>
<td>NK10C</td>
<td>Chloride trap (incl. overhead reformers streams)</td>
<td>beads &amp; pellets</td>
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<td>NK20C</td>
<td>LPG sweetening</td>
<td>various</td>
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<td>NG50 &amp; NPL50</td>
<td>n/iso paraffins separation in gas or liquid phase</td>
<td>various</td>
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<tr>
<td>13X</td>
<td>Phy51 &amp; Phy53</td>
<td>CO &amp; N2 removal in PSA H2 units</td>
<td>various</td>
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<tr>
<td>13X</td>
<td>G5</td>
<td>Sweetening and purification (incl. Penex® &amp; Butamer™)</td>
<td>various</td>
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<tr>
<td>3A ETHANOL DRYING</td>
<td>EPX3B</td>
<td>Ethanol drying in PSA ETOH systems</td>
<td>beads</td>
<td>1/8” &amp; 1/16”</td>
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<tr>
<td>3A</td>
<td>EHP</td>
<td>Dehydration of high purity ethanol grades</td>
<td>beads</td>
<td>1/8”</td>
</tr>
<tr>
<td>MERCURY REMOVAL</td>
<td>HG series</td>
<td>Hg removal grades for dry or wet gas streams (guard beds)</td>
<td>beads</td>
<td>various</td>
</tr>
</tbody>
</table>
RANGE OF SERVICES:
"BEFORE, DURING AND AFTER"

Together with products, CECA offers a real partnership to its customers to support them from concept stage until full operation.

This is the "Before, During and After" approach, based on a wide range of capabilities:

• **R&D pilot plant facilities**: specific testing programs for new developments are possible within a very short time schedule

• **Oil & Gas technical group**: a team of knowledgeable and responsive engineers working on worldwide projects with engineering companies from feasibility studies to detailed engineering stage; more than 1,500 tons of Molecular Sieves are installed yearly for new projects

• **After-sales Services**: specialists are available for start-up, training and optimization, providing analytical services, performance evaluation, operator training, and loading assistance

• **Worldwide Sales Network**: available at any time to support customer needs around the world
WORLDWIDE PRESENCE

- Plants
- Research and Development Centers
- Marketing and sales offices
HEADQUARTERS:

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CECA, a subsidiary of the Arkema Group, is a world player in Specialty Chemicals. CECA constantly strives to improve its customers’ performance by creating and developing chemical intermediates and additives. CECA operates in over 100 countries, with an extensive international network of industrial facilities, together with two research centres (GRL and CRRA) dedicated to customer innovation.