Activated Alumina & Molecular Sieves

Quality and advanced technology

Axens
IFP Group Technologies

Procatalyse Catalysts & Adsorbents

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About Axens Catalysts & Adsorbents

Axens, formed through the merger of Procatalyse Catalysts & Adsorbents with IFP's Technology Licensing and Service Division, is an international provider of technologies, catalysts and adsorbents as well as services to the refining, petrochemical and natural gas processing industries. Backed by strong R&D and a unique understanding of the interactions between catalysts, adsorbents and processes, we offer our customers advanced and comprehensive catalytic solutions to suit their needs. Our catalysts and adsorbents service program includes training, start-up assistance, performance follow-up, analysis of spent material, advice for regeneration and extensive experience to enhance product performance under your operating conditions. Our adsorbents, suited for applications in the refining, petrochemical, chemical and gas processing industries, are produced in our ISO-9001 certified manufacturing facilities in Salindres, France, which uses the most advanced technologies in this field.

Adsorbent types

Many types of adsorbents exist, of which the most important ones are activated alumina, zeolite, silica gel and activated carbon.
Axens' Procatalyse Catalysts & Adsorbents produces both special alumina and zeolite based adsorbents (molecular sieves). This enables us to offer our customers the most suitable adsorbent or combination of adsorbents to optimize their drying or purification process.

This brochure provides basic information concerning activated alumina and molecular sieves and their possible applications. We also discuss our patented and industrially proven Multibed™ Technology which features combinations of our adsorbents for improved performance.

Activated Alumina

Manufacturing process

Axens starts with gibbsite as the raw material to manufacture activated alumina, using the Bayer process, in which bauxite reacts with soda and precipitates as alumina. The gibbsite is then dehydrated according to the original Pechiney Flash process, developed initially at Salindres in 1954, in such a way that only negligible quantities of inactive boehmite are formed.

Another Pechiney process patent described the production of activated alumina in the form of extrudates and smooth surfaced beads.
During the agglomeration process, the extremely high reactivity of the alumina powder leads to a significant crystalline change resulting in an increase in specific surface area and pore volume and the development of very high mechanical strength.

Adsorption

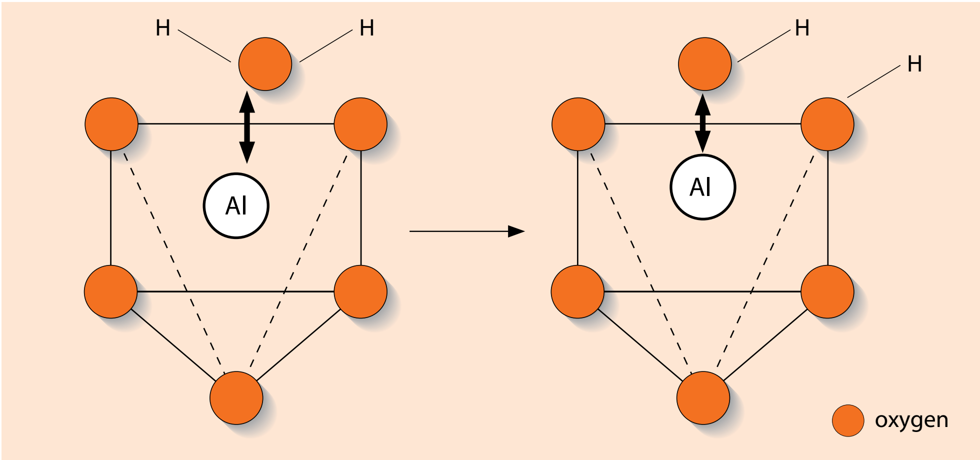
Adsorption is the fixation of molecules by reversible reaction on the surface of a solid. The adsorption of a compound on alumina is the sum of three different phenomena:

❶ Chemisorption, forming the first layer at low partial pressures.

❷ Physisorption, due to the formation of multiple layers by hydrogen bonding in the alumina pores.

❸ Capillary condensation, where localized condensation takes place at temperatures above that of the bulk fluid's dew point.

Chemical bonding of water oxygen with surface aluminum occurs, leading to unstable tri-coordinated oxygen which is transformed into two surface bonded hydroxyl ions. This is called dissociative adsorption. Then, other water molecules can link to the hydroxyl groups by hydrogen bonding. As a consequence, the volume of adsorbed water is not limited to a single layer.
The volume of adsorbed water per unit of surface area depends on the surface site reactivity and is expressed as adsorption capacity. Axens uses the terms E0.1 and E0.6 to express the adsorbent capacity at 10% and 60% relative humidity, respectively.



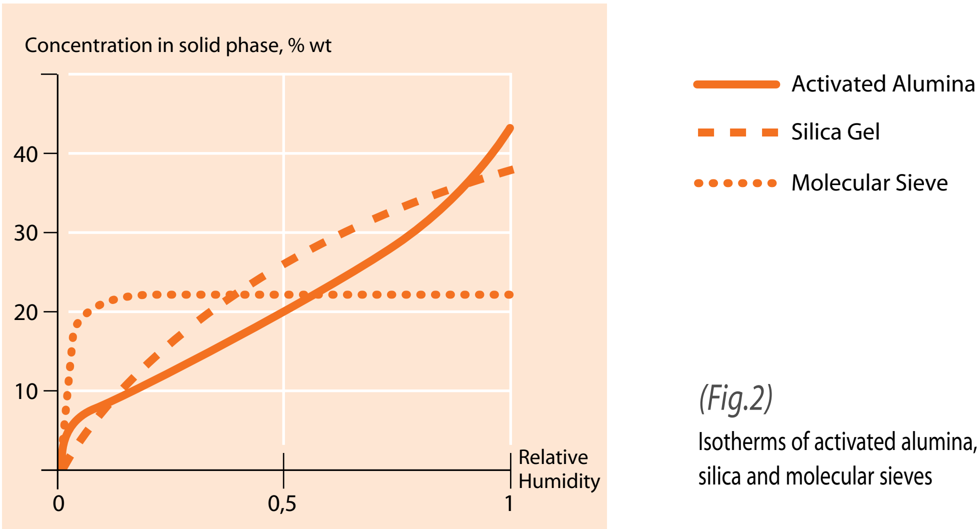
(Fig.1)
Adsorption of water to the alumina surface

These phenomena are surface reactions, which control the reaction rate. This is the reason why specific surface area is an important feature for designing adsorbents in dehydration and other applications.

A high internal surface area through the presence of pores (capillaries) is necessary to create adsorption sites. Alumina is the most widely used adsorbent because of the chemical properties of its surface and its ability to be shaped with well-defined pores defined as follows:

- (Ultra) Macropores (> 1000 Å) to enhance diffusion into the pore system.
- Mesopores (30 to 1000 Å) to accommodate medium size molecules.
- Micropores (< 30 Å) to accommodate small molecules like water.

One strength of Axens is the ability to optimise the pore size distribution for a specific adsorbent duty, keeping high mechanical strength. Chemical species are sometimes used to alter acidity or basicity. Low temperature, high partial pressure and high condensation temperature of the gaseous compound all favor physical adsorption. Generally, alumina has high affinity to polar compound like water. The higher the condensation temperature of a gaseous compound, the greater is its adsorption.
Adsorption also increases with the partial pressure of the compound, and this relationship is represented at a constant temperature by an adsorption isotherm. Figure 2 represents isotherms of three types of adsorbent.



(Fig.2)
Isotherms of activated alumina, silica and molecular sieves

Regeneration *(desorption)*

After saturation has been reached, one can restore the original adsorption properties by desorption. Usually the adsorbed molecules (adsorbate) are desorbed by addition of heat by a hot inert gas between 160 and 220°C at reduced partial pressure. If only the partial pressure is reduced, the adsorbate concentration on the solid phase will be higher than that predicted by the adsorption isotherm. This phenomenon is called hysteresis. The most common configuration consists of two adsorbers, one operating in the adsorption mode while the other operates in the regeneration mode.

Aging

A gradual reduction in adsorption capacity is caused by aging of the adsorbent. Two types of aging exist;

1. *Hydrothermal aging is an irreversible change of adsorbent structure caused by hydrothermal treatment during regeneration, resulting in reduced active area. Aging is therefore dependent on the number of regenerations and quality of the adsorbent. The rate of adsorption capacity reduction is more rapid at the beginning of the adsorbent's life. With time, the rate stabilizes.*

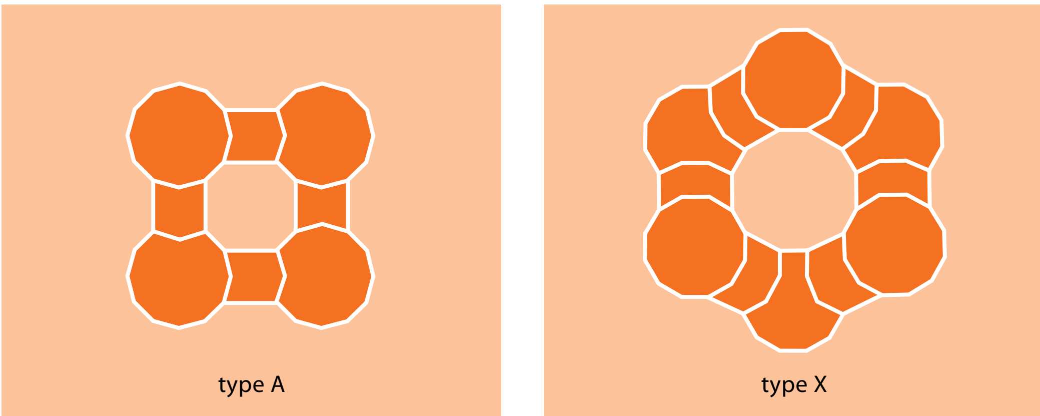
2. *Aging from contamination caused by coadsorption of undesired species and coke formation on the active surface of the adsorbent. This phenomenon is not completely reversible, and carbon deposits increase with each regeneration*

Alumina product range

Type	Application
AA 1.5 - 3 mm	Highest adsorption when pressure drop is not a problem
AA 2 - 5/4-8 grade A	Drying of organic liquids (LPG, gasoline, and from the steam cracker), drying and purification of air and gases (MeCl, NLG, LNG), drying of H_2, O_2, N_2
AA 2-5/4-8 grade P	Purification, like selective elimination of fluorinated hydrocarbons (HF alkylation process and purification of gases and liquids)
AA 2-5/4-8 grade D	Specifically developed for air dryers with a very high water adsorption range and high mechanical resistance
SAS 351, 1.5-3 mm	Polymer purification, purification of COS, H_2S en CO_2, MeCl removal
SAS 357, 2-5 mm	CO_2 removal from air
SAS 820, spheres	Polymer purification
SAS 830, extrudates	TBC elimination
SAS 857	Elimination of HCl and water from CCR hydrogen product
C.B.L./C.B.R./C.B.T	Separation for gas chromatography purposes
SPH 501	Guard bed top layer in Multibed™ system
SPH 513	Guard bed top layer in Multibed™ system

Molecular Sieves

Molecular sieves are zeolite-based adsorbents consisting of crystalline aluminosilicates (zeolites) and clay. The zeolite represents the active phase. Zeolites occur only as small crystals (1 - 6 µm) which are too small for use in dynamic adsorption systems. A small amount of clay is therefore employed as a binder enabling fabrication of shaped products to adjust the mechanical properties of the adsorbent.

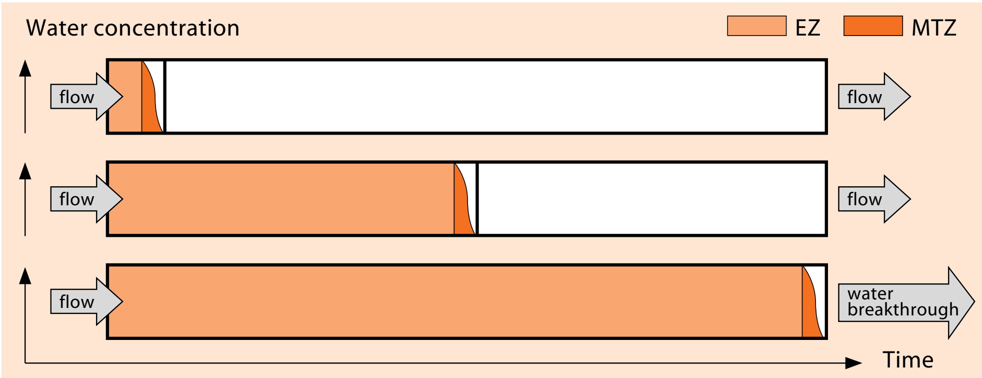


(Fig.3)
A and X type zeolites

The special characteristics of molecular sieves include reversible adsorption of various gaseous compounds and a network of cavities and narrow pores giving very high internal surface area. Type A zeolite with sodium cations has a pore width of 4 Å, and is called MS4A. Replacement of sodium by calcium cations leads to 5 Å pores, and is called MS5A. In the same way replacement of sodium by potassium leads to molecular sieve MS3A. Zeolite of type X gives pores of 10 Å and the calcium type corresponds to MS13X.

Adsorption

The zeolite is responsible for the physical adsorption of the molecule to the surface. It is therefore necessary to develop the largest possible internal surface as is obtained by the presence of well defined pores and cavities. Adsorption increases with the partial pressure of the adsorbate.
Contrary to other adsorbents like activated alumina and silica, zeolites have a high adsorption capacity at low partial pressures. Adsorption capacity decreases with increasing temperatures, but zeolites keep their efficiency for drying up to 100°C, whereas alumina has its more favorable adsorption characteristics below 50°C. When the mass transfer zone (MTZ), which preceeds the adsorbate saturating the adsorbent in the equilibrium zone (EZ) reaches the bottom of the reactor (breakthrough condition), the adsorber reactor is switched to the regeneration mode.



(Fig.4)
Picture of EZ/MTZ

Regeneration

Molecular sieves can be regenerated by changing the isotherm (thermal swing) by heating the adsorbent with a hot gas or by changing the partial pressure (pressure swing). Regeneration gas flows countercurrently to the process gas at temperatures between 200 and 280°C. If a fast regeneration is required, temperatures up to 320°C could be considered.

Normally adsorber units are used with one adsorber in adsorption mode and the other in regeneration mode. Depending upon volumes being treated a multi-adsorber system can be implemented.

Regeneration is generally performed countercurrently to the drying direction. This prevents the adsorbate from coming into contact with the bottom part of the adsorbent. This reduces hydrothermal aging (see next part) and enhances the number of cycles. When a dry gas (like nitrogen) is used, lower regeneration temperatures can be employed reducing aging. Wet gas is less costly, but requires higher regeneration temperatures (> 250°C), causing faster aging.

Subsequent cooling with dry cold gas is necessary. If dry gas is not available, it is recommended to perform the cooling step in the same direction (co-current) as the adsorption. Care must be taken to avoid the pick-up of water from the condensor or from unpurged parts of the unit.

If there is a limitation in regeneration temperature we advise using a combination of activated alumina and molecular sieves, taking advantage of the lower temperature needed to regenerate activated alumina. For some applications however molecular sieves are preferred over activated alumina because of possible co-adsorption effects (see next part), such as the use of MS 3A SC molecular sieves for cracked gas drying.

Co-adsorption

Several types of molecules can adsorb simultaneously on the surface, competing for active sites. Highly polar molecules will displace less polar molecules, causing the less polar ones to emerge first. Suppose both water and CO_2 are present, then we can expect the less polar CO_2 to emerge first.

Applications

Zeolite type adsorbents (Molecular sieves) can be applied in two ways:

1. *Separation according to molecular size: only those molecules with a diameter smaller than the zeolite pore will enter and be adsorbed, e.g., iso- and normal paraffins separation or removal of CO or CH_4 in a H_2 stream.*

2. *Separation according to molecular polarity: zeolite adsorbents tend to adsorb molecules of higher polarity by affinity, e.g., removing CO from hydrogen.*

Molecular sieves product range

Type	Application
MS 3A	drying of alcohols and olefins
MS 3A SC	drying of cracked gases and olefins
MS 4A	• drying of gases and liquids • methanol removal from gases and liquids
MS 4A NG	drying and CO_2 removal from natural gas
MS 5A	• drying and CO_2 removal from gases and LPG's • methanol removal from gases and liquids • H_2S, mercaptan and COS removal from gases and LPG's
MS 5A PS	• CO and N_2 removal from H_2 rich streams in PSA • O_2 production from air by PSA
MS 5A SP	separation of iso/normal paraffins in vapor phase processes
MS 13X	• drying and mercaptan separation from natural gas and LPG • NH_3 and CO_2 removal from gas streams
MS 13X ASP	drying and CO_2 removal from air or gas streams

Choice of adsorbents

A great variety of adsorbent types exists on the market. Hence it is very difficult for the user to make the right and most economic selection of adsorbent type for his specific process.

In the case of drying under conditions of high relative humidity, activated alumina displays a larger adsorption capacity. Whereas in the case of drying at low relative humidity and higher temperature, molecular sieves would be more suitable. When drying temperatures for hydrocarbon species over 60°C are applied, it is recommended to use molecular sieves.

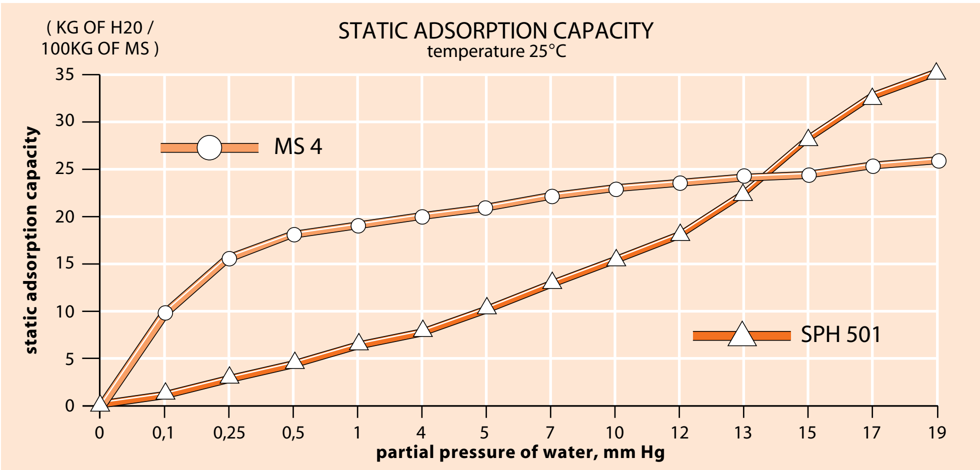
Every process provides its own specific problems, and therefore it is best to contact the Axens' adsorbent team or our local representative to discuss the best solution for your adsorbent selection.

Procatalyse, now Axens, was the first company to produce both activated alumina and zeolite type adsorbents. In this way, our company has accumulated extensive technical knowledge to advise you which adsorbent type or combination of adsorbent types (Multibed™ Technology) to choose.

We have tried to provide you with an overview of which adsorbent to select by using the 'Application List' included at the end of this brochure.

Multibed™ Technology

The patented MultiBed™ technology combines optimally the advantages of Spheralites and molecular sieves when dealing with water saturated contaminated feeds. Spheralites have a higher adsorption capacity for water at high partial pressure (reactor inlet conditions), while molecular sieves exhibit higher adsorption capacity for water at lower partial water pressure.



(Fig.5)

Isotherms of Spheralites and 4A molecular sieves

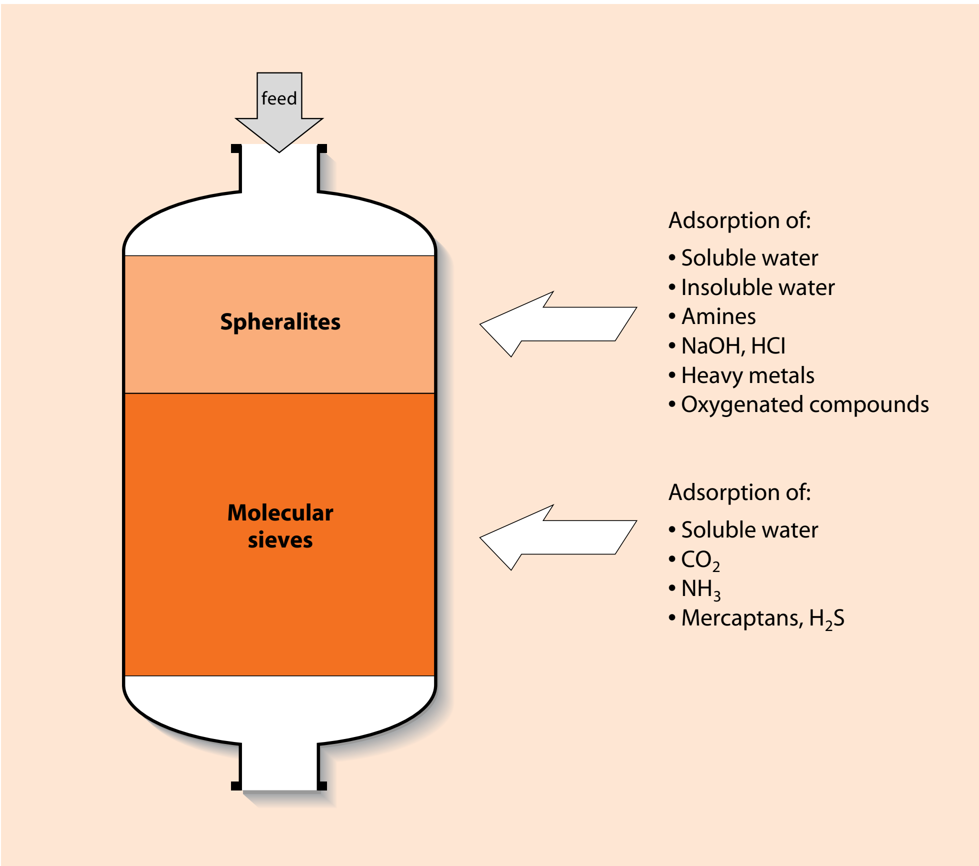
Molecular sieves are excellent adsorbents for soluble water. Insoluble (condensed) water though destroys the bond between the binder and zeolite, causing the zeolite and clay to fall apart into micro particles, creating major pressure drop problems. Also, during regeneration condensation takes place at the cold section of the reactor. Spheralites adsorb condensed water while keeping their mechanical properties, so Spheralites can act not only as a better adsorbent but also as guard bed at the top of the reactor.

The advantages of Spheralites in the upper section of the reactor are:

- Higher static adsorption capacity
- Promotion of catalytic reactions, such as COS hydrolysis and chloride removal
- Adsorption of chemical species such as amines and heavy metals.

Application of a top layer of Spheralites will prevent aging of the adsorbent.

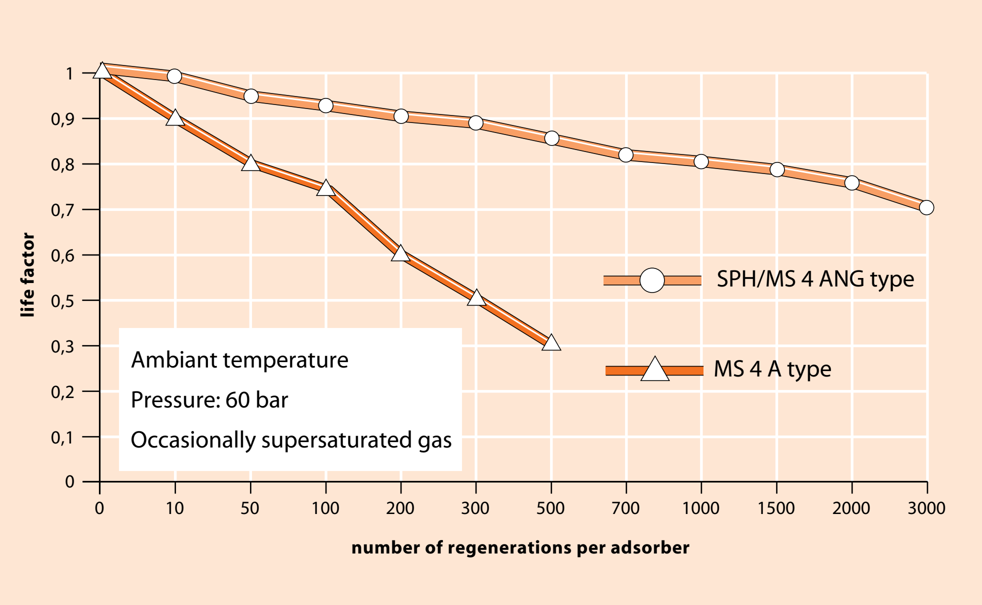
Combinations of Spheralites and (several types of) molecular sieves can tackle almost any adsorption problem.



(Fig.6)

Applications of the Multibed™ Technology

Below industrial results are presented in the case of natural gas drying with MS4A molecular sieves alone or in combination with spheralites.



(Fig.7)

Life factor vs number of regenerations for SPH/MS4ANG vs MS4 in natural gas drying.

The results of the Multibed™ technology are:

- **Improved adsorption capacity**
- **Improved purification capability**
- **Improved lifetime of the adsorbent.**

Packaging

At its fully ISO-9001 certified facilities, Axens can supply both alumina specialty and molecular sieve products either in metal drums, fiber drums, big bags or in bulk. Every lot is regularly and methodically sampled and analyzed at the laboratory with the latest and most advanced analytical equipment to ensure constant product quality.

Application List

REFINING

SERVICE / BASIC ADSORBENT	ALUMINA	MS 3A	MS 4A	MS 5A	MS 13X	SPECIAL	
CATALYTIC REFORMING							
Naphtha drying			■				*Multibed™*
Naphtha sweetening					■		*Multibed™*
Hydrogen recycle treatment						*MS 4A*	*Multibed™*
Regeneration catalyst gas treatment	■					*MS 4A*	*Multibed™*
Produced hydrogen gas treatment	■					*SAS 857*	
ISOMERIZATION							
Feedstock drying	■		■				*Multibed™*
Feedstock sweetening					■		*Multibed™*
Hydrogen make-up drying	■		■				*Multibed™*
Hydrogen purification	■			■			*Multibed™*
HYDROTREATMENT							
Hydrogen purification	■			■			*Multibed™*
HF ALKYLATION							
Feedstock drying	■	■	■				*Multibed™*
Defluorination of recycle product	*AA 2-5 P*			*AA 2-5 P*			
STEAM REFORMING							
Hydrogen purification	■			■			*Multibed™*
ETHYLENE-BENZENE ALKYLATION							
BF_3 removal	■						
Benzene drying			■				
Ethylene drying	■	■					
AROMATICS							
Benzene drying			■				*Multibed™*
Toluene drying			■				*Multibed™*
Xylene drying			■				
Cyclohexane drying	■		■				
FINISHING							
Propane drying	■		■				*Multibed™*
Propane sweetening				■	■		*Multibed™*
Butane drying	■		■				*Multibed™*
Butane sweetening				■	■		*Multibed™*
Pentane drying	■		■				
Pentane sweetening					■		*Multibed™*
Hexane drying	■		■				*Multibed™*
Hexane sweetening	■		■				*Multibed™*
LPG drying	■		■				*Multibed™*
LPG sweetening				■	■		*Multibed™*
Kerosene drying			■				*Multibed™*
Jet fuel drying			■				*Multibed™*
Gas oil drying	■		■				*Multibed™*
Solvent drying	■		■				*Multibed™*
B.T.X. drying			■				*Multibed™*
SEPARATION							
Normal and isoparaffins separation				*MS 5A SP*			
Paraxylene recovery						■	

PETROCHEMICALS

SERVICE / BASIC ADSORBENT	ALUMINA	MS 3A	MS 4A	MS 5A	MS 13X	SPECIAL	
STEAM CRACKING							
Cracked gas drying	■	■				*Multibed™*	
Cracked liquid drying		■				*Multibed™*	
C_2 cut drying	■	■				*Multibed™*	
C_3 cut drying	■	■				*Multibed™*	
Monomer over-drying and purification	■					*SAS 351*	*Multibed™*
Hydrogen drying	■	■	■				*Multibed™*
CO_2 removal			■	■	■		
Propylene drying	■	■					*Multibed™*
Butadiene drying		■					*Multibed™*
Other olefins drying		■					*Multibed™*
Other diolefins drying		■					*Multibed™*
SYNTHETIC RUBBER							
Methyl chloride drying	■					*MS 4A*	*Multibed™*
Propylene drying		■					*Multibed™*
POLYMERIZATION							
Feedstock drying	■	■					*Multibed™*
Feedstock purification	■	■				*SAS 820*	*Multibed™*
Polymers purification	■					*SAS 351*	*Multibed™*
Solvent drying	■	■					*Multibed™*
Styrene-TBC removal	■					*SAS 830*	*Multibed™*
Butadiene-TBC removal	■					*SAS 830*	*Multibed™*
LAB PRODUCTION							
Benzene drying			■				
HF removal from recycle paraffins	■						
Polynuclear aromatics removal	■						
Paraffins drying			■				

CHEMICALS

SERVICE / BASIC ADSORBENT	ALUMINA	MS 3A	MS 4A	MS 5A	MS 13X	SPECIAL	
TEREPHTHALIC ACID							
Effluent gas treatment	■						
ACETIC ACID							
Process gas treatment	■		■		■		
Air separation plant	■				■		*Multibed™*
HYDROGEN PEROXYDE							
Recycle feed treatment	■					*SAS 351*	*Multibed™*
AMMONIA							
Synthesis gas drying and purification			■	■	■		
Purge gas treatment			■				
HYDROGEN UNIT							
Hydrogen recovery	■			■			*Multibed™*
Hydrogen purification	■			■			*Multibed™*
OTHERS							
Alcohol drying		■					
Chlorofluorohydrocarbons drying	■		■			*MS 4A*	
Chlorofluorohydrocarbons purification	■				■		
Solvent drying	■	■	■	■			
Solvent purification	■			■	■		

NATURAL GAS

SERVICE / BASIC ADSORBENT	ALUMINA	MS 3A	MS 4A	MS 5A	MS 13X	SPECIAL	
Natural gas drying	■	■	*MS 4A NG*	■			*Multibed™*
Natural gas sweetening				■	■		
Condensate drying	■		■	■			*Multibed™*
Condensate sweetening				■	■		
LPG drying	■	■	■				*Multibed™*
LPG sweetening				■	■		*Multibed™*
Propane drying	■		■				*Multibed™*
Propane sweetening				■	■		*Multibed™*
Butane drying	■		■				*Multibed™*
Butane sweetening				■	■		*Multibed™*
LNG drying	■		■	■			*Multibed™*
LNG sweetening				■	■		*Multibed™*
CO_2 removal from natural gas			■	■	■		
H_2S removal from natural gas				■	■		*Multibed™*

MISCELLANEOUS

SERVICE / BASIC ADSORBENT	ALUMINA	MS 3A	MS 4A	MS 5A	MS 13X	SPECIAL	
Instrument air	■		■				
Air before cryogenic processing	■				■		*Multibed™*
CO_2 drying	■		■				
Drying of CO_2 (breweries)	■		■				
Oxygen/Nitrogen separation				■			*Multibed™*
Nitrogen drying	■		■				
Argon drying	■		■				
Helium drying	■		■				
Hydrogen drying	■		■				
Hydrogen purification	■			■	■		*Multibed™*
Inert gas drying	■		■				
Blanket gas drying	■		■				
CO_2 removal from blanket gases			■	■	■		
Propellent drying/sweetening	■				■		

Axens
Procatalyse Catalysts & Adsorbents
89, Boulevard Franklin Roosevelt - BP 50802
92508 Rueil-Malmaison Cedex- France
Tél: + 33 (0) 1 47 14 21 00
Fax: + 33 (0) 1 47 51 87 95
www.axens.net

Axens North America, Inc.
Procatalyse Catalysts & Adsorbents
1800 St James Place, Suite 500
Houston, Texas 77056-4199 USA
Tel: + 1 (713) 840 1133
Fax: + 1 (713) 840 8375
www.axens.net

SEPTEMBRE 2002 / 2000 ex. CRÉATION ET RÉALISATION OT PRODUCTION

Axens is an international provider of technologies, catalysts and services to the hydrocarbon industries. We offer commercially proven products including processes, catalysts, adsorbents and equipment backed by nearly fifty years of R&D and industrial success. Our mission is to enhance customer performance.