Zeolites: Absorbents,Adsorbents

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By

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Our Mission:
"To utilize innovative science and technology to create advanced zeolite products and applications."

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Abstract

Utilization of the unique properties of natural zeolites has advanced beyond the usual crushed and screened granules to specialty absorbents and adsorbents. The complex physio-chemical properties of natural zeolites, once understood, can be manipulated to perform as selective absorbents and adsorbents. All zeolites are molecular sieves which, depending on their internal structure, can selectively adsorb molecules according to their size and shape. Zeolites exhibit a high degree of hydration, a state producing a stable low density and a large void volume crystal structure. Utilization of innovative science and technology is creating advanced zeolite absorbents and adsorbents.

Introduction

It is important in the discussion of natural zeolites as absorbents and adsorbents, that the terminologies used be clearly understood.

The term zeolite refers to a group of hydrated aluminosilicates of the alkali or alkaline earth metals, which are predominately sodium, calcium, potassium and magnesium. Zeolites have three-dimensional crystalline frameworks of tetrahedral silica or alumina anions strongly bonded at all corners. The zeolite structures contain (-Si-O-Al-) linkages that form surface pores of uniform diameter and enclose regular internal cavities and channel ways of specific shapes and pore sizes of about 2 to 10 angstroms. Within the cavities are water molecules and the metal cations. The water molecules can be reversibly driven off and the cations, which are bonded loosely, can be ion exchange.

The term zeolite refers to natural zeolites. Forty zeolites have been identified, as well as a large number of compositional variants, all of which were named from the locations where they were first found or after early scientists who discovered them. Synthetic zeolites number in the hundreds with no systematic naming system.

Physio-Chemical Properties of Zeolites as Absorbents and Adsorbents

Zeolites share, to varying degrees depending on genesis and purity, the following characteristics.

1. Low density with significant porosity and permeability.

2. Large molecular void volume and channel ways in the dehydrated crystal; large surface area.

3. A high degree of hydration.

4. Stability of the crystal structure when dehydrated.

5. Significant physical strength in all size ranges.

6. Cation exchange properties and catalytic properties.

7. Ability to absorb and adsorb.

8. All zeolites have molecular sieves properties that are a function of the specific zeolite species.

Molecular sieves are materials that can selectively adsorb molecules on the basis of the molecules electrical charge and size. All natural zeolites are molecular sieves.

Activated clays and carbon, as well as alumina powder and silica gels, are also molecular sieves.

Definitions for Absorption, Adsorption, Sorbents, Sorbates Diffusion and Molecular Sieves

Different industry segments tend to develop their own meanings for the definition and terminologies they use to explain, in simple terms, their products and services. For the purposes of clarity the following definitions are used to define the reactions presented here.

Absorption: to take up or drink-in, as a sponge imbibes water. The process of assimilation of molecules into the structure of a solid. One substance taken into the body of another substance.

Adsorption: a physical separation process occurring when liquids, gases, colloids, and suspended matter adhere to the surfaces of any internal pores of a medium.

Sorbent: the term “sorb” is used in water processing when the distinction is not clear as to whether the phenomenon is either absorption or adsorption or a combinations of these processes. The term also refers to the selective adsorption of cations within a sorbent, based on physical dimensions and charge distribution in molecular sieving.

Sorbates: are the materials either solids, liquids or gasses that are absorbed or adsorbed by the zeolite.

Diffusion: is the migration of sorbate within the zeolite crystal and affects molecular sieving and selective adsorption, as well as desiccation. Diffusion in zeolites is very complicated and difficult to predict. Often what does happen, shouldn’t, and what shouldn’t happen, does. Diffusivity is determined by direct measurement. Some of the variables that influence diffusion rates are zeolite lattice defects, channel geometry, impurities, structural changes by penetrants or physical and chemical treatments. An important element of the functionality of diffusion in any given application is the time of reaction. The time of reaction is influenced by temperature, pressure, and concentration of the sorbate, as well as volume changes from liquid sorbate to vapour phase sorbate. Direct measurements of time of mass transport should be obtained by direct measurement, not modeling.

Pore Volume: The presence and availability of large volumes of internal space is a distinguishing and exceptional feature of zeolites. The inherent variables of species, purity, micropore accessibility the functional data must be obtained by direct measurement. The effects of temperature, time and pressure on any given sorbents size and shape, as well as the size, shape, number and location of the cations affect performance.

Markets for Absorbents and Adsorbents

For the past two decades zeolites have been used as an absorbent in non-technically demanding, non-regenerative applications. These zeolite uses as industrial absorbents, including animal bedding, horticultural applications, animal feeds, anticaking agents, and consumer odour control products are, for the most part, simply crushed, screened granular and powdered zeolites.

Most of the development for absorbents and adsorbents has been, and continues to be, in the synthesis of performance specific synthetic zeolite products produced by chemical companies.

However, in the past decade zeolite producers have begun to produce functional products with specific physio-chemical properties matched to the application. These new innovative applications range in diversity from new lightweight cementing systems for oil and gas completions, to new modified zeolite adsorbents for removing metals or organics from water. Zeolite gas treatment systems, pressure swing adsorption systems, odour control systems, and other specialty application systems are under development.

The largest value applications for zeolites and synthetic zeolites are as inorganic adsorbents, especially for environmental applications, industrial gas production and specialty chemicals.

Applications

Synthetic zeolites account for approximately 85% of the value of the inorganic microporous adsorbent market in 2001. Activated aluminas, silica gels, specialty clays and miscellaneous materials account for the balance. The market can be broadly segregated into regenerative and non-regenerative applications.

Non-regenerative markets

1. Desiccating, thermo pane windows, refrigerants, radioisotope removal and storage, odour control, NH_4+ removal.

Regenerative markets

Separations based on molecular sieving or separations based on ionic selectivity.

1. Gas phase bulk separation - adsorbents (Nitrogen-oxygen, oxygen-nitrogen, CO, methane, CO_2, N_2).

2. Gas purification - adsorbents (NOX/ N_2/ SO_2/organics/ vent streams/ cell-gas effluent).

3. Liquid bulk separation - adsorbent concentration approximately 10% weight or higher in the feed (fructose/glucose, aromatics, normal paraffins /iso-paraffins).

4. Liquid purification - adsorbent concentrations less than 3 weight % in the feed (sulphur compounds, water/organics).

Discussion

The “one size fits all mentality” that has plagued the zeolite industry in the past is rapidly disappearing as producers create new products and systems to solve specific problems for a wide range of industrial applications.

A systematic and detailed examination of the target zeolite to determine an accurate characterization of both the zeolite and related microporous materials is critical to successful utilization. This is accomplished using qualitative and quantitative chemical analysis, XRD, SEM, and particle size analysis. Techniques for the determination of surface area, ion exchange and ion-trapping capacities including rates, TGA/DTA are utilized.

Processing and treatment of the zeolite ore is equally important for utilization in new technically demanding systems and applications. At the processing facilities the particle size curves, as well the actual particle shape is critical to performance of the zeolite. The molecular pore water must, as well as any modification, peptizing or treatment must be precisely controlled.

Until recently the focus of zeolite development has been on sedimentary zeolite deposits containing predominantly clinoptilolite. The deposits are substantive in size and are available in western North America. A few of these deposits have the necessary characteristics to meet the criteria for value added applications as specialty adsorbents. A deposit of the chabazite zeolite, in Arizona, has been subject to intensive research and development resulting in the creation of a number of adsorbent applications, which are currently being introduced and marketed.

Other Zeolite Sources

C2C has been conducting exploration, zeolite extraction process research, as well as product research and development on “high purity zeolites” contained within volcanic flow rocks since 1993.

Large deposits have been located in Nova Scotia, Canada, where zeolite occurrences have been known for over 100 years. Nova Scotia is the type locality for Mordenite. In 2001 C_2C located a significant occurrence of zeolite contained in volcanic flow rocks in British Columbia.

An effective process has been developed which enables the production of zeolite with purities in excess of 96%. The identified zeolites having the greatest economic potential in these deposits for use as adsorbents are; Chabazite, Mordenite, Stilbite and Thomsonite. These zeolites will be produced when the product development work can create sustainable demand.

Conclusions

The use of zeolite as simple absorbents is historic, requiring very little in the way of processing or preparation. Zeolites are sold as absorbents but function as both an absorbent and adsorbent, as in the case of animal bedding and barn deodorizers. Here the zeolite absorbs liquids and adsorbs the ammonia produced by microbial activity on the liquids. A similar set of circumstances occurs with zeolite industrial absorbents or zeolite encapsulation of hazardous waste, such as treating inverted drilling wastes containing petroleum products with a high saline content.

The use of zeolites as inorganic adsorbents in environmental applications is increasing annually.

Significant expansion of the use of zeolites as adsorbents in gas separation and treatment systems will occur within the next five years.

A number of innovative applications and specialty systems, utilizing zeolite, will be introduced within the next one to four years.

The driver for this increased usage is the current disciplined approach to zeolite research and development, combined with additional zeolite species becoming available. Zeolites have some physio-chemical advantages over their synthetic counter parts, or analogs, besides a cost of production advantage. Current product research and development for these elite minerals is focusing on those advantages such as crystal strength and crystal size.

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