

CHAPTER II

BACKGROUND AND LITERATURE SURVEY

This chapter starts with some information on natural gas dehydration. Then, details of solid desiccant properties and their applications are discussed. It is followed by details of zeolites and clinoptilolite. Previous works related to the applications of clinoptilolite are also concluded comprehensively in this chapter.

2.1 Natural Gas Dehydration

Reservoir fluids flowing to the surface during production operations normally contain water. Water vapor is probably the most common undesirable impurity found in untreated natural gas. Moreover, normal line flowing conditions, whether in gathering systems or transmission lines, reach the hydrate forming temperature. Even in areas where line temperatures will not reach the hydrate range, temperature variations lead to water condensation. Exactly, natural gas transported through common carrier pipelines must meet a moisture specification of 7 pounds of water per million standard cubic feet of natural gas. The principal reasons for the removal of water vapor from natural gas for long-distance transmission include the following:

1. Liquid water and natural gas can form solid, ice-like hydrates that plug equipment.
2. Natural gas containing liquid water is corrosive, particularly if it also contains CO_2 or H_2S .
3. Water vapor in natural gas may condense in pipelines potentially causing slugging flow conditions.
4. Water vapor increases the volume and decreases the heating value of natural gas; this leads to reduced line capacity.

Four important methods are employed for the dehydration of natural gas: compression, refrigeration, treatment with drying substances or absorption, and adsorption.

A plant for water removal by compression consists of a natural gas compressor, followed by a cooling system to remove the water vapor by condensation. Unless the cooling process reduces the temperature to the lowest value that the gas will encounter at the prevailing pressure, cooling does not prevent further condensation of water. For the refrigeration, passing dehydrated gas over the refrigerated coils is more costly than the others; however, where exhaust steam is available to operate the refrigeration cycle, refrigeration charges can be reduced. In the absorption, the water vapor is removed from natural gas by intimate contact with liquid desiccant. Glycols are used most widely for this purpose because of their high affinity for water, low cost, chemical stability, low foaming, and low solvent action for natural gas. For the adsorption process, the water vapor from the natural gas is concentrated and held at the surface of solid desiccants by forces thought to be caused by residual valency. For water dew points in the range of -90 to -100°C , molecular sieves are used in many plants. Other solid desiccants are activated alumina and silica gel.

At present, adsorption process is the most widely used for the natural gas dehydration because it can remove practically all water from natural gas as low as 1 ppm and there are various choices of adsorbents to be used (Ruthven, 1984).

2.2 Solid Desiccants

A solid desiccant is simply an adsorbent, which has a high affinity and capacity for adsorption of water so that it can be used for selective adsorption of water from a gas stream. The main requirements for an efficient desiccant

are a highly polar surface and a high specific surface area (small pores). The most widely used desiccants are silica gel, activated alumina, and zeolites. The equilibrium adsorption isotherms for moisture on these materials have characteristically different shapes making them suitable for different applications (Perason and Grant, 1992).

Zeolites have high affinity and high capacity of water at low partial pressures, shown by the nearly rectangular form of the isotherm. This makes them useful desiccants where a very low humidity or dew point is required (Perason and Grant, 1992). *Zeolite 3A* excludes most molecules except water. It is used for natural gas dehydration, cracked gas drying, olefins drying, and ethanol drying. It is usually made by ion exchanging potassium onto a *Type 4A* in place of sodium. *Zeolite 4A* or sodium form of the crystal *Type A* is an inexpensive adsorbent usually used for drying. Further processed forms can be used for carbon dioxide removal. The major disadvantage of zeolite desiccants is that a high temperature is required for regeneration ($>300^{\circ}\text{C}$), which makes their use uneconomic when only a moderately low dew point is required.

Compared to zeolites, the initial slope of the isotherm of alumina is not as steep as that of a zeolite, indicating a lower moisture affinity at low partial pressure, but the capacity at high humidities is often higher than that of a zeolitic adsorbent. Regeneration temperatures of alumina are typically in the $250\text{-}350^{\circ}\text{C}$ range. Alumina adsorbents are more robust than zeolites and less sensitive to deactivation by organic, but they are generally less suitable than the zeolites where very low humidity is the primary requirement (Perason and Grant, 1992).

For silica gel, its isotherm is more nearly linear over a wide range of partial pressure, although the affinity for moisture is lower than that of either alumina or zeolites. However, a regeneration temperature is as low as 120°C , making silica gel the most suitable candidate for pressure swing driers,

desiccant cooling systems, and other applications where low grade heat is used for regeneration of the adsorbent (Perason and Grant, 1992).

Recently, a new solid desiccant $AlPO_4-5$ was studied. The zeolite, a member of the aluminophosphate molecular sieve family, has a structure comprising alternating tetrahedra of Al and P linked together to form a microporous structure with unidimensional 4-, 6-, and 12-membered ring channels. Unlike other zeolites, $AlPO_4-5$ has a neutral framework with mild hydrophilicity. The water sorption isotherm over $AlPO_4-5$ was studied and found that low sorption capacity in the initial region followed by a steep rise in sorption was observed. The typical water sorption behavior observed in $AlPO_4-5$ is related to its structural characteristics and results from pore filling of the six-membered ring channels followed by the capillary condensation in the 12-membered ring channels (Newalkar *et al.*, 1998).

2.3 Zeolite

Zeolites were first recognized as a new type of mineral in 1756 by a Swedish mineralogist, Cronstedt. They were considered to occur typically as minor constituents in basaltic and volcanic rocks (Hernandez *et al.*, 2000a). Nowadays, more than 200 synthetic zeolite types and 50 natural zeolites are known. Zeolites have been intensively studied in the first half of the 20th century although attention has concentrated mainly on synthetic zeolites and it is only in recent years that natural zeolites have started gaining interest.

As shown in Figure 2.1, a zeolite is an aluminosilicate with a skeletal structure, containing void occupied by ions and molecules of water having a considerable freedom of movement that leads to ion exchange and reversible dehydration. The primary building block of the zeolite framework is the tetrahedron, four atoms of oxygen at the vertices. Each oxygen atom is shared between two tetrahedra. Hence, the tetrahedra form a continuous framework.

Substitution of Si^{4+} by Al^{3+} defines the negative charge of the framework, which is compensated by monovalent or divalent cations located together with water molecules in structural channels. Cations in the channels are substituted easily, unlike *Si* and *Al*, which are not exchanged under ordinary conditions. The water molecules can serve as bridges between exchangeable cation. Perhaps the most typical situation involves a cation bound to the channel wall on one site and to a water molecule on the other (Tsitsishvili *et al.*, 1992). It is convenient to express the zeolite composition by the so-called oxide formulas of the type $\text{M}_{2/n}\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$ where x is 2 or greater, M is the charge balancing cation, n is the cation valence, and y represents the moles of water contained in the zeolitic voids.

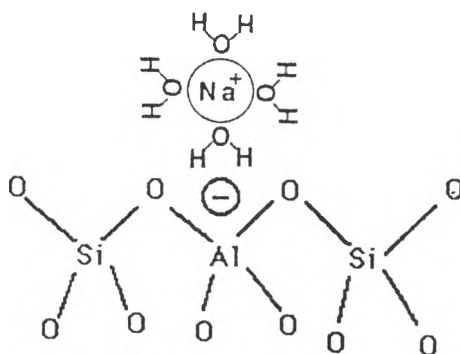


Figure 2.1 Zeolite topology.

2.4 Clinoptilolite

2.4.1 Clinoptilolite Structure

Of the about 50 known zeolite minerals, clinoptilolite occurs in sufficient quantity and purity to allow their use as commercial products and less expensive than synthetic zeolite. Clinoptilolite is a member of the heulandite group of natural zeolites and is isostructural with the zeolite

heulandite. The unit cell is monoclinic *C*-centered with *Na*, *K*, *Ca*, and *Mg* as the most common charge-balancing cation. *Si/Al* ratio is usually in the range of 4.5 to 6. The structure of clinoptilolite, as shown in Figures 2.2 and 2.3, consists of a two-dimensional system of three types of channels: two parallel channels, *A* (10-member ring) and *B* (8-member ring), perpendicularly intersected by channels *C* (8-member ring). The dimensions of channels *A*, *B*, and *C* are $4.4 \times 7.2^\circ \text{A}$, $4.1 \times 4.7^\circ \text{A}$, and $4.0 \times 5.5^\circ \text{A}$, respectively. Gas or vapor molecules can only move in plane and penetrate the crystalline structure through a series of intersecting channels, each layer of channels separated by a dense gas-impermeable layer of tetrahedra.

The selectivity, diffusion rate of uptake gases, and adsorption capacity of clinoptilolite are influenced by the type, nature, polarizing power, number, and location of the charge-balancing cations residing in the *A*, *B*, and *C* channels (Ackley and Yang, 1991a,b; Ackley *et al.*, 1992; Tsitsihvili *et al.*, 1992; and Arcoya *et al.*, 1996).

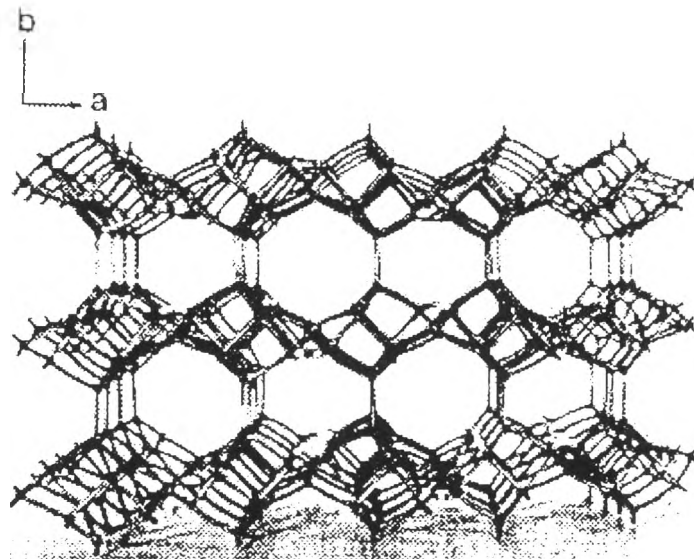


Figure 2.2 Clinoptilolite structure.

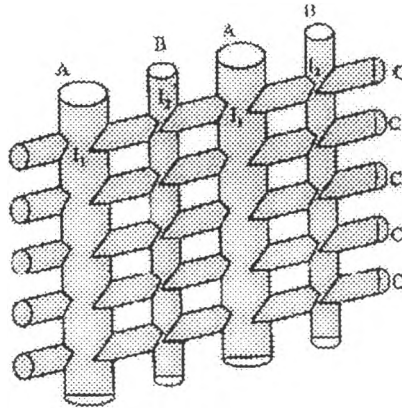


Figure 2.3 Clinoptilolite structure showing channels *A*, *B*, and *C* and intersection I_1 and I_2 .

2.4.2 Properties and Applications of Clinoptilolite

Clinoptilolite has ion exchange and gas adsorption properties. Its applications include pollution control, energy conservation, agriculture and aquaculture, mining and metallurgy. The adsorption properties of clinoptilolite and its ion exchanged derivatives have been investigated for the following applications: natural gas purification and drying (removal of CO_2 , H_2S , N_2 , and H_2O), air separation (both O_2 and N_2 production), flue gas cleanup (SO_2 removal), and in coal gasification (NH_3 removal) (Tsitsishvili *et al.*, 1992; Ackley *et al.*, 1992).

2.4.2.1 *Ion Exchange Properties*

The ion exchange capacity is basically a function of the degree of substitution of aluminium for silicon in the framework structure. The greater the substitution, the greater the charge deficiency, and the greater the number of cations required for electrical neutrality. In practice, however, the ion exchange capacity depends on other factors, notably the nature of the cation species (size, charge, etc.), the temperature, the concentration of the

cation species in solution and the structural characteristics of the zeolite (Bernal and Lopez-Real, 1993).

The clinoptilolite-rich tuffs of Bigadic are in the form of coarse-grained glassy ash tuffs at the bottom and fine-grained glassy dust tuffs on the top. Samples taken from different locations in the coarse and fine-grained zones were tested for their NH_4 -exchange capacities. NaCl treatment improves the capacities of most samples, but acid treatment followed by conversion to *Na*-form is significantly beneficial in increasing the capacities for only group of samples from the coarse grain zone. If not followed by conversion to *Na*-form, only very dilute (0.01 N) acid treatment can improve the capacities to an extent, for some sample from the same zone (Ballmoos *et al.*, 1992)

Effects of treatment and conditioning on the removals of *Pb* and *Cd* from effluent wastewater were studied with clinoptilolite. The as-received clinoptilolite contained a complement of exchangeable *K*, *Ca*, and *Na* ions but exposing them to concentrated NaCl solutions converted them to a homoionic state in the *Na* form, which improved significantly their exchange capacity. The particle size had no effect on the exchange suggesting that the mechanism is not surface controlled. NaOH-treated clinoptilolite performed best with optimum *Pb* and *Cd* exchange capacities exceeding 200 mg/g. Metal removal efficiencies exceeding 99% were achieved; therefore, effluent contaminated with high levels of *Pb* and *Cd* can be treated by this modified clinoptilolite (Kesraoul-Oukl *et al.*, 1993).

Clinoptilolite was treated in the same procedure, but its selectivity and removal performance were focused on the treatment of effluents contaminated mixed heavy metals (*Pb*, *Cd*, *Cu*, *Zn*, *Cr*, *Ni*, and *Co*). The pH has an effect on the metal removal as it can influence both the characteristics of the exchanging ions and the zeolite itself. The removal

mechanism was controlled by ion exchange and precipitation was proven negligible (Ouki and Kavannagh, 1999).

2.4.2.2 Adsorption Properties

The use of natural zeolites as gas adsorbents has a great commercial interest due to their availability and low cost. Molecular sieve properties of clinoptilolite have been investigated for molecules of different dimensions. Since the nature of the counterions can significantly affect these properties, ion exchange with protons and different cations has been frequently used as a method to enhance the adsorptive capacity of clinoptilolite toward different molecules.

Clinoptilolite modified by ion exchange method to the ammonium form and then treated with a dilute solution of a strong acid has high capacity for acid gases and life than unmodified clinoptilolite (Kiovsy and Koradia, 1977).

Natural clinoptilolites and its modified forms of *Li*, *Na*, *K*, *Ca*, *Ba*, *Sr*, *Zn*, *Cu*, *Co*, *Fe*, *Mn*, and *Mg* were useful for the removal of traces of carbon dioxide, water (Chao, 1990), and ammonia (Chao and Rastelli, 1991) from streams of hydrocarbons having kinetic diameters of not more than about 5°A. For *Mg*-clinoptilolite, it also selectively adsorbs and separates gases having molecular dimensions equal to or smaller than N₂ from other gases with molecules equal to or larger than CH₄ (Chao and Rastelli, 1990).

The adsorption of pure N₂ and CH₄ gases on natural Turkish clinoptilolite was studied. The pure-gas adsorption isotherms of N₂ and CH₄ reveal that this natural zeolite has higher capacities for CH₄. An increase in the operation temperature did not appear to reduce the adsorption capacity drastically (Predeseu *et al.*, 1995). Moreover, the adsorption of N₂ and CO was studied again on the Turkish clinoptilolite at near ambient

conditions. The result showed that clinoptilolite was a particularly promising sorbent for the separation of CO and N₂ (Triebe and Tezel, 1995a).

Clinoptilolite from Castilla (Cuba), activated at 673 K, is an adequate molecular sieve to separate N₂ and O₂ from air, and less expensive than the synthetic zeolites. Ion exchange treatments with NH₄⁺, Na⁺, K⁺, Cs²⁺, Mg²⁺, Ca²⁺ and, particularly Ba²⁺, substantially modify its adsorptive capability and enables a suitable separation of gases such as N₂, O₂, CO and CH₄. The nature polarizing power and location of the cations in the framework play an important role on the adsorption capacity of clinoptilolite towards O₂, N₂, CO, and CH₄ (Arcoya *et al.*, 1996).

Bigadic clinoptilolite and its *Na*-, *K*-, *Ca*-, and *H*-enriched forms were used to study the adsorption of H₂S and SO₂. Higher adsorption capacities were observed for SO₂, in agreement with its higher permanent dipole moment. There was also a larger increase in the amount of adsorbed SO₂ at higher pressure, arising from the stronger dipole-dipole interaction between SO₂ molecules. Channel blockage of the *Ca*-form resulted in not adsorbing SO₂ and very low capacities for H₂S. The highest capacities for both gases were obtained with the *H*-form, which was followed by the *Na*- and *K*-forms for SO₂, parallel to the decrease in the electronegativity and ionic potential and the increase in the polarizability of the cation. For H₂S adsorption, the *H*-form had the highest capacity followed by the *K*-form and the *Na*-form, respectively. The *Na*-form yielded very low adsorption capacities resulted from the initial dissociative adsorption of H₂S on certain *Na* sites, the formation of *SH* and *OH* species and the channel blockage. (Sirkecioglu *et al.*, 1995).

Acid treatment is one technique used to improve or modify adsorbent, via the mechanisms of decationization and dealumination, and also by dissolving any amorphous silica blocking the channels in the structure. The cation blocking effect in this clinoptilolite is thus eliminated or

lowered by the acid treatment, i.e. substituting large ions by protons. Eventually, a continued acid treatment also lowers further cation exchange by leaching Al^{3+} from framework positions while introducing H^+ into the few remaining cation locations (Hernandez *et al.*, 2000b).

Hydrochloric acid, sulfuric acid and phosphoric acid were used to treat clinoptilolite. Treating with hydrochloric acid, the adsorbed amount increased to 5-fold for N_2 , to 3-fold for C_6H_6 , but for CH_3OH no significant change was observed. As acid strength increased further, there were declines both in the adsorption capacity and crystallinity. The increase of adsorbed amount was caused by the rearrangement of the pore entrance and cation exchange (Chon and Seo, 1976).

Clinoptilolite treated by orthophosphoric acid affected extra-framework and impurity materials. *Fe* was mostly extracted from the extra-framework octahedral sites. *Fe* and *Al* tetrahedral framework were less affected, preserving the zeolite crystallinity. Acidity decreased, because the Bronsted sites were partially destroyed by the dealumination, and was rebuilt by the creation of moderately acidic *POH* groups (Pozas *et al.*, 1996).

The skeletal isomerization of n-butene to isobutene of clinoptilolite was studied by treating the zeolite with various acid strengths, boric acid, phosphoric acid, and nitric acid. Among the treated samples, only those modified with boric acid showed an improved catalytic performance of skeletal isomerization in terms of activity and stability. The main effect of boric acid treatment was the selective increase in the number of acid sites of moderate strength required for efficient catalysts in skeletal isomerization without collapse of its framework. These acid sites of moderate strength were considered to be selective and stable reaction sites for skeletal isomerization of n-butenes (Lee *et al.*, 2000).

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Natural zeolite, in contrast to synthetic materials, has a limited crystallinity thus indicating a certain degree of contamination of the structure with other minerals or amorphous glassy material. The presence of cations or minerals blocking the pore channels of a zeolite and the limited extent of its crystalline structure drastically reduces its sorption activity by diminishing the microporous volume accessible to the adsorbate. Exactly, acid treatment of a high-silica natural clinoptilolite improves the N₂ adsorption (Hernandez *et al.*, 2000a).

In general, N₂ sorption isotherms of clinoptilolites gradually evolve from the *Type IV* isotherm (natural samples) to the *Type I* isotherm (modified samples). Nevertheless, the irreversible adsorption of N₂ at the pore entrances of clinoptilolite modified by acid treatment affects characteristics of its adsorption isotherm. In addition, the treatment also results in the hysteresis loop at the low N₂ pressure (Hernandez *et al.*, 2000b).