

Utilization of Zeolite 3A Adsorbent for the Measurement of Extremely Low Moisture Concentrations in Gaseous Flow Streams

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Abstract- In chemical process industries, a network of piping system holds gases in huge quantities and contains a low, moderate, and high concentrations of water moisture. The presence of moisture in these gas streams is highly undesired, particularly in the case of natural gas lines. At low temperatures water condenses in the pipelines and may be a reason for a number of technical problems. An adequate method for the gas dehydration is decided on the basis of moisture concentrations. The detection and quantification of the actual values of water vapour concentrations in gas streams is very important. Measurement of the low concentration of water vapors is very difficult. This work presents that one may determine an extremely low water vapour concentrations in a continuous flow system by placing a fixed mass of zeolite 3A molecular sieves. For example, an air gas mixture having a known dilute concentration of water vapours (5470 ppm) when passed over a zeolite 3A adsorbed 7.6 mmol kg^{-1} of water vapours.

Keywords- : Adsorption; Breakthrough curve; Zeolite 3A.

I. INTRODUCTION

Petrochemical and pharmaceutical industries are well-known for having water moistures in gaseous flow streams. The presence of moisture has a substantial detrimental impact on the downstream processes [1]. Therefore, moisture content and other impurities including dirt particles are removed before transferring the gas into later sections of the plants. Dehydration process is carried out in dedicated units and is essential because water vapours causes corrosion, forms hydrates salts, and sometimes blocks the flow lines due to ice formation, particularly in the environments having extremely low temperatures. The detection of the low concentrations of moisture in gas streams is usually difficult for many process industries. Moisture presence, even in ppm amounts is sometime damaging consequences and may result in

the pipe explosions [2,3]. Different dehydration processes, for example (1) the gas is compressed to a greater pressure followed by a rapid cooling, (2) or simply cooling of gas below a dew point, (3) and absorption by a desiccant may be used to reduce the moisture concentrations [3,5, 6]. For example, the moisture of natural gas streams is reduced in many stages prior to its use in the petrochemical or domestic industries. In these type of the applications, concentration of water vapours is ideally reduced to a zero ppm levels [4,5]. In short, the most important parameter that determines the choice of the dehydration method is the water concentration level of the gas streams [5, 7].

Moisture detectors are usually installed with some gap along the pipe lines in order to maintain a safe and continuous flow process. These instrumental sensors are ceramics materials with complex electrical instrumentations. Adsorption/desorption of the water vapours from the ceramic sensors surface and in presence of charged plates system generates a defined signal to indicate the level of the moisture concentrations. Problem with most of these materials is that they catch false signals in presence of changed vapours. This work is an effort to highlight the selective adsorption property of zeolite 3A sieves to develop an earliest method to precisely measure the extremely low water concentration of the gas streams [8]. Zeolite 3A was chosen as an adsorbent because it has a strong hydrophilic nature, water holding capacity, and uniform pore size [9]. Moreover, Zeolite 3A only adsorbs water molecules, i.e. adsorbent has no interaction with CO_2 and charged vapours [10 - 13]. Barrer and Milton were the pioneer in studying the synthetically prepared zeolites (1948 to 1955) [14, 15]. At Present, the international association of zeolites (IZA) mostly regulates and publish the data of newly determined zeolite structures and properties. From the elemental prospective, zeolite consist of aluminium, silicon, oxygen, and several ex-framework cations [10]. The presence of aluminium in the structural framework creates negative charges and therefore a

holding sites of the water molecules [16]. Ideally, AlO_4 and SiO_4 tetrahedra combine together and forms a well-organized three dimensional macro molecular structures. These aluminosilicate structural arrangements may result into thin (0.4-0.5 nm), intermediate (0.5-0.6 nm), and wide (0.7-0.75 nm) pore size openings [12, 17].

Generally, zeolites are preferred over other water sorbents porous materials such as organic polymers, clays, and metallic organic frameworks [18]. The reason for this preference is for having stable framework, thermal, and chemical structure [19]. Moreover, the bonding of zeolites with the gaseous or liquid species are very selective [20]. The ex-framework sites of the zeolites can be exchanged with the other cations species and may alter the adsorption capacity [21]. In this short paper the authors studied the applicability of Zeolite 3A as a hygroscopic material to adsorb a fixed concentration of water vapours in a continuous air streams having a few ppm of water moisture.

I. METHODOLOGY

2.1. Experimental Setup

The experimental setup for adsorption/ desorption of water vapours consists of a cylindrical furnace, temperature control unit, humidifier, flow meter, adsorption column with valve at both ends, and several gas flow lines as shown in Fig 1. The adsorption column and flow lines were of quarter inch and made up of stainless steel. Flow lines were split in to two separate paths, i.e. the first line passed through a humidifier and then entered into adsorption column, whereas the other line directly opens into the adsorption column. The first channel was used to introduce moisture in a carrier gas (dry air), while the other line was installed for the purpose of adsorbent activation. The adsorption column was uniformly packed with zeolite 3A sample. This adsorption bed having a mass of 1.746×10^{-4} kg was kept in the middle of the adsorption column. The flow rate (Q) of gaseous stream was maintained at about 0.2 Lmin^{-1} . The adsorbent was activated by heating in presence of a lower flow rate of air, while the temperature was increased with a ramp rate of 2°Cmin^{-1} to a temperature of 300°C and the system was kept under this condition for about 24 hours. After that, the adsorption bed was cooled down to a room temperature. For each adsorption experiment, dry air first passes through a humidifier bottle placed inside the container having moderate sized ice cubes (0°C). The air leaving the humidifier carried 5470 ppm of water vapours. After a fixed time, this humidified air saturates the adsorbent bed. Finally, the equilibrium adsorption capacity was determined by analyzing the breakthrough curves.

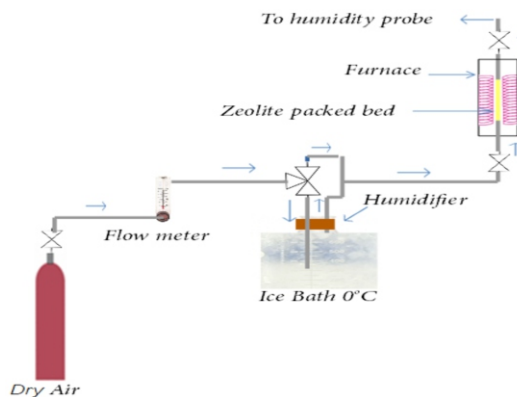


Fig.1 Representation diagram of experimental apparatus.

2.2. Theory/Calculation

The addition of a very low ppm of water vapours in dry air stream was achieved by passing the air through an aqueous solution. This aqueous solution was prepared by dissolving a 68 g of sodium chloride in 200 g of distilled water and left for 30 minutes and then cooled to 0°C , however the solution was still in a liquid phase. The non-volatile sodium chloride molecules occupy some portion of water surface and therefore displacing some of the volatile water molecules. Within the solution and on the surface, these water molecules retain their kinetic energy distributions, just like in its pure state, where the rate of collision at which molecules of water in vapor phase hits the surface of the solution and re-entered is also the same. However, due to presence of salt the dynamic equilibrium between liquid and vapor phases is perturbed in such a way that more molecules re-enter the solution rather than they leave as presented in Fig 2. This phenomenon leads to decrease in the vapour pressure of the solution. Also, by lowering the temperature more molecules in the vapor phase were forced to remain in the aqueous solution.

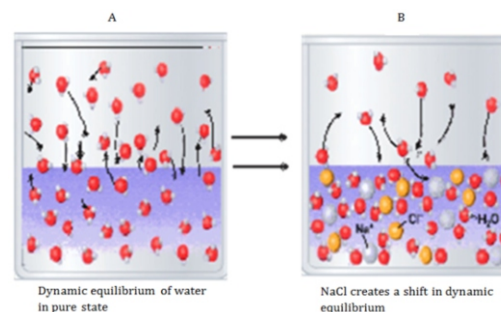


Fig. 2 Lowering of water vapor pressure.

The adsorption capacity of the zeolite 3 A was determined by solving the break through curve equation. The amount of total trapped moisture was calculated by the equation (Eq 1)

$$q = \frac{1}{m} \int_0^{t_b} [Q_{in}C_{in} - Q_{out}C_{out}] dt \quad (1)$$

Where m is molar mass (mol kg^{-1}), Q is the flow rate of gas (L min^{-1}), t_b is a break through time, and C is the concentration of moisture (mol/L).

III. RESULTS AND DISCUSSION

Air feed containing a 5470 ppm of water vapours was allowed to flow over a fixed bed column of zeolites in order to determine the breakthrough curve or the water adsorbing capacity. The kinetics of the adsorption, i.e. after a definite time period the diffusion of water vapours from the bulk of gas phase to the surface of adsorbent establishes an equilibrium between the moisture content and solid phase. This equilibrium defines the shape of the concentration profile curve. Within the early interval of the adsorption, the concentration of the water vapour in the effluent stream is zero. As the time passes, the bed gets saturated and the time t_b (breakthrough time) approaches. If the flow of moisture stream continues uninterrupted, the effluent stream regains its initial inlet concentration level, i.e. 5470 ppm.

Fig 3 shows the breakthrough curves over zeolite 3A and zeolite 4A. For Zeolite 3A, the traces of water vapor in the effluent stream were noticed within the first 50 minutes, whereas a complete breakthrough occurred in 110 minutes. When compared with the break through curve over Zeolite 4A adsorption bed, the slope of the curve over a zeolite 3A is relatively steep, showing that mass transfer and channeling effects are minimum. The potential reason for the variation of curve over zeolite 4A can be attributed to pore size or gas channeling. The quantity of moisture adsorbed till the saturation point over zeolite 3A was 7.6 mmol kg^{-1} .

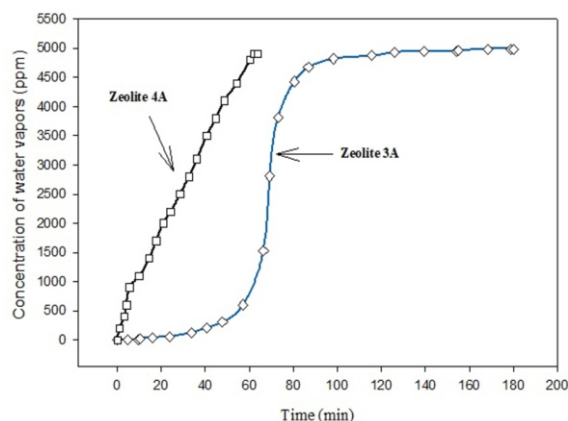


Fig 3 The water vapour breakthrough curve over zeolite 3A ($\diamond$) and zeolite 4A ($\square$) (carrier gas = Air, $Q = 0.2 \text{ L min}^{-1}$, Conc. (water) = 5470 ppm)

As discussed, gas stream channeling may be a cause for the steady slop of curve over zeolite 4A. Thus, considering the system in hand, the particle size of the

sample was kept at minimum, i.e. almost powder form was used for all adsorption experiments in order to minimize the channeling phenomena. Large size pellet size can easily introduce haphazardness in the bed packing, thus allowing channeling effects as shown in Fig 4.



Fig. 4 A representation of channelling in the adsorption bed

IV. CONCLUSION

Gas stream of many process industries are usually a mixture of different chemical species and also contains water moisture. The removal of moistures is needed for many reasons. The detection of a low concentrations of water vapours in a gas flow lines is usually very difficult, i.e. gaseous system consisting of changed vapours generates a similar signal output as it produces for the water molecules. Zeolite 3A adsorbs a fixed mass of water moisture. This zeolite property when combined with the instrumentations will be helpful to determine a real time data. The data presented in this work shows that the amount of water adsorbed over a $1.746 \times 10^{-4} \text{ kg}$ of sample of zeolite 3A was 7.6 mmol kg^{-1} .

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