

The feasibility of desorption on Zeolite-water pair using dry gas

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Abstract. The increase in temperature, reduction in partial pressure, reduction in concentration, purging with an inert fluid, and displacement with a more strongly adsorbing species are the basic things that occur in the practical method of desorption. In this study, dry gas at constant temperature and pressure was employed as the aid to reduce the partial pressure in the water desorption on the zeolite 13X. The objective of this study is to confirm the feasibility of desorption using dry gas experimentally and numerically. The implication of heat and mass transfers were numerically investigated to find the most influential. The results of numerical simulation agree with the experimental ones for the distribution of local temperature and average water adsorbed in the packed bed.

1. Introduction

Adsorption heat pump systems using zeolite-water pairs have been developed since long time ago [1]. Direct contact system between water as working fluid and zeolite as adsorbent has been proposed to develop the adsorption heat pump system for steam generation [2]. The reason for proposing this direct contact system was described in the previous study [2,3]. The possibility for steam generation using this system has been confirmed experimentally although it still could not reach the prediction/theoretical value. Steam generation is on the adsorption stage. For regeneration of saturated zeolite after adsorption process, inert gas is chosen to strip/release the water content which is believed in vapor/gas phase in the zeolite. From the experimental study before [1], inert gas such as dry nitrogen and dry air can regenerate zeolite for almost 80-90%. But there is problem in desorption study such as long time needed to release/remove water in the zeolite particle in the packed bed which means impractical to be applied in the industries. Long time needed for desorption accomplish means reaction rate occurs slowly.

Study about the solution to increase desorption rate was found in some report used microwave to shorten the time and also could decrease the energy level needed to remove water content in the zeolite [4,5]. Methods for regeneration of saturated zeolite have been investigated in various types [6]. General problem in desorption /regeneration process of zeolite is low reaction rate that may be because of high energy required to desorb water vapor from zeolite. Practical methods of desorption and regeneration including one, or more usually a combination, of the following such as increase in



the temperature, reduction in partial pressure, reduction in concentration, purging with an inert fluid, displacement with a more strongly adsorbing species, and change of chemical condition such as pH. As a variable for changing thermodynamic potential, a change in temperature is much more effective than a change in pressure. However, the final choice of regeneration method(s) depends upon technical and economic considerations. The most common methods are changes in temperature (thermal swing adsorption) and changes in pressure (pressure swing adsorption). The general advantages and disadvantages of each method together with some process examples.

The main objective of whole study is to regenerate steam from waste water in the industries such as petrochemical industries using the dry inert gas in medium/low level energy (noticed by the temperature degree). Because in the plant, there are plenty amount of gas at around 150 °C exhausted from the cracking furnace. It is wiser to use this gas for the regeneration of saturated zeolite after it producing the steam. In terms of the type of zeolite 13X is hydrophilic adsorbent, thermal swing is better method for desorption [7]. The purpose of this study is to find the best condition of desorption process of zeolite 13X to release the water vapor using dry gas stripping. Therefore the gas condition as the stripper was investigated experimentally and numerically.

2. RESEARCH METHODS

2.1 Experiment

Similar with the previous study [2], zeolite 13X was investigated in this study. Two different particle shape of 13X were examined. Initially, zeolite was calcined in furnace at 350 °C for 4.5 hours. Then the dry zeolite were put in a box at high humidity 98% until reached equilibrium condition to get saturated zeolite with water vapor. The mass fraction of water adsorbed in 13X at 25°C under atmospheric pressure is 0.271 kg-water/kg-dry zeolite as theoretical value. In the experiment, the amount of water adsorbed was also around 0.27 kg-water/kg-dry zeolite.

Figure 1 shows the schematic diagram of experimental apparatus. Saturated zeolite was packed in the reactor and kept at constant temperature. Water content in the zeolite particles at 110 °C at initial condition was 0.27 kg water/kg dry zeolite without free water. Free water was obtained from the difference between water concentration in the zeolite after experiment subtracted by the the maximum value of water can be adsorbed in the zeolite (for 13X was 0.27 kg water/kg dry zeolite). Dry N₂ at temperature 80 and 140 °C with various flow rates at 10, 30 and 50 L/min were then introduced to the reactor. The mass of water released was obtained by measuring the mass of water vapor in the air at outlet of the reactor.

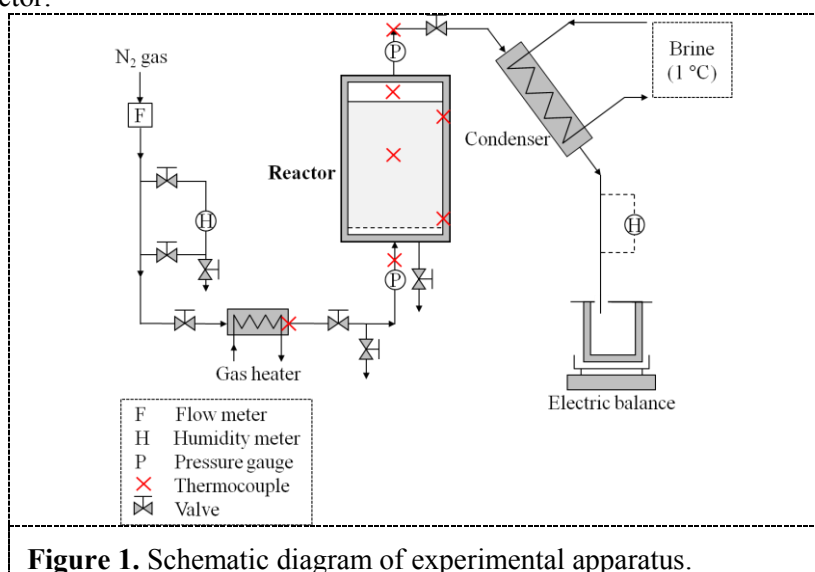


Figure 1. Schematic diagram of experimental apparatus.

2.2 Mathematical Model

Phenomenon during desorption using N_2 gas in packed bed was studied using a two-dimensional cylindrical model (r-z axes). Fig.2 shows scheme of module of the packed bed from the experiment that would be numerically calculated.

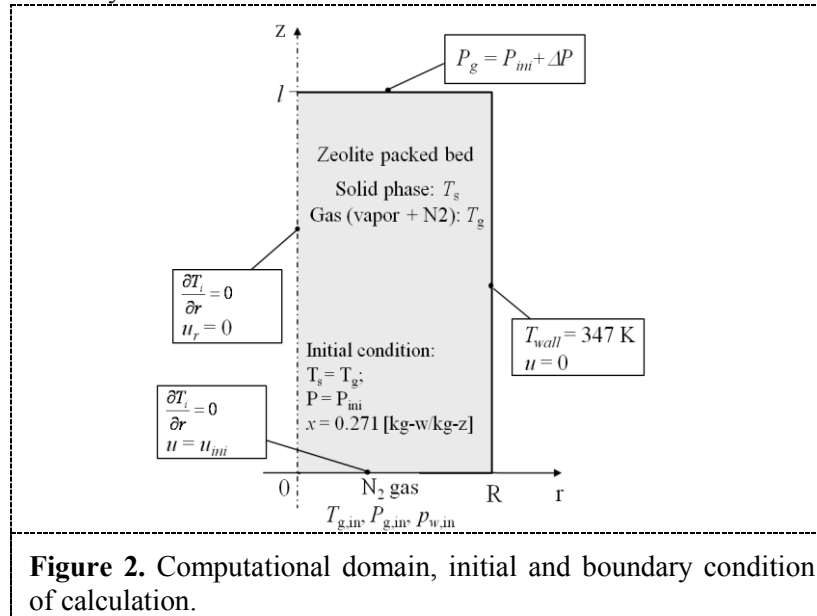


Figure 2. Computational domain, initial and boundary condition of calculation.

The main assumptions in the modeling are:

- All the zeolite particles have uniform properties such as geometry and size
- The gas velocity (including vapor) in the packed bed is determined using Darcy's equation
- The gaseous phase behaves as an ideal gas
- The particle is covered by laminar film, bounding the particle from the gas fluid.
- Macropore conducts the transportation of gas molecule from inside to the surface of particle.
- Molecules of water vapor are only adsorbed on the surface of zeolite crystal, therefore effect of micropore diffusion is not considered.

The governing equations of the studied system consist of energy balance of solid and gas (water vapor and N_2 gas) and mass balance in the solid related to the gas in the pores. Model equations of energy balance, mass balance, momentum, and kinetic model are shown in the following and the computational domain including initial and boundary conditions is shown in Fig. 3. The temperature of gas and solid is solved separately.

- Energy balance for solid phase (the zeolite):

$$(1 - \varepsilon_s) \rho_s C_{ps} \frac{\partial T_s}{\partial t} = (1 - \varepsilon_s) \nabla \cdot k_s \nabla T + (1 - \varepsilon_s) Q_0 \frac{dv}{dt} + S_{sg} h_{sg} (T_s - T_g) \quad (1)$$

- Energy balance for gas phase (N_2 and vapor):

$$\varepsilon_s \rho_g C_{pg} \frac{\partial T_g}{\partial t} + \rho_g C_{pg} u_g \nabla T = \varepsilon_s \nabla \cdot k_g \nabla T + S_{sg} h_{sg} (T_s - T_g) \quad (2)$$

- Mass balance for the zeolite:

$$(1 - \varepsilon_s) \frac{\partial \rho_s}{\partial t} = m \quad (3)$$

- Mass balance for gas phase:

$$\frac{\partial}{\partial t} \varepsilon_t \rho_g + \nabla \cdot (\rho_g u) = -m \quad (4)$$

where m is the desorption rate of water desorbed from zeolite which is defined as the following:

$$m = (1 - \varepsilon_t) \Delta \rho_s \frac{\partial v}{\partial t} \quad (5)$$

Gas diffusive velocity u is calculated using Darcy's equation as the momentum equation:

$$u = -\frac{K}{\mu} \nabla P \quad (6)$$

with K as the permeability calculating using Kozeny-Carman's:

$$K = \frac{1}{5} \frac{\varepsilon_t^3}{(1 - \varepsilon_t)^2} \frac{1}{S_p^2} \quad (7)$$

The specific surface area S_p depends on the particle shape is determined by $6/d_p$ and $4/d_p$, for spherical and cylindrical particles, respectively.

Reaction rate model is expressed as below:

$$\frac{\partial v}{\partial t} = k(v_{eq} - v) \quad (8)$$

where v is the reacted fraction defined from the water content in the zeolite based on thermal analysis (TG/DTA) measurement. Reacted fraction is obtained from:

$$v = \frac{x_0 - x}{x_0 - x_f} \quad (9)$$

Reaction rate controller k is defined using Linear Driving Force (LDF) model because diffusion on the surface (external film) of particle and macropores influence the desorption rate.

$$k = k_{LDF} \quad (10)$$

$$\frac{1}{k_{LDF}} = \frac{\wedge r_p}{3(1 - \varepsilon_b)k_f} + \frac{\wedge r_p^2}{15(1 - \varepsilon_b)\varepsilon_p D_p} \quad (11)$$

Therefore, the rate controller consists of effect of external film and macropores region, respectively. \wedge is partition ration that represent the fraction of water vapor as adsorbate that is exactly adsorbed in the zeolite particle, expressed as follow:

$$\wedge = \frac{\rho_b x}{\rho_g} \quad (12)$$

k_f as the mass transfer coefficient on the external film is defined using Wakao equation as:

$$k_f = \left(2.0 + 1.1 \text{Sc}^{1/3} \text{Re}^{0.6} \right) \frac{D_{AB}}{r_p} \quad (13)$$

The gas diffusivity is calculated assuming both Knudsen and molecular diffusion:

$$\frac{1}{D_p} = \tau_p \left(\frac{1}{D_K} + \frac{1}{D_{AB}} \right) \quad (14)$$

with

$$D_{AB} = 1.8583 \times 10^{-3} \sqrt{\frac{T^3}{MM_g}} \frac{1}{p \sigma^2 \Omega_D} \quad (15)$$

and

$$D_K = 4.85d_{pore}\sqrt{\frac{T}{MM_g}} \quad (16)$$

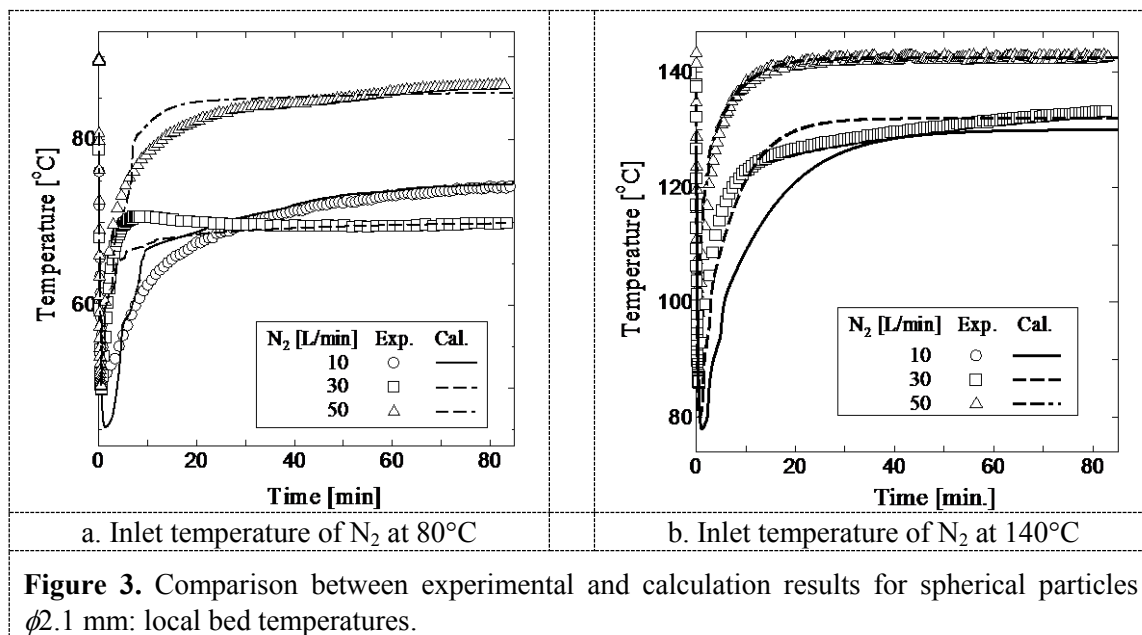
where τ_p as the particle tortuosity is determined as the inverse of particle pore ($1/\varepsilon_p$) based on Wakao while the molar mass of gas (nitrogen and vapor) MM_g , defined as:

$$\frac{1}{MM_g} = \left(\frac{1}{MM_{N_2}} + \frac{1}{MM_{H_2O}} \right) \quad (17)$$

Enthalpy of desorption (ΔH), heat capacity (C_{ps}) obtained from DSC measurement and such as frequency factor (A) and activation energy (E_a) obtained from TG/DTA measurement. Kunii and Smith's equation is used to get λ_{eff} . The total number of mesh points in the computational domain are 80×15 with the time step is 10^{-3} s.

The governing equations above are numerically solved using finite element method (FEM). The followings are the discretization of the governing equations which are solved for mass and heat balances separately.

3. Results and discussion



Good agreements of temperature variations with time were obtained for desorption using spherical particles which the flow-rate of Nitrogen gas varies at 10, 30 and 50 L/min at temperatures 80 and 140°C (Fig. 3). According to the temperature variations in the center of the bed, flow-rate of Nitrogen gas has big influence in desorption. This is confirmed from the peak of temperature distribution becomes narrower when flow-rate of inlet gas increased. Higher flow-rate will influence the distribution because it can reduce the pressure drop in the bed (Eq. 6) and increase the heat transfer coefficient (Eqs. (1) and (2)).

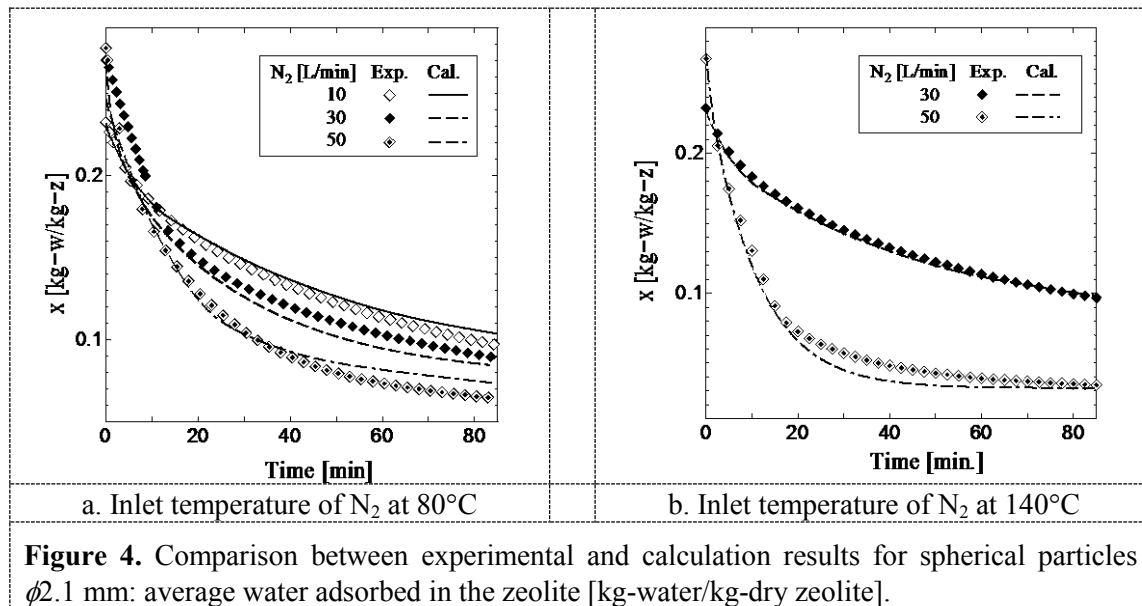
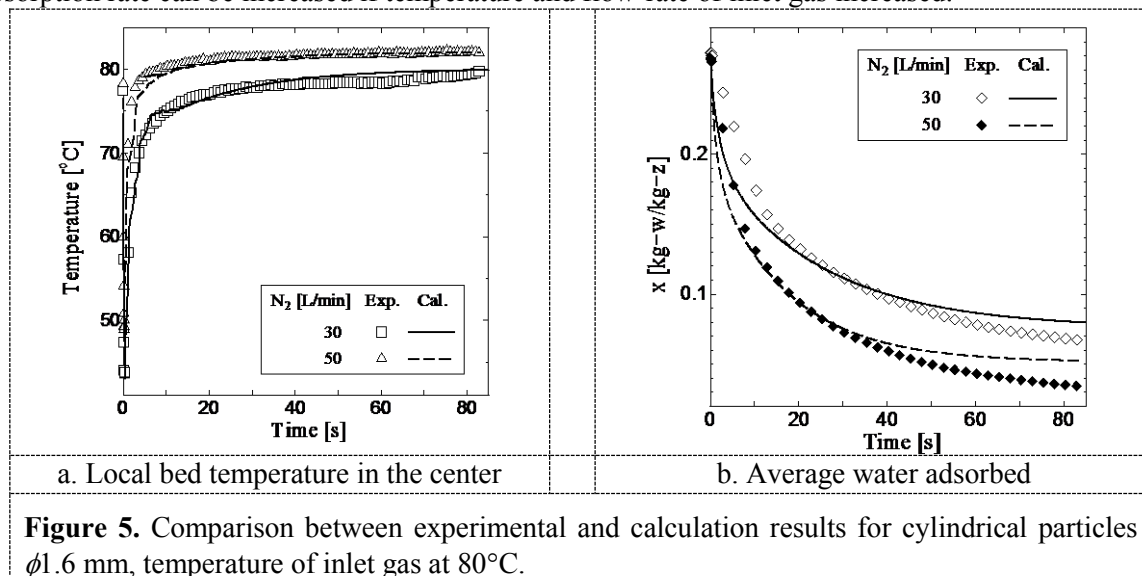


Fig. 4 shows water adsorbed variations with time between experiment and calculation confirmed good agreement for various flow-rate and temperature of Nitrogen gas. Initial value of water adsorbed in the zeolite is not uniform for each desorption condition due to difficulty to get uniform temperature in the preparation of saturated zeolite. The amount of water released from zeolite depends on the flow-rate and temperature of Nitrogen gas. Higher flow rate and temperature, more water can be desorbed. Furthermore, time required to release 80% of water adsorbed in zeolite can be shortened if the flow rate increased. Temperature of inlet gas also has effect in the shortening desorption time. This implies desorption rate can be increased if temperature and flow-rate of inlet gas increased.



Desorption on cylindrical particles of zeolite 13X was investigated using Nitrogen gas at 80°C with flow-rate 30 and 50 L/min . Fig. 5 shows a good agreement of temperature variations with time can be obtained for desorption using spherical particles which the flow-rate of Nitrogen gas varies at 30 and 50 L/min at 80°C . The temperature distribution becomes narrower when flow-rate of inlet gas increased similar tendency with using spherical particles. More amount of water adsorbed can be

released if higher flow rate used to desorb zeolite. This is confirmed experimentally and numerically through Figure 5-8. However, theoretical calculation predicted the amount of water released from zeolite is 0.015 [kg-w/kg-z] higher than experimental one.

4. Conclusion

This study could confirm the feasibility of desorption using dry gas where the results were summarized as below:

1. According to the overall heat balance of desorption, the drying time is theoretically calculated. From the comparison of drying time between experiments and calculations, the relative errors were within 9%. The relative errors show that heat transfer was dominant in desorption.
2. The results of numerical simulation agree with the experimental ones for the distribution of local temperature and average water adsorbed in the packed bed.

From the calculations, there was limitation in the operating condition of desorption. There was almost no different when the gas flow rate was more than 50 L/min and the gas temperature was more than 100 °C.

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