A Multi-scale Approach for the Discovery of Zeolites for Hydrogen Sulfide Removal

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Abstract

Removing H₂S from industrial gases is important to avoid operational hazards and to meet environmental regulation. Microporous zeolites are potential adsorbents for separating H₂S from other gases. While large number of candidate zeolites exists, it is not trivial to select cost-effective zeolites capable of satisfying process constraints and specifications. In this work, a novel method for the zeolite-based H₂S separation is put forward which pertains to a multi-scale modeling, simulation, and optimization framework for combined material screening and process optimization to reduce the overall process cost. The framework spans the atomistic and mesoscopic scales for the screening and selection of zeolites and the macroscopic scale for the simulation and selection of optimal conditions for pressure swing adsorption (PSA)-based H₂S separation technology. Applying this framework, several novel zeolites have been identified for the first time for separation of H₂S from representative H₂S/CO₂, H₂S/N₂, and H₂S/CH₄ mixtures. The zeolites which are screened are capable of removing H₂S from natural gas, acid gas, tail gas, flue gas, refinery gas, biogas, landfill gas, and other gases of industrial importance. Results show that it is possible to perform cost-effective H₂S removal by exploiting reverse selectivity of the gas molecules using novel micro-porous materials. We have also identified zeolite ABW as an adsorbent with high potential for commercialization for multi-purpose gas separation including acid gas removal from natural gas and carbon capture from power plants.

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1 Introduction

H₂S is a toxic, odorous and corrosive gas found in many fuels and chemicals including natural gas, refinery gas, tail gas, biogas, landfill gas, synthesis gas and coke-oven gas. It is often produced from industrial activities such as petroleum refining, natural gas processing, power generation, coal gasification, pulp and paper manufacturing, food processing, wastewater treatment and semiconductor manufacturing. More than 14% of the U.S. natural gas reserves are contaminated by unacceptable levels of H₂S (Dalrymple, Trofe, and Leppin, May 23, 1994), which broadly range from 4 ppm – 42.5 mole % (Alexander and Winnick, 1994), but can be as high as 90% (T-Raissi, 2002). Examples of “ultra-sour” gas reserves include the Cotton Valley pinnacle reef in East Texas of U.S. (87% H₂S), Zhaolanzhuang in China (60–90% H₂S), and Caroline and Bearberry gas field in Alberta, Canada (70–90% H₂S). H₂S is also present in coal and other petroleum-based fuel gases, and is a major air pollutant from chemical and power plants.

H₂S must be removed or reduced to a permissible level from gaseous fuels before they can be transported or used. The presence of H₂S leads to pipeline corrosion during natural gas transportation. It is also considered as a serious corrosive contaminant for fuel processing during coal gasification and diesel reforming (Burke, Winnick, Xia, and Liu, 2002).

Several technologies are available for H₂S removal, including absorption, membrane separator, catalytic oxidation, catalytic membrane contactor, and microbial treatment (Stewart and Arnold, 2011; Kidnay, Parrish, and McCartney, 2011; Towler, Shethna, Cole, and Hajdik, 1997; Cnop, Dortmund, and Schott, 2007; Syed, Soreanu, Falletta, and Béland, 2006). Industrial processes to remove H₂S typically employ absorption to separate concentrated H₂S, followed by Claus treatment to convert to elemental sulfur. However, these processes are highly energy intensive, and can be as extensive and complicated as the rest of the processes (Nowacki, 1994). While alkanolamine absorption processes are widely deployed to reduce acid gas contents to about 10 ppm (Towler, Shethna, Cole, and Hajdik, 1997), high energy consumption and cost of solvent regeneration and solvent degradation are major challenges which still need attention. Bioprocesses involving microorganisms for the biooxidation of H₂S are suitable mostly for the H₂S removal from biogas (Syed, Soreanu, Falletta, and Béland, 2006).

Adsorption-based gas separation (Ruthven, 1984; Yang, 1987) provides promising alternatives

for gas sweetening and H₂S separation applications. Adsorption offers multiple operational modes such as pressure-swing adsorption (PSA), vacuum-swing adsorption (VSA), and temperature-swing adsorption (TSA). Many PSA processes have been studied in the literature (Ruthven, Farooq, and Knaebel, 1994; Agarwal, Biegler, and Zitney, 2010; Hasan, First, and Floudas, 2013; Reynolds, Ebner, and Ritter, 2006; Ho, Allinson, and Wiley, 2008; Webley and He, 2000). PSA, which involves passing a gas mixture through a column packed with a microporous adsorbent that selectively adheres one gas over others, has been shown to be cost-effective for many important gas separations including carbon capture (Hasan, First, and Floudas, 2013; Hasan, Baliban, Elia, and Floudas, 2012b; Hasan, Boukouvala, First, and Floudas, 2014; Hasan, First, Boukouvala, and Floudas, 2015) and natural gas purification (First, Hasan, and Floudas, 2014).

Hasan *et al.* (Hasan, Baliban, Elia, and Floudas, 2012a,b) optimized different separation processes including absorption, membrane, and adsorption for CO₂ separation from flue gases, and showed that a single material is not always the best for all feed compositions and flow rates. In fact, the cost of a PSA process significantly varies depending on the material selected for separation. To this end, microporous zeolites have large internal surfaces for adsorption, and can significantly reduce the energy consumption and cost of a PSA-based gas separation. More than 200 zeolites have been found or synthesized and numerous hypothetical zeolite frameworks can be considered. However, it is a challenge to simultaneously find the optimal zeolite and PSA process for H₂S removal. The existence of large number of alternative materials and different operating conditions make the design and optimization of PSA process very challenging. An efficient computational framework is therefore required to screen for the most promising candidates.

Previously, we introduced a computational framework that effectively combines material selection and process optimization to efficiently screen large databases of microporous materials (Hasan, First, and Floudas, 2013; First, Hasan, and Floudas, 2014). In this work, a novel method for the adsorption-based H₂S separation is put forward which pertains to a multi-scale modeling, simulation, and optimization framework for combined material screening and process optimization to reduce the overall separation cost. The framework spans the atomistic scale and the mesoscopic scale for the screening and selection of zeolites and the macroscopic scale for the selection of optimal process conditions for the removal of H₂S from several important gas mixtures including power plant flue gas, natural gas, biogas, tail gas, and acid gas. The framework is developed and

applied toward achieving the following goals for adsorption-based H₂S removal:

- identify the most effective and feasible materials and processes for PSA-based H₂S removal from binary gas mixtures (e.g., CO₂/H₂S, H₂S/N₂, H₂S/CH₄)
- obtain high purity and high recovery to limit product losses and greenhouse (GHG) emissions, and
- minimize total investment, operating and material costs.

This is the first study reported in the literature that addresses in a quantitative way the trade-offs at material and process scales for zeolite-based H₂S separation. The novel features of our approach also include (i) hierarchical use of shape-, pore- and size-selectivities for zeolite screening for H₂S removal, (ii) discovery of zeolites with reverse adsorption selectivities for H₂S removal from CO₂/H₂S mixtures, (iii) design and optimization of PSA processes for both favorable and reverse adsorption selectivities for H₂S removal, (iv) calculation of investment and operating costs to evaluate the performance of PSA-based H₂S removal process while satisfying design specifications on both purity and recovery, and (v) detailed mathematical process modeling, rigorous optimization, and combined material selection with process optimization for adsorption-based H₂S removal.

2 Multi-scale Framework

Our overall *in silico* screening approach is shown in Fig. 1. We start our analysis with a zeolite database (First, Gounaris, Wei, and Floudas, accessed on August 15, 2015). From this database, we identify potential zeolites based on their pore sizes using ZEOMICS – a three dimensional pore characterization method developed by Floudas and co-workers (First, Gounaris, Wei, and Floudas, 2011). The zeolites are ranked based on shape selectivity (First, Gounaris, and Floudas, 2013), pore selectivity and size selectivity (First, Hasan, and Floudas, 2014). Adsorption isotherms of H₂S and other guest molecules are then generated for the top selected structures. These isotherms provide a basis for performing next filtering based on adsorption selectivity. The structures with highest adsorption selectivities are short listed as remaining candidates. For each of these candidate materials, we optimize a PSA process to obtain the optimal separation cost, purity, and recovery.

The optimized process is obtained by optimizing a detailed PSA model. The purity, recovery and overall separation cost are used as the final metrics to evaluate those zeolites.

[Figure 1 about here.]

A more detailed description of the method at each scale is provided below.

2.1 Atomistic Scale: Pore Characterization, and Screening based on Shape, Size and Pore Selectivities

The transport and adsorption of guest molecules inside a zeolite are affected by their shapes, sizes and affinities, as well as by the pore characteristics of the zeolite framework. Therefore, our multi-scale screening procedure (shown in Figure 1) starts with a three-dimensional pore characterization method to filter a database of 199 zeolite structures to obtain a short list of candidate zeolites as potential adsorbents for H₂S separation. The characterization of the zeolite frameworks is performed using ZEOMICS. Starting from the crystallographic data of a zeolite, ZEOMICS applies graph, geometry, and optimization algorithms to identify portals, channels, cages, and their connectivity. These provide a comprehensive description of the void spaces within a zeolite that molecules such as H₂S, CO₂, CH₄ and N₂ can access. The description includes pore size distribution, accessible volume, accessible surface area, largest cavity diameter (LCD), and pore limiting diameter (PLD). The framework geometry-based characterization allows us to calculate shape selectivity, size selectivity, and pore selectivity of a gas molecule (e.g., H₂) with respect to other molecules in a mixture (e.g., CO₂, N₂, or CH₄).

The three-dimensional shape selectivity of zeolites considers the energetic cost of transport through possible pathways. In the case of a binary gas mixture, shape selectivity describes the difference in energetic cost of transport of two gases through a zeolites pores and their networks due to strain and distortion caused by shape and size (Gounaris, Floudas, and Wei, 2006a; Gounaris, Wei, and Floudas, 2006b; Gounaris, Wei, Floudas, Ranjan, and Tsapatsis, 2009; First, Gounaris, and Floudas, 2013). Depending on the energetic cost, E , of transport, a guest molecule may have free passage ($E = 0$), hindered diffusion (low E), or no passage (high E). Shape selectivity, $S_{shape,A/B} \in [0, 1]$, of gas A over gas B, for a given zeolite is, therefore, calculated as the absolute difference in Boltzmann factors of the minimum pathway energies of A and B. For instance,

considering a binary mixture of CO_2 and H_2S , we compute the shape selectivity between CO_2 and H_2S , $S_{\text{shape},\text{CO}_2/\text{H}_2\text{S}}$, as a measure of the degree to which the zeolite can separate CO_2 from H_2S based on hindrance to molecular transport through the most dominant path-way. A value of $S_{\text{shape},\text{CO}_2/\text{H}_2\text{S}} \rightarrow 1$ indicates that CO_2 diffusion is severely hindered, while H_2S enjoys free passage, and a value of $S_{\text{shape},\text{CO}_2/\text{H}_2\text{S}} \rightarrow 0$ indicates that both CO_2 and H_2S have similar energetic penalties to travel through the zeolite.

The metric of size selectivity was first introduced by Hasan et al. (Hasan, First, and Floudas, 2013) to consider the entire distribution of pore sizes inside zeolites for carbon capture. While shape selectivity is focused on the most dominant pathway through a zeolite, size selectivity, $S_{\text{size},A/B} \in [0, 1]$, is calculated as the relative difference in accessible pore volume between two gases by approximating the gas molecules as hard spheres to determine accessibility. In adsorption-based gas separation, size selectivity may determine the separability if the side channels of a zeolite structure play a dominant role.

Pore selectivity, $S_{\text{pore},A/B} \in [0, 1]$, another metric originally proposed for natural gas purification (First, Hasan, and Floudas, 2014), is calculated as the relative difference in energetically-accessible pore volume. The concept of pore selectivity is based on combining the energetic calculations of shape selectivity with the accessible pore volume calculations of size selectivity.

Each of the above metrics is calculated as a number between 0 and 1, with 0 indicating low selectivity and 1 indicating high selectivity. The selectivity values are used to perform a preliminary screening of the large database of zeolites. In this work, minimum cut-off values of 0, 0.1, and 0.1 are introduced for shape, size, and pore selectivity, respectively, to filter the full database of zeolites. Zeolites satisfying one or more of these cut-off values are included for further consideration.

2.2 Mesoscopic Scale: Molecular Simulation, and Screening based on Adsorption Selectivity

While each of the metrics of shape-, size- and pore-selectivity is readily computed using the automated 3D zeolite pore characterization method, the calculation for adsorption selectivity requires more detailed simulation of equilibrium gas adsorption behavior at the molecular level. Adsorption selectivity is determined by performing grand canonical Monte Carlo (GCMC) simulations to cal-

culate the Henry constants of gases in each zeolite. We employ the GCMC method in the software package MCCCSTowhee (MCCCSTowhee). The details of the GCMC simulations are reported elsewhere (First, Hasan, and Floudas, 2014). The Henry constant ($H_{i,z}$) is useful to understand the interaction between the adsorbate molecule i and the surface of zeolite z . We estimate the Henry constant from the pure-component adsorption isotherm generated by GCMC data as follows:

$$H_{i,z} = \lim_{p \rightarrow 0} \frac{\partial q_{i,z}}{\partial p_{i,z}} = \lim_{q \rightarrow 0} \frac{\partial q_{i,z}}{\partial p_{i,z}} \quad (1)$$

where $q_{i,z}$ is the molar loading of gas i in equilibrium with a bulk fluid phase at partial pressure $p_{i,z}$ in zeolite z . We evaluate the adsorption selectivity, S_{ads} , as follows:

$$S_{ads,z} = \frac{q_{CO_2,z}/p_{CO_2,z}}{q_{N_2,z}/p_{N_2,z}} \approx \frac{H_{CO_2,z}}{H_{N_2,z}} \quad (2)$$

2.3 Process Scale: Optimization of Pressure Swing Adsorption (PSA) Processes for H₂S Separation

The purpose of the process optimization is to evaluate and compare the performances of top adsorption-selective zeolites for H₂S removal. While typical PSA processes refer to above-atmospheric pressure operations, we allow the pressure to go as low as 0.01 bar during desorption. In this context, our PSA process includes both above-atmospheric, atmospheric, and vacuum operations. While PSA and TSA are both suitable, we select PSA over TSA since PSA is often the preferred method for gas separation involving natural gas, carbon capture and many industrially important gases. To fully evaluate the PSA performance for each selected zeolite, we use (i) a 3-step PSA cycle with detailed process configuration, (ii) a detailed model for the PSA process, and (iii) a grey-box constrained optimization method for PSA process optimization.

2.3.1 PSA Configuration

The PSA process for H₂S removal is illustrated in Fig. 2a. The feed is first compressed to bring it to the desired adsorption pressure. One or more columns packed with zeolite are used for adsorption. For CO₂/H₂S and H₂S/CH₄ mixtures, the clean gas (CO₂ and CH₄, respectively) is collected using a desorption vacuum pump. When we separate H₂S from H₂S/N₂ mixture, H₂S is collected using

the desorption vacuum pump. Multiple adsorption columns are used to maximize the utilization of the feed compressor and the desorption vacuum pump.

[Figure 2 about here.]

PSA is a cyclic process in which each column undergoes a number of operational steps. Even the simplest cycle requires at least two steps, namely adsorption and desorption, but for improved performance, additional steps are used. Our PSA process is operated using a 3-step PSA cycle (Fig. 2b) consisting of (i) column pressurization, (ii) adsorption and (iii) counter-current desorption of the more adsorptive gas. During pressurization, each PSA column is filled with feed gas from the feed-end until the column pressure reaches the adsorption pressure, P_{ads} . During the adsorption step, the other end of the column is kept open so that the less adsorptive gas can exit the column while the more adsorptive gas is adsorbed by the zeolite. During the desorption step, the other end of the column is closed, and the more adsorptive gas is evacuated from the feed-end of the column at the desorption pressure, P_{des} . A typical pressure profile during a cycle is illustrated in Fig. 2b.

2.3.2 PSA Modeling

The PSA process is modeled using a system of nonlinear algebraic and partial differential equations (NAPDE). These equations describe mass and energy balances, flow through porous media, temperature and pressure effects, and heat transfer resistance across the column wall. The NAPDE model is described below.

Let i represents the components in a binary gas mixture (e.g., i represents CO_2 and H_2S when a $\text{CO}_2/\text{H}_2\text{S}$ mixture is considered). Since the mole fractions must add up to 1 and we consider binary mixtures, the mole fractions in the NAPDE model will be represented in terms of the more adsorbing component. Let, j represents mover (compressors and vacuum pumps), k represents cooler, and n represents column packed with zeolite. The model parameters are defined and described in Table 1.

[Table 1 about here.]

The 5 decision variables for process optimization are L (column length), P_{ads} (adsorption pressure), t_{ads} (adsorption time in each cycle) P_{des} (desorption pressure), and t_{des} (desorption time in

each cycle). The feed flow rate, feed velocity and column diameter are fixed. The number of required PSA columns is calculated using a procedure described elsewhere (Hasan, Baliban, Elia, and Floudas, 2012b).

We consider the variation both in time t and along the column length l . The following system variables are defined to describe the system: $P(l, t)$ for pressure, $T(l, t)$ for temperature, $T_w(l, t)$ for column wall temperature, $u_z(l, t)$ for velocity, $y_i(l, t)$ for mole fraction of component i in the gas phase, $x_i(l, t)$ for fractional loading of component i in the solid phase, $x_i^*(l, t)$ for equilibrium fractional loading of component i in the solid phase, $k_i(l, t)$ for mass transfer coefficient of component i , $b_i(l, t)$ for temperature dependent parameter for component i , $B_i(l, t)$ for an isotherm parameter for component i , $\Delta H_i(l, t)$ for the change in internal energy for component i , and $\rho_g(l, t)$ for the density of gas obtained from the ideal gas law. These system variables remain the same for fixed values of the decision variables. Therefore, the NAPDE model can be treated as a simulation model when all the decision variables are fixed. However, if the decision variables are allowed to change within their lower and upper bounds, then the NAPDE model becomes an optimization model, where the goal is to obtain the optimal decision variables which minimize the total cost while satisfying all process constraints.

We nondimensionalize the NAPDE model by defining the following dimensionless variables:

$$Z = \frac{l}{L}, \tau = \frac{tu_0}{L}, \bar{P} = \frac{P}{P_{ads}}, \bar{P}_{des} = \frac{P_{des}}{P_{ads}}, \bar{T} = \frac{T}{T_0}, \bar{T}_w = \frac{T_w}{T_0}, \bar{T}_a = \frac{T_a}{T_0}, x_i = \frac{\bar{q}_i}{q_s}, x_i^* = \frac{q_i^*}{q_s}, \text{ and } \bar{u}_z = \frac{u_z}{u_0}.$$

To calculate the mole fraction of component i in the gas phase, we use a component mass balance:

$$\frac{\partial y_i}{\partial \tau} = \frac{1}{Pe} \left(\frac{\partial^2 y_i}{\partial Z^2} + \frac{1}{\bar{P}} \frac{\partial y_i}{\partial Z} \frac{\partial \bar{P}}{\partial Z} - \frac{1}{\bar{T}} \frac{\partial y_i}{\partial Z} \frac{\partial \bar{T}}{\partial Z} \right) - \bar{u}_z \frac{\partial y_i}{\partial Z} + \frac{\psi \bar{T}}{\bar{P}} \left((y_i - 1) \frac{\partial x_i}{\partial \tau} + y_i \frac{\partial x_{N_2}}{\partial \tau} \right) \quad \forall i \quad (3)$$

where $\psi = \left(\frac{1-\varepsilon}{\varepsilon} \frac{RT_0 q_s}{P_{ads}} \right)$, and $Pe = \frac{u_0 L}{D_L}$ is the Peclet number.

Since $\sum_i y_i = 1$, we can write the overall mass balance as follows:

$$\frac{\partial \bar{P}}{\partial \tau} - \frac{\bar{P}}{\bar{T}} \frac{\partial \bar{T}}{\partial \tau} = \left(-\bar{P} \frac{\partial \bar{u}_z}{\partial Z} - \bar{u}_z \frac{\partial \bar{P}}{\partial Z} + \bar{u}_z \frac{\bar{P}}{\bar{T}} \frac{\partial \bar{T}}{\partial Z} \right) - \bar{T} \psi \frac{\partial}{\partial \tau} \left(\sum_i x_i \right) \quad (4)$$

The dimensionless interstitial gas velocity is computed using the following form of Darcy's

law:

$$\bar{u}_z = - \left(\frac{k_p P_{ads}}{\mu u_o L} \right) \frac{\partial \bar{P}}{\partial Z} \quad (5)$$

Since we allow heat transfer across the column wall, we have:

$$\frac{\partial \bar{T}_w}{\partial \tau} = \pi_1 \frac{\partial^2 \bar{T}_w}{\partial Z^2} + \pi_2 (\bar{T} - \bar{T}_w) - \pi_3 (\bar{T}_w - \bar{T}_a) \quad (6)$$

And, the following energy balance is used to compute the temperature inside the column:

$$\frac{\partial \bar{T}}{\partial \tau} = \pi_4 \frac{\partial^2 \bar{T}}{\partial Z^2} - \pi_5 \bar{u}_z \frac{\partial \bar{T}}{\partial Z} + \sum_{i=1}^N (\pi_{6i} + \pi_7 \bar{T}) \frac{\partial x_i}{\partial \tau} - \pi_8 (\bar{T} - \bar{T}_w) \quad (7)$$

where $\pi_1 - \pi_8$ are dimensionless parameters, and their complete expressions can be found in the Appendix.

The mass transfer is assumed to depend linearly with the driving force for adsorption loading. The linear driving force (LDF) model is as follows:

$$\frac{\partial x_i}{\partial \tau} = \frac{k_i L}{u_o} (x_i^* - x_i) \quad \forall i \quad (8)$$

The rate constant (k_i) is calculated using the following expression:

$$k_i = \Omega \frac{\varepsilon D_p}{r_p^2} \left(\frac{c}{q} \right)_i \quad \forall (i) \quad (9)$$

To evaluate x_i^* , we use the following dual-site Langmuir model:

$$x_i^* = \sum_{s=1}^2 \frac{\left(\frac{q_{i,s}^{sat}}{q_s} \right) b_{i,s} c_i}{1 + \sum_i b_{i,s} c_i} \quad \forall i \quad (10)$$

where $q_{i,s}^{sat}$ is the saturation loading of component i at site s ($s = 1, \dots, 2$). The temperature dependent parameter $b_{i,s}$ follows the Arrhenius-type expression:

$$b_{i,s} = \frac{b_{i,s}^o e^{-\frac{\Delta U_{i,s}}{RT}}}{RT} \quad \forall (i, s) \quad (11)$$

Note that a candidate zeolite is represented in the model by the Langmuir parameters describing the adsorption isotherms and heats of adsorption of the gases present in the feed, which are readily available through Grand Canonical Monte Carlo (GCMC) simulation.

We also apply appropriate boundary and initial conditions to describe the three steps, since they are different for different steps. The complete set of initial and boundary conditions for the 3-step PSA process are provided in the Appendix.

To ensure that the PSA process satisfies the minimum purity and recovery specified for the separation, we impose

$$Pu = \frac{\int_o^{t_{evac}} \bar{u}_z y_{CO_2} \frac{\bar{P}}{RT} dt}{\sum_i \int_o^{t_{evac}} \bar{u}_z y_i \frac{\bar{P}}{RT} dt} \geq Pu_{min} \quad (12)$$

$$Re = \frac{\int_o^{t_{evac}} \bar{u}_z y_{CO_2} \frac{\bar{P}}{RT} dt}{\int_o^{t_{pr}} \bar{u}_z y_{CO_2} \frac{\bar{P}}{RT} dt + \int_o^{t_{ads}} \bar{u}_z y_{CO_2} \frac{\bar{P}}{RT} dt} \geq Re_{min} \quad (13)$$

The total investment cost, TIC , of the PSA process is calculated as follows:

$$TIC = \alpha_c (\bar{W}_{ads})^{\gamma_c} + \alpha_v (\bar{W}_{des})^{\gamma_v} + \sum_n PC_n \quad (14)$$

where, α and γ are the cost parameters obtained from literature (Uppaluri, Linke, and Kokossis, 2004; Hasan, Baliban, Elia, and Floudas, 2012a,b), and PC_n is the purchase cost of column n . $\bar{W}_{ads}$, and $\bar{W}_{des}$ are the power requirements of the feed compressor and the desorption vacuum pump, respectively. The expressions for calculating PC_n , $\bar{W}_{ads}$ and $\bar{W}_{des}$ are provided in the Appendix.

The annual operating cost, AOC , is given by:

$$AOC = \left[8000 \times 3600 \sum_j UC_j W_j + 8000 \times 3600 \sum_k UC_k W_k + UCM \times \frac{\pi}{4} D^2 L N \rho_s \right] \quad (15)$$

where, UC_j is the unit operating cost for equipment j , W_j is the duty of equipment j as computed above, and UCM is the unit material cost. We consider 8000 hours as the total annual operation time.

The objective of the optimization is to minimize the total annualized cost of the overall PSA process:

$$MIN [\phi TIC + AOC] \quad (16)$$

where, ϕ is the annualizing factor, TIC is the total investment cost, and AOC is the total annual operating cost. The annualizing factor ϕ is calculated based on the capital recovery factor, the total plant cost, and the annual maintenance cost. A value of 0.154 is used for the capital recovery factor. The total plant cost includes the total equipment installed costs, the indirect cost, and the balance of plant cost. We consider the indirect cost and the balance of plant cost be 32% and 20% of the total installed cost, respectively. The annual maintenance cost is taken to be 5% of the total plant cost. The installed cost of an equipment includes the equipment purchase cost and the installation cost. We consider the installation costs to be 4% of the purchase costs for general equipment (columns and heat exchangers) and 80% of the purchase costs for movers (compressor and vacuum pump) (Fisher, Searcy, Rochelle, Ziaii, and Schubert, 2007). A detailed discussion on the economic parameters and their values used to calculate the investment and operating costs can be found elsewhere (Hasan, Baliban, Elia, and Floudas, 2012a,b).

Equations (3)–(16) define the nonlinear algebraic and partial differential equation-based (NAPDE) model for the optimization of the 3-step PSA process for H_2S separation.

2.3.3 PSA Optimization

We first identify the most significant input variables which affect the cost, purity and recovery. While the pressurization time is fixed to 20 s (Hasan, First, and Floudas, 2013), the NAPDE model is optimized to identify the column length (L), adsorption (P_{ads}) and desorption (P_{des}) pressures, and adsorption (t_{ads}) and desorption (t_{des}) step durations. The column diameter and number of columns are determined using analytical expressions described in Hasan et al. (Hasan, Baliban, Elia, and Floudas, 2012b).

The NAPDE model includes coupled and nonlinear partial differential equations describing the mass and energy balances, time integration in purity and recovery constraints, nonlinear constraints describing the isotherms, and a concave objective function. While the model is detailed

and accurately captures the equilibrium, kinetic and transport behavior of gas adsorption inside a packed column, it is challenging to solve the model to optimality. In our previous works (Hasan, First, and Floudas, 2013; Hasan, Baliban, Elia, and Floudas, 2012b; First, Hasan, and Floudas, 2014), we introduced an iterative surrogate-based optimization method, where the objective function and the key constraints related to purity and recovery were approximated by multiple Kriging models (Jones, Schonlau, and Welch, 1998; Henao and Maravelias, 2010; Davis and Ierapetritou, 2007). The advantage of such surrogate-based optimization is that the PSA process can be efficiently optimized for different zeolites in a reasonable time. A similar approach is followed in this work, however, a quadratic approximation of the following form is used for the surrogate models representing the objective and constraints.

$$y^l = \beta_0^l + \sum_n \beta_n^l x_n + \sum_n \sum_{n' \geq n} \beta_{nn'}^l x_n x_{n'} \quad (17)$$

Here, l represents cost, purity, and recovery; x_n represents the decision variables (L , P_{ads} , P_{des} , t_{ads} , and t_{des}), and β are the model parameters which are fitted based on maximum likelihood method using NAPDE simulation data.

We take a discretized version of the NAPDE model to generate samples (i.e., input data required for the development and subsequent improvement of the surrogate model). We simulate the PSA process for different values of the decision variables, and obtain the corresponding cost, purity and recovery values. Each set of fixed decision variables for which the discretized NAPDE model is solved is considered a sample. With this, the optimization encompasses the following aspects: initial sampling based on Latin Hypercube designs (LHD), explicit handling of constraints through individual surrogate models, optimization of quadratic parameters and finally, optimization of the surrogate quadratic model. Initially, a simplified version of the NAPDE model is solved for a limited number of cycles, and a coarser discretization scheme is used to extract useful information about the feasible region of the system. A larger set of simulations of this fast approximation are performed based on LHD, and subsequently a subset of these points is chosen to build the quadratic models. We develop the following three surrogate models:

$$y^c = \beta_0^c + \sum_n \beta_n^c x_n + \sum_n \sum_{n' \geq n} \beta_{nn'}^c x_n x_{n'} \quad (18)$$

$$y^p = \beta_0^p + \sum_n \beta_n^p x_n + \sum_n \sum_{n' \geq n} \beta_{nn'}^p x_n x_{n'} \quad (19)$$

$$y^r = \beta_0^r + \sum_n \beta_n^r x_n + \sum_n \sum_{n' \geq n} \beta_{nn'}^r x_n x_{n'} \quad (20)$$

where, y^c , y^p , and y^r are the surrogate variables representing the PSA cost (TIC), purity (Pu), and recovery (Re), respectively. The quadratic model parameters ($\beta_0^c, \beta_n^c, \beta_{nn'}^c, \beta_0^p, \beta_n^p, \beta_{nn'}^p, \beta_0^r, \beta_n^r, \beta_{nn'}^r$) are identified via least-squares error minimization to produce quadratic surrogate models separately for cost, purity and recovery. For instance, the nonlinear (NLP) error minimization problem to produce the surrogate model for the cost is described as follows:

$$MIN \quad \sum_i \left(\frac{TIC^i - y^{i,c}}{TIC^i} \right)^2 \quad (21)$$

s.t.

$$y^{i,c} = \beta_0^c + \sum_n \beta_n^c x_{i,n} + \sum_n \sum_{n' \geq n} \beta_{nn'}^c x_{i,n} x_{i,n'} \quad (22)$$

where, i represents a sample and TIC^i is the original cost value at sample i obtained from NAPDE simulation. Similar NLP problems are solved to generate surrogate functions for purity and recovery.

Subsequently, the optimization of the surrogate models is performed. The surrogate-based PSA optimization is defined as:

$$MIN \quad y^c \quad (23)$$

s.t.

$$y^c = \beta_0^c + \sum_n \beta_n^c x_n + \sum_n \sum_{n' \geq n} \beta_{nn'}^c x_n x_{n'} \quad (24)$$

$$y^p = \beta_0^p + \sum_n \beta_n^p x_n + \sum_n \sum_{n' \geq n} \beta_{nn'}^p x_n x_{n'} \quad (25)$$

$$y^r = \beta_0^r + \sum_n \beta_n^r x_n + \sum_n \sum_{n' \geq n} \beta_{nn'}^r x_n x_{n'} \quad (26)$$

$$y^p \geq Pu_{min} \quad (27)$$

$$y^r \geq Re_{min} \quad (28)$$

New sampling of the NAPDE model is performed at the solution. The above steps are performed iteratively until a convergence is met related to the accuracy of the approximation and consecutive iteration improvement. **The parameter estimation and optimization of the surrogate models are performed in GAMS.** There is a possibility that the surrogate optimization may not have a feasible solution in terms of purity or recovery or both. In that case, we solve the following alternative model to generate the new sample, where the priority is set to obtain solutions with purity and recovery values as close as possible to the minimum specified values.

$$MIN \quad (y^p - Pu_{min})^2 + (y^r - Re_{min})^2 \quad (29)$$

s.t.

$$y^p = \beta_0^p + \sum_n \beta_n^p x_n + \sum_n \sum_{n' \geq n} \beta_{nn'}^p x_n x_{n'} \quad (30)$$

$$y^r = \beta_0^r + \sum_n \beta_n^r x_n + \sum_n \sum_{n' \geq n} \beta_{nn'}^r x_n x_{n'} \quad (31)$$

$$(32)$$

Using the above strategy, the optimal purity, recovery and process costs are obtained for selected zeolites. Cost is used as the final metric to obtain a ranked ordered list of the most promising zeolites for H₂S removal. We rank the feasible zeolites, which satisfy the minimum purity and recovery constraints, according to cost in decreasing order.

3 Results & Discussion

In this work, 199 existing zeolites are considered for screening. The zeolites data are taken from the ZEOMICS database (First, Gounaris, Wei, and Floudas, accessed on August 15, 2015). Selectivities are calculated based on CO₂ for CO₂/H₂S mixture, and H₂S for both H₂S/N₂ and H₂S/CH₄ mixtures. All shape and pore selectivities are calculated at 298 K. Minimum cut-off values of 0, 0.1, and 0.1 are introduced for shape, size, and pore selectivity, respectively, to filter the full database of zeolites. The multi-scale framework is applied for different separation systems involv-

ing H₂S. The results are discussed below.

3.1 H₂S removal from CO₂/H₂S Mixture

We consider the removal of H₂S from a feed acid gas (CO₂/H₂S) mixture containing 5% H₂S. The feed flow rate is 0.1 kmol/s. We would like to purify CO₂ with a minimum purity of 98%. Most importantly, we also want to reduce the loss of CO₂ during the separation. A minimum recovery target of 90% for CO₂ is set. Therefore, the objective is to identify the most cost-effective zeolites and the optimum PSA process which would separate CO₂ with at least 98% purity and 90% recovery from the feed acid gas mixture. This is a challenging problem for several reasons. First, CO₂ and H₂S are both acid gases, and exhibit similar affinities. Second, although the change in CO₂ purity is not very significant, the requirement for both extremely high purity and high recovery makes the H₂S removal a challenging task. The trade-off between purity and recovery often prohibits a separation process to obtain a product with both high purity and high recovery.

Applying our computational framework, we have identified 57 out of 199 zeolites which show either shape selectivity, size selectivity or pore selectivity for CO₂ over H₂S. Among the 57 zeolites, which exhibit shape/size/pore selectivity for CO₂, only 15 of them show favorable adsorption selectivity for CO₂ (i.e., $S_{ads,CO_2/H_2S} > 1$), while 42 zeolites show moderate to high adsorption selectivity for H₂S ($S_{ads,H_2S/CO_2} > 1$). Tables 2 and 3 report the most selective zeolites for CO₂/H₂S separation, arranged in decreasing order of adsorption selectivity for CO₂. The zeolites listed in Table 2 have CO₂ adsorption selectivities higher than 1, while the zeolites listed in Table 3 have H₂S adsorption selectivities higher than 1. This reverse selectivity for CO₂ is in contrast to the typical adsorption characteristics considered for microporous materials. It is typically considered that in microporous materials, the adsorption affinities for gases follow: CO₂ > H₂S > CH₄ > N₂. However, we observe that zeolites may also exhibit adsorption selectivity in favor of H₂S (Table 3).

[Table 2 about here.]

[Table 3 about here.]

The observation of many H₂S-selective zeolites has important implications in the design and optimization of PSA processes for CO₂/H₂S separation. First, due to the change in selectivity

from CO₂ to H₂S, CO₂ would no longer be preferably adsorbed inside the column. The PSA design would need to consider more H₂S adsorption during the adsorption step than CO₂. Second, instead of CO₂, H₂S would be extracted during the desorption step. Third, the product CO₂ would be obtained in a different step. The final product CO₂ pressure would be also different. Fourth, the purity and recovery constraints would need to be implemented differently. When CO₂ is more adsorptive, then these constraints are imposed on the CO₂ out flows during the desorption step. However, when H₂S is more adsorptive, then the constraints must be imposed on the CO₂ out flows from the opposite end of the column during the adsorption step. Fifth, since the feed typically contains less H₂S than CO₂ in terms of molar flow rates, the operating and investment costs for H₂S selective PSA processes would be different than those of the CO₂ selective PSA processes, even when the composition of the feed mixture remains the same.

Therefore, we have considered two different PSA configurations to address both typical (CO₂-selective) and reverse (H₂S-selective) zeolites. The PSA configuration shown in Fig. 3a is developed for CO₂-selective zeolites, where H₂S leaves the column during adsorption and CO₂ is extracted as product during desorption. The purity and recovery constraints are imposed on the CO₂ flows at the feed end of the column during desorption at vacuum, P_{des} .

The PSA configuration illustrated in Fig. 3b considers H₂S-selective zeolites, where CO₂ is extracted as product at the far end of the column during the adsorption step, while H₂S is first desorbed from the column at the feed end of the column using the vacuum pump, and then left as concentrated H₂S stream during the desorption step. The purity and recovery constraints are imposed on the CO₂ flows at the far end of the column during adsorption at highest pressure, P_{ads} .

[Figure 3 about here.]

For both process configurations, we consider the same feed mixture with the same target separation while optimizing the total annualized cost (TAC) of the PSA process. TAC includes the investment, operating and material costs.

The results for CO₂-selective zeolites are shown in Table 4. Through multi-scale modeling, simulation and optimization, we have identified 4 zeolites (BIK, NSI, AEN, MON) as the top CO₂-selective zeolites for H₂S removal. Each of these four zeolites can remove H₂S while satisfying the CO₂ purity and recovery of 98% and 90%, respectively. BIK is the top zeolite which separates

CO₂ from the H₂S/CO₂ mixture with 98% purity and 92% recovery at a total cost of \$3.35 MM for every 0.1 kmol/s of the feed.

[Table 4 about here.]

The optimal design of the PSA columns remain the same for all zeolites. The column lengths are selected to be the shortest length allowed (i.e., 1 meter) for all cases. While smaller columns are possible, a further reduction in column length would decrease the L/D ratio to an operationally impractical level. The desorption pressure is 0.01 bar in most cases, highlighting that unless the columns are regenerated at deep vacuum, the desired recovery would not be attained. The majority of the energy consumed in PSA process is attributed to the vacuum regeneration of the adsorbents. The desorption is preferred to occur at low vacuum, which can be the consequence of sharp isotherm curvatures of the more adsorbing component (in this case, CO₂) at low partial pressures. The same phenomenon was observed in our previous study on CO₂/N₂ separation (Hasan, First, and Floudas, 2013). The adsorption times are found to be much shorter than the desorption times.

Interestingly, BIK, NSI and AEN zeolites were also previously identified as top materials for CH₄ purification from CO₂/CH₄ mixtures (First, Hasan, and Floudas, 2014). Therefore, we anticipate that these zeolites will be excellent candidates for CH₄ separation from ternary mixtures containing CH₄, CO₂ and H₂S. They will provide cost-effective and single-step acid gas removal (both CO₂ and H₂S) from sour natural gas, shale gas, biogas, and landfill gas.

For comparison, we further list the top zeolites involving CO₂ separation from H₂S, CH₄ and N₂ in Table 5, based on the results obtained in this work and by (First, Hasan, and Floudas, 2014) and (Hasan, First, and Floudas, 2013). We observe that ABW ranks in top ten for all three important separations (7th in H₂S removal from acid gases, 7th in natural gas purification, and 4th in carbon capture). Therefore, ABW shows high potential for commercialization as an adsorbent for multiple applications, including acid gas removal from natural gas.

[Table 5 about here.]

We also optimized PSA processes for the zeolites which show more adsorption affinity toward H₂S than that for CO₂. We consider the same feed composition to evaluate these zeolites. The top zeolites with reverse selectivity are listed along with their optimal PSA performance in Table 6.

Results suggest that H₂S-selective zeolites (Table 6) can be in fact more effective than CO₂-selective zeolites for H₂S removal from CO₂/H₂S mixtures (Table 4). We have identified three novel zeolites (TOL, TON, and MOR) which cost-effectively separate CO₂ from H₂S with 98% purity and 90% recovery for CO₂. The top H₂S-selective zeolite is TOL which separates CO₂ from H₂S with 98% CO₂ purity and 93% recovery at a cost of \$2.11 million, which is 37% less than the cost estimated for the best CO₂-selective zeolite BIK. In fact, all three H₂S-selective zeolites which are feasible for the separation have less separation cost than that of BIK. This is a non-intuitive result obtained for the first time which shows that it is possible to perform cost-effective H₂S removal by exploiting reverse selectivity of the gas molecules using novel microporous materials.

[Table 6 about here.]

The regeneration of the PSA columns significantly contributes to the energy consumption and cost. The desorption pressure is a key factor that governs the energy consumption toward achieving a more cost-effective separation. It is observed that the H₂S-selective zeolites are capable of removing H₂S by desorbing H₂S at elevated pressures (0.02–0.04 bar) compared to the desorption pressures (0.005–0.01 bar) required for CO₂ by the CO₂-selective zeolites. Since the vacuum pump needs to achieve a significantly large pressure ratio (P_{atm}/P_{des}) compared to the pressure ratio for feed compression (P_{ads}/P_{atm}), even a slight improvement in the desorption pressure (P_{des}) is highly desirable. To illustrate, the change of P_{des} from 0.01 to 0.02 bar reduces the pressure ratio by half from 100 to 50 for the vacuum pump which has a constant outlet pressure of 1 bar. This in turn significantly reduces the energy consumption and cost. While regenerating the column at higher pressure reduces the cost, we also need to remember that this reduces the purity and recovery. Therefore, it is important to perform detailed process optimization in tandem with material selection to appropriately address the trade-offs.

3.2 H₂S removal from H₂S/N₂ Mixture

64 candidate zeolites are screened as preliminary candidates for H₂S removal from H₂S/N₂ mixture, which exhibit either shape, size and pore selectivity. Table 7 provides the list of the top candidate zeolites for the separation of N₂ from a H₂S/N₂ mixture. Among the 64 zeolites, which

meet the minimum cut-off values for at least one of the selectivities (shape, size, pore and adsorption selectivities of H_2S over N_2), the top 31 zeolites are listed in Table 7 which exhibit H_2S adsorption selectivity of 50 or more.

[Table 7 about here.]

The top zeolites according to their process performance for $\text{H}_2\text{S}/\text{N}_2$ separation are listed in Table 8. These results are based on feed containing 10% H_2S and 90% N_2 . Four zeolites (ATV, AWO, MER and BRE) can separate N_2 with 99% purity and more than 90% recovery. ATV, the best zeolite for $\text{H}_2\text{S}/\text{N}_2$ separation, can separate N_2 with 99% purity and 94% recovery. The highest purity of 99.99% is achieved by SOD, highlighting the fact that zeolite-based adsorption can perform ultra-purity separation. However, such separation has lower recovery (about 86%), which signifies the trade-off between purity and recovery in a separation process.

The design of the PSA columns is found to be similar to other separations. The column length is selected to be 1 meter for all cases, which is the lowest value allowed for the length during separation. The adsorption times are at least 2 to 3 times shorter than the desorption times for most zeolites. The desorption pressures (0.01 – 0.04 bar) are also found in the similar the range identified for $\text{CO}_2/\text{H}_2\text{S}$ separation as discussed earlier. Again, majority of the energy consumed in PSA process are attributed to the vacuum regeneration of the adsorbents.

[Table 8 about here.]

3.3 H_2S removal from $\text{H}_2\text{S}/\text{CH}_4$ Mixture

Out of 199 zeolites, 29 zeolites show shape selectivity, 26 zeolites show size selectivity, and 33 zeolites show pore selectivity higher than 0.1 for H_2S for $\text{H}_2\text{S}/\text{CH}_4$ system. All 33 zeolites which are pore-selective also show shape and size selectivities for this separation. Table 9 lists the top candidate zeolites for the separation of H_2S from a $\text{H}_2\text{S}/\text{CH}_4$ mixture. Only 13 zeolites meet one or more selectivity criteria.

[Table 9 about here.]

We consider a methane source which is contaminated by 5% H_2S . The objective is to reduce the H_2S level to less than 2% while recovering 90% of the methane from the feed. We have investigated the top zeolites suggested by the materials-centric metrics, and found that the zeolite MER is a promising zeolite which has not been suggested in any previous studies for H_2S separation for removing H_2S from natural gas (CH_4). MER can increase the purity of CH_4 from 95% to 99.99%, while recovering 90% of the CH_4 fed to the PSA process.

The costs of the PSA processes described in this work are obtained for fixed economic parameters. While the absolute costs are sensitive to the values used for the economic parameters, the overall ranking of the zeolites do not change significantly. Similar observations were made in previous studies related to CO_2 , N_2 , and CH_4 (Hasan, First, and Floudas, 2013; First, Hasan, and Floudas, 2014). Furthermore, the shape, size and pore selectivity-based rankings are not sensitive to the equilibrium parameters, as they do not depend on the nature of the adsorption isotherms. However, the absolute purity and recovery values may change if the isotherm parameters are changed significantly.

4 Conclusions

Using the combined material screening and process optimization methodology, we have discovered several new zeolites for removing H_2S from a variety of industrial gas mixtures with applications in carbon capture, acid gas removal, natural gas purification and tail gas purification. We have identified TOL, TON, MOR, BIK, NSI, AEN, and MON to be the most cost-effective zeolites for H_2S removal from acid gas. We have also found several novel zeolites for H_2S removal from nitrogen and methane. The PSA process can achieve CO_2 purity to 98 – 99% with CO_2 recovery of 90 - 94% for 95/5% $\text{CO}_2/\text{H}_2\text{S}$ system, 10/90% $\text{H}_2\text{S}/\text{N}_2$ system, and 99.99% purity and 90% recovery for 5/95% $\text{H}_2\text{S}/\text{CH}_4$ system. The costs of separation are also reasonable. Lowest adsorption and desorption pressures, fast adsorption but slow desorption are found to be effective for adsorption-based H_2S removal using zeolites. Several zeolites are identified with potential for commercial use. Especially, zeolite ABW ranks as one of the top materials for the removal of both H_2S and CO_2 (acid gases) from natural gas. It has been found that cost-effective H_2S removal can be obtained by exploiting reverse selectivity of H_2S over CO_2 in zeolites. All screened zeolites are among the

top materials for gas sweetening and H₂S removal from natural gas, acid gas, tail gas, flue gas, refinery gas, biogas, landfill gas, and other gases of industrial importance. We anticipate that our approach is suitable for the discovery of novel materials for other molecular gas separation.

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Appendix

A1. Dimensionless groups in the NAPDE model

$$\pi_1 = \frac{K_w}{\rho_w C_{pw} u_o L} \quad (33a)$$

$$\pi_2 = \frac{2r_i h_{in} L}{\rho_w C_{pw} u_o (r_o^2 - r_{in}^2)} \quad (33b)$$

$$\pi_3 = \frac{2r_o h_o L}{\rho_w C_{pw} u_o (r_o^2 - r_{in}^2)} \quad (33c)$$

$$\pi_4 = \frac{K_z}{\epsilon \left(\rho_g C_{pg} + \frac{1-\epsilon}{\epsilon} (\rho_s C_{ps} + C_{pa} q_s) \right) u_o L} \quad (34a)$$

$$\pi_5 = \frac{\rho_g C_{pg}}{\left(\rho_g C_{pg} + \frac{1-\epsilon}{\epsilon} (\rho_s C_{ps} + C_{pa} q_s) \right)} \quad (34b)$$

$$\pi_{6i} = \frac{\frac{1-\epsilon}{\epsilon} (-\Delta H_i) q_s}{T_0 \left(\rho_g C_{pg} + \frac{1-\epsilon}{\epsilon} (\rho_s C_{ps} + C_{pa} q_s) \right)} \quad (34c)$$

$$\Delta H_i = \Delta U_i - RT \quad (34d)$$

$$\pi_7 = \frac{\frac{1-\epsilon}{\epsilon} (C_{pg} - C_{pa}) T_0 q_s}{T_0 \left(\rho_g C_{pg} + \frac{1-\epsilon}{\epsilon} (\rho_s C_{ps} + C_{pa} q_s) \right)} \quad (34e)$$

$$\pi_8 = \frac{2h_{in} L}{\epsilon r_i u_o \left(\rho_g C_{pg} + \frac{1-\epsilon}{\epsilon} (\rho_s C_{ps} + C_{pa} q_s) \right)} \quad (34f)$$

A2. Initial and Boundary Conditions for the 3-Step PSA

Pressurization: The initial conditions for the first pressurization step are given by equation (35).

$$\begin{aligned} y_i &= y_{i,0} \\ \bar{P} &= \bar{P}_{des} \\ \bar{T} &= 1 \\ x_i &= x_i^*|_{y_{i,0}} \end{aligned} \quad (35)$$

Let $Z = 0^+$ and $Z = 1^-$ be the two ends of an adsorption column where the boundary conditions

must be applied. The boundary conditions at $Z = 0^+$ for the pressurization step are as follows:

$$\begin{aligned}\frac{1}{Pe} \frac{\partial y_i}{\partial Z} &= -\bar{u}_z (y_{i,f} - y_i) \\ \frac{1}{Pe_H} \frac{\partial \bar{T}}{\partial Z} &= -\bar{u}_z (1 - \bar{T}) \\ \bar{T}_w &= \bar{T}_a \\ \bar{P} &= f(\tau); \bar{P}_{des} \rightarrow 1\end{aligned}\tag{36}$$

The boundary conditions at $Z = 1^-$ are:

$$\begin{aligned}\frac{\partial y_i}{\partial Z} &= 0 \\ \frac{\partial \bar{T}}{\partial Z} &= 0 \\ \bar{T}_w &= \bar{T}_a \\ \frac{\partial \bar{P}}{\partial Z} &= 0\end{aligned}\tag{37}$$

Adsorption: The boundary conditions at $Z = 0^+$ and $Z = 1^-$ for the adsorption step are given by equations (38) and (39), respectively.

$$\begin{aligned}\frac{\partial y_i}{\partial Z} &= -Pe(y_{i,f} - y_i) \\ \frac{1}{Pe_H} \frac{\partial \bar{T}}{\partial Z} &= -(1 - \bar{T}) \\ \bar{T}_w &= \bar{T}_a \\ \bar{P} &= 1 + \frac{\Delta}{P_{ads}}\end{aligned}\tag{38}$$

$$\begin{aligned}\frac{\partial y_i}{\partial Z} &= 0 \\ \frac{\partial \bar{T}}{\partial Z} &= 0 \\ \bar{T}_w &= \bar{T}_a \\ \bar{P} &= 1\end{aligned}\tag{39}$$

where Δ is a user defined parameter to set the pressure drop across the bed, and $Pe_H = \frac{\epsilon u_o L \rho_g C_{pg}}{K_z}$.

Desorption: The boundary conditions at $Z = 0^+$ and $Z = 1^-$ for the evacuation step are given

by equations (40) and (41), respectively.

$$\begin{aligned}\frac{\partial y_i}{\partial Z} &= 0 \\ \frac{\partial \bar{T}}{\partial Z} &= 0 \\ \bar{T}_w &= \bar{T}_a \\ \frac{\partial \bar{P}}{\partial Z} &= 0\end{aligned}\tag{40}$$

$$\begin{aligned}\frac{\partial y_i}{\partial Z} &= 0 \\ \frac{\partial \bar{T}}{\partial Z} &= 0 \\ \bar{T}_w &= \bar{T}_a \\ \bar{P} &= f(\tau) : \bar{P}_{ads} \rightarrow \bar{P}_{des}\end{aligned}\tag{41}$$

A3. Expressions for Calculating Power consumption

$$\dot{W}_{ads} = \frac{W_{ads}}{t_{ads} \times 746}\tag{42}$$

$$\dot{W}_{des} = \frac{W_{des}}{t_{des} \times 746}\tag{43}$$

$$W_{ads} = \frac{1}{\eta} \varepsilon \pi D^2 u_0 P_{ads} \frac{\gamma}{\gamma-1} \int_0^{t_{ads}} (\bar{u}_z \bar{P}|_{Z=0}) \left[\left(\frac{P_{ads} \bar{P}|_{Z=0}}{P_f} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right] dt\tag{44}$$

$$W_{des} = \frac{1}{\eta} \varepsilon \pi D^2 u_0 P_{ads} \frac{\gamma}{\gamma-1} \int_0^{t_{des}} (\bar{u}_z \bar{P}|_{Z=0}) \left[\left(\frac{P_{atm}}{P_{ads} \bar{P}|_{Z=0}} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right] dt\tag{45}$$

A4. Expressions for Cost Calculations

The purchase cost (PC_n) of column n is calculated using the following expressions:

$$PC_n = F_M C_{V,n} + C_{PL,n} + V_{P,n} C_{PK} + C_{DR,n}\tag{46}$$

where F_M is the factor for materials-of-construction, $C_{V,n}$ is the free-on-board (f.o.b.) purchase cost of empty vessel with the weight W_n , $C_{PL,n}$ is the added cost for adsorber platforms and ladders, $V_{P,n}$ is the adsorber packing volume, C_{PK} is the installed cost of the packing for unit volume, and $C_{DR,n}$

is the installed cost of flow distributors and redistributors of column n . These are expressed as follows:

$$C_{V,n} = \exp \left\{ 7.2756 + 0.18255 \ln(W_n) + 0.02297 [\ln(W_n)]^2 \right\} \quad (47)$$

$$W_n = \pi (39.37 D_n + t_S) [39.37 (0.8 D_n + L_n)] t_S \rho \quad (48)$$

$$C_{PL,n} = 300.9 (3.281 D_n)^{0.63316} (3.281 L_n)^{0.80161} \quad (49)$$

$$V_{P,n} = \frac{\pi}{4} (3.281 D_n)^2 (3.281 L_n) \quad (50)$$

$$C_{DR,n} = 3 \times 125 \times \frac{\pi}{4} (3.281 D_n)^2 \quad (51)$$

where L_n and D_n are the length and diameter of column n , t_S is the shell thickness, and ρ is the density of the carbon steel. We use $F_M = 2.1$, $C_{PK} = 40$, $\rho = 0.284 \text{ lb/in.}^3$, and $t_S = 2$.

A5. Cost Breakdown Results

The following Table provides the breakdown of the costs and the compressor work duties for $\text{H}_2\text{S}/\text{CO}_2$, $\text{H}_2\text{S}/\text{N}_2$, and $\text{H}_2\text{S}/\text{CH}_4$ separations:

[Table 10 about here.]

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Figure 1: Flowchart of the multi-scale zeolite screening and process optimization method for H_2S separation.

Figure 2: PSA process for H_2S separation: (a) process flow diagram with multiple columns, feed compressor and desorption vacuum pump, and (b) pressure profile of the 3-step PSA cycle, which includes (i) pressurization, (ii) adsorption, and (iii) desorption.

Figure 3: PSA configurations for (a) CO_2 adsorptive, and (b) H_2S adsorptive processes.

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Table 1: PSA process model parameters.

Parameter	Description
F	feed flow rate
$y_{i,f}$	mole fraction of component i in the feed gas
T_o	feed temperature
P_f	feed flow rate
u_o	feed velocity
T_a	outside air temperature
$y_{i,0}$	initial mole fraction of component i in the column
P_{atm}	atmospheric pressure
K_z	effective heat conductivity
K_w	thermal heat conductivity of column wall
h_{in}	heat transfer coefficient inside the column
h_o	heat transfer coefficient for outside the column
C_{pw}	specific heat capacity of column wall
C_{pg}	specific heat capacity of gas mixture
C_{pa}	specific heat capacity of adsorbed gas in solid
C_{ps}	specific heat capacity of adsorbent
R	gas constant
q_s	saturation capacity
b_i^o	isotherm parameter for component i)
D_M	molecular diffusivity
D_p	macropore diffusivity, $D_p = \frac{D_M}{\tau_p}$)
D_L	axial dispersion coefficient defined by the correlation: $D_L = 0.7D_M + 0.5u_o d_p$)
UC	unit operating cost
d_p	particle diameter
r_p	particle radius, $\frac{d_p}{2}$)
k_p	bed permeability defined by the correlation: $k_p = \frac{d_p^2}{150} \left(\frac{\epsilon}{1-\epsilon} \right)^2$
r_{in}	inside radius of the packed column
r_o	outside radius of the packed column
Pu_{min}	specified minimum purity
Re_{min}	specified minimum recovery
ΔU_i	heat of adsorption for component i
τ_p	tortuosity factor
ϵ_p	particle porosity
ϵ	bed porosity
ρ_w	density of column
ρ_s	density of solid particle
μ	gas viscosity
ϕ	annualization factor
α	unit capital cost
β	coefficients of the quadratic surrogate models
γ	exponent of power cost

Table 2: CO₂-selective zeolites for CO₂/H₂S separation, based on shape, size, pore and adsorption selectivities.

Zeolite	LCD (Å)	PLD (Å)	Shape selectivity ($S_{shape,CO_2/H_2S}$)	Size selectivity ($S_{size,CO_2/H_2S}$)	Pore selectivity ($S_{pore,CO_2/H_2S}$)	Adsorption selectivity ($S_{ads,CO_2/H_2S}$)
AHT	4.6	3.4	0	0.396	0.4258	38849.16
LOS	7.0	3.1	0	0.5864	0.9765	2276.41
ABW	4.1	4.1	0	0	0.2836	627.46
NSI	4.8	3.4	1	0.2461	0.3365	200.77
BIK	4.8	3.6	1	0	0.1283	51.97
MON	4.9	3.5	1	0	0.0762	50.88
AEN	5.1	3.7	1	0	0.0083	29.93
APC	4.9	3.8	1	0	0.1936	26.4
YUG	5.1	3.7	1	0	0.006	4.74
GME	7.7	7.7	0.4688	0	0.0065	2.01
GOO	5.1	3.6	1	0	0.2329	1.41
ITW	5.4	3.4	0	0.1296	0.165	1.37
RSN	5.8	3.4	1	0	0.0419	1.23
PAU	11.1	4.7	0.3314	0	0.0087	1.18
SZR	6.9	5.3	0.3812	0	0.0155	1.04

Table 3: Zeolites for CO₂/H₂S separation which shows high shape, size and pore selectivity but reverse adsorption selectivity for CO₂.

Zeolite	LCD (Å)	PLD (Å)	Shape selectivity ($S_{shape,CO_2/H_2S}$)	Size selectivity ($S_{size,CO_2/H_2S}$)	Pore selectivity ($S_{pore,CO_2/H_2S}$)	Adsorption selectivity ($S_{ads,CO_2/H_2S}$)
LOV	5.8	3.4	1	0.3201	0.3352	0.95
AFN	5.9	3.7	1	0	0.0513	0.93
DOH	8.5	3.3	0	0.732	0.8382	0.9
CAS	5.7	3.5	1	0.185	0.2141	0.81
AFX	7.8	4.1	0.4114	0	0.0097	0.76
MOR	6.5	6.5	0.4499	0	0.0008	0.67
DFT	5.7	4.3	0.2742	0	0.0024	0.57
LTA	11.7	4.9	0	0	0.0061	0.57
EAB	7.4	3.4	0	0.1258	0.2609	0.56
VNI	5.4	3.2	0	0.0286	0.1281	0.49
NES	6.6	5.7	0	0	0.0189	0.43
BRE	5.9	3.5	1	0.2561	0.2645	0.42
LTF	8.1	8.1	0.6381	0	0.1184	0.41
MFS	6.0	6.0	0.2353	0	0.0412	0.41
MAZ	8.1	8.1	0.611	0	0.1817	0.37
GIU	7.0	2.9	0	0.7056	0.9127	0.32
MEI	7.5	7.5	0.3602	0	0.112	0.31
TON	5.7	5.7	0	0	0.265	0.31
CGF	6.4	3.5	1	0.1784	0.5212	0.28
IWW	7.2	6.9	0.6153	0	0.0469	0.28
FRA	7.3	3.3	0	0.5771	0.6507	0.26
ESV	6.9	3.7	1	0	0.0124	0.22
SOD	7.0	3.2	0	0.7035	0.9216	0.21
APD	5.6	3.8	1	0	0.0716	0.2
SAT	7.5	3.6	1	0	0.012	0.2
NON	7.1	2.9	0	0.2442	0.96	0.18
FAR	6.7	2.7	0	0.5574	0.9149	0.13
TOL	7.0	2.6	0	0.4305	0.9141	0.1
SBN	5.7	3.4	1	0.2701	0.2707	0.08
AFG	7.0	2.7	0	0.0934	0.9967	-
ANA	4.9	3.0	0	0.4387	0.99	-
AST	8.6	2.5	0	0.0182	0.9956	-
BCT	4.4	3.2	0	0.4994	0.7834	-
JBW	3.8	3.8	1	0	0.2571	-
LIO	6.3	2.5	0	0.009	0.9997	-
LTN	10.8	2.4	0	0.009	0.9979	-
MAR	7.0	3.0	0	0.4298	0.9904	-
MEP	6.1	2.3	0	0.0071	0.9983	-
MTN	8.0	2.5	0	0.0155	0.9994	-
MVY	4.4	3.1	0	0.529	0.8016	-
RUT	6.6	2.2	0	0.0005	0.9998	-
SGT	8.4	2.7	0	0.0677	0.9901	-

Table 4: PSA results for the top CO₂-selective zeolites for H₂S separation from CO₂/H₂S mixture.

Zeolite	<u>Adsorption step</u>		<u>Desorption step</u>		Column length (m)	CO ₂ purity (%)	CO ₂ recovery (%)	Cost (MM\$)
	pressure (bar)	time (s)	pressure (bar)	time (s)				
BIK	2	18.74	0.01	300	1	98	92	3.35
NSI	1.03	15	0.01	200	1	98	92	3.45
AEN	2.31	15.32	0.005	231	1	99	90	3.57
LOS	3.13	8.34	0.01	121	1	98	90	3.67

Table 5: Zeolite ranking for CO₂ separation from H₂S, CH₄ and N₂.

Zeolite	H ₂ S removal CO ₂ /H ₂ S	Natural gas purification CO ₂ /CH ₄	Carbon capture CO ₂ /N ₂
BIK	1	5	> 26
NSI	2	9	> 26
AEN	3	2	> 26
LOS	4	>10	24
ABW	7	8	4

Table 6: PSA results for the top H₂S-selective zeolites for H₂S for CO₂/H₂S mixture.

Zeolite	<u>Adsorption step</u>		<u>Desorption step</u>		Column length (m)	CO ₂ purity (%)	CO ₂ recovery (%)	Cost (MM\$)
	pressure (bar)	time (s)	pressure (bar)	time (s)				
TOL	12.23	72.96	0.04	272.73	2.00	98	93	2.11
TON	14.62	90.08	0.02	267.78	1.10	98	90	2.23
MOR	19.21	69.54	0.03	295.00	1.95	98	91	2.55

Table 7: H₂S selective zeolites for H₂S/N₂ separation, based on shape, size, pore and adsorption selectivities.

Zeolite	LCD (Å)	PLD (Å)	Shape selectivity ($S_{shape,H_2S/N_2}$)	Size selectivity ($S_{size,H_2S/N_2}$)	Pore selectivity ($S_{pore,H_2S/N_2}$)	Adsorption selectivity ($S_{ads,H_2S/N_2}$)
AWO	5.8	4.3	0	0.22	0.22	227.8
APD	5.6	3.8	0	1.00	0.12	170.4
DFT	5.7	4.3	0	0.27	0.00	122.0
ATV	5.4	4.1	0	0	0.22	118.0
SBN	5.7	3.4	0.27	1.00	0.28	108.7
TOL	7.0	2.6	0.84	0	0.96	89.79
ZON	6.5	4.0	0	0.17	0.06	88.89
SOD	7.0	3.2	0.94	1.00	0.94	81.77
BRE	5.9	3.5	0.26	1.00	0.27	77.07
MER	7.3	4.8	0	0.20	0	73.83
GIU	7.0	2.9	0.90	0	0.95	70.18
ATN	6.6	4.7	0	0.25	0.16	69.63
MOR	6.5	6.5	0	0.45	0.01	68.20
ESV	6.9	3.7	0	1.00	0.03	67.13
CGF	6.4	3.5	0.18	1.00	0.62	66.85
FRA	7.3	3.3	0.62	1.00	0.67	66.52
TON	5.7	5.7	0	0.30	0.38	64.99
THO	5.8	4.1	0	0.18	0.01	64.32
LTF	8.1	8.1	0	0.70	0.14	60.06
MAZ	8.1	8.1	0	0.63	0.20	58.39
UOS	6.5	4.2	0	0.10	0.10	58.33
MFS	6.0	6.0	0	0.25	0.05	57.90
EON	7.3	7.3	0	0.48	0.17	55.69
ATO	6.1	6.1	0	0	0.12	55.20
LOV	5.8	3.4	0.32	1.00	0.36	54.67
OFF	7.3	7.3	0	0.45	0.02	54.43
SAT	7.5	3.6	0	1.00	0.05	53.36
FAR	6.7	2.7	0.90	0	0.95	52.83
NON	7.1	2.9	0.65	0	0.98	51.65
LEV	7.7	3.4	0	1.00	0.13	51.08
IHW	6.2	4.0	0	0.52	0.04	50.14

Table 8: Top zeolites for H₂S separation from H₂S/N₂ mixture.

Zeolite	<u>Adsorption step</u>		<u>Desorption step</u>		Column length (m)	N ₂ purity (%)	N ₂ recovery (%)	Cost (MM\$)
	pressure (bar)	time (s)	pressure (bar)	time (s)				
ATV	5.00	50.00	0.01	113.46	1.0	99	94	1.65
AWO	4.40	49.65	0.03	137.00	1.0	99	93	1.49
MER	5.00	50.00	0.01	113.46	1.0	99	92	1.66
BRE	4.48	46.15	0.04	147.00	1.0	99	90	1.50

Table 9: H₂S selective zeolites for H₂S/CH₄ separation, based on shape, size, pore and adsorption selectivities.

Zeolite	LCD (Å)	PLD (Å)	Shape selectivity ($S_{shape,H_2S/CH_4}$)	Size selectivity ($S_{size,H_2S/CH_4}$)	Pore selectivity ($S_{pore,H_2S/CH_4}$)	Adsorption selectivity ($S_{ads,H_2S/CH_4}$)
AWO	5.8	4.3	0	0	0.1095	32.9
SBN	5.7	3.4	0.2701	0	0.2736	19.71
MER	7.3	4.8	0	0.3879	0	14.17
LOV	5.8	3.4	0.3201	0	0.3188	13.59
RWR	5.1	3.8	0	1	0	13.01
DAC	5.8	4.8	0	0.4487	0	12.71
JRY	5.2	3.9	0	1	0.0046	11.75
GOO	5.1	3.6	0	0	0.1838	11.53
GIS	5.6	3.9	0	1	0	11.3
ATN	6.6	4.7	0	0	0.1272	11.04
SIV	6.0	4.4	0	0.5369	0.0016	10.33
SOF	4.8	4.7	0	0.3975	0.0001	10.14
ITW	5.4	3.4	0.1296	0	0.1472	10.1

Table 10: Cost breakdown results

Zeolite	Investment cost (\$/yr)	Operating cost (\$/yr)	Duty of feed column compressor (kW/kmol)	Duty of vacuum pump (kW/kmol)
<u>H₂S/CO₂ separation</u>				
TOL	1,281,884	826,668	1	12,098
TON	1,341,497	888,051	1	13,337
MOR	1,509,647	1,036,792	1	15,359
<u>H₂S/N₂ separation</u>				
ATV	1,052,258	599,331	1	6,759
AWO	963,808	529,332	1	6,102
MER	1,054,996	601,461	1	6,760
BRE	969,712	534,017	1	6,193
<u>H₂S/CH₄ separation</u>				
MER	1,094,053	632,809	1	6,268