Adsorption (2014) 20:201–210
DOI 10.1007/s10450-013-9563-y

Microwave assisted vacuum regeneration for CO_2 capture from wet flue gas

Paul A. Webley · Jun Zhang

Received: 20 January 2013 / Accepted: 23 July 2013 / Published online: 8 August 2013
© Springer Science+Business Media New York 2013

Abstract Small scale processing of flue gas with the goal of enriching the stream in CO_2 for sequestration or use is an interesting application area for adsorption technology. For example, boiler flue gas which may contain up to 10 % (v/v) CO_2 in air can be readily enriched to a stream containing >70 % CO_2 which may be ideal for use within a process such as acidification, precipitation, stripping, etc. The challenge in these applications is producing high purity CO_2 without excessive energy use and handling high concentrations of water vapor without the added complication of a pre-drying stage. In this study we have examined the use of microwave assisted vacuum as a way of rapidly directing thermal energy to the adsorbent surface to liberate water and CO_2. Preliminary "proof-of-concept" pump down experiments were conducted on a small transparent adsorption column of 13X zeolite pre-saturated with a 12 % CO_2 in N_2 gas mixture. Both wet and dry gas tests were conducted. The addition of microwave radiation improved the rapid desorption of CO_2 and water and improved the integrated CO_2 purity in the blowdown stream from 60 to 80 %. In the case of dry CO_2 mixtures, the enhancement is due to microwave heating of the 13X zeolite facilitated by the high cation density in the faujasite structure. In the case of water and CO_2 desorption, the temperature rise of the adsorbent upon microwave heating was much lower than that predicted by simple heating suggesting that the microwave radiation is absorbed primarily by the adsorbed water. A simplified energy analysis suggests that brief exposure of an adsorbent to microwave radiation will raise the required vacuum level for regeneration of high humidity flue gas streams and may lead to an overall lower energy penalty. The selective ability of microwave radiation to target different species provides scope for optimized, compact, flue gas treatment systems.

Keywords CO_2 capture · Microwave regeneration · Zeolite 13X · Vacuum swing adsorption

List of symbols

C	Total gas concentration (mol/cm^3)
C_i	Concentration of species i (mol/cm^3)
t	Time (s)
ε_b	Bed voidage
ρ_{ads}	Adsorbent density (g/cm^3)
$\bar{n}_i$	Loading of component i (mol/g)
$\bar{n}_T$	Total loading (mol/g)
$\bar{n}_i^*$	Equilibrium loading of component i (mol/g)
u	Gas interstitial velocity (cm/s)
z	Axial distance (cm)
k_i	Linear driving force constant (1/s)
D_{eff}	Effective diffusion coefficient for i in the adsorbent (cm^2/s)
R_p	Pellet radius (cm)
$C_{p,\ ads}$	Adsorbent specific heat (J/g K)
$C_{p,\ gas}$	Gas specific heat (J/mol K)
T	Temperature (K)
ΔH_i	Isosteric heat of component i (J/mol)
$\dot{Q}_{gen}$	Rate of heat generation by external means (W/g)
h_w	Bed-wall heat transfer coefficient (W/cm^2 K)
T_w	Wall temperature (K)
D	Bed inner diameter (cm)
m_{1i}, m_{2i}	Isotherm parameters (mol/g)
b_{10i}, b_{20i}	Isotherm parameters (1/bar)

P. A. Webley (✉) · J. Zhang
Department of Chemical and Biomolecular Engineering,
The University of Melbourne, Parkville, VIC 3010, Australia
e-mail: pwebley@unimelb.edu.au

Q_{1i}, Q_{2i}	Isotherm parameters (J/mol)
P	Pressure (bar)
P_{MW}	Microwave power per unit volume (W/m^3)
ω	Microwave frequency (rd/s)
ε_o	Dielectric permittivity of vacuum (F/m)
ε''	Dielectric loss coefficient
E	Microwave electric field (V/m)

1 Introduction

The use of adsorption technology to capture CO_2 from a variety of process streams had been extensively investigated particularly in the last 15 years (Casas et al. 2013; Xiao et al. 2012; Won et al. 2012; Wang et al. 2012; Su and Lu 2012; Liu et al. 2012; Kelley et al. 2010; Tlili et al. 2009). A very large number of promising adsorbents have been developed for this purpose with properties tailored for particular process gas streams (Sumida et al. 2012; Lin et al. 2012; Lee et al. 2012; Wang et al. 2011a; D'Alessandro et al. 2010; Choi et al. 2009). The economic assessment of an adsorption system for CO_2 capture is often driven by energy costs and in adsorption technology the energy is needed for regenerating the beds. The suitability of the regeneration option is dependent on the application (feed conditions and product specifications) and even the specific site location for the process as well as integration options at the site. For example, a remote site without ready access to steam may favor electrical energy provided by on-site generators as an input (e.g. vacuum swing adsorption) rather than thermal energy. On the other hand, locations with available low quality waste heat (e.g. a power plant) make temperature swing operation more attractive. In the suite of regeneration options are pressure reduction (PSA or VSA), temperature swing processes (either heating through the vessel walls or internal heaters or hot gas purge), electrical swing processes (which are an alternative heating option and really fall within the TSA field), and purge desorption (e.g. moisture swing adsorption, Wang et al. 2011b). Combinations of these regeneration options have also been investigated (Su and Lu 2012; Wurzbacher et al. 2011).

As is well known, temperature swing processes provide a stronger driving force for desorption of CO_2 giving a larger working capacity but are hindered by the large time scale involved in heating and cooling large vessels of adsorbent. In this respect, research towards rapid thermal processes is a logical next step in TSA development. In addition, the use of a hot purge gas (such as steam) dilutes the recovered CO_2 and a separate downstream separation is required. On the other hand, pressure swing processes can operate extremely fast but require more valuable, high quality electrical energy input and, depending on how tenaciously the CO_2 is held to the surface, may require very low pressures to regenerate. These low pressures (often less than 10 kPa) lead to large piping and valve sizes to minimize pressure drop and therefore restrict the scalability of the technology. One of the key challenges for pressure or vacuum swing adsorption separation of CO_2 from N_2 (e.g. flue gas applications) is to produce sufficiently pure CO_2 product (often >95 %) without requiring excessively low vacuum levels. Past reported studies (e.g. Su and Lu 2012) suggest that for 13X zeolite, vacuum levels below 10 kPa are needed to produce CO_2 product purities of greater than 95 %. Alternatively (or in addition), a CO_2 product purge is often required to enhance the system purity. This step may lead to a reduction in CO_2 recovery as the effluent from this step may contain CO_2. It is therefore interesting to investigate alternative regeneration methods which may lessen the severity of the vacuum levels needed to achieve satisfactory CO_2 purity.

In addition to the energy required for CO_2 removal, the high water levels present in the system offer additional challenges. Often flue gas contains almost as much H_2O as CO_2. Our earlier studies attempted to deal with this high water level by a multilayered approach or process modifications (Li et al. 2011, 2008). While it is possible to control the location of the water loaded zone in the bed, high water levels require unreasonably deep vacuum levels for regeneration and not all zeolites can be regenerated in this way.

One interesting option for rapid adsorbent regeneration is the application of microwaves. This regeneration method has been investigated for over 50 years particularly for dehydration and VOC removal (Chandrasekaran et al. 2012). The interaction of microwaves with a material may show thermal and athermal effects, the latter particularly exploited in microwave chemistry. The presence of water in many CO_2 capture applications makes the microwave technique particularly attractive. Zeolites and CO_2 are transparent to microwave radiation whereas water shows substantial absorption. The dielectric loss coefficient (ε'') of water (which directly relates to the conversion of radiation to heat) is substantially larger than for zeolite or CO_2 (Turner et al. 2000), therefore adsorbed water is selectively heated rather than heating the entire adsorbent and gas system, resulting in a potential enhancement of desorption with lower energy consumption. Studies utilizing microwave radiation for regenerating desiccant zeolite rotors used in air dehumidification (Ohgushi and Nagae 2003; Kubota et al. 2011a, b) found that the desorption rate was about 5 times higher for microwave heating at 800 W than for hot-air heating. Also, the amount of water desorbed from the zeolite by microwave heating was 1.6–2.0 times larger than by hot-air heating.

Pure silica zeolites have low dielectric loss and do not heat appreciably under microwave radiation. However, as suggested by others (Turner et al. 2000), the silica bonds which end in silanols at the surface or defects may have substantially higher dielectric loss coefficients—in particular, dangling OH bonds can become rotationally excited producing heat which is transferred directly to the bulk of the crystal. This suggests that the surface can be deliberately targeted in a microwave desorption process. Dry NaX zeolite can be heated to greater than 1,200 °C by microwave radiation over 6 min while a wet NaX sample reached only 33 °C in 6 min (Whittington and Milestone 1992). This study speculated that the Na^+ cations in the supercage are excellent microwave absorbers and substantially increased the thermal effect, in contrast to high silica materials such as de-aluminated Y zeolite (DAY). Zeolites with different water loading levels exhibit different overall dielectric properties and consequently respond differently to microwave radiation (Carreras et al. 1987).

To take advantage of the excellent microwave selectivity of water in the adsorbed phase, a novel approach in flue gas CO_2 capture, for both dry and wet systems, is put forward in this study. Microwave energy is introduced into the CO_2 separation system during the desorption step to enhance the overall performance. Preliminary proof of concept experiments were conducted to quantify the effect and a simple mass and energy balance were developed and validated with the data to provide insight into the underlying mechanisms. A system energy consumption analyses was also performed to assess this idea. Our goal in this study was not to utilize microwave radiation alone but to examine the features of a hybrid vacuum-microwave system. Our intention is to retain the vacuum as the primary source of regeneration energy while using microwave assist to mitigate the deep vacuum levels needed for conventional vacuum desorption—we denote this process microwave assisted vacuum swing adsorption (MVSA). We are particularly interested in using microwave assist for wet gas systems with high gas humidity. For flue gas streams with high water content (>5 % water) very low vacuum levels are often required (<3 kPa) to provide sufficient purge to remove the water (Li 2010). It may be possible to elevate these vacuum levels to more practical values (e.g. ~20–30 kPa) by a short exposure of part of the bed to microwave radiation.

The experiments presented in this study are preliminary and were conducted to assess the merits of MVSA in the first instance.

2 Experimental work

2.1 Materials and isotherms

In this study, 13X zeolite (UOP APG I, (8 × 12 beads) was chosen as the adsorbent because of its high CO_2/water adsorption capability, the presence of numerous studies on CO_2 capture using 13X, and stability under repeated cycling. Adsorption isotherms for CO_2, N_2 and water were measured over the range 20–90 °C and are reported in our earlier work (Zhang et al. 2009). Isotherms for CO_2 and N_2 were measured by a Micromeritics ASAP2010 and water isotherms were measured by an Intelligent Gravimetric Analyser (IGA), Hiden Isochema, UK.

2.2 Microwave desorption experiments

A transparent plexiglass adsorption column (ID 20 mm, OD 30 mm, Packed Length 100 mm) was packed with 20 g of dry, activated UOP APG I adsorbent The column was placed inside a microwave chamber (2.45 GHz) in a vertical orientation. A schematic of the column-microwave system is provided in Fig. 1. The temperature of the adsorbent was not measured in the column since conventional thermocouples are microwave absorbing. The temperature of the gas entering and leaving the column was measured outside the microwave chamber as shown by the location of the thermocouples in Fig. 1. To control the rate of pump down, we placed a valve in the suction line between the bed and the vacuum pump. The bed pressure was measured between the valve and the suction of the vacuum pump during the pump down experiments. A premixed gas mixture of 12 % CO_2 in N_2 was used for the experiments.

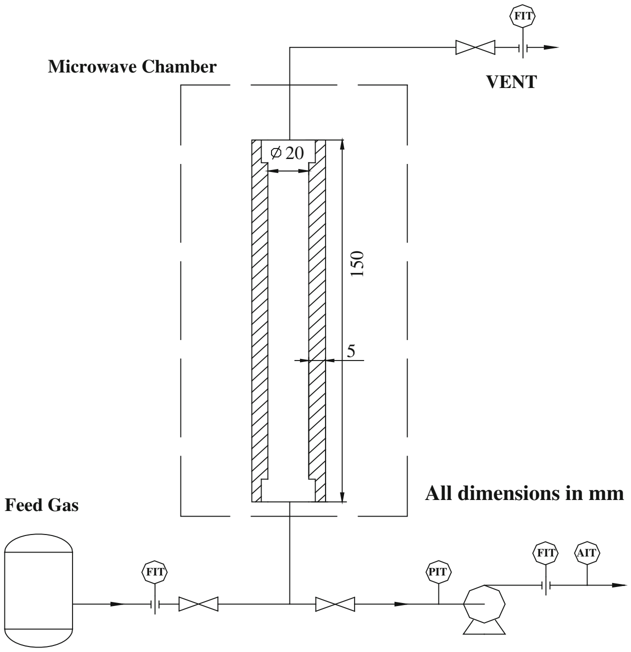

Fig. 1 Schematic of the microwave-adsorption experimental apparatus

Pump down experiments were performed by first saturating the column with the premixed gas by doing a full breakthrough experiment and ensuring that the temperature and composition were uniform. Thereafter, the exit of the column was closed and a vacuum applied (BOC Edwards E2M1.5 vacuum pump) to the feed end (countercurrent to the feed) for a fixed duration.

Pump down experiments were conducted for (a) the column pre-saturated with a dry CO_2/N_2 (12 % CO_2 in N_2) gas mixture at 120 kPa and 20 °C; and (b) a column pre-saturated with a wet CO_2/N_2 (12 % CO_2 in N_2) gas mixture in which the relative humidity of the mixed gas was 18 % at 120 kPa and 20 °C (H_2O mole fraction of 0.0048). The wet gas was prepared by passing the dry gas through a water filled bubbler controlled at a fixed temperature and blending the wet gas with a dry gas stream of 12 % CO_2. The dew point of the blended feed gas was measured with an in situ water sensor (HMT330, VAISALA, Finland, ±0.05 % full scale).

In each case the pump down was conducted with and without the presence of microwave radiation. The response parameters included integrated CO_2 purity in the pump down gas, temperature history, pressure history, gas flow history and energy consumption, either measured or calculated.

It was found that the microwave oven has an uneven distribution of microwave radiation, as expected. Careful calorimetric experiments were conducted to "map" the energy profile within the oven. After mapping the energy field, the column was placed in a uniform radiation field to achieve more homogeneous heating. These same calorimetric measurements showed that the power received at the column when filled with water was approximately 840 W when the microwave setting was 1,100 W. Furthermore, only short durations of microwave radiation were used. It was found that excessive radiation time (>40 s) could lead to damage of the column and its contents.

2.3 Adiabatic model for MVSA

To help interpret the experimental results and provide a basis for comparison with alternate regeneration strategies, a simple pump down model of the MVSA process was developed. The model is a conventional set of mass and energy balance equations written for a single desorption step for a three component system: H_2O, CO_2 and N_2. The model only captures first order effects and omits features such as axial dispersion of mass and energy, thermal conductivity in the axial direction, and heat loss to the wall. The major equations are:

Species i balance where i is CO_2 and H_2O (N_2 determined by difference: $C_{N2}=C–C_{H2O}–C_{CO2}$):

$$\frac{\partial C_i}{\partial t}+\left(\frac{1-\varepsilon_b}{\varepsilon_b}\right)\rho_{ads}\frac{\partial \bar{n}_i}{\partial t}=-\frac{\partial uC_i}{\partial z} \tag{1.1}$$

Total mass balance:

$$\frac{\partial C}{\partial t}+\left(\frac{1-\varepsilon_b}{\varepsilon_b}\right)\rho_{ads}\frac{\partial \bar{n}_T}{\partial t}=-\frac{\partial uC}{\partial z} \tag{1.2}$$

Rate of adsorption for each species:

$$\frac{\mathrm{d}\bar{n}_i}{\mathrm{d}t}=k_i\left(\bar{n}_i^*-\bar{n}_i\right),\quad k_i=\frac{15D_{eff}}{R_p^2}\ i=\ \mathrm{CO_2},\ \mathrm{H_2O},\ \mathrm{N_2}\varepsilon'' \tag{1.3}$$

Energy balance

$$\rho_{ads}\left(\frac{1-\varepsilon_b}{\varepsilon_b}\right)C_{p,ads}\frac{\partial T}{\partial t}-\rho_{ads}\left(\frac{1-\varepsilon_b}{\varepsilon_b}\right)\sum_{i=1}^{3}\Delta H_i\frac{\partial \bar{n}_i}{\partial t}=\rho_{ads}\left(\frac{1-\varepsilon_b}{\varepsilon_b}\right)\dot{Q}_{gen}-C_{\mathrm{p,gas}}\frac{\partial uCT}{\partial z}-\frac{4h_w}{\varepsilon_b D}(T-T_w) \tag{1.4}$$

Dual Site Langmuir Equilibrium Model

$$n_i=\frac{m_{1i}b_{1i}y_iP}{1+b_{1i}y_{1i}P}+\frac{m_{2i}b_{2i}y_iP}{1+b_{2i}y_iP};\ \mathrm{i = H_2O, CO_2, N_2} \tag{1.5}$$

$$b_{1i}=b_{10i}\exp\left(\frac{Q_{1i}}{RT}\right);\ b_{2i}=b_{20i}\exp\left(\frac{Q_{2i}}{RT}\right)$$

The velocity at the exit of the column, u_{exit}, was calculated from the actual volumetric flow rate as supplied by the vendor pump curve which was a function of the suction pressure. A valve placed between the column and the pump also changed the profile of the pump down curve and this was modeled using a valve equation (Chou and Huang 1994). It should be noted that the molar flow rate is not constant over the pump down period. The model is run with a constant actual volumetric flow rate of the Edwards vacuum pump (which, over the pressure range is very flat and constant) together with a valve equation between the vacuum pump and the bed. The boundary condition on the bed can also be quite well represented as a constant velocity. The instantaneous and integrated molar flow rate is calculated and the integrated CO_2 concentration is then calculated from the integrated moles which have been accumulated at each time. The isotherm data were fit to a Dual Site Langmuir Equation for each individual species and the isosteric enthalpies, ΔH_i were determined as a function of loading by the Clausius–Clapyron Equation. For the dry gas simulations, the competitive adsorption of CO_2 and N_2 was modeled using the extended Langmuir Equation with the parameters shown in Table 1. For the wet gas cases, the adsorption of CO_2 and N_2 were first calculated as indicated in the dry case and then reduced in line with the experimental observation of Wang and Levan (2010) according to the water loading. The rate constants for CO_2, N_2 and H_2O were

Table 1 Model parameters used in simulation

Item	Value		
Bed properties			
Bed voidage	0.37		
Adsorbent internal voidage	0.50		
Adsorbent density (g cm^3)	1.011		
D_{eff}, H_2O	6×10^{-6}		
D_{eff}, CO_2	5×10^{-5}		
D_{eff}, N_2	7×10^{-5}		
Particle diameter	8 × 12 mesh		
Bed internal diameter (cm)	2.0		
Bed length (cm)	10.0		
Operating conditions			
Initial column pressure (bar)	1.2		
Initial column temperature (K)	300		
Initial column mole fraction	Dry	Wet	
H_2O	0.00	0.0048	
CO_2	0.12	0.119	
Isotherm parameters	H_2O	CO_2	N_2
m_1 (mmol/g)	5.699	2.610	2.456
b_{10} (1/bar)	1.169×10^{-6}	1.510×10^{-6}	2.89×10^{-4}
Q_1 (J/mol)	47,965	30,180	16,000
m_2 (mmol/g)	9.262	2.081	0.000
b_{20} (1/bar)	3.088×10^{-6}	7.090×10^{-5}	0.000
Q_2 (J/mol)	58,488	35,181	0.000

determined by matching the breakthrough curves to the simulation data to get the effective diffusivity values, D_{eff}. The instantaneous bed pressure was calculated from the ideal gas equation once the gas concentration C was solved for. The set of PDE's described in Eqs. (1.1–1.4) were discretized spatially using the finite volume method with Sweby flux limiters and solved using the MATLAB routine ode15 s to provide the dynamic and integrated information. The program was also used in scale up calculations to estimate the total energy required. All of the model parameters are provided in Table 1.

3 Results and discussion

3.1 Dry gas experiments with and without microwave

Figure 2 shows the integrated concentration of CO_2 in the suction gas from the bed during the pump down step for the case of the adsorbent bed pre-saturated with dry, 12 % CO_2 in N_2 gas. The curves are continuous output from the Servomex CO_2 analyzer attached to the discharge of the vacuum pump. The concentration is therefore not instantaneous CO_2 concentration of the gas leaving the bed since accumulation within the vacuum pump, analyzer line etc. will cause integration of the CO_2 profile. From 0 to 360 s there is no application of microwave radiation and the concentration of CO_2 in the vacuum line increases as expected. The model is able to capture the rise quite well. The simulation predicts a rise in CO_2 concentration to a final integrated CO_2 purity of 63 %, in good agreement with the experimental data. The microwave is applied at 360 s for 25 s. The model shows a rapid rise in CO_2 concentration in the integrated pump down gas to 80 %, in good agreement with the data. The additional desorption of CO_2 can be interpreted entirely as a thermal effect since CO_2 is transparent to microwave radiation. Thus, heating of the adsorbent is rapid and, unlike using a hot purge gas which would dilute the CO_2 product, the effluent CO_2 concentration is significantly improved. The microwave heating in our model is represented as a simple Joule heating effect (inclusion of Q_{gen} in the energy balance) which appears to be adequate for this case.

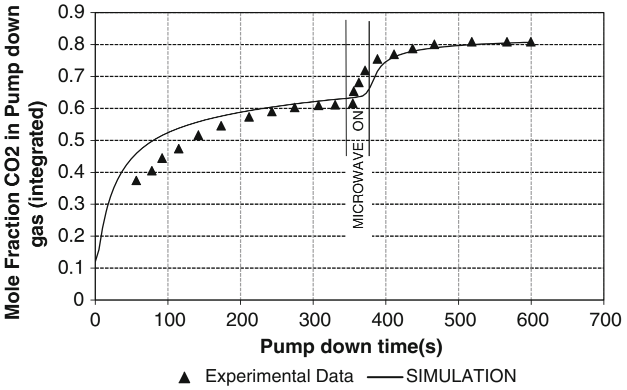

Fig. 2 Integrated mole fraction of CO_2 in the pump down gas during the pump down process—dry gas case

The pressure and temperature history of the gas leaving the bed entering the vacuum pump is shown in Fig. 3a, b. The pressure profile matches the data well.

The simulated temperature history shows the instantaneous bed temperature and the temperature of the integrated gas leaving the bed, assuming no heat transfer to the piping leaving the bed. In practice, the rather small scale of the experiment and large surface to volume ratio means that ambient heat transfer will mitigate temperature changes, as shown by the experimental data in Fig. 3c. Nevertheless, it is clear that there has been a considerable temperature rise on application of the microwave radiation which has more than offset the drop in temperature due to desorption of the CO_2 in the bed.

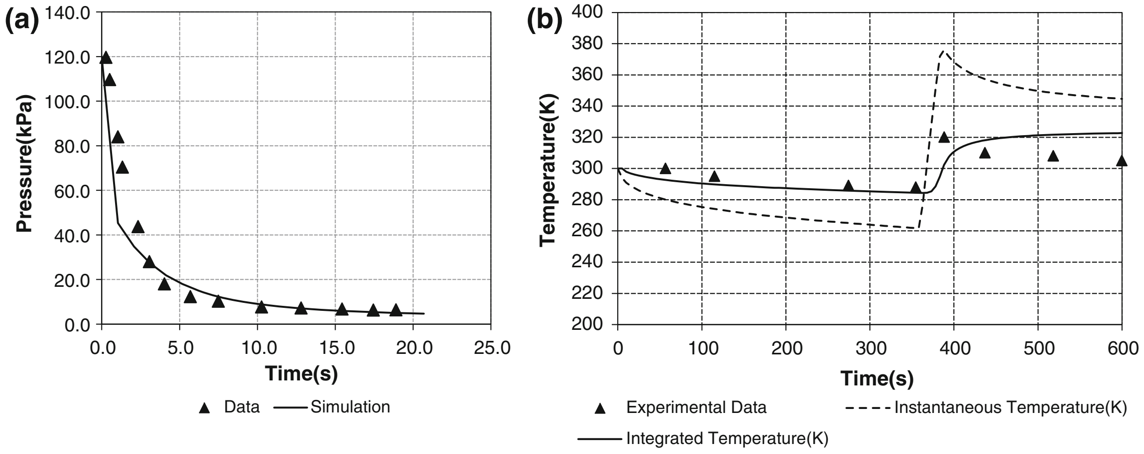

Fig. 3 **a** Bed pressure and **b** exit gas temperature during pump down of the bed (dry gas)

This is consistent with a pure thermal effect as zeolite heating under microwave radiation is well known (Whittington and Milestone 1992).

3.2 Pumpdown of bed pre-saturated with wet gas

Figure 4 shows the integrated CO_2 concentration (dry basis) in the gas leaving the bed for the case where we have pre-saturated the column with a wet CO_2/N_2 mixture also containing 12 % CO_2. The relative humidity of the stream was 18 % as measured by the Vaisala humidity meter corresponding to a water mole fraction of 0.0048. Microwave radiation is applied at 400 s for 20 s. Figure 4 also shows the prediction from the simulation which is reasonably close but under predicts the final CO_2 level. We see that in a wet gas system, the peak integrated CO_2 purity increase upon microwave addition (from ~55 to ~68 %) is less than that in a dry system (~60 to ~80 %). This is due to the lower CO_2 loading on the bed initially in the presence of water vapor as well as the lower temperature increase of the system. Figure 5 shows the temperature of the gas leaving the bed. In this case, the desorption of water by microwave radiation has attenuated the temperature rise in the bed far below that predicted by the model. It is clear that the absorption of microwave radiation by water is not satisfactorily represented by a simple heating term as in the case of a dry gas. Comparison with Fig. 3b shows that the maximum experimentally measured temperature rise for the dry case (320 K) is considerably higher than that observed for the wet case (305 K). This trend is consistent with that observed by Turner (2000) in their study of cyclohexane and methanol desorption from silicalite and DAY. In that study, it was found that virtually all of the heating came from the microwave's interaction with the adsorbent when the material with low dielectric loss (such as cyclohexane) was adsorbed.

In summary, the adsorbent temperature in the dry gas cases increased considerably more than the wet gas system,

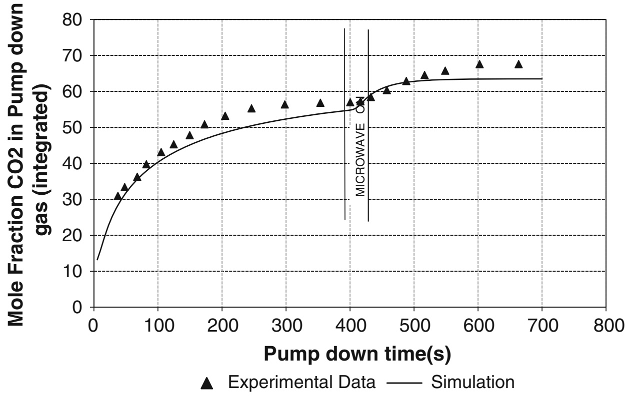

Fig. 4 Integrated mole fraction of CO_2 in the pump down gas—wet gas case

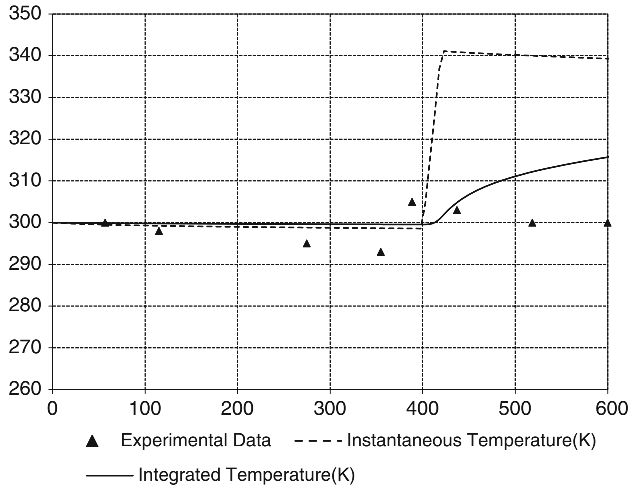

Fig. 5 Temperature of the gas leaving the bed for the case in which the bed is initially saturated with wet gas

which indicates that in the wet gas case, the radiation has been directed at liberating water from the surface of the adsorbent with little increase in adsorbent temperature. This is a useful *athermal* feature of microwave radiation for wet adsorbents and deserves closer study to understand the role of zeolite surface chemistry such as cation density (the cations acting as microwave absorbers) and silanols groups on water desorption.

3.3 Model analysis

To provide some theoretical insights and to assess the merits of the microwave assisted proposal, numerical simulations were performed using the model described above. In this instance we have assumed a dry feed (no water). Figure 6a shows the effects of heat generation on the integrated CO_2 purity obtained by desorption from the bed for different heat inputs. As before, we have represented the heat input solely as $\dot{Q}_{gen}$ in Eq. (1.4). In practice, the absorbed power per unit volume of material is:

$$P_{MW} = \varepsilon'' \varepsilon_o \omega E^2 \tag{1.6}$$

where ω is the angular microwave frequency, ε'' the dielectric loss coefficient (imaginary part of the complex relative dielectric permittivity), ε_o the dielectric permittivity of vacuum, and E the microwave electric field. The absorption of the microwave radiation by the system therefore depends on ε'' and the relative amount (volume) of the components in the system. Of the components, the adsorbent (NaX) has the largest relative volume but low ε''. The adsorbed water has high ε'' but a low volume and the CO_2 and N_2 have both low volume and ε''. Therefore we expect an interesting change in P during the desorption process as the water is first removed and then, depending on its adsorbed amount (and isotherm shape), the zeolite is thermally heated. Regardless, this level of detail is not yet available and our analysis simply uses a single $\dot{Q}_{gen}$ term regardless of specificity. In addition, we have not accounted for losses (i.e. <100 % effectiveness of heating)—the power scale in Fig. 6 should therefore be regarded as indicative only. As shown in Fig. 6(a), with the increase of microwave power level, the CO_2 purity steadily increases with the marginal gain decreasing with continued increase of microwave power level. We expect this as the non-linear isotherm for CO_2 would make initial temperature increases advantageous but after some temperature, additional desorption would be negligible given the drop in CO_2 capacity.

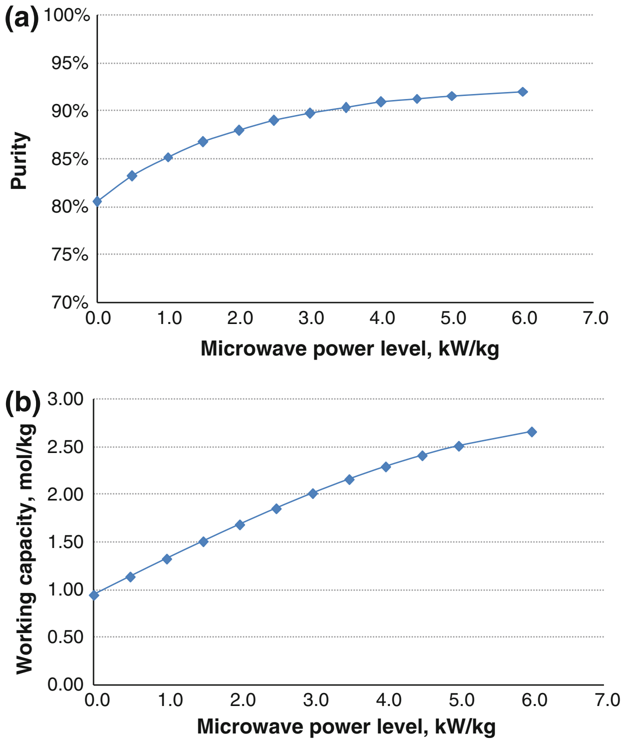

Fig. 6 Effect of microwave power level on **a** CO_2 purity, **b** CO_2 working capacity

A similar pattern was also observed with the working capacity of the adsorbent (Fig. 6b). We have defined working capacity as the net amount of moles of CO_2 removed during the desorption step, per unit mass of adsorbent. With the help of microwave energy, the purity exceeds 92 % and the productivity reaches 2.66 mol/kg adsorbent (a typical CO2VSA system working capacity is usually less than 1 mol/kg). This represents a large decrease in bed volume with corresponding capital savings. Figures 7 and 8 show the effect of the microwave radiation on the vacuum level needed to achieve the required purity. This was important to our study and shows that with the assistance of microwave, we may be able to save pumping energy to achieve the same purity and working capacity as that achievable only under deep vacuum. The addition of microwave energy has changed the desorption path and provided a more isothermal pump down process. For

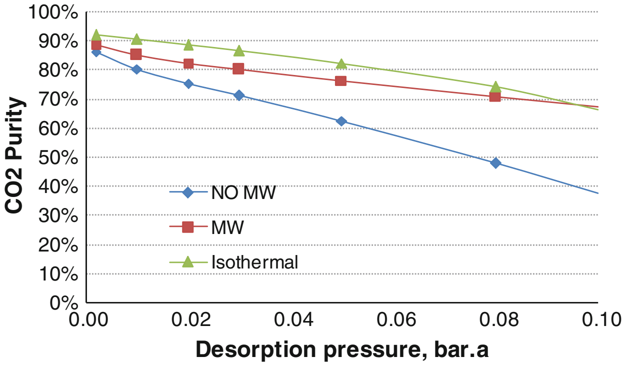

Fig. 7 Effect of desorption pressure on CO_2 purity with and without microwave radiation. Isothermal case included as reference

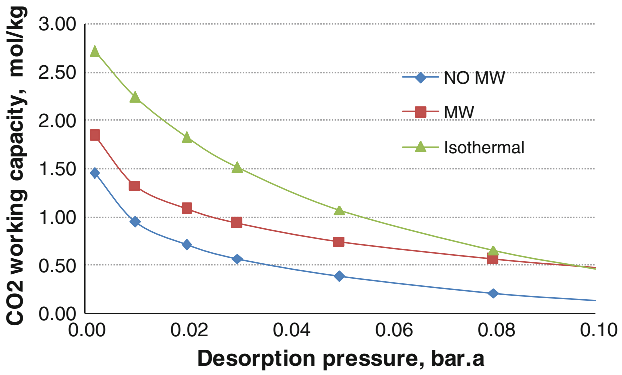

Fig. 8 Effect of desorption pressure on CO_2 working capacity with and without microwave radiation. Isothermal case included as reference

example, in the absence of microwave-assist, a vacuum level of 3 kPa is needed to achieve 70 % purity. This vacuum level of 3 kPa is frequently needed to achieve high CO_2 purities in CO2VSA systems (Li et al. 2011, 2008) and is difficult to achieve at large scale. The addition of microwave energy raises this to 8 kPa for the same purity. The microwave power only plays a minor role in this process compared with the additional vacuum pump energy needed. Considering the large improvement of working capacity and adsorbent regeneration achieved after microwave desorption, it may be worthwhile to spend this extra energy on the separation process depending on individual applications. An optimized combination of microwave power and vacuum power may be able to reduce the overall energy requirements.

These simple calculations are based on a bed uniformly saturated with a gas of a fixed composition (12 % CO_2 in N_2, dry). During an actual vacuum swing cycle, the composition profile in the bed at the start of the pump down step will not be uniform. It is likely that there will be far less CO_2 adsorbed near the exit of the bed. In addition, if a CO_2 product purge is used, the entrance region of the bed will contain a much higher concentration of CO_2 (close to the product concentration). In this case we expect the results shown in Figs. 5, 6, 7 and 8 to change. It is not possible to predict these without a full cycle simulation since the presence of microwave radiation during a full cycle and its effect on the extent of require product purge is not known. Given the promise suggested by our initial proof of concept experiments, we are currently undertaking an analysis of this situation.

3.4 Calculation of energy requirements

To assess the effectiveness of microwave energy and vacuum energy in achieving CO_2 desorption, we have used our model to calculate the desorption energy needed and purity attainable for 4 cases of pump down of a bed: (a) a bed saturated with dry gas (12 % CO_2/N_2) employing vacuum only down to 30 kPa (b) a bed saturated with dry gas (12 % CO_2/N_2) employing vacuum and microwave energy (c) a bed saturated with wet gas (12 % CO_2/N_2) employing vacuum only down to 30 kPa and (d) a bed saturated with wet gas (12 % CO_2/N_2) employing vacuum and microwave energy. We have chosen 30 kPa as a reasonably achievable vacuum pressure using a single stage blower. The results are shown in Table 2. It is seen that with a small amount of microwave energy, a dry gas system yields much higher purity and productivity. The addition of microwave energy helps attenuate the temperature drop [which was from 20 to 7 °C in case (a)] providing higher productivity and purity. The additional recovery has lowered the vacuum energy costs by more than the required additional microwave energy resulting in an overall lower total energy.

For a wet system, since water is a very strong energy absorber (high ε''), we expect much of the microwave power to be absorbed by the adsorbed water (Eq. 1.6). The wet gas case (d) shows lower purity and productivity due to reduction in CO_2 capacity in the presence of competing water. As mentioned earlier, we have found experimentally that under the same microwave irradiation conditions, a wet system temperature rise is much smaller than a dry system. This contrasts with our calculation in Table 2 which shows a temperature increase to 56.3 °C. This reason for this discrepancy is the way in which we have represented the addition of microwave power through a simple $\dot{Q}_{gen}$ term. Clearly, the effect of microwave radiation on removal of water is not a simple thermal effect and we will need to understand and improve our representation

Table 2 Comparison of the energy requirement for four pump down scenarios

	Dry gas, no MW	Dry gas, MW	Wet gas, no MW	Wet gas, MW
Integrated CO_2 purity (%)	28.33	39.60	24.04	31.63
Productivity (mol/kg)	0.618	1.108	0.30	1.046
Vacuum pump energy (MJ/kg CO_2)	1.47	0.93	1.96	0.82
Microwave energy (MJ/kg CO_2)	0	0.10	0	1.07
Total energy (MJ/kg CO_2)	1.47	1.03	1.96	1.90
Final desorption temperature (°C)	7.0	12.0	5.0	56.3

of this effect in our model to match our experimental data. As suggested by Carreras et al. (1987), zeolites with different water loading levels exhibit different overall dielectric properties and respond differently to microwave radiation. The addition of a component-specific "absorption" fraction to $\dot{Q}_{gen}$ will be needed based on Eq. (1.6). The total energy for the wet case may therefore be lower than that calculated in Table 2.

The different effects of microwave radiation on the dry case and wet case provide scope for innovative design of the microwave system. In usual practice, the wet and dry zones in an adsorbent bed may be spatially separated with the wet zone coincident with the feed and may even use a different adsorbent. On the other hand, the dry zone is usually located towards the exit of the bed. Application of the microwaves to the wet zone only (or perhaps differing amounts to the two zones) can provide an optimal irradiation profile to minimize total energy in concert with an appropriate vacuum level. In addition, the use of intermittent microwave radiation during the pump down process can be optimized to correspond to changes in the isosteric heat of water as the loading decreases.

3.5 Practical aspects and implementation

The practical application of microwave technology to adsorption systems is restricted to small systems. Microwave compressed air desiccant dryers are already industrially available (Arrow Pneumatics 2011). The penetration distance of the microwaves dictates the largest diameter which can be used. This penetration distance depends on the system characteristics, especially the dielectric constants and must usually be determined experimentally. Low Si:Al ratio zeolites are expected to have relatively short penetration depths. A rough estimate for NaX is 15 cm (Bathen 2003) whereas more transparent zeolites such as DAY may provide >100 cm penetration depth. This raises an interesting option of using high silica adsorbents in the water guard layer of the system to achieve high penetration depths and assist in water desorption without large temperature increases. A penetration depth of 100 cm translates to a bed diameter of at least 200 cm which is useful for the scale of CO_2 capture from flue gas systems of small boilers. The ability to raise the vacuum level from <5 to >30 kPa is a large benefit because of the associated reduction in gas velocity in the suction lines and correspondingly lower pipe and valve sizes. Far more study is needed to understand the impact of microwave radiation on the cyclic stability of an adsorption process, especially the integration of a microwave system into a complex cycle and the quantification of microwave energy needs for different adsorbent systems. The need to cool the bed before re-admitting feed gas for the next cycle remains but the rapid heating and smaller temperature rise we have observed for water desorption suggests that this cooling may be accomplished more rapidly than in conventional TSA.

The MVSA process appears at first glance to be similar to electrical swing adsorption (ESA). However, the latter relies entirely on Joule heating and the impact on the system is independent of the molecules—all are heated together with the heating of the adsorbent. Furthermore, ESA is restricted to conducting adsorbents (e.g. carbon monoliths) and the risk of fire in systems containing high voltage, carbon and oxygen is significant. In contrast, MVSA requires transparent adsorbents (such as high silica zeolites), is specific to adsorbed species with high dielectric loss coefficients, and can be rapidly applied and removed during a cycle.

Finally, it should be recalled that we are converting high quality electrical energy into thermal energy for desorption of molecules and comparison with true TSA processes which use low quality heat should always include the Carnot factor associated with the heat-work conversion. Based on the energy penalty at a typical power plant, this factor is approximately 3.2 (DOE/NETL-2012/1557 2012). Therefore, an electrical specific energy of 1 MJ/kg CO_2 for adsorption systems which use vacuum only to regenerate the adsorbent translates to 3.2 MJ/kg of thermal energy which is currently comparable to or slightly greater than than that required for conventional liquid-scrubbing MEA based systems.

4 Conclusions

We have examined the action of microwave radiation on the CO_2 capture characteristics of the pump down process for adsorbent regeneration. Experiments conducted on wet and dry CO_2/N_2 mixtures with and without microwave radiation indicated that in the dry case, the microwaves provided simple heating of the zeolite which led to an improvement in CO_2 desorption and an improvement in product purity. Unlike the usual temperature drop accompanying desorption, the action of microwave radiation could keep the bed more nearly isothermal improving purity and capacity. In the case of wet CO_2/N_2 mixtures, the desorption of water (a strong microwave absorber) attenuated the temperature rise and indicated that microwave assisted vacuum could provide improved CO_2 desorption and column regeneration compared to the case with no microwave radiation. A simple model was developed to describe the effect of heating on the process. Representing the heating as a simple uniform heat generation process was not successful in duplicating the data for the wet case. A more detailed microwave power model is needed which captures the targeted nature of the radiation. The analysis indicates that there is scope for integration of a microwave process into a vacuum desorption system and it may be possible to elevate the vacuum levels and provide capital and energy savings. Far more work is needed though to understand the complex relationship between the microwave radiation and the interaction of the zeolite chemistry and guest molecules CO_2, H_2O and N_2.

Acknowledgments We acknowledge funding for this CO2CRC project provided by the Australian Government through its CRC program.

References

Arrow Pneumatics: Microwave compressed air desiccant dryers. Fact Sheet. (2011)

Bathen, D.: Physical waves in adsorption technology—an overview. Sep. Purif. Technol. **33**, 163–177 (2003)

Carreras, M., de Roque-Malherbe, R., las Pozas, C.: Dielectric-differential thermal analysis. IV. The role of water. J. Therm. Anal. **32**, 1271–1276 (1987)

Casas, N., Schell, J., Joss, L., Mazzotti, M.: A parametric study of a PSA process for pre-combustion CO_2 capture. Sep. Purif. Technol. **104**, 183–192 (2013)

Chandrasekaran, S., Ramanathan, S., Basak, T.: Microwave material processing-a review. AIChE J. **58**, 330–363 (2012)

Choi, S., Drese, J.H., Jones, C.W.: Adsorbent materials for carbon dioxide capture from large anthropogenic point sources. ChemSusChem **2**, 796–854 (2009)

Chou, C.T., Huang, W.C.: Incorporation of a valve equation into the simulation of a pressure swing adsorption process. Chem. Eng. Sci. **49**, 75–84 (1994)

D'Alessandro, D.M., Smit, B., Long, J.R.: Carbon dioxide capture: prospects for new materials. Angew. Chem. Int. Ed. Engl. **49**, 6058–6082 (2010)

DOE/NETL-2012/1557: Current and future technologies for power generation with post-combustion carbon capture. Final Report. (2012)

Kelley, B.T., Deckman, H.W., Herschkowitz, F., Northrup, P.S., Ravikovitch, P.I.: Temperature swing adsorption of CO_2 from flue gas utilizing heat from compression. (2010)

Kubota, M., Hanada, T., Yabe, S., Kuchar, D., Matsuda, H.: Water desorption behavior of desiccant rotor under microwave irradiation. Appl. Therm. Eng. **31**, 1482–1486 (2011a)

Kubota, M., Hanada, T., Yabe, S., Matsuda, H.: Regeneration characteristics of desiccant rotor with microwave and hot-air heating. Appl. Therm. Eng. (2011b). doi:10.1016/j.applthermaleng.2011.11.044

Lee, Z.H., Lee, K.T., Bhatia, S., Mohamed, A.R.: Post-combustion carbon dioxide capture: evolution towards utilization of nanomaterials. Renew. Sustain. Energy Rev. **16**, 2599–2609 (2012)

Li, G.: Capture of carbon dioxide from post-combustion flue gases by vacuum swing adsorption. Influence of water vapor. Monash University (2010)

Li, G., Xiao, P., Webley, P., Zhang, J., Singh, R., Marshall, M.: Capture of CO_2 from high humidity flue gas by vacuum swing adsorption with zeolite 13X. Adsorption **14**, 415–422 (2008)

Li, G., Xiao, P., Xu, D., Webley, P.A.: Dual mode roll-up effect in multicomponent non-isothermal adsorption processes with multilayered bed packing. Chem. Eng. Sci. **66**, 1825–1834 (2011)

Lin, L.C., Berger, A.H., Martin, R.L., Kim, J., Swisher, J.A., Jariwala, K., Rycroft, C.H., Bhown, A.S., Deem, M.W., Haranczyk, M., Smit, B.: In silico screening of carbon-capture materials. Nat. Mater. **11**, 633–641 (2012)

Liu, Z., Wang, L., Kong, X., Li, P., Yu, J., Rodrigues, A.E.: Onsite CO_2 capture from flue gas by an adsorption process in a coal-fired power plant. Ind. Eng. Chem. Res. **51**, 7355–7363 (2012)

Ohgushi, T., Nagae, M.: Quick activation of optimized zeolites with microwave heating and utilization of zeolites for reusable desiccant. J. Porous Mater. **10**, 139–143 (2003)

Su, F., Lu, C.: CO_2 capture from gas stream by zeolite 13X using a dual-column temperature/vacuum swing adsorption. Energy Environ. Sci. **5**, 9021 (2012)

Sumida, K., Rogow, D.L., Mason, J.A., McDonald, T.M., Bloch, E.D., Herm, Z.R., Bae, T.H., Long, J.R.: Carbon dioxide capture in metal-organic frameworks. Chem. Rev. **112**, 724–781 (2012)

Tlili, N., Grévillot, G., Vallières, C.: Carbon dioxide capture and recovery by means of TSA and/or VSA. Int. J. Greenhouse Gas Control **3**, 519–527 (2009)

Turner, M.D., Laurence, R.L., Conner, W.C., Yngvesson, K.S.: Microwave radiation' s influence on sorption and competitive sorption in zeolites. AIChE J. **46**, 758 (2000)

Wang, L., Liu, Z., Li, P., Yu, J., Rodrigues, A.E.: Experimental and modeling investigation on post-combustion carbon dioxide capture using zeolite 13X-APG by hybrid VTSA process. Chem. Eng. J. **197**, 151–161 (2012)

Wang, Q., Luo, J., Zhong, Z., Borgna, A.: CO_2 capture by solid adsorbents and their applications: current status and new trends. Energy Environ. Sci. **4**, 42 (2011a)

Wang, T., Lackner, K.S., Wright, A.: Moisture swing sorbent for carbon dioxide capture from ambient air. Environ. Sci. Technol. **45**, 6670–6675 (2011b)

Wang, Y., LeVan, M.D.: Adsorption equilibrium of binary mixtures of carbon dioxide and water vapor on zeolites 5A and 13X. J. Chem. Eng. Data **55**(9), 3189–3195 (2010)

Whittington, B.I., Milestone, N.B.: The microwave heating of zeolites. Zeolites **12**, 815–818 (1992)

Won, W., Lee, S., Lee, K.S.: Modeling and parameter estimation for a fixed-bed adsorption process for CO_2 capture using zeolite 13X. Sep. Purif. Technol. **85**, 120–129 (2012)

Wurzbacher, J.A., Gebald, C., Steinfeld, A.: Separation of CO_2 from air by temperature-vacuum swing adsorption using diamine-functionalized silica gel. Energy Environ. Sci. **4**, 3584–3592 (2011)

Xiao, G., Xiao, P., Lee, S., Webley, P.A.: CO_2 capture at elevated temperatures by cyclic adsorption processes. RSC Adv. **2**, 5291–5297 (2012)

Zhang, J., Xiao, P., Li, G., Webley, P.A.: Effect of flue gas impurities on CO_2 capture performance from flue gas at coal-fired power stations by vacuum swing adsorption. Energy Procedia **1**(1), 1115–1122 (2009)