Microwave assisted regeneration of zeolite

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Abstract
This paper presents an experimental study on zeolite NaX dehydration under microwave irradiation at a laboratory scale. Dehydration rates vary linearly with the absorbed power and show no influence with the purge gas flowrate. A pulsed mode of irradiation enhances dehydration due to higher level of temperature reached and improved mass transport rates. A thermal balance model is developed in order to assess the maximum temperature reached in the adsorbent bed and the use of the dissipated energy inside the solid is discussed. From these results, this paper evaluates the economic interest in a microwave regeneration process and discusses the technical feasibility at an industrial scale.

Key-words : microwave - desorption – zeolite

1. Introduction

Among the electro-heat technologies, microwave heating is a potentially attractive technique, offering an energy-efficient alternative to current heating technologies (Thostenson and Chou, 1999). Microwaves are already employed in food and rubber industry and more recently find new applications in other industrial processes such as waste-streams treatment (Jones et al., 2002; Appleton et al., 2005).

In contrast with classical heating processes, for which energy is transferred due to thermal gradients by conduction, convection or radiation through a heated surface, microwave energy is directly delivered to materials through molecular interaction with the electromagnetic field. Materials differ in their response to microwave heating and molecules or atoms must exhibit a dipole moment in order to absorb microwave energy. Ability to convert electromagnetic energy into thermal energy depends on the dielectric properties of each material and can be described using complex relative permittivity $\varepsilon_r$. The real part $\varepsilon'_r$ characterizes a material’s ability to store charge, and $\varepsilon''_r$, the imaginary part, measures the heat related to electromagnetic losses in the material. Dielectric properties are not only dependent on frequency but also on composition and temperature, which are often time-dependent variables of the process. In addition, because the microwave equipment design determines the electromagnetic field, the size and shape of the object being heated is also important.

When a composite material of different dielectric properties is placed within an alternative field, microwaves will selectively couple with the higher loss material. Some solids being very efficient to convert electromagnetic energy into heat when gas and some liquids are totally transparent to microwaves, it is thus well established that the solid phase of a liquid-solid or a gas-solid fixed bed can be selectively heated (Bonnet, 2003; Estel et al., 2003). Heat is directly provided to the solid phase then flow is inverted compared to classical heating, being from the center to the outer boundary of the particles. Microwaves appear as a very attractive technology for gas-solid separation or adsorbent regeneration for which mass and heat flow then in the same direction.

Concerning the regeneration of adsorbents under microwave, studies have essentially been performed at a laboratory scale. Some papers, dealing with the dehydration of zeolite 13X demonstrate the ability of microwaves for fully desorbing water with an outlet gas temperature lower than 150°C (Roussy et al.,...
1981, 1984). The dehydration rate is proportional to the applied power and is governed by the thermal evolution of the material under the electromagnetic field, acting essentially with the supply of calorific energy (Benchanaa et al., 1989). Studies performed with other adsorbates such as ethanol on silicalite (Burkholder et al., 1986), or ethanol/toluene on zeolite DaY (Reuβ et al., 2002), show that adsorbate polarity is important for electromagnetic energy conversion and the more polar an adsorbate is, the higher the desorption rate is. Co-adsorption studies of volatile organic compounds (VOC’s) in moist air on various adsorbents (Kobayashi et al., 1996; Turner et al., 1998, 2000; Lopez et al., 2004; Kim et al., 2005; Hashisho et al., 2005) also confirm this result. The initial water content of the solid is then a key parameter for desorption processes: for dry zeolites, often exhibiting weak absorbing properties at ambient temperature, heating is rather difficult while it becomes easy when containing small amounts of water. The nature of the adsorbent and of the exchange cation in particular, is also of major importance (Whittington et al., 1992; Weissenberg et al. 1994; Ohgushi et al., 1998). From all these studies, microwave regeneration processes appear of main interest for desorbing polar adsorbates on solid materials exhibiting low thermal conductivity such as polymers or ceramics.

The aim of this paper is now to evaluate the economical interest of a microwave regeneration process and discuss the technical feasibility at an industrial scale. Three industrial processes of adsorbent regeneration are already reported in Bathen, 2003. The first two deal with the recovery of solvents from a polymeric adsorbent or of VOC’s adsorbed on activated carbon. The last one deals with alumina regeneration in an air drying process. For the recovery of VOC’s from activated carbon used in gold ore beneficiation, Canada Ontario Hydro Technologies has built a pilot plant of a 30 kg/h capacity and the next scale up to 120 kg/h is underway. This study is concerned with the regeneration process of zeolite NaX used as an adsorbent in the dehydration process of natural gas. The actual thermal regeneration process is highly energy consuming. Five percent of the dry natural gas produced has to be heated up to 300°C for the regeneration step and recycled, leading to important heating/cooling cycle times.

In a first step, an experimental study using microwave heating is performed in order to optimize energy conversion by optimisation of the cavity and the wave guide design and as well, to evaluate the dehydration rates and power consumptions in various operating conditions. In a second step, a thermal balance model is proposed to assess the maximum temperature reached inside the adsorbent bed and avoid the zeolite degradation. In the last step, extrapolation to an industrial unit and the design of the process is discussed. The economical interest of such a microwave process is evaluated based on the global energy consumption compared with conventional heating.

2. Experimental section

2.1 Materials and apparatus

Commercial NaX zeolite beads (G5 type), the main characteristics of which are summarised in Table 1, were provided by Ceca. Classical characterization of this sample has been carried out by nitrogen adsorption at 77 K (Micromeritics ASAP 2010). Prior to measurements, samples were outgassed at 773 K for 12 hours. Microporous volume is calculated from the Dubinin-Raduskevitch equation and mesoporous volume is obtained by difference between nitrogen adsorbed volume at a relative pressure P/P₀ equal to 0.99 and microporous volume. Nitrogen and synthetic air N₂/O₂ (80/20) were purchased from Air Liquide and used as vector gases at a flowrate ranging from 2 to 30 NL/h.

<table>
<thead>
<tr>
<th>Table 1. Zeolite NaX properties</th>
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<tbody>
<tr>
<td>Average diameter (µm)</td>
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<tr>
<td>Particles density (kg/m³)</td>
</tr>
<tr>
<td>Bed density (kg/m³)</td>
</tr>
<tr>
<td>B.E.T Surface Area (m²/g)</td>
</tr>
<tr>
<td>Microporous Volume (cm³/g)</td>
</tr>
<tr>
<td>Mesoporous Volume (cm³/g)</td>
</tr>
<tr>
<td>Water adsorption capacity at ambient (kg water/kg dry zeolithe)</td>
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</tbody>
</table>
Hydration and dehydration cycles were performed in a fixed bed reactor introduced in the chimneys of a waveguide. As shown on Figure 1, the microwave heating system consists of a magnetron working at 2.45 GHz with a maximal power of 1950 W. Microwaves are carried out in a WR 340 waveguide applicator for a resonant single mode $TE_{013}$. The applicator length is manually adjusted at the beginning of the experiment to achieve reflected power at a minimum. The circulator protects the magnetron by conducting reflected power into a water load. Reflected and incident powers are measured and recorded. Experiments were performed in a continuous mode or in a pulse mode of microwave irradiation with incident power ranging from 30 to 250 W.

The fixed bed reactor consists of a glass tube of 2.9 cm internal diameter equipped with a PTFE grid at the bottom. Adsorbent bed height is about 3.75 cm and its position is adjusted so that all the zeolite is in the irradiated zone. The reactor is introduced through the chimneys that prevent possible microwave leakage and is supported on a microbalance which records its weight evolution with time. During the hydration step, full saturation of the solid is obtained by bubbling of the gas in a water containing vessel before flowing through the adsorbent bed. During dehydration step under microwave irradiation, the gas flows through a desiccant bed of silica gel before being introduced at the bottom of the reactor. The gas flowrate is controlled by a rotameter. An optical fiber is used in the irradiation area to measure the solid temperature inside the bed or the gas temperature a few millimetres above the bed surface.

2.2 Experimental results

Typical results of dehydration obtained under microwave heating are presented on Figure 2a and Figure 2b, showing respectively the weight loss of the bed and the absorbed power versus time. Experimental results confirm the ability of microwave radiation to fully and rapidly dehydrate zeolite NaX as the weight loss value of 27% in weight corresponding to the adsorption capacity is reached at the end of each experiment. The weight loss response to an incident power step is of first order with a delay mainly attributed to desorbed water molecules diffusion inside the pores of the zeolite and transport outside of the bed. The shape of this curve is typically linked to the fact that the absorbed power remains nearly constant during the whole experiment (Figure 2b). During dehydration, electromagnetic energy conversion into heat leads simultaneously to solid heating and water desorption. The absorbed power increases in a small extent at the beginning of the experiment due to the applicator length adjustment and then, due to the favourable evolution of the dielectric properties of the system with increasing temperature. At the beginning, energy conversion is mainly due to the presence of adsorbed water while at the end, it can certainly be attributed to the favourable value of the $\varepsilon'$ of the dry zeolite at elevated temperature (Whittington et al., 1992).
In a typical experiment, about 60% of the incident power is absorbed by the system. By placing additional impedance adaptors within the wave guide, absorption of almost 95% of the incident power has been obtained demonstrating that the microwave system can quite easily be optimised by working in the resonant conditions of the irradiated object or by adding impedance adaptors.

Experiments performed at various gas flowrates demonstrate that this operating parameter has hardly no influence on desorption rates. Weight loss curves are quasi-identical when gas flowrate is varied from 2 to 30 NL/h corresponding respectively to gas superficial velocities from $8.4 \times 10^{-4}$ to $1.26 \times 10^{-2}$ m.s$^{-1}$. Under microwave irradiation, the role of the gas is no longer to supply energy but to carry away desorbed molecules outside of the bed and favour external mass transfer by maintaining a low partial pressure in the gas phase as well as turbulence at the solid surface. At an industrial scale, it will then be possible to considerably reduce gas consumption by operating at a minimum value of the gas flowrate, just high enough to ensure a good distribution in the bed and the draining of the desorbed molecules.

Figure 3 shows the strong influence of the incident power on the weight loss curves. Average values of the corresponding absorbed power are also reported. The higher the incident power is, the shorter the initial delay is, the faster dehydration occurs, and the higher the final temperature of the outlet gas is, indicating a higher temperature reached in the zeolite bed. This last parameter will be discussed in detail in the next section. From this graph, the dehydration rates have been evaluated from the slope of the curves in their linear part and are reported in Figure 4. The calculated dehydration rate is shown to be quasi-proportional to the absorbed power. This result can simply be used for extrapolation to another scale, the key extrapolation parameter being the absorbed power density (in W/m$^3$ of reactor). Nevertheless, for the energy consumption comparison, precise values will preferentially be taken from experimental weight loss curves.

**Figure 2.** Dehydration of zeolite: $m_{\text{dry zeolite}} = 16 \text{g}$, $P_i = 50 \text{W}$, $Q_g = 12.82 \text{NL/h}$

(a) Weight loss of the bed, (b) Absorbed power

**Figure 3.** Weight loss versus time: Influence of the incident power: $m_{\text{dry zeolite}} = 16 \text{g}$, $Q_g = 12.82 \text{NL/h}$

**Figure 4.** Dehydration rates versus absorbed power $m_{\text{dry zeolite}} = 16 \text{g}$, $Q_g = 12.82 \text{NL/h}$
The mode of irradiation is also of main importance on dehydration curves. Some additional experiments were performed in pulse mode (15s ON at 250W and 60s OFF corresponding to a mean incident power value of 50W) and compared to the same experiment performed in continuous mode (50 W of incident power, constant during the whole experiment). Dehydration rates 30% higher were obtained in pulsed mode while absorbed power was only few percents higher. The fact that the absorbed power is higher in pulsed mode can be easily explained by the higher temperature the bed reaches (detected by the outlet gas temperature and confirmed by the model described in Section 3). During the first seconds in pulsed mode, the bed is irradiated with an elevated value of the incident power leading to a rapid increase of the temperature bed, leading also to improved dielectric properties. Natural convection is not important enough to observe an efficient cooling of the bed during the following sixty seconds (power OFF) and the next step of 250W is applied to an already hot bed, the dielectric properties of which lead to a better energy conversion. Higher level of the bed temperature favours desorption and mass transfer within the pores of the zeolite leading to faster desorption rates in a pulsed mode of irradiation compared to rates obtained in a continuous mode for the same energy consumption.

3. Thermal balance model

As mentioned above, the temperature of the outlet gas, a few millimetres above the bed surface has been measured but this value is obviously not really representative of the real temperature of the zeolite bed. The precise evaluation of this last parameter is important for two reasons: first of all, zeolite can deteriorate at high temperature (above about 500°C) leading to structural changes of the material and modified adsorption capacities, compromising the life time of the process. Second, the temperature reached during the desorption step conditions the cooling step duration. Our main objective by using microwave heating is to maximize the desorption rates while minimizing the solid heating. The absorbed power can be written as the sum of five terms (Roussy et al, 1984) detailed in equations 1 to 5, corresponding respectively to the power used for gas heating, for solid heating, for heating of the adsorbed molecules, for desorption and for thermic losses.

\[
P_{u_{\text{gas}}} = Q_{\text{gas}} C_{pg} \left( T_{e_g} - T_{e_g} \right) \quad (1)
\]

\[
P_{u_{\text{zeolite}}} = m_{\text{zeolite}} C_{p\text{zeolite}} \frac{dT_{\text{zeolite}}}{dt} \quad (2)
\]

\[
P_{u_{\text{w}}} = m_w C_{pw} \frac{dT_{\text{zeolite}}}{dt} \quad (3)
\]

\[
P_{u_{\text{desorption}}} = -\frac{dm}{dt} \Delta H_{\text{des}} \quad (4)
\]

\[
P_{u_{\text{losses}}} = hA(T_{\text{zeolite}} - T_{\text{amb}}) \quad (5)
\]

This thermal model is based on the assumption of a uniform distribution of the energy and, as well of a uniform temperature within the whole bed. In order to verify this assumption, a local modelling of the repartition of the electromagnetic field would be required. For that, evolutions of the dielectric permittivities of the complex medium adsorbate/adsorbent during dehydration are needed. Very few data are available in literature and values given are quite dispersed, depending strongly on the solid characteristics. Dielectric properties of the zeolite 13X used by Roussy et al., (1984) vary from 3.7 to 2.6 for \( \varepsilon_r' \) and from 0.6 to 0.35 for \( \varepsilon_r'' \) during dehydration, leading to penetration depth values, calculated from equation 6, ranging from 12.53 to 17.98 cm. But depending on crystal water and ion content, zeolites can allow penetration depth from 10 to 100 cm (Bathen, 2003).
The temperature was measured inside the zeolite NaX bed at several axial and radial positions and moderate variations of about 20% were observed, justifying in a first approach, the use of this simplified model. The typical mean values used for parameters are: $C_{pg} = 1.028 \text{ kJ/kg/K}$; $C_{p\text{zeolite}} = 1 \text{ kJ/kg/K}$; $\Delta H_{\text{des}} = 76 \text{ kJ/mol of water}$; $C_{pw} = 4.18 \text{ kJ/kg/K}$, corresponding to the heat capacity of liquid water, the adsorbed water being in a condensed phase. The heat transfer coefficient was experimentally evaluated in our system by analysis of the cooling of the dry bed. Depending on the level of temperature reached, heat transfer coefficient values varying from $5 \text{ to } 10 \text{ W.m}^{-2}.\text{K}^{-1}$ were found to fit well our experiments.

From absorbed power and weight loss curves, the zeolite temperature is calculated as a function of time (Figure 5). Two additional experiments were performed in the same operating conditions in order to validate our calculations: the first one, with the optical fiber placed in the center of the zeolite bed in order to reach experimentally the zeolite temperature and the second one, with an infra-red thermometer placed above the bed, measuring the surface temperature of the zeolite bed. The optical fiber technology does not allow measurements above 250 °C explaining why the first experiment was stopped before end.

The infra-red thermometer was calibrated before use and a linear dependence of zeolite emissivity with temperature was taken into account. Figure 5 shows a good agreement between the experimental and calculated values. Temperature of the bed increases regularly before stabilisation and a temperature of about $430^\circ\text{C}$ is reached when total dehydration is obtained for the operating conditions of figure 5. In these conditions, 10% of weight loss is reached in 13.5 minutes when the temperature of the bed is only $240^\circ\text{C}$ while a temperature of $300^\circ\text{C}$ is used in the classical thermal process to reach this dehydration level. This result indicates that under microwave radiation, dehydration could be achieved at a lower temperature of the solid bed than in the classical process.

Figure 6 shows the absorbed power distribution between the five terms described by equations 1 to 5. At the beginning of the experiment, absorbed power is mainly used for solid and adsorbed water heating, but desorption quickly becomes dominant, reaching about 50% at its maximum. Gas heating term remains negligible. When dehydration is nearly complete, the zeolite temperature is that all the absorbed power is such transferred as thermal losses. The thermal model used in various operating conditions shows on one hand, that the higher the power density is, the higher the contribution of the desorption term is. On the other hand, the higher temperature of the zeolite reached could lead to its melting. Microwaves are then more interesting when high power density is applied for short intervals.

$$Dp_m = \frac{\lambda_0}{\pi} \left( \frac{1}{2\varepsilon_r \left( (1 + (\tan \delta)^2) - 1 \right)} \right)$$

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'}$$

$$\text{Figure 5. Temperature of the zeolite versus time}\quad P_{abs} = 30\text{W}, \quad m_{\text{dry zeolite}} = 16g, \quad Q_g = 12.82 \text{NL/h}$$

$$\text{Figure 6. Repartition of the absorbed power versus time}\quad P_{abs} = 30\text{W}, \quad m_{\text{dry zeolite}} = 16g, \quad Q_g = 12.82 \text{NL/h}$$
4. Process Design and Economical comparison

In the classical thermal swing adsorption (TSA) process, the typical dynamic quantity of desorbed water, representing the mass of adsorbed and desorbed water during each cycle is 10% of the dry solid weight (water content of the bed oscillates between 25% to 15%). The regeneration step uses 5% molar (and sometimes up to 20%) of the dry natural gas produced. This gas is preheated from 30°C to 300°C before regeneration which operates at 30 bars. Based on the methodology described in Campbell, (1984), Chapter 19 « Adsorption Dehydration », typical energy consumption of this TSA process is: 20300 kJ/kg of desorbed water. Based on our experimental results presented in Section 2, Table 2 gives energy consumptions for several power densities applied in the microwave process. The corresponding residence times and energy savings are also reported.

Table 2. Energy consumption of the microwave process for a water dynamic quantity of 10% w/w

<table>
<thead>
<tr>
<th>Power Density (kW/kg dry zeolite)</th>
<th>0.75</th>
<th>1.69</th>
<th>2.26</th>
<th>8.92</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy consumption (kJ/kg desorbed water)</td>
<td>17007</td>
<td>13693</td>
<td>12195</td>
<td>11600</td>
</tr>
<tr>
<td>Residence time (min)</td>
<td>38.0</td>
<td>13.5</td>
<td>9.0</td>
<td>2.2</td>
</tr>
<tr>
<td>Energy savings (%)</td>
<td>16.0</td>
<td>32.5</td>
<td>39.9</td>
<td>42.8</td>
</tr>
</tbody>
</table>

From these results, it can be concluded that using microwave technology in the dehydration process of zeolite can lead to important energy savings if high power densities can be applied. In addition, gas consumption can also be reduced considerably (from 30 to 10 times) since under microwaves, gas is only required for the good draining of the desorbed molecules. Calculations performed at higher dehydration levels (until 15% w/w of water dynamic quantity) lead to even lower energy consumptions suggesting even better performances for further levels of dehydration. The volumetric character of the microwave heating coupled to good adsorbing properties of the system lead to a better use of the energy inside the solid as indicated by the thermal balance model. Energy is mainly used for desorption and to a lesser extent for solid heating. The final temperature of the bed is then lower compared to the classical process. Inside the particle, heat flow is in the same direction as the mass flow leading to better desorption and transport efficiencies. The higher the power density applied is, the shorter the residence times and lower energy consumptions are. Nevertheless, high power densities require a powerful magnetron or reduce the reactor capacity of treatment. In addition, overheating of the solid and thermal runaway can occur due to local enhancement of the dissipated energy. A power density of about 2.2 kW/kg of dry zeolite appears as an optimum value in our case.

In order to extrapolate these results to an industrial scale, a technical solution could be to work in a continuous mode on the solid phase. Several reasons can be given: a) the need of a high power density; b) short residence time; c) magnetron maximum power available (about 50 kW). By applying microwave irradiation on a circulating bed of solid or a fluidised bed, residence times of several minutes could be respected and large quantities of solid could be regenerated. The main difficulty remains in the microwave cavity design and scale up. Large quantities of zeolite used in a classical TSA process (typically about 30-40 tonnes per bed) require the conception of larger microwave reactors and larger applicators. Multimodal microwave applicators have been designed and are already used in pilot plants (Internet references) for industrial applications. The wave guide is equipped with slots of a precise size and the multimode cavity is a well designed shape in order to obtain as homogeneous an electromagnetic field as possible. The role of the moving solid bed is preponderant and helps in preventing hot spots formation. Such a design requires further investigations on dielectric characterisation of adsorbent systems, depending on the shape and structure of the adsorbent, structure of the bed, adsorbate contents and temperature as well. Electromagnetic modelling of the field needs to be coupled to a local mass and heat transfer model at the pores scale for a better understanding of the dehydration mechanisms under microwave irradiation and a good prediction of the adsorbent/adsorbates couple for which a microwave process could be worthwhile developing.
5. Conclusion

The use of microwave technology for regeneration of zeolite NaX at an industrial scale appears to be of potential economical interest, especially in a context of global energy consumption reduction and limiting of the production of gases responsible for the greenhouse effect. The microwave process is particularly interesting when high power density is applied on short residence times. Major savings could be achieved by reducing not only the global energy consumption but also the purge gas flowrate and the levels of temperature reached. With respect to the available maximum power of magnetrons, one of the technical solutions to scale-up of a microwave process could be to work in a continuous mode on the solid phase. The main difficulty remains in the microwave waveguide and applicator design which requires further investigations on dielectric characterisation of adsorbent systems.

Notations

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_{gas}$</td>
<td>Gas flowrate (kg/s)</td>
</tr>
<tr>
<td>$C_p$</td>
<td>Heat capacity (kJ/kg/K)</td>
</tr>
<tr>
<td>$T_s$</td>
<td>Outlet temperature (K)</td>
</tr>
<tr>
<td>$T_i$</td>
<td>Inlet temperature (K)</td>
</tr>
<tr>
<td>$m_{zeolite}$</td>
<td>Zeolite bed weight (kg)</td>
</tr>
<tr>
<td>$m_{zeolite, dry}$</td>
<td>Zeolite dry bed weight (kg)</td>
</tr>
<tr>
<td>$m_w$</td>
<td>Weight of adsorbed water (kg)</td>
</tr>
<tr>
<td>$P_u$</td>
<td>Power used for (W)</td>
</tr>
<tr>
<td>$\Delta H_{des}$</td>
<td>Water enthalpy of desorption (kJ/kg)</td>
</tr>
<tr>
<td>$t$</td>
<td>Time (s)</td>
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</table>

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$h$</td>
<td>Global heat transfer coefficient (W/m²/K)</td>
</tr>
<tr>
<td>$A$</td>
<td>Heat exchange surface (m²)</td>
</tr>
<tr>
<td>$D_p$</td>
<td>Penetration depth in the material (m)</td>
</tr>
<tr>
<td>$\lambda_0$</td>
<td>Wave length in vacuum (m) = 0.1224</td>
</tr>
</tbody>
</table>

Subscripts

- $g$: Gas
- $zeolite$: Zeolite
- $w$: Adsorbed water
- $amb$: Ambient

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