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## Reversibility studies of clay hydration degree in its natural and composite condition

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### Abstract

In this work, the regeneration of desiccant compounds materials was studied after of its adsorption capacity. Also, reuse of the materials was evaluated after progressive regenerations. For this, the effect of regeneration temperature on adsorption capacity of the desiccant compounds materials was analyzed. For the tests adsorption of water a certain amount of dry sample was placed in a desiccator at 98% RH and 298 K, until reach the time of equilibrium, in which the final weight was recorded. In order to check the reversibility of the process re-adsorption studies were performed with water. To do this, before starting the second adsorption cycle, the same portion of sample was dried again to release the adsorbed water (drying temperatures: 343 K and 373 K). Later was proceeded similarly to first adsorption cycle. After to this procedure was reiterated 5 times the test results showed no significant decrease in the efficiency of the material when the samples were regenerated at 373 K. In this way, was possible to maintain approximately constant the hygroscopic characteristics of the material. From the results it was determined that the optimum temperature of drying for the regeneration process is to the corresponding to 373 K since at this temperature the rate of desorption of water is facilitated, which allows to adapt the material in order to initiate a new cycle, being in evidence a good behavior of the material in reversibility

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## 1. Introduction

The control of humidity is important for achieving adequate levels of comfort during the development of human activities in general and business in particular. Moreover various industries require humidity control. Conventional processes that controlled humidity use desiccant materials. These are dehydrating agents which adsorb vapor of water from the atmosphere. One advantage of use of desiccant materials in adsorption processes is its ability to be regenerated. The step of adsorbent regeneration is very important in adsorption processes because it reduces the operating costs of the overall process, and determines the feasibility of the adsorption process. The purpose of regeneration is returned to the saturated adsorbent material its original drying capacity by removing molecules of water adsorbed on its surface, but with the least possible disruption of chemical, physical or textural properties of the material. Desiccants regeneration is often performed by heat treatment [Clausse et al. (2008)]. However, disadvantages are presented. After thermal regeneration, the material must go through a process of grinding and sifting according to grain size of selected job. This manipulation of the solid material leads to despondency of material and assumed losses. Another disadvantage is the energy consumption, although any type of oven is suitable for regeneration.

In recent decades many types of porous desiccants adsorbents such as activated carbons, silica gel, zeolites, etc have been investigated [Cortes Correa (2009), Le Bec et al. (2010), Yang (2003)]. These materials are capable to adsorb physically a significant amount of water at room temperature. Alternatively new types of adsorbents clay have been developed [Bulut et al. (2009), Castrillo et al. (2013), Thoruwa et al. (2000), Mekhamer, (2011)]. The scientific interest of these materials is due to their physicochemical properties, which result from its small particle size and its ability to exchange ions. Moreover they are able to accommodate molecules into the interlayer space, showing a considerable chemical activity on the surface of the sheets and physical changes of the laminar structure, such as swelling, which are reversible [Bergaya et al.(2006)]. Desiccant compounds consisting of porous physical adsorbents and hygroscopic salts have better characteristics than common physical adsorbents. A common method to preparation of these adsorbent compounds is mechanical mixing [Castrillo et al. (2013)]. The used porous matrix are mostly clays, silica gel and zeolites. During the mixing process, the hygroscopic salt is dispersed in the pores of the adsorbent without agglomeration. A portion of the salt is deposited into the pores, and the rest on the external surface of the matrix. Both processes are important for the composite material due to the salt into the pores exhibits lower hydration pressure than bulk salt which favors the adsorption in the composite material [Cortes Correa (2009)]. Thus, the importance of the composites materials is that the favorable properties and characteristics of the constituent materials are combined when the composite material is prepared correctly. Previous studies indicate that adsorption of water on the bentonite presents a considerable increase when the content of Calcium in the clay material is increased up to 15%, by mechanical mixing [Castrillo et al. (2013)]. The bentonite was called BR-15-m, which reached 1.3 g water / g adsorbent at 98% RH and 298 K, higher than reported in the literature [Cortes Correa (2009), Bulut et al. (2009), Thoruwa et al. (2000), Montes-Hernandez et al. (2004)].

In this paper the degree of reversibility of materials with hydrophilic characteristics were studied, in order to determine the performance and establish conditions for regeneration.

## 2. Experimental

For this study, a natural bentonite, designated BR, with high smectite content was selected as desiccant material [Castrillo et al. (2012)] and a composite material prepared from BR and a hygroscopic salt of Calcium, called BR-15-m, which was previously studied for their preparation and their optimal adsorption characteristics [Castrillo et al. (2013)]. A preliminary step of grinding and screening was performed until a particle size <100 mesh. Finally, the adsorbents were dried in oven at 343 K and stored in a desiccator until use.

The nomenclature used for the regenerated samples was specified in Table 1 and corresponded to the name of the desiccant material, followed by an indication of the number of saturation and regeneration cycles.

Table 1. Nomenclature used for regeneration of studied desiccants.

Desiccant	N° cycles of saturation	N° cycles of regeneration	Nomenclature
BR	i saturations (Ci) (i= 0, 1, ...6)	j regenerations (Rj) (j= 0, 1, ...6)	BR Ci Rj
BR-15-m	i saturations (Ci) (i= 0, 1, ...6)	j regenerations Rj (j= 0, 1, ...6)	BR-15m Ci Rj

The water adsorption tests were carried out in closed systems at 298 K and 98% RH. The value of RH desired was obtained with a saturated solution of  $K_2SO_4$ . The test consisted of placing a certain amount of sample in the desiccator with appropriate RH. The amount of adsorbed water was determined by periodic weights until to obtain constant mass [Spanish rule UNE-EN ISO 12571 (2000)]. Equation (1) describes the calculation of the relative amount of adsorbed water (g / g).

$$m_e (gg^{-1}) = \frac{m_e - m_s}{m_s} \quad (1)$$

where  $m_e$  represents the weight of the wet sample (g) in the equilibrium and  $m_s$  represents the weight of the dry sample (g).

When adsorption equilibrium was reached, thermal regeneration tests at 343 K and 373 K were carried out. The treatment was performed until constant mass, obtaining the regeneration of the desiccant material by desorbing water. The residence time of the materials at each temperature, necessary to achieve the first regeneration (24 hours) was used as a parameter for subsequent regenerations, in order to compare the obtained results. Once the sample was regenerated, five successive cycles of adsorption-regeneration were performed under the same conditions described above, showing the effect on the adsorption capacities of the material after the different cycles.

The specific surface was determined from the nitrogen adsorption isotherms at 77 K on a Micromeritics ASAP 2020 analyzer. Before nitrogen adsorption, the samples were subjected to a process of degassing at 343 K in vacuum. For the treatment of the data and calculation of specific surface, the equation given by Brunauer, Emmett and Teller was applied.

### 3. Result and Discussion

Determination of time that sample took until to be saturated was important to finish the adsorption cycle and begin the regeneration cycle. In Figure 1, water adsorption in function of time was performed. It showed precisely how adsorption was happening. It was observed that at about 96 hours the samples were saturated with water.

The adsorption for modified bentonite was higher than natural bentonite, as expected, because of hydrophilicity increase. The amount of adsorbed water increased fastly in the first 24 hours. At the beginning, the sample was effective because the surface area, which was in direct contact with vapor of water, was the first to become saturated. Then the water molecules had to go beyond of that area of the saturated solid to adsorption could occur. The maximum amount of vapor of water adsorbed to 98% RH and 298 K was 0.34 and 1.36 g / g for natural bentonite BR-C1-R0 and modified bentonite BR-15-m-C1-R0, respectively.

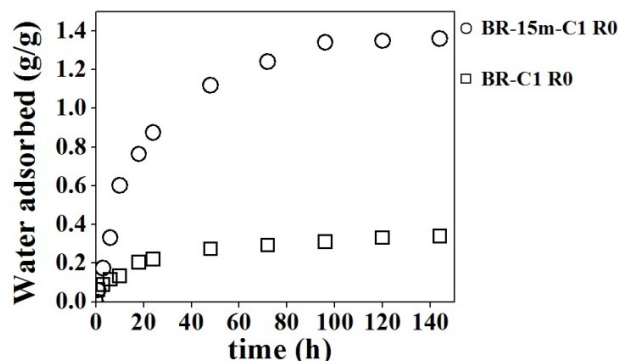


Fig. 1. Water adsorption progress in samples respect to time at 98% RH for natural BR and modified BR-15-m samples.

Most water retention capacity by sample BR-15-m-C1-R0 could be attributed at least two different adsorption processes: an adsorption process provided by the clay material which implied interactions with surface charges and hydration of interlaminar natural cations, in which hydration decreased in the following order:  $\text{Ca}^{2+} > \text{Na}^{+} > \text{K}^{+}$  [Dios Cancela et al. (1997)]. The other adsorption process would involve the  $\text{CaCl}_2$ -clay composite material, in which the adsorption of water was favored by the dispersion of the salt in the adsorbent surface. Moreover, the crystal size of hydrate suitable for the pore size of the material, would allow the growth of such crystals by adsorbing water molecules, resulting a favorable hydration process [Cortes Correa (2009), Tretiak et al. (2009), Tokarev et al. (2002)].

Figure 2 showed the evolution of water adsorption observed in the materials after being regenerated five consecutive times, using drying temperatures of 343 and 373 K.

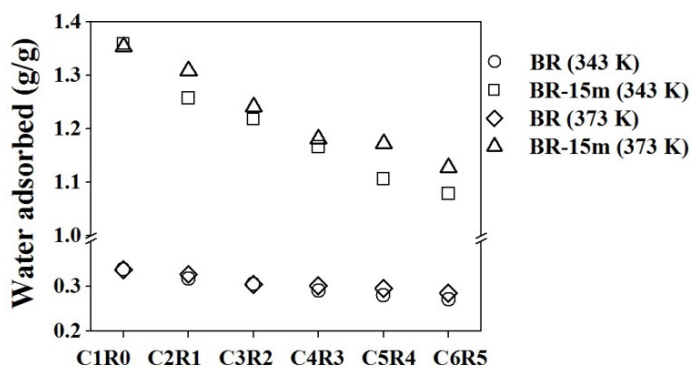


Fig. 2. Thermal regeneration effect at 343 and 373 K on water adsorption in the samples at 98% RH (Ci: adsorption cycles, Ri: number of regenerations).

The material BR-15-m had a higher hydrophilicity, as shown in figure 1, so the amount of vapor of water released during the heat treatment was much greater than untreated bentonite, BR. Considering the processes that occur during heating of the materials was feasible that internal rearrangements occur in addition to partial drying as a result of removing of water molecules adsorbed on the surface. Evaporation of water occurred throughout the material and vapors diffused outside through the porous structure of material. When the volume of vapor of water was very large, vapor pressure generated produced the rupture of the walls of the material, resulting in degradation of them. It would alter the porous structure comparing with the starting material, leading to the formation of structures that would block the access to the pores causing a narrowing in porosity of treated material.

The desorption process at 343 K induced a greater decrease in adsorptive capacity compared to desorption at 373 K after 1 cycle of adsorption, because in the samples the rate of desorption of water were not favored, increasing the amount of water for the beginning of each cycle.

For the sample BR-15-m, a greater reduction in the adsorption process after regenerations was observed, due to the large volume of released vapor. Instead, the sample BR maintained very similar drying properties to the starting material, regardless of the regeneration temperature, because the volume of vapor released during the successive heat treatment was small because of the less amount of adsorbed water.

In Figure 3 the percentages of reduction in the adsorption of regenerated material to 343 and 373 K depending on the adsorption-regeneration cycles were observed. Considering a regeneration temperature, either 343 K or 373 K, with increasing of regeneration cycles, the adsorption capacity of water decreased in case of natural and modified bentonite, although this increase was less evident in the first case.

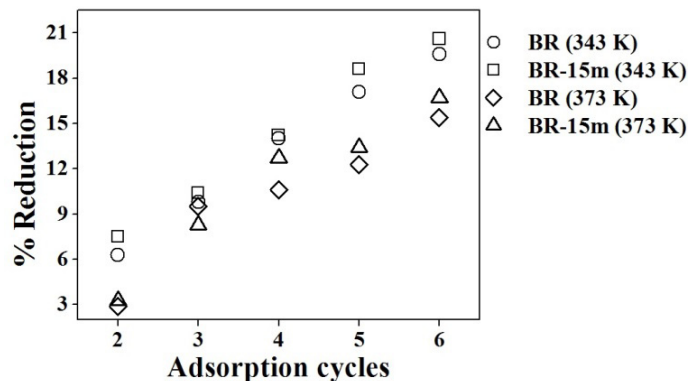


Fig. 3. Percentage of reduction in the adsorption of regenerated materials at 343 and 373 K depending on the adsorption cycles.

It would imply the samples showed ever smaller percentage of accessible pores to vapor of water, probably because water removal did not occur quantitatively. Similarly, the adsorption process was less obvious for the regeneration of natural bentonite comparing with modified bentonite; it would mean natural bentonite retained more weakly the molecules of water.

This result was consistent with the behavior observed before in the adsorption for these materials [Castrillo et al. (2014)]. Moreover, considering a particular sample, the percentage of reduction when the regeneration was performed at 343 K was greater than 373 K, because of the process of releasing of vapor of water would occur to a greater extent 373 K reducing the amount of water for the beginning of each cycle.

Figure 4 showed the isotherms of adsorption / desorption of  $N_2$  of the starting and regenerated materials. Taking into account the classification of the IUPAC isotherms, all materials exhibited type IV isotherms.

From the obtained data, the addition of  $CaCl_2$  led to a decrease of the volume of  $N_2$  adsorbed and therefore, a decrease in specific surface due to the occlusion of pores of the clay material by the  $CaCl_2$ .

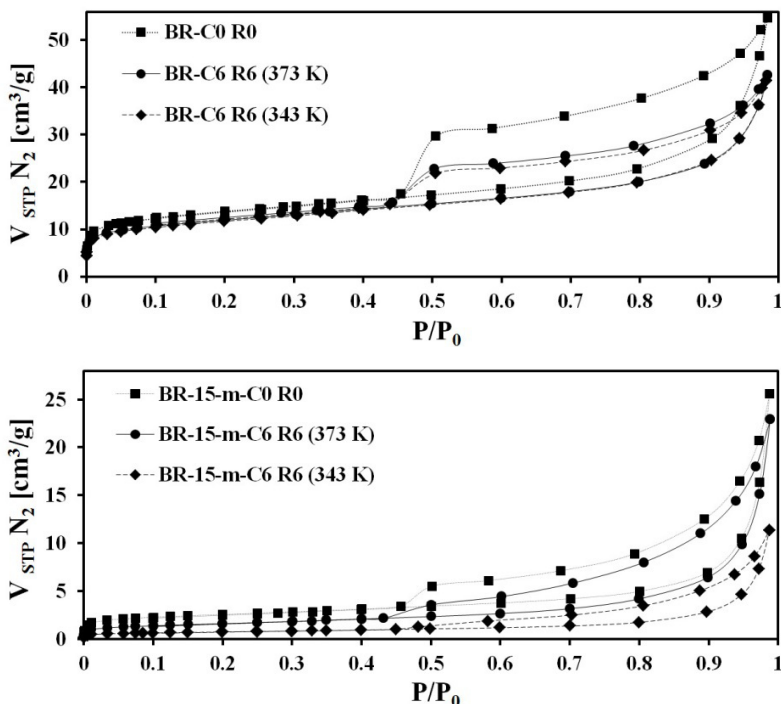


Fig. 4. Adsorption / desorption of  $N_2$  (a) of starting and regenerated materials 343 y 373 K.

Also, regeneration produced a decrease of the specific surface comparing with the starting material, which would indicate a decrease of pore volume because the pores would be occupied by molecules of water. When the temperature of regeneration was low the surface area decreased (Table 2), which negatively affected the physisorption of water. The specific surfaces obtained applying the BET method were shown in Table 2.

Table 2. Specific surface of starting and regenerated materials obtained from the  $N_2$  adsorption/desorption isotherms.

Desiccant	$S_{BET}$ ( $m^2/g$ )
BR-C <sub>0</sub> R <sub>0</sub>	45
BR-C <sub>6</sub> R <sub>6</sub> (373 K)	43
BR-C <sub>0</sub> R <sub>0</sub> (343 K)	42
BR-15 m - C <sub>0</sub> R <sub>0</sub>	9
BR-15 m - C <sub>0</sub> R <sub>0</sub> (373 K)	6
BR-15 m - C <sub>0</sub> R <sub>0</sub> (343 K)	3

In the modified samples with Ca water molecules were adsorbed more strongly. It would imply that in regeneration process, thermal energy was not enough to remove such water molecules, resulting in a further decrease of the surface respect to the natural sample.

#### 4. Conclusions

The drying capacity of the materials varied depending on initial water content in the samples at the beginning of each cycle; because of regeneration was not 100% effective, drying capacity slowly decreased after successive regenerations.

After fifth regeneration cycle at 343 K, the adsorption was reduced by 15% and 17% in BR and BR-15-m samples, respectively, based on the drying capacity of the first adsorption cycle (0.34 g water / g material and 1.36 g water / g material).

Thermal regeneration of materials depended on the nature of the adsorbent and regeneration temperature (343 or 373 K). In this sense, thermal desorption in natural bentonite was maintained approximately constant regardless of the regeneration temperature.

Analysis in progress will allow to continue with the evaluation of influence of the thermal regeneration in the characteristics of the starting materials.

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