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Sorption Water By Modified Bentonite

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Abstract

In order to improve adsorptive properties and provide a viable alternative to humidity control techniques, the desiccants can be modified with chemical aggregates such as calcium chloride (CaCl_2), the latter often used as dehydrating due to its hygroscopicity and low cost. Its use as a drying agent has disadvantages because of its particles form a liquid film. However, the CaCl_2 may be mixed with other materials for preparing desiccant products. In this work we studied, at 298 K and different relative humidities (RH), the adsorption processes of desiccants mixtures composed of a bentonite clay Argentinian and CaCl_2 . The results showed a better performance of the desiccant mixture with respect to natural clay in the whole HR working range. It was also observed that addition of CaCl_2 favors adsorptive properties with respect to a purification treatment.

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1. Introduction

The application of desiccants as a viable alternative to traditional techniques of humidity control had received considerable attention in recent years. Many solids such as activated carbon, silica gel and molecular sieve, although potentially useful, were considered unsuitable due to the high cost and high temperatures of regeneration. Molecular sieve was unsuitable due to its lower hygroscopicity (Aldis et al., 1980; Tomilson and Miller, 1981). Therefore the

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water adsorption in clays in controlled conditions of RH had received considerable attention in recent years. When the sheets of expandable clays had been balanced with water vapor by increasing of RH, a successive adsorption of water in layers was observed. It was deduced from the shape of the adsorption isotherms and from changes of certain features of the patterns of X -ray diffraction related with basal spacing (Montes-Hernandez and Geraud, 2004; Dios Cancela et al., 1997). Thus, these materials were potentially important to use as a desiccant due to its high adsorption capacity. They could be improved by purification and addition of chemicals such as CaCl_2 to obtain desiccant mixtures of higher hygroscopicity and higher stability (Thoruwa et al., 2000). In this work it is studied the effect of purification and modification of a bentonite from Argentina with CaCl_2 in humidity retention, in order to evaluate the conditions for improving the desiccant capacity.

2. Experimental

It was used a natural bentonite from the province of Neuquén, called BQ. The purified clay fraction (<2 microns), called BQp, was obtained by sedimentation according to Stokes' Law. Both samples, BQ and BQp, were characterized in previous studies (Castrillo et al., 2012) which were summarized in the results section. Natural bentonite was modified by addition of CaCl_2 by mechanical mixing and maintaining a ratio of 5, 10 and 15 grams of Ca^{2+} per 100 grams of clay. The obtained mixtures were named BQ 5, BQ 10 and BQ 15, respectively.

The tests were carried out at 298 K in closed systems at 11, 33, 56, 75 and 98 % RH. RH desired values were obtained with saturated salt solutions LiCl (11%), MgCl_2 (33%), $\text{Mg}(\text{NO}_3)_2$ (56%), NaCl (75%) and K_2SO_4 (98%). BQ 5, BQ 10 and BQ 15 were pre-dried at 343 K for 24 hours. The test consisted of placing 0,500 g of sample into the appropriate RH desiccator. The amount of adsorbed water was determined by periodic weight until to obtain constant mass (ISO 12571, 2000). Calculation of the amount of adsorbed water (g/g) was determined from the equation:

$$\text{Adsorbed water} \left(\frac{\text{g}}{\text{g}} \right) = \frac{(m_e - m_s)}{m_s} \quad (1)$$

where m_e represented the weight of the wet sample (g) in the equilibrium and m_s represented the weight of the dry sample (g). Knowledge of the amount of adsorbed water for each RH allowed plotting the adsorption curve.

As to the desorption curve, starting point corresponded to the amount of adsorbed water in the samples at 98% RH. This value corresponded to the last point of the adsorption curve. Then, the samples were placed successively in a series of test environment with stepwise decreasing RH (i.e. at 56% RH and then at 11% RH). The water content was determined when equilibrium was reached with each environment. The knowledge of water content for each RH allowed to plot the desorption curve.

3. Result and Discussion

The results of analyzes by X-ray diffraction indicated that the BQ sample contained smectite as majority mineral. (Fig. 1).

Between the phases associated with the smectite (E), it was included quartz (Q), gypsum (Y) and feldspar (F) as impurities. It was observed that the purification treatment enriched clay content in the sample.

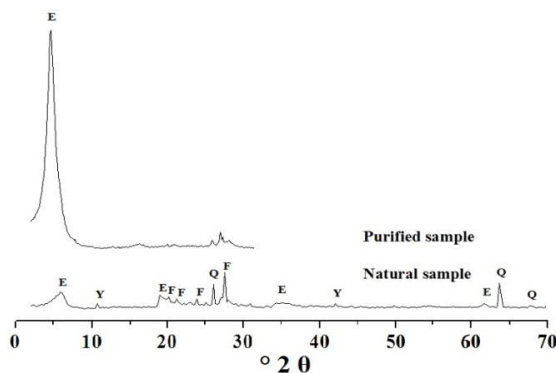


Fig. 1. Mineralogical composition of natural and purified sample.

Likewise, the chemical composition of the adsorbent materials was determined (Table 1). It was observed that the results obtained for the natural sample and the clay fraction were closed to literature values reported for smectites (Dolinar, 2012).

Table 1. Chemical analysis of the studied adsorbents.

Oxides	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	TiO ₂	LOI
BQ (%)	62.67	16.60	5.78	0.04	2.02	2.66	3.09	1.00	0.11	0.63	5.42
BQ 5 (%)	53.11	14.18	5.55	0.03	1.54	4.44	2.23	0.78	0.08	0.65	17.41
BQ 10 (%)	45.66	11.12	4.77	0.03	1.38	6.16	2.16	0.68	0.05	0.57	27.44
BQ 15(%)	41.20	10.45	4.14	0.02	1.24	7.78	1.68	0.59	0.07	0.49	32.35
BQ p (%)	56.67	16.42	6.43	0.03	1.89	1.36	3.48	0.71	0.13	0.69	12.20

As expected, the % CaO of the mixtures was increasing from 2.66 for natural sample to 7.78% for the sample with the highest amount of CaCl₂ added. Chemical analysis showed a higher content of CaO in the natural sample in relation to the purified sample, which could be attributed to the gypsum impurities found by X-ray diffraction. As to the ignition loss (LOI) there was a significant difference between BQ and BQp. The mixtures had higher LOI values which would be related to its character of calcic bentonites.

To check how much Ca²⁺ ions were incorporated into the clay structure by mechanical mixing, it was put in contact 1 to 2 grams of sample with 20 to 25 mL of distilled water. It was stirred 24 hours and centrifuged at 4000 rpm for 10 minutes. The concentration of Ca²⁺ in the supernatant was determined by atomic absorption. This procedure showed that Ca²⁺ ions added by mechanical mixing were incorporated between 60 and 80% in the clay structure, according to the results reported in Table 2.

Table 2. Calcium exchanged by mechanical mixing vs % Ca added.

	%Ca _{added}	%Ca _{incorporated}
BQ	0	0
BQ 5	5	4
BQ 10	10	8
BQ 15	15	9

The results of progress of water adsorption vs contact time at 56 and 98% RH was shown in Figure 2.

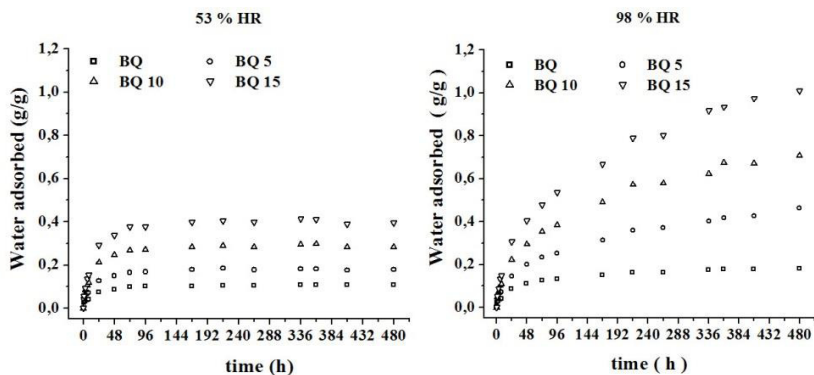


Fig. 2. Progress of water adsorption vs. time in natural and modified bentonite at 53% and 98% RH.

It was observed that the trend of the curves were logarithmic in all cases. The adsorption occurred at a high initial velocity and then declined slowly until reaching the equilibrium, which was reached about 7 days at 56% RH. At 98% RH the equilibrium time was reached after 17 days. However, it was observed a slight increase in adsorption above the 17 days with addition of Ca²⁺, but this increase was negligible for practical purposes. After 17 days, the amount of adsorbed water remained almost constant under the studied conditions. The results from the tests performed to 11, 33 and 75% RH conditions showed a similar behavior to those obtained at 56 and 98% RH. However, at lower RH conditions, equilibrium was reached before. The results of amount of adsorbed water vs % CaO were represented graphically in Figure 3.

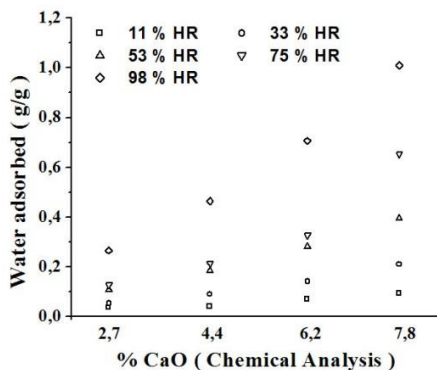


Fig. 3. Adsorption of water vs. % CaO added (determined by chemical analysis) in the adsorbent materials in order to RH studied.

It was observed a trend due to specific interactions in the adsorption centers of the sample surface, where the water molecules were coordinated with different cations and silanol groups. These water molecules would interact through hydrogen bonding with other water molecules producing a significant increase in retention (Mekhamer, 2011).

The results of adsorption of humidity obtained from the comparative tests between the natural, purified and modified samples were shown in Figure 4. The water retention capacity increased substantially with increasing of RH of environment in all samples. After reaching the equilibrium state, BQp and BQ samples achieved a adsorption of maximum humidity of 0.27 and 0.44 g water/g sample respectively, while modified samples, BQ 5, BQ 10 and BQ 15, exhibited a adsorption of maximum humidity of 0.46, 0.71 and 1.01 g water/g sample, respectively.

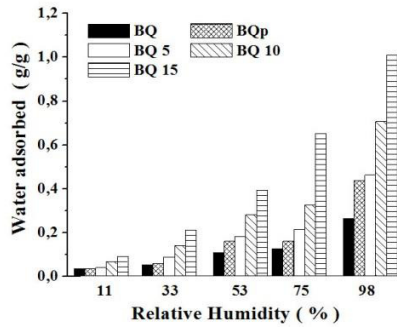


Fig. 4. Water adsorption in natural, purified and modified bentonite in different RH environments.

These results showed a gradual improvement in the drying behavior of the mixtures, with increasing of calcium relative content to the natural and purified samples, which would be consistent with results reported in the literature. In this respect the retention capacity was improved in the Turkish bentonite from 0.059 g/g for the natural sample to 0.238 g/g for the sample with 15% of Ca²⁺ (Bulut, 2009). This can be explained in terms of the interaction of calcium with water compared to other exchangeable cations such as sodium, lithium and magnesium (Thoruwa et al., 2000), although mechanical mixing of the bentonite with CaCl₂ would not involve a full cation exchange.

On the other hand, the main advantage of the drying mixture bentonite - CaCl₂ on CaCl₂ was the formation of liquid films. This effect was produced because CaCl₂ was adsorbed by the support material, i.e. the bentonite.

Consequently, the mixture could be considered as a manipulable desiccant with better efficiency for industrial applications. Because of low cost, drying mixtures could be replaced after a loss of efficiency.

The results of adsorption - desorption tests of water was showed in Figure 5. Not observed large difference between the curves, which would allow reusing the material after desorption, keeping yield grade in the adsorption process.

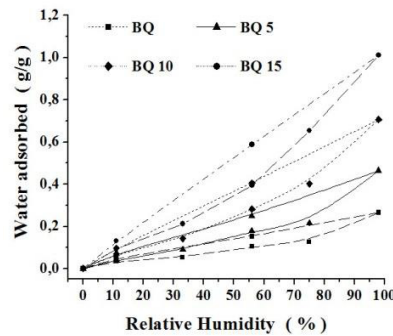


Fig. 5. Adsorption-desorption of water in natural and modified bentonite.

The drying behavior at 80% RH of commercial products such as silica gel and molecular sieve of Desipack signature (Süd-Chemie Performance Packaging) with the samples analyzed in this paper at 75 and 98% RH were compared in Figure 6.

If it was analyzed the behavior of commercial desiccants at 80 % RH respect to the behavior of the studied samples, at lower RH (75 %) the treatment using CaCl₂ was necessary to achieve comparable values of adsorption. At high RH (98%) all samples had higher efficiency of adsorption.

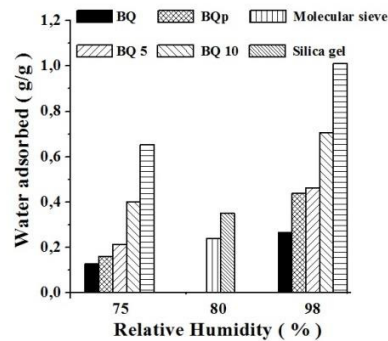


Fig. 6. Water adsorption in commercial desiccant and natural, purified and modified bentonite.

Therefore, it was observed that high RH conditions of the purified sample were more efficient in adsorption when they were treated with CaCl_2 than using commercial desiccants.

4. Conclusions

It was possible to obtain mixtures which had good behavior as desiccant using bentonite and CaCl_2 as starting materials. Natural bentonite modified with a subsequently addition of 5, 10 and 15% of Calcium and the purified bentonite (BQ, BQp BQ 5, BQ 10 and BQ 15) achieved a maximum absorption of humidity of 0.27, 0.44, 0.46, 0.71 and 1.01 g water/g sample, respectively.

Desiccants mixtures were obtained by simple mechanical mixing. This could played an important role in the ability to industry-level applications that required desiccants in quantity and whose price was determined more by the preparation process than by the price of raw materials.

The results indicated a close relationship between the drying power and purity of the clay mineral. However, the treatment of calcium added enhances the drying behavior more than a purification treatment.

Subsequent analysis will allow to continue a more detailed study about physicochemical aspects of clay- CaCl_2 mixtures in relation to their drying capacity. The regeneration process of the material will be investigated to estimate the life cycle of these drying materials.

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