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MOISTURE DESORPTION ISOTHERMS AND THERMODYNAMIC CHARACTERISTIC OF PREHYDRATED AND EXTRUDED GCL

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Abstract: An experimental investigation into the drying of pre-hydrated and extruded GCL is presented in this paper. Moisture desorption isotherm at temperature from 20 to 40°C and water activity from 0.20 to 0.70 were determined using the static gravimetric method. The moisture isotherms were sigmoid shaped and were influenced by the thermal environment. The Guggenheim-Aderson-DeBoer (GAB) was used to fit experimental values using a non-linear regression analysis. GAB model was appropriate to predict the desorption equilibrium moisture content of pre-hydrated and extruded GCL for the range of temperatures and water activities studied. Finally, an expression for predicting the thermal property was developed.

1. Introduction

Geosynthetic Clay Liners (GCLs) are sealing elements and commonly known as factory-manufactured contaminant / leachate / fluid barriers that consist of a thin layer of either calcium or sodium bentonite core sandwiched between two geomembranes or geotextiles.

Over the past decade, design engineers and environmental agencies have developed a growing interest in the application of GCLs as an alternative / preference to compacted

clays in cover systems or as bottom lining of waste containment facilities. They have also gained widespread use in a variety of sealing applications, predominantly in hydraulic engineering, structural water proofing and groundwater protection.

In order to meet the potential to be an effective contaminant barrier in hostile geochemical environments, a factory controlled prehydration with cation exchange resisting polymer is added to an appropriate manufacture moisture condition. This prehydration of GCLs prior to

installation is always necessary (McLoughlin, 2004, Wijeyesekera, 2003). It is also critical that the consistency of the bentonite core is preserved to ensure that the prehydrated GCL remains flexible in order that there will be reduced possibility of it drying and consequently developing brittle fractures when exposed to a hostile thermo-environmental condition.

The knowledge of the desorption isotherm, which represents the relation at a fixed temperature between the moisture content of the product and the water activity is essential in the study of drying. The thermodynamic analysis of these isotherms makes it possible to determine the energies involved during the process which help to comprehend and control the drying of the prehydrated GCL.

To this end, the aims of the present study are to determine the desorption isotherms of two sets of prehydrated GCL at three temperatures, to fit the data with suitable models and evaluate the thermodynamic properties, which is a basic parameter for moisture retention determination.

2. Mathematical Models

Numerous models have been developed and studied for the prediction of the relationship between equilibrium solid moisture content, water vapour pressure and temperature. These models can be theoretical, semi-

theoretical or empirical. The choice of a suitable model depends on a certain number of factors.

Past literature helps to define desorption isotherms as the relationship between the equilibrium water content of a given material and the water activity or relative humidity at a certain temperature. In principle, desorption isotherms are obtained by maintaining the sample at a given temperature, under a partial pressure of constant water vapour until thermodynamic equilibrium is reached.

The Guggenheim-Anderson and de Boer (GAB) model is more appropriate and often used to describe the sorption isotherms of clay (Mihoubi et al, 2002). The general expression of this model is:

$$w = \frac{w_m C K A_w}{(1 - K A_w)(1 - K A_w + C K A_w)} \quad (1)$$

where w is the material moisture content; A_w is the water activity; w_m , K and C are three constants to be determined.

3. Materials and Methods

2.1. Sample Preparation

Two sets of specimens, namely PA and PB were used in the experimental measurements. PA and PB were formed with the addition of distinctively different

liquid polymers; A and B with a maximum moisture of 40% (d.b.), and vacuum extruded to a thickness of 5 mm. One of the primary purposes of the liquid polymer treatment is to lower water activity and improve the mechanical properties of the sample. Discussion of these polymers is beyond the remit of this paper.

Five circular samples approximately 100mm in diameter were cut from each of the extruded sections using a stainless steel ring and removed using an extractor for each test.

2.2. Desorption Isotherm Measurements

The equilibrium moisture content (EMC) of specimens PA and PB were determined using the standard gravimetric technique, in which the weight was monitored discontinuously with an analytical balance with an accuracy of ± 0.001 g.

The samples of the specimens under investigation were kept in an environmental chamber at constant relative humidities of 20, 30, 40, 50, 60 and 70% ($\pm 1.5\%$) and for each of these the temperatures were maintained at 20, 30 and 40°C ($\pm 1^\circ\text{C}$). The samples were weighed continuously and allowed to equilibrate over a period of one to two weeks, depending on the sample. The equilibrium was considered reached when a constant weight was obtained (± 0.001 g). The dry mass was determined

gravimetrically after drying in a convectional oven at 105°C for 24 hours.

2.3. Experimental Results:

Figures 1 and 2 contain, respectively, the experimental desorption isotherm of specimens PA and PB at temperatures of 20, 30 and 40°C. Figure 3 presents the information on the same graph, for the purpose of comparing the two desorption isotherms of specimen PA and PB at 30°C. In these figures, m is the moisture content of the specimen expressed on a dry basis (kg water per kg of dry clay) and A_w is the water activity, defined as the ratio of the partial pressure to the saturated vapour pressure at the temperature of equilibrium and defined as:

$$A_w = \frac{P}{P_0} \quad (2)$$

It is noted from these figures that: (i) the isotherms are of the normal S-type following the Brunauer (1945) classification, (ii) the EMC of both specimens decreases with increasing temperature, (iii) the EMC of specimen PA varies from 0.0 to 0.18 kg.kg^{-1} , but for specimen PB varies from 0.0 to 0.31 kg.kg^{-1} , (iv) for a given temperature, a notable difference exists between curves of specimens PA and PB (Figure 3). The last

observation may be explained by the higher polarity of water molecules and the tendency for better hydrogen bonding. This implies that desorption of moisture from specimen PB may be more difficult than from specimen PA. As a consequence, the physical desorption of moisture is reduced. This effect is uniquely responsible for the plasticizing properties of polymer B.

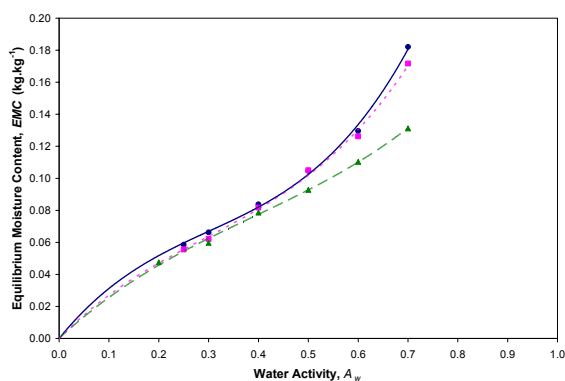


Figure 1 Experimental desorption isotherm of specimen PA (● = 20°C, ■ = 30°C, ▲ = 40°C).

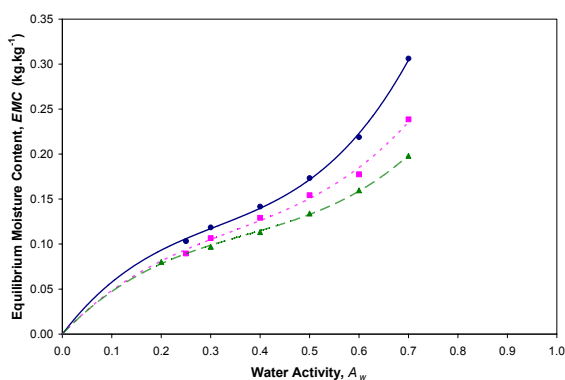


Figure 2 Experimental desorption isotherm of specimen PB (● = 20°C, ■ = 30°C, ▲ = 40°C).

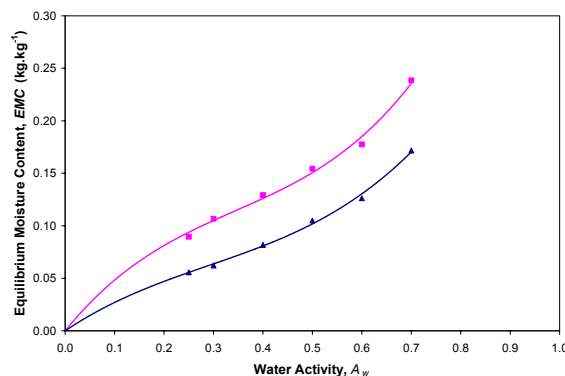


Figure 3 Desorption isotherm of specimen PA (▲) and PB (■) at 30°C

3. Thermodynamic Analysis

3.1 Modelling of Desorption Isotherm

The parameters for the selected GAB equation were estimated by non-linear least squares regression analysis. To evaluate the ability of the GAB model to fit the experimental data, the mean relative percent error (P), the standard error (SE) and the coefficient of correlation between the experimental and predicted data (r^2) were determined using the following equations:

$$P = \frac{100}{N} \sum_{j=1}^N \left| \frac{y_{jcal} - y_{jexp}}{y_{jexp}} \right| \quad (3)$$

$$SE = \sqrt{\frac{\sum_{j=1}^N (y_{jcal} - y_{jexp})^2}{N - n_p}} \quad (4)$$

$$r^2 = \frac{S_t - SCE}{S_t} \quad (5)$$

where

$$S_t = \sqrt{\frac{\sum_{j=1}^N (\bar{y} - y_j)^2}{n-1}} \text{ being } \bar{y} = \frac{\sum_{j=1}^N y_j}{N}$$

and

$$SCE = \sum_{j=1}^N (y_{jcal} - y_{jexp})^2$$

The results obtained are presented in Tables 1 and 2. The fitting of experimental data of both specimens using the GAB model over the chosen temperature and water activity ranges were acceptable for specimen PA ($P = 1.42\%$) and specimen PB ($P = 1.58\%$).

The value of the monolayer moisture content (w_m) obtained by the GAB model is an important parameter. It is regarded as the sorption capacity of the adsorbent and the indicator of available polar sites of binding water vapour. As with the EMC, the w_m of specimen PA increases with increasing temperature whereas for specimen PB it decreases with increasing temperature. The latter phenomenon might be attributed to the water molecules in the vapour state surrounding the sample with their higher kinetic energy at increased temperature resulting in decreased w_m as the temperature is raised.

The value of the K parameter in the GAB equation ranged from 0.7 – 1.0, which may

be an indication that the desorption isotherms of both specimens PA and PB are multilayered. The GAB constant, K , is a parameter that corrects for the properties of the multilayer molecules with respect to the bulk liquid. This constant describes the profile of the isotherm in a high water activity range, thereby regulating the upswing after the plateau in a medium range of water activity.

Table 1 Estimated value of constant and the statistical parameters obtained for sorption model applied to experimental desorption data of PA

Constants	20°C	30°C	40°C
w_m	0.057	0.066	0.075
C	9.8963	5.8282	6.8645
K	0.9954	0.9208	0.7174
$\%P$	1.13	1.72	1.42
SE	0.0024	0.0030	0.0018
r^2	0.9984	0.9973	0.9980

Table 2 Estimated value of constant and the statistical parameters obtained for sorption model applied to experimental desorption data of PB

Constants	20°C	30°C	40°C
w_m	0.098	0.096	0.080
C	21.35	10.51	22.94
K	1.00	0.88	0.86
$\%P$	1.74	2.76	0.25
SE	0.0053	0.0066	0.0005
r^2	0.9985	0.9910	0.9991

4. Conclusion

In this study, desorption isotherms of polymer treated bentonite specimens PA

and PB, in the temperature range 20 – 40°C were determined. The desorption isotherm of both specimens presented a sigmoid shape characteristic, and a clear effect of temperature was observed. For the same temperature condition, specimen PB tends to have a higher water activity at EMC comparable with specimen PA. This implied that polymer B treated bentonite has a higher moisture retention capacity. The GAB model proved to be appropriate for predicting the desorption moisture isotherm for the clay material.

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