The Florite-Water Vapor Sorption Therm

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The sorption isotherms for moist air and Florite were determined at a total pressure of one atmosphere and 75°, 100°, 125°, 150°, 175°, and 200°F. No hysteresis was evident.

An investigation of the sorption isotherms showed that a concentration-temperature coordinate could be identified, which when plotted against amount sorbed, causes all sorption isotherms to collapse into a single sorption therm.

For purposes of sorption curve fitting the concentration-temperature coordinate was incorporated into a version of BET theory. This relation produced an excellent fit of data without resorting to more complicated versions of BET theory.

The concentration-temperature coordinate was also incorporated into a modified version of Langmuir-Hey theory to show that this interpretation also leads to a very satisfactory fit of sorption data.

Some additional observations are made concerning the computerized curve fitting technique as applied to silica gel, the data for which were reported in an earlier publication.

This is another report in a series concerning sorption therms as discussed in an earlier paper (*11*). Previous papers covered silica gel (*8*), Drierite (*11*), Linde molecular sieve 4A (*10*), and activated alumina (*9*). Here we consider Florite.

In the 1947 work of Amero, Moore, and Capell (*1*), very little Florite equilibrium data are given. Eagleton and Bliss (*5*) presented limited Florite equilibrium data along with experimental effluent curves.

Strictly speaking, Florite is a particular bauxite activated by the Floridin Company. In addition to the preceding works which deal with this specific bauxite, several other papers have dealt with activated bauxites generally; it is assumed that these adsorbents should be very similar to Florite in properties, but the differences—if any—between various activated bauxites are not indicated in the literature at the present.

Heinemann, Kreger, and McCarter (*6*) presented a study of the physical properties of activated bauxite. The key findings of this study related to changes in physical properties with temperature of activation. It was found that there are in activation five clearly distinguishable temperature ranges: 1. 100 to 450° F; 2. 450 to 650° F; 3. 650° to 1000° F; 4. 1000° to 1100° F; and 5. 1100° to 1800° F. During the first, third, and fifth of these little, if any, chemical change occurred; between 450° to 650° F and again between 1000° and 1100° F indications were that chemical changes were occurring in the bauxite.

Takizawa (*16*) presented a series of room temperature isotherms for bauxite and a number of other adsorbents. According to Takizawa the bauxite isotherm at 25° C could be described fairly well by the simple BET (*2, 3, 4*) expression

$$\frac{p}{V(p_0 - p)} = \frac{1}{V_m\, C_b} + \frac{C_b - 1}{V_m\, C_b}\, p/p_0$$

It is evident that sorption isotherms have continually aroused interest over the years for reasons that have varied from time to time. However, attempts at analytical fits of these are either incomplete or otherwise unsuccessful.

EQUIPMENT AND PROCEDURE

The sorption isotherms were determined using a dynamic method that involved equipment previously described (*8*). The same three humid air sources were used with laminar flow gages to produce intermediate humidities by mixing.

The 2-4 U.S. mesh Florite was donated by the Floridin Company. It was reduced to 12-16 U.S. mesh for use in the various runs. All samples were regenerated in thin layers in an oven for 14 hr. at 350° F prior to charging the sample holder for use in the sorption runs. The oven was equipped with a blower for forced air circulation.

THE SORPTION THERM

Florite isotherms at 85°, 100°, 125°, 150°, 175°, and 200° F were determined, covering the range of humidity from 20 to 15,140 lb. water/million lb. dry air.* Data obtained are presented in Figures 1 and 2. No hysteresis was observed. A comparison of these data with equilibrium data that are available for Florite and activated bauxite in general shows that these curves resemble the activated bauxite curves of Takizawa (*16*), particularly in regard to the rapidly rising portion evidenced (see Figure 1) at the high adsorption end of the 85° F isotherm and to a lesser extent in the 100° F isotherm. A comparison of these data with Eagleton and Bliss' (*5*) Florite data shows one significant difference: Eagleton and Bliss' curve (measured at 80° F) tends to level out after experiencing a less marked rise than the data of the present study. A comparison of Amero, Moore, and Capell's (*1*) single 70° to 75° F isotherm with the 85° F isotherm of the present study shows the two to be similar except that the curve determined in the present work rises more steeply on the upper end. In the case of Florite, discrepancies between two

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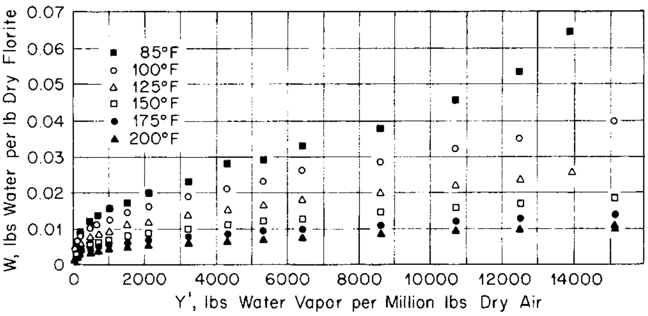

Fig. 1. Florite data: high humidity region.

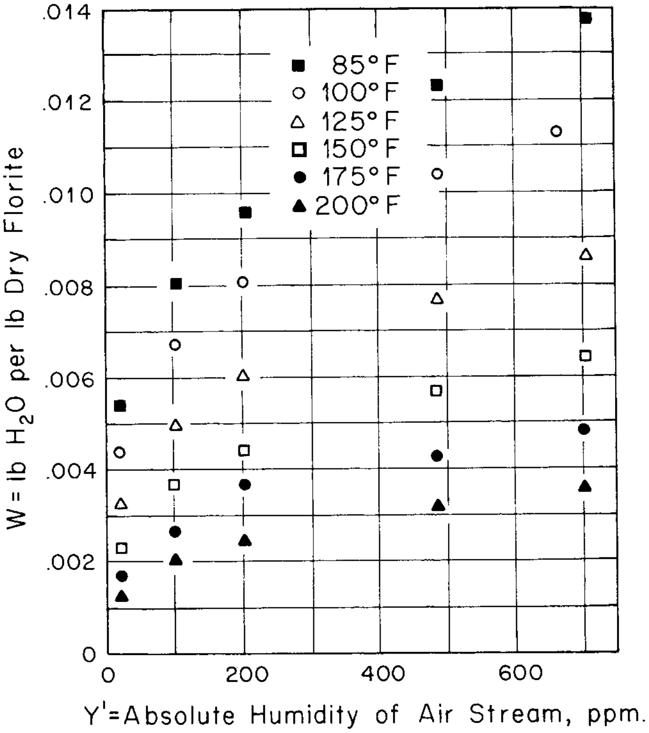

Fig. 2. Florite data: low humidity region.

studies are not surprising because bauxite is after all a naturally occurring material, whose composition and structure can vary considerably.

The Polanyi function

$$X_p = T \ln \frac{p_0}{p} \qquad (1)$$

was tried in plotting isotherms and found to bring all isotherms together quite well. Other functions were tried without success. Florite data are plotted using this relation in Figure 3.

ANALYTICAL FIT OF THE SORPTION THERM

Although X_p defined by Equation (1) brings all isotherms into a single curve, when plotted against amount sorbed, this kind of curve is not recognizable as a conventional isotherm. In order to switch the equilibrium curve to a conventional type isotherm the following function is introduced

$$X_t = e^{-X_p/A} \qquad (2)$$

$$A = \text{constant, } ^\circ\text{R}$$

By substitution of Equation (1) into Equation (2), one can obtain the following function:

$$X_t = \frac{p}{p_0}^{\,T/A} \qquad (3)$$

In this current work we used a computerized nonlinear regression type analysis (*13*) to determine the best least square fit of the collapsed data while at the same time varying A to also reduce the value of the sum of the squares of the deviations from the sorption therm expression under test. Because of this, A can vary somewhat with the sorption therm expression being tested because the criterion for measuring deviations differs. To show this more vividly we will also apply the same method of analysis to the silica gel data that was reported and analyzed earlier (*8*).

The first sorption therm expression tested in the case of Florite was

$$W = \frac{a_1\, b_1\, X_t}{1 + b_1\, X_t} + \frac{a_2\, b_2\, X_t\, Y_e}{1 + b_2\, X_t\, Y_e} \qquad (4)$$

where

$$Y_e = \frac{1}{2}\left[1 + ERF\,(V_e)\right]$$

$$ERF\,(V_e) = \frac{2}{\sqrt{\pi}} \int_0^{V_e} e^{-s^2}\, ds$$

$$V_e = B_e\,(X_t - X_{ta})$$

$$X_t = (p/p_0)^{T/A}$$

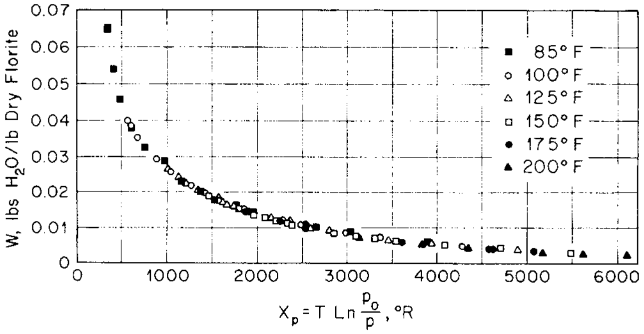

Fig. 3. Characteristic curve for Florite.

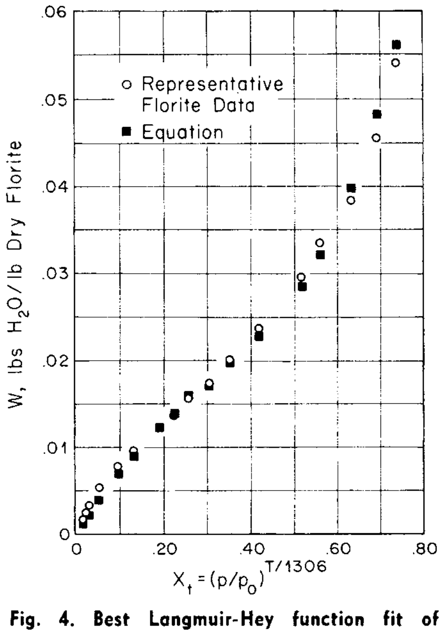

Fig. 4. Best Langmuir-Hey function fit of Florite data.

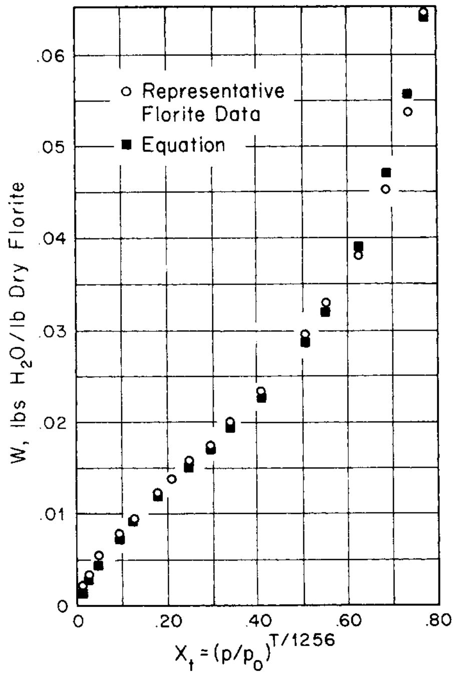

Fig. 5. Best simple BET fit of Florite data.

$a_1, b_1, a_2, b_2, B_e, X_{ta}$ = constants, dimensionless

T = absolute temperature, °R

This is a modified version of Langmuir-Hey theory (*7*, *12*). The specific best-fit function was determined to be

$$W = \frac{0.085\ X_t}{1 + 1.70X_t} + \frac{23.0\ X_t\ Y_e}{1 + 230X_t\ Y_e} \qquad (5)$$

where

$$a_1 = 0.05$$

$$a_2 = 0.10$$

$$Y_e = \frac{1}{2}\ (1 + ERF\ (V_e))$$

$$V_e = 1.60\ (X_t = 1.98)$$

$$X_t = (p/p_0)^{T/1306}$$

This fit is compared to representative Florite data in Figure 4. Maximum error occurs at $X_t = 0.69$, an error in W of 0.0025 lb. H_2O/lb. dry Florite, which represents a percent error of 5.5%.

The next sorption therm expression tested was based on the simple BET equation expressed in $W(X_t)$ form as

$$W = \frac{KC_b}{[1 - X_t]} \cdot \frac{X_t}{[1 + (C_b - 1)\ X_t]} \qquad (6)$$

The best fit was found to be

$$W = \frac{0.1188}{1 - X_t} \cdot \frac{X_t}{1 + 6.298\ X_t} \qquad (7)$$

where

$$X_t = (p/p_0)^{T/1256}$$

Equation (7) is compared to representative Florite data points in Figure 5. As can be seen from this figure, the maximum error occurs around $X_t = 0.68$, an error in W of 0.0015 lb. H_2O/lb. dry Florite, which represents a percentage error of around 3%. The value of A differs by about 4% compared to its previous value in Equation (5) for reasons already discussed.

It should be considered that the foregoing fits of data represent final results. Other expressions were, of course, tested and the best fits of data were inferior to those reported here.

We now turn to the silica gel data reported earlier and apply our new method of analysis to it. Equation (4) is the first one to be fit to the data. The values of the parameters for the best least-square fit were found by the computer to be such that the specific function is

$$W = \frac{1.715\ X_t}{1 + 17.15\ X_t} + \frac{941\ X_t\ Y_e}{1 + 3765\ X_t\ Y_e} \qquad (8)$$

where

$$a_1 = 0.10$$

$$a_2 = 0.25$$

$$Y_e = \frac{1}{2}\ 1 + ERF\ (V_e)$$

$$V_e = 1.55\ (X_t - 1.75)$$

$$X_t = (p/p_0)^{T/555}$$

$$T = \text{Temperature, °R}$$

The fit is compared to representative silica gel data points graphically in Figure 6. This fit has a maximum error in W of 0.01 lb. H_2O/lb. dry silica gel at $X_t = 0.53$, which is a percent error of around 3%.

Next we fit a BET type equation. There are several BET equations (*2*, *3*, *4*) which are not often used due to their greater complexity. The simplest of these expressed in $W(X_t)$ form is

$$W = \frac{(KC_b\ X_t)\left[\ 1 + \left(\frac{1}{2} n_a\ g - n_a\right) X_t^{n_a - 1} - (n_a\ g - n_a + 1) X_t^{n_a} + \frac{1}{2} n_a\ g\ X_t^{n_a+1}\right]}{(1 - X_t)\left[\ 1 + (C_b - 1)\ X_t + \left(\frac{1}{2} C_b\ g - C_b\right) X_t^{n_a} - \frac{1}{2} C_b\ X_t^{n_a+1}\right]} \qquad (9)$$

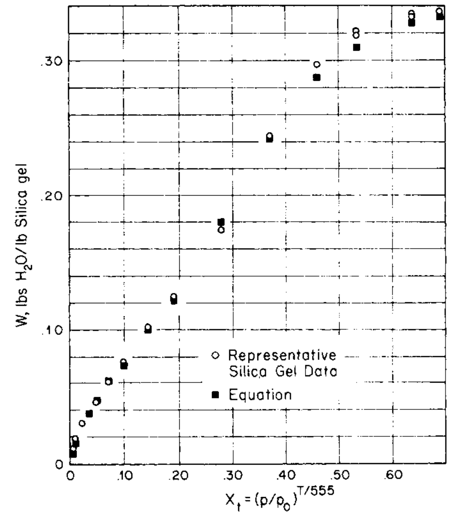

Fig. 6. Best Langmuir-Hey function fit of silica gel data.

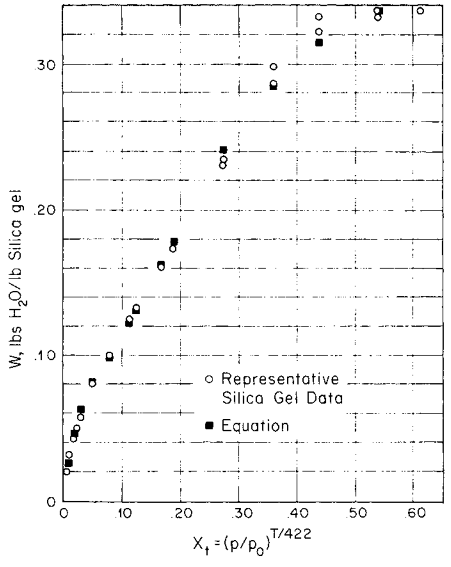

Fig. 7. Best BET fit of silica gel data.

where

K, g, C_b = constants, dimensionless
n_a = number of adsorbed layers, dimensionless

The computer determined that the parameters

$$K = 0.1040$$
$$C_b = 49.28$$
$$n_a = 3.64$$
$$g = 75$$
$$A = 422$$

gave the best fit. Substituting the above values of the parameters into Equation (9) gives

$$W = \frac{5.12X_t\,[1 + 132.8X_t^{2.64} - 270.2X_t^{3.64} + 136.5X_t^{4.64}]}{[1 - X_t][1 + 48.3X_t + 1798X_t^{3.64} - 1847X_t^{4.64}]} \qquad (10)$$

where

$$X_t = (p/p_0)^{T/422}$$

Equation (10) is compared to representative silica gel data in Figure 7. The maximum error occurs at $X_t = 0.43$, an error in W of 0.012 lb. H_2O/lb. dry silica gel, an error of around 3%.

DISCUSSION

The best description of the Florite equilibrium data lies in the BET theory. It should be noted, however, that there is an essential difference between Equation (7) and the BET equation of the same form. Brunauer et al. used the temperature concentration function

$$X_b = \frac{p}{p_0}$$

whereas we used the function

$$X_t = \frac{p}{p_0}^{T/A}$$

Therefore, Equation (7) cannot be derived directly from the BET theory—at least not without making some modifications. However, Equation (7) does have a practical advantage over the original BET equation in that the temperature dependence is more nearly correct. This temperature dependence of course derives from the macroscopic theory of Polanyi (*14, 15*).

Similar comments can be made regarding the modified version of Langmuir-Hey theory. In this case exponential dependence on temperature was envisioned in the original theory whereas here we used the temperature dependence shown in the definition of X_t.

Application of the nonlinear regression analysis to silica gel data shows that A can vary from 422 to 555 depending on the criterion used for measuring deviations during the computerized fitting process. In our work that was reported earlier the value of A was found to be 500.

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NOTATION

A = constant, °R
$C_b, K_b, B_e, X_{ta}, a_1, b_1, a_2, b_2, K, g$ = constants
$ERF\ (V_e) = \frac{2}{\sqrt{\pi}} \int_0^{V_e} e^{-s^2}\, ds$
n_a = number of molecular layers of sorbate on sorbent
p = partial pressure of water vapor, mm Hg
p_0 = saturation vapor pressure of water at T, mm Hg
T = absolute temperature, °R
V = amount sorbed, cc at STP
V_m = maximum amount sorbed, cc at STP
W = concentration of water on sorbent, lb. water/lb. dry sorbent
$X_t = (p/p_0)^{T/A}$
$X_p = T \ln (p_0/p)$
Y' = absolute humidity, ppm
$Y_e = (1 + ERF\ (V_e))/2$
$V_e = B_e\ (X_t - X_{ta})$

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