The Activated Calcium Sulfate-Water Vapor Sorption Therm

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The sorption isotherms are reported for the β-soluble anhydrite form of calcium sulfate (Drierite) exposed to moist air at one atmosphere total pressure and 90, 100, 125, 150, 175, and 200°F. A concentration-temperature coordinate has been identified which when plotted against the amount sorbed caused all isotherms to collapse into a single sorption therm. The latter has been fit by a three-term expression based on a combination of sorption theories. A graphical comparison is made between a curve calculated from the analytical expression and actual experimental datum points.

Curve fitting was done by machine and involved minimizing the square of the deviations. Maximum deviations up to 4% are experienced in the high range. In the low range these tend to increase but so do the experimental errors.

Realistic analytical expressions for sorption therms would simplify and/or improve the accuracy of numerical analyses (*1, 5, 6, 22, 24, 25*) recently devised for studying and designing the percolation operations. The latter involve flow of a sorbate laden fluid stream through a tower packed with adsorbent. During the operation sorbate is transferred between the fluid and solid phases. In past numerical work idealistic expressions have been used and consequently sorption data are poorly represented and the precision of the results suffer.

The work reported here is a part of a larger research project in which percolator kinetic mechanisms were investigated. While we were formulating some new mathematical concepts and stability criteria applicable to a numerical analysis of percolators (*14*), it became obvious that analytical expressions for sorption therms improved the precision of and subsequently simplified the analysis while reducing computer time. In the light of this experience a study was made of the sorption therms for the systems moist air and silica gel, activated calcium sulfate, Linde molecular sieve 4A, activated alumina and Florite. A report on the first of these appears elsewhere (*15*). Reports on the last three adsorbents will be published subsequently (*16* to *18*). As far as we are aware, no one has reported analytical expressions that fit the five systems under investigation over a broad range of concentration and temperature.

A three-step study is needed for each sorbent system to arrive at the desired result. The first step involves careful determination of the adsorption and desorption isotherms for a known material over a sufficiently wide temperature range to cover the full range of application. Next, a temperature-concentration function that causes the various isotherms to merge into a single sorption therm curve on a plot of amount sorbed versus temperature-concentration function must be identified. Finally one must find an analytical expression, either theoretical or empirical if need be, that represents the sorption therm with the required precision. This is the basis for the past, present, and subsequent reports.

The foregoing procedure has the advantage that it leads to a positive result with immediate usefulness. In those cases where it is necessary to use empirical expressions, the procedure permits deferring to subsequent studies the matter of accounting on theoretical grounds for the empirical expression.

The sorption isotherms for activated calcium sulfate-moisture with or without air have continually aroused interest over the years for various reasons. In some cases (*23, 31, 33*) the basic mechanism of hydration constituted the focal point of investigation. In another case (*19*) the isotherms were determined and reported as a result of implementing the analysis of percolation data wherein calcium sulphate was involved. Some investigators (*9, 20, 28*) were more interested in the thermodynamic properties associated with the hydration and dehydration process. Others (*4, 30, 33*) concentrated on crystal structure as related to the degree of hydration. None were concerned with mathematical expressions of the sorption therms.

Over the years the sorption theories of Langmuir (*21*), Brunauer, Emmett, and Teller (*2, 3*), Harkins and Jura (*11*), Hey (*12*), Polanyi (*26, 27*), and Dubinin (*7, 8*) and others have emerged. The results have been used to characterize adsorbents. In some instances they have been used to judge adequacy of the theory and in others to imply values of surface area or the number of sorbate layers.

The Polanyi theory leads to a method of plotting which takes temperature into account, but the resulting curve is so distorted that it is difficult to recognize for purposes of expressing the phenomenon explicitly.

Sorption data have been plotted as amount sorbed versus relative humidity (*13*) but the collapse of isotherms to a single sorption therm is incomplete.

EQUIPMENT AND PROCEDURE

The sorption isotherms were determined using a dynamic method that involved equipment previously described (*15*). The same three humid air sources were used with laminar flow gages to produce intermediate humidities by mixing.

The commercial grade of activated calcium sulfate, that is, "Drierite," was used in sizes 10-14 U.S. mesh and 12-16 U.S. mesh. Samples were regenerated in thin layers in an oven at 400°F. for 2 hrs. The oven was equipped with a blower for forced air circulation.

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THE SORPTION THERM

The original data are plotted in Figure 1. They are based on normal adsorption and desorption runs and no hysteresis was observed.

The Hey (*12*) or Langmuir (*21*) type isotherm suggests that the equilibrium partial pressure is related to amount sorbed and temperature; thus

$$p = Kf(C1)\sqrt{T}\,e^{-A/T} \qquad (1)$$

where $f(C1)$ is a function of sorbed concentration $C1$. At a constant value of $C1$, one can reduce Equation (1) to

$$\ln(p/\sqrt{T}) = \ln C - A/T \qquad (2)$$

where C is a constant. A plot of $\ln(p/\sqrt{T})$ versus $1/T$ should yield a straight line if the theories are applicable. To test this we used points from our data located at the point of maximum slope ($W \cdot 100 = 2.5\%$) and plotted as shown in Figure 2. The value of A is 13,720°R. If one chooses $W \cdot 100$ at 1.5% a slightly larger value of A results, and vice versa for $W \cdot 100$ equal to 3.5%. This point corresponds to the socalled decomposition of the hemihydrate. The data of Lescoeur (*23*) given in the International Critical Tables (*32*) were also plotted in Figure 2. The results are in excellent agreement. Both the slopes and the intercepts agree. This comparison further confirms our experimental data and the value of A used in the reduced coordinate.

Figures 3 and 4 show the two-dimensional plots of our data wherein the reduced coordinate X_R is actually being tested.

ANALYTICAL FIT OF THE SORPTION THERM

Having determined the reduced coordinate, we directed attention to fitting the sorption therm. Figures 3 and 4 show the data and the curve resulting from the following equation:

$$W \cdot 100 = \frac{ABX}{1+BX} + \frac{C \cdot V1 \cdot X}{1 + V1 \cdot X} + \frac{E \cdot V2 \cdot X}{1 + V2 \cdot X} \qquad (3)$$

where

$$V1 = D[1 + ERF(G1(X - XR1))]/2$$

and

$$V2 = F[1 + ERF(G2(X - XR2))]/2$$

$$A = 0.34$$
$$B = 15.0$$
$$C = 4.80$$
$$D = 3.90$$
$$XR1 = 1.70$$
$$G1 = 5.26$$
$$E = 3.85$$

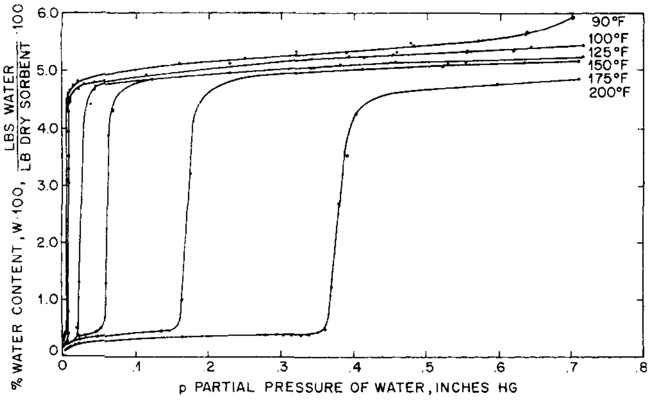

Fig. 1. Sorption isotherms.

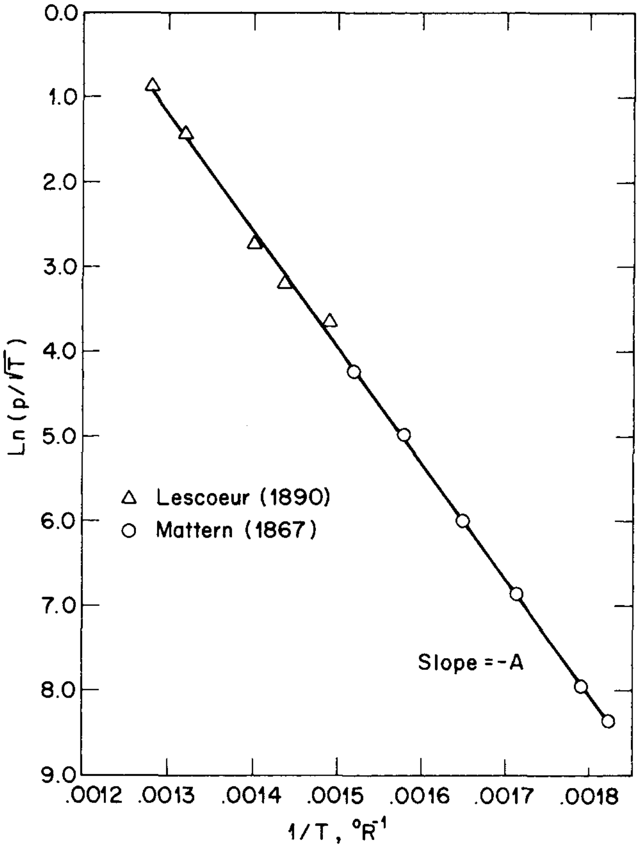

Fig. 2. Comparison of data.

$$F = 0.0028$$
$$XR2 = 260.0$$
$$G2 = 0.005$$

If one converts $W \cdot 100$ to $C1$ and the pressure to lb.$_f$/sq.ft., the constants (using the same symbols) in Equation (3) are

$$A = 0.209313E - 01$$
$$B = 0.212081E - 07$$
$$C = 0.295500$$
$$D = 0.551411E - 08$$
$$XR1 = 0.120237E + 10$$
$$G1 = 0.743697E - 08$$
$$E = 0.237016$$
$$F = 0.395884E - 11$$
$$XR2 = 0.183892E + 12$$
$$G2 = 0.706937E - 11$$
$$X\ (=)\ \text{lb.}_f\,\text{ft.}^{-2}\,{}^\circ\text{R.}^{-1/2}$$
$$C1\ (=)\ \text{lb. moles water/cu.ft. granule}$$

The best values of the constants were determined by a curve fitting procedure that was programmed for the IBM 7040 and 360 digital computers. This procedure involved minimizing the square of the deviations.

DISCUSSION OF RESULTS

It should be noted that in Figure 4 even up to $X_R\ 10^{-7} = 450$ in Hg · °R.$^{-1/2}$ · 10^{-7} there is no indication of a sharp step in the curve corresponding to the formation of the dihydrate, that is, $100 \cdot W = 26.5$. On the other hand, Weiser (*33*) has measured a "dehydration isobar," and if these data were plotted on Figure 4, one would see that the dihydrate exists down to $X_R \simeq 40$ in Hg · °R.$^{-1/2}$ · 10^{-7}. At this point a sharp decrease in sorbed moisture occurs. In addition, the decomposition pressures reported

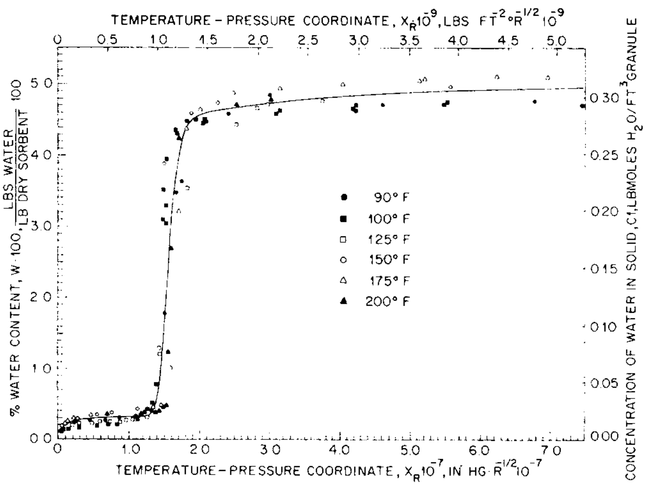

Fig. 3. Sorption therm, low X_R.

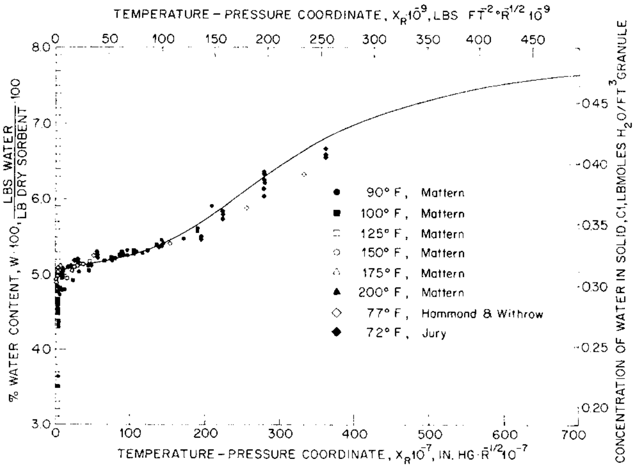

Fig. 4 Sorption therm, high X_R.

by Van't Hoff (*31*) are similar to the values of Weiser et al. in that they indicate that dehydration takes place over the range $85 < X_R < 176$ in Hg · °R.$^{-1/2}$ · 10^{-7} for temperatures $90 < T < 200$°F. The reasons for the range of values is that the X_R coordinate with $A = 13{,}720$°R. does not reduce Van't Hoff's dihydrate decomposition pressure data to a single point as is the case for Lescoeur's (*23*) hemihydrate decomposition pressures. The recent work of Razouk et al. (*30*) supports our data and that of Hammond and Withrow (*10*). Their experiments indicated that the transformation from the hemihydrate to the dihydrate does not occur significantly at pressures below saturation. In essence the transformation is "a 'through solution' mechanism involving the passage of structural units of a solid hemihydrate through solution followed by a crystallization." Appreciable changes of lattice parameters are associated with this transformation. This confirms Bunn's (*4*) findings that adsorption occurs up to 0.66 moles water and that the crystal then dissolves and is replaced by the dihydrate crystal.

Considering all of these facts resolves the paradox, that is, Weiser et al. and Van't Hoff were observing the desorption, or dehydration, process of the dihydrate, while we, like Hammond and Withrow, were reporting sorption data for β-soluble anhydrite. In essence, then, there is a large hysteresis effect, but in normal sorption processes involving calcium sulfate, the dihydrate does not form. Hence, the third sorption step shown in Figure 4 is a small effect probably due to a Langmuir type sorption (but not of significant dihydrate formation).

The sum type analytical expression assumed for the sorption therm is not new and does a remarkable job of representing the data. Rabinowitch and Wood (*29*) suggested use of a sum type expression based on theoretical grounds but no one seems to have used it. Our sum expression differs from theirs in that the functions $V1$ and $V2$ have been inserted. These functions are fractions which increase with increases in X. They bring into account the extent to which the corresponding Hey or Langmuir type process enters into the overall sorption process.

Three processes enter the overall sorption process. The first term of the sum apparently represents the Langmuir sorption that occurs along intergranular boundaries. The second term represents the Hey type hydration of a zeolitic type structure corresponding to hemihydrate formation. The third term probably represents a Langmuir type sorption on exposed surfaces.

The precision of the fit of Equation (3) involves deviations of up to 4% in the high range. In the low range there are larger individual deviations, but this is also in the range where experimental errors increase.

ACKNOWLEDGMENT

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NOTATION

$A, B, C, D, E, F, G1, G2, K, XR1, XR2$ = constants
$C1$ = concentration of water in solid, lb. mole/cu.ft.
p = partial pressure of water vapor, in Hg
p_0 = saturation partial pressure of water vapor at temperature T, in Hg
T = absolute temperature, °R.
$V1 = D[1 + ERF(G1(X - XR1))]/2$
$V2 = F[1 + ERF(G2(X - XR2))]/2$
W = concentration of water in sorbent solid, lb. water/lb. dry sorbent
X = reduced pressure-temperature coordinate, in Hg · °R.$^{1/2}$ · 10^{-7}

$$= X_R \cdot 10^{-7} = \frac{p\, e^{A/T}}{T^{1/2}}$$

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Flow Attachment to Solid Surfaces: The Coanda Effect

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The phenomenon of flow attachment to solid surfaces, occurring with both liquids and gases, is the long-known though inadequately understood Coanda effect.

A flow visualization study was made using a birefringent milling yellow dye solution flowing over a deflection surface consisting of flat plates. A two-dimensional flow channel with transparent side walls was used. Photographic observations of the development of the Coanda effect reveal the method of flow attachment and confirm a number of literature predictions. One of the most interesting of these phenomena is the existence of a well defined mixing region along the deflection surface.

A simplified model of the flow field has been proposed in order to describe the mechanism governing the Coanda effect. The model is supported by experimental data consisting of pressure profiles obtained along the deflection surface and secondary flow entrainment measurements.

Place a cube of salt in a beaker of water and slowly dissolve it by pouring a stream of water over it. As the salt dissolves, a horizontal surface, instead of the expected irregularly shaped surface, is maintained along the top of the cube. Pour a cup of tea out of a teapot spout. The tea will often flow down the spout and even flow up the underside of the teapot before becoming detached. If the pouring angle from the horizontal is increased, the liquid stream partially adheres and partially detaches itself from the spout. When the teapot is tilted still further, the entire stream detaches completely but the downward jet follows an unexpected diversion from the vertical in that it bends towards the spout. Finally, upon tilting the teapot lower yet and thereby increasing the flow again the expected ballistic curve flow path is obtained.

An extensive qualitative investigation by the noted rheologist Marcus Reiner (*18*) points up the occurrence of these and similar effects. Having noticed the flow attachment of fluids to surfaces against the pull of gravity, Reiner and Block (*18*) designed several experiments to show that adhesion as a surface-tension property can be excluded as an explanation of the effect.

It is well known that if a stream of air is blown through a nozzle slit it will be deflected along the external portion of the nozzle and that it entrains several times the amount of air in the original jet. Furthermore, the pressure along the nozzle surface is much less than atmospheric. This has been called the Coanda effect (*2*).

The Coanda effect has potential applications in the areas of water purification (U.S. Pat. 2,761,292 and 2,803,591), liquid atomizers (U.S. Pat. 2,713,510 and 2,826,454), spraying devices (U.S. Pat. 2,988,303), moving devices (U.S. Pat. 2,920,448), and smoke control (U.S. Pat. 2,173,550 and 2,187,342). The cooling effect of a Coanda pump makes it feasible for the pumping of cryo-

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