



**METER**  
ENVIRONMENT

## USE ISOTHERMS TO DETERMINE THE SPECIFIC SURFACE AND SWELLING POTENTIAL OF SOIL

Dr. Gaylon S. Campbell

One would not normally expect there to be a connection between food physics and geotechnical engineering, but there are several. METER builds instruments for measuring water activity in foods and for characterizing food moisture relations. We also build instrumentation for geotechnical engineering. In many cases, the instruments are the same. METER recently introduced the [VAPOR SORPTION ANALYZER](#) (VSA) to research markets in foods and pharmaceuticals. This report briefly discusses results of experiments using the VSA to measure isotherms of soils.

The term isotherm, as used in food physics and physical chemistry, refers to the relationship between sample water content and water activity (think relative humidity) for a sample at some specified temperature. In geotechnical engineering, we call such a relationship a soil moisture characteristic (see “Measures of soil suction”, which relates water activity to other suction units).

The VSA has a sensitive balance inside which records the mass of a sample that is enclosed in a temperature-controlled chamber. Moist or dry air is passed through the chamber, increasing or decreasing the water content of the sample. Periodically the flow of air stops, and the sample water activity is determined by a cooled-mirror sensor in the sample chamber. In 24 to 48 hours a sample can be dried to around 3% relative humidity, wet to 90% humidity, and dried again to 3%. Since the data points are collected automatically, detailed moisture characteristics with hundreds of points are easily obtained.

## MEASURES OF SOIL SUCTION

In geotechnology, soil suction is typically expressed in pressure units such as kPa, with a positive sign representing negative pore water pressure. In soil physics, the negative sign is retained, and the quantity is called water potential. Water potential and water activity are related by the Kelvin equation from thermodynamics

$$\Psi = RT \ln a_w$$

where  $R$  is the gas constant for water (462 kPa K<sup>-1</sup>), and  $T$  is the Kelvin temperature. Suction can also be expressed in head units as cm of water. One kPa is equivalent to 10.2 cm of water. Schofield (1935) noted that a logarithmic scale was better suited to soil suction measurements than a linear scale so introduced the pF scale, which has been used in geotechnology (McKeen, 1992). pF is the base 10 logarithm of the suction in cm of water. The pF scale has several advantages. Most importantly, it makes the moisture characteristic almost linear. Disadvantages are that it is based on antiquated (non SI) suction units and commits a serious mathematical faux pas by taking the logarithm of a number with units. Another disadvantage is that the numerical value increases with decreasing moisture. These problems are conveniently sidestepped by the chi measure advocated by Condon (2006). Chi is defined as

$$\chi = -\ln [-\ln(a_w)]$$

Table 1 compares chi with other measures of soil suction.

	kPa	cm of H <sub>2</sub> O	a <sub>w</sub>	pF	Pore Diam. μm	Freezing pt - C	chi χ
	1	10	0.999993	1.01	290.080	-0.001	11.82
	10	102	0.999926	2.01	29.0008	-0.008	9.51
Field capacity	33	337	0.999756	2.53	8.790	-0.025	8.32
	100	1020	0.999262	3.01	2.901	-0.076	7.21
	1000	10204	0.992640	4.01	0.290	-0.764	4.91
Permanent wilt	1500	15306	0.988980	4.18	0.193	-1.145	4.50
	10000	102041	0.928789	5.01	0.029	-7.635	2.61
Air dry	100000	1020408	0.477716	6.01		-76.35	0.30
Oven dry	1000000	10204080	0.000619	7.01			-2.00

Table 1. A comparison of chi against other measures of soil suction

## THE EXPERIMENT

We ran samples of 5 soils along with a sample of Bentonite clay in the VSA. Clay content of the various samples is shown in Table 2. Figure 2 shows the isotherms for the six samples. Clearly, increasing amounts of clay in samples increases the amount of water adsorbed at any given water activity. Low clay isotherms show little structure, but the Bentonite sample shows distinct regions where the energetics of the clay/water interaction change.

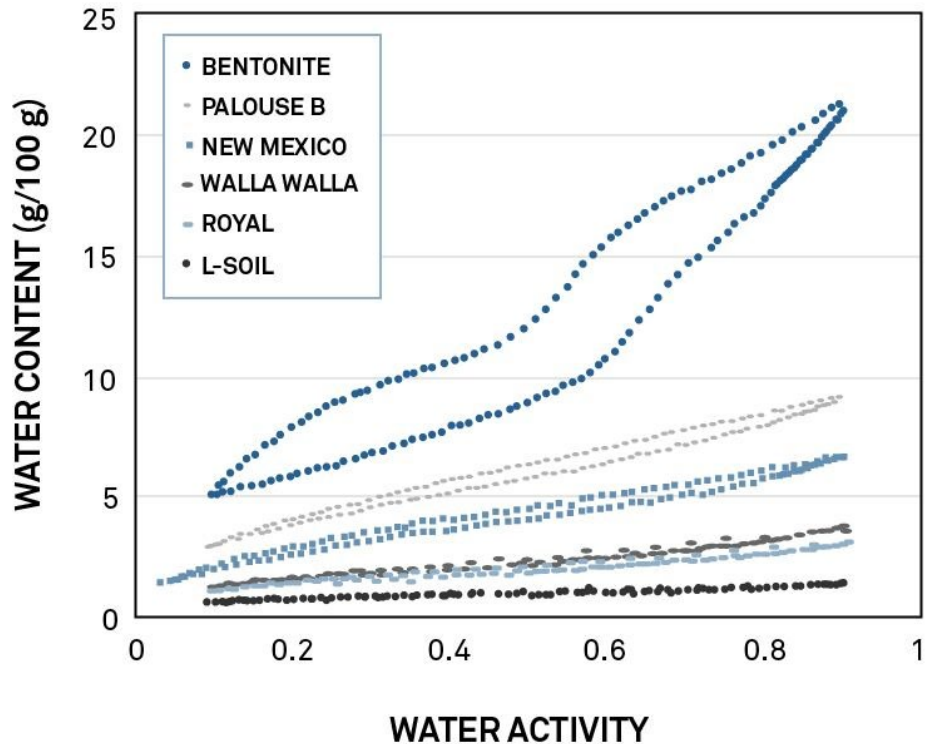


Figure 2. Isotherms for six soil materials showing adsorption (lower) and desorption (upper) arms of the hysteresis loop for each material

The adsorption and desorption processes are reversible. Subsequent trips around the sorption-desorption loops (not shown) give data points that fall on top of those shown in Figure 2. Sorption follows a different path than desorption. This phenomenon is called hysteresis. It results from the fact that, at a given water content, more energy is required to remove water from a drying soil than a wetting.

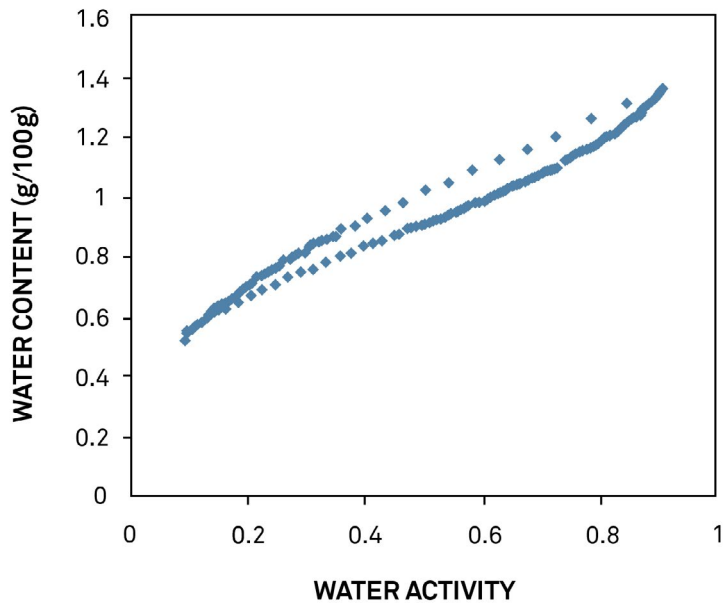


Figure 2a. L-soil isotherm with expanded water content scale

## USE THE VSA TO DETERMINE SURFACE AREA

The isotherms are interesting, but what can one do with them? Likos and Lu (2002, 2003) built an apparatus to generate isotherms similar to those shown here. They used the apparatus to determine the specific surface of materials and to assess the swelling potential of soils. The use of water vapor adsorption to measure specific surface is not a new idea. Orchiston (1953) published an excellent paper more than 50 years ago using isotherm data to determine the specific surface of 7 New Zealand soils (but see Quirk and Murray, 1999 for some more recent interpretations). Orchiston used three different methods to determine specific surface. The first was the standard method of determining the monolayer value using the BET model (Brunauer et al. 1938). We used that method to determine the specific surface areas of our samples. The results are shown in Table 2.

Sample	clay fraction	BET area m <sup>2</sup> /g	Figure 3 slope m <sup>2</sup> /g	Figure 3 condon area m <sup>2</sup> /g	Slope a <sub>w</sub> < 0.3	Area slope < 0.3 a <sub>w</sub> m <sup>2</sup> /g	EGME area m <sup>2</sup> /g
L soil	0.04	19	0.43	28	0.33	21	25
Royal	0.15	38	0.8	52	0.69	44	45
Walla	0.14	43	0.93	60	0.81	52	70
New Mexico	0.35	84	1.67	107	1.81	117	
Palouse B	0.47	119	2.43	157	2.43	156	203
Bentonite		168	3.77	243	3.76	242	

Table 2. Sample characteristics, chi plot slopes and specific surface areas computed using the different methods

Interestingly, Orchiston also used the chi plot method as outlined by Condon (2006). It is clear that this “new” idea goes back more than 50 years. In fact, it is based on earlier work originally published in 1929. Sometimes one wonders whether we should call the work we do research or re-search. In any case, Figure 3 shows the chi plots of the data for the soils studied here along with eye-fit straight lines, which intersect the chi axis at the oven dry value. The lines, for the most part, are excellent fits to the adsorption arm of the isotherm (the desorption side is also plotted to show its shape on a chi plot but is not used for the analysis).

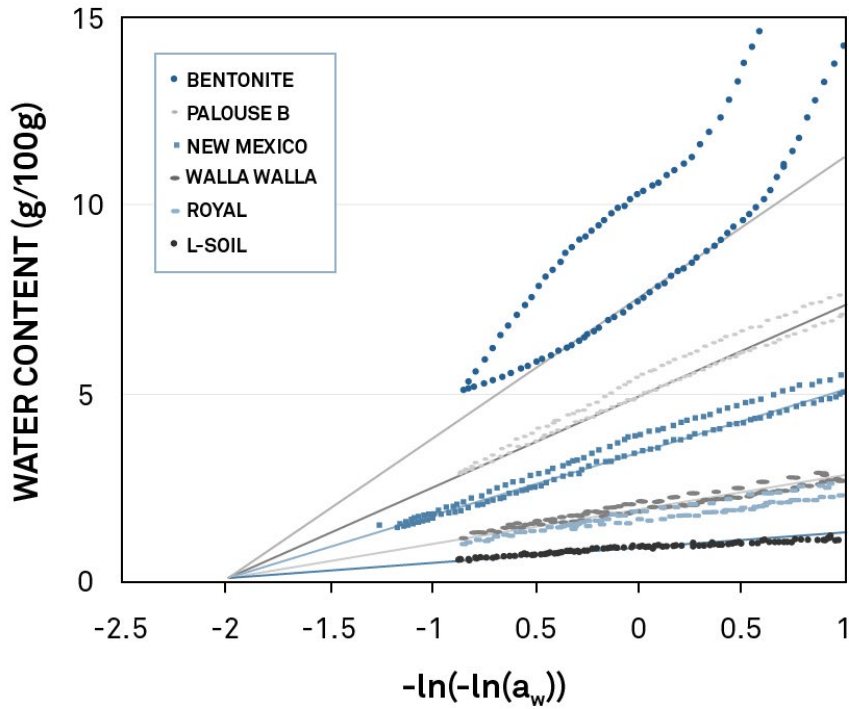


Figure 3. Chi plots of the moisture release data for the 6 soil materials

Figure 4 shows the slopes of the straight lines as a function of clay content for the five soil samples. Clearly, the slope is highly-correlated with clay content for this particular set of samples (since clays differ drastically in their properties, this would not generally be the case; the correlation would be with clay activity, not clay content).

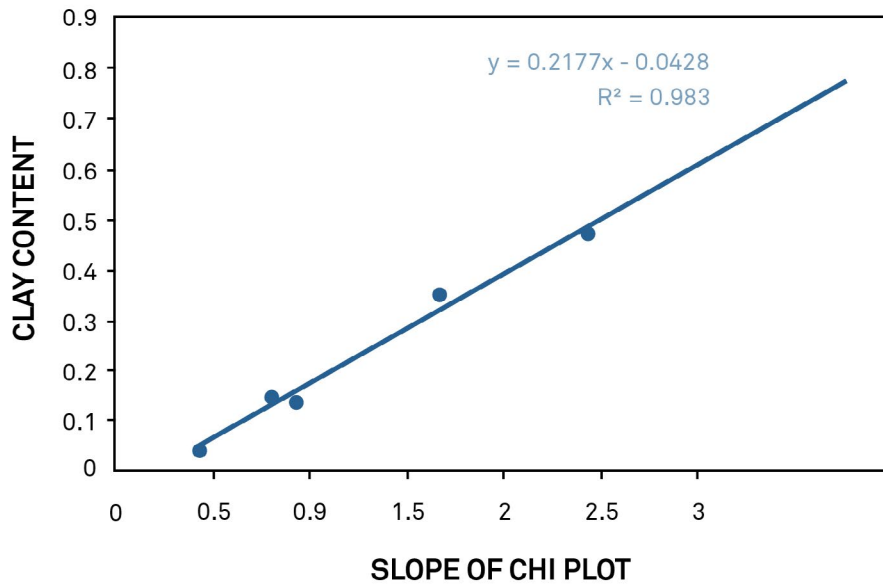


Figure 4. Relation between clay content and slope of the chi plot for the sample analyzed here

The surface area can be computed directly from the slopes of the chi plots. Condon gives the following formula for computing the specific surface

$$A = fSa$$

where  $S$  is the slope of the chi plot (g/g; note that the values plotted in Figure 3 are g/100 g),  $a$  is the monolayer area covered by unit mass of water (here taken as 3500 m<sup>2</sup> g<sup>-1</sup>), and  $f$  is a factor from Condon (2006) equal to 1.84. Table 2 shows these values. The chi plot values, in all cases, are greater than the BET values. Surface area measurements, using the EGME method, were available for samples similar to some of those run in this experiment. Those also are shown in Table 2. They tend to agree best with the chi plot method.

One additional column is shown in Table 2. In it, a least squares line was fit to the chi plot for samples below 0.3  $a_w$  (the same range of data used for the BET analysis). This gives a less subjective method for determining the slopes of the lines than the eye fit shown in Figure 3. These slopes and the corresponding areas are shown in column 8 of Table 2 and are essentially the same as those from the Figure 3 slopes.

## ANOTHER VSA APPLICATION: SWELLING POTENTIAL

According to McKeen (1992), the slope of the chi plot is closely related to the swelling potential of a soil. That is perhaps easy to see in Figure 3. At a chi value of 1, which is already well below suctions typical of soils in nature, the water content of the sand is around 2%, while the Bentonite is 14%. This added water represents a substantial increase in soil volume and has a very large swelling pressure (> 10 MPa). A modification of McKeen's classification is shown below. His method is based on pF, which uses base 10 logarithms, and pF is plotted vs. water content, rather than water content vs. suction, as we have here.

To convert his slopes to the ones shown in Table 3, we took the reciprocal and multiplied by -0.434 to convert from common to natural logarithms. Also, our slopes are given in g/100 g, or percent, so we multiplied his transformed values by 100. The

results are shown below. The highest slope is for the Bentonite, which has a value of 3.8 g/100 g. This would place it in McKeen’s moderate range. Palouse B, with a slope of 2.4 g/100 g is in the low range. All others in our sample set are nonexpansive. The slope for a Wyoming Smectite sample analyzed by Likos and Lu (2003) is 5.3 g/100 g, which would put it in the high range.

It should be pointed out that McKeen’s scheme was developed using [filter paper](#) to measure suction. The measurements were much less precise than those of Likos and Lu (2003) and those presented here. He also concentrated more on the wet end of the moisture characteristic. No precautions were taken to assure that only the sorption arm of the isotherm was used for computing the slope. Because of these uncertainties, the numerical values given by McKeen probably do not correspond exactly to the slopes from the VSA, but the approach is correct. The ranges should be reevaluated using more precise measurement methods that are now available.

Swelling potential	Slope range g/100 g
Very High	> 7.2
High	4.3-7.2
Moderate	3.3-4.3
Low	2.2-3.3
Nonexpansive	< 2.2

Table 3. Expansive soil ranges based on the chi plot, modified from McKeen (1992)

## ISOTHERM ANALYSIS OFFERS ADDITIONAL UNDERSTANDING OF CLAY WATER INTERACTION

The Bentonite sample in Figure 2 is clearly different from the other samples. We wondered if this could be the result of measurement artifacts. We therefore reduced the sample size and flow rate and made the measurement over a larger water activity range. The results are compared to the original isotherm in Figure 5. Several things are clear from these measurements. First, the method appears repeatable, and samples apparently are very near equilibrium, even at the higher scan rate, since the low and high scan rates match on the desorption arms. Having established that, it is very interesting that the desorption arm appears to be almost independent of where the isotherm starts, while the adsorption arm appears to be completely dependent on where it starts. The initial drydown is shown starting around 0.35  $a_w$ .



Even this comes quickly to the limiting desorption line. The low-speed desorption line lies almost on top of the high-speed line, even though the low line starts at a higher water activity. The absorption line, on the other hand, seems completely dependent on where it starts. Even the two low adsorption lines differ slightly because they start at slightly different places. An isotherm analysis would appear to offer opportunity for additional understanding of clay water interaction.

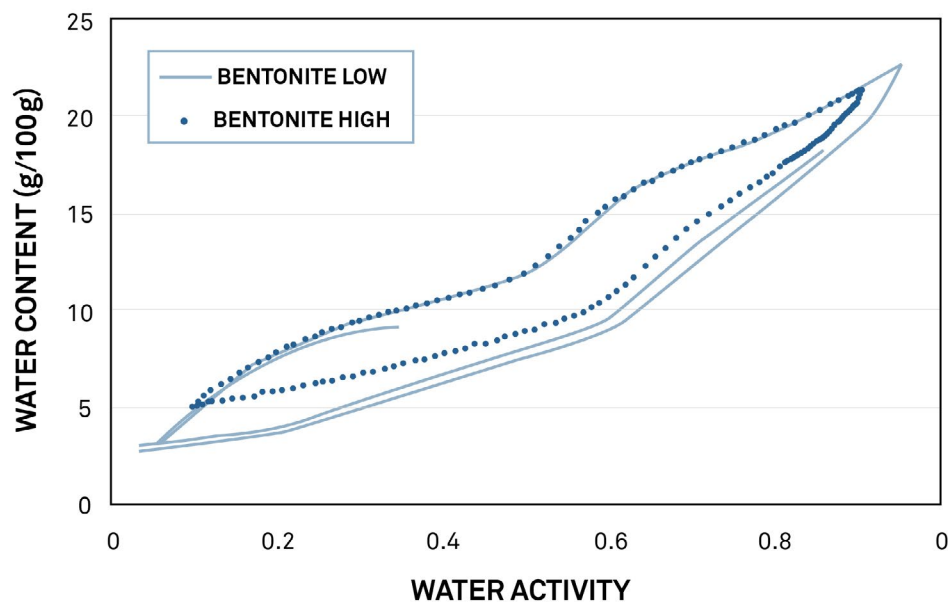


Figure 5. The Bentonite sample isotherm after reducing the sample size and flow rate compared to the original Bentonite isotherm.

## CONCLUSION

Analysis of dry soil characteristics is just in its infancy, but some things are already clear. First, hysteresis is apparent in all samples, even sands. Second, the response is closely related to the clay content and the activity of the clay in the sample. Third, adsorption isotherms appear to be useful for determining the specific surface and swelling potential of soil samples. Finally, the chi variable shows distinct advantages over other measures of suction for some applications and should find wider use in geotechnical applications.

## REFERENCES

Brunauer, Stephen, Paul Hugh Emmett, and Edward Teller. "Adsorption of gases in multimolecular layers." *Journal of the American Chemical Society* 60, no. 2 (1938): 309-319. [Article link](#).

Condon, James B. *Surface area and porosity determinations by physisorption: measurements and theory*. Elsevier, 2006. [Book link](#).

McKeen, R. Gordon. "A model for predicting expansive soil behavior." In *Proc., 7th Int. Conf. on Expansive Soils*, vol. 1, pp. 1-6. Reston, VA: ASCE, 1992.

Likos, William J., and Ning Lu. "Water vapor sorption behaviour of smectite-kaolinite mixtures." *Clays and Clay Minerals* 50, no. 5 (2002): 553-561. [Article link](#).

Likos, William J., and Ning Lu. "Automated humidity system for measuring total suction characteristics of clay." (2003): 1-12. [Article link](#).

Orchiston, Hector Douglas. "ADSORPTION OF WATER VAPOR: I. SOILS AT 25 [degrees] C." *Soil science* 76, no. 6 (1953): 453-466. [Article link](#).

Quirk, J. P., and R. S. Murray. "Appraisal of the ethylene glycol monoethyl ether method for measuring hydratable surface area of clays and soils." *Soil Science Society of America Journal* 63, no. 4 (1999): 839-849. [Article link](#).

Schofield, R. K. "The pF of the water in soil." In *Transactions of the 3rd International Congress of Soil Science*, vol. 2, pp. 37-48. 1935.