Isotherm Analysis: New (and Old) Ways to Look at Soil

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One would not normally expect there to be a connection between food physics and geotechnical engineering, but there are several. Decagon 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. Decagon recently introduced the AquaSorp IG isotherm generator to research markets in foods and pharmaceuticals. This report briefly discusses results of experiments using the AquaSorp IG 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 sidebar which relates water activity to other suction units).

The AquaSorp IG is shown in Figure 1. It 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 dew point 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.

Figure 1. Aquasorp Isotherm Generator

Sidebar:

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^{-1}),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

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

The following table compares *chi* with other measures of soil suction.

	kPa	cm of H_2O	a_w	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	29.008	-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

The Experiment

We ran samples of 5 soils along with a sample of Bentonite clay in the Aquasorp. 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. 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 Fig. 2.

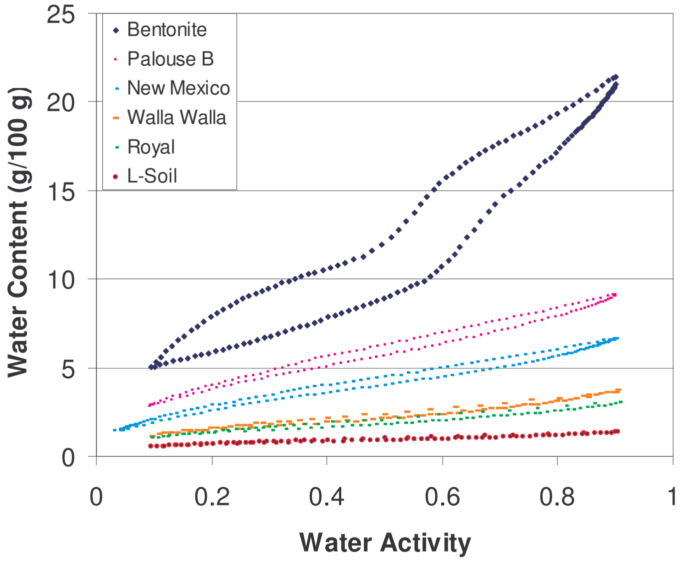


Figure 2. Isotherms for 6 soil materials showing adsorption (lower) and desorption (upper) arms of the hysteresis loop for each material.

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 soil. The hysteresis loop is obvious for the Bentonite. At the scale of the figure the L-Soil hysteresis is too small to be seen, but when it is blown up, the Aquasorp is sufficiently sensitive to show hysteresis even in this sandy soil as shown in Figure 2a.

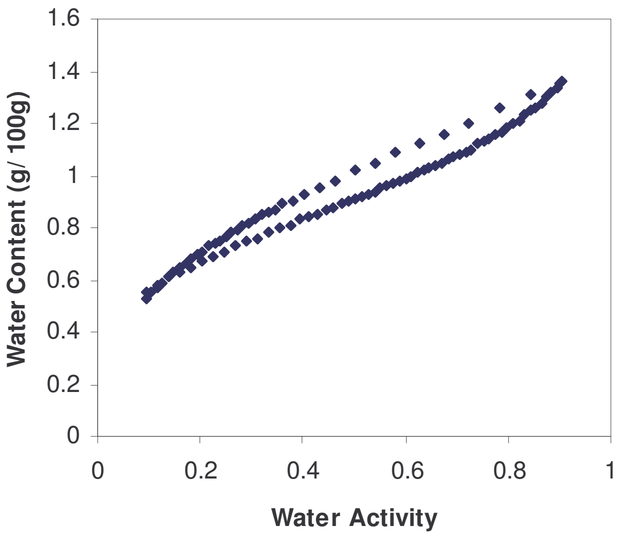


Fig. 2a. L-Soil isotherm with expanded water content scale.

Applications: Surface Area

The isotherms are interesting, but what can you 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 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.

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

Sample	clay fraction	BET Area m^2/g	Fig 3 slope m^2/g	Fig. 3 Condon Area m^2/g	slope $a_w < 0.3$	Area slope < 0.3 a_w m^2/g	EGME Area m^2/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	

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

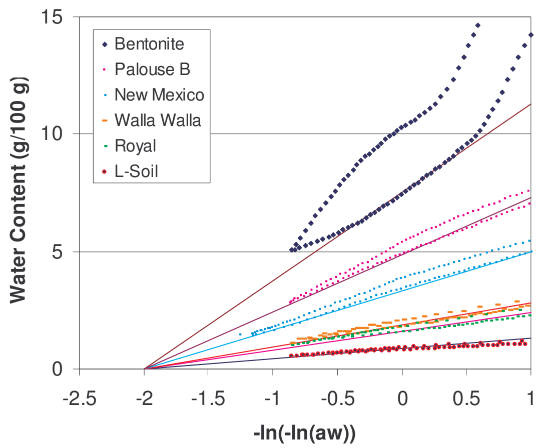


Figure 3. *Chi* plots of the moisture release data for the 6 soil materials

(the desorption side is also plotted to show its shape on a *chi* plot but is not used for the anysis). 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).

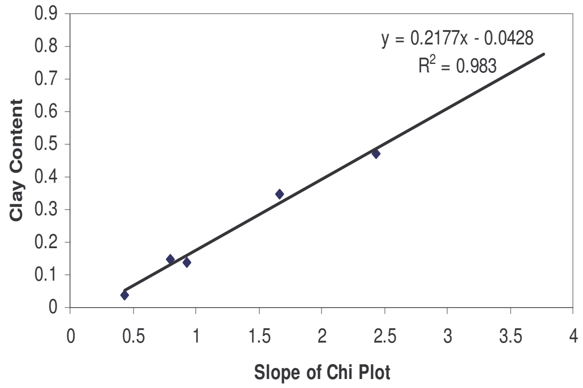


Figure 4. Relation between clay content and slope of the *chi* plot for the soil samples analyzed here.

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 Fig. 3 are g/100 g), a is the monolayer area covered by unit mass of water (here taken as 3500 $m^2\ g^{-1}$), 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 Fig. 3. These slopes and the corresponding areas are shown in column 8 of Table 2, and are essentially the same as those from the Fig. 3 slopes.

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 Fig. 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.

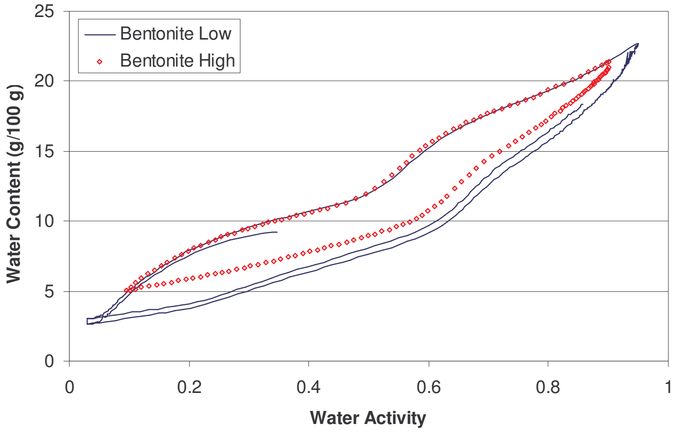
It should be pointed out that McKeen's scheme was developed using filter paper to measure suction. The measurements were much less precise than those of Likos and Lu (2003) and those presented here. He also concentrated more on the wet end of the moisture characteristic. No precautions were taken to 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 AquaSorp, but the approach is correct. The ranges should be re-evaluated using more precise measurement methods that are now available.

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

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

Further Observations

The Bentonite sample in Fig. 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 Fig. 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 of 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 adsorption 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.



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 used in geotechnical applications.

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