Fundamentals of Moisture Characteristic Curves in Ceramics

Moisture relations play a key role in ceramic manufacturing. Getting the correct moisture level in green bodies can make the difference between a successful firing or a failure. “With moisture sorption isotherms (also called moisture characteristic curves), it may be possible to infer the behaviors of clay at higher temperatures (during sintering) based on its performance at room temperature, by observing how water is moving in and out of the 2:1 clay layers during wetting and drying.” Dr. Colin S. Campbell, soil physicist.

This application note will introduce the concept of moisture characteristic curves, and discuss the results of experiments using the Vapor Sorption Analyzer (VSA) benchtop instrument.

Understanding Moisture Characteristic Curves

To completely understand water relations in a material requires an understanding of the amount of water (moisture content) that can be held at a given energy state (water potential). Moisture characteristic curves describe the relationship between water potential and moisture content at a constant temperature. The amount of water vapor that can be absorbed by a material depends on its chemical composition, physical-chemical state, and physical structure. Consequently, the moisture characteristic curve shape is unique to each material or mixture due to differences in capillary, surface, and colligative effects.

The VSA: What Does it Do?

The Vapor Sorption Analyzer (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 potential is determined by a sensor in the sample chamber using the chilled mirror dew point. 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 characteristic curves with hundreds of points are easily obtained.

Hysteresis Curves

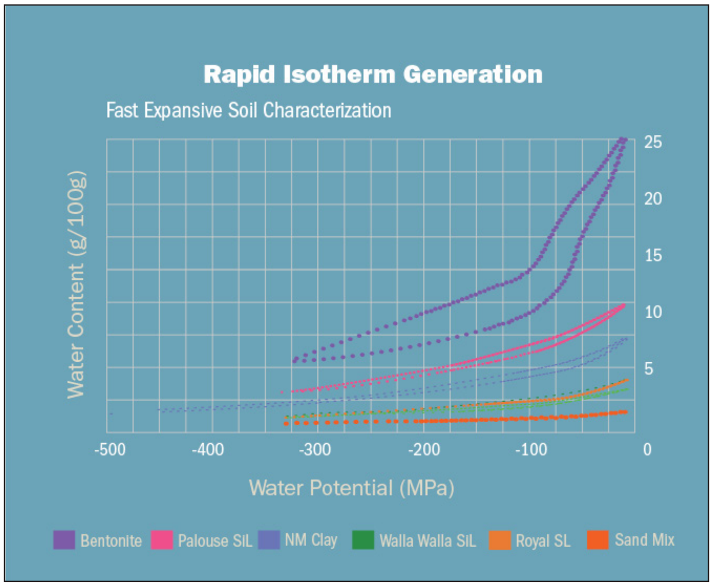

Figure 1. Moisture characteristic curves for six soil materials showing adsorption (lower) and desorption (upper) arms of the hysteresis loop for each material.

Figure 1 shows soil moisture characteristic curves obtained by wetting a sample from a dry state and drying a sample from wet state. The arrows indicate wetting and drying of the sample. The moisture content at each water potential is higher during desorption than adsorption.

As this example illustrates, a soil moisture characteristic curve is not a single valued function but depends on the wetting and drying history of the sample. This phenomenon is called hysteresis.

Non-Equilibrium

If diffusion of water into or out of a material is slow, and sufficient time is not allowed for complete diffusion, there will be a large amount of apparent hysteresis that could be reduced by allowing sample equilibration.

Uses For Moisture Characteristic Curves

For a manufacturer drying a material, the moisture characteristic curve can be used to assist in process control by determining drying rates and optimal endpoints. The moisture characteristic curve also shows whether a material exhibits hysteresis and what impact that has on water potential after drying to a given moisture content. In a hysteretic sample, the moisture content is higher at a given water potential for desorption than for adsorption. The practical impact of hysteresis is that a moisture content that is correct when drying a sample because it corresponds to a correct water potential may not be correct during adsorption because it corresponds to a higher water potential level. Thus, when a material is dried to a correct water potential, but then exposed to humid conditions during storage, the impact of these events can be predicted.

Using the VSA on Soils

We ran samples of five soils along with a sample of Bentonite clay in the VSA. Clay content of the various samples is shown in Table 2. Figure 1 (above) shows the moisture characteristic curves for the six samples. Clearly, increasing amounts of clay in samples increases the amount of water adsorbed at any given water potential. Low clay-rich moisture characteristic curves show a consistent, near linear behavior, but the Bentonite sample shows distinct sections where the energetics of the clay-water interaction change. Also note that 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. 1.

Table 2: Clay fraction of five tested soils

Sample	Clay Fraction
L soil	0.04
Walla	0.14
Royal	0.15
New Mexico	0.35
Palouse B	0.47
Bentonite	

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

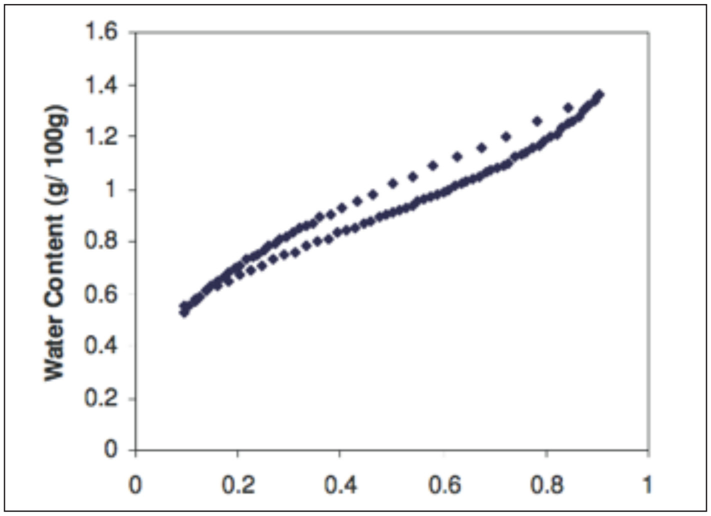

Figure 2. L-Soil moisture characteristic curve with expanded water content scale.

The Bentonite sample in Fig. 1 is clearly different from the other samples. To ensure that this is the result of measurement artifacts, we reduced the sample size and flow rate, and made the measurement over a larger water potential range. We then compared the results to the original moisture characteristic curve in Fig. 3.

Several things are clear from these measurements. First, the method appears repeatable. Second, the samples are apparently very near equilibrium, even at the higher scan rate, since the low and high scan rates match on the desorption arms. Having established this, it is very interesting that the desorption arm appears to be almost independent of where the moisture characteristic curve starts, while the adsorption arm appears to be completely dependent of where it starts. The initial dry down 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 potential. Even the two low adsorption lines differ slightly because they start at slightly different places. A moisture characteristic curve analysis would appear to offer opportunity for additional understanding of clay-water interaction.

What We Learned

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, the change in slope associated with water uptake into clay layers can be seen easily in moisture characteristics curves on the VSA.

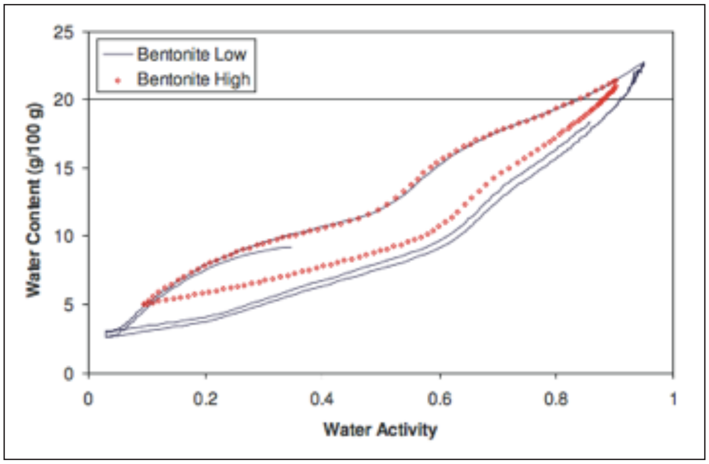

Figure. 3 Bentonite clay hysteresis loops tested at high and low scan rates.

A Blueprint for Moisture Relations

Moisture characteristic curves serve as a blueprint for moisture relations in any material. Modern instrumentation has made it possible for anyone to analyze the moisture relations of almost any material. The efficacy of moisture characteristic curves in a material depends on being able to achieve high data resolution without drastically increasing test times; the VSA is able to do both. These high resolution moisture characteristic curves make it possible to model and engineer materials in ways not previously possible. You can create automated moisture characteristic curves, even holding the humidity constant to show the kinetics of water uptake into crystal structures (2:1 clays). The reward is maximizing the quality and profitability of materials.

Reference List

1. Bell L.N., & Labuza, T.P. (2000). Moisture sorption: practical aspects of moisture characteristic curve measurement and use. *American Association of Cereal Chemists*, St. Paul, MN.

2. Brunauer, S (1945). *The Adsorption of Gases and Vapors*. Princeton, NJ: Princeton University Press.

3. Campbell, G.S. & Norman, J.S. (1998). E*nvironmental Biophysics*. New York, NY: Springer Science.

4. Condon, J.B. (2006). Theories behind the chi plot. *J.B.Condon (ed.) Surface area and porosity determinations by physisorption,* 91-125. Elsevier, Oxford.

5. Brunauer, S., Emmett P.H., & Teller E. (1938). Adsorption of gases in multi-molecular layers. *Journal of American Chemistry Society*, 60:309-319.

6. Condon, J. B. (2006) *Surface Area and Porosity Determination by Physisorption: Measurements and Theory.* Elsevier, Amsterdam.

7. McKeen, R. G. (1992). A model for predicting expansive soil behavior. *Proceedings of the 7th International Conference on Expansive Soils*, 1:1-6.

8. Likos, W. J., & N. Lu. (2002). Water vapor sorption behavior of smectite-kaolinite mixtures. *Clays and Clay Minerals,* 50: 553-561.

9. Likos, W. J., & N. Lu. (2003). Automated humidity system for measuring total suction characteristics of clay. *Journal Geotechnical Testing,* 26:2-12.

10. Orchiston, H. D. (1953). Adsorption of water vapor: I. Soils at 25 C. *Soil Sciences* 73:453-465

11. Quirk, J. P., & Murry, R.S. (1999). Appraisal of the ethylene glycol monoethyl ether method for measuring hydratable surface area of clays and soils. *Soil Science Society of America Journal* 63:839-849.

12. Schofield, R.K. (1935). The pF of water in soil. *Trans. of the 3rd International Congress of Soil Science* 2:37