Fundamentals of Water Potential in Ceramics

Why Measure Water Potential?
In many situations, water content data can be limiting because they don't predict how water moves or behaves in a system. Water potential measures the energy state of water and helps explain the behaviors of water movement that otherwise defy intuition. For example: soil, clay, sand, potting soil, and other media, all hold water differently. Imagine a sand with 30% water content. Due to its low surface area, the sand will be close to saturation. Now consider a fine-textured clay also at 30% water content. The clay may only appear moist due to the surface of the clay binding the water and making it less available.

Moisture relations play a key role in ceramic manufacturing. Water also plays a key role in ceramic manufacturing. Achieving the right moisture level in green bodies can make the difference between a successful firing or a failure.

Defining Water Potential
Water potential is the energy required, per quantity of water, to transport an infinitesimal quantity of water from the sample to a reference pool of free water. To understand what that means, compare the water in a soil sample to water in a drinking glass. The water in the glass is relatively free and available; the water in the soil is bound to surfaces, diluted by solutes, and under pressure or tension. In fact, the soil water has a different energy state from "free" water. The free water can be accessed without exerting any energy. The soil water can only be extracted by expending energy. Water potential expresses how much energy you would need to expend to pull that water out of the sample.

Water potential is a differential property. For the measurement to have meaning, a reference must be specified. The reference typically specified is pure, free water at the soil surface. The water potential of this reference is zero. Water potential in the environment is almost always less than zero, because energy would have to be spent to get the water to the surface as free water.

We can use a thought experiment to better understand water potential. Take a glass of water, and a dry sponge. Dip the corner of the sponge into the glass of water. The water will move from the glass into the sponge.

What is the difference between the water in the glass and the water in the sponge? The answer is that the water in the glass is free, while that in the sponge is, to some extent, bound. It has a lower energy state than the water in the glass. We know that because, to retrieve the water from the sponge, we need to apply energy to it by squeezing the sponge.

That reduction in the water's energy reduces its vapor pressure and freezing point while increasing its boiling point. In other words, the water in the sponge is different from the water in the glass in measurable ways.

Let's consider the reduction in vapor pressure. We can calculate the change in energy that accompanies a change in pressure using the first law of thermodynamics. If we let the symbol U represent the energy in a system, and calculate the change in U that occurs when we change the volume, at constant pressure (assuming no heat is added or removed) we can write equation 1:

1 $$dU = -pdV$$

dU represents a small change in energy, and dV represents a small change in volume. The relationship between pressure and volume, called the ideal gas law, is represented in equation 2:

2 $$pV = nRT$$

where *n* is the number of moles of gas, *R* is a constant, known as the gas constant (8.31 J/mol K) and *T* is the temperature of the gas in kelvins. We can differentiate the ideal gas law to get equation 3:

3
$$dV = -nRT\frac{dp}{p^2}$$

Combining equation 1 and 3 we get equation 4:

4
$$dU = nRT\frac{dp}{p}$$

The energy required to go from the vapor pressure of the pure water in the glass, which we call the saturation vapor pressure and give the symbol *po*. The vapor pressure of the water in the sponge is:

5
$$U = nRT\int_{po}^{p}\frac{dp}{p} = nRTln\left(\frac{p}{po}\right)$$

The ratio *p/po* represents water potential, or water activity (a_w), when we are talking about the water in the sponge, or water in solids or liquids. We call it the relative humidity when we apply it to water in the air, and sometimes multiply it by 100 to express it as a percent. The ratio *U/n* is the energy per mole of water is called water potential. Water potential is represented by the greek letter Ψ and has units of Joules/mole. With this substitution, we finally arrive at equation 6 relating the energy of the water in the sponge and its water potential.

6
$$= RT\ lna_w$$

Equation 6 tells us that we can express the energy state of the water in a material either as a water potential or as a water activity. Some fields of science use water potential and others use water activity. There are some others that use freezing point depression or osmolality, which are equivalent concepts. There are advantages and disadvantages to each, but the important thing to understand is that both are measures of the energy state of the water and have a strong theoretical basis. We focus on water potential here because that is the measure most widely used in soils.

What Determines Water Potential?

Now consider what factors influence water potential. We can lower the water energy by adsorbing the water in the sponge. Water adsorbed onto any surface lowers its energy state. The water is bound by hydrogen bonds, capillary forces and van der Walls -London forces, so it has less energy than free water. We call these matrix effects. The water energy can be decreased in another way as well. We can dilute the water with solutes. Since work is required to restore the water to its pure, free state, this also reduces the water activity and water potential. We call these effects osmotic effects. We sum the reduction in energy from matric and osmotic effects to get the total change in energy.

The WP4C determines water potential by measuring the temperature of the sample and the dew point of the air in a sealed head space.

How Do We Measure Water Potential?

Equation 6 provides a convenient way of measuring water potential or water activity. If we enclose a sample in a sealed container, the relative humidity of the head space will equilibrate with the water potential of the sample. At equilibrium the two will be equal, and we can measure the relative humidity of the headspace to know the water potential of the sample.

The best method for measuring water potential is suggested by the ratio *p/po*. The saturation vapor pressure *po* depends only on the temperature of the sample, as shown in the accompanying graph. If we know the sample temperature, we know *po*. The vapor pressure of the water in the sample can be measured by measuring the vapor pressure of water in the sealed head space of the sample.

The most accurate way of measuring that vapor pressure, and one that goes back to first principles, is to measure the dewpoint of the air. The WP4C dewpoint instrument measures those two variables, so gives a direct and fundamental measurement of water potential. If you want water activity, it is easy to convert between the two measurements.

Other Methods for Measuring Water Potential

Essentially, there are only two primary measurement methods for water potential—tensiometers and vapor pressure methods. Tensiometers work in the wet range—special tensiometers that retard the boiling point of water (UMS) have a range from 0 to about -0.2 MPa. Vapor pressure methods work in the dry range—from about -0.1 MPa to -300 MPa (0.1 MPa is 99.93% RH; -300 MPa is 11%).

Historically, these ranges did not overlap, but recent advances in tensiometer and temperature sensing technology have changed that. Now, a skilled user with excellent methods and the best equipment can measure the full water potential range in the lab.

Conclusion

Water potential is a thermodynamic measure of the energy of water in a material. It defines what water is available for physical-chemical processes at a particle level. In ceramics, measuring water potential may be useful to determine if the water in the clay is at the optimum energy state for sintering. Since consistent results are the goal of ceramic processes, water potential may be particularly well-suited to being a specification for quality.