Lecture No. 3

Moisture content and loss on ignition:

The moisture content of raw materials is a very important consideration as it varies between wide limits in the same materials owing to such factors as condition of shipping and storage and the chemical and physical nature of the materials. Water may occur in materials in tow different ways as water mechanically held (mechanical water), or as water of constitution. Water of constitution is water tied up as an integral part of the molecule, as in ($Al_2O_3.3H_2O$) or as water of crystallization as in borax ($Na_2B_4O_7.10H_2O$). This water of constitution is generally constant for any one particular material. The mechanically held water is the water or moisture on the surface or between the particles of the material.

To determine the water mechanically held or, in some cases, some of the water of crystallization, a weighed sample is placed in a dryer at 110°C until it comes to constant weight. The difference between the weight of the sample when dry and its original weight is the weight of the mechanical water contained in it. The percentage moisture may be based either on the original weight or on the dry weight. The latter is the better practice.

Example

Suppose a 100 g sample of clay, after being dried to constant weight at 110°C, weights 87 g. what is the percentage moisture based on 1) The wet weight? 2)The dry weight?

100 - 87 =13 g of moisture

Percentage moisture (W. W.)= (Grams of moisture/ Wet weight) X 100

=13/100X100= 13%

Percentage moisture (D. W.)= (Grams of moisture/ Dry weight) X 100

= 13/87)X100= 14.9%

Many ceramic materials contain other volatile constituents, beside water, which are driven off only at higher temperatures. Clay for instance, may contain carbonaceous materials, which decompose, carbon, which oxidizes and carbonates, which decompose along with sulphides, sulphates, and other salts, which break down under oxidation, reduction, or heating. The temperatures at which these changes take place vary in different materials and for different constituents.

The determination of these volatile constituents is important in the calculation of melted weights of frits for enamels, glazes etc. The loss on ignition, as this difference is called, gives an indication of the carbon content of clays.

The loss on ignition is determined by ignition of all of the volatile constituents. In the laboratory such a test is made by heating a weighed sample in a porcelain crucible, first over a dull flame and latter over a blast lamp. The difference between the original weight of the sample and its weight after ignition is the loss on ignition, and it represent as a percentage based on unignited sample weight or on ignited weight.

Percentage loss on ignition = (loss in weight/ weight of original sample)X 100

On heating a sample of clay, the mechanical water left from drying is first driven off. Near red heat, the water of constitution is driven off, carbonaceous material decompose, and if there is sufficient air present, the carbon burns to carbon dioxide.if the sample is not heated too fast all the carbon burns out, but if it is heated too fast the carbon becomes entrapped by the fusion of the material and is thereby protected from further oxidation. The sulphides begin to decompose and oxidize to the oxides of sulphur, which go off as a gas, at higher temperature the carbonates decompose into the oxides of the metal and carbon dioxide gas, and at still higher temperature, under proper conditions, even the sulphates decompose.

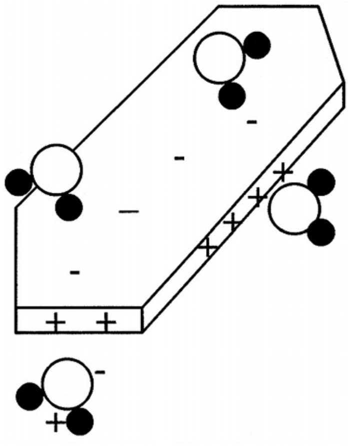
Introduction to Drying:

Drying of ceramics is much more complicated than drying many other objects because unfired ceramics typically exhibit shrinkage during drying. This shrinkage can lead to cracking and loss of acceptable quality in production.

(***Drying is the process of removing water from an unfired ceramic object or raw material in the green or as-formed state or in the as-received state)***. As such, drying is accomplished by supplying energy to the ceramic in order to accomplish evaporation.

Adding Water to a Completely Dry Ceramic and Subsequently Removing that Moisture:

When water is added to a completely dry ceramic powder, the initial portion of water will cover the surface of the particles,(this water is usually called the **surface water or the hygroscopic water**). The phenomena in this initial coverage of the surface involve the electrical nature of the surface and the polar nature of the water molecule as shown in figure below.



Attraction of water molecules to kaolinite surfaces.

When water is added to a ceramic powder, the water generally “sees” a negative charge cloud at the ceramic surface. In order to minimize the energy of the surface, the ceramic surface attracts the positive side of the polar water molecule toward the surface to achieve a degree of wetting. Van der Waals forces develop, holding the water molecules onto the surface.

After the water covers the surface in thin molecular layers — the water next fills voids between fine particles known as capillaries (called the **capillary water**). Capillaries are generally defined as voids or pores of a diameter less than about 1 μm in diameter or size. It can be shown that the diameter of a pore between three spherical particles in contact is 0.154 times the radius of the spheres. In other words, if the average particle size of spherical particles is 1 μm, the average pore size is about 0.2 μm given perfect packing of the spheres.

Since most ceramic compositions also contain some larger pores (generally ~50–100 μm in size) due to imperfect particle packing or gradation, these pores are gradually filled with water. In mixes that exhibit plasticity. This water quantity is called the **pore water**.

Finally, additional water tends to significantly separate particles in the material. In plastic forming processes, this separation adds lubricity to the system to facilitate forming. This last water quantity that causes separation of particles is called the **forming water**.

In drying, water is removed from the ceramic, and the sequence in which the various waters are removed is exactly the reverse of the theoretical sequence of water addition given above; that is, first forming water, then pore water, then capillary water, and finally surface waters are removed.

WATER ADDED TO A DRY CERAMIC POWDER

- First, covers the surface of the particles. (assuming ideal mixing to prevent agglomeration).
- Second, fills small capillaries (space between particles).
- Third, fills pores.
- Fourth, causes a separation of particles.

DRYING REMOVES

- Forming water first (if present).
- Pore water next (if present).
- Capillary water (usually present).
- Surface water (always present).

Stages of drying:

The generalized rate of drying of a ceramic product is shown in Fig. A. The rate of drying is defined as the change in the weight of moisture in the ceramic per unit time, the rate of drying is the slope of the line defined by the drying process. It is clear that the slope of the line is constant during the initial drying of the ceramic, for example, on progression from Point A to Point B in the drying process of Fig.A . For this reason, the initial period is called the **constant rate period of drying**.

As drying continues beyond Point B, the drying rate declines with the rate of decline constant. In other words, the slope of the line in (Fig A) as drying progresses from Point B to Point C is declining at a consistent rate. This period of drying is called the **first declining rate period**.

In the next period of drying (progression from Point C to Point D) the rate of drying declines at an increasing rate; this period is called the **second declining rate period**.

THE PROGRESSION OF DRYING IS:

- The constant rate period.
- The first declining rate period.
- The second declining rate period.

The information presented in Fig. A can be presented in a plot of drying rate versus time. As shown in Fig. B, at the start of drying the rate of drying is constant on progression from Point A to Point B. Beyond Point B, the rate of drying declines constantly until Point C is reached. Then, the drying rate progressively slows until drying is completed. The moisture content at Point B in Figs. A and B is called the critical moisture content (Mc) because shrinkage takes place as drying continues down to Mc, but shrinkage is negligible below Mc, this is the point at which the product can be moved without fear of warpage.

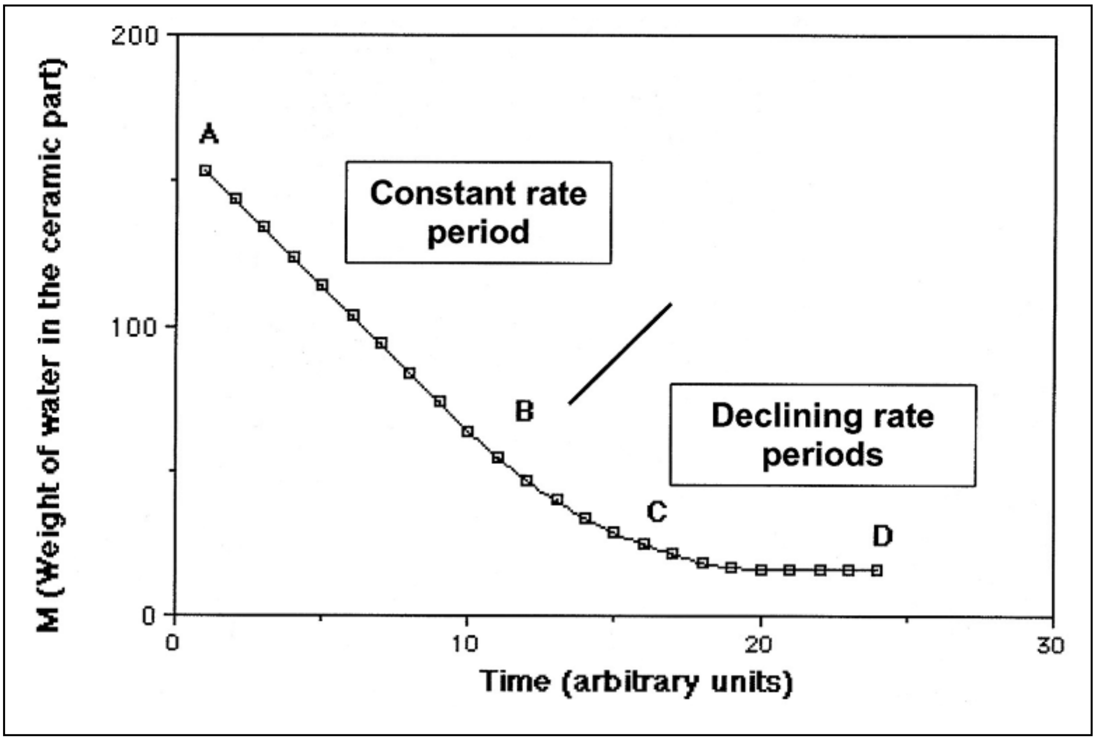


Figure A: Change in moisture content in ceramics during drying.

Rate of Drying:

The rate of evaporation in drying, R, is the rate of water removed in weight of water per unit area of exposed surface in the water (lb/ft^2 or kg/m^2). The rate is proportional to the enthalpy difference between the surface (h_{surf}) and the bulk of the air segment h_{amb}:

$$R=\zeta\left(h_{surf}-h_{amb}\right)$$

where ζ is a proportionality constant called a mass transfer coefficient.

The rate of evaporation is also governed by convective heat transfer,

$$R=h(\,T- Tw)/\Delta h_{vap}$$

where h is the coefficient for convective heat transfer and Δh_{vap} is the heat of vaporization of water. The terms T and Tw denote dry bulb and wet bulb temperatures, respectively.

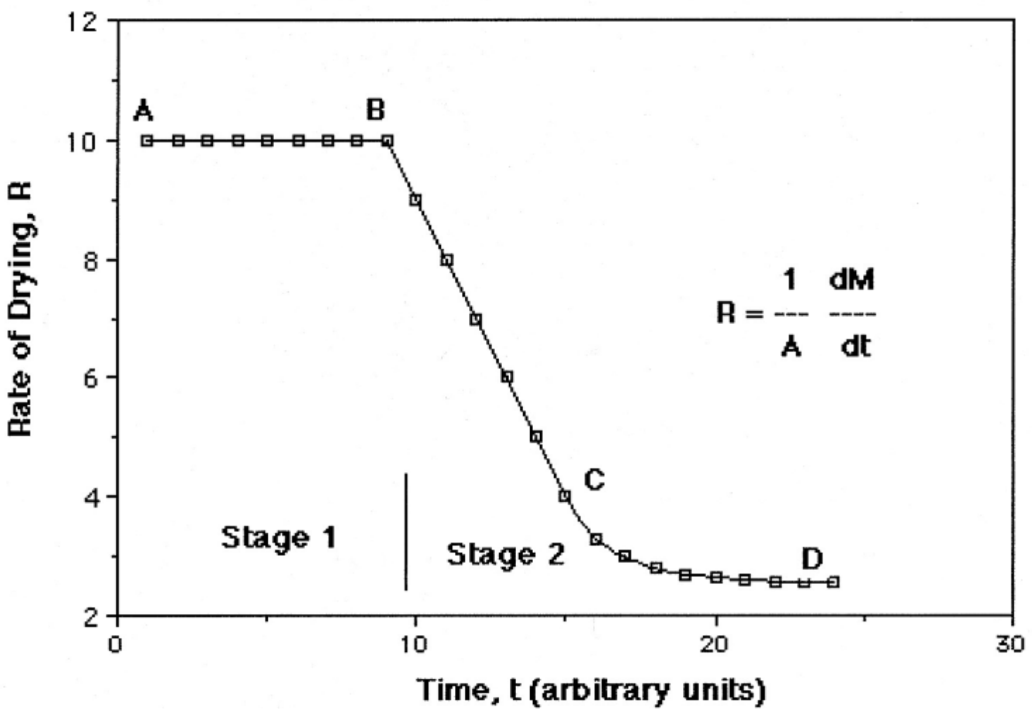


Figure B: Drying rate plot. M = weight of water in the ceramic; A = surface area of the ceramic exposed to the drying environment.

The film coefficient h is found to vary with air velocity. In the simplest case, h is described as follows:

- For air flow parallel to a surface:

$$h= 0.0128G^{0.8}$$

where G is the mass velocity of the air in lb/ft2-h. The dimensions of h are (Btu/h-ft^2-°F).

- For air flow perpendicular to a surface:

$$h= 0.037G^{0.37}$$

Throughout the history of ceramic processing, it has been known that there are three primary factors in avoiding defects in drying:

- The rate of drying during Stage I must be sufficiently slow to avoid stress development, which initiates cracks.
- The moisture content of the ceramic mix affects drying shrinkage.
- The particle size distribution of the ceramic material has a significant effect on the drying shrinkage that is observed.

Drying and firing shrinkage determination:

Calculate the linear drying shrinkage as a percentage of plastic length, as follows:

$$S_d =(L_p – L_d)/L_p X 100$$

where:

S_d = linear drying shrinkage, %,

L_p = plastic length of test specimen, and

L_d = dry length of test specimen.

Calculate the total linear shrinkage after drying and firing of clay shrinkage specimens as a percentage of plastic length, as follows:

$$S_t = (L_p - L_f)/L_p \times 100$$

where:
St = total linear shrinkage after drying and firing, %,
Lp = plastic length of test specimen, and
Lf = fired length of test specimen.

When desired, volume shrinkage may be calculated from linear shrinkage, as follows:

$$\text{Volume shrinkage, \%} = [1 - (1 - S/100)^3]\ 100$$

where: S = linear shrinkage, %.

Water of plasticity: is the water necessary to bring the clay to a good working consistency and expressed as a percentage as

$$T = [(Wp - Wd)/ Wd] \times 100$$

Where:

Wp: weight of plastic piece. Wd: weight of dry piece

Shrinkage water: is that portion of the water of plasticity which is given off up to the point where shrinkage ceases and pore water: that portion of the water of plasticity which is given off from the point where shrinkage ceases until the clay piece has reached constant weight at 100C.

$$\text{Shrinkage water} = t = [(Vp - Vd)/ Wd]\times 100$$

Where:

Vp: plastic volume.

Vd: dry volume.

$$\text{Pore water} = t_2 = T - t$$

References:

1- "Introduction to DRYING of CERAMICS", **Denis A. Brosnan and Gilbert C. Robinson**.
2- ASTM manuals.
3- "ceramic tests and calculations", A. I. Andrews.