

FLOW PROPERTIES OF THE KAOLINITE-WATER SYSTEM

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INTRODUCTION

For the last 20 years, the Ceramic Division at the Massachusetts Institute of Technology has been carrying on basic work with the kaolinite-water system. The results have been published from time to time in the *Journal of the American Ceramic Society* under the title of "Fundamental Study of Clay."

At the start, it was realized that natural clays were so complex that it would be impossible to consider them as a basis for quantitative calculations. Therefore, most of our research has been carried out on specially prepared samples taken from the natural clay. These kaolinite samples had a known particle size, were free from organic matter, and had controlled adsorbed ions. In this way, the effect of any one variable on the rheological properties could be studied in a logical way.

The preparation of the clean kaolinite fractions is an exacting and time-consuming process, which has been fully described in our publications (Norton and Speil, 1938; and Johnson and Norton, 1941), so it need not be discussed here. It should be mentioned, however, that the finer fractions may well contain traces of minerals other than kaolinite, too small in amount to show up by X-ray diffraction methods, yet sufficient to influence the colloidal properties.

FLOW PROPERTIES

The flow properties of kaolinite-water systems must be divided into two groups: the pastes, and the slips. The intermediate range is so sticky that at present we have no satisfactory way of measuring its properties.

Pastes

This region goes all the way from dry powder to a mass so wet that it will just support itself under gravity forces. The flow properties may be measured by twisting a bar in torsion (Norton, 1938; and Graham and Sullivan, 1939), or deforming it in shear (Norton, 1952), very much as the flow properties of a metal are studied. The rate of deforming is quite important, as well as maintaining a uniform water content during a test. Also, the previous history of the specimen must be considered, as strains existing in the piece prior to testing influence the results.

Slips

As this consistency has such a low yield point that it cannot resist gravity forces, the specimen must be held in a container. Usually, the test is carried out in a concentric cup viscometer (Johnson and Norton, 1941), where the rate of shear may be varied and the yield point determined under static conditions.

Sticky Region

Little work has been done with this consistency as the material is too stiff to flow well, and yet too soft to support itself. The only possibility is that suggested by Greger and Berg (1954), where the material is tested in a completely enclosed concentric cup viscosimeter under pressure. There is little practical value in these tests, but they are of immense theoretical value in giving us a picture of the whole system.

PASTES

The flow properties of pastes may be varied by changing the water content, the particle size, the rate of deformation, the surface tension of the water, and the adsorbed ions. These variables will be discussed in turn, and then a probable theory of plasticity will be built around them.

Water Content

Increasing water content, as everyone knows, decreases the yield point and increases the maximum extension. This is shown clearly in Figure 1. If the product of the yield point and the maximum extension is plotted

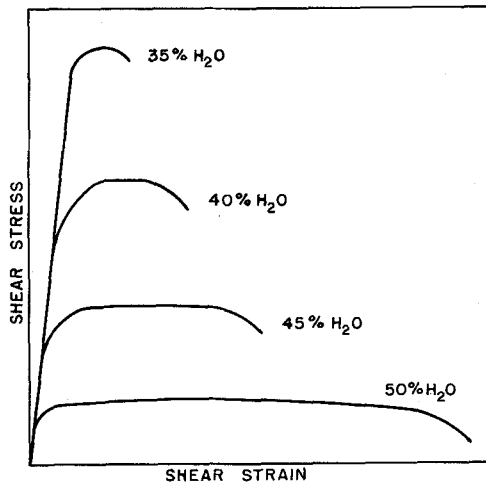


FIGURE 1. — Stress-strain diagram for kaolinite and water.

against water content, a maximum will occur where the mass actually feels as if in the most workable condition (Figure 2).

Particle Size

There seems to have been little quantitative work done (Speil, 1940) on the flow properties of monodisperse fractions in the form of pastes. In general, the finer fractions give greater workability and higher yield points.

Rate of Deformation

Again, little precise work has been carried out on the influence of rate of deformation. It seems evident from a few tests made in our laboratory that high deformation rates give increased yield points and greater extensions. In other words, clay pastes are more workable when rapidly deformed.

Orientation of Clay Particles

When a clay paste is deformed, there is at once a turning of the clay particles closely into alignment along a plane parallel to the direction of shear. This preferred orientation is much like that occurring in deformed metals and, similarly, influences the over-all properties. This condition makes it very difficult, if not impossible, to form a specimen that is uniform throughout. This phenomenon has been reported on by Popov (1944) and more recently by Weymouth and Williamson (1953). In any measurement of the stress-strain values, this orientation must be considered.

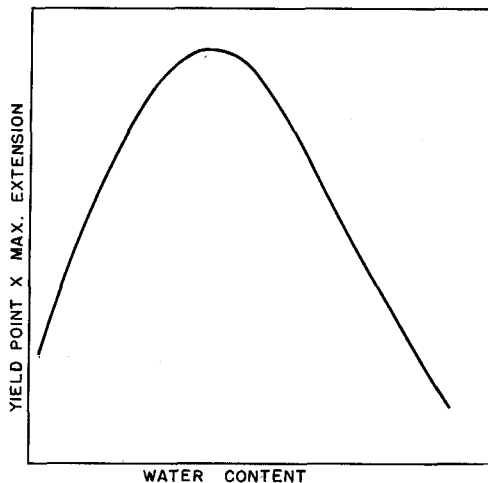


FIGURE 2. — Workability of kaolinite and water.

Adsorbed Ions

The flow properties of pastes are greatly influenced by the adsorbed ions on the clay. Everyone is familiar with the effect of deflocculents which supply mono-valent cations and OH ions for adsorption. With a pure hydrogen clay, little change in flow properties occurs until all of the ions are exchanged, and there are free OH ions available. Then the properties change with great suddenness. For this reason, a paste will change into a slip with only a small addition of deflocculent. Thus, it has been almost impossible to obtain quantitative values, as the properties of the paste must be measured in a different way from the slip.

In general, it may be said that adsorbed hydrogen and calcium ions cause high yield points, while the alkali ions produce low ones (Speil, 1940).

Surface Tension of the Water

The surface tension of water, which normally has a value of 72 dynes-cm., may be depressed by small amounts of non-ionic wetting agents to around 16 dynes-cm. This lowering of the surface tension causes a corresponding lowering of the workability, as shown by Kingery and Francl (1954) in Figure 3. With the lower surface tension liquids, the workability is so low that it is very difficult to form even the simpler specimens.

Theory of Plasticity

There are many theories that account for the flow properties of pastes such as clay and water. The only one that seems to account for all the known facts is the stretched membrane theory (Norton, 1948). This theory

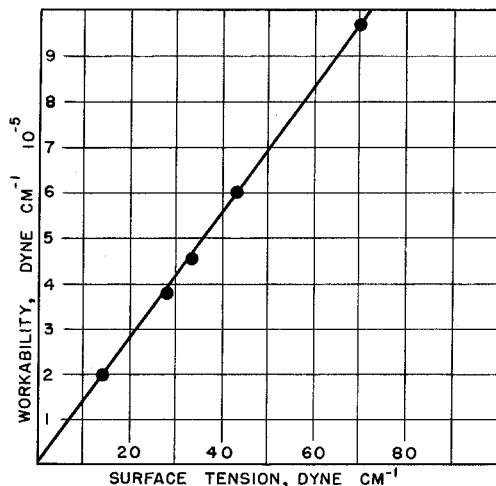


FIGURE 3.— Influence of surface tension on workability.

may be illustrated by the two kaolinite plates surrounded by water films shown in Figure 4. The particles are held together by the surface tension forces in the surrounding water surface and held apart by an equal repulsive force, caused perhaps by like charges on the two plates (electro-kinetic).

These repulsive forces may be measured quantitatively by pressing the plastic paste between permeable pistons (Norton and Johnson, 1944) and measuring the force against water content. The force on a single plate may be computed for a monodisperse fraction, and the water film thickness from the shrinkage in drying. The curvature in the outer water film to give the capillary forces needed to balance the repulsive forces may then be calculated, and come out to be reasonable values.

The fact that the kaolinite plates are thin and flat allows one to slide over the next a small amount without breaking the water envelope, thus giving extensibility to the mass. On the other hand, should the extension become too great, the envelope is broken and the piece ruptures.

The results on pastes made up with a series of water and wetting agents, shown in Figure 3, are an excellent confirmation of this theory, for the same analysis may be applied to a finite specimen with millions of particles. Here it is seen that the forces pressing the particles together are lowered in proportion to the surface tension, and the forces necessary to slide one plate along the next are also reduced in the same way.

SLIPS

This consistency comprises suspensions of kaolinite in water with a low enough yield point to flow under gravity forces. The flow properties are influenced by the concentration of solids, the particle size, and the adsorbed ions.

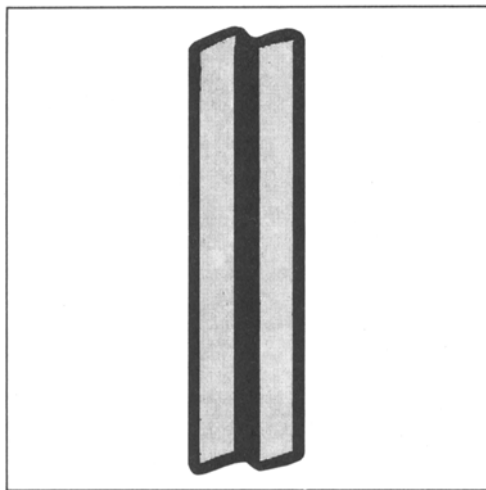


FIGURE 4.— Two plates of kaolinite with their water film.

Suspensions of kaolinite particles are not truly viscous but have an apparent viscosity which varies with the rate of shear. In other words, they are thixotropic. Therefore, to get comparative values, the suspension must be compared under like flow conditions. It has seemed best to run the samples at various shear rates, and then extrapolate to infinite rate of shear in all cases.

Influence of Solid Concentration

The flow properties of water are well known. As solid is added, the apparent viscosity may be expressed (Norton *et al.*, 1944) as:

$$\eta_s = (1 - C)\eta_1 + kC + k_1C^3 \quad (1)$$

where: η_s = apparent viscosity of the suspension.

η_1 = viscosity of the water.

C = solid concentration.

k, k_1 = constants depending upon particle size and adsorbed ions.

The first term in the right side of the equation represents the energy adsorbed by the water; the second term, the energy adsorbed by the individual particles rotating in a velocity gradient (shear); the last term, only important in high concentrations, is the energy adsorbed by interaction of one particle with the next.

The yield point of a suspension of H-kaolinite is given by:

$$F_0 = k_2C^3 \quad (2)$$

In other words, this is the third term of equation (1), which represents the interference factor. This is to be expected, for a suspension of completely independent particles could hardly have a yield point.

Kaolinite suspensions, where the hydrogen ions have been replaced by sodium ions, have no measurable yield point even at high concentration. This indicates that the forces between the particles are not attractive forces.

Deflocculation and Base Exchange

It has been maintained that the yield point and apparent viscosity fall rapidly when the adsorbed hydrogen ions have been replaced with sodium ions. The exact mechanism of deflocculation is not known, as no completely satisfactory theory has been proposed. We do know that deflocculents must have mono-valent cations and give an alkaline reaction (Johnson and Norton, 1941), that is, produce OH^- ions. Bases, as well as salts of strong bases and weak acids having alkalies as cations comprise most of the deflocculents.

The colloidal chemist explains deflocculation on the basis of the Gouy-Freundlich double layer theory of water hulls around the kaolinite particles. The OH^- are supposed to be selectively adsorbed on the "broken edges" of the crystals with Na^+ counter ions. When more OH^- is added than can be

adsorbed on the crystal, an excess occurs in the free water and profoundly changes the forces between the particles (Speil, 1940).

Base exchange may occur in the following ways:

1. On the "broken edges" of crystals where the bonds are unsatisfied.
2. Crystal lattice unbalance due to iso-substitution of an ion of one kind of co-ordination for that of a higher or lower co-ordination, thus resulting in a net charge to be neutralized by an adsorbed ion.
3. Dissociation of structural (OH) radical.
4. Exchange of structural cations.

Number 2 seems to be the most important cause of base exchange in clay minerals, especially in the three-layer types. There is little proof that any of the other three are operative with kaolinite. Therefore, we come to the conclusion that kaolinite, which has no lattice substitutions, should have no base exchange capacity. Measurements show that it does have a relatively small value, varying with the particle size, as shown in Figure 5, as compared with montmorillonite and talc. The former has a high value, somewhat dependent on particle size, while the talc (Kingery *et al.*) has substantially no base exchange. Several people have made the suggestion that kaolinite actually has no base exchange and that values measured are due to admixture of three layer minerals too small in amount to be detected directly, or to poorly crystallized regions where lattice substitution is possible.

When kaolinite is ground to break up the crystals into smaller sizes, the base exchange increases and the perfection of the crystal decreases until an amorphous structure results. Here the increased base exchange may be due only to the possible substitution in this zeolite type of structure.

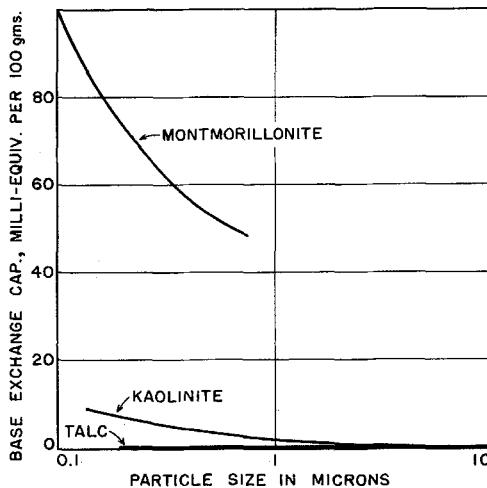


FIGURE 5.— Base exchange capacity.

Altogether, we need to know a great many more facts before we can paint a true picture of base exchange in kaolinite.

CONCLUSIONS

More basic information is needed on the kaolinite-water system to enable us to interpret the facts we have now, and still more is needed to enable us to understand the complex behavior of natural clays.

There is the hope that we may be able to produce tailor-made clays with controlled minerals, particle size, adsorbed ions, organic matter, etc., to give the manufacturer a constant supply of a clay best suited to his purpose.

In the future, perhaps the clay producers will supply a ready-mixed body to rigid specifications more cheaply than a single plant can make it up. One has only to look at the change that has come about in the concrete industry, where now a considerable proportion of the concrete used in construction is delivered ready mixed.

There is a great need for better methods of measuring the workabilities of clay bodies to be used on the automatic jigger in our potteries. The machine is not as adaptable to small changes in plasticity as the experienced jiggerman.

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