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THE ROLE OF WATER IN SLIP CASTING

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16. Abstract

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THE ROLE OF WATER IN SLIP CASTING

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ABSTRACT

Slips and casting are considered in terms of pnysical and colloidal chemistry. Casting slips are polydisperse suspensions of lyophobic particles in water, whose degree of coagulation is controlled by interaction of flocculating and deflocculating agents. Slip casting rate and viscosity are functions of temperature. Slip rheology and response to deflocculating agents varies significantly as the kinds and amounts of colloid modifiers change. Water is considered as a raw material. Various concepts of water/clay interactions and structures are discussed. Casting is a de-watering operation in which water moves from slip to cast to mold in response to a potential energy termed moisture stress. Drying is an evaporative process from a free water surface.

INTRODUCTION

The role of water in ceramics is of the utmost importance. If a normal piece of whiteware clay(ball clay or china clay) is placed into a large volume of water, the water gradually penetrates the clay lump, loosening and separating the particles until the mass falls apart, or slakes. Mixing with a propellor device (blunging) or milling in a ball mill speeds up the disintegration. The result is a slip or slurry.

By reducing the amount of water to one-third to one-half the weight of the clay (depending upon clay fineness), a plastic state is attained. When the plastic mass is dried it forms a hardened lump. By proper treatment with certain chemicals the plastic material can be converted to a creamy, fluid slip.

Slip casting is a consolidation or drawing together of the particles of a casting slip into a semi-rigid, plastic mass through removal of a portion of the liquid phase by an absorbent mold, which brings the particles close enough together to allow certain natural forces of attraction to function.

Slips designed for slip casting operations may be thought of as consisting of one or more polydisperse, particulate ceramic materials dispersed in a liquid (most usually water) at high-volume solids by action of one or more deflocculating agents, forming a suspension that is fluid enough to enter

and completely fill an absorbent mold. Slip casting with low-volume solids ceramic particle suspensions and absorbent plaster molds was practiced as early as the 18th century[1] but use of alkali hydroxides and/or hydrolyzable alkali salts to produce fluidity in high-volume solids slips for casting goes back with certainty only to about 1890[2]. Various refractory oxides were being made into high solids casting slips by acid deflocculation by around 1910[3].

A slip casting operation demands apparently contradictory qualities. The slip must be fluid while being pumped through pipes or poured into molds. Yet the slip must not allow its larger, heavier grains to segregate from the finer particles while the slip is quiescent in the mold. These demands are met by a slight thickening which occurs upon cessation of shear. The degree of gellation, however, cannot be so great as to interfere with a quick clean draining of excess slip at the end of the casting period. The resulting cast must be firm enough to stand and be handled without distortion yet have sufficient plasticity to permit trimming and cutting to allow its ready release from the mold. All this requires an understanding of the physical and colloidal character of deflocculated, high-volume solids systems.

Particles of ceramic materials used in slip casting can range downward from perhaps $5,000\mu m$ (in certain refractory products) to $0.001\mu m$. The large majority of casting formulas, however, are classed as "fine"[4], with an upper size limit

of around 100-200μm. Particles of ceramic materials are most often platey or blocky in shape despite the fact that sizes are here expressed in terms of spherical diameters. Mathematical complications with nonspherical geometries are avoided by using the principle of hydrodynamic similarity (equivalent spherical diameter or ESD) where particle size is given as the diameter in microns of a sphere having the same density and sedimentation velocity as the nonspherical particle under test. As the size of particles is made smaller, there is a gradual change in certain important physical properties (Brownian motion, sedimentation rate, diffusion, rate of coagulation) until particle sizes reach approximately 0.2-0.5μm. Below this diameter there is a sharp increase in the rate of property change. The particles in this state of subdivision are said to be colloidal. A suspension of minus 0.2μm particles in a liquid is termed a lyosol or more simply a sol. If D is taken as a characteristic linear dimension (the diameter, for example) of a particle then its surface is proportional to D^2 and its mass to D^3. The ratio of surface-related forces to inertial (or mass) forces varies as D^{-1}, which accounts for the very large changes in properties as the particles become more and more colloidal.

COLLOID CHEMISTRY

Two main types of colloid are recognized; lyophilic and lyophobic. Lyophilic substances disperse spontaneously

in appropriate liquids to form sols that are not coagulated
or flocculated by electrolytes (substances, such as NaCl or
H_2SO_4, that dissociate into ions in solution). Lyophobic
materials do not spontaneously disperse in liquids but re-
quire mechanical (grinding, for example) and/or chemical
(deflocculation, for example) assistance to form sols.
Lyophobic colloids coagulate or flocculate readily in the
presence of electrolytes which allow the van der Waals forces
to hold the particles together to form agglomerates[5].
Coagulation of lyophobic suspensions can be reduced or elim-
inated by developing a diffuse double-layer of electrical
charges around the particles[6] or by neutralizing acidic
groups of adsorbed organic compounds[7] or by combining
these effects. Nearly all ceramic materials are lyophobic
in nature and require deflocculants to form stable, non-
coagulating slips.

The mechanism by which lyophobic particles are brought
into proximity, where van der Waals forces can function, is
diffusion by Brownian motion[8]. The smaller the particles
the faster they move, so that flocculation of ceramic slips
will depend upon (a) the fineness of the colloid fraction,
(b) the percentage of colloid, and (c) the extent to which
the forces of attraction have been offset by deflocculating
agents.

Some high solids (i.e., concentrated), deflocculated
slips can be made to flow readily when stirred or shaken

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gently but will resist stirring at higher rates of shear, assuming a dry grainy appearance that disappears in a few moments after stirring is stopped. Slips that act in this manner are referred to as dilatant or shear-thickening slips[9]. The particle size distributions of the solid phases of dilatant slips have characteristically narrow ranges and are generally low in colloid. By way of contrast, other high solids, deflocculated slips become progressively more fluid as shearing rate is increased and will thicken with time when allowed to stand quietly. This phenomenon is termed thixotropy or shear-thinning[9]. The particle size distributions of thixotropic slips always have appreciable percentages of colloidal-size particles.

It was found[10] that the deformation and flow (rheology) of ceramic slips can be made to vary by simply altering the extension of the particle distribution (i.e., broadening or narrowing the size limits) or by altering the intermediate distribution between fixed size limits (e.g., substituting one coarse-grained body constituent for another having a differing particle size distribution). Changes of intermediate distribution can also result in marked changes in the ease with which the liquid can pass through the developing cast into the mold.[11]

STABILITY OF LYOPHOBIC SLIPS

In the case of clay slips sodium carbonate and the

various sodium silicates are the commonly used thinning or
deflocculating agents. It has been shown that ions such as
Ca^{++}, Mg^{++}, $SO_4^=$, and Cl^- tend to reduce deflocculation or
even cause flocculation. The presence of limited amounts
of certain types of organic matter associated with ball
clays improves deflocculating efficiency of sodium carbonate
in the presence of flocculating ions. An excess of such
organic material, however, can result in lessened fluidity
of clay slips[7].

Experience has shown that metal oxides can be defloc-
culated either at low pH with HCl or HNO_3 or at high pH with
NaOH, with complete flocculation at some intermediate pH.
The intermediate pH slip, however, can be deflocculated by
introducing alkali salts of a carboxylated or sulfonated
polyelectrolyte[12]. All slips become progressively more
fluid as the amount of deflocculating agent is increased,
pass through a minimum viscosity, and then become progressively
more viscous as the deflocculant is further increased.

DEFLOCCULATION OF CERAMIC MATERIALS

Clay particles gain their surface charges both by ioniza-
tion and ion adsorption. The lattice structure of the clay
minerals of the ceramic clays either permit isomorphous re-
placement of higher valence cations by lower valence cations
or allow occasional cation vacancies[13]. Either way, the
resulting positive charge deficit causes the clay platelets
to have a net negative charge on their basal planes (or faces),

neutralized in nature by the presence of exchangeable cations that ionize when the clay is placed into water thus forming the counterion cloud for the faces of the clay particle. The edges of clay platelets may be positive under acid conditions, neutral in the region of pH 7.0, and negative at higher pH levels [13]. With an excess of H^+ (low pH) the edges are positively-charged. Where OH^- and H^+ are in balance the edges are neutral and at high pH, OH^- is adsorbed and the clay particle is fully negatively-charged. Metal oxides, on the other hand, adsorb H^+ or OH^-, whichever is in excess, and so become either positively or negatively charged, depending on pH[6]. Surfaces that are already charged, as, for example, clay platelet edges or calcined alumina particles at a moderate acidity (say pH 6.0), show a preferential tendency to adsorb surfactant ions, which in turn may form hemi-micelles[14] with other surfactant ions so that a surface charge reversal may occur with little or no change in pH. Or counterions having a high charge number may be adsorbed and reverse the existing surface charge[6]. The mechanism of deflocculation has been shown to be an exchange reaction in which cations low in the series H^+, Al^{3+}, Ba^{2+}, Mg^{2+}, Ca^{2+}, NH_4^+, K^+, Na^+ replace those higher in the series while at the same time hydroxyl ions are made available to charge the surface of colloidal particles[15].

The interaction of the clay particles with the ions of the bulk is dynamic, in that ions pass from the liquid to the solid and in the reverse direction. This process is

termed "ion exchange".

Various mechanisms have been suggested as the basis of ion exchange. Brindley[16] is of the opinion that no single mechanism is involved; rather several mechanisms are involved but to different degrees for the different clays. It is necessary to consider ion exchange in light of the nature of clays and the liquid medium.

Two main causes are assigned to exchange of cations by clays. One is related to the presence of dissociable ions on the surfaces of the particle; this is the so-called "broken bond" hypothesis. Unsaturated bonds on the clay surface are thought to take up H^+ or OH^- ions from the water phase to satisfy these valences. Then, if the H's are dissociable they can be displaced by cations in an exchange reaction.

The other hypothesis relates to the effect of isomorphous replacements of higher valence cations by lower valence cations in the crystal lattice. Cations are adsorbed from solution to balance the charge deficit. The adsorbed cations may be displaced by other cations in an exchange reaction.

Although anion exchange by clay minerals is certainly possible, much less attention has been paid to this than to cation exchange. Various mechanisms can be visualized by which anions can be adsorbed and exchanged by clays. Anions forming part of the crystal structure and anions in water solution can exchange; these would be easily accessible surface

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ions. Or the exchange may involve all anions of a clay lattice by means of solid-state diffusion. Or, as is more likely, anion exchange may occur at the boundaries of the silicate layers.

An exchange of F^- for OH^- is a likely reaction in view of the similarity of size, charge, and polarizability. F^- frequently occupies OH^- positions in natural minerals, such as mica. Dickman and Bray[17] and Samson[18] used NH_4F as a source of F^- ions, while Romo and Roy[19] employed NaF. In all cases there was an attack on the clay with formation of $(NH_4)_3AlF_6$ or Na_3AlF_6, respectively. The work of Romo and Roy[19] left doubt as to whether any F^- for OH^- exchange had occurred. Samson[18] concluded that for kaolinite surfaces OH^- was displaced by F^-, but Al ions were dissolved from near edges, thus exposing more OH^- for replacement by F^-.

EFFECT OF TEMPERATURE

Weber[20] referred to the effect of temperature on slip consistency and later McDougal[21] showed that variable slip temperatures led to variable casting performance. Hall[22] and Schramm and Hall[23] noted that the lowered viscosity of slips due to increased temperature was out of proportion to purely viscous considerations, suggesting a possible modification of the state of aggregation as being responsible.

Russell and Mohr[24] found the rate of cast of kaolin slips to be relatively stable over the 15-27°C range, rising

sharply at 35°C, and dropping again at 39°C. Rolke[25] reported that heating slip to 35-40°C increased the rate of clay dispersion about four-fold over cooler slip, and that heating to 30-70°C reduced the viscosity 40 percent, raised the casting rate 40 percent, and increased the green strength by 45 percent. Van Wunnik, et al.[26] showed that slip and mold temperatures were important factors in governing the quality and rate of casting. As slip temperature increased, viscosity decreased and the range of deflocculation widened. Even though the viscosity of a warm slip was appreciably lower than that of a comparable colder slip, the warm slip still cast more rapidly, sometimes by as much as 25 percent. Where a slip was warm (e.g., 40°C) and molds were cold (e.g., 20°C), draining was poor and casts remained soft for long periods after draining. When molds were held in the 25-40°C range even cool slip cast well.

Herron and Cutler[27] studied casting kinetics and reported that the rate of diffusion of water through the accumulated cast adjacent to the wall of the mold governed the casting process, and that the rate of cast was inversely proportional to viscosity of slip water at all temperatures. Roy[28] established experimentally that the rate of cast was a direct function of the water temperature of the mold and of the slip. Faster movement of water through porous structures, such as a cast and the plaster mold, is expected because of lowered water viscosity at higher temperature.

Cold plaster cools warmer water coming from the slip and the rate of cast is reduced. Lower slip viscosity at higher temperature was attributed to freer movement of the water.

SLIP RHEOLOGY AND CAST PROPERTIES

One of the more difficult aspects of slip casting is insuring constant cast properties such as rate, amount of water retained by the moist cast, and dry strength; all of which are some way related to the consistency of the slip and its tendency to thicken upon standing (i.e., its thixotropy). It is common practice in the industry to attempt control of casting qualities by maintaining a constant solids content and adjusting the viscosity and thixotropy by varying the amounts and kinds of deflocculating agents and the kinds and amounts of colloid modifiers (i.e., organic substances that enhance deflocculation and various inorganic cations and anions that retard or inhibit deflocculation). Consistency measurements and thixotropic tendencies of slips are commonly measured with rotational viscometers, such as the Brookfield RVT[29] viscometer or the Gallenkamp Technico[30] viscometer. Less frequently used are flow tubes.

WATER-CARRIED SOLUBLE SALTS

Slip rheology and response to deflocculating agents will vary significantly as the kinds and amount of colloid modifiers change. Two very common ways in which this can

happen are (a) changes in the soluble constituents of pro-
cess water and (b) development of soluble sulfates in ball
clays. Assurance of potability and softness in municipal
water supplies must presuppose content of natural variation
in the amount of dissolved substances, while soluble con-
tent of natural water sources may vary with seasonal floods
or droughts or contamination by industrial wastes. Some
idea of changes from source to source and season to season
for various city water supplies can be gained from the

analyses in Table I. Ball clays contain sulfides which
oxidize in the presence of air and water to form soluble
sulfates in storage. From these data it may appear that
a wide variation can be tolerated in body forming but it
must be remembered that chloride and sulfate salts are some-
times quite soluble and rapidly dried ware can develop large
surface concentrations that might be detrimental to glazes.

In one such instance soluble sulfates in a municipal
water supply were so high that the filterpressed body con-
tained several times as much sulfate ion as had the original
raw clays. Casting slips made from this filterpressed body
developed so much sodium sulfate from interaction of de-
flocculant and sulfate ion that the dried ware had a heavy
surface concentration on the upper areas of the dried ware.
The result was badly scrambled engobe and glaze.

The possibility of wide, rapid changes in the kinds
and amount of water soluble salts in process water (or clays)

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can lead to marked differences in performance of ceramic
formulations; in particular casting slips and glaze slips.

Treatment of municipal water supplies to insure pota-
bility can mean variation in the amount and kind of ions,
especially when the raw water changes with seasonal floods,
droughts, or industrial waste contamination. The major water-
borne ions affecting the degree of deflocculation of clay-
based slips are Ca^{2+}, Mg^{2+}, Fe^{2+}, Cl^-, and $SO_4^=$. Hardness
is expressed in terms of $CaCO_3$ although this figure covers
the sum of Ca^{2+}, Mg^{2+}, and Fe^{2+} present, regardless of its
original form. Very soft water contains as little as 15 ppm
of hardness while a hard water carries 100-200 ppm. The
alkalinity of water usually consists of calcium or magnesium
bicarbonate. Softening of water with lime and soda ash in-
troduces carbonate and hydroxyl ions. Sulfate may enter as
alum used in clarifying water or from industrial sources while
chloride may come from chlorine-treating or naturally occurring
salts.

The presence of calcium hardness in whatever form is
reflected in increased defloculant requirement of casting
slips and reduced fluidity, even at maximum deflocculation.
Non-deflocculating chloride and sulfate ions also increase
deflocculant requirement and further reduce fluidity. Rate
of cast and percent retained water are increased by the
presence of alkaline earth chlorides and/or sulfates. The
sulfate ion reduces the production of hydroxyl ion from

sodium carbonate and lessens neutralization of acidic groups of clay-associated organic matter.

WATER AS A RAW MATERIAL

It is not difficult to appreciate why the inter-relationships between clay, especially, and water should be so hard to understand. Water itself is a highly complex entity. Clays and related minerals also have complicated structures, possessing many unusal groupings and configurations that could affect their relationships with polar water molecules.

Three features of crystal surfaces can influence water molecules that come into contact with them:

(a) distorted ionic groups on the solid surface,

(b) broken bonds at fractures or on cleavage planes,

and (c) isomorphous replacement lattice charge deficits. Further complications occur where minerals have lattice holes large enough to accommodate water molecules (e.g., the zeolites).

A detailed survey of available literature led Drost-Hansen[31] to conclude that (a) the ordering of water molecules near most solid interfaces differs significantly from that of the bulk water and (b) the interfacial structure extends in a gradually modified form over some distance from the surface. The character of the solid surface was thought to govern the kind and extent of structuring of vicinal water, but this relationship could be modified by the kind and amounts of ions present in the water solution[32].

It is not possible to explain the plastic behavior
of clay-water masses without assuming some form of adsorption
of water by the clay particles. The inherent negative
charges, which can be demonstrated for clay particles[33],
and the unsatisfied valences at broken edges[34] lead to
intense electrical fields near the particle surface. Some
authorities postulate simple adsorption of polar water mole-
cules held in an oriented structure by hydrogen bonds[35].
Others believe the water dipoles are attracted by reason
of the good geometric fit between hexagonal network of ice
and the clay lattices and are thus held by hydrogen bonds
in an ice configuration.

Almost certainly the Frank-Wen[36] concept of im-
mobilization of water in compact A-region hulls near ions,
and the development of zones of highly mobile water dipoles
in "broken structure" B-region layers can be used (in pos-
sibly modified form) in considering development of water
hulls on clays. Clay lattices fracture in such a way as to
expose unsaturated ionic bonds at the edges of the plate-
lets. Exposed Al^{3+}, Si^{4+}, $O^=$, and OH^- each will provide
active sites for attraction of water molecules[34]. It is
probable that the OH-layer of the kaolinite layer unit and
the O-layer of the three-layer units can adsorb H_2O by
hydrogen bonding.

There is a large volume of literature dealing with
the general problem of water/clay interactions[31]. Some

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investigators favor the idea of long-range ordering[37].
On the other hand, we find van Olphen[38] arguing that long-
range ordering of water at clay-mineral surfaces is not
needed to explain the rheological properties of clay-water
systems.

It is difficult to separate structural phenomena from
geometric effects because of such things as packing of clay
platelets or the action of exchangeable cations on water
structure. In general, Drost-Hansen[31] thought that the
necessarily high concentration of ions near the clay sur-
face resulted in concentrated "local solutions" that made
experimental work difficult.

In the course of an X-ray study of water in frozen
clay-water paste it was found that ice crystals had formed
with their c-axis perpendicular to the c-axis of the clay
lattice[31]. Apparently the ice was not formed by direct
epitaxis upon the solid. Two alternative explanations of
the nucleating power of clays were considered:

> (a) there was possible nucleation at "favorable"
> sites on the clay with the ice nucleus grow-
> ing parallel along the platelet surface,
> all the while being separated from the clay
> (except for occasional points of attachment)
> by unfrozen structured water containing ex-
> changeable cations, hydrated oxides, and any
> electrolyte that might be present,

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or (b) nucleation occurred at some distance from

the clay surface and as ice formed any ions

present   were excluded, so that salts

concentrated in a layer between ice and clay.

It would appear that the nucleation may occur in a disordered

zone between vicinal ordered water and bulk water.

Drost-Hansen[31] made reference to interesting studies

of clay-water bonding by Wu, who used a nuclear magnetic

resonance method. Spin-spin and spin-lattice relaxation

times were determined with water and heavy water adsorbed

onto kaolinite and montmorillonite. It was concluded that

below 0°C the water near the clay surface had a structure

different from that of ice. For sodium-montmorillonite at

100% water a viscosity of 110 poises was found for the

layer water; but at 40% water an apparent vicinal water

viscosity of 330 poises was found. By assuming the energy

of activation for viscous flow as approximately the 8 kilo-

calories/g-mol found for ion movement in the two molecule

layers of water in bentonite, this would correspond to a

water layer viscosity of 700 times that of ordinary water.

Mestik and Aidanoda[31] measured heat conductivity of

water between layers of mica. Thermal conductivity of water

lying between mica sheets was found to be at least 10 times

greater than that of the bulk water. The thermal con-

ductivity of ice was only 3.5 times that of bulk water. So

this study appears to indicate substantial structural changes

of water near a mica surface, and that the structure is
not that of ice.

The thickness of the adsorbed water film seems to vary
with the degree of deflocculation[39]. Negatively charged clay
particles suspended in water attract cations to their surfaces.
A simple picture shows a layer of positive ions at or near the
negatively charged surface neutralizing the negative charge.
Beyond this is a distribution of anions and cations similar
to that of the bulk solution. This is the Helmholtz electri-
cal double layer concept. However, the orginal Helmholtz
double-layer was unsatisfactory in many respects and has been
modified over the years. The more realistic Gouy-Chapman-
Stern concept is given by Figure 1. As proposed by Stern[40],
the double-layer is divided into two parts separated by the
Stern plane, which is located at a distance from the charged
plane equivalent to the radius of a hydrated ion. Specifically
adsorbed ions are those that are temporarily attached to the
charged surface by electrostatic and/or van der Waals forces.
These ions are in dynamic equilibrium with the ions of the
diffuse layer. Ions with centers located beyond the Stern
plane form the diffuse portion of the counterion double-layer.

The potential drops sharply from ϕ_o at the charged clay
surface to ϕ_s (the Stern potential) in the Stern layer, then
decays exponentially from ϕ_s to zero beyond the diffuse double-
layer. The potential at the plane of shear between bound
water and bulk water is termed the zeta potential and is a

measure of the repelling force between two similarly charged clay particles. The "thickness" of the double-layer is taken as the reciprocal of the Debye parameter kappa. Kappa is an index of the concentration of ions in the bulk solution. The larger k is the more attraction there is for counter-ions and the more rapidly ϕ decays. The smaller the counter-ions and the greater their charge the closer they are drawn toward the charged surface, so that the double-layer thickness, 1/k, is reduced.

The Frank-Wen[36] concept of an immobilized hull of water around ions of small size and high charge allows one to consider a mechanism of formation of a solvated hull a-round clay platelets. The surface of clay has positive and negative ionic sites owing to exposure of Al^{3+}, Si^{4+}, $O^=$, and OH^-, especially at broken edges. Since free ions have been shown to attract water molecules into ordered structures it is logical to assume that unsaturated valencies of the clay lattice must also attract and order water dipoles, or other ions dissolved in the water, to satisfy charge deficits.

Just how thick a layer of water can build up must, therefore, depend to a large extent upon those types of ions found in the water. It can be shown that structure-promoting free ions such as Ca^{2+}, Mg^{2+}, and Al^{3+} tend to immobilize tightly held, organized layers (A-region) of water molecules. Since cations are attached to the clay surface it is reasonable to assume that the thickness of

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the solvated layer around the particle would depend to some extent upon the character of exchangeable cations.

Various means have been used to determine the thickness of the adsorbed water on clay particles. Most measurements have been derived from adsorption of water vapor on clays under controlled humidity conditions. For kaolinites, measurements of this kind indicated film thicknesses of around 15Å; however, calculations from particle-particle distances near the lower plastic limit gave thicknesses up to 1000Å. East[41] calculated water thickness from shrinkage measurements and water volume loss. For a hydrogen-kaolin he found a hull thickness of 80Å, for calcium-kaolin 106Å, and for sodium-kaolin 186Å.

Davis and Worrall used an interesting technique involving adsorption of water from a glucose solution. For various mono-ionic ball clays and kaolins Davis and Worrall[42] reported values of clay film thickness as shown in Table II. In discussing their results, Davis and Worrall were of the opinion that there was no correlation between water adsorption and zeta potential. The cation-exchange capacities of their clays (around 5.0 meq/100g for china clay and 15.0 meq/100g for ball clay) were too low for any primary hydration of ions to be much of a factor in the relatively high amounts of water found to be adsorbed. Reference is made to the Frank-Wen[36] concept of "structure-breaking" (by a particular kind of ion that randomizes the water dipoles by preventing

the "flickering cluster" structuring occurring in ion-free water) and "structure-promoters" (those ions that tend to attract compact, ordered layers of water dipoles). The B-region lying between structurally normal bulk water and the ordered, immobilized A-region water is the zone of "structure breaking".

Lawrence[43] indicated that increases of ordered structure involved entropy losses, while decreases of structure involved entropy gains. He used the entropy of solution $\triangle S$ (the entropy change in calories per degree-mol occurring as the hypothetical mol fraction of unity is passed in solution) as a basis for correlating structure effects of ions. From $\triangle S$ he calculated $\triangle S^{st}$ (the contribution to entropy change due to effect of ions on water structure). Table III gives $\triangle S$ and $\triangle S^{st}$ values for a number of different ions. The $\triangle S^{st}$ value for Li^+ was indicative of some ordering whereas those for Na^+ and K^+ indicated an increase in disorder of bulk water structure. The F^- ion promoted some ordering while Cl^- had a $\triangle S^{st}$ that meant an increased disorder. The negative $\triangle S^{st}$ for Mg^{2+}, Ca^{2+}, and Al^{3+} were indicative of promotion of long-range order in ionic water hull strucutre.

Figures 2 and 3 are plots of the ionic field strength, Z/a^2, (where Z= valence and a= ionic radius) against $\triangle S^{st}$ and ionic elevations of fluidity by a number of ions. In the case of Z/a^2 vs $\triangle S^{st}$ there is an excellent correlation for cations and anions considered separately. Naturally,

one would expect a difference between anions and cations be-cause of the difference in bonding for M^+-H_2O and A^--H_2O.

Hydrogen bonding[44] has to be taken into account for A^--H_2O. The data for Z/a^2 vs fluidity do not quite show the good correlation seen in Figure 2; the data of Figure 3 indicates the Na^+ to be a structure promoter where entropy data shows it to be a structure breaker. Structure promotion is a function of field strength of the ion; the smaller the ion and the larger its charge, the greater the field strength.

In an assessment of their data Davis and Worrall[42] noted some qualitative agreement between structure-promotion theory and their results. The rather low Li^+ values were possibly due to hydrolysis of the clays, which results in a partial conversion to H-clay. Note that H-clay water layers were thin for both ball and china clay. Their china clay was 95% kaolinite; whereas the ball clay approximated 54% disordered kaolinite, 32& mica, and 14% fine quartz.

DE-WATERING

Most of the water in a ceramic formulation never actually makes it into the kiln but is removed in forming and drying steps. The peculiar nature of water makes these de-watering steps rather interesting.

The degree of deflocculation of a given casting slip, for example, governs the rate at which water is removed by the mold. A casting operation is basically a concentrating process by means of which the colloid density is raised and

coagulation increased. For a given slip viscosity and thix-
otropy index, Ryan[45] found that clays containing Ca^{2+} and
Mg^{2+} as exchangeable cations cast more rapidly than clays
containing Na^+. The water retention of the alkaline-earth

clay casts was in all instances higher than in the sodium-
clay casts, although cast quality was acceptable in all cases.
In similar fashion the filtering rate of non-deflocculated
slips is increased by introduction of polyvalent cations.

The temperature of casting slips and filtering slips
has a profound effect upon slip viscosities and the rate of
cast and filtration rate. It has been shown that as slip
temperature is increased its viscosity drops and rate of
de-watering increases[46]. Roy[46] has demonstrated that
rate of cast is a direct function of the changes in viscosity
and surface tension of the water phase of slips with temperature.

Once the cast, plastic-formed, or dry-pressed item has
been made the manufacturer is faced with the necessity of
removing residual moisture as quickly and safely as possible.
A mistake ceramists often make is to consider water content
as a basic parameter for movement of water. This is not the
case; soil scientists long ago showed that water only moves
in response to a gradient of potential energy of the water[47].
This gradient was termed moisture stress. The ability of a
moist system to retain its water ranges from approximately
zero (zero moisture stress) in dilute clay suspensions to

about 10^{10} ergs/g for nearly dry clay. A soft plastic clay body has a moisture stress around 4×10^5 ergs/g, the leather-hard state 5×10^7 ergs/g, and an air-dried mass about 10^9 ergs/g. By plotting moisture content versus log of moisture stress it is seen that reduction of moisture in drying requires little expenditure of energy in the early stages of drying. At an inflection point in the curve the shrinkage will have ceased and the slope of the curve becomes much less steep over a moisture content ranging from around 18 percent down to around 5 percent where a second inflection point shows up. From this point down to zero moisture content the moisture stress increases sharply.

Roy[46] has demonstrated that the mechanism of transfer of moisture from the moistware is an evaporative process from a free water surface. Rate of drying thus depends upon temperature, relative humidity, and volume of air movement across the free water surface.

During the early stages of drying, especially of large items, it is desirable to maintain a blanket of moist air over the piece to lessen moisture movement from its surface to prevent differential shrinkage, while the interior water is being warmed up to approximately the dryer temperature. Humidity may then be dropped moderately during the intermediate drying period and once the "5 percent" level is reached temperature can be raised and humidity dropped.

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TABLE I

City Water Analyses

Locality	Hardness, ppm CaCO$_3$	Alkalinity	Sulfate
Atlanta, Ga.	10 - 16	8 - 15	5-- .20
Mansfield, Oh.	122 - 387	98 - 330	50 - 175
Trenton, NJ.	21 - 68	4 - 60	10 - 35
New Castle, Pa.	57 - 180	18 - 72	20 - 65
S.W. Illinois	315 - 560	105 - 232	250 - 505
S.E. Ohio	312 - 484	65 - 110	110 - 215
S. Central Texas	0 - 12	400 - 494	0 - 10

TABLE II

Adsorption of Water on Mono-Ionic Clays

Clay Type	Exchangeable Cation	Calculated Thickness, Å
China Clay	H^+	68
" "	Li^+	117
" "	Na^+	106
" "	K^+	49
" "	Mg^{2+}	138
" "	Ca^{2+}	117
" "	Sr^{2+}	85
Ball Clay	H^+	33
" "	Li^+	40
" "	Na^+	104
" "	K^+	37
" "	Mg^{2+}	143
" "	Ca^{2+}	82
" "	Sr^{2+}	87

TABLE III

Entropy of Solution of Monatomic Ions in Water

Ion	$\triangle s$	$\triangle s^{st}$
F^-	-40.9	- 3.5
Cl^-	-26.6	+10.2
H^+	-38.6	
Li^+	-39.6	- 1.1
Na^+	-33.9	+ 4.0
K^+	-25.3	+12.0
Mg^{2+}	-84.2	-27.6
Ca^{2+}	-65.5	-10.6
Al^{3+}	-133.0	-42.0

STERN LAYERS

SOLID

(K)*

SOLID

[a]

DIFFUSE LAYERS

ϕ_o

ϕ_s

POTENTIAL

(K)*

ϕ_o

ϕ_s

POTENTIAL

[b]

o

$1/K$

o

$1/K$

DISTANCE

DISTANCE
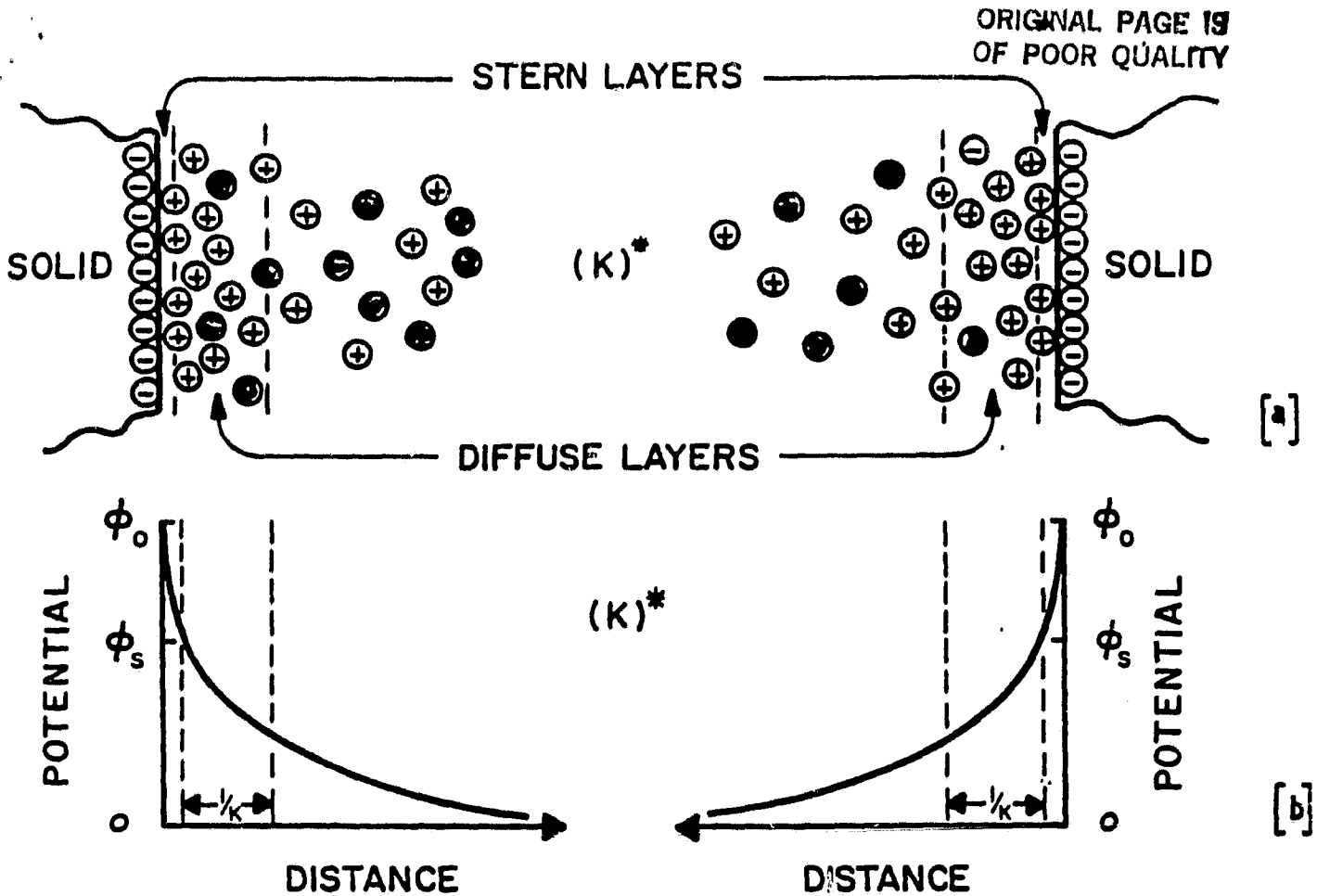
(K)* = ELECTROLYTE CONCENTRATION FUNCTION

Figure 1.   Diagram (a) shows two charged surfaces with their
attendant diffuse double-layers approaching one
another. The Greek letter kappa is an index of
ion concentration in the bulk solution beyond the
double-layers. Diagram (b) shows that the potential
drops abruptly across the Stern Layer, then more
slowly through the diffuse counterion cloud. The
reciprocal of the Debye parameter K is arbitrarily
taken as the measure of double-layer thickness.
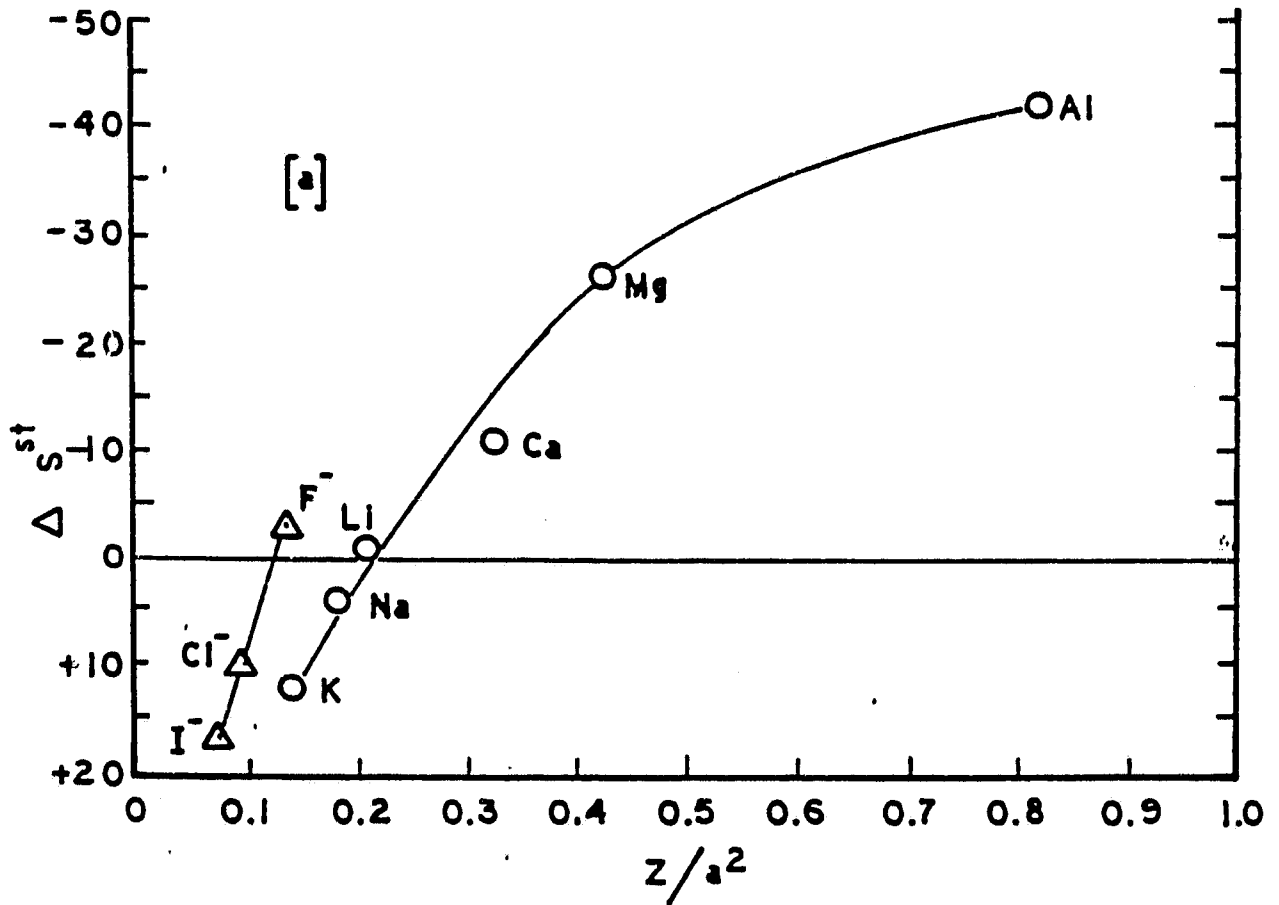
All k's = kappa

Figure 2. Plot of ΔS^{st} against charge per unit areas of
various anions and cations. Diminishing ΔS^{st}
indicates increased A-region ordering. Increasing
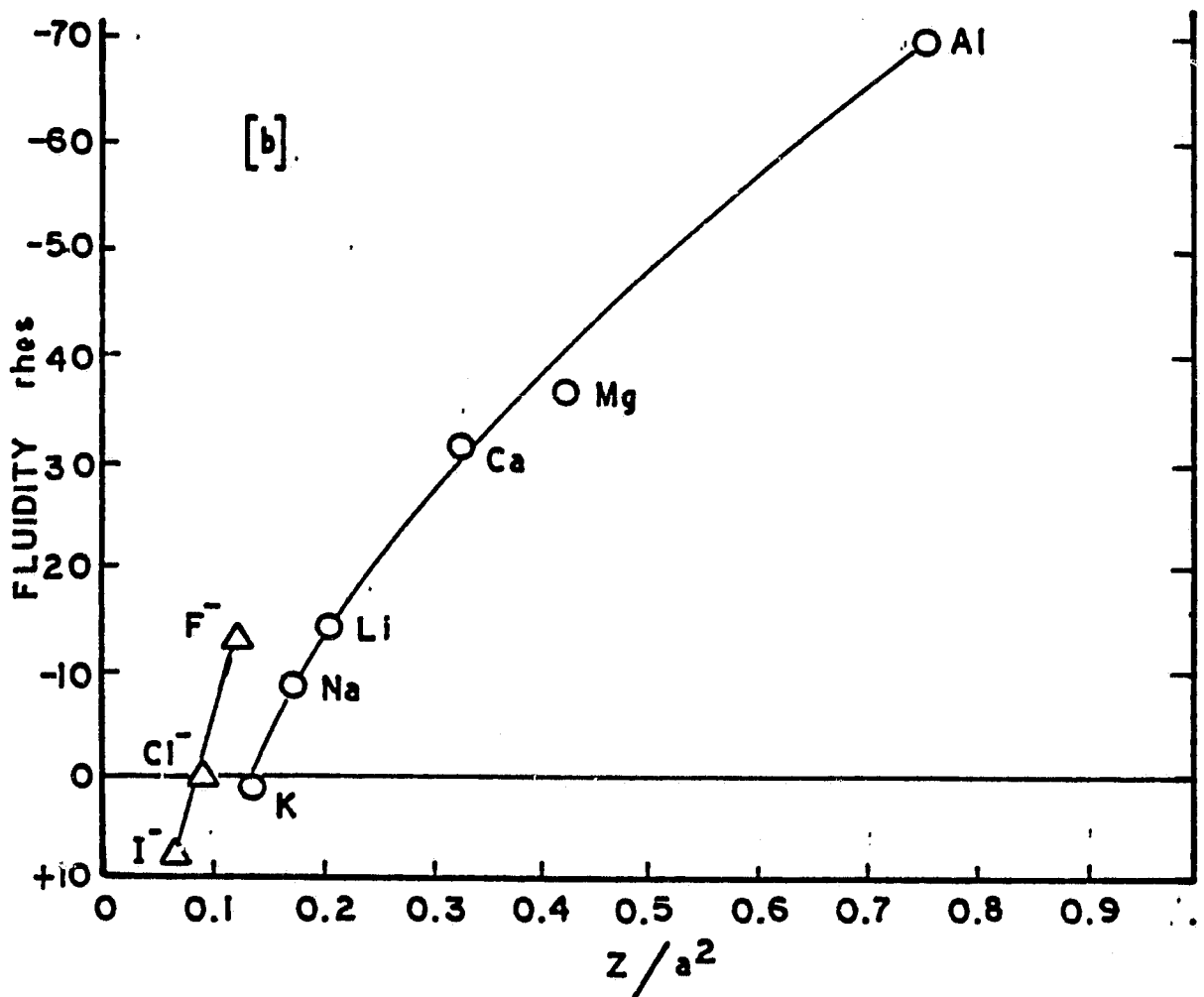ΔS^{st} indicates wider B-region disordered zones.

Figure 3. Effect of charge per unit areas of various anions and cations upon fluidity (reciprocal of viscosity) of water solutions. Decreasing viscosity indicates tighter bonding of the Λ-region water.