The role of water in sludge dewatering

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ABSTRACT: While the dewatering of wastewater sludges has received considerable research attention, it has been assumed that the water continuum surrounding the sludge particles has the physical properties of bulk water. This paper suggests that such an assumption may not be valid. The existence of vicinal water, consisting of ordered and layered water molecules on the surfaces of submerged solids, is demonstrated using research from various disciplines. The meaning of "bound water" as used in sludge technology is discussed, and it is shown that bound water can be defined in several ways, depending on the test used. It seems reasonable that bound water as it is usually defined actually consists of three different types of water—water captured in the interstitial spaces within flocs and within cells, vicinal water on the surfaces of solids, and water of hydration. Only some of the interstitial water can be removed by mechanical dewatering. Because of the large surface area of sludge particles, including living cells, it is likely that much of the bound water is vicinal water, and this cannot be removed mechanically. The determination of the various fractions of these waters may lead to a better understanding of mechanical sludge dewatering. *Water Environ. Res.,* **66,** 4 (1994).

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The separation of water from solids, or sludge dewatering, continues to be a major problem in wastewater treatment. Some sludges are easier to dewater than others, but the reasons for these differences are not well understood. It is usually agreed that particle shape, size, and surface characteristics are important in determining a sludge's amenability to thickening or dewatering.

In all research on sludges, it has been assumed that the water that surrounds the particles behaves as ordinary water, and that this water has all of the chemical and physical properties of common water. The purpose of this paper is to suggest that this may not be a safe assumption, and that there may be different physical states of water in sludge and that these different forms of water may play an important role in determining whether or not it is easy to separate the water from the solids.

Properties of Water in Aqueous Slurries

As early as 1935, Derjaguin measured the viscosity of water with a rotating viscometer and observed unexpectedly high values of viscosity as the clearances become very small. These early experimental results were discounted by most scientists, and were thought to reflect either contaminated or inadequate equipment (Etzler and Drost-Hansen, 1983).

In the early 1960s, Fedyakinin found that a strange type of water collected with time on top of tiny glass capillaries, a water that was more dense than the bulk water below. His discovery became the centerpiece of a major research effort at the Moscow Institute of Physical Chemistry, where the head of the Surface Forces Laboratory was Derjaguin. Further research indicated that when this water vapor condensed on a solid surface it appeared to have distinctly different physical properties from bulk

liquid water. It was thought that a new water phase had been found, and this anomalous water was later dubbed "polywater" by other researchers. Numerous laboratories in Britain and the United States conducted confirming experiments on polywater, and produced theoretical calculations to explain its existence. Eventually, however, it was concluded that the experimental results could be explained by other less dramatic means, such as impurities leached from the solid surface, and polywater became a historical scientific curiosity to all and an embarrassment to some (Frank, 1981).

The polywater episode probably set back experimental surface water chemistry for decades, and only in the last few years have surface chemists rediscovered the anomalous nature of water when it is in contact with a solid surface. The mistake made by the Soviet researchers was that they assumed that this anomaly persists even in the absence of surfaces, while in fact the properties of water seem to indeed be altered close to surfaces. This is due entirely to the presence of the surfaces. An excellent recent summary of the research into this phenomenon is provided by Granick (1991).

Vicinal water. The idea that water molecules next to solid surfaces behave differently from normal water was discussed by Szent-Gyorgyi (1957) who suggested that the liquid water molecules, in the presence of a solid surface, will layer themselves on a solid surface and are "ice-like" in structure and physical behavior. Based on overwhelming and diverse experiments, there seems to be little doubt today that while the term "ice-like" seems inappropriate to describe the water molecules immediately adjacent to a solid surface, these molecules do seem to behave differently from water molecules in bulk water.

The layers of water molecules at the solid boundaries are known as "vicinal water," described as "interfacial water (usually near a solid interface) the properties of which differ from the corresponding bulk properties due to structural differences induced by proximity to the surface" (Drost-Hansen, 1981). When the solid surfaces are particles, water forms a layered shell of essentially immobile water molecules around the particle. The water molecules in this shell do not form a rigid structure, and are therefore not "ice-like" as originally thought, but continue to be in a dynamic equilibrium with the surrounding bulk water.

The structuring of water molecules on the surface is thought to be due to the fact that hydrogen bonding between water molecules is enhanced near solid surfaces. The surface interrupts the normal pattern of packing, and the water molecules compensate by arranging themselves in an orderly fashion on the surface.

The structuring of the water molecules seems to continue well away from the surface, as indicated by the changes in physical properties of this water. Intuitively, it is reasonable to expect that the effect of surfaces on water structure decreases as the distance from the surface increases, much like the particle charge

effect. Thus it is not possible to state the actual depth or thickness of this surface boundary layer because the depth of the layer becomes dependent on the method of measurement. Accordingly, the effects of this layer of rearranged molecules have been noted to range from at least 30 A (3 nm) to perhaps several hundred Angstroms.

Most researchers have reported that the thickness of the closely ordered surface layer of molecules is in the 2.5 to 5 nm range. For example, Strenge (1978) used viscosity measurements to estimate the vicinal layer to be of the order of 2.5 nm, or about 10 molecular diameters, defined as a layer that is completely immobile. Similarly, Etzler and Fagundus (1987) found that the influence of vicinal water extends to approximately 3 to 5 nm. Israelachvili and Kott (1989) agree that "certain liquid properties can no longer be described by their bulk (continuum) properties once the number of molecular layers in the gap falls below about 10."

While the layers of completely immobile water molecules seem to be in the range of 3 nm, the effect of this layering may extend far into the bulk water. Peschel and Adlfinger (1970), for example, measured the viscosity of thin films between two quartz plates and found that the viscosity of interfacial water is significantly greater than that of bulk water, and that this effect is hundreds of molecular diameters thick.

Support for the conclusions of Peschel and Adlfinger comes from experiments conducted many years ago on the tobacco mosaic virus. When solutions of the tobacco mosaic virus, a cylinder about 342 nm long and 15 nm in diameter, are concentrated, the particles tend to line themselves up in an orderly parallel fashion, even though the space between them is as much as 50 nm, suggesting that the influence of the water molecule structuring on surfaces extends this far into the solution. (Bernal and Fankuchen, 1941).

The structure of water molecules near surfaces can be demonstrated by the oscillatory nature of the forces on two very smooth plates as they are squeezed together. During the progressive squeezing, the water molecules are rearranged and the pressure oscillates with a frequency of one molecular diameter. Layers of water molecules are progressively squeezed out, and the pressure necessary to squeeze out the next layer increases as the surfaces converge (Israelachvili and Kott, 1989). These forces are known as "solvation" forces and this effect seems to extend to about 3 nm or about 10 molecular diameters from each surface.

At these distances, electrostatic and van der Waals forces become minor compared to solvation forces (Chan and Horn, 1985). Double layer theories seem to be valid only for both low ionic strength solutions and at substantial distances away from the particle surface. (Israelachvili, 1985; Israelachvili and Adams, 1976).

The second experimental justification for hypothesizing the existence of vicinal water comes from calorimetric studies in clay. The interstitial spaces between clay particles, 2 to 5 nm, are small enough to create the possibility of substantial amounts of vicinal water. Anderson and Tice (1973), using a scanning calorimeter, found that when clay samples are frozen and then thawed, unexpected endotherms appear at temperatures as low as −30°C, indicating the thawing of frozen water at these very low temperatures. If the water molecules are arranged on the solid surfaces in orderly structures, it seems reasonable that these

molecules would resist incorporation into the ice crystal, and higher energies would be required to make them freeze.

A further indication of the presence of vicinal water comes from the measurement of dielectric properties in water/particle mixtures. Ballario et al. (1980) studied the behavior of water in water-cellulose mixtures, measuring the permittivity and dielectric loss for a number of cellulose concentrations. They found that these mixtures of water and cellulose exhibit unexpected behavior, as shown by the dielectric curves. The authors conclude that this anomalous behavior may be best interpreted as a three-component system: cellulose, normal water and water with abnormal properties.

It can be concluded that there is general agreement in the literature about the existence of vicinal water on solid surfaces. This water has two interesting physical properties that relate to the potential for sludge dewatering—density and viscosity.

Density. Using a pycnometer, (Figure 1) Drost-Hansen (1985b) and his colleagues have shown that the volume of a slurry is reduced when the particles settle into a concentrated mass. As the particles come closer together, the shells of the surface water overlap, and some water is expelled into the bulk water (or in sludge, most likely the interstitial water). Because
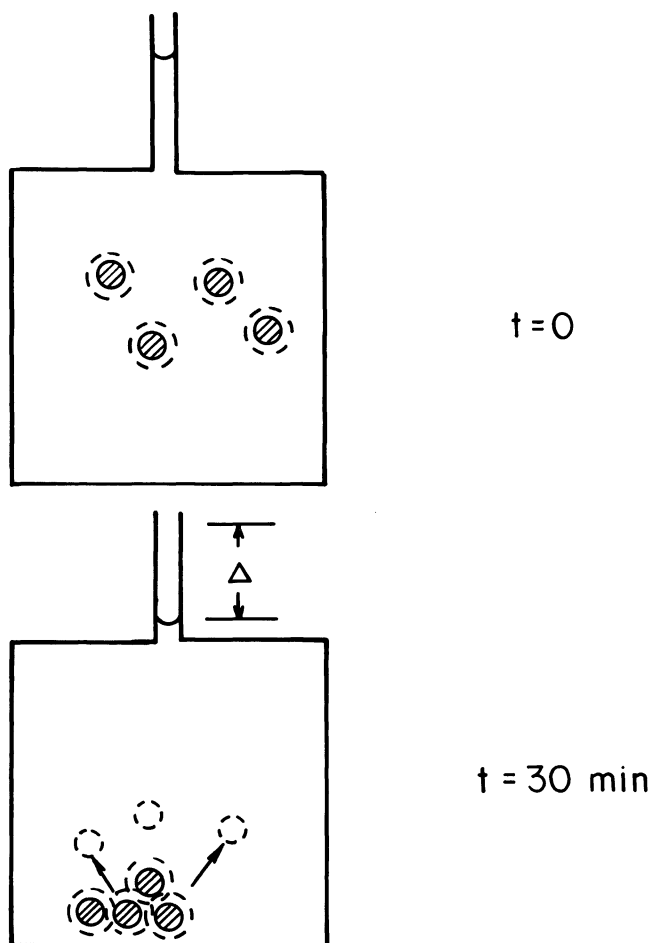

Figure 1—Representation of pycnometer experiments of Drost-Hansen (1977).

the specific volume of vicinal or surface water is about 3% greater than that of bulk water, the transfer of water from the surface to the bulk water results in a smaller volume (Drost-Hansen et al., 1985b). They conclude from these experiments that vicinal water has a density of about 0.965 g/cm₃.

Etzler and Fagundus (1987) also found that the density of vicinal water is in the range of 0.965 to 0.970. Similar studies with organic liquids which would not be expected to develop vicinal structures on solid surfaces indicated that the density was essentially that of the bulk liquid density, enhancing the confidence in the experimental results for water.

Viscosity. The viscosity of vicinal water has been measured by several means, including the "blow off" method of Derjaguin and Churaev (1981). The method consists of blowing a wetting liquid film off a well-polished solid surface by a stream of air. Their results indicate a substantially higher viscosity for vicinal water over bulk water.

In experiments where two solid surfaces are brought together and the liquid between them is sheared, it has been shown that as the space is decreased to several molecules thick, the liquid no longer undergoes shear. At these distances continuum Reynolds theory breaks down, with drainage occurring in abrupt steps that tend to match the diameters of the molecules (Chan and Horn, 1985; Gee et al., 1990; Israelachvili and Adams, 1976). In effect, the molecules are ordered in layers and when the pressure is sufficiently high, one layer is pushed out and the pressure relieved.

Viscosity of thin liquid interlayers has also been measured using ultrathin quartz capillaries, and it has been found that for polar liquids like water, the mean viscosity increases as the radius of the capillaries decreases (Churaev et al., 1970). Etzler and Drost-Hansen (1983) suggest that the viscosity of vicinal water, as it affects particle interaction, is in the range of 2 to 10 times higher than bulk water viscosity. Other researchers suggest that the viscosity of vicinal water can be as much as 30 times that of bulk water (Peschel and Adlfinger, 1971).

Derjaguin and Churaev (1981) show that non-polar liquids such as carbontetrachlorine do not show any increase in viscosity with smaller capillaries, suggesting that the increased viscosity is indeed due to the polar nature of water molecules. While the viscosity of vicinal water is much higher than that of bulk water, studies using filtration through a porous glass membrane have shown that even in very fine pores the water exhibits Newtonian flow characteristics (Churaev, 1976).

Capillary tubes were also used to measure viscosity at temperatures well below 0°C. It was found that the nonfreezing boundary layers show viscosity levels many times higher than the viscosity of supercooled bulk water (Derjaguin and Churaev, 1981).

Elevated viscosities seem to decrease with increased temperature and disappear completely at about 70°C, suggesting that high temperature destroys the vicinal water boundary water layers (Churaev et al., 1970). Similarly, Derjaguin and Churaev (1981) found that the thickness of a polymolecular film of water on a quartz surface is reduced to zero at about 65°C. It may be more than a coincidence that this temperature is also pasteurization temperature. The destruction of vicinal water layers at the pasteurization temperature offers interesting possibilities in explaining the effect of heat treatment on sludge dewaterability. One may speculate that the destruction of pathogenic organisms

at Pasteurization temperatures is due to the elimination of the vicinal water that the cells need in order to remain viable. The destruction of vicinal water may also be contributory to the effectiveness of heat in sludge conditioning prior to dewatering.

Sludge Thickening and Dewatering

Sludge is made up of diverse solid particles suspended in an impure water continuum. Attempts to define a sludge particle have been hampered by the problem that as soon as attempts are made to measure or even look at these particles, they will change. Within the treatment system, sludge particles are dynamic—dispersing and reforming depending on biological, chemical, and physical conditions.

Perhaps the only means of defining a sludge particle is to continually dilute the sludge with water under low shear conditions until the particles define their own size and structure. Using the dilution technique, laser particle size analyzers can be used to obtain particle size distribution curves as shown in Figure 2. Note that the size of the particles, 6 μm, is larger than the size of common microorganisms, so that the particle measured by the laser particle analyzer, which required an 1:8000 dilution, is most probably a small floc. Larger flocs occur as well, but in smaller numbers.

If sludge flocs are studied microscopically, they seem to resemble the form shown in Figure 3 (Rasmussen, 1991). There seems to be a great deal of slime and detritus captured within a structure held together with filamentous organisms. Bacterial colonies, resembling small villages, are collected within the structure.
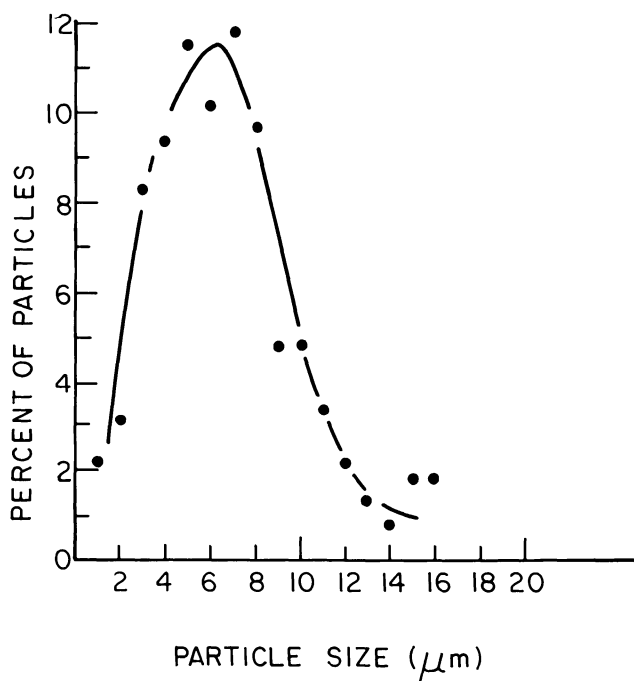

Figure 2—Particle size distribution for an anaerobically disgested sludge as measured by laser particle size analyzer, solids concentration 1.3%, diluted 1:8000).
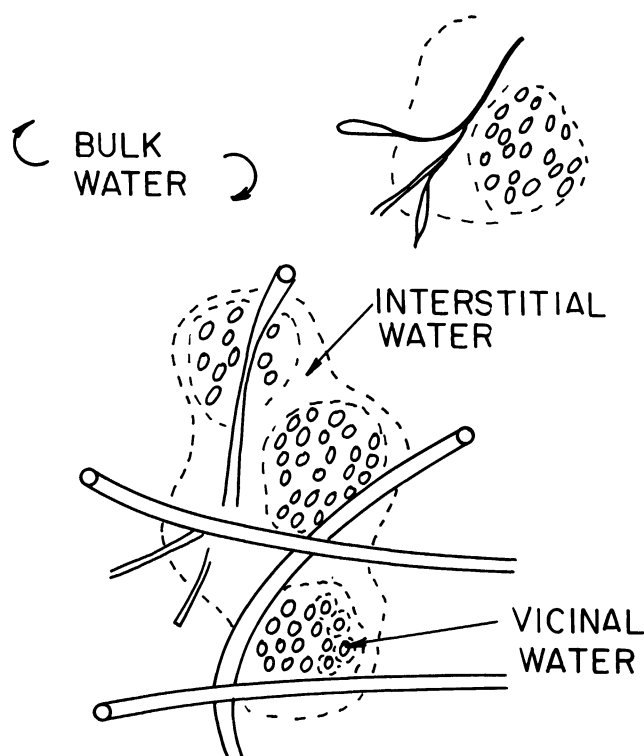
Figure 3—Representation of a sludge floc (after Rasmussen, 1991).

Water, with various dissolved chemicals, is the continuum surrounding the sludge floc. The various water fractions associated with the sludge floc can be defined on the basis of the sludge floc structure. Although the names given to the various water fractions have evolved over the years (Vesilind, 1974; Moller, 1983; Smollen, 1988), the following descriptions of different physical states of water in sludge (illustrated in Figure 2) will be useful.

Free (or bulk) water: water not associated with and not influenced by the suspended solids particles.

Interstitial water: water trapped in the crevices and interstitial spaces of the flocs and organisms. Some of this water is held within the floc structure, and can become free water if the floc is destroyed. It is conceivable that some interstitial water is held within the structure of microbial cells, and can become free water only if the cells are destroyed. The effect of the solid surfaces on this water are unclear, but evidence presented below suggests that some of this interstitial water may not behave physically as bulk water.

Vicinal water: multiple layers of water molecules held tightly to the particle surface by hydrogen bonding. This force is believed to be short-ranged but very intense close to the particle surface resulting in the appearance of highly structured water molecules. This water can be within cells as well, as long as it is associated with a solid surface. The major distinction between vicinal water and interstitial water is that the latter is free to move when the physical confinement is eliminated. Vicinal water is not free to move but adheres to solid surfaces.

Water of hydration: the water chemically bound to the particles and removable only by the expenditure of thermal energy.

For example, water associated with the aluminum hydroxide floc can be removed only by thermal drying. Also, the thermal conversion of slaked lime [$Ca(OH)_2$] to quicklime [CaO] releases water of hydration.

The easiest water to remove from a wet sludge is bulk water, which can be eliminated by drainage, thickening, or mechanical dewatering. Interstitial water, however, is trapped within the flocs and its release can be attained only by either the destruction or compression of floc structures using sufficient mechanical energy to squeeze the water out. Most dewatering processes are designed to remove both bulk water and interstitial water from sludge.

Possibly the most interesting water fraction in dewatering is vicinal water, because it cannot be mechanically removed unless some prior conditioning is affected. Similarly, mechanical dewatering cannot remove the water of hydration that is chemically bound to the solids. It is of interest to know exactly how much vicinal water and water of hydration exists in a given sludge, because this represents the limit of mechanical dewatering.

Bound water in sludge. The application of the concept of different types of water to sludge technology is complicated by the historic definition of "bound water." Most past researchers have divided water in sludge into two categories—bulk water and bound water. By devising a measure of one water, the other is calculated by subtraction from the total water as measured by evaporation.

For example, if bulk water is defined as the clear water fraction resulting from 30 minutes of settling in a liter cylinder (the SVI test), then the water captured within the settled sludge is bound water. Conversely, it is possible to use some measurement for the bound water and calculate the free water by subtraction. For example, in 1969, Vesilind hypothesized that sludge water can be classified using a test tube centrifuge. It was found that sludge in high speed centrifuges does not compact as a smooth curve with increased centrifugal acceleration, but rather seems to hold its volume for a time, and then suddenly collapse. These periodic reductions in sludge volume were thought (probably incorrectly) to indicate the release of different fractions of water (Vesilind, 1974).

In some definitions, bound water is assumed to be held to the sludge particles by capillary forces, and some of the earlier definitions of different physical states of water included a "capillary water" category (Moller, 1983, and Vesilind, 1974). This "capillary water" seems to represent only part of the bound water. By introducing a detergent to sludge and reducing the surface tension of the water so that capillary forces would not come into play, Katsiris and Kouzeli-Katsiri (1987) found that about 30 to 20% of the bound water (as defined by their measurement technique) is held on the particles by capillary forces.

A widely accepted definition of bound water in sludges is water that does not freeze at some given temperature, usually $-20°C$. The first researchers to define bound water in sludges in this manner were Heukelekian and Weinberg (1956). Using dilatometers for their studies, and an activated sludge sample, they found that the quantity of bound water is about 0.3 g/g of dry solids.

Barber and Veenstra (1986) also used freezing techniques to evaluate the thickening and dewatering characteristics of sludges and showed that increased unfrozen water as measured by dilatometry correlates with both increased sludge volume index and specific resistance to filtration. Forster (1983) found that

increased unfrozen water (again measured by dilatometry) correlated with increased sludge viscosity.

Katsiris and Kouzeli-Katsiri (1987), in an excellent paper that first drew attention to the role of water in sludge dewatering, used dilatometric techniques to find that unfrozen water in a 0.4% solids activated sludge is between 9 and 12 g/g of dry solids (by weight). For digested sludge with a 2 to 2.5% solids concentration, the values are between 3.0 and 3.5 g/g of dry solids, or 7 to 8% of the total water content. They also found that the fraction of unfrozen water decreases with increasing solids concentration. Robinson and Knocke (1992) demonstrated that the dilatometric method gives excellent reproducibility in the measurement of unfrozen water. They confirmed the results of Katsiris and Kouzeli-Katsiri and found that the unfrozen water content increases (expressed as a fraction of the dry solids) with increased solids concentration for all sludges tested, and that the effect is not influenced by polymer conditioning. They found that the unfrozen water content ranged from about 1 to 5 g/g dry solids, depending on the sludge and the method of dewatering prior to measurement. The wetter the sample, the more unfrozen water it contained. A similar conclusion was reached by Carberry and Prestowitz (1985) who used nuclear magnetic resonance spectroscopy to measure bound water in sludges.

Confirmation of the dilatometric results were recently obtained by the use of a time domain reflectometer (TDR), a device for measuring the dielectric constant of solids and liquids. It was found that the amount of water in sludge that does not freeze depends on the temperature, and that at the freezing point of water, fully 10% of the sludge water can still be unfrozen (Shannon and Wilson, 1991).

Another method for measuring the quantities of different types of water is evaporation. Vesilind and Tsang (1990) used thin layers of sludge dried at normal temperatures and with the mass continually monitored to show that as the sample dries, the rate of weight loss at first is constant because the water molecules cover the surface of the sludge and evaporate at a constant rate. As drying continues, the rate of evaporation suddenly decreases. This critical drying point is followed by a second decrease at a second critical point, ending with no further weight loss, at which point the sample contains only water of hydration. The two different slopes of the drying curve demonstrate the presence of different types of water driven off at various stages of drying. A model postulating the existence of several types of water is shown to be a good descriptor of the evaporation curve.

A similar study was conducted by Halde (1979), who also found that the drying curve has two discernable critical points, indicating that there are at least two mechanisms for water retention in sludge. Halde conducted his tests at two different temperatures, 25 and 35°C, and found that while the rate of drying changes markedly, the location of the critical points in the drying curve does not change with temperature, thus suggesting that the amount of vicinal or interstitial water does not change with temperature. He also conducted drying tests with chemically conditioned sludges, and found that while polymer conditioning moves the first critical drying point, it does not affect the second one. The explanation not offered by Halde for this result is that polymers reduce the amount of interstitial water by compressing the flocs, but they do not change the surface area, and therefore do not change the amount of vicinal water.

Smollen (1988) concludes from her drying studies that bound water content does not seem to affect the solids in a dewatered cake. This result adds credence to the idea that sludge cakes contain mostly vicinal water, with the interstitial water having been squeezed out during the dewatering operation. In a later study, she shows that different sludges have different bound water content, and that a correlation exists between bound water (as measured by evaporation) and the ability of sludge to dewater (1990).

The recognition that a substantial fraction of water is unfrozen at quite low temperatures also suggests the potential for the survival and even multiplication of pathogenic organisms in sludge. Ongoing studies suggest that the survival of pathogens is dependent not only on the lowest temperature attained by the frozen sludge, but also the rate of freezing, confirming the role of the unfrozen water in the survival of pathogens. (Sanin, Vesilind and Martel, 1992).

It is clear that sludge contains types of water that have different properties from bulk water as a result of the presence of solid surfaces. It seems reasonable to assume that "bound water", as the term is used in the environmental engineering and sciences literature, is actually a gross estimate of several forms of water, including some fraction of interstitial water, vicinal water and water of hydration.

Perhaps the most interesting form of bound water in sludge is vicinal water. Two arguments can be advanced to suggest the existence of vicinal water in sludge. First, it can be shown that studies with aqueous slurries consisting of particles similar to what might be found in sludge have indicated the presence of vicinal water. Second, measurements directly on sludge samples have shown that sludge does indeed contain substantial amounts of vicinal water.

Sludge particles can be made of almost anything, including organic and inorganic solid surfaces, living matter, or dead organic detritus. Etzler and Drost-Hansen (1983) found that the type of surface does not seem to affect the presence or absence of vicinal water, and that this type of layering is present for all types of surfaces.

The fact that water can be bound to organic material has been known for a long time. Kauzmann (1959) distinguishes two types of water bound to proteinaceous systems: one that fills cavities between the molecules, and one that is tightly bound to the molecules. Hazelwood, Nichols, and Chamberlain (1969) also argue for the existence of at least two types of ordered water in skeletal muscles, based on their work with nuclear magnetic resonance. Kuntz et al. (1969), also using NMR techniques with frozen samples, confirm that there are at least two types of water that are prevented from joining the ice lattice until the temperature is very low. Charm and Moody (1966) found that in haddock muscle with 80% water content, about 14% of the water remained unfrozen at −20°C, indicating that while the layers of water molecules immediately adjacent to organic molecules is strongly oriented, their transformation to ice is energetically unfavorable.

Especially interesting in relation to sludge dewatering is the question of vicinal water on macromolecules. Jacobson (1955), basing his conclusions on x-ray, dielectric and nuclear magnetic resonance studies, suggests that macromolecules possess vicinal hydration structures. Forsling (1952) proposes that water molecules close to macromolecules may exist in a state somewhere between a solid and liquid. Evidence seems to indicate that the

critical size of particles below which no vicinal water occurs and above which vicinal water tends to always occur is between a molecular weight of 1 000 and a few thousand Daltons (Etzler and Drost-Hansen, 1983, and Drost-Hansen, 1981). In short, there seems to be no reason a dirty mixture such as sludge would not exhibit vicinal water just like other aqueous slurries.

Evidence for the existence of water with properties similar to vicinal water comes from freezing studies (Vesilind and Martel, 1990) in which sludge samples were frozen at a given rate (same temperature) and after freezing, placed in various progressively colder temperatures. After thawing, the sludge dewaterability was measured with a capillary suction time apparatus. There seems to be little measurable effect of progressively colder temperatures until about −30°C, when the dewaterability dramatically improves. This is taken as indirect empirical evidence that some fraction of water which has not frozen at −20°C finally freezes at −30°C. When the water molecules join the ice crystal, the flocs are squeezed, creating a sludge structure that is easier to dewater after thawing. Laser particle analyses indicate that the sludge particle size actually tends to decrease after freeze/thaw, even though the dewaterability is dramatically improved.

Additional evidence for the existence of vicinal water in sludge comes from differential scanning calorimetry studies conducted by Black and Vesilind (unpublished data, 1992). These results indicate that sludge behaves quite similarly to clay, showing minor endotherms as the frozen sludge sample in the calorimeter is warmed, with the peaks indicating the points at which some of the ice melts.

All available evidence therefore tends to support the assumption that sludge does not behave any differently from other fine particle slurries, and certainly seems to contain substantial amounts of vicinal water.

Role of vicinal water in sludge thickening and dewatering. In gravitational thickening, the presence of vicinal water, with its higher viscosity and layered shells around fine particles, would greatly affect the hindered settling or thickening of sludge. Drost-Hansen *et al.* (1985a) show that the inclusion of the effect of vicinal water shells around the particles can explain some part of the inability of models to predict concentrated settling behavior. Barford (1972) studied the settling rates of aqueous suspensions of aluminum oxide particles, and devised a model for predicting the settling rate. The model, however, fails at both the very low and very high concentration range. The failure at the high range is understandable due to the mysterious particle-particle interactions, but the problems at the very low range are not obvious. One explanation, offered by Drost-Hansen, would be that the actual size of the particles was substantially larger due to the vicinal water shells. The effect can be manifested both in the increase in effective diameter, the change in effective density as the result of the low density vicinal water surrounding the particle, and an increase in the viscosity of the fluid immediately surrounding the particles. The latter is of special interest because all hydromechanics approaches assume that the property of the water flowing around particles has the same physical properties as the bulk water.

Mechanical sludge dewatering cannot hope to remove any more than bulk and interstitial water from the sludge matrix. Neither vicinal water nor water of hydration would be affected by these processes. It would therefore be of interest to know, before a dewatering operation is planned, what the available

water for dewatering (bulk plus interstitial water) is, recognizing that vicinal water and water of hydration can never be removed by mechanical means. If it is possible to accurately measure the distribution of water in sludge, it might then be possible to estimate the highest possible cake solids concentration that can be achieved for a given sludge.

One approach to this might be to develop a relationship between the sum of bulk, interstitial, and vicinal water (and continue to call this sum "bound water") versus the solids concentration. Assume first that each sludge floc carries a given quantity of non-bulk (bound) water. At very low solids concentrations, where the floc particles are highly dispersed, the grams of water per gram of dry solids should be low because there is little interstitial water. With increasing solids concentration, as the flocs start to grow and trap more water in the interstitial spaces, the fraction of bound water can be expected to increase. At even higher solids concentrations, when the sludge flocs are compacted by either centrifugation or filtration, the interstitial water is squeezed out, and only vicinal water and the water of hydration remain. Thus, a curve showing the amount of bound water at varying solids concentrations should first show an increase with solids concentrations and then a decrease with further increasing solids concentration, finally leveling off at a very high solids concentration.

Robinson and Knocke (1992) conducted dilatometer tests at various solids concentrations, and found that bound water does in fact decrease with increasing solids concentration. As the sludge solids concentration is increased by dewatering, more of the interstitial water is expelled, and the bound water concentration per mass of solids decreases with increased solids concentration. As the solids concentration is increased, progressively increased quantities of interstitial water are expelled until finally the compacted cake contains only vicinal water plus water of hydration. Such a curve (Figure 4) might be highly useful in defining the limits of dewatering.

Katsiris and Kouzeli-Katsiri (1987) found results similar to those of Robinson and Knocke. Using one of the curves by Katsiris and Kouzeli-Katsiri (Figure 5), and assuming that, if the authors would have (or could have) continued to increase the solids concentration of this activated sludge, the curve would have leveled off. That is, the bound water concentration would have leveled off at about 1 200% of dry solids. Assuming that this water is the combination of vicinal water and water of hydration that cannot be extracted by mechanical means, it is pos-
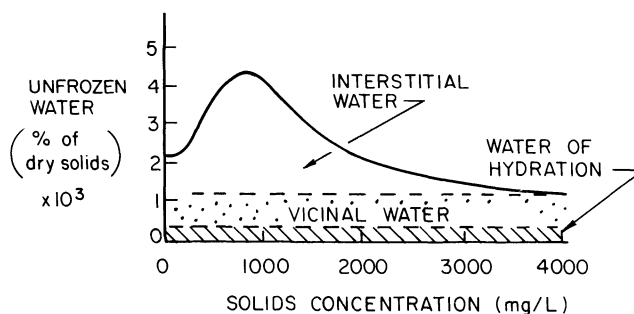

Figure 4—A hypothetical curve showing the change in water distribution with solids concentration.
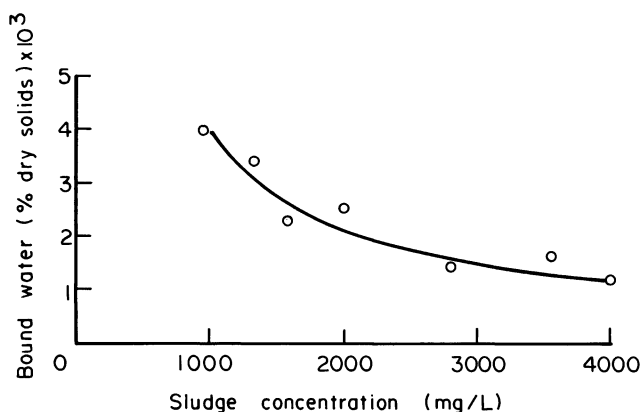
Figure 5—Effect of solids content on bound water content for an activated sludge measured by dilatometry (Katsiris and Kouzeli-Katsiri, 1987).

sible to show by calculation that the best cake solids that can ever be achieved for this sludge are 8% solids. It is unreasonable therefore to expect a mechanical dewatering device to achieve higher solids concentrations, and if this is required, the sludge has to be modified by chemical, biochemical, physical, or thermal conditioning.

It is interesting to speculate where all this vicinal water is in a biological sludge such as the one used by Katziris and Kouzeli-Katsiri. Certainly the exterior surface area of particles is great, but this would not explain all of the vicinal water. It seems likely, therefore, that some of the vicinal water is within the cell structure of microbial organisms.

At the present time, the question of what types of water are in living cells is unresolved. Some researchers hold that the vast majority of water in a cell is interstitial water having the physical characteristics of bulk water (Cooke and Kunz, 1974) while others believe that *all* of the water in cells behaves physically different from bulk water (Ling, 1979). Ling believes that "all or nearly all water molecules in a living cell can be considered to exist as polarized multi-layers, oriented on the surfaces of cell proteins."

Clegg (1981) summarizes the evidence and concludes that "a very substantial amount of water in cells manifest significantly different properties and behavior than does water in the bulk liquid." He bases his conclusion on a number of lines of reasoning, but perhaps most importantly on the simple structure of cells. The interior of cells seems to be composed of microtrabeculae, or scaffolding that supports the outer skin of the cell, having interstitial spaces between 50 and 150 nm. If the thickness of the vicinal layer is 3 nm, a typical cell would only have 15% vicinal water, and 85% interstitial or trapped water. If, however, the surface effects extend to over 50 nm, as claimed by some researchers, then it seems likely that *all* water within living cells has anomalous physical properties. If this is true, then there is no difficulty in explaining the poor solids concentrations achieved in mechanical dewatering. Even if cells are broken, the surfaces will remain, and vicinal water will still exist as long as the surfaces are present. The fraction of vicinal water can be reduced by reducing the amount of surface area, and breaking cells will probably not result in less surface area. If sludge is to be chem-

ically or physically altered to enhance dewatering, then the surface area of the particles must be decreased.

Conclusions

One of the reasons that sludge dewatering is often unsuccessful is that some of the water tends to be attached to particle surfaces as vicinal water, and this can only be removed by changing the amount of surface that water can adhere to. Polymers will only influence the interstitial water, and will make it possible for the bulk and much of the interstitial water to be separated by mechanical means. These chemicals probably do not, however, affect the vicinal water, and thus mechanical devices cannot be expected to dewater polymer conditioned sludge past the point of removing the bulk and interstitial water.

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