

SURFACE FORCES IN FILTRATION

By

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After graduating with an honours degree in Chemistry, John Gregory spent three years in the Chadwick Public Health Engineering Laboratories at University College carrying out research on surface forces in filtration for a Ph.D. degree. Three years were spent as a research chemist with the Natural Rubber Producers Research Association and in October 1965 Dr. Gregory was appointed Lecturer in the Department of Civil Engineering at University College, London with special responsibility for physical chemistry in relation to Public Health Engineering).

INTRODUCTION

Ultimately the success of any filter depends on the adherence of particles to be removed from suspension to the surfaces of the filter media. The operation of the filter is also dependent on the success with which these adherent particles can be removed during the washing process which cleans the media. Only the first of these, the adhesion process, will be considered here, although it can lead to speculative considerations of the washing process.

In the field of water filtration only one previous account has been published of a theory of adhesion in filters. This was by the Czech workers Mackrle and Mackrle¹ who equated the van der Waals' force between the filter grain and suspension particle to the Stokes' hydrodynamic drag on the particle. From this a dimensionless criterion of adhesion, called the Ma number, was developed, which was related to the Reynolds' number representing the flow conditions in the filter. Their theory neglected forces due to the electrical double layer, and appears incorrect in certain assumptions as will be shown later.

In some technologies similar to water purification there have been theoretical developments of surface force interactions between particles in aqueous suspension and fixed or moving surfaces. In the field of mineral flotation Deryagin² has contributed a theory of collection of particles on to air bubbles. However, the presence of surface active agents, the importance of surface tension and a non-laminar flow system combine to make the theory not directly applicable to water filtration. Of more direct application has been the study of the flow of colloidal suspensions through porous media, in connection with soil science, by Hunter and Alexander³. As the suspensions used were principally colloidal in size, in the range 0.2 to 2.4 microns, only the larger particles could be considered similar to those experienced in rapid filtration in waterworks practice.

Some experimental work has explored the effects of surface forces in water filtration by changing the surface chemistry of the filter grains or suspension particles, or by changing the ionic dissolved material in the water. Particularly significant was the work of Crapps and O'Melia² who modified the surface potentials of ferric hydroxide flocs in demineralised water by addition of phosphates, sulphates or chlorides. They demonstrated that filter performance was drastically modified by the addition of 25 ppm of phosphate ion, and that the effect was pH dependent. Sandford and Gates³ coated sand grains with a hydrophobic stearate and showed that the presence of this coating had no effect on the removal of aluminium hydroxide flocs and bacteria. Hunter and Alexander showed experimentally that when the sand surface was rendered positive by adsorption of cetyl trimethylammonium ions the removal of colloidal clay particles from suspension was enhanced. Heertjes and Lerk⁴ studied the filtration of ferric hydroxide sols and flocs through a filter composed of small glass spheres and measured the electrokinetic potentials on the spheres as the sol particles adhered to them. They concluded that surface forces accounted for the removal of colloidal particles, but that the removal of flocs a few microns in size was purely mechanical. Oulman, Burns and Baumann⁵ measured the electrokinetic potential of diatomite with various aluminium salts and polyelectrolytes, giving more favourable filtration. This however is not the same as sand filtration, and their experimental solutions were very close to distilled water with low conductivities. The relevance of these various experimental observations to the present work will be discussed later.

Many other authors have made reference to electrical double layer forces in filtration, but such comments have been speculative without quantitative theoretical or experimental evidence. Some work has been reported (Zaghloul⁶) on electrokinetic effects due to the passage of water through a porous sand bed. Such streaming potential effects only occur at a significant level when the media grains are very small, or flow rates are very high, both well outside the range of normal water filtration operations.

There appeared to be sufficient evidence that surface forces may be important in filtration, particularly when particles are too small for straining action to be significant. Consequently an investigation was undertaken of the physico-chemical aspects of surface forces.

PHYSICAL CHEMISTRY OF SURFACE FORCES

A suggestion has been made by Oulman and his colleagues that solvation layers of water hydrogen bonded to silica surfaces may account for surface force phenomena, and that when wetted particles come in contact they are held together by hydrogen bonding of water between their surfaces. Although such very short range forces may exist up to about 10 angstroms, experimental evidence for their effect is slight, and in dispersed systems such water layers usually contribute to stability of the dispersion, not to its flocculation.

On the other hand, there is considerable evidence in colloid science for forces due to electrical double layer interactions, and long range molecular forces of the van der Waals' type. Consequently these aspects of the surface forces are considered here.

Solvation
forces

100. ELECTRICAL DOUBLE LAYER

At the boundary between a solid and an electrolyte solution, the concentration of the ionic components is not the same as in the bulk of the solution, and the solid surface generally carries an electric charge. This charge is balanced by an appropriate number of oppositely charged ions in the adjacent solution, forming what is known as an electrical double layer. This comprises two regions: an inner fixed layer of almost immobile ions across which there is a sharp potential drop due to a partial balance with the surface potential, and an outer diffuse layer of mobile ions across which the potential falls off more slowly to electrical neutrality (zero potential) in the bulk of the solution. This is presented diagrammatically in Figure 1. The potential just outside

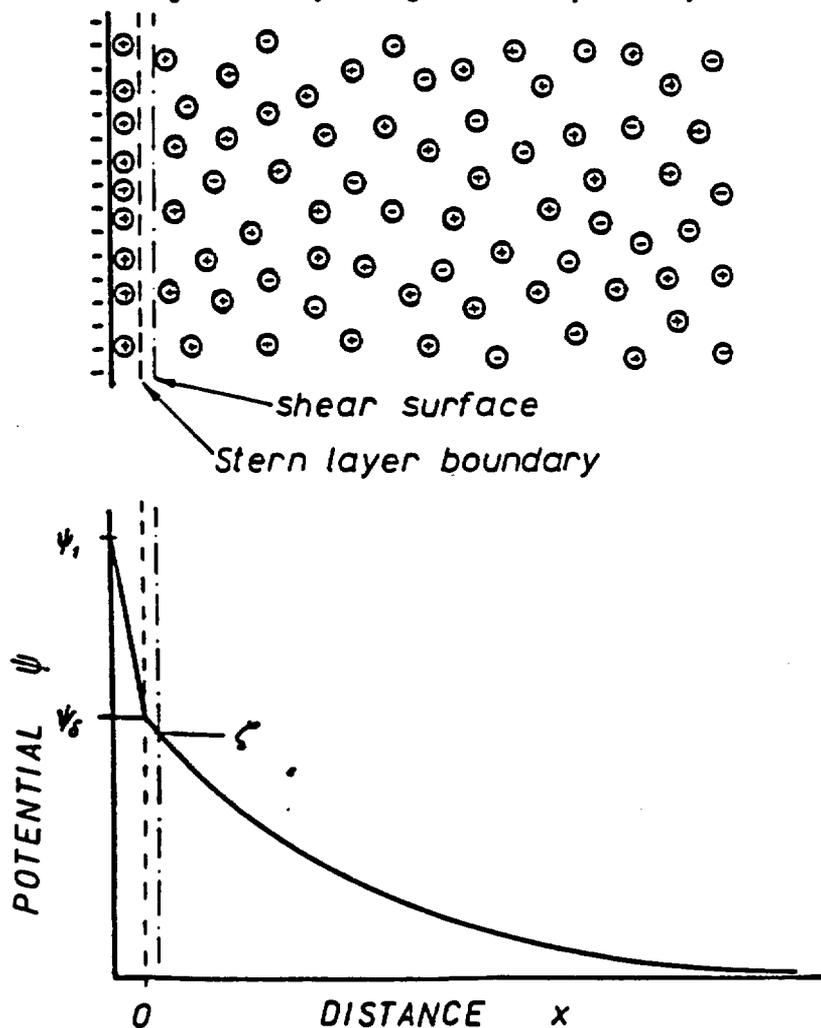


Fig. 1. Diagram of the electrical double layer, showing potential ψ as a function of distance x from Stern layer boundary.

z e ψ_0 potential

the fixed layer, ψ_0 , depends largely on the ionic strength of the solution as this will determine the electrical capacity of the diffuse layer, which will in turn determine how the potential drop from the surface potential, ψ_0 , to zero is divided between the two layers. This potential, ψ_0 , is important physically because it is closely related to the zeta potential calculated from electrokinetic measurements, and for some approximations the two are considered identical.

From considerations of the relationships between electric charge density and potential in the double layer it can be shown (strictly, only for symmetrical electrolytes) that

$$\psi = \psi_0 \exp(-\kappa x) \dots\dots\dots (1)$$

if $z e \psi_0 < 25$ mV,

where ψ is the potential at distance x from the fixed layer,

z is the valency of the ions (in the double layer),

κ is the reciprocal of the double layer thickness,

$$\kappa = \left(\frac{4\pi e^2 \sum c_i z_i^2}{\epsilon kT} \right)^{\frac{1}{2}} \dots\dots\dots (2)$$

where e is the charge on the electron,

c_i is the concentration of the ions of valency z_i , (number per cc.),

ϵ is the dielectric constant of the liquid,

k is Boltzmann's constant,

T is the absolute temperature.

The double layer thickness, $1/\kappa$, is the separation of two theoretical condenser plates at potential ψ_0 to give the same capacity as the diffuse layer; from Equation 1 it is also the distance at which the potential has fallen to 1/exponential constant (that is 1/2.7183) of the potential ψ_0 .

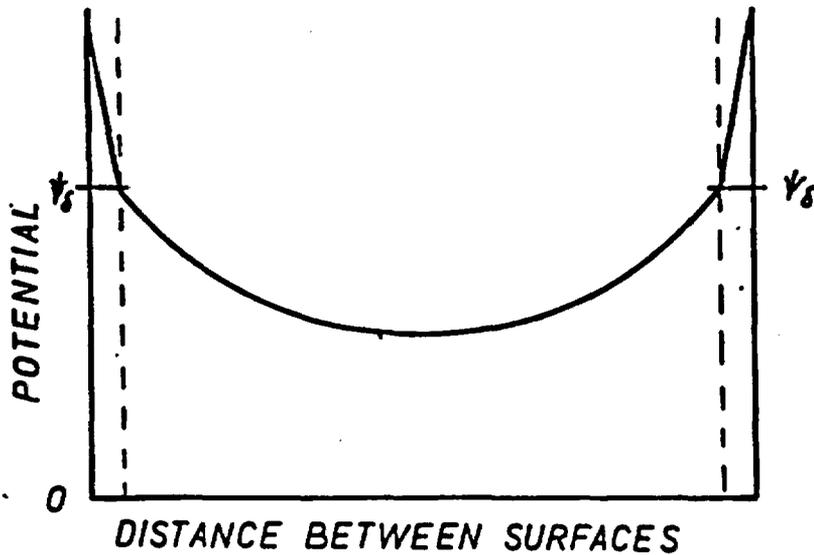


Fig. 2. Distribution of potential between two close surfaces with equal ψ_0 potentials.

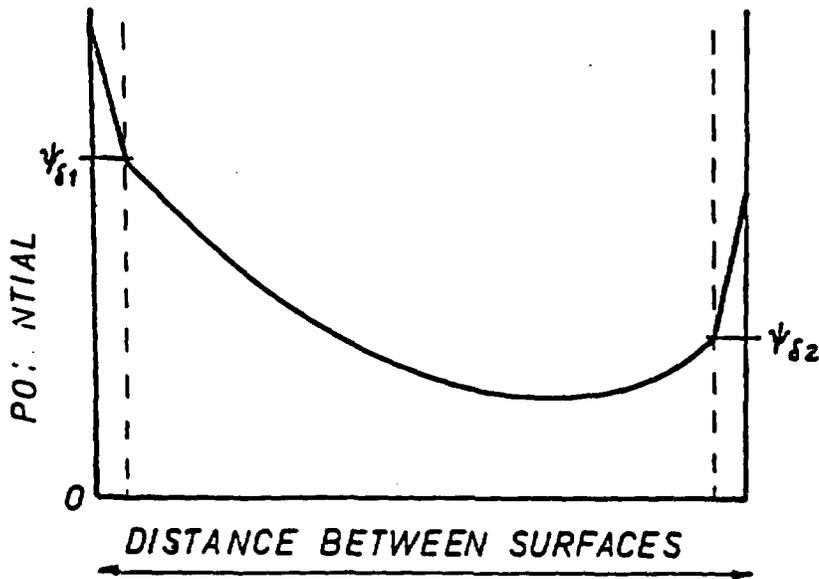


Fig. 3. Distribution of potential between two close surfaces with unequal ψ_δ potentials.

When two surfaces approach one another so that the double layers overlap the potential distribution between them will be as shown in Figure 2 if the potentials ψ_δ are equal, or as shown on Figure 3 if they are unequal. Verwey and Overbeek⁹ have shown how the new potential distribution can be calculated for the symmetrical case of Figure 2. This has been extended by Gregory¹⁰ to deal with the unsymmetrical case of Figure 3.

The size of particles to be filtered from water compared with that of the filter grains allows their surface force relationships to be considered as a small sphere approaching an infinite flat surface. The method of Deryagin¹¹ for two spheres can be adapted for the sphere-flat plate interaction to find the double layer interaction energy. This is only valid for close approach of the sphere when the separation is less than the sphere radius. By integrating the interactions of individual pairs of parallel concentric infinitesimally thin rings on the flat plate and on the sphere surface Gregory¹⁰ showed the interaction energy to be given by equation (3).

$$\frac{V_r}{a} = \frac{128\pi kTc}{\kappa^2} \gamma_1 \gamma_2 \ln [1 + \exp(-\kappa d)] \quad \dots \dots \dots (3)$$

- where V_r is the double layer interaction energy,
- a is sphere radius,
- c is number of ions of one type per cc.
- d is sphere — flat plate separation.

$$\gamma = \frac{\exp(z\psi_\delta/2KT) - 1}{\exp(z\psi_\delta/2KT) + 1} \quad \dots \dots \dots (4)$$

subscripts 1, 2 refer to sphere and flat plate respectively. Substituting for κ^2 in Equation (3) and inserting numerical values pertaining to water at 25°C, Equation (3) becomes

$$\frac{V_r}{a} = 9.24 \times 10^{-4} \frac{\gamma_1 \gamma_2}{z^2} \ln [1 + \exp(-\kappa d)] \dots\dots\dots (5)$$

Equation (5) will be used subsequently in calculations of double layer interaction in filter systems.

MOLECULAR FORCE INTERACTIONS

The universal attractive forces between atoms and molecules are generally known as van der Waals' or molecular forces. From consideration of interacting molecular dipoles, both fixed and induced, and most importantly of dispersion forces (due to the same fundamental properties which cause dispersion of light or other electromagnetic radiation), it can be shown that the energy of attraction for molecules or atoms falls off as the inverse sixth power of distance.

$$V_s \propto 1/x^6 \dots\dots\dots (6)$$

Only the dispersion forces are additive, i.e. the total interaction between two aggregates of atoms or molecules can be determined simply by adding the contributions of all interacting pairs. In this way, Hamaker¹² showed that for two equal spheres the interaction energy becomes

$$V_s^{11} = - \frac{Aa}{12d} \dots\dots\dots (7)$$

where A is the Hamaker constant
a is the sphere radius
d is the separation

Equation (7) only applies for very close approach such that $d \ll a$. The corresponding expression for sphere-flat plate interaction is

$$V_s = - \frac{Aa}{6d} \dots\dots\dots (8)$$

The negative sign designates the interaction as attractive, whereas V_r in Equation (5) is repulsive interaction if the potentials Ψ_s are of the same sign.

When the separation is of the same order as the wavelength of the electromagnetic transmission of the energy, the energy is less than that given by Equation (8), and is given by Equation (9).

$$\frac{V_s}{a} = \frac{-A}{6d} \left(\frac{2.45}{5p_s} - \frac{2.17}{15p_s^2} - \frac{0.59}{35p_s^3} \right) \dots\dots\dots (9)$$

where $p_s = 2\pi d/\lambda$, and λ is a characteristic wavelength (of the order of 10^{-3} cm). Equation (9) derived by Schenkel and Kitchener¹³ is only valid at $p_s > 0.5$ and extrapolation is necessary to very close approach where $p_s \rightarrow 0$ and Equation (8) holds. At large separations when $p_s \gg 1$ the energy is said to be fully retarded and can be obtained by using the first term only in Equation (9).

An alternative method of calculating the molecular force interactions has been proposed by Lifshits¹⁴ and extended by Dzyaloshinskii¹⁵ to take into account the presence of a liquid between the surfaces. This method deals with the macroscopic properties of the materials and does not rely on the additivity of molecular or atomic interactions. For similar materials in water, the sphere-flat plate interaction energy is given by Equation (10).

$$\frac{V_s}{a} = - \frac{h v \pi^2}{4120 n_0 d^2} \left(\frac{n_1^2 - n_0^2}{n_1^2 + n_0^2} \right)^2 \dots\dots\dots (10)$$

where h is Planck's constant
 v is velocity of light,
 n_1 is the refractive index of the solid materials,
 n_0 is refractive index of water
 d is separation ($\ll a$, therefore, for large particles) $> 2000\text{\AA}$,
 "long range".

For intermediate ranges optical data on the materials are required which are not available, consequently the interaction energies cannot be calculated.

A difficulty arises in the use of Equations (8) or (9) because of the calculation of the Hamaker constant A . Verwey and Overbeek⁹ have suggested a value of 2×10^{-12} ergs for most materials, but some experimental data reviewed by Gregory¹⁰ indicate that lower values hold for many aqueous systems. For two different materials (subscripts 1, 2) in water (subscript 0) the value of A is given by Equation (11).

$$A = \frac{1}{n_0^2} (A_{12} - A_{10} - A_{20} + A_{00}) \dots\dots\dots (11)$$

The values A_{12} , A_{10} etc. can be calculated by methods given by Ottewill and Wilkins¹⁶ or Schenkel and Kitchener¹⁷. Gregory¹⁰ has given a table of values of A , comparing experimental values, those calculated from Equation (10) and some calculated from the simplified London Equation (12), for similar materials in water.

$$A = 2.09 \times 10^{-13} \frac{\pi^2 q^2 s^2}{v^2} \dots\dots\dots (12)$$

where q is the number of molecules per cc,
 s is the effective number of dispersion electrons,
 v is an empirically derived frequency for the molecules, probably closely related to the frequency of fundamental electronic oscillations within the molecules.

Gregory indicated where tabulated values of s and v for many substances could be found, thus allowing Equation (12) to be calculated.

PARTICLES IN SUSPENSION

ELECTROKINETIC POTENTIALS OF NATURAL PARTICLES AND PRECIPITATES

The particles in water to be removed by filtration are generally too small or not dense enough to be removed efficiently by sedimentation. Some of these particles are naturally present in the water as inorganic,

or dead organic or living organic material. Other particles may be the residues of precipitation or flocculation processes which have been carried over from sedimentation tanks.

Natural
Particles
Clay or silica
Change
clay \rightarrow edge

The natural inorganic materials are generally clays or silica particles, either colloidal or microscopic. Occasionally certain well waters can carry fine suspensions of chalk. The size range may be considered to be from 0.01 micron to 30 microns, i.e. including colloidal and microscopic particles. Below this range the particles are approaching a solution state, and above the range the particles may be removed by straining or sedimentation. The clays exhibit an overall negative surface potential at normal water pH values, although the plate-like structure of many clays may have negative potentials on the flat surfaces, but positive potentials along their edges. A full review of clay colloid chemistry has been made by van Olphen¹⁷. Silica particles also have a negative surface potential in water (see, for example, Smith¹⁸), which for clean surfaces can be as high as -80 mV.

The natural organic materials may be bacteria, algae and other micro-organisms, or decomposition products of plants or animals. It is well-known that bacteria carry a negative surface potential in water (see, for example, Bean, Campbell and Anspach¹⁹), and this has also been demonstrated for both live and dead freshwater planktonic algae (Ives²⁰). It appears probable that the same is true for other micro-organisms and Coackley's investigations²¹ on sewage sludge particles also indicated that dead organic particles also have a negative potential; the same was true for the organic colour colloids investigated by Black and Willems²².

With regard to precipitated and flocculated material in water the most commonly encountered will be ferric and aluminium hydroxide colloids and flocs from coagulation processes and magnesium and calcium precipitates from softening reactions.

F₂O₃
Change reversal

Unlike the natural particulates in water which exhibit a negative potential throughout the pH range for natural waters, the hydroxide precipitates of iron and aluminium show a sign reversal of potential. For aluminium hydroxide floc at about pH 8.0 the potential reverses from negative at higher pH to positive at lower pH. The exact pH of the isoelectric point depends on the other ions present in the water (see, for example, Black and Hannah²³). For ferric hydroxide floc the isoelectric point pH appears to be lower. Crapps and O'Melia⁴ reported a reversal of sign between pH 5.0 and 6.5, with negative potentials at the higher pH values. However, the addition of various salts affected this, phosphate in particular rendered the potential more negative, and reversed the sign from positive to negative even at pH 5.0. For colloidal ferric oxide Heertjes and Lerk⁷ reported a reversal of sign of potential at pH 6.7, the particles having a negative potential above this pH. With regard to the precipitates resulting from lime-soda softening, Black and Christman²⁴ have reported that magnesium hydroxide particles carried a positive potential over the pH range 10.0 to 11.6, and the calcium carbonate particles exhibited a low negative potential from pH 9.0 to pH 10.5. However, due to adsorption of magnesium ions on the calcium carbonate this negative potential is reduced and may be reversed above about pH 10.0.

This brief review of the electrical potentials carried by particulates in water leads to the conclusion that most particles carry a negative surface potential, the exceptions being softening precipitates at high pH, alum flocs below pH 8 and ferric flocs and colloids at low pH. This statement is a generalisation; the presence of specific counter-ions and indifferent electrolytes will both modify the potential at the shear surface and alter the double layer thickness.

ELECTROKINETIC POTENTIAL OF A MODEL SUSPENSION

For the purpose of theory and laboratory experiment a model suspension was required which would be similar in characteristics to the particulates in water, but which would be spherical and have a known chemical composition. This was provided by a powder of polyvinylchloride (pvc) microspheres, of density 1.4 g/cc and diameter about

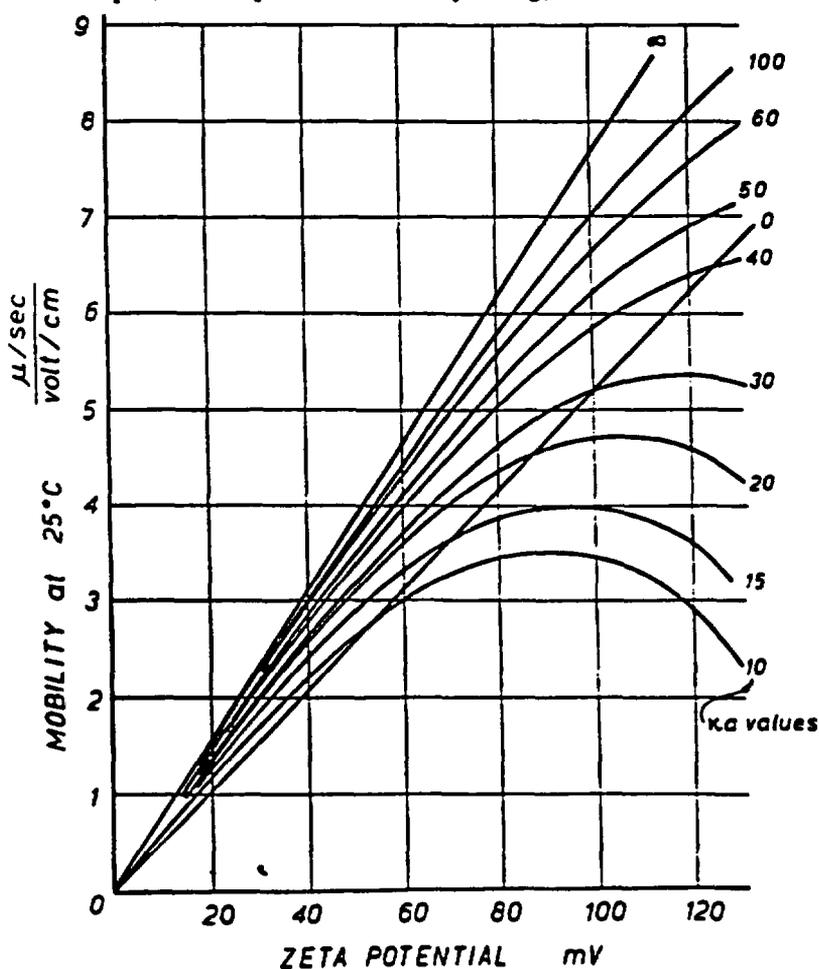


Fig. 4. Electrophoretic mobility V_e/F as a function of electrokinetic potential ζ for various values of κa in a uni-univalent electrolyte.

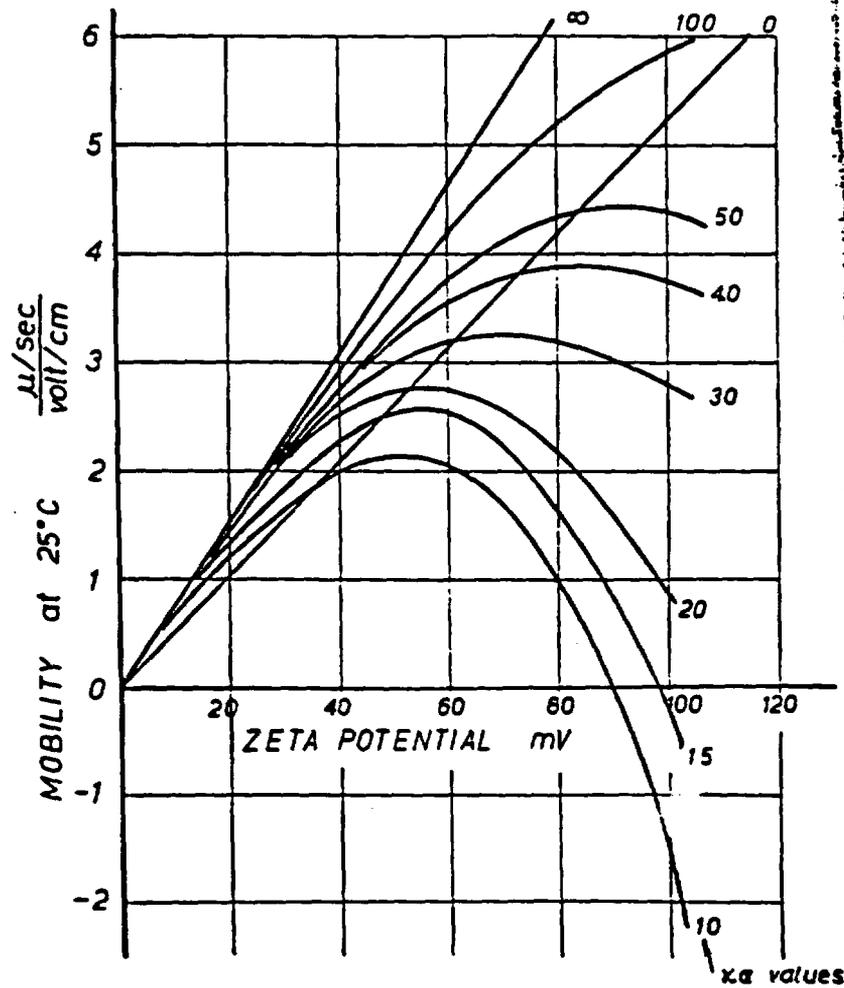


Fig. 5. Electrophoretic mobility V_e/F as a function of electrokinetic potential ζ for various values of ka in a di-divalent electrolyte.

1.3 micron. (Geon. 121 : British Geon Ltd., Devonshire House, Piccadilly, London, W.1). This had already been used for many filtration experiments in the authors' laboratories.

The pvc particles were dispersed in various electrolytes in distilled water, and their electrokinetic potentials calculated from electrophoretic mobility observations in a flat electrophoresis cell similar to that used by Ives²⁰. In such a flat cell it is usually necessary either to observe mobilities through a completely vertical traverse of the cell, or to focus on the stationary levels to obtain the electrophoretic mobility independently of the electro-osmosis caused by the potential between the glass walls of the cell, and the solution. The first of these methods is tedious, the second can be inaccurate as the observed mobilities vary

Electrophoretic cell

sharply with the depth of observation near the stationary levels and small errors in location would cause large errors in obtaining the true electrophoretic mobility. A method that involves neither of these disadvantages was employed by measuring the velocity observed at the mid-depth and at the top and bottom boundaries of the cells. Let v_m be the observed velocity at mid-depth (max. observed velocity), v_b be the observed velocity at the top and bottom boundaries, v_e the true electrophoretic velocity and v_o be the electro-osmotic velocity. The velocity of the liquid v_l at any depth y from the boundary is given by the parabolic equation (see, for example, Overbeek²³).

$$v_l = v_o \left[1 - 6 \left(\frac{y}{y_m} - \frac{y^2}{y_m^2} \right) \right] \dots\dots\dots (13)$$

where y_m is depth of cell.

From (13) it may be shown that the true electrophoretic velocity can be determined using Equation (14).

$$v_e = (v_b + 2 v_m) / 3 \dots\dots\dots (14)$$

The advantages of this method are that the maximum velocity v_m can be observed quite readily even if focus is not exactly on the mid-depth, and the boundary velocity v_b can be observed as the boundary is easily located optically. This method was checked against complete depth traverses, yielding parabolic velocity profiles, for the pvc suspension and the agreement was satisfactory.

Due to the size of the microspheres (radius a) and the double layer value (κ), the normal equation relating electrophoretic mobility to electrokinetic potential (ζ) has to be modified to allow for distortion of the double layer during migration of the particle. This is known as the relaxation correction, and has been thoroughly developed by Overbeek²³, to the form of Equation (15) where $f(\kappa a)$ comprises a series of correction functions which he tabulated.

$$v_e = \frac{\epsilon \zeta F}{6\pi \eta} f(\kappa a) \dots\dots\dots (15)$$

where η is the viscosity of the liquid,
 F is the electric field strength,
 $f(\kappa a)$ is the Overbeek correction factor.

Using Equation (15) and substituting numerical values for certain constants for water at 25°C, graphs of v_e/F (i.e. electrophoretic mobility in microns/sec. per volt/cm.) against ζ (i.e. electrokinetic potential in millivolts) have been prepared on Figures 4 and 5, for uni-univalent and di-divalent electrolytes respectively. For temperatures below 25°C, down to 15°C, an approximate temperature correction is given by

$$\zeta_t = \zeta_{25}(1 + 0.0213 (25 - \theta)) \dots\dots\dots (16)$$

where θ is temperature in °C.

The electrokinetic potential of the pvc microspheres was always negative in potassium nitrate and magnesium sulphate solutions of varying strength, with values ranging from -16mV to -90mV. Particular values will be given in relation to calculations of double layer interactions in a later part of this paper.

FILTER GRAIN SURFACES

ELECTROKINETIC POTENTIALS ON FILTER MEDIA

There is much less published information on the electrical potentials on filter grain surfaces, partly due to the fact that the experimental methods for this have not been so well developed as those for particle electrophoresis. Van de Vloed²⁴ suggested that clean sand should exhibit an electrokinetic potential of -50mV , as this was the value for silica. Hunter and Alexander³ observed an electrokinetic potential of -45mV on silica grains at pH 7.4 in a phosphate buffer solution after washing with NaOH followed by distilled water rinsing. They demonstrated that this potential could be reversed to about $+5\text{ mV}$ by immersing the silica in 10^{-4} molar cetyl trimethylammonium bromide solution. Heertjes and Lerk⁷ observed electrokinetic potentials of about -55 mV on glass

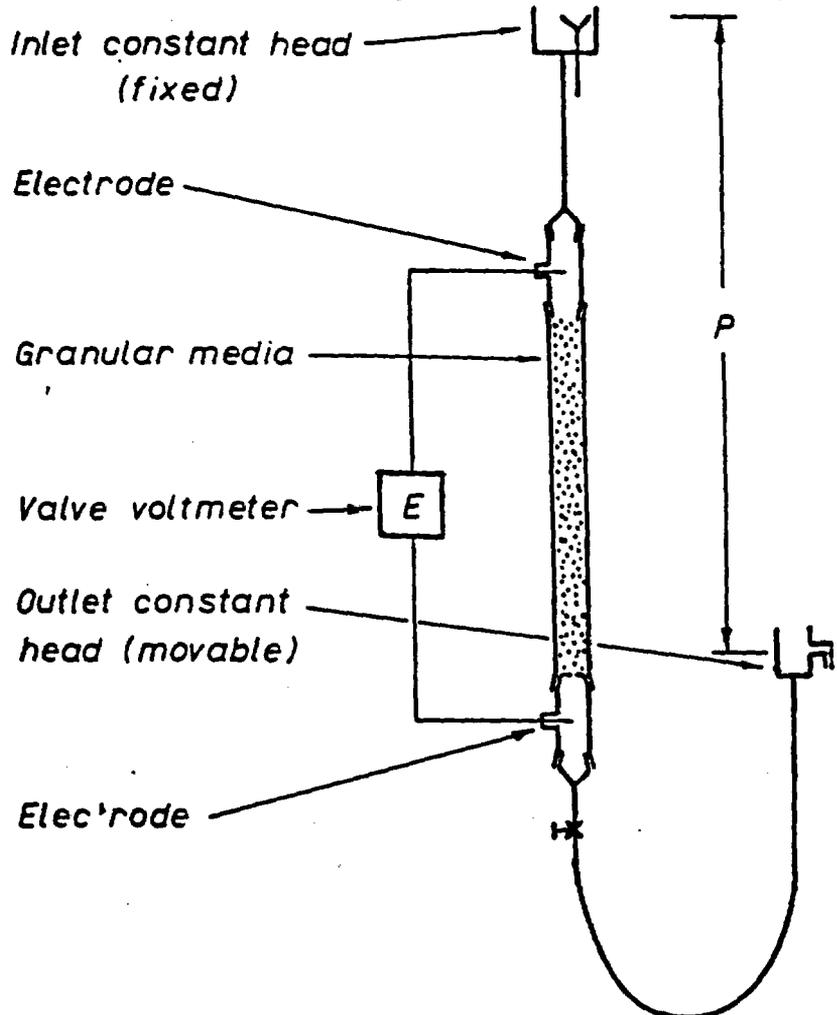


Fig. 6. Diagram of streaming potential apparatus.

spheres (about 0.5 mm in diameter) in water at pH 6. This was reversed by a ferric oxide sol, to a maximum of +16 mV, during a filtration experiment accompanied by a slight rise in pH to 6.5. Crapps' reported mobility values for sand crushed fine enough to be used as a suspension in an electrophoresis cell, corresponding to electrokinetic potentials of -27 mV to -38 mV in the pH range 5 to 8.

STREAMING POTENTIAL STUDIES

An experimental investigation of the electrokinetic potentials of sand, anthracite and ballotini (spherical glass beads) was conducted using a streaming potential cell built for this purpose. This apparatus is shown diagrammatically in Figure 6. The passage of an electrolyte through a column of the filter grains, under the static head or pressure difference P , causes an electrical potential E to be set up across the electrodes. This streaming potential was measured on a valve voltmeter. The streaming potential of the column of grains had to be much larger than that of the porous sintered glass plug retaining the grains. Consequently, the column of grains was about 34 cm. long for most experiments. To avoid certain experimental and contamination errors the electrodes of silver-silver chloride or platinum had to be most carefully prepared (Gregory¹⁰) and the apparatus maintained scrupulously clean, particularly avoiding surface active agents, rubber tubing and stopcock grease. The water for preparation of the electrolyte was glass double-distilled, as de-ionised water has been shown to be quite unsuitable for electrokinetic work²⁷.

The relationship between electrokinetic potential (ζ) and streaming potential (E) is given in Equation (17)

$$\zeta = \frac{E}{P} \cdot \frac{4\pi \eta K_0}{\epsilon} \dots\dots\dots (17)$$

where P is the pressure difference across the column of grains.

η is the viscosity of the electrolyte.

ϵ is the dielectric constant of the electrolyte.

K_0 is the conductivity of the electrolyte.

At 25°C in water this reduces to

$$\zeta = 1.312 K_0 \cdot \frac{E}{P} \dots\dots\dots (18)$$

where ζ and E are in mV, P in cm water and K_0 in micromho/cm. Within the temperature range 15°C-25°C the variations in viscosity, dielectric constant and conductivity just cancel, making Equation (18) valid within this range, if the value of K_0 is corrected to 25°C. Under certain conditions the conductivity of the solution in the pores of the filter grains would be different from that of the bulk solution (K_0). This is due to the double layers providing a surface conductance higher than that of the bulk solution. In the case of the sand and anthracite a surface conductance correction could not be applied due to the irregular geometry of the grains. With the ballotini, however, such a correction was applied using Equation (19), substituting K_D for K_0 in Equation (18).

$$K_D = \frac{R_1}{R_2} K_0 \dots\dots\dots (19)$$

where K_D is the conductivity allowing for surface conductance, R_1 is the resistance of the porous column calculated from its geometry and the resistance measured when saturated with a strong electrolyte (to swamp surface conductance effects) and R_2 is the measured resistance of the porous column with the experimental electrolyte.

As a preliminary check on the accuracy of the method a sample of crushed sieved quartz (about 120 microns in size) was washed in boiling aqua regia and then in distilled water. The electrokinetic potential in 5×10^{-4} N. potassium chloride was found to be -65 mV. in good agreement with previously published values.

SAND (LEIGHTON BUZZARD) (425 MICRONS)

The streaming potential experiments were carried out in potassium chloride solutions of strength varying from 1×10^{-4} to 9×10^{-4} N. as potassium chloride is an indifferent electrolyte to quartz and the quartz/potassium chloride system has been previously investigated. The difference in the electrokinetic potentials of pure quartz and sand should be due to surface impurities on the sand. These were removed either by acid washing in boiling hydrochloric acid, or crushing to expose new surfaces, or both. The following results were obtained in 5×10^{-4} N. potassium chloride (corresponding to a conductivity of about 80 micromho/cm).

Natural water washed sand:	$\zeta = -17$ mV.
Acid washed:	-27 mV.
Crushed:	-57 mV.
Crushed, acid washed:	-28 mV.

As the strength of the potassium chloride increased so the electrokinetic potential fell, but it was not possible to measure its value at potassium chloride concentrations equivalent to London tap-water (about 500 micromho/cm.) because as K_D increases in Equation (18) so E/P diminishes and the streaming potential is too small to be measured reliably on the valve voltmeter. However, ζ for natural sand in London tap-water was estimated as -8 mV.

The fact that the electrokinetic potential can be raised by acid washing and crushing demonstrates that the surface impurities have a positive charge. The major impurity on the sand appeared to be limonite, containing ferrous iron. In Crapps' experiments²¹ and in some directed by one of the authors (Oeben and Haines²²), where ferric hydroxide floc was filtered through previously unused sand, the filtration performance of the sand changed from run to run. This was in spite of the sand being water washed and restored to its original hydraulic state after each run. Consequently, in the case of Crapps' experiments, the sand was washed in 50 per cent hydrochloric acid, and then in demineralised water to restore the surface of the sand to a constant condition. In the other experiments the sand appeared to become a progressively better filtering medium for retaining iron floc. At pH 8.2 this is consistent with the negative surface potential of the sand being reduced in magnitude by either Fe^{++} or Fe^{+++} or some positive species of ferric oxide.

The variation of electrokinetic potential with pH was also investigated, but this proved difficult with natural sand as the acid solutions attacked the sand surface and no steady readings could be obtained. For acid-washed and crushed sand the effect of pH change was as expected: the

negative electrokinetic potential diminished in magnitude in solutions of lower pH.

BALLOTINI (GLASS SPHERES) (460 MICRONS)

In solutions of potassium chloride or potassium nitrate the ballotini exhibited an electrokinetic potential of about -50 mV initially, but this diminished to about -30 mV on prolonged contact with the electrolyte. This was almost certainly due to penetration by water. Variation of electrokinetic potential with potassium nitrate concentration was quite regular: the potential diminished by about 11 mV for a tenfold increase in concentration. At 5×10^{-4} N. potassium nitrate, $\zeta = -23$ mV. The variation of electrokinetic potential with pH in solutions of constant ionic strength appeared to be small. In the di-divalent electrolyte 5×10^{-4} N. magnesium sulphate the electrokinetic potential was significantly smaller, $\zeta = -13.5$ mV.

ANTHRACITE (CRUSHED COAL) (460 MICRONS)

The anthracite was similar to the ballotini, but with negative potentials of greater magnitude

At 5×10^{-4} N. KNO_3 , $\zeta = -32$ mV.
 5×10^{-4} N. $MgSO_4$, $\zeta = -24$ mV

In potassium nitrate solutions the magnitude of the electrokinetic potentials fell about 20 mV for a tenfold increase in electrolyte concentration.

The results of these streaming potential experiments are summarised on Figure 7.

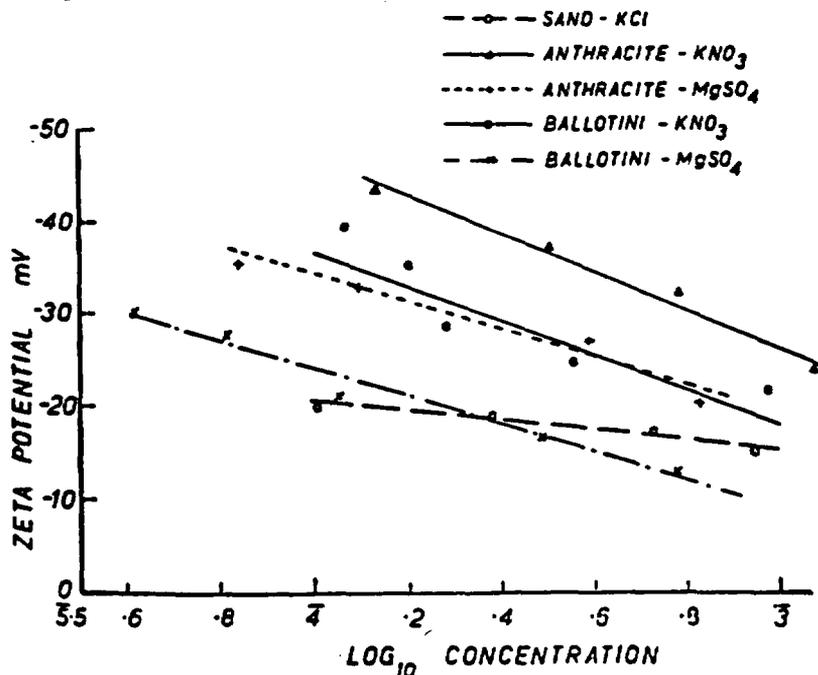


Fig. 7 Electrokinetic potentials for sand, anthracite and ballotini obtained from streaming potential measurements.

CALCULATION OF INTERACTIONS

DOUBLE LAYER REPULSION

With a known electrolyte, or with the ionic strength of the water known, it is possible to calculate the double layer parameter κ from Equation (2). For water at 25°C, this equation simplifies to

$$\kappa = 2.32 \times 10^7 (\sum c_m z^2)^{1/2} \quad \dots \dots \dots (20)$$

where c_m is molar concentration.

- | | |
|--|---|
| For 5×10^{-4} N.KCl or KNO ₃ | $\kappa = 0.74 \times 10^6 \text{ cm}^{-1}$ |
| 5×10^{-4} N.MgSO ₄ | $\kappa = 1.48 \times 10^6 \text{ cm}^{-1}$ |
| London tap-water (Burkin and Bramley ¹⁰) | $\kappa = 2.8 \times 10^6 \text{ cm}^{-1}$ |

If the potential at the outer edge of the Stern layer ψ_s is assumed the same as the electrokinetic potential ζ , then Equation (4) can be rewritten as

$$\gamma = \frac{\exp(\phi/2) - 1}{\exp(\phi/2) + 1} \quad \dots \dots \dots (21)$$

where $\phi = \frac{z\zeta}{25.6}$ at 25°C, with ζ mV.

Equation (5) can be used to calculate the repulsion energy quantity V_r/a for various particle grain separations d , or more conveniently for the product κd . For convenience Equation (5) is restated:

$$\frac{V_r}{a} = 9.24 \times 10^{-8} \frac{\gamma_1 \gamma_2}{z^2} \ln [1 + \exp(-\kappa d)] \text{ erg/cm.} \quad \dots \dots (5)$$

The data from two sets of experiments will be used to compute the interactions.

The first five of these experiments were conducted in the Public Health Engineering Laboratories at University College, London, using a suspension of polyvinylchloride microspheres (diameter just over 1 micron). In the first four experiments a filter 3 cm. deep was used, with a particle size analysis of the influent and filtrate carried out with a Coulter Counter (Coulter Electronics Ltd., High St. South, Dunstable, Beds.), shortly after filtration had commenced. The fifth experiment was in a column 75 cm. deep, with turbidimetric measurements of concentration changes as the suspension passed through the column. Table 1 gives the principal details of the experiments.

TABLE 1
FILTRATION EXPERIMENTS AT UNIVERSITY COLLEGE, LONDON
(Using pvc microspheres; flow-rate 45 gal/sq. ft/hr)

Expt. No.	Medium	Electrolyte	Temp. °C	Filter Coefficient	Ref. 10, 11
1	Ballotini	5×10^{-3} N.KNO ₃	21	0.024	Gregory Expt. 23
2	Ballotini	10^{-3} N.KNO ₃	23	0.033	" 27
3	Ballotini	10^{-3} N.MgSO ₄	18.5	0.070	" 31
4	Anthracite	10^{-3} N.MgSO ₄	20	0.067	" 38
5	Sand	MWB tap-water	18	0.110	Sholji Expt. 11

The filter coefficient given in column 5 of Table 1 is used in modern theory as a measure of filter performance. It is the change of concentration divided by the inflow concentration, per unit depth. The higher the value of the filter coefficient, the better is the filter for retaining particles from the suspension. The basic data for computing the double layer interactions from Equation (5) are given in Table 2 and the resulting repulsion energy curves are plotted on Figure 8. The ordinate scale is in terms of the thermal energy for a particle of 1 micron radius ($kT = 405 \times 10^{-16}$ erg).

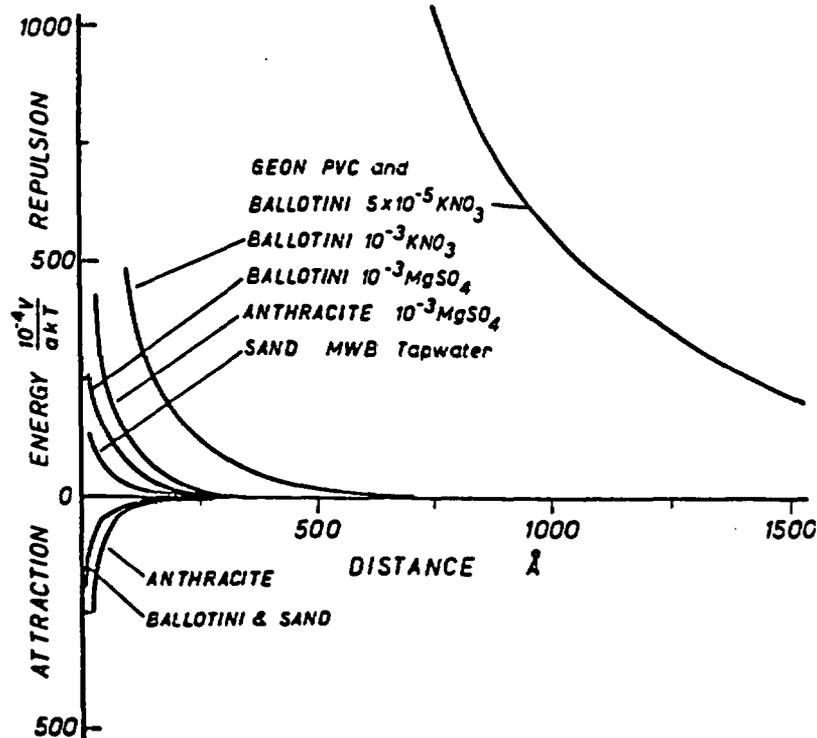


Fig. 8. Attraction and repulsion energy curves between pvc microsphere and sand, anthracite and ballotini grain surfaces in various electrolytes.

TABLE 2
ELECTROKINETIC DATA FOR UNIVERSITY COLLEGE
EXPERIMENTS

Expt. No.	ζ grain	ζ part	z	ϕE	ϕP	γE	γP	κ cm ⁻¹	$\delta = 1/\kappa$
1	-43	-90	1	1.68	3.50	0.40	0.71	0.23×10^6	430 Å
2	-18	-39	1	0.70	1.50	0.18	0.36	1.04	96
3	-9	-28	2	0.70	2.11	0.18	0.48	2.08	48
4	-19	-25	2	1.48	1.95	0.35	0.45	2.08	48
5	-8*	-20†	1.8	0.56	1.40	0.13	0.34	2.8	36

* untreated Leighton Buzzard sand, estimated value

† estimated value

The second set of experiments consisted of filtration of ferric floc (diameter approx. 20 microns) through sand, reported by Crapps. Filtration was observed in long columns of sand and penetration of floc was noted by visual observation of a brown stain on the white sand in the column. Head losses were also noted; these are used here as a comparative basis for measuring filter efficiency. The rate of head loss per unit time is given as a "filter index" with Experiment 9 as unity. The principal details of the experiments are given in Table 3.

TABLE 3
FILTRATION EXPERIMENTS AT GEORGIA INSTITUTE OF TECHNOLOGY

(Ferric floc filtered through sand at 100 gal/sq. ft/hr; Temp. 22°C.)

Expt. No.	Electrolyte (all at pH 7)	Filter Index	Ref. ²⁰
6	Demineralised water	10	Crapps 6.1
7	25 ppm Cl ⁻	15	" 6.2
8	25 ppm SO ₄ ⁻²	9	" 6.3
9	25 ppm PO ₄ ⁻³	1	" 6.4

The basic data for computing the double layer interactions are given in Table 4. Although the electrokinetic potential of acid washed Ottawa sand is given it has not been used as the majority of the filter

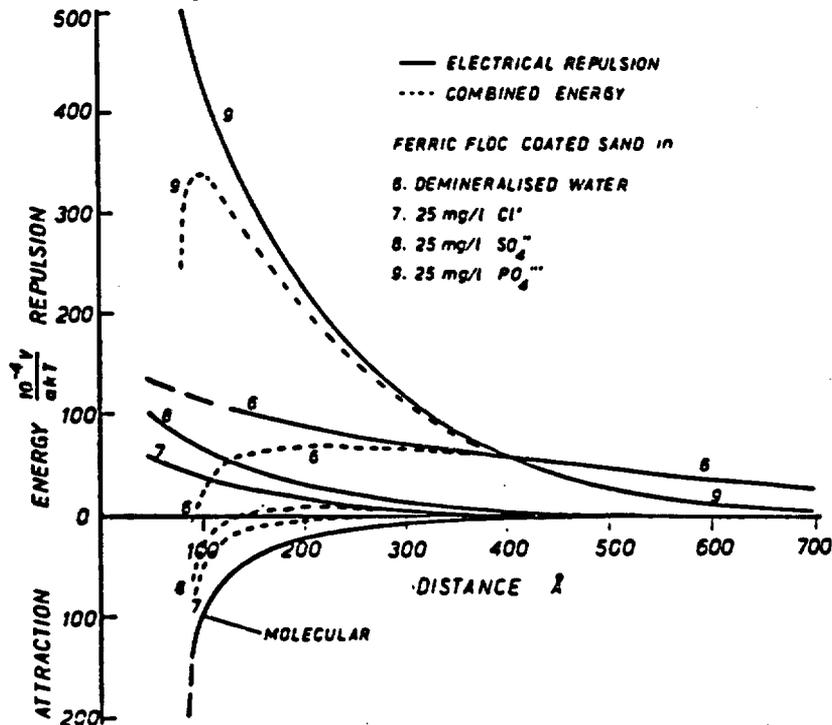


Fig. 9. Attraction, repulsion and combined energy curves between ferric floc particles and ferric floc coated sand grain surfaces, in various electrolytes.

run would be with floc coated sand being approached by floc particles. Therefore the calculations are based on floc-floc double layer interactions for which the repulsion energy curves are given on Figure 9.

TABLE 4
ELECTROKINETIC DATA FOR GEORGIA EXPERIMENTS

Expt. No.	ζ grain	ζ floc	z	ϕ floc	γ floc	κ cm ⁻¹	$\delta = 1/\kappa$
6	-33	-10	1	0.39	0.09	0.25×10^6	403 Å
7	-38	-8	1	0.31	0.07	0.90	111
8	-36	-10	2	0.78	0.19	0.95	105
9	-35	-24	1.4	1.32	0.31	0.75	135

MOLECULAR ATTRACTION

In order to calculate the molecular attraction as a function of distance from Equation (9) it is necessary to know the Hamaker constant A and the characteristic wavelength λ for the two materials and the liquid separating them.

From considerations of the physical and optical data available, and by making checks between the retarded Hamaker equations and the long-range macroscopic theory the following values have been calculated (Gregory¹⁰).

Glass (also sand)—pvc in water $A = 5.5 \times 10^{-14}$ erg
 $\lambda = 81.7$ m μ
 Anthracite—pvc in water $A = 1.4 \times 10^{-13}$ erg
 $\lambda = 77.8$ m μ

Using these values and equation (8) for the unretarded region (up to 50 Å separation) and equation (9) for the retarded region (over 150 Å separation), with interpolation between, the attraction energy curves have been calculated and are plotted on Figure 8. The values for A are considerably less than the general 2×10^{-12} erg given by Verwey and Overbeek⁹, and used by Hunter and Alexander³. However, there is increasing experimental evidence that lower values than this should be used in many cases.

In the case of the ferric floc coated sand and ferric floc particles of experiments 6-9 it is not simple to obtain adequate data to compute the required values for A and λ . Mackrle and Mackrle computed a value for A for the interaction of ferric floc to ferric floc of about 2×10^{-12} erg. In computing this value, however, they made an error by including orientation and induction terms. These only apply to an isolated pair of molecules as do the dispersion effects, unless there is strong dipole orientation. Although water has a relatively high dipole moment it is doubtful if it can contribute at the high frequencies of interaction that are involved. A lower value of A would, therefore, be indicated.

A method of calculating A is to compare the fully retarded Hamaker expression developed by Schenkel and Kitchener¹¹ (equation (9), first term only), with the long range macroscopic equation of Dzyaloshinskii¹² (Equation 10).

$$\text{Fully retarded Hamaker} \quad \frac{V_a}{a} = \frac{-2.45A\lambda}{60\pi d^2} \quad \text{from (9)}$$

$$\text{Long-range macroscopic} \quad \frac{V_a}{a} = \frac{-hv\pi^2 \left(\frac{n_1^2 - n_0^2}{n_1^2 + n_0^2} \right)^2}{4120n_0 d^2} \quad (10)$$

where h = Planck's constant = 6.547×10^{-27} erg-sec.

v = velocity of light = 3×10^{10} cm/sec.

n_0 = refractive index of water = 1.33.

n_1 = refractive index of $\text{Fe}(\text{OH})_3$ = 2.1.

$$\text{Equating } \frac{2.45A\lambda}{60\pi} = 2.5 \times 10^{-20}$$

If λ is taken at $80 \text{ m}\mu = 0.8 \times 10^{-5}$ cm (see previous values),
 $A = 4.9 \times 10^{-11}$ erg

The characteristic wavelength λ is usually of the order of 10^{-5} cm., and so variations in the estimated value of this will affect A slightly, but not to the order of magnitude difference compared with the Mackrle figure. Using these values and interpolating between the unretarded and retarded regions as before the calculated attraction energies have been plotted on Figure 9.

COMBINED INTERACTION ENERGIES

In the case of the first five experiments using the pvc particulate suspension the combined curves have not been drawn on Figure 8, to avoid confusion. However, inspection of the two curves indicate an enormous energy barrier of several thousand times kT for Experiment 1 in very dilute uni-univalent electrolyte. This corresponds with a low filter efficiency (see Table 1). In Experiment 2, with higher concentration of uni-univalent electrolyte, there is again a large energy barrier probably of the order of 1000 kT , and again filter efficiency is low. In Experiments 3 and 4, with moderate concentrations of di-divalent electrolyte the energy barriers are substantially diminished, being not more than 100 to 200 kT , and there is a corresponding increase in filter efficiency. In the case of Experiment 5 in M.W.B. tap-water the energy barrier is not more than 10 kT , and may not exist at all due to uncertainties in the precision of calculations of the interaction energies. This is accompanied by a substantially higher filter efficiency. This reveals an inverse correlation between height of energy barrier, and filtration efficiency. However, the presence or absence of an energy barrier cannot be the only criterion of efficiency, as some removal of particles by the filter did take place even with the largest energy barrier. Some other mechanism is, therefore, also involved.

Consideration of the combined energy curves for the other four experiments involving ferric floc particles, as shown on Figure 9, reveals a similar situation. As the energy ordinate is in terms of the thermal energy of a 1 micron radius particle, and the floc particles had a mean radius of 10 microns, the ordinate scale must be multiplied by 10 to be brought into terms of kT . The floc in water containing phosphate (Experiment 9) has an energy barrier of nearly 3500 kT . This is compatible with a low rate of increase of head loss in the filter, indicating

little removal. (See Table 3). The floc in demineralised water has a barrier about 700 kT high (Experiment 6), and has a substantially better performance than Experiment 9. Experiment 8 with sulphate in the water, shows an energy barrier of less than 100 kT. The absence of an energy barrier (chloride) is associated with the highest filter efficiency. Again, there is an inverse correlation between height of energy barrier and filtration efficiency, but again some floc was removed continuously by the filter (although at a slow rate) in Experiment 9 in spite of the very large barrier.

These energy barriers are at a separation of about 100 to 200 Å, that is 0.01 to 0.02 micron. Considering the surface roughness of filter media, and the non-spherical geometry of most particulates in water, it is questionable whether this separation is not tantamount to contact as surface "peaks" on either grain or particle will protrude greater distances than this.

Generally the whole range of these surface forces is less than 500 Å, and less than about 200 - 300 Å for most natural waters containing moderate amounts of dissolved salts. The special cases of Experiment 1 (very dilute potassium nitrate, almost distilled water), Experiment 6 (demineralised water) and Experiment 9 (25 ppm of phosphate, a specifically adsorbed ion for ferric floc) are not likely in practice. Consequently surface forces cannot be responsible for actions in the bulk of the pore space in between filter grains, and some other physical or hydrodynamic action has to be proposed to explain the translation of particles from the flow to the vicinity of the grain surfaces where surface forces have effect.

CONCLUSIONS

Physico-chemical, or surface, forces come into action when suspension particles are close to grain surfaces. Their range in distilled, or near-distilled, water may be several hundred Angströms, but is not likely to exceed 2000 Angströms (0.2 micron). In most natural waters containing moderate amounts of dissolved salts their range is less than about 200 Angströms (0.02 micron).

Most particles in water carry a potential of like sign to that exhibited by grain surfaces (negative). Softening precipitates, alum flocs below about pH8 and ferric flocs below about pH6 usually carry a positive potential. If grain and particle have opposite potentials there is no barrier to adsorption of the particle; if they have similar potentials a barrier may exist. In either case, once the grain is coated with particles a barrier is possible, depending principally on the potential carried by the particles.

It has not been possible to compare the kinetic energies of particles with calculated energy barriers. However, from certain experimental data it does appear that $200kT$ (0.81×10^{-11} erg) is a critical value for 1 to 2 micron pvc microspheres, and about the same order of magnitude for 20 microns ferric hydroxide flocs. Energy barriers higher than this slow down filtration removal significantly, and below this filtration proceeds more efficiently.

In any case some particles always do adhere to the grains. They may be physico-chemically atypical, but it is more likely that there are

adherence mechanisms which are independent, or almost so, of surface forces. Interstitial straining is an example of such a mechanism; the surface roughness of grains and particles may be another such factor. However, by drastically modifying the chemical conditions, it is possible to change filter performance very significantly.

Previous estimates of the van der Waals-Hamaker constant, A , appear to have been between one and two orders of magnitude too high, but methods of calculating these values are still not precise.

SYMBOLS USED

a	radius of suspension particle	cm
A	Hamaker constant (subscripts 0, 1, 2 indicate liquid and first and second solids respectively)	erg
c	concentration of ions	no./cc
c_i	concentration of ions of the i -th kind	no./cc
c_n	concentration of ions	molar
d	particle to grain separation	cm
e	charge on the electron	
E	streaming potential	
F	field strength	
h	Planck's constant	erg-sec
k	Boltzmann's constant	erg per °
K_D	conductivity of electrolyte, allowing for surface conductance	micromho/cm
K_v	bulk conductivity of electrolyte	micromho/cm
n_0	refractive index of water	
n_1	refractive index of solid phase	
p_c	function in equation for retarded molecular attraction	($= 2\pi d/\lambda$)
P	pressure difference across streaming potential cell	cm H ₂ O
q	number of molecules per cc.	
R_1	resistance of streaming potential column from its geometry	
R_2	resistance of streaming potential column saturated with strong electrolyte	
s	effective number of dispersion electrons	
T	absolute temperature	
v	velocity of light	cm/sec
v_b	observed velocity of particle at electrophoresis cell boundary	cm/sec
v_e	true particle electrophoretic velocity	cm/sec
v_m	observed maximum velocity of particle	cm/sec
v_o	electro-osmotic velocity	cm/sec
v_y	observed velocity of particle at distance y from cell boundary	cm/sec
V_a'	potential energy of attraction between a pair of atoms	erg
V_a''	potential energy of attraction between a pair of spheres	erg
V_a	potential energy of attraction between sphere and flat plate	erg

V_r	potential energy of repulsion between sphere and flat plate	erg
y	distance from surface	cm
y_0	distance from electrophoresis cell boundary	cm
y_0	depth of electrophoresis cell	cm
z	valency of electrolyte	
z_i	valency of the i-th kind of ion	
γ_1	function of ϕ_1 in repulsion potential equation	
γ_2	function of ϕ_2 in repulsion potential equation	
δ	thickness of double layer	cm
ϵ	dielectric constant	
ζ	electrokinetic potential	
η	absolute viscosity	poise
θ	temperature	$^{\circ}\text{C}$
κ	reciprocal of double layer thickness	cm^{-1}
λ	characteristic wavelength	cm
ν	empirical frequency	
ϕ_1	function of electrokinetic potential for material 1	(= $z\zeta_1/25.6$)
ϕ_2	function of electrokinetic potential for material 2	(= $z\zeta_2/25.6$)
ψ	electrical potential	
ψ_1	electrical potential at surface	
ψ_0	electrical potential at the outer edge of Stern layer.	

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