

# THEORY OF FLOCCULATION, SUBSIDENTENCE AND REFILTRATION RATES OF COLLOIDAL DISPERSIONS FLOCCULATED BY POLYELECTROLYTES

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## ABSTRACT

The flocculation and subsequent subsidence of colloidal suspensions are markedly increased by the addition of flocculating agents; for example various starches and recently developed synthetic polymers.

The rate of flocculation depends not only upon the extent of adsorption of the agent (flocculant) but also upon the order of mixing and the character and extent of the subsequent agitation which determines the character of the floc formed. Electrolytes flocculate by reducing the electrostatic repulsions between charged particles, but long chain polymers produce flocs by a bridging mechanism which overcomes electrostatic repulsions.

Quantitative relationships are developed between the optimum concentration of flocculant and the rates of flocculation, subsidence, and particularly rate of filtration through the filter cake.

## INTRODUCTION

This investigation was undertaken in June 1951 at the request of the U.S. Atomic Energy Commission as a fundamental study of colloidal stability for the purpose of developing methods to dewater and recover dispersions of uraniferous ores for chemical processing. Originally the study dealt only with the waste slurries of the Florida Phosphate Fertilizer Industry, but later was extended to the ores of the Colorado Plateau and finally to pure compounds of known structure such as  $\text{Ca}_3(\text{PO}_4)_2$ ,  $\text{AlPO}_4$  and  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . The waste slurries did not settle and could not be filtered, thus presenting a problem for recovery and chemical treatment. The present paper reviews the salient features of the investigation for the purpose of

interpreting and developing more fully our basic theories of flocculation and filtration.

The major results for the remarkable effects of the newly discovered flocculating aids in promoting flocculation, subsidence and filtration have been published in a series of six papers in the *Journal of Colloid Science*, culminating in a theory of the rate of filtration through the filter cake (Smellie and La Mer, 1958).

The dispersions employed have been characterized and described by La Mer and Smellie (1952, 1953, 1954a, 1956a, 1956b, 1956c), La Mer *et al.* (1953, 1954b, 1956, 1957a, 1957b) and Smellie and La Mer (1958). For the most part the Florida phosphate slimes consist of fine particles ranging from 1 to 10  $\mu$ , with a few larger sandlike particles and some very fine particles. The slimes settled very slowly. The Hopewell Mine slimes were somewhat gelatinous in character.

The colloidal dispersions prepared in the laboratory were obtained by grinding the native leached phosphate rock under water in a pebble mill and retaining all fractions passing a  $-200$ -mesh ( $74\ \mu$ ) sieve. The same procedure was employed for the pure compounds,  $\text{Ca}_3\text{PO}_4$ , etc. These dispersions, in the absence of any added flocculant, settle appreciably in 24 hr and almost completely in 3 days leaving a turbid supernatant. The time needed to filter these slurries (of 5 percent solids) was from 350 to 1500 sec depending upon the fineness of the grinding process. The small native particles of interest in this investigation are, for the most part, flat platelike structures of substituted kaolin, gibbsite and wavellite types, in addition to larger irregular particles of calcium phosphate, aluminum phosphate, and silica.

The smaller (clay type) particles consist of more-or-less rigid layers of silicate, aluminum hydroxides, and calcium hydroxides. Stability is attributed to hydrogen bonding between the exposed OH groups and the solvent water molecules. It is known that water molecules can penetrate at least partly into some of the lattice structures, but swelling in kaolinite is not as pronounced as in the montmorillonite or bentonite structure. The fine particles have major axes of less than 1 to 2  $\mu$  and are negatively charged with an electrophoretic velocity of  $2\text{--}4\ \mu\text{sec}^{-1}\ \text{V}^{-1}\ \text{cm}^{-1}$ . The charge is a function of the pH and is modified by the presence on the surface of the particle of potential-determining ions such as  $\text{Al}^{3+}$  and  $\text{PO}_4^{3-}$ .

The slurry particles exhibit primarily a hydrophilic behavior. The electric charges on the particles and the electrolyte environment (Gouy–Chapman–Debye ion atmosphere) play a minor role in producing stability. One cannot correlate the stability with the so-called “zeta potential” calculable from the measured electrophoretic mobility without profound modification of that simple theory. We have achieved our most spectacular increases in rates of flocculation, subsidence and filtration by the *addition of negatively*

*charged polyelectrolytes* (at pH = 6–7), such as Lytron, Separan, and particularly by polyacrylamides of various molecular weights modified in this laboratory by partial hydrolysis, mixing and cross linking with formaldehyde upon negatively charged clay-type particles. These observations cast serious doubts upon the pertinence of the prevalent theory of electric charge interactions, as measured by the “zeta potential,” for an interpretation of stability. The futility of obtaining a simple explanation in terms of “zeta potentials” becomes more evident when we recognize, as Verwey and Overbeek (1948, p. 48) have emphasized, that it is the electrostatic part of the thermodynamic potential  $\psi$  which controls stability and not the zeta potential. This latter potential is produced by shearing kinetically one layer of electrolyte from another.

$\psi$  and  $\xi$  may run parallel in many cases but one cannot assume this *a priori* since the two quantities occasionally have opposite signs!

The addition of lime water, aluminum salts, or ferric salts reduces the electric double layer potential  $\psi$  thus producing *flocculation with moderate improvements in the rate of subsidence but without producing any significant improvement in the filtration rate*. Electrolytic coagulation does not improve the porosity of the filter cake. On the other hand potato starch produces a loose type of floc with large pores which filters well. These findings require digression.

## POLYELECTROLYTES

A polyelectrolyte is a type of macromolecule in which the polymer possesses a number of electrical charges (or ionized sites) along the molecular chain of carbon atoms. New properties are conferred upon the polymer as a result of the electrical forces arising from the position of the charges along the chain. These forces can produce drastic changes in the shape of the molecule by converting a long threadlike chain molecule into a coil and vice versa.

Polymethacrylic acid and polyvinyl pyridine are typical examples of synthetic polyelectrolytes of established structure. In alkaline solution the former becomes the negatively charged polymethacrylate ion whereas the latter becomes the positively charged polyvinyl pyridinium ion in solutions of strong acid. The coiled molecules in neutral solvents stretch out as long threads when acidified or made alkaline as a result of the repulsions of the created charges of the same sign along the molecular chain. These changes in shape have a profound effect upon the viscosity of dilute solutions; they are also extremely sensitive to neutral salt additions. It is therefore not surprising that markedly different behaviors in molecular bridging and consequent flocculation powers of polyelectrolytes appear as a function of pH and added salts. In some cases the polyelectrolyte possesses positive and negative charges within the same macromolecule. They are then called

*polyampholytes*; the juxtaposition of opposite charges in an ampholyte make their behavior correspondingly more complicated.

Proteins and polypeptides are time honored typical examples of polyampholytes. The pectins of plants and the hyaluronic acids in animal tissues are acidic derivations of polysaccharides. More recently it has been recognized that the various starches belong to this class.

## PHOSPHORUS IN STARCH

The different properties of corn, tapioca and potato starches arise from differences in the degree of electrolyte character and the molecular structure (branched or straight chain) as well as the content of phosphorus monoester (La Mer and Smellie, 1956 a, 1956 b). Chemical analysis shows between 0.07 and 0.13 percent of phosphate for potato starches, whereas corn starch is practically devoid of phosphate. The fatty acid contents also differ. Fig. 1 gives Staudinger's structure of the branched amylopectin fraction

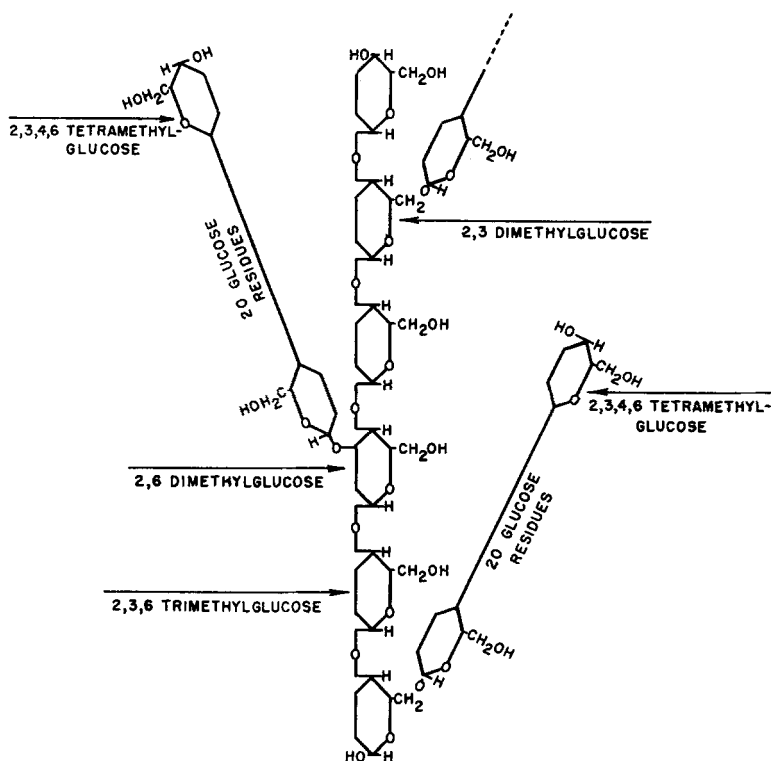


FIGURE 1.—Diagram of amylopectin with principal chain. Formula of Staudinger. Phosphate groups are missing.

of starch which can be separated from the amylose fraction by electrophoresis. Meyer *et al.* (1948) give more details of these structures but neglect the important role of phosphorus content. The presence of phosphorus in the molecule is an old finding of Samec which has been exploited in a series of independent investigations in the Columbia University Chemical Laboratories, commencing in 1916 up to the present time under the direction of Professors. A. W. Thomas, T. C. Taylor, Mary Caldwell and Charles O. Beckmann. We are indebted to Professor Beckmann for reminding us of these neglected investigations on phosphorus content and for suggesting, in the fall of 1951, the role phosphate could play in flocculation by starch. The branched type of molecule is obviously better for producing the *haphazard-type floc structure needed for good filtration*. The Botany Department of Columbia University has also shown that branched structures of starch, and perhaps also the phosphate content, are chromosome linked. More attention to corn breeding and the selection of the resultant types of starch (waxy maize, etc.) should yield significant improvement in the flocculation efficiency of starches. At present a million dollars worth of caustized corn starch is being used in the U.S.A. for flocculation purposes each year.

La Mer and Smellie (1956b) give the evidence that the flocculating powers of starches are correlated closely with their phosphate content in the presence of cations such as Ca, Ba and Ag which form insoluble phosphates, whereas they are ineffective when these cations are replaced by Na, K,  $\text{NH}_4$ .

Human saliva, which contains a muco protein, and the mucilaginous extracts obtained from the boiling of cactus plants have also been shown to be excellent flocculants at extremely low concentrations for the colloidal dispersions under consideration.

## MECHANISM OF FLOCCULATION

These findings led us to the hypothesis that flocculation by starch is produced by a cross-linking mechanism. The carbohydrate portion of the starch molecule is adsorbed on the surface of the ore particle, probably by hydrogen bonding between the OH groups. The calcium ions present in the water then cross link via the phosphate groups, yielding a floc. Starches having branched chains appear to be more effective than the straight-chain varieties.

The hypothesis that flocculation occurs by the binding together of particles by adsorbed long-chain molecules appears to be of general applicability and in turn it led us to a study of the effects of synthetic polyelectrolytes. As a working model the theory of flocculation by polyelectrolyte through cross linking of particles has also served well in the interpretation

of our results with all types of gums, mucoproteins and, in particular, the specially synthesized polymers of the vinyl, polyacrylamide and polyethylene series. These materials are immensely superior to simple electrolytes as flocculants although the further addition of certain electrolytes often affects the polyelectrolyte efficiency. The effectiveness of the polymers thus depends on many factors, such as molecular weight, degree of cross linking and hydrolysis of the polymer.

Independently of our starch studies of 1951, the Monsanto Chemical Company conducted a series of investigations for the improvement of soils by using such conditioners as humus, algin and finally the polyelectrolyte "krilium," a co-polymer of vinyl acetate and maleic anhydride marketed under the trade name of Lustrex, later called Lytron. Ruehrwein and Ward (1952) proposed a mechanism similar to that which we were using to explain our results for starches. Later Michaels and Morelos (1955) gave added weight to the ideas of Ruehrwein and Ward.

## EXPERIMENTAL

By controlling the mixing and subsequent agitation with respect to character and time, laboratory procedures have been developed which yield highly reproducible quantitative data. Although quantitative differences appear in the individual behavior of chemically different ores toward a specific flocculant, the typical sedimentation and filtration rate curves found for the Florida phosphate rock slimes hold generally for the more important Colorado Plateau ore slimes with respect to type of flocculant, amounts needed and improvement in filtration rate. *With increasing additions of flocculant, the filtration rate always passes through a maximum, i.e. there is a minimum in the time needed for filtration.* The improvement in filtration rate often reaches 50- to 70-fold, and in special cases even 200-fold for the addition of as little as 50-100 ppm of polymer for a dispersion containing 5-10 percent solids. Typical results are shown in Table 1.

To achieve these reproducible rates of flocculation, subsidence and finally of filtration, it became necessary first to carry out detailed systematic studies of the effects of order of mixing and of the intensity and length of agitation. The detailed data are cumbersome to reproduce and are not given, particularly since it sufficed to locate the optimum conditions which are most important for controlling the kinetics of flocculation. By locating the optimum conditions it became possible to develop techniques that were relatively insensitive to minor changes in the variables. It was only by rigorously adhering to these standard techniques that it was possible to obtain the highly reproducible results reported for rates of subsidence and rate of filtration which led to the development of a consistent theory.

TABLE 1—IMPROVEMENT IN FILTRATION RATES BY FLOCCULANTS<sup>1</sup>

Flocculant	Filtration Improvement Factor	Optimum Flocculant Concentration (ppm)
Amer. Cyanamid Co.		
Reagent S-3000 .....	16	200
Polyacrylamide PAM-50 .....	20	400
Polyacrylamide PAM-75 .....	12	250
Polyacrylamide PAM-100 .....	50	250
Dow Chemical Co.		
Separan 2610 .....	70	200
General Aniline and Film Co.		
PVM/MA (copolymer of methyl vinyl ether and maleic anhydride series; sp. visc. 0.5-0.8) with 0.2% added CaCl <sub>2</sub> .....	30	80
PVM/MA (sp. visc. 7.4) with 0.2% added CaCl <sub>2</sub> .....	30	80
A. F. Goodman and Sons		
Potato starch .....	9.3	400
W. A. Scholten, Netherlands (agent Morningstar Nicol)		
Starch ether: Solvitose H 4 .....	8	800
Monsanto Chemical Co.		
Lytron 886 (partial Ca salt of copolymer of vinyl acetate and maleic anhydride) .....	9	30
Lytron 886 with 0.05% added CaCl <sub>2</sub> .....	50	80
Lytron 887 (copolymer of vinyl acetate and maleic anhydride) .....	9	30
National Starch		
613-645 (cationic starch derivative) .....	8	1500

<sup>1</sup> These are thirteen of the best products out of a total of 150 commercial samples tested.

## REPRODUCIBLE SUBSIDENCE AND FILTRATION TECHNIQUES

### *Subsidence*

The slime and the flocculating reagent were mixed by the 100-ml cylinder (10-40 times in 2 min) to obtain uniform mixing; the subsidence measurements were then made by recording the height of the solid-liquid boundary as a function of time. The subsidence rates of untreated slimes and slimes with Ca(OH)<sub>2</sub> only, were used as controls in each series of experiments.

### *Filtration*

Vacuum filtration rates were the most reproducible. A 5.5-cm Buchner funnel and Whatman no. 2 filter paper were used. A pump reduced the pressure inside the filter flask and maintained a constant pressure difference

of 74 cm Hg. The rate of filtrate collection was measured with a 100-ml graduated cylinder placed inside the filter flask.

#### *Agitation and Mixing Reagents*

The flocculating agents must be added progressively in measured doses, and the mixing by agitation controlled with respect to the number of inversions of the container (*shaking is not advisable*) and the total time in which a given number of inversions is made. Flocculating agents were added to the slime as 0.1–1 percent solutions in water. When all the reagent is added at one time, the adsorption will be greater at the top of the container than below. Under such conditions the result differs from that obtained when the reagents are added dropwise and mixed after each addition, even if the total number of inversions of the container is the same in each case.

#### *Method of Mixing-Agitation*

The results with vacuum filtration were reproducible to  $\pm 5$  percent if a given number of inversions was performed within a given period of time. The number of inversions giving optimum results was 40 in 2 min. However, variation of the number of inversions between 10 and 40 in 2 min was permissible in some cases, leading to a variation in filtration rate of about 10 percent. A device was constructed which rotated the cylinders at certain speeds, determined by gearing, to eliminate the variations due to the manual technique of different operators.

Floc size can be affected significantly by varying the agitation when all other factors are controlled. This is particularly evident in the filtration rates since differences in floc size lead to great differences in the porosities of the filter cakes. The effect of mechanical agitation is more dependent on the total number of revolutions than on the revolutions per minute for a given total number.

### TYPICAL SUBSIDENCE AND FILTRATION RATES OF FLOCCULATED SLIMES

Our observations on subsidence fall into two distinct types (Fig. 2). Curve I represents cases in which flocculation is relatively slow. The initial region represents slow flocculation with a gradually increasing subsidence rate due to gradually increasing floc size (o–a). This is followed by a region of constant subsidence after flocculation is complete (a–b). Finally, packing or compression occurs (b–c) when the flocs make contact with each other near the bottom of the cylinder. Curve II represents cases in which flocculation is completed rapidly, and a constant subsidence rate is observed immediately. The differing final volumes have been omitted in the schematic Fig. 2.



Fig. 3 shows the typical subsidence behavior of a phosphate slime when treated with various amounts of Floegel, a modified starch. Note that very small amounts of flocculating agents (up to 20–30 ppm) are detrimental. Amounts of flocculant greater than 30 ppm produce increasing improvement in subsidence rate up to about 200 ppm. This subsidence behavior is typical of all our observations with a variety of suspensions (phosphates, clays, etc.)

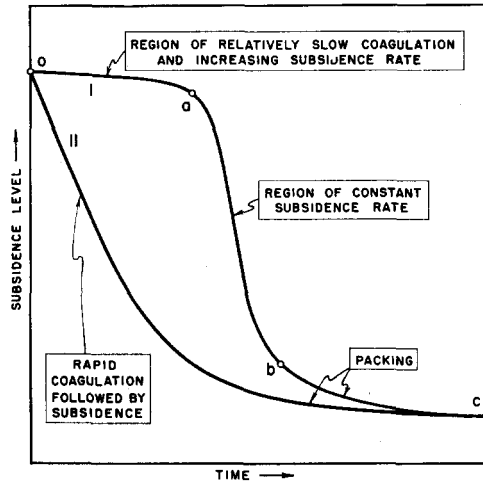


FIGURE 2.—Variation of subsidence *vs.* time for unflocculated and well flocculated slimes.

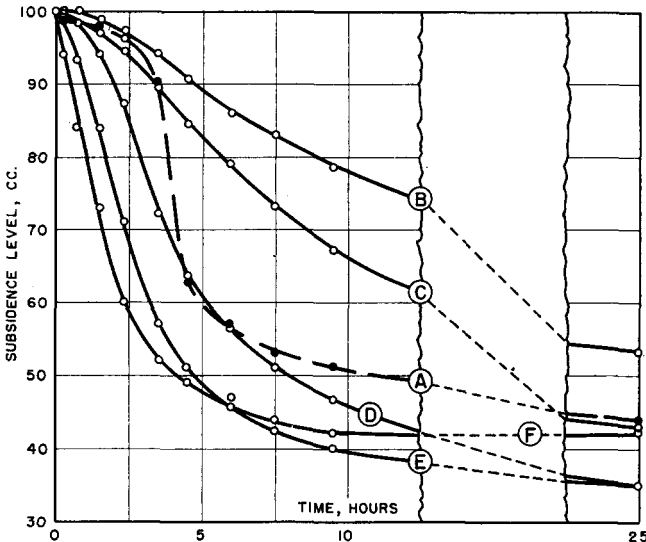


FIGURE 3.—Subsidence level *vs.* time.

and polymeric flocculating agents (starches, gums, synthetic polymers). The equation of continuity of a flow process yields an equation which accounts accurately for the subsidence of well-flocculated slimes.

La Mer and Smellie (1956c) develop mathematically their original qualitative ideas of subsidence as a compression of flocs leading to an expression valid for well flocculated suspensions, namely that

$$t/(h_0 - h) = \alpha + \beta t, \quad (1)$$

where  $t$  is time,  $h_0$  and  $h$  the heights of the subsiding column at times  $t = 0$  and times  $t$ .  $\alpha$  and  $\beta$  are constants.

It was also found that, for a *well flocculated slime*, an exact linear relation over the range  $a$  to  $b$  in Fig. 2 was obtained when the relative filtration rates were plotted against the square of the relative subsidence (see Fig. 3 in La Mer and Smellie, 1956c). This simple relation follows when one recognizes that free-falling particles obey Stokes' law; *i.e.* rate of fall is inversely proportional to the square of the equivalent radius of the particles. The size of the pores  $R$  in the resulting filter cake should be governed by the packing of these spheres and hence  $r$  and  $R$  should be proportional. The flow of liquid through capillaries (pores) is governed by Poiseuille's law; *i.e.* inversely as  $R^4$ . Hence  $R^4$  is proportional to  $r^2$ , or  $R^2$  to  $r$ , yielding the linear relation referred to above. See La Mer and Smellie (1956c) for mathematical details.

The range of flocculant concentration in which the optimum in filtration rate occurs is often narrow. Hence, the experiments should be designed for small increments of flocculating agents. The position of the optimum depends on the chemical composition of the solids, their particle size, the percentage of solids and the particular flocculant being used. Fig. 4 shows typical filtration data. The sharp decrease in flocculating efficiency with consequent decreases in filtration rates for flocculant concentrations greater than optimum should be noted. Microscopic observations show that the average floc size decreases with the higher concentrations of polymeric flocculating agents.

Approximately 200 polymeric flocculating agents have been tested quantitatively over the past three years. The majority of these agents were commercially available products, research samples provided by various companies, or modified (phosphorylated or carboxylated) starches and synthetic polymers prepared by Professor C. O. Beckmann and Dr. M. Roger of Columbia University. Pertinent data are summarized in Table 1. The optimum concentrations of the various flocculants which produce the maximum filtration rates are given with the "filtration improvement factor" (F.I.F.), which represents the ratio of the filtration rate at the optimum concentration of the flocculant to that of the untreated slime. Since all polymeric agents show the same pattern of behavior, although often differing con-

siderably in effectiveness as flocculants, the interpretation of such factors as percentage of solids and particle size in relation to the optimum flocculant concentrations becomes feasible. The variation of the filtration rate with the concentration of flocculant is explained by a relatively simple theory relating the surface adsorption of flocculating agents to the floc size and filtration rate.

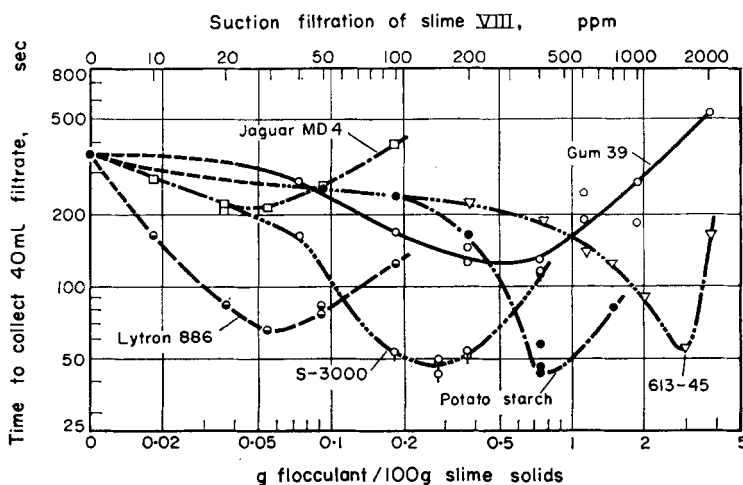


FIGURE 4.—Suction filtration of slime VIII. Time to collect 400 ml filtrate in seconds vs. grams flocculant for 100 g slime solids.

### THEORY OF FILTRATION

The extensive experimental data on filtration shown in Figs. 4, 5 and 6 indicate that the forms of all filtration curves are of the same general type and are governed by the maximum value for the filtration rate (or minimum value of filtration time) for a given value  $P_M$  of the concentration of flocculant. Two numbers characterize this value of  $P_M$ ; namely, the improvement of filtration rate ( $Q - Q_0$ ) and  $P_0$  (the ppm of flocculant needed to achieve it). Since the curve about  $P_M$  exhibits a sharp rise to a maximum followed by a sharp decrease in value as  $P_0$  is increased, any theory of filtration for added flocculants must yield an equation for  $(Q - Q_0)$  which involves  $P_M$  to a high positive power (exponent) for values of  $P_0 < P_M$  followed by a high negative power for  $P_0 > P_M$ . As we shall see, the origin of these high powers in  $P_M$  arises from variations in  $\theta$ , the fraction of the surface covered by flocculant, as the concentration of flocculant is varied. Hence the extent of adsorption is of the greatest importance in the theory.

The mathematical development of our theory of filtration involves four stages (A, B, C, D).

A. The flocculant is adsorbed on the particles in accordance with Langmuir's adsorption isotherm involving  $\theta$  and  $(1 - \theta)$ . The assumption that Langmuir's equation applies has been confirmed recently by direct measurements (Lazlo Jankovics—unpublished).

B. An equation for the kinetics of flocculation–deflocculation and the repair of flocs by the coagulation of fine particles upon the flocs is developed.

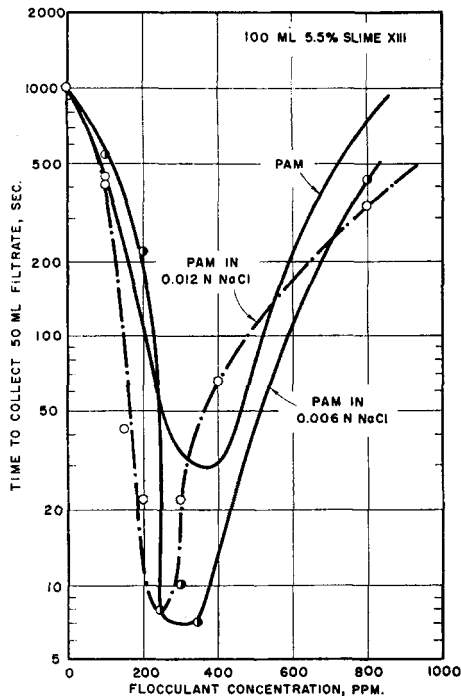


FIGURE 5.—Salt effects on filtration rate using polyacrylamide (PAM).

This yields an equation for  $R$ , the equivalent equilibrium radius of the floc.

C. The Kozeny–Carman (K–C) equation which relates the flow through the pores of the filter cake to the square of the surface area ( $S^2$ ) of the pores is introduced. Details of the use of this equation and the measurements of surface areas by stearic acid adsorption are given by La Mer *et al.* (1954 b, 1956 d).

D. Experiments varying the weight percent of solids and of fineness of grinding (La Mer *et al.*, 1957 b) show that the amount of flocculant ( $P_M$ ) that must be added to achieve the optimum or maximum rate in filtration varies as the square of the weight percent of solids ( $W^2$ ), which in turn is proportional to the square of the surface area ( $S^2$ ) of the particles as determined by the fineness of grinding.

$$P_M \sim W^2 \sim S^2.$$

The K-C equation thus permits one to connect the rate of filtration with the weight of solids used and then in turn with A and B above. The development, limitations and improvements upon the K-C equation have been treated in an exhaustive fashion by Scheidegger (1957, pp. 100-108).

In the customary conduct of a filtration test, the slurry is filtered through a cake whose initial thickness is zero and increases in thickness progres-

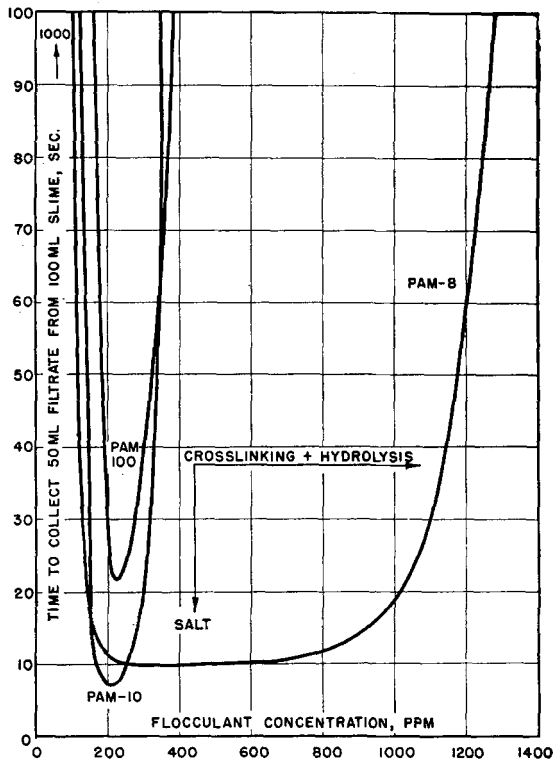


FIGURE 6.—Effect of cross-linking a partially hydrolyzed polyacrylamide (PAM-8) on filtration. PAM-10 and PAM-100 differ in molecular weight only.

sively with the elapsed time. When the flocculated slurry is poured upon the filter, the filtration rate approximates that of a first-order equation of chemical kinetics as modified by this increase in filter cake thickness. In the experiments testing our theory we have avoided these difficulties by also measuring the rate of refiltration through the cake produced by the first filtration.

The refiltration rate measures faithfully the basic factors considered in the theory. Corrections for the growth of the filter cake can then be super-

imposed if desired. In refiltration the thickness and porosity ( $\epsilon$ ) remain constant so that the simplest form of the K-C equation is applicable.

According to Smoluchowski's theory the coagulation of particles in colloidal solutions is essentially a bimolecular rate process controlled by the diffusion towards one another of the elementary particles designated for the moment by the symbols  $A$  and  $B$  (Umberger and La Mer, 1945).

A. When the adsorption of the polyelectrolytes obeys Langmuir's isotherm,

$$\theta = \frac{bP}{1 + bP}, \tag{2}$$

or

$$(1 - \theta) = \frac{1}{1 + bP}. \tag{3}$$

Here  $b$  is a specific constant depending upon the chemical character of the adsorbent and the adsorbate.  $P$  is the *equilibrium concentration* of polyelectrolyte remaining in the solution after the (slow) adsorption process is completed. If  $P_0$  is the initial concentration of flocculant added, then

$$P = P_0 - kw\theta. \tag{4}$$

Here  $kw\theta$  is the decrease in the bulk concentration of flocculant arising from adsorption.  $W$  is the solid content of adsorbate and  $k$  is a constant which depends upon the specific area of the solids and hence varies with the fineness of grinding,  $kw$  being a measure of total surface area.

By straightforward but somewhat tedious algebra,  $\theta$  and  $(1 - \theta)$  can be expressed in terms of  $P_0$  yielding finally

$$\theta = \frac{P_0}{\frac{(1 + bkw)}{b} + \frac{P_0}{(1 + bkw)}}, \tag{5}$$

$$1 - \theta = \frac{1 + bkw}{b} \left/ \left[ \frac{1 + bkw}{b} + \frac{P_0}{1 + bkw} \right] \right. \tag{6}$$

B. In the particular case of flocculation, the coagulation process involves the postulated cross-linking mechanism described above in which a flocculant molecule (or molecules) holds the two particles  $A$  and  $B$  together. The elementary process proceeds in two steps. First the flocculant threadlike molecule represented by a dash (-) adsorbs on particle  $A$ .



$A-$  and  $B$  then diffuse towards each other and become cross-linked by the flocculant forming the elementary floc particle  $A-B$  by the process



at a rate determined by Smoluchowski's diffusion equation.

This elementary floc  $A-B$  can then grow by further adsorption of flocculant molecules and by further coagulation with particles which can be designated either as  $A$  or  $B$  or by  $(A-B)$ . The kinetics of these successive steps is the same as that of the elementary process since  $A$  and  $B$  are in principle indistinguishable.

If  $n_0$  is the number concentration per unit of volume of the  $A$  and  $B$  particles, the number of  $A$  particles having adsorbed flocculant molecules is  $n_0\theta$ , where  $\theta$  represents the fraction of the total surface covered by adsorbed flocculant molecules.

For a  $B$  particle to become attached to an  $A$  particle the free end of the flocculant on  $A$  must now be adsorbed on the uncovered surface of this particle. The number of  $B$  particles having uncovered surface is  $n_0(1 - \theta)$  so that the overall rate of flocculation  $df_1/dt$  becomes

$$df_1/dt = k_1 n_0^2 \theta (1 - \theta). \quad (7)$$

The method of mixing or agitating the slime and flocculant is the critical factor in determining the ultimate floc size for any given slime, slime content and flocculation agent concentration. The floc reaches an optimum size for a particular slime, solid content of elementary particles, and flocculant concentration, and for a given intensity of agitation measured by the number of rotations of the container at a certain rpm.

An optimum in floc size indicates that the flocculation process involves not only the formation of flocs, but the destruction of flocs or their decrease in size due to the mechanical action of agitation. At the optimum size a steady state exists between the rates of construction of flocs and their destruction.

This disintegration of flocs should proceed at a rate that is proportional to the mass or the size of flocs and also to a repair process which is inversely proportional to the surface of the floc and the binding or stabilizing influence of the factor  $\theta(1 - \theta)$ . Assuming for convenience that the flocs are essentially spherical, then the overall rate of disintegration of flocs  $-df_2/dt$  can be set equal to

$$-df_2/dt = \frac{k_2 P^3}{R^2 \theta(1 - \theta)} = \frac{k_2 R}{\theta(1 - \theta)}. \quad (8)$$

Here  $R$  is the radius of the floc and hence  $R^3$  is proportional to the mass of the floc.  $R^3$  represents a factor tending to pull the floc apart.  $R^2$ , which is proportional to the surface area of the floc, retards the decrease in floc size as a result of the repair process of picking up particles from the surroundings. The magnitude of the factor  $\theta(1 - \theta)$  determines the probability of the binding of fine particles upon the floc by adsorption of flocculant as in the primary process. Therefore, the overall net rate becomes

$$df/dt = k_1 n_0^2 \theta(1 - \theta) - \frac{k_2 R}{\theta(1 - \theta)}. \quad (9)$$

At the optimum in floc size, the net rate = 0, consequently yielding an equilibrium value for the floc radius  $R$

$$R = \frac{k_1}{k_2} n_0^2 \theta^2 (1 - \theta)^2,$$

which is proportional to  $n_0^2$  or proportional to  $W^2$ , the square of the weight percents of solids.

C. The K-C equation discussed previously relates the rate of filtration through a filter cake to the specific surface area of particles in the cake. When a slime is flocculated, the effective specific area of the filter cake is reduced to smaller values corresponding to increasing filtration rates.

The K-C equation predicts that the filtration rate ( $Q$ ) will be inversely proportional to the square of the surface area of the particles in the cake. If the flocs are considered as essentially spherical in shape and are made up of closely packed primary particles (as usually observed under the microscope), it may be shown that the other factors in the K-C equation such as ( $\epsilon$ ), the porosity of the filter cake, and ( $L$ ), the thickness of the cake, will be essentially constant. The cross-section of the cake is the same in all cases since the same cylindrical funnel is used throughout for filtration. Therefore, the volume of the filter cake will be essentially constant for slimes in different degrees of flocculation. The filtration rate ( $Q$ ) is then proportional to  $S^{-2}$ , where  $S$  is the surface area of particles (or flocs) in a unit volume of the filter cake for a given series of experiments using the same slimes, percent of solids, and flocculant.

It is shown (Smellie and La Mer, 1958) that the simplified K-C equation applicable to our conditions; namely,

$$Q = K^1/S^2 = K/R^2, \quad (11)$$

when combined with the value of

$$R = k_1/k_2 n_0^2 \theta^2 (1 - \theta)^2$$

gives

$$R = kw^2 \theta^2 (1 - \theta)^2, \quad (12)$$

since  $n_0$  is proportional to  $W$  for a fixed particle size distribution.

When no flocculant is present,  $\theta = 0$  and  $R$  approaches zero. Actually in the untreated slime  $R = R_0$ , the average radius of primary particles. Therefore eq. (12) should be corrected.

According to Kozeny-Carman,

$$Q/Q_0 = R^2/R_0^2, \quad (13)$$

where the subscript zero refers to no added flocculant and  $R^2 = R_0^2$  when  $Q = Q_0$ .



Adding unity to each side of the equation and rearranging:

$$Q - Q_0 = Q_0 \frac{R^2 - R_0^2}{R_0^2}. \quad (14)$$

When no flocculant is present,  $R = R_0$ . Therefore, it is reasonable to represent  $R^2 - R_0^2$  in terms of the square of eq. (12) as follows:

$$R^2 - R_0^2 = k^2 w^4 \theta^4 (1 - \theta)^4, \quad (15)$$

and

$$Q - Q_0 = k^2 w^4 \theta^4 (1 - \theta)^4. \quad (16)$$

Substituting for  $\theta$  and  $1 - \theta$  in terms of eqs. (5) and (6) gives

$$Q - Q_0 = \frac{k^1 P_0^4}{\left( \frac{1 + b k w}{b} + \frac{P_0}{1 + b k w} \right)^8}, \quad (17)$$

where

$$k^1 = \frac{(Q/R_0^2) k^2 w^4 (1 + b k w)^4}{b^4}. \quad (18)$$

A plot of the measured filtration rate  $Q$  versus  $P_0$  gives a curve that goes through a maximum at the optimum in filtration rate. This behavior is typical for a variety of slimes and flocculants.

At the maximum  $dP/dP_0 = 0$ . Differentiating eq. (17) and setting the derivative = 0 and noting that

$$P_0 \text{ (optimum)} = (1 + b k w)^2 / b = \frac{1}{b} + 2 k w + b k^2 w^2$$

we obtain the working equation

$$Q - Q_0 = P_0^4 / (A + B P_0^4) \quad (19)$$

where

$$A = \frac{1 + b k w}{b (k^1)^{1/8}} \quad (20)$$

and

$$B = \frac{1}{(k^1)^{1/8} (1 + b k w)}. \quad (21)$$

This equation may be rearranged into a linear form

$$P_0^{1/2} / (Q - Q_0)^{1/8} = A + B P_0. \quad (22)$$

By plotting, as in Fig. 7, the experimental quantity  $P_0^{1/2} / (Q - Q_0)^{1/8}$  against  $P_0$ , the parts per million of added flocculant, we find a linear relationship, for a variety of slimes and flocculating agents have an intercept  $A$  and a slope  $B$ .

The ratio of the intercept  $A$  to the slope  $B$  is equal to  $(1 + b k w)^2 / b$  or to  $P_0 \text{ (optimum)}$ , *i.e.*  $A/B = P_0 \text{ (optimum)}$ . It is thus possible to determine the value of  $P_0 \text{ (optimum)}$  from the intercept and slope of the above plot, where it has not been determined directly by experiment.

The particular criticism that can be made of eq. (22) above, concerns the lack of sensitivity of the eighth root of the filtration rate. Where the data include an experimental determination or close estimate of the value of  $P_0$  (optimum), *i.e.*  $P_m$ , the following procedure can be used to test the validity of the function.

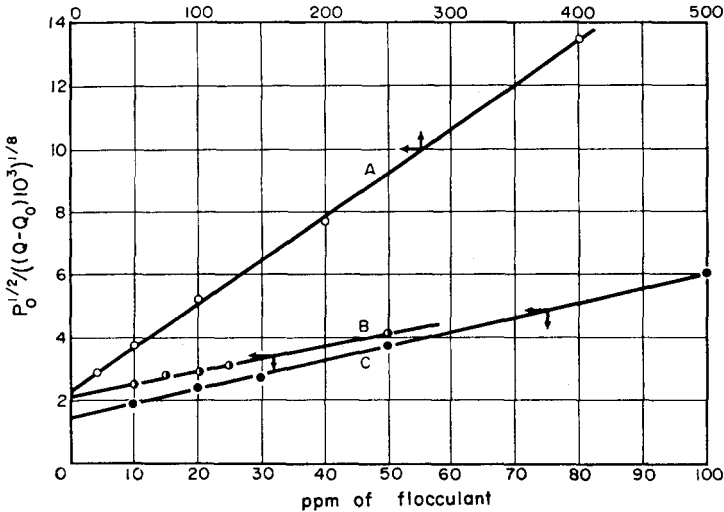


FIGURE 7.—Tests of filtration theory. Legends of curves on figure.

Since  $P_0$  (optimum) =  $A/B$ , then

$$Q - Q_0 = \frac{P_0^4}{(A + BP_0)^8},$$

$$Q - Q_0 = \frac{P_0^4}{(BP_m + BP_0)^8},$$

$$= \frac{P_0^4}{B^8[P_m + P_0]^8},$$

$$\frac{P_0^4}{Q - Q_0} = B^8[P_m + P_0]^8,$$

and

$$\log \left[ \frac{P_0^4}{Q - Q_0} \right] = 8 \log B + 8 \log [P_m + P_0].$$

Therefore a plot of  $\log [P_0/(Q - Q_0)]$  vs.  $\log [P_m + P_0]$  should be linear with slope 8.

Fig. 8 shows two sets of data plotted in this way. The slopes obtained are 8.10 and 8.07, respectively. Plots of the data assuming other powers such as 4, 6 and 10 either deviate from a straight line or give incorrect slopes so that the eighth power function is well established.

From data that are now being obtained with techniques for determining the adsorption of polymers, we expect to develop the filtration theory to a higher degree of refinement.

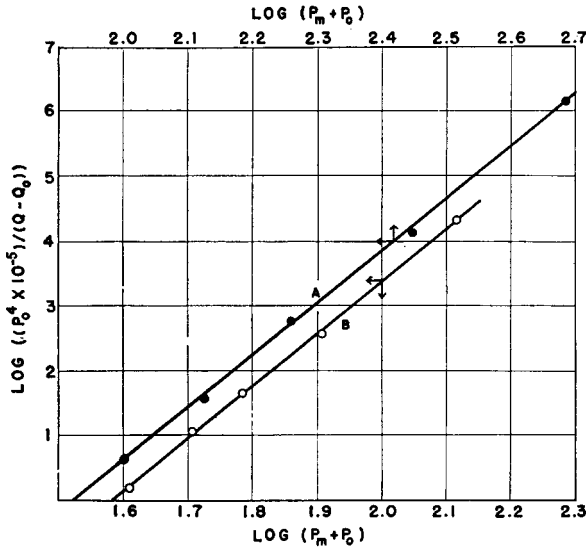


FIGURE 8.—Further tests of filtration theory. Legends of curves on figure.

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