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# REMOVAL OF MICROORGANISMS FROM WATER

A review, in four parts, dealing with the problem of water-borne disease, the epidemiology, the microorganisms involved and methods of their removal, including details of new results obtained in research. Part 1 (Introduction, Water-borne Disease and the Microorganisms Involved) was published in *Water and Water Engineering* for August 1967 at pages 321-325, Part 2 (Coagulation) in the September 1967 issue at pages 360-363, Part 3 (Flocculation) in the October issue at pages 414-417 and Part 4 (Data) in the November issue at pages 454-459.

## PART I: INTRODUCTION, WATER-BORNE DISEASE AND THE MICROORGANISMS INVOLVED

### INTRODUCTION

WATERS differ greatly in physical and chemical quality and in content of microorganisms. The quality of the water is clearly related to the contents and types of organisms present and both of these aspects are the subject of intensive study at present. The control and removal of microorganisms has been studied to some extent in the past, the latter more frequently, however, as part of a process and not so much for its own sake. It is also generally known, and accepted, that a major objective in water treatment is to make it chemically acceptable for drinking purposes. It is probably not as widely realised that in rendering a raw water attractive the more important purification benefit achieved: the water is also made safer from a health aspect. This is the aspect of particular interest here.

That water may spread infectious disease was realised by Hippocrates, who describes it in his essay on airs, waters and places<sup>1</sup>. Pollitzer states<sup>2</sup> that the only convincing feature amidst the calamities resulting from the cholera infection of the third pandemic was that observations made (by Snow) in England in 1854 clearly showed, those who were not obsessed by fanciful theories, that contaminated water played a major role in the spread (this) disease.

Forward strides taken since, in sanitation and water supply practice, have all but eliminated the incidence of the major water-borne diseases as cholera and typhoid fever in the western world. The improvements which have been effected are of such magnitude that the biological importance of water as a medium of transmission is now debated<sup>3,4</sup>.

This has come about in a period during which, however, the re-use of water was progressively increasing. According to Heukelekian and Dondero, 70 million people out of a total of 180 million in the U.S.A. were in 1963 using water from sources already used once for domestic sewage and industrial waste<sup>5</sup>. Outbreaks of infections resulting from penetration of water purification plants by disease producing organisms are considered by Berger to be a potential danger<sup>6</sup>. That this is a real danger is illustrated<sup>7</sup> by the fact that a bacterial strain originally isolated in 1931 was still present in sewage effluent in 1958, and also that organisms the size of free living amoeba and algae were found<sup>8</sup> to survive intensive water treatment.

With increase in population on a world-wide scale the influence of human activity on water supplies can only become greater. There has been a large increase in

bacterial content of waters which have been studied over the past 40 years in the U.S.A.<sup>12,13</sup>. This has resulted in a change in approach to sewage and water treatment in that country. Sewage plant effluent is now commonly chlorinated before being released into streams, and whereas prechlorination of water entering a purification plant was virtually unknown 30 years ago<sup>12</sup>, it is now practised almost without exception<sup>13</sup>. This is, however, not general practice elsewhere in the world where more reliance is placed on the efficiency of water purification unit operations, such as sand filtration, coagulation, flocculation and sedimentation, for the removal of microorganisms.

Whatever the pretreatment or control measures applied, it is clear that removal or control of bacteria is not the only biological problem to be dealt with in water purification. Smaller organisms such as viruses are much more resistant to normal concentrations of disinfectant and this is equally true for larger organisms such as fungi, crustacea and nematodes. Methods of control of these organisms are problematical. A study of the methods of removal of microorganisms is, therefore, indicated. Removal fits naturally into the water treatment process which is by nature extractive.

Nematodes and smaller organisms all have some sanitary significance in water purification and have, therefore, to be taken into account. Algae, although an important group of microorganisms have little or no hygienic significance and will, therefore, not be dealt with.

The objectives with this review is to outline the problem of water-borne disease—the epidemiology thereof: the microorganisms involved and the methods of removal of these, including the chemical and physical aspects involved in the pertinent unit operation. Some data do exist on removal of microorganisms and new results have been obtained in research into this subject. These will be presented here.

### WATER-BORNE DISEASE

There is a long history and extensive literature of epidemics of water-borne disease<sup>1, 2, 4, 14, 15, 16</sup>. The major epidemics of the past were due to clearly defined diseases—possibly only such were chronicised. Attention is now also being paid to less clearly defined diseases. Attempts are only now being made at a systematic study of the occurrence of water-borne diseases<sup>17-18</sup>. Water engineers should know the nature of such diseases: for this purpose it is necessary to consider the diseases and also the epidemiology.

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## Diseases

Out of a total of 148 communicable diseases, some 14 are water-borne or suspected to be so<sup>9a</sup>. Ten years earlier these figures were 118 and 11 respectively<sup>9b</sup>. Included in the 14 diseases, mentioned above, is a grouping termed acute diarrhoeal disease; these are mainly water-borne and demonstrate the increasing significance attached to such disease. The diseases, their manifestation and morbidity, the agent of infection, and their geographical distribution are<sup>9</sup> as shown in Table 1.

Table 1  
Water-borne Diseases

Disease	Manifestation	Morbidity	Agent of Infection	Geographical Distribution
Amebiasis	Wide clinical	Low	<i>E. histolytica</i>	World-wide
Acute Diarrhoeal Disease	Enteric	Low	Enteropathogenic <i>E. coli</i> , Enteroviruses, Protozoa and Helminths	World-wide
Cholera	Intestinal	10—80% fatal within 24 hours	<i>Vibrio comma</i>	India, S.E. Asia
Dracontiasis	Subcutaneous	Non-fatal	<i>Dracunculus medinensis</i>	India, Pakistan, Middle East, Africa, West Indies
Echinococcosis	Liver and Lungs	Can be fatal	<i>Echinococcus granulosis</i>	Wide
Infectious hepatitis	Liver	0.2% fatal	Hepatitis virus	World-wide
Leptospirosis	Wide Systemic	Low	Leptospira	World-wide
Paratyphoid fever	Generalised	Low	<i>Salmonella</i> and Paratyphoid bacilli	World-wide
Poliomyelitis	Acute febrile	Low	Polioviruses	World-wide
Schistosomiasis	Debilitating	High eventual	<i>Schistosoma</i>	East, Middle East, Africa, S. America
Shigellosis	Acute diarrhoea and fever	Rarely fatal	<i>Shigella</i> bacteria	World-wide
Taeniasis and Cysticercosis	Benign and severe somatic	Non-fatal	Tape worms	Wide
Tularemia	Ulceration	5% fatal	<i>Pasteurella tularensis</i>	Europe, Asia, Africa
Typhoid fever	Systemic	10% fatal	<i>S. typhosa</i>	World-wide
Fungal	In mucosa	Non-fatal	Pathogenic fungi	Wide

## Epidemiology of Water-borne Diseases

Snow, by deductive reasoning was the first investigator, in modern times, to determine a causal relationship between a disease outbreak and a water supply. He asserted that if the effect of contaminated water be admitted, it must lead to the conclusion that it acts by containing the true and specific cause of the malady (cholera). Koch, because of his newly acquired ability to isolate pure strains of bacteria from single colonies, demonstrated in his investigation of the Calcutta water supplies, the presence of *Vibrio comma* which caused the cholera epidemic<sup>2</sup>.

It is apparent from modern reporting that the considerations applied in deciding on whether or not a disease is water-borne are ill defined and sometimes doubtful. Maxcy states<sup>3</sup> that it must be convincingly shown that the behaviour of a disease in human communities is such as would be expected if the causative, parasitic microorganisms were dependent for continued dissemination, in part or at times, upon the medium of contaminated water.

Continuous doubt has been cast upon poliomyelitis being a water-borne disease at all; this may be due to repeated quotation<sup>19,20</sup> of the view on the relationship of this disease to water supplies put forward by Maxcy<sup>3</sup>. It appears that subsequent workers deduced<sup>19,20,21</sup> from Maxcy's reasoning that to be water-borne an outbreak must be explosive; their deduction is understandable as Maxcy refers the reader to the classic epidemics of the past. It would, however, be expected that the classical type of outbreak would occur only in a small community or in case of gross pollution of purified water in a large community.

Studies in the United States of America, on occurrence of water-borne outbreaks, do not indicate that disease necessarily occurs on a widespread scale even where the distribution system is extensive. Weibel *et al* state<sup>17</sup> that if any of the outbreaks for the large cities involved the whole distribution system, the statistics would have been different, but cross-connection or back siphonage resulted in outbreaks limited to only small parts of distribution systems probably due to dilution.

That a large distribution system is involved does not necessarily mean that any outbreak should be explosive. The very extent of a system would result in attenuation of pathogens. Sanderson and Kelly calculated<sup>22</sup> that if raw sewage enters a water supply resulting in a coliform count of 2500/100 ml and if there were 1 virus to 10<sup>6</sup> coliform, then after conventional treatment of the water 1 in 16,000 persons would ingest 1 virus particle. Only 10 per cent of these would develop recognisable disease. This illustrates that in an extensive supply system, even with known pollution, disease outbreak need not be explosive. If, however, this fact were to be ignored, water would be the ideal vehicle to maintain a number of diseases in an endemic state.

With the increase in consumption of repeatedly used surface water, epidemic proportions of disease may well recur. Walton found<sup>13</sup> that 48.3 per cent of outbreaks, studied by him, resulted from surface water which constituted only 18.9 per cent of the facilities from which water was obtained.

It would appear from the above that all that may be said with confidence about epidemiology of water-borne disease is that if the pathogens are known to be water-borne, whether or not they result in disease, the water

ould be treated in such fashion as to remove or  
erely limit them.

### conclusions

Our knowledge of communicable diseases, including  
se which are water-borne, is continuously expanding.  
Epidemiology of water-borne disease is clearly dependent  
on this knowledge which has been lacking in the past,  
and this may be the reason for the paucity of reported  
demics. This paucity may reflect the relative insen-  
sitivity of present epidemiological techniques for the  
detection of small but frequent outbreaks of water-borne  
disease. It does reflect a lack of enlightened interest in  
the aspect of water supplies in various parts of the  
world.

## WATER-BORNE MICROORGANISMS

Water as found in nature, nearly always contains some  
microorganisms. With few exceptions, natural waters  
at some stage in their history come into contact with  
sludge which acquire soil and sewage or manurial matters, all of  
which are rich sources of organisms. The population  
of these waters hence include organisms of natural water,  
sludge and sewage<sup>23</sup>. It is nevertheless no simple matter  
to isolate any particular organism from water when they  
are present in low concentrations<sup>8, 24, 25</sup>. On the other  
hand, a high bacterial content is not unusual in some  
waters which are perfectly wholesome and remote from  
pollution<sup>26</sup>. Water-borne organisms known to be  
pathogenic to man or which are carriers of pathogens  
include also some indicator organisms which will be dealt with  
separately. The characteristics of these bacteria, helminths,  
protozoa and viruses and the factors which influence  
their occurrence are of interest.

### Indicator Bacteria

It is not known whether the natural water or soil  
bacteria are at all pathogenic, and sewage bacteria are,  
therefore, the only ones considered to be of direct im-  
portance. Many sewage bacteria are normal inhabitants of  
the intestines of man and animals; some are, however,  
specifically adapted to sewage. Occasionally, pathogenic organ-  
isms are included amongst these.

The intestinal bacteria of importance as indicators of  
pollution are the *Coliform* group, *Clostridium perfringens*,  
and *Streptococcus faecalis*. The water-borne pathogenic  
bacteria are the cholera *Vibrio comma*, the *Salmonella*  
group, the *Shigella* group, the spirochaete *Leptospira*,  
*Pasteurella tularensis* and *Pseudomonas aeruginosa*. The  
characteristics and properties of these bacteria and their  
occurrence in water will be dealt with.

### Properties of Bacteria

The characteristics of the bacteria which are of particu-  
lar interest are their morphology and physical proper-  
ties. Some of these are shown in Table 2. The electro-  
phoretic phenomena, relating to bacteria, are also of  
interest but it is not possible to tabulate these because  
of the extensive variation of this characteristic with en-  
vironment, nutrition and age of any given culture. This  
is depicted to some extent in the diagrams<sup>27</sup> of Fig. 1.  
The diagrams show the effect of age of cultures of rough  
and smooth forms of *E. coli* on their electrophoretic  
mobility when they are suspended in different buffers at  
various pH. It will be clear from Fig. 1 why it is not  
possible to generalise on the electrophoretic properties  
of bacteria. The other characteristics however, can be  
generalised, and are as shown in Table 2.

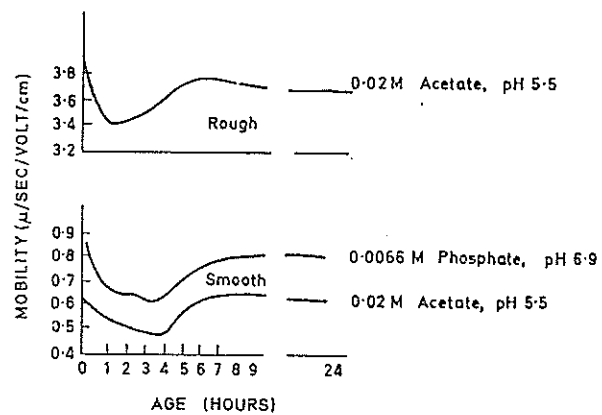


Fig. 1—Electrophoretic mobility of *Escherichia coli*

Table 2  
Characteristics of Indicator and Pathogenic Bacteria<sup>28</sup>

Bacterial Species	Shape and Form	Size ( $\mu$ )	Flagella	Motility	Gram
<i>Clostridium perfringens</i>	Rods. Single, pairs frequently chains.	1.0-1.5 x 4.0-8.0	none	—	+
<i>Coliform Group (Escherichia coli)</i>	Rods. Nearly coccoid to long rods. Single, pairs and short chains.	0.5-1.0 x 3.0	Peritrichous	+ or —	—
<i>Streptococcus faecalis</i>	Ovoid. Pairs or short chains.	0.5-1.0	none	—	+
<i>Leptospira biflexa</i>	Spiral. Amplitude 0.2 $\mu$ , 22-30 waves per cell.	0.2-0.25 x 5-7	none	—	—
<i>Pasteurella tularensis</i>	Rods and cocci, extremely pleomorphic. Single. Rough, smooth and mucoid.	0.2 x 0.2-0.7	—	—	—
<i>Pseudomonas aeruginosa</i>	Rods. Pleomorphic. Single, pairs and short chains.	0.5-0.6 x 1.5	3 polar	+	—
<i>Salmonella (4 species)</i>	Rods. Single, pairs.	0.6-0.7 x 2.0-3.0	Peritrichous	+, —	—
<i>Shigella (6 species)</i>	Rods. Single.	0.4-0.6 x 1.0-3.0	—	—	—
<i>Vibrio comma</i>	Rods. Curved. Single and spiral chains.	—	1 polar	+	—

It will be seen from Table 2 that there is a wide variation in the properties of the bacteria. The table lists genus and species only; a large number of serotypes of these exist<sup>28</sup>.

Taylor in a study<sup>29</sup> of 800 bacterial cultures, taken mainly from sewage polluted lakes and streams in the English Lake District, found that 95 per cent were (short) rods and Gram negative; 4 per cent were rods and Gram positive, also spore forming; and less than 1 per cent were cocci. Taylor was of the opinion that these were not soil bacteria but typical of those found in water. Collins subsequently confirmed these findings in an extensive survey of the bacterial ecology of the

same waters<sup>30</sup>. It will be seen that most of the organisms listed in Table 2 are also rods and Gram negative.

#### Occurrence of Bacteria

It is not possible to give quantitative data on the natural occurrence of pathogenic bacteria as these are rarely determined even when a direct search is made for them. The occurrence of pathogens can, however, be inferred from their numbers in faeces and the numbers of indicator organisms commonly found in surface waters and sewage.

Allen reported<sup>10</sup> average counts of 288,000 coliform bacteria per 100 ml and 41,000 *S. faecalis* per 100 ml for the effluent from 7 large scale sewage works. Stander reported<sup>11</sup> that sewage which had been settled, applied to a biological filter and then to a humus tank contained 420,000 *E. coli* per 100 ml. After sand filtration, this effluent would still contain some 226,000 *E. coli* per 100 ml.

Walton reporting<sup>13</sup> on 27 water purification plants in the U.S.A., found that they received raw water containing 2300 to 1,700,000 coliforms per 100 ml; 14 of the plants had maxima of over 50,000 coliform per 100 ml. The River Thames at Walton contains<sup>7</sup> some 900 to 23,000 coliforms per 100 ml.

#### Helminths

It is well known that water purification plant units are vulnerable to nematodes and trematodes. Some of these organisms, while possibly not pathogenic, cause severe disease conditions and result in great discomfort or debilitation of humans. It has also been conjectured by Chang *et al* that<sup>31</sup> free living nematodes may have sanitary significance. Chaudhuri *et al* state<sup>32</sup> that the possibility that nematodes, by ingesting pathogens, could protect organisms from destruction by chlorination has been demonstrated in the past. An aspect common to these organisms is that they are resistant to disinfection<sup>33</sup>.

The Guinea worm, *Dracunculus medinensis* is carried in larval form into the human system by the crustacean Cyclops. This copepod measures<sup>34</sup> some 0.5 × 2.0 mm and is frequently found in filters.

Chang *et al* found<sup>31</sup>, in their survey of free living nematodes, that 16 out of 22 of the water supplies investigated contained nematodes in both raw and finished water. Of the 7 genera identified, 3 are sewage, trickling filter nematodes.

The three types of *Schistosoma* (*S. mansoni*, *S. haematobium* and *S. japonica*) which cause schistosomiasis in humans have an intricate life cycle; this includes as host also certain species of water snails. The cercariae are some 1.5 mm in length and have a forked tail which is discarded after entry into its host. The worm form is then transported via the bloodstream to various body organs and eggs are periodically released and excreted. The ova hatch in water and the larval form enters the snail host thus completing the life cycle.

Granuloma results from subcutaneous invasion of cercaria, similar to the schistosoma type, and the organism is common in swimming bath water in the U.S.A.<sup>35</sup>.

#### Protozoa

According to Kabler *et al*<sup>35</sup> at least 5 species of amoebae have been found in the intestinal tract of man. Metzler *et al* found<sup>8</sup> that the cysts of free living amoeba

—comparable in size to *Entamoeba histolytica* regularly appeared in treated, reclaimed water (sewage) demonstrating the vulnerability of water treatment plants to this kind of organism. Chang reported<sup>36</sup> the presence of live cysts of free living nematodes and amoebae in 6 out of 22 water supplies examined in the United States. *E. histolytica* is, however, the only protozoon known to be pathogenic to man.

#### Viruses

Certain well-known viruses such as poliomyelitis and infectious hepatitis are excreted by humans and occur in sewage and water. Little significance is attached to the occurrence of non-enteric viruses in excreta. It has, however, been demonstrated that the presence of enteric viruses in water do result in disease<sup>37</sup>. Some viruses, because of their known pathogenicity and greater simplicity of detection than others, can now be isolated from water. The extent to which they are isolated varies considerably because, unlike bacteria which multiply in various nutrients, viruses are obligate parasites and require living animal cells for subsistence or reproduction. The properties and occurrence of the viruses are of interest.

#### Properties of Viruses

The classification of microorganisms is in a constant state of change and uncertainty, this is particularly so for viruses. Of the three suborders of Virales<sup>28</sup> the Zoophaginae are of interest and in particular a group which Andrewes named the Picorna viruses<sup>38</sup> and the group named Reovirus by Sabin<sup>39</sup>. The picorna virus group includes poliomyelitis virus, Coxsackie virus and ECHO virus. Table 3 shows the variety of the morphological characteristics of enteroviruses and of phage.

Table 3  
Morphological Characteristics<sup>38, 39, 40</sup> of Water-borne Enteroviruses and Phage

Virus	Shape and Form	Size (m $\mu$ )
Adeno		30
Coxsackie A, B.	Sphere with dense core of 15 m $\mu$ ; no outer membrane.	28
ECHO	Sphere with nucleoid of 13 m $\mu$ ; no outer membrane.	24-25
Infectious Hepatitis	Polyhedral; no membrane or protein.	40-150
Poliomyelitis	Cubical; 42 capsomeres in 5:3:2 symmetry; no outer membrane.	25
REO	Cubical with nucleoid of 35 m $\mu$ ; 92 capsomeres; no outer membrane.	60-90
Bacteriophage	Polyhedral head and cylindrical tail, like tadpole.	Head dia. 100-150 Tail length 100-150

#### Occurrence of Viruses

There is not much literature available on the relative numbers of enteric viruses in water. This is due to the difficulty involved in recovering them and also, especially in the past, difficulty in demonstration of viruses. The plaque technique now makes demonstration of a number of enteroviruses possible, but Poynter recently demonstrated<sup>41</sup> that inhibiting substances in water constitute a severe limitation.

Kelly *et al*, in a study of 308 sewage samples, found that the number and types of agents isolated differed according to the isolation method used; they found 244 PFU/100 ml in raw sewage. McMichael and Kee monitored sewage effluent in a water reclamation project and found<sup>43</sup> that, during a polio vaccination campaign, settled sewage showed 102 PFU/litre poliovirus; activated sludge effluent contained 252 PFU/litre.

#### Conclusion

Certain properties of the various microorganisms are fully well established. The magnitude of their occurrence is, however, not known very well; this is especially for the helminths and protozoa, and also the viruses.

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## PART 2 : COAGULATION

**I**N his pioneering studies of coagulation von Smoluchowski distinguished between the rapid process which takes place when colloids are in the presence of sufficient electrolyte, and the slow process when there is insufficient electrolyte<sup>54, 66</sup>. He considered the two types of coagulation to be perikinesis where particle collisions are effected by diffusion and orthokinesis where collision is effected by shear flow. The term coagulation will be used here to refer to the perikinetetic process which is physico-chemical by nature and the term flocculation will be used to denote the orthokinetic process which is in addition hydrodynamic.

The factors involved in the coagulation of solids in water include the nature of the suspended colloids of the disperse phase and the nature of the water constituting the continuous phase. Colloidal particles are the main constituents of a stable suspension in water, and the properties of colloids are, therefore, of prime interest. Stability as used here is, however, relative; the extent to which colloids remain in suspension or are removed will be determined not only by their own characteristics but also by the qualities of the water in which they are suspended.

Extensive reviews were recently carried out by Black<sup>44, 45</sup>, by Packham<sup>46, 47</sup>, by Stumm and Morgan<sup>48</sup> and by Sennett and Olivier<sup>49</sup> on coagulation in water. In these reviews considerable attention is given to colloid theory and some attention is given to some of the particular factors which affect coagulation. The relationship between the theory and these factors does, however, not emerge at all clearly from these reviews.

Black concludes<sup>44</sup> that there is still no logical explanation of the fact that certain polyelectrolytes may be quite effective in one situation and relatively ineffective in another. He finds that the mode of action of non-ionic, natural materials is not clear. Black states<sup>44</sup> that there are no fixed rules to guide the selection of a coagulant for use with a given water—the jar test is still the only aid.

Packham states<sup>47</sup> that until there is a comprehensive theory, applicable to colloidal systems, of the complexity of raw water, investigations will have to proceed largely on empirical lines.

Stumm and Morgan conclude<sup>48</sup> that a more comprehensive chemical theory of coagulation is required.

Sennett and Olivier state<sup>49</sup> that only in the past few decades has anything like an adequate basis for a theoretical development of coagulation been available.

They find, however, that colloid chemistry of lyophobic systems is the surface chemistry of the dispersed phase; this is an aspect which is hardly discussed by the other workers mentioned above, possibly because they are more directly concerned with the continuous phase.

Considerable progress has nevertheless been made in the interpretation of coagulation effects. This has been done with the aid of the double-layer theory; and a knowledge of the implications of the factors which affect coagulation is valuable. Black and Walters state<sup>50</sup> that because of the numerous variables that affect coagulation, a theoretical analysis of a given set of conditions and a diagnosis of coagulation resulting therefrom is practically impossible. They state, however, that the discovery of any systematic relationship must result in a better understanding of the coagulation mechanisms. There can be very little to disagree with in this view. The brief review which follows will thus be directed towards a consideration of the properties of colloids, and their stability, the kinetics of coagulation and physico-chemical factors of coagulation.

### General Properties of Colloids

The term colloid arises from a classification of all substances in terms of their ability to diffuse through water and parchment membranes. Crystalloids were said to have the ability to diffuse through a membrane but colloids not. This we now know to be untrue<sup>27</sup>; certain proteins and indeed viruses are crystallisable and practically all crystalloids may be brought into the colloidal state.

Perrin distinguished<sup>46</sup> between colloids formed by substances such as starch, protein and gum on the one hand and metals and their oxides on the other. Starches, etc., react with water spontaneously, giving rise to sols which can be dehydrated to the original material and then redispersed any number of times. Metallic sols can, however, only be formed by special techniques and suffer irreversible coagulation if dehydrated. Perrin ascribed this behaviour to differences in affinity of the disperse phase for water and used the forms hydrophilic for the usually organic substances and hydrophobic for the usually inorganic substances.

Hydrophilic sols are formed by starch and by proteins and the result strongly resembles a true solution. Their molecules are, however, large enough to be of colloidal dimensions and exhibit colloidal properties. Hydrophobic sols generally have a much larger particle size than the hydrophilic sols. Some of the properties of the two types of colloid are compared in Table 4.

Table 4  
Properties of Colloids 51, 52

Property	Type of Colloid	
	Hydrophilic	Hydrophobic
Coagulation	Results in a gel.	Results in granules.
Concentration	High concentration of disperse phase frequently stable.	Only low concentration of disperse phase stable.
Coagulation	Residue after desiccation will take up water immediately.	Residue will not become decoagulated.
Colloidal	Unaffected by small amounts of electrolytes; salted out by large amounts.	Very easily precipitated by electrolytes.
Stability	Governed by electric charge and solvation.	Governed by electric charges of the particle only.
Light effect	Usually yields a weak Tyndall beam.	Tyndall beam and light scatter is marked.

The distinction between the two types of colloid is not definitely not definite—a series of substances exist with properties intermediate between the extremes indicated in Table 4. Clay minerals are an example of an intermediate type; they are readily coagulated by an electrolyte but also result in stable sols on contact with water.

Bacteria also behave like colloids; although some are larger than the arbitrary size range usually accepted for colloids. They are subject to Brownian motion<sup>27</sup>, exhibit light scattering to some degree but do not result in granules when coagulated. According to Verwey and Overbeek<sup>52</sup> they can be classified as hydrophilic colloids.

Surface area is well known to be one of the most important properties of colloids. It is important for its determination of the surface area; a given mass of particles with greater surface area the smaller their size. Colloids exhibit surface effects and these determine the degree of stability in dispersion; this can be explained by the electrical repulsion between particles. This particle interaction can clearly be effective only if particle size is below a certain level; above this level the force of gravity becomes dominant. The stability of colloids is affected by a number of factors and these will be dealt with.

### Stability of Colloids

Two broad theories exist to explain the basic mechanism of colloid stability and coagulation<sup>46</sup>. The physical theory emphasises the concept of the electrical double layer surrounding a colloid and also the significance of electrolyte physical factors such as ionisation, ion pair formation, ion adsorption and zeta potential. The chemical theory assumes that colloids are aggregates of primary chemical structure, that the primary charge of dispersed particles arise from the complex ionogenic groups present on the surface of the dispersed particles, and that destabilisation of colloids is due to chemical interactions such as complex formation and proton transfer.

Both theories are both considered to be of importance here as the former primarily affects the particulate matter which is to be removed whereas the latter deals with the water medium in which they exist and the electrolytes with which removal is attempted.

The most generally accepted picture of the charge

carrying phenomenon of colloidal particles is that put forward by Stern. This is based on the simple Helmholtz fixed layer theory as modified by the diffuse layer concept of Gouy and Chapman. The inner, fixed layer has a sharp fall of potential across it. The outer, diffuse layer consists of mobile ions decreasing in concentration away from the particle and across which the potential gradient is more gradual. This may be shown diagrammatically<sup>51</sup>, in a simplified form, as in Fig. 2.

Because colloidal particles diffuse slowly and their motion is random, the problem cannot be treated as a chemical reaction involving an energy barrier. It becomes necessary to know the total shape of the potential energy curve rather than its height.

Verwey and Overbeek explained the interaction of sol particles having an electrical double layer<sup>52</sup>. They consider first the free energy of the double layer and then show how, on close approach of two surfaces, the overlapping double layers interact to increase the free energy

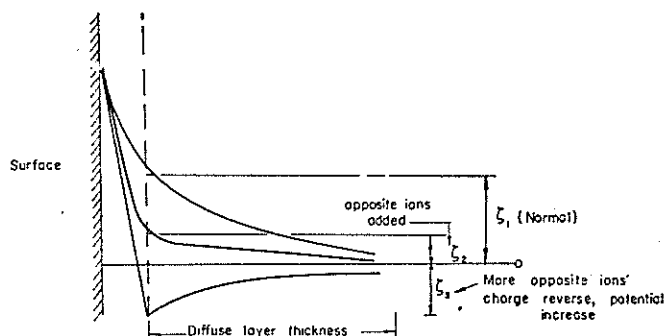
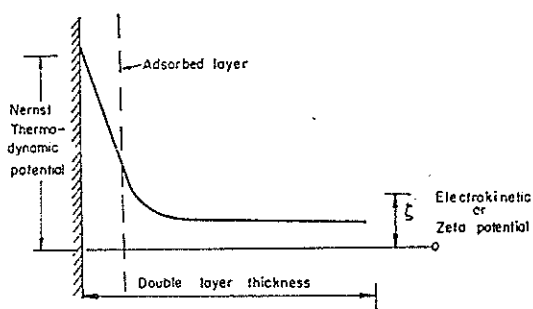


Fig. 2—Effect of ions in solution on zeta potential

of the system thus leading to a potential energy of repulsion. The energy of repulsion between particles was then related, as a function of their separation, to the ionic make-up of the solution. The explanation is completed by a consideration of the London dispersion force as applied to particles of colloidal size which, as an approximation, leads to an energy of attraction varying with  $d^{-1}$  for small distances, and with  $d^{-2}$  at larger separations.

Fig. 3 shows<sup>52</sup> the net potential energy of interaction of a colloid under the influence of an electrolyte. A combination of the curves of repulsion and attraction yields a resultant curve representing the equilibrium state; this state varies depending on the opposed forces.

An important point that emerges from this work<sup>53</sup> is that zeta potential cannot be considered to be the only electrokinetic factor governing stability. The total potential of the whole double layer should be considered; this remains constant and independent of the electrolyte

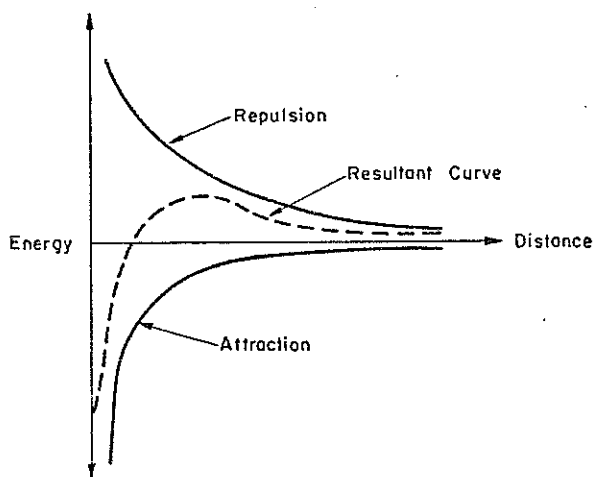


Fig. 3—Energy of interaction of colloid and electrolyte

concentration. The important variable factor is the distribution of this potential with distance from the colloidal particle, i.e. the thickness of the double layer. The effect of electrolytes is to decrease the thickness of the double layer thus allowing the particles to come closer together and the London—Van der Waals forces of attraction to come into operation.

The work of Verwey and Overbeek also provides the theory for the Schulze-Hardy rule, i.e. that the coagulating concentration of an electrolyte is inversely proportional to the 6th power of valency.

#### Kinetics of Coagulation

The observed range of coagulation indicates that even when the coagulated condition is, as is thermodynamically always the case, the lowest energy state of the system, an energy barrier can exist that prevents particle to particle adhesion on contact. The rate of coagulation will, therefore, depend on the collision frequency of the sol particles and their energy with respect to the energy barrier. Colloidal particles undergo Brownian motion and, thereby, diffuse and collide; they are in kinetic-thermal equilibrium, with the suspending fluid. In the absence of an energy barrier, the coagulation rate will be determined solely by the collision frequency. The theory of the kinetics of coagulation was evolved by von Smoluchowski<sup>54</sup>. He considered a monodisperse suspension of spherical colloids of  $n_0$  particles per unit volume at time  $t = 0$ , and envisaged each particle to have an attraction sphere of radius  $R$ . Stating that the diffusion constant  $D$  can have no influence on the absolute course of coagulation, which, therefore, must be a function of the product  $Dt$ , he arrives by dimensional analysis at the equations

$$n_1 = \frac{n_0}{1 + 2t/T}$$

where the half time of coagulation, i.e. the time required for the number of particles to be halved,

$$T = \frac{1}{4\pi \cdot D \cdot R \cdot n_0}$$

and perikinetic collision frequency

$$P = 4\pi \cdot D \cdot R \cdot n_0$$

The further analysis by von Smoluchowski relates to the rate of decay of number of particles with time. He did also consider slow coagulation and showed how his theory can be expanded to become applicable to it.

Fuchs subsequently put forward a further theory<sup>55</sup> of slow coagulation. He deduced a factor by which the time of coagulation in von Smoluchowski's theory should be increased. Müller extended the theory to include polydisperse systems<sup>56</sup>.

#### Physico-chemical Factors

The early work of Theriault, Clark and Miller still forms a part of the basis of our understanding of the chemical factors involved in coagulation of waters containing turbidity or colour colloids. They found in the first instance that a certain minimum amount of cation should be present for effective coagulation; from the colloid stability theory outlined above, this is to be expected. They also found that an anion of strong coagulating power should be present. Lastly, they found that pH must be carefully adjusted.

There is some evidence that turbidity of the water has some influence on the effective dosage of coagulant<sup>57</sup>. The studies by Langelier and Ludwig, on the influence of various clays on coagulation were, however, in the first instance directed towards the effect of the cation exchange capacity of the clays<sup>58</sup> and secondly to the size of particles<sup>59</sup>.

The importance of the nature of the cation present was studied extensively by Schulze and Hardy, leading to the establishment of their rule with regard to coagulating power and valency<sup>52</sup>. The importance of this finding was borne out by subsequent tests on a large number of coagulants, leading to the finding that the salts of the trivalent Al and Fe were the most effective coagulants<sup>47</sup>. Black, however, points out<sup>45</sup> that Mattson's electrophoretic study of coagulation of clay colloids minimised the importance of the Schulze-Hardy rule in that he demonstrated that the products of hydrolysis of aluminium and ferric salts are more effective than the trivalent cations in reducing or neutralising the zeta potential of colloidal particles. Stumm and Morgan also point out<sup>48</sup> that, under coagulation conditions, relatively small concentrations of 'free'  $Fe^{+++}$  and  $Al^{+++}$  ions, with a charge of plus three, are present in the solution; they do, however, not draw any conclusion from this.

The importance of the presence of certain anions has been confirmed in investigations by Packham. He states<sup>47</sup> that the effect of anions was found to be more marked than that of cations and increases with ionic charge. Black's findings confirm this<sup>45</sup>.

The significance of pH in the coagulation process has been extensively confirmed in investigations by Black and co-workers<sup>44, 60, 61</sup>, by Packham<sup>62, 63, 64</sup>, and by Stumm and Morgan<sup>48</sup>.

Black and Willems found<sup>60</sup> that organic colour removal with alum was optimum at lower pH values than for turbidity removal. Electrophoretic measurements showed that at these low pH values, the charge on the organic colloids was neutralised or reduced considerably. They concluded that binder action was not important in colour removal and that the reduction of potential by positively charged basic sulphates of aluminium was more significant.

Black and co-workers found<sup>50, 61</sup> that the mobilities of the particles of three different clay suspensions decreased to the isoelectric point at pH 5-7. An overdose of coagulant at this stage marked the beginning of the zone of efficient coagulation for all three suspensions. Base exchange capacities were not found to be directly or proportionately related to the coagulant doses



quired to effect satisfactory coagulation, but the base change capacities significantly affected the coagulant doses required to cause charge reversals at low pH.

An extensive investigation by Packham, of various factors affecting coagulation, lead to a number of findings<sup>62, 63</sup>. A concentration of 50 p.p.m. of various clay minerals, including kaolinite, illite, quartz and montmorillonite were individually tested and it was found that all showed a minimum dosage required to give turbidity ( $D_{1/2}$ ) at pH 6.8 to 7.8 except bentonite which is at a minimum for pH up to 7.5. The suspended solids from nine rivers were tested with the same result. Coagulation exchange capacity was not found to be an important factor in coagulation. Electrophoretic measurement showed that the precipitating aluminium hydroxide has a weak positive charge while the clay particles have a negative charge. The attraction between oppositely charged particles will enhance the initial position of the hydroxide on the surface of the clay particles, which, it is stated, becomes completely and evenly coated. Insufficient work was done at various concentrations of the different clay minerals to allow of conclusions on the influence of concentration.

Packham determined<sup>64</sup> that maximum precipitation of aluminium hydroxide occurs at pH 7; the pH range 6 to 10 was tested.

In their carefully controlled coagulation tests, Stumm and Morgan found<sup>48</sup> that the minimum coagulant concentration required for satisfactory colour removal depends on the initial alkalinity, as does the width of the range of favourable colour removal. This is in agreement with Langelier and Ludwig's finding<sup>58, 59</sup>. According to Stumm and Morgan a more comprehensive chemical theory of coagulation phenomena is required. Such a theory should explain<sup>48</sup> coagulation effectiveness in terms of pH, buffer capacity, hydrolysis, equilibria of the coagulant metal ions, complex formation equilibria and chemical equilibria of the colloidal and dissolved substances to be removed. They point out that coagulant metal ions are hydrolysed in aqueous solution and that considerable evidence exists to support the view that iron and aluminium hydroxide precipitates are polymeric complexes. Complex formation reactions between aluminium or iron coagulant metal ions and hydroxylic, phosphate, sulphate or aromatic hydroxy functional groups are stated to be important in the destabilisation of such naturally occurring impurities as dyes, proteins and carbohydrate materials. These workers finally find that the great importance of pH in determining both the nature of coagulant metal hydrolysis products and the charge of colloidal impurities points to the necessity of an experimental coagulation technique in which the pH can be kept constant while the concentration of metal ions are varied.

#### Conclusions

Microorganisms which are larger than bacteria would not be considered to be colloidal and are, therefore, subject to coagulation only by physical enmeshing. Bacteria and viruses may be considered to behave as colloids and will accordingly take part in coagulation.

The stability of a colloidal suspension is determined principally by the double layer thickness. This dimension is subject to variation due to the presence of an electrolyte which chemically exerts an influence inversely proportional to the sum of the product of concentrations of the squares of the valencies.

A theoretical formulation of the kinetics of coagulation

does exist, and although many simplifying assumptions were made in its derivation, it has been found to be valid for coagulating systems.

The factors, in addition to those mentioned above, which affect coagulation of a suspension are pH, alkalinity, total dissolved solids, turbidity and coagulant.

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## PART 3: FLOCCULATION

**D**ESTABILISATION of a suspension resulting in coagulation, is in practice followed so closely by the commencement of flocculation that it is hardly possible to say when one stage ends and the other begins. They invariably overlap to some degree. If the chemical conditions are incorrect then some or all of the colloidal particles may remain dispersed regardless of the efficiency of the flocculation operation. Given appropriate treatment of the water flocculation of the particles in suspension depends on physical conditions only.

Flocculation is the most important engineering unit operation in the removal of microorganisms. The other operations like sedimentation and filtration are dependent for their success in this removal process on flocculation; they effect the necessary phase separation but cannot be expected or relied on to increase micro-organism removal in their own right.

Although sedimentation and filtration are *per se* relatively ineffective in removal of microorganisms, they are of prime importance in phase separation. Flocculation should, therefore, be considered in terms of these unit operations. Most important are those floc characteristics desirable for any one or other of these operations. Floc should be as large and dense as possible for sedimentation. For filtration, a less dense floc will obviate undue clogging and allow flow to take place.

The colloid theory and perikinesis were dealt with under coagulation; orthokinesis will be dealt with now. It will be seen that the theory of orthokinetic flocculation is a further development of perikinetic flocculation theory; the basis for both of these were developed, by von Smoluchowski, from a consideration of particle collisions.

Particles must collide in order to flocculate. To facilitate collision there must be motion and a sufficient concentration of particles. The rate at which collisions can occur, during flocculation, is thus a function of the number of particles involved, their size and the rate of motion. Collisions take place as a result of diffusion or Brownian motion, flow past an obstacle, differential sedimentation, velocity gradient, and turbulence. Some of these mechanisms have been treated earlier in this article and they have been reviewed elsewhere<sup>65</sup>. Collisions due to velocity gradient in laminar flow or due to turbulence is, however, of particular interest and will be

dealt with here. Various other factors influencing flocculation are also of interest but these may be considered separately from laminar and turbulent flow.

### Laminar Flow

The stirring of water, whether by mechanical or other means, imparts velocity to it and to the colloids or suspended matter that it contains. Differences in velocity across the path of flow create velocity gradients. Most flocs formed in water are quite fragile. As they grow in size, the velocity gradient across them increases and they tend to be broken up. The expression of collisions due to velocity gradients has been achieved but numerous simplifying assumptions are necessary for the purpose.

Von Smoluchowski formulated his theory<sup>54</sup> for rapid coagulation which would take place when a complete discharge of colloidal gold particles takes place in the presence of abundant electrolyte. This theory was extended by him to apply to slow coagulation without and with agitation. The basic assumptions to this theory is that every particle is surrounded by a definite sphere of attraction, and any other particle will execute Brownian motion undisturbed outside this sphere. If, however, the particle should enter the sphere, it combines permanently. The gas theory of molecule and atomic radii are used although the particles are clearly not spherical.

With these simplifying assumptions as basis, von Smoluchowski stated<sup>66</sup> the equation for the number of particles entering the reaction sphere per second to be

$$f = \frac{4}{3} R^3 n \frac{du}{dz}$$

Where  $\frac{du}{dz}$  is the velocity gradient ( $G$ ) and the other terms are as before.

This equation expresses the rate of change of concentration of the particles. It is evident from the equation that aggregation by shear flow, i.e. flocculation, becomes increasingly important as particle size increases. It should also be noted that flocculation appears, according to this theory, to be independent of temperature and viscosity.

Müller pointed out<sup>67</sup> that von Smoluchowski's theory describes coagulation of hydrophobic colloids well, but that it is limited to simple systems. Tuorilla verified<sup>68</sup> von Smoluchowski's theory as modified by Müller<sup>56</sup>, and Fuchs showed<sup>55</sup> that only small error was involved

the static state assumption which was made. Camp and Stein reviewed these concepts and indicated their application in fluid mechanics<sup>78</sup>. Extensive flocculation studies of dynamic systems have since been carried out by Mason and others<sup>69-72</sup>, indicating the general applicability of the von Smoluchowski theory despite the numerous assumptions.

In his mathematical presentation, of coagulation and flocculation, von Smoluchowski considered the relative numbers of particles at given time intervals and arrived at the plot shown in Fig. 4. In this figure,  $n_0$  is the initial number of particles,  $n_1$  is the number of particles after time  $t$ ;  $n_2$  consists of two particles  $n_1$ ;  $n_3$  consists of three particles  $n_1$  or one  $n_1$  and one  $n_2$  particles, and  $\Sigma n$  is as previously defined.

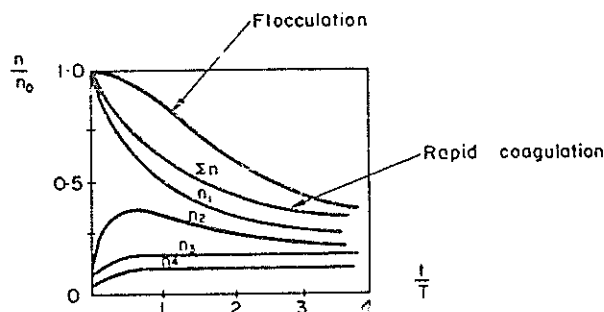


Fig. 4—Progress of rapid coagulation and flocculation of particles

The von Smoluchowski equation was developed for a monodisperse suspension—a gross simplification of the polydispersity found in a flocculating system. The integration of the differential equation is clearly complex except to the extent that von Smoluchowski shows in his diagram or as done numerically by Ritchie<sup>73</sup>, by Zebel<sup>74</sup> and by Gemmel<sup>75</sup>.

Zebel studied the course of coagulation of a heterogeneous aerosol determining initial size distribution experimentally and finding distributions for succeeding times by stepwise calculations on a digital computer. Gemmel carried out a numerical study by means of a digital computer and subsequently carried out confirmatory experimental work. He made size determinations, using flocculation, by a photographic process.

In the above, quiescent or laminar flow conditions only were considered, this is however not the case in the present application of flocculation nor is it necessarily desirable. Viscous flow, because of lower system energy may be expected to result in low density floc, of wide size range. This may be suitable for filtration but not for sedimentation. Turbulent flow on the other hand may well be expected to result in dense floc of narrower size range. A consideration of turbulence as it affects flocculation is, therefore, of particular interest.

### Turbulent Flow

In turbulent flow, the velocity at a point fluctuates at random with high frequency; a high concentration of momentum is, therefore, readily dispersed resulting in a much more uniform velocity distribution than in laminar flow. For laminar flow in a pipe, energy dissipation is proportional to the mean speed  $v$ ; for turbulent flow it is proportional to nearly  $v^2$ . The relation between inability of laminar flow and transition to turbulent flow as not yet been rigorously established. Even instability not sufficient for transition to turbulent flow; an unstable laminar flow may turn into another mode of

laminar flow. This has been well demonstrated<sup>76</sup> by Taylor for flow between concentric cylinders.

Formulations thus far evolved, for quasi-steady incompressible flows involve the unknown quantities of Reynolds stress components, i.e. shearing due to turbulence. To overcome this, a statistical study may be made of direct observations which can be taken in a turbulent system. Empirical equations evolved by Prandtl, Taylor and von Karman have been found to yield usable results in many cases<sup>77</sup>.

Prandtl's momentum conservation theory has the advantage of simplicity and ease of application and forms the basis of what follows.

For eddy kinematic viscosity  $\nu_e$  and mixing length  $\lambda_e$ .

$$\begin{aligned} \nu_e &= \rho \lambda_e^2 \frac{du}{dy} \\ &= \rho \lambda_e^2 G \end{aligned}$$

$$\text{hence } G = \frac{\nu_e}{\rho \lambda_e^2}$$

(The mixing length  $\lambda_e$  is the distance at right angles to the flow, over which an eddy must travel before it suffers a complete change of fluid within itself.)

The von Smoluchowski equation may be modified to become

$$f = \frac{4}{3} R^3 n \frac{\nu_e}{\rho \lambda_e^2}$$

The term  $\frac{\nu_e}{\lambda_e^2}$  is a rate factor here, and is the magnitude of turbulent transport in the system.  $\nu_e$  and  $\lambda_e$  can usually not be determined directly, but in the case of a paddle stirred vessel these are a function of the paddle drag. The mixing length can be determined by calculation from observation of length of travel of eddies by using dye and observing change of material.

The velocity gradient is readily definable for laminar flow but not for a turbulent flow regime. In the latter case a root mean square velocity gradient corresponding to the Stokes dissipation function can, however, be determined<sup>78</sup>. Robinson, in a study of the viscosity of colloids stated<sup>79</sup> that the flow of a Newtonian liquid is characterised by the fact that its maintenance requires the expenditure of energy at a rate proportional to the volume of the liquid and to the square of the velocity gradient maintained in it. The constant of proportionality, he stated, varies from one liquid to another. This constant is the coefficient of viscosity. Expressed in mathematical terms

$$\begin{aligned} P &\propto V G_m^2 \\ \text{and } P &= \mu V G_m^2 \\ \text{Hence } G_m &= \sqrt{P/\mu V} \end{aligned}$$

where  $P$  is power,  $\mu$  is viscosity, and  $V$  is volume. This is similar to the expression arrived at by Camp and Stein<sup>78</sup> and the term root mean square of velocity gradient ( $G_m$ ) was used.

### Physical Factors

The factors which may affect flocculation include temperature and viscosity, agitation and time, particle characteristics and floc properties.

#### Temperature and Viscosity

Camp, Root and Bhoota found<sup>80</sup> that temperature had no remarkable effect on time of floc formation under optimum coagulation conditions. This was amply borne out by results obtained in the work by Ritchie<sup>73</sup>. Temperature is, however, significant in its effect on viscosity

and thermal energy and this does affect the initial, coagulation stage to some extent.

It will be seen that the von Smoluchowski equation does not contain a viscosity term. The consideration of mean velocity gradient on the other hand contains this term and it is stated by Camp and Stein to be of significance in both laminar and turbulent flow<sup>78</sup>. Taylor pointed out the significance of extreme care to be taken if viscosity effects were to be ascertained<sup>76</sup>. This is as may be expected from the very slight variations which do take place in this variable at ambient temperatures of tests.

#### Agitation and Time

Velocity differentials, resulting in gradients or turbulence, is a well known factor in floc formation. Von Smoluchowski indicated the significance of velocity gradient and time in his work<sup>54, 66</sup>. He did, however, consider only the building effect of a velocity gradient and not disruption due to it. In the field of water treatment Camp and co-workers<sup>78, 80, 81</sup>, Bean<sup>82</sup>, Ritchie<sup>73</sup>, and Gemmel<sup>75</sup> have all demonstrated the dependence of flocculation on agitation and time.

The particular significance of agitation was clearly demonstrated by Stamberger<sup>83</sup> who found that a concentrated latex which had been stable for several years coagulated rapidly when subjected to moderate agitation.

Ritchie showed<sup>73</sup> that the variation in floc size with velocity gradient follows a pattern as indicated in Fig. 5. It can be shown that the maximum radius of floc

$$r_m = \frac{k}{\mu G}$$

where  $k$  is a constant of velocity and of toughness of the floc.

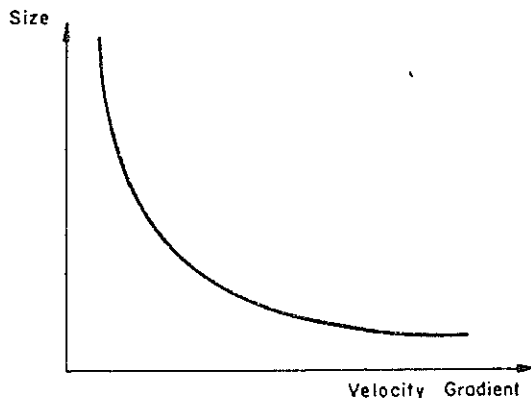


Fig. 5.—Floc growth and agitation

LaMer and Healy, in an investigation of adsorption-flocculation of macro-molecular substances such as starches and gums, found<sup>84</sup> that agitation determines the rate and extent of polymer surface reaction. This in turn determines bridging conditions at the surface of adjacent particles in a dispersion. They found that the flocculation equilibria are agitation controlled but that there is also a time effect.

The time factor in flocculation is seen to contain a chemical and a physical aspect. In a consideration of these aspects the properties of the continuous medium and additives to it, and the properties of the particles are both important. These properties have to some extent been dealt with under coagulation but will be expanded further on with regard to the particles.

Quantitative values have been put to velocity gradient and time for flocculation. These values can, however, at present only be taken as tentative as they are not qualified by defined quality criteria.

Fair and Geyer state<sup>85</sup> that velocity gradients of 10 to 75 seconds<sup>-1</sup> generally pertain in flocculation units. They also state that the dimensionless product of velocity gradient ( $G$ ) and time ( $t$ ) having values  $10^4$  to  $10^5$  result in good flocculation in practice. This is in close agreement with values calculated from American practice<sup>86</sup>.

Camp proposes<sup>81</sup> that since high velocity gradients yield small floc, the best economy should result from staged flocculation in a series of tanks. He put forward the concept that the sum of  $Gt$  values for all the tanks should be the same as for a single high rate tank; this he suggests would result in optimum flocculation. Fair and Geyer suggest<sup>85</sup> an initial value of 100 seconds<sup>-1</sup> and a final value of 10 seconds<sup>-1</sup>.

The values put forward for  $G$  and  $t$  are applicable to a system where floc concentration is kept very low due to continuous efflux of floc. In a floc blanket process, the floc concentration would constitute a further factor to be taken account of.

#### Properties of Particles

Müller indicated<sup>56</sup> the importance of particle size distribution in flocculation. He showed that the probability of collision for unequal sized particles is greater than for monodisperse particles. He also showed that in a polydisperse suspension, large particles disappear at the same rate as they would in the absence of small particles. The small particles disappear more rapidly however. This he explained by saying that the small micelles form a layer on the larger particles and then disappear more rapidly than predicted by the von Smoluchowski theory.

Langelier and Ludwig carried out tests with clay particles of various sizes and found<sup>59</sup>, that for optimum flocculation, water must contain a suitable number of particles less than  $1\mu$  in size, and a sufficient number  $1\mu$  to  $5\mu$ .

Camp and Stein demonstrated<sup>78</sup> that at a point in a fluid, the rate of flocculation which is caused by the motion of the fluid is directly proportional to the concentration of flocculable particles at that point. This was also found by Manley and Mason<sup>72</sup>.

LaMer and Healy found<sup>84</sup> that maximum flocculation is specific for each system and occurs over a narrow concentration range. They also found that for low percentage solids dispersion, i.e. in the 100 to 1000 mg/l region, orthokinetic flocculation effects will certainly be important. It was noted that change of system from dispersed to flocculated to dispersed occurred over a narrower range with increase in intensity of agitation. They state that this is not understood.

#### Properties of Floc

Black and Walters state<sup>50</sup> that the choice of a satisfactory criterion of good coagulation is particularly difficult. This is, by the same token, true also for flocculation. They state that adequate coagulation must result in a high degree of turbidity removal and then point out that the use of this property is complicated by numerous aspects.

Von Smoluchowski pointed out<sup>54</sup> these difficulties and

entions that toughness or stickiness had been used in the past as measures of flocculation.

In his study<sup>87</sup> of the physical aspects of flocculation, Hudson used a size and settling velocity as parameters for flocculation. He found that volume of floc is greater at low agitation speeds than for larger speeds. He also used excellent settling with flocs less than 0.5 mm in diameter; these were produced at higher  $G$  than slower settling particles. He found floc volume to be proportional to coagulant dosage and small particles to be denser than large particles. Hudson also found that floc can be made more compact at a  $Gt$  value of 0,000 than for a limited agitation— $Gt$  value of 10,000.

#### Conclusions

Flocculation due to velocity gradient in laminar flow has been theoretically formulated and has been verified by experimentation.

The theory of flocculation evolved for laminar flow velocity gradients can be modified in order to apply to turbulent flow. The applicability of the theory involved in turbulent flow has not been experimentally verified.

Temperature and viscosity may well be factors in flocculation, they are however, not significant.

There is evidence to support the conclusion that both agitation and time are factors which affect flocculation. Flocculation equilibria are, however, agitation controlled. Size and concentration of particles are important factors in flocculation.

There is as yet no well defined quantitative measure for the properties of floc and how these may be achieved; this is possibly because the necessary desiderata have not been put forward.

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## PART 4: DATA

**E**ACH phase of the conventional water purification process is related to and is affected by those preceding and following it and it is, therefore, not simple to determine to what extent any particular process or unit operation affects removal of particulate matter.

Removal of the larger bacteria, cysts and helminths may be effected by simple sedimentation as found in nature. The smaller bacteria and the viruses can be removed directly by ion exchange or adsorption processes or indirectly by coagulating and flocculating them into an agglomerate which is then removed. In the latter case, phase separation is effected either by sedimentation or by filtration or both. Slow sand filtration will effectively remove most microorganisms; the mechanisms and processes involved are, however, manifold. Even rapid filtration may, however, under special circumstances be effective in the removal of microorganisms without being preceded by coagulation.

Coagulation and flocculation are undoubtedly of primary importance in the removal of microorganisms from water. There is nevertheless very little quantitative data available on the removal of particulate matter by coagulation; this is to some extent due to the practical problem involved in phase separation, which is necessary to determine the efficacy of this particular process. Even a combination of coagulation and the flocculation unit operation has yielded very little data unless phase separation was effected by subsequent sedimentation or filtration. An attempt will, however, be made to deal with the data on these processes and unit operations separately in so far as it is possible, and in the sequence in which they usually occur in the water purification process except for adsorption which will first be dealt with.

### Adsorption

This process takes place to greater or lesser extent in all the processes and unit operations of water purification; it is of special applicability in coagulation. Adsorption or attachment is, however, dealt with here as a process in its own right because of its importance as indicated by the amount of data available on ion exchange removal of bacteria; attachment of viruses to cells; adsorption of virus to non-biological surfaces; and adsorption of non-biological matter.

### Bacteria

Bacteria (and protozoa) can be considered to be

hydrophilic biocolloids. They carry a net negative charge<sup>27</sup> at neutral pH, and their isoelectric point is at pH, 3 to 4. The surface charge density of bacteria is strongly pH dependent as it acquires this charge through acid-base interactions. Porter states<sup>27</sup> that bacteria behave in many respects like colloids in various liquid media. Stability of a bacteria dispersion does, however, depend on the physiological condition of the cell.

Gillisen carried out experiments with coliforms and ion exchange material and found<sup>88</sup> anion exchanger effective in removal but cation exchanger ineffective, indicating that these bacteria carry a negative charge. He found that removal takes place throughout the depth of an exchange column, indicating that a straining (or filtering) action is not primarily involved. Removal was found to be not as dependent on the amount of bacteria removed as on their concentration in suspension. The charge characteristic was proven by repeated successful regeneration. Mitchell and Nevo found<sup>89</sup> that the major factor involved in clogging of sand during infiltration is accumulation of polysaccharide, i.e. adsorbed bacterial matter.

Gillisen's and Mitchell's findings may, therefore, indicate that adsorption of bacteria in a filter can progress to the stage of physical clogging.

### Viruses

Viruses are not motile and must rely for their transport on their random Brownian motion or the movements of the suspending fluid. Of the two mechanisms the former is most important in adsorption.

Allison and Valentine found<sup>90</sup> that adsorption of virus and similarly sized non-biological particles could be almost exactly predicted by diffusion theory. They found that both virus and the polystyrene latex particles used in the study are negatively charged and that there are no barriers to their adsorption.

Puck and Sagik carried out experiments with phage and ion exchange resins and found<sup>91</sup> that the phages used are absorbed by anion exchangers indicating that they were negatively charged. The electrical charge differed for the two phages though they were tested under the same conditions.

Dieterich carried out research into removal of bacterial virus in sand filtration and found<sup>92</sup> that clean washed sand has a high adsorptive capacity. He found that various electrolytes influenced removal of phage differently, indicating that electrostatic forces are involved. Treatment of the sand with an anionic detergent

used a reduction in virus removal leading Dieterich to the conclusion that clean sand is probably positively charged and the phage negatively. The electrokinetic potential of silica surfaces has, however, been found by various workers to be negative unless impurities are present<sup>93</sup>.

#### Non-biological Particles

Microorganisms are generally accompanied in water by some non-biological organic and inorganic particulate matter and some interaction may take place between these particles. Hudson carried out an extensive study<sup>94</sup> on this subject and came to the conclusion that there is a parallelism between the removal of turbidity and microorganisms. The problem of detecting bacteria in turbid water is well known and has been demonstrated by Portzfeld and Thon<sup>95</sup>. The implication of these findings is clear and it is, therefore, necessary to view some of the data on adsorption of non-biological matter.

Black and Willems suggest<sup>60</sup> that the coagulation of turbidity in water takes place in two stages, the primary stage is the adsorption of trivalent aluminium and iron ions into the lattice structure of the clay particles by ion exchange. This results in a reduction in the negative zeta potential of the clay particles. Black previously stated<sup>44</sup> that it has been shown that the metallic ions in a diffuse double layer surrounding a clay particle constitute an ion exchange system in equilibrium.

Hemphill and Swanson reported<sup>96</sup> that sorption of the organic acids tested by them, is related to the structure of the clay mineral and the size of the sorbate molecule. Some sorption is stated to take place on the surface and some by slower reaction, in the interlayers.

Weber and Morris found<sup>97</sup> that when there are a number of dodecyl benzene sulphonate compounds present at the same time in water, that adsorption to activated carbon is affected. Each solute was found to affect adversely both the rate of adsorption and the equilibrium capacity for adsorption of the other compound present.

#### Coagulation—Flocculation

These are considered to be the most important processes in unit operations involved in the facilitation of phase separation in water purification. Until recently, however, very little investigation had been carried out on either of these. Most of the investigation which has been carried out on removal of suspended particles is meaningless because of lack of control of factors which affect coagulation and flocculation, and also because performance parameters were not even determined<sup>98</sup>. This may to some extent be due to a lack of clear understanding or definition of these processes. The data presented below should be viewed in the light of the above remarks.

#### Bacteria and Protozoa

Streeter carried out pioneer plant scale studies on removal of bacteria from water<sup>12</sup> in the U.S.A. These extended over a number of years and involved 17 municipal purification plants and one experimental filtration plant treating Ohio river, Eastern and Midwestern states water. He also studied 14 other plants treating Great Lakes water. A considerable amount of comparative data, bearing on the efficiency and limitations of water purification processes was obtained at the time. On the basis of these studies Streeter put forward limiting raw

water coliform indexes for the various processes, operations and combinations of these as indicated in Table 5.

Table 5  
Efficiency of Treatment Processes in Bacteria Removal

Treatment	Limiting Raw Water Coli Index per 100 ml	
	Ohio River	Great Lakes
(a) Chlorination only	80	50
(b) Coagulation, sedimentation and rapid filtration	80	60
(c) (b) + prechlorination	3 500	?
(d) (b) + postchlorination	6 000	4 500
(e) (b) + pre and post chlorination	20 000	?
(f) (d) and two stage sedimentation or long period of sedimentation	60 000	?

It is seen from Table 5 that a combination of coagulation, sedimentation and rapid filtration was considered to be capable of dealing only with a relatively small bacterial content—as small as chlorination alone. This tabulation no doubt set the pattern for future development in water purification with respect to the importance of chlorination in addition to coagulation; it possibly created an impression of superior importance of disinfection *per se*.

Walton carried out an extensive study of a large number of municipal water purification plants and reported<sup>13</sup> on 27 of these situated in 17 states of the U.S.A. His findings were in general agreement with those of Streeter. He found that removal of coliforms by coagulation, sedimentation and rapid filtration approximated the 98 per cent reduction reported by Streeter. Based on this finding, and evidently allowing for only 1 coliform organism per 100 ml Walton arrives at the conclusion that the upper limit with which the mentioned operations can successfully cope is 50 per 100 ml.

Chang *et al* determined the removal of native Ohio river water bacteria and *E. coli* in laboratory coagulation-flocculation tests of virus and phage studies<sup>99</sup>. Interpretation of the results obtained in these tests is complicated in the first instance because of the extensive sedimentation period of 90 minutes which was used in both of two stages, and secondly because of the pH control procedure. There is presumably some natural die-off at the low temperature over the extended period of the experiment. The pH control procedure involved ferric chloride and calcium oxide both of which may well have a bactericidal effect and one of which was moreover used as coagulant in the tests.

Tenney investigated coagulation-flocculation of sewage bacteria suspensions. He found<sup>100</sup> a stoichiometric relationship between the concentration of bacteria and the metal ion dose required; for aluminium sulphate, optimum pH of the bacterial suspension was found to be 5 to 6. He concludes that coagulation of bacteria is caused by the bridging action of linear polymeric substances and by metal ion hydrolysis products; this he says is supported by the finding that the non-hydrolyzable calcium ion, which will reduce surface charge will not cause coagulation.

Panicker *et al* carried out tests to determine the removal of *Entamoeba histolytica* cysts from water by coagulation-flocculation-sedimentation<sup>101</sup>. They found that at a given turbidity of the water the concentration of cysts that can be removed from the water is directly related to the sedimentation time for a given dosage. The tests showed that the settling rate could be increased by coagulation-flocculation which facilitates sedimentation.

#### *Bacteriophage and Virus*

One of the early tests on the removal of virus from water was that dramatically performed by Neefe *et al*<sup>102, 103</sup>. The treatment was carried out on distilled water containing infectious hepatitis virus. To this water was added sodium carbonate as a buffer, aluminium sulphate as coagulant and activated carbon; all of which was then stirred, and the resulting floc was allowed to settle, and to complete this multiple effect treatment, the supernatant was strained through cotton gauze. Each of 5 volunteers was then required to ingest 2715 cc of the water so treated. Two of these volunteers developed mild hepatitis after 33 and 37 days (as opposed to 21 to 23 days for untreated water). It is not possible to say which of the many processes involved were responsible for the attenuation or removal of the virus as measured by the qualitative results obtained.

Chang, Isaac and Baine investigated the removal of a bacterial virus in water, by coagulation-flocculation with aluminium sulphate<sup>104</sup>. They used distilled water in all these tests in order to avoid variation in chemical constituents as found in surface waters. They made the water up with phosphate buffer and 5 p.p.m. 5 $\mu$  diameter suspended silica. They state that preliminary tests were carried out to determine the smallest dose of alum for 'good' floc formulation; at pH 5.2 this was found to be 40 p.p.m., and dosages up to 100 p.p.m. were used in further tests. A flocculation period of 30 minutes was followed by 90 minutes sedimentation which is stated to have been still too short. Removals of 99.9+ per cent were obtained. Chang states, however, that high removal occurred at pH 4.5 and 9.0 despite small amounts of floc and that this was possibly due to adsorption by glassware despite preventive treatment given it.

The investigators concluded<sup>104</sup> from their tests that for given conditions of pH, temperature, flocculation and sedimentation time, the percentage removal of phage from the treated water is a function of coagulant concentration. This is, however, clearly applicable only within limits and although not ignored, the mechanisms of coagulation were not fully taken into account by these workers. No indication is given as to criteria used for effectiveness of the processes used apart from the assay of phage. Removal may well have been primarily adsorption but possibly to a large extent on the apparatus and equipment. For the amount of suspended particles present, the coagulant dosages applied were excessive.

Chang *et al* carried out an investigation into the removal of Coxsackie virus and bacteriophage<sup>105</sup>. The effect of final pH on removal of virus and phage was determined, and it was found that at optimum pH 7.2, 99.0 per cent of Coxsackie virus was removed with a dosage of 80 p.p.m. alum. Optimum pH for phage was 6.2 and 99.1 per cent removal was effected. It was found that increasing dosages of alum resulted in increased removal of both virus and phage.

In further tests<sup>99</sup> carried out on Ohio river water by

Chang and co-workers, a two-stage coagulation process was used. Supernatant resulting from first stage treatment was used after addition of calcium oxide. Removals in excess of 99 per cent were obtained for the phage and virus at temperatures of 5°C and 25°C by this two-stage procedure. This means an improvement of 4 per cent over a single stage process. In these studies the removal of virus was consistently, slightly higher than phage removal.

A test was carried out on significance of floc formation to virus removal and it was found<sup>99</sup> that once the floc had fully formed no removal took place if virus was then added. If, however, there was a very high dosage, some removal resulted. The finding is, however, contradictory to that of Kempf *et al*<sup>106</sup> and Carlson *et al*<sup>107</sup> who found that a layer of floc on top of a filter results in removal of viruses: both found that the more floc there is on the filter, the better is the removal.

The pH control procedure used by Chang *et al* in these studies<sup>99, 105</sup> is subject to the same criticism given above. Apart from virus and phage assay no other parameters or criteria were consistently used to control the effectiveness of the processes applied. This leads to doubts as to the site of removal of the particles—the effect of glassware and equipment has been remarked upon above. In view of these considerations, their results are thus seen to be qualitative only.

Robeck, Clarke and Dostal carried out experiments on removal of attenuated poliovirus; this included some work with a pilot water treatment plant in which alum was used as a coagulant. They found<sup>108</sup> that only with 'sufficient' alum dosage and 'good' floc formation was virus removal effective. These results are difficult to interpret as a variety of waters and a number of processes and operations were used in series but only final results are given.

Woodward, in a review of the relation of raw water quality to treatment, mentions<sup>109</sup> the modern tendency to reduce the size of coagulation facilities to the extent of reverting to the 19th century practice of carrying out coagulation in the filter. The reason for this is no doubt that coagulation and flocculation can be carried out more efficiently in a filter than in some of the units evolved for these operations.

It is stated<sup>98</sup> that virus removal roughly parallels the removal of coliforms, total bacteria and turbidity. There was, however, until recently (apart from some field data<sup>94</sup>) very little definitive information on this aspect.

#### **Sedimentation**

If unaided, this unit operation can only remove the larger bacteria and organisms except where the smaller biota are attached to heavier particles. It is, however, of considerable importance as a secondary, phase separation process.

#### **Filtration**

Microorganisms of all sizes can be removed by filtration as its mechanisms include adsorption, flocculation, straining, sedimentation and biological activity<sup>85, 92, 110, 111</sup>. In the slow sand filter all of these mechanisms of removal are involved and biological activity is of particular importance as opposed to a rapid filter where this latter action is limited. Straining by means of Kieselguhr or membranes is a well known operation and is extensively used to remove particles as large as or larger than bacteria.



## ent Investigations

vious investigators in this field often employed a ber of processes and unit operations simultaneously, complicating the evaluation of the efficacy of any le process. In the few cases when one process only used, no measurement was made of removal of er colour or turbidity from water. It is therefore possible to say whether the process applied was ssary nor to comment on its sufficiency or otherwise. s clearly desirable that the removal of microor- isms should be related to physical parameters which used to judge the efficiency of the water purification essage.

was decided, for the reasons given, to investigate oval of bacteria by coagulation and flocculation, at same time measuring removal of clay mineral. eria of differing characteristics and two different s, all of which occur commonly in water, were thus l in tests recently carried out. A general indication he methods and the findings is given here.

suspensions of quartzite and of bentonite were made in distilled, demineralised water which was buffered result in a conductivity of 350  $\mu$  mho/cm. The pH he water after addition of different dosages of alum- m sulphate, was maintained at 7.0 by keeping the l acidity added to the suspension constant. Acetic l was used for this purpose.

he bacteria were added to the 500 ml samples of clay ensions, various dosages of alum added and these e then subjected first to rapid mixing for 2 minutes then to flocculation for 8 minutes. The resulting was allowed to settle for 15 minutes and samples e then taken for determination of bacterial and clay centration in the supernatant.

ig. 6 shows the results obtained with bentonite, ptococcus faecalis and *Escherichia coli* when these e simultaneously present in suspension. *E. coli* is

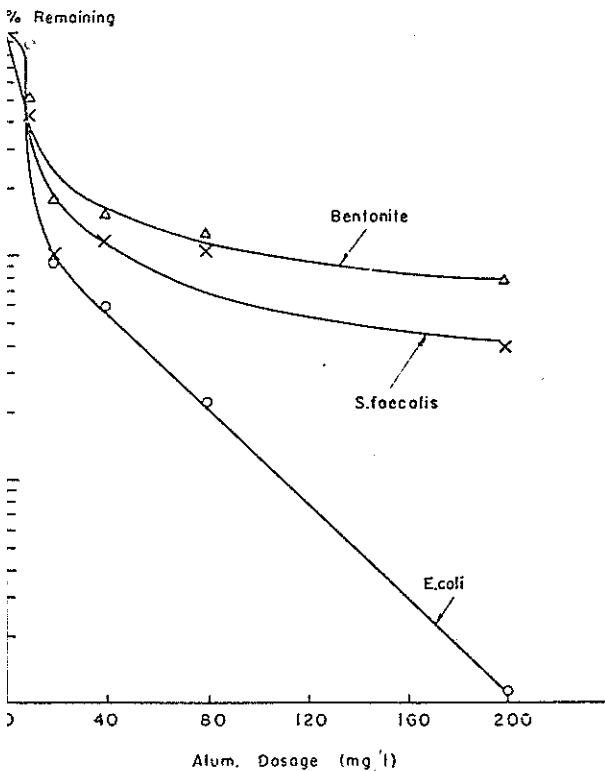


Fig. 6—*E. coli*, *S. faecalis* and 20 mg/l Bentonite

more extensively removed than bentonite or *S. faecalis*, showing that removal of the indicator organism cannot be taken as an indication of removal of the other bacteria. The close agreement in removal of *S. faecalis* and bentonite may also be noted.

It was found that the removal of these bacteria and clays from suspension may be expressed in the form of a law of the nature:

$$R D^m = c$$

where  $R$  = percentage bacteria or clay remaining,  
 $D$  = dosage of alum (mg/l) and  $m$  and  $c$  are constants.

This is similar to the Freundlich adsorption equation. The results expressed in terms of the above equation and plotted to log scale are as shown in Fig. 7.

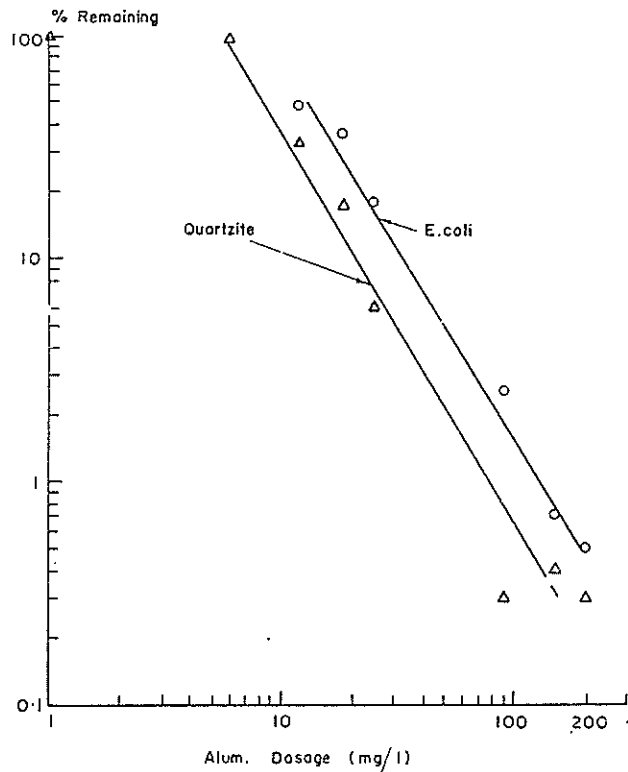


Fig. 7—*E. coli* and 500 mg/l Quartzite

The influence of the concentration of quartzite in suspension on *E. coli* removal is shown in Fig. 8. The competition for the available coagulant is clear from the inverse variation between clay concentration and *E. coli* removal. The latter thus appears to be coagulation controlled. It was found on the other hand that removal of *S. faecalis* was flocculation controlled and *Pseudomonas aeruginosa* is equally affected by coagulation and flocculation.

The effects and importance of both the chemical and the hydro-dynamic processes in the removal of bacteria was thus established. Most significant are the relative removals of bacteria and clays.

It was shown that flocculation affects aggregation and thus removal of bacteria in the same way as it affects clay minerals. Quartzite is thus now being used in further studies of flocculation. For this purpose a Couette device, capable of applying a definable velocity gradient to the water has been developed and will be used. Of especial interest is the influence of flocculation

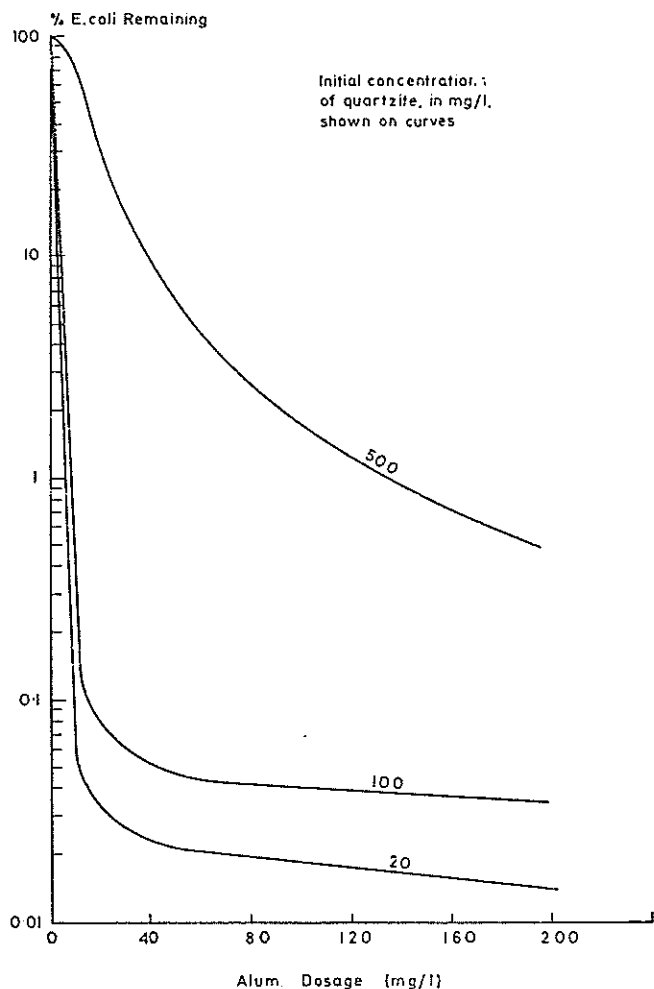


Fig. 8—Effect of concentration of Quartzite on *E. coli* removal

on sedimentation and filtration as these are the commonly used phase separation unit operations and will in the final instance thus affect removal of microorganisms.

### Conclusions

Adsorption is clearly an important process in the removal of bacteria and viruses, and its influence is present to various degrees in the different unit operations. Adsorption may well be seen to be the prime removal process especially in the case of the minute virus particles.

From the available data and knowledge of the various microorganisms it may be concluded that sedimentation is only an effective removal mechanism in the case of the larger biota. Sedimentation is, however, an important phase separation process.

Filtration is nominally capable of removal of microorganisms but cannot be seen as being an effective method for this purpose. It might in fact provide a favourable culture bed for some organisms. Filtration has value as a phase separation operation in the removal of particles containing microorganisms.

Some laboratory data are available on phage and virus removal by coagulation—limited, however, because of the complexity of assaying these particles. Laboratory and field data exist on removal of bacteria by coagulation and flocculation. The significance of these two processes was, however, seldom individually determined. The various factors which influence them were given

insufficient attention and their effects were not related to quality criteria otherwise commonly used to determine the effectiveness of water treatment. An attempt was made, in recent investigations, to apply such criteria to tests carried out; the factors affecting coagulation and flocculation were controlled. It is hoped that the results obtained will be of interest to those involved in water purification.

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