6-1-1939

The Use of Acidified Sodium Silicate in Chemical Coagulation of Sewage

Conrad W. Christenson

Follow this and additional works at: https://commons.und.edu/theses

Recommended Citation
Christenson, Conrad W., "The Use of Acidified Sodium Silicate in Chemical Coagulation of Sewage" (1939). Theses and Dissertations. 470.
https://commons.und.edu/theses/470

This Thesis is brought to you for free and open access by the Theses, Dissertations, and Senior Projects at UND Scholarly Commons. It has been accepted for inclusion in Theses and Dissertations by an authorized administrator of UND Scholarly Commons. For more information, please contact zeineb.yousif@library.und.edu.
THE USE OF ACIDIFIED SODIUM SILICATE IN CHEMICAL COAGULATION OF SEWAGE

by

CONRAD W. CHRISTENSEN

(E.S. University of North Dakota, 1936)

A thesis submitted to the Graduate Division of the University of North Dakota in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE IN CHEMICAL ENGINEERING

Grand Forks, North Dakota

June 9, 1939
This thesis is submitted by Conard W. Christenson in partial fulfillment of the requirements for the degree of Master of Science. It is hereby approved by the committee of instruction in charge of the work.

Chairman

C. L. Finm

W. J. Westmoreland

Director of Graduate Division
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Industrial Importance of Research.</td>
<td>1</td>
</tr>
<tr>
<td>Nature of Sewage</td>
<td>6</td>
</tr>
<tr>
<td>Methods of Analysis of Sewage</td>
<td>8</td>
</tr>
<tr>
<td>Historical</td>
<td>9</td>
</tr>
<tr>
<td>General Methods of Sewage Treatment</td>
<td>12</td>
</tr>
<tr>
<td>Sewage Treatment at Grand Forks.</td>
<td>34</td>
</tr>
<tr>
<td>Review of the Literature</td>
<td>38</td>
</tr>
<tr>
<td>Experimental Procedure</td>
<td>52</td>
</tr>
<tr>
<td>Data and Results</td>
<td>61</td>
</tr>
<tr>
<td>Plant Test Run</td>
<td>70</td>
</tr>
<tr>
<td>Form of Silica that Aids Coagulation</td>
<td>73</td>
</tr>
<tr>
<td>Discussion</td>
<td>85</td>
</tr>
<tr>
<td>Summary</td>
<td>89</td>
</tr>
</tbody>
</table>
Gordon M. Fair has stated that, "Sewage research is concerned with the physical, chemical and biological forces that act and interact to bring about changes in the composition and condition of the complex and unstable substances that constitute sewage. Orderly sewage research, like all research, includes the following:

1. Statement or definition of the project for the purpose of clarifying and delimiting the objective of the work to be done.

2. Deductive analysis of the problem for the purpose of suggesting possible answers and developing a hypothesis of the various elements involved and of their probable relations.

3. Design and construction of apparatus, determination of observational procedures and securing of measurements of all the elements that enter significantly into the problem and represent the hypothetical factors.

4. Assembly, classification and, where possible, graphical presentation of the measurements.

5. Mathematical analysis of the results for the purpose of testing the different elements of the hypothesis and determining its agreement with the observed results, followed, where necessary, by modification of the hypothesis in the light of the clearer and more definite thought that has been brought to bear upon the problem by the analysis. Mathematical verification and generalization of the hypothesis should provide, as its ultimate goal, a 'law' that formulates the nature of the relationships that have been observed and measured.
Types of Research Problems. Sewage treatment offers a very broad field for research. The problems involved include:

1. Physical (mostly hydraulic) problems, such as control of flow through sedimentation units, trickling filters and aeration tanks.

2. Chemical problems, such as the precipitation of solids and the conditioning of sludge for dewatering.

3. Biological problems, such as the conversion, by aerobic or anaerobic processes of unstable compounds into the relatively stable substances and the destruction of living organism." 

In sewage treatment, as well as any other industrial field, research is necessary to improve the product at lower cost. The direct benefits resulting from improvements are more difficult to evaluate in sewage practice than in many other fields because it is difficult to place a direct dollar and cent value on the benefits accruing from the clearer, more sanitary and less putrescible effluent. Willem Rudolfert states further that: "In order to prove the value of sewage research it is necessary to indicate clearly that (1) the art advances by producing better results, alleviating the gross pollution of our streams, reducing the health hazards, removing the nuisances and increasing the welfare of the people, (2) the improvements are obtained at relatively lower costs."

In order to more clearly present the value of sewage research it is well to consider the advancements made in the field during the last 15 years.

Separate sludge digesting was considered to be useless in
this country until, when in 1925, research was begun to prove its practical applicability. Previously, it was thought that the operation was too complicated, that a poorer quality of gas was produced and that the units would be too large. By introducing heat and carefully controlling the reaction, the digestion time was cut from 650 days to 30 days. The importance of this improvement over the Imhoff tank and the practicability of separate sludge digestion is evidenced by the fact that hundreds of such plants have been built in hundreds of cities both large and small. Here again it is difficult to evaluate the actual benefits from separate sludge digestion but it is certain that much money and time have been saved.

1925 also saw the beginning of a practice that is now widespread—chlorination. The advancements in this field have been due largely to the organization known as the Chlorine Institute. The Institute enlisted the cooperation of sanitary engineers, health departments, sewage experiment stations and various other agencies and have developed chlorination to a point where now it is difficult to think of sewage treatment at all without chlorine treatment in some form. The use of chlorine is of inestimable value in controlling odors, preventing corrosion and safeguarding streams, bathing beaches, etc. from pollution.

The nuisance of sewage flies was another problem that could not be solved until a state entomologist became interested in the life history of the most prevalent of sewage flies (psychoda). He found among other things that the larvae would leave their habitat when too much water was present. This led to the practice of
flooding the filters where these flies were most numerous. The elimination of these flies cannot be appreciated to the fullest extent except by the operators and laborers working where they are present. To them the riddance of this nuisance was of prime importance.

In sludge drying and disposal of sludge the larger plants have done most of the research because they do have a big problem in the disposal. Some of the smaller plants have taken care of the problem by running the sludge into greenhouses. This eliminated the odor nuisance and resulted in more rapid drying of the sludge. This method of disposal requires, for large plants, the use of excessive areas of land. Especially is this true in densely settled areas where land valuation is high. As a result the larger plants have taken to more intensive use of chemicals and Oliver filters to dewater the sludge. It is easy to see the problems that would arise for larger plants if these advancements had not been made. In recent years, incineration of the dried sludge has received impetus from the building of a few plants such as the Twin Cities development, that utilize this type of treatment. Much has been learned of the fuel value of the sludge and its volatile gases but there still remains a vast amount of work to be done in this field. Sale of sludge for fertilizer has also been practiced to some extent.

The practice of activated sludge is quite old (dating back to 1882) but was not used extensively until 1915 and the investigation of the principle and possible improvements did not really get started until 1930. Indeed, there is still some controversy
as to the relative importance of the physical, chemical and biological processes. But, with the large number of investigators and advancements being made the fundamental concepts are gradually becoming well known.

The old reliable trickling filters have received a great deal of attention due to the widespread use of this method of treatment and the fact that it has been in use for such a long time. Results have been very gratifying since the present capacities of filters are far greater than those of the old, slow type. The amount of time and money saved in this field alone exemplifies the value of research in sewage treatment.

Chemical treatment of sewage has only recently become of prime importance. This type of treatment was used quite extensively in early sewage practice but was discarded in favor of biological methods. Of late years the method has come back largely because of flexibility of use and its ease of handling. Research has developed new chemicals and their practicability is shown by the large number of such plants being built in the past few years.

Of course none of the above developments could have been made were it not for the fact that equipment necessary for the operation of plants had not kept pace of the other developments. The time and labor saving devices in sewage treatment is fundamentally the same as in other fields and results are essentially the same. Truly, sewage treatment would be quite stagnant without the benefits resulting from improved equipment.
Sewage has been defined by the Committee on Sewerage and Sewage Disposal of the American Public Health Association as a "combination of (a) the liquid wastes conducted away from residences, business buildings and institutions and (b) from industrial establishments, with (c) such ground, surface and storm water as may be admitted to or finds its way into the sewers." It is extremely putrescible, its decomposition produces large quantities of malodorous gases, and it may contain numerous pathogenic or disease producing bacteria such as dwell normally in the intestinal tract or are present in certain industrial wastes, as from tanneries or laundries. Its immediate and unobtrusive removal from its source in residences and industrial plants to a point sufficiently remote from densely settled areas to permit of its discharge or suitable treatment without offense, is most desirable.

Sewage is composed largely of water (99.9%) but contains sufficient quantities of offensive and dangerous substances to make its sanitary disposal of great importance.

Physically, its appearance is that of dirty dish water or bath water to which has been added floating matter such as fecal matter, bits of paper, matches, grease, vegetable debris, etc. Solids are present in both suspended and dissolved form. Some of the suspended solids will settle out when the velocity of the sewage is decreased but some will remain in suspension even after long periods of quiescence. A large part of the solids is in the colloidal state and presents an especially difficult problem. The Metropolitan Sewerage Commission of New York estimated the city's sewage contained, per thousand population, annually, 14 tons of
feces, 8 tons of toilet paper and newspaper, 11 tons of soap and washings, 8 tons of street wastes, and 4 tons of miscellaneous substances, a total of 45 tons. If this sewage is discharged into rivers without treatment, a large amount of solids will settle to the bottom and sides forming sludge banks which interfere with the flow of the water. Floating solids, fats and oils form an unsightly scum. These present a visible objection to the discharge of untreated sludge.

Chemically, sludge consists of animal, vegetable and mineral materials. It is the organic matter that causes the real trouble. This material is very complex and is oxidized, in presence of bacterial enzymes, to more stable, simple materials. This oxidation is accompanied by objectional odor and other noxious conditions in the streams to which they are admitted. They take up all available supply of oxygen in the stream and it is this oxygen demand that causes river decay. That is, it prohibits the growth of fish and vegetable matter in the rivers. It also causes stagnation and results in making the water unfit for animal or human consumption.

Biologically, sewage contains a vast number of living organisms among which bacteria predominates. One gallon of sewage may contain 20 to 250 billion bacteria. A large part of the bacteria are harmless to man and can be used to oxidize the complex organic matter in the sewage. They are those organisms normally present in the intestinal tract. It is not uncommon, however, to find disease-producing or pathogenic organisms in the sewage. These are composed of cholera, typhoid fever, dysentery, etc., and are the so-called water born diseases. These disease-producing bac-
teria are what cause the real danger to public health.

Sewage is generally spoken of as being domestic or industrial and the terms are self explanatory. Sometimes storm water is admitted to the sewerage system and these are called combined sewers. Where the two flows are separated they are called separate sewers and are spoken of as being storm water and sanitary sewers. Concentration is a means of designating sewage and is a measure of the ratio of sewage matter to water. The condition of sewage is also used to designate it as fresh or septic. Sewage becomes septic and offensive if allowed to remain in tanks or other receptacles long enough for all of the oxygen present to be used up.

Part III

Method of Analyses of Sewage

The quantity of solid matter in sewage is determined by evaporating a known amount of sewage and weighing the residue. This is known as total solids. If the residue is ignited the amount driven off is known as the volatile solids or an approximation of the amount of organic matter. Suspended and dissolved solids can be obtained by filtering. This does not indicate the amount of colloids and there is no simple method at present for determining this factor. Settleable solids is that amount that will settle out in a certain interval of time. It is measured in an "Imhoff Cone", a conical glass 4 inches in diameter at the top and 16 inches tall. The cone holds 1 liter and is graduated in cubic centimeter at the bottom where amount of deposited sludge is read. The pH, a measure of the acidity or alkalinity of the sewage, is measured by a pH electrometer or by comparing, colorimetrically, with known stan-
Alkalinity is measured by titrating a known volume with \( \frac{N}{50} \) Sulfuric acid. The biochemical oxygen demand (commonly known as B.O.D.) is the oxygen demanded by bacteria during the oxidation of the organic matter present in sewage. It is determined by diluting some of the sewage with aerated water and determining the oxygen present before and after an incubation period (generally 5 days at 20°C.) Bacteria are determined by plating out on an agar plate a known quantity of sewage and incubating the plate 24 to 48 hours. The number of colonies present is the number of bacteria present before incubation. Another test is for Bacterium Coli (B-Coli). This is done by inoculating a broth containing lactose sugar and litmus indicator. Acidification and gas production show the presence of B Coli. B Coli are present in the intestines of man and animals and this test is a good index of sewage pollution.

**Part IV**

**Historical**

The treatment and controlled disposal of sewage is a very recent development. Sewars are known to have existed in antiquity, mention being made of them in old Grecian cities and in Nineveh and Babylon as early as the seventh century before Christ. It is surprising to note, however, that very little was done between days of the Early Roman Empire and 1842 which marked the beginning of modern sewerage practice.

The city of Hamburg, Germany was partly destroyed by fire in 1842 and, as the section destroyed was the oldest in the city, it was decided to rebuild it according to the then modern practice. These sewers of Hamburg were a marked improvement over anything
prior to that time and twenty five years after construction they were found to be clean and without odor.

**Early London sewerage** - A statute was passed in 1531 that regulated and controlled the sewerage practices of London until 1847. This same law prevailed in spite of the growth of the city and the subsequent problem resulting from a concentration of people in the city. The conditions prevailing in London in the early 19th century were appalling. Filth, stench and unsanitary surroundings were the rule rather than the exception.

In 1847 an epidemic of cholera broke out in India and started spreading westward. This served as the impetus to start a comprehensive study of conditions in London. A Royal Commission was formed and although some sewer construction work resulted, these sewers were poorly constructed and did not last for very long. Cholera broke out in 1849 and continued until 1854, finally proving conclusively the effect of polluted water and unsanitary conditions. More sweeping laws were passed in 1855, and with the appointment of J. W. Bazalgette as Chief Engineer began the elimination of London's problem.

The sewerage system of Paris was inaugurated as a result of the cholera epidemic of 1832. They were a little earlier than the London renaissance and did not have so much trouble due to administrative boundaries as did London.

Records of sewers in Paris date back to 1412 and were well known through the publication of a number of books in which the sewers of Paris were used for background. These sewers, as well as those built after 1833, were very large—about 6 ft. in
height and have been criticized very much in this respect but when
one realizes that they were designed to carry away all storm water
and street refuse as well, it is easier to see the reason for this
exceptionally large size.

Parisians insisted on having cesspools for disposal of their
sewage but their continued use soon made the whole subsoil of Paris
practically a cesspit and the resulting odors were very offensive.
This was one of the reasons for the passage of their newer ordin­
ance. At that time there was also the controversy of dry versus
water carriage. The former method consists of collecting excre­
mentitious matter in pails and removing it that way. In the latter
method it is flushed into sewers with water. The dry method is ad­
vantageous for those sections of a city whose topography prevents
the practical disposal of sewage into the mains. It is still used
to some extent in Europe but is quite unsanitary and is used in
only a small scale in the United States.

Cesspools are to be preferred to the dry method but they pre­
sent the problem of offensive odors and disease spreading by flies.
Here the sewage is dumped into holes and the liquid allowed to per­
colate through the soil, the solid matter being collected and dis­
posed of in some other place. The pollution of water supplies re­
sulting from their use has gradually brought about the deplacement
of this method.

Earlier practices, where the flushing or water carriage method
was used, was to dispose of the sewage in the easiest way possible.
In Europe the sewage was used extensively for irrigation purposes
or where convenient it was discharged into rivers or streams. Be­
cause of the large areas for irrigation and the cheapness of land in the United States these practices were prevalent here until the beginning of the 20th century. Large bodies of water and freely flowing streams presented a convenient way of disposing of an objectionable waste and hence sewerage practice here lagged far behind those of the more densely populated European countries.

In the United States almost all progress in sewage treatment has taken place during the past 50 years. True, there was an extensive sewerage program in Chicago in 1855 but aside from this, very little was done until the 1880's. The industry has progressed rapidly until in 1935, 91 percent of all urban population was served by sewered communities. Three methods, other than the earlier dilution method, are in general use here—broad irrigation, chemical precipitation and intermittent sand filtration. These came into use only after several years of discharging into large bodies of water or running streams had made the people realize that further treatment was necessary. Continued use of the dilution method resulted in contamination of these waters and general nuisances due to sludge and floating matter.

Part V

General Methods of Treatment

Irrigation. Irrigation as a method of treatment is quite old because of its ease of operation and convenience. There are two types, sewage farming and subsurface irrigation. In sewage farming the sewage is caused to flow over cultivated fields or to percolate through the ground and join the ground water. In subsurface irrigation the sewage is distributed beneath the surface and allowed to penetrate into the ground through openjointed pipes.
The latter method presents more problems and this treatment is confined to very small communities, hotels, resorts, etc.

As the sewage passes through the soil the larger particles are removed by straining and small particles are removed by sedimentation or adsorption onto the soil grains. The quantity of sewage that can be percolated through soil depends, of course, on the nature of the soil. Sandy soils have a much greater capacity than a clay which allows but a small amount of water to pass through it.

When the sewage is on the surface, oxygen is absorbed from the atmosphere while within the soil it is taken up from the ground air. As the sewage percolates through the soil it draws behind it fresh quantities of air and maintains aerobic conditions in the soil. This breathing of the soil is what makes possible the stabilization of the sewage. Continuous application of sewage to the soil is impossible because the oxygen must be replenished, hence a rest period has to be provided for. Best results are obtained on an open, sandy soil because of its greater permeability to both air and water.

The most important chemical process in the irrigation method is oxidation. This oxidation is accomplished by bacterial enzymes and carries the cycle of organic matter to a point where the end products are not only inoffensive but also become available as plant foods.

The fertilizing value of sewage has been largely overestimated. Nitrogen, to be used as a fertilizer, must be present in the form of nitrates, and this is very seldom the case in sewage as the nitrogen is usually in the form of nitrites.
These nitrites require nitrifying bacteria to convert them to the available nitrate condition. Conditions for the action of these bacteria are quite stringent—oxygen, mild temperature and presence of lime or other bases are essential. The phosphates and potash-es are present in only very small amounts; fats and soaps are also present and tend to clog the land causing what is known as "sewage sick" land. This "sewage sickness" can be prevented by screening or sedimentation. Another disadvantage is that fertilizers should be applied at certain stages in the crop rotation and this cannot be accomplished with sewage disposal as the sewage must be disposed of continuously.

The method of application is essentially the same as irrigation with water. A few exceptions are when an underdrainage system constructed of agricultural tile drains or large open ditches is installed. This is to provide for better aeration and removal of effluent to some waterway.

The area required for irrigation depends on the type of soil and previous treatment of the sewage. Common values given are 2,000 to 40,000 gals. per acre per day. A good average is 8,000 gals. but pre-settling will raise this figure somewhat. The nature of the effluent is essentially the same as that given artificial treatment, very good results being obtained on suitable soils.

The dangers to health arising from this sort of irrigation are not very great, but dairying and raising of produce to be consumed raw should not be permitted. Grazing is practiced in some places but its use should not be encouraged. Ground water pollution has not been proved but is a source of danger.
The foul odors emanating from an over-sewered farm present an objection as does the spreading of disease by the ever-present fly.

Disposal of sewage by irrigation is economical only where large tracts of land are available or where water is scarce. This treatment is still used in Europe and the British Isles but in the United States it is confined to the semi-arid land in the southwest. Here, the scarcity of water and suitability of the soil have combined to make this a satisfactory method of treatment.

**Dilution.** Dilution as a method of disposal had its inception when the communities started admitting human excreta into the drains built previously for carrying away storm water from the streets. This practice was prevalent in the United States until recently and in most European countries until the water pollution became too objectionable.

Sewage disposal by dilution is limited by the following factors:

**A. Hygienic considerations**

1. Contamination (introduction of bacteria and other substance which tend to make water unfit for domestic use) of
   
   (a) private and public water supplies.
   
   (b) natural ice.
   
   (c) shell fish.
   
   (d) water at bathing beaches.

2. Pollution (introduction of substances causing water to be objectionable in appearance or to give off
objectionable odors) resulting in

(a) nuisance affecting the public health and comfort.
(b) impairment of recreational facilities.

B. Esthetic Conditions, creation of conditions offensive to

1. The eye.
2. The sense of smell

C Economic consideration, damage to

1. Industrial water supplies.
2. Livestock.
3. Fish and the useful aquatic life.
4. Property with resulting depreciation of values.
5. Private and public river and harbor improvements and navigation, (such as silting due to sewage deposits.)

D. Legal considerations, interference with the rights of riparian owners.

Dilution is employed both for the disposal of raw sewage and of sewage treated artificially. The admission of untreated sewage to waterways is still used to a very large extent in this country. About 55 per cent of the sewered communities discharge their sewage untreated into inland waterways. The coastal cities discharge their sewage, largely untreated, into the Pacific or Atlantic Oceans.

When dilution is the only method of treatment, legal rights of property owners below the river outfall present another problem. This pollution of streams becomes of paramount importance to farmers in semi-arid states where the use of all of the available water is absolutely necessary. The communities have no right
to pollute the streams to such an extent that they are unfit for use to riparian owners. It is for this reason that the volume and nature of sewage to be discharged into streams should be known exactly, before dilution, so as to be able to predict its effect on the river.

When sewage is discharged into a running stream, self-purification takes place. Whipple defines self purification as "the natural process or combination of natural agencies that tends to render stable or innocuous foreign substances that find their way into water and so to restore the water to its natural condition of purity."

As stated above, sewage contains a certain amount of insoluble solids which, in slow-moving streams, settle to the bottom forming a sludge which decomposes under anaerobic conditions forming obnoxious gases. These anaerobic (bacteria that live in absence of oxygen) organisms liquefy and split up the more complex constituents forming a simpler compound that can be acted upon by the aerobic (bacteria that live in presence of oxygen) organisms forming more stable, simpler substances. Oxygen, to maintain aerobic conditions in the upper layer, is obtained from the atmosphere by absorption. The amount of oxygen absorbed depends upon velocity, turbulence and general condition of the stream.

Sunlight is also a valuable aid, as it acts as a disinfectant to destroy many objectionable bacteria and also by stimulating plant life which, in turn, by photosynthesis, give off oxygen and use up the carbon dioxide. Coagulation also takes place in the moving stream. This may be accomplished by the addition of industrial wastes which form a floc in the stream and settle down,
taking with it some of the colloidal and suspended matter.

The presence of bacteria and other living organisms is of prime importance in the self-purification. These bacteria, or their enzymes, convert the complex organic matter into simple substances that can be used up by the plankton (algae and fungi). Animal forms such as protozoa, rotifera and crustacea also destroy organic matter in much the same manner as bacteria. Rooted plants that are present utilize food products in the bottom sludge. Worms, insect larvae, etc., live on the sludge material. Fish may also be scavengers or live on plankton and insect larvae.

The changes that occur in a stream are progressive and to further understand the factors involved a brief discussion of these changes follows.

The first stage is one of degradation. To begin with, the sewage causes the water to become turbid, shutting out the sunlight, causing the green plants to die. Some types of fish, who relish fresh organic matter, gather around the outfall. Bacterial activity, in the oxidation of organic matter, soon diminishes the available oxygen supply making the stream unsuitable for life except in its lowest forms. These lower forms of life—saprophytes, bacteria, fungi and protozoa—develop in enormous numbers. Reaeration takes place but cannot keep pace with the deoxygenation. Sludge is also deposited to the bottom of the stream and anaerobic bacteria and little red worms (Limnodulus and Tubifex) appear here to work on the sludge and stabilize it. The stench arising in this period is quite high and undesirable. The oxygen content is decreased to about 40 per cent.

Then follows the period of active decomposition in which the
process of splitting up complex organic matter and oxidation is more active because of the presence of more oxygen in the water. Soluble, volatile and gaseous compounds are formed. In periods of low flow this process is slowed up and septic or anaerobic conditions may prevail. Foul odors arise, sludge from the bottom may be floated by gas inclusions and the stream becomes black. Further down the stream, as the organic matter is decreased, the bacteria die because of a lack of food supply, and decomposition ceases. The oxygen content begins to rise.

Following this period the stream begins to get clearer, the oxygen content rises slowly through reaeration and photosynthesis, nitrogen is converted to nitrites and nitrate, sulfur to sulfates, carbon to carbonates and small fish life begins to reappear. Pathogenic organism may still be present, however, because long periods of flow are required for their complete destruction.

The above processes are not very well defined in a stream and various factors such as temperature, comparative amounts of sewage and water, discharge of new wastes, entrance of cleaner water, etc., all enter into the scheme of things to interrupt or accelerate the purification.

Various means have been devised to further dilute the sewage in cases where the river flow is too low. The city of Chicago reversed the flow of the Chicago river by pumping Lake Michigan water. The city of Milwaukee also pumped water from Lake Michigan. Federal legislation has, however, prohibited this type of treatment now.

In case the city discharges the sewage into the ocean, essentially the same process takes place. The purification is slower,
However, in salt water due to the smaller dissolved oxygen content. Then, too, sludge seems to settle faster in brackish water, due perhaps to coagulation of the colloids. The sewage and sludge are dispersed throughout the sea water by the action of tides, and wind.

The standard of dilution requirement varies, of course, with the type of sewage and the type of stream into which it is being discharged. Some authorities use the B Coli count as the measure of dilution requirements. The most commonly accepted value of dilution are 3.5 to 6.0 cubic feet per second per 1,000 persons. Thus sewage is diluted from 25 to 1 to 60 to 1 and this seems to afford ample purification in an ordinary stream.

The process of irrigation and dilution are the treatments using natural methods. To get better results, faster, other more concentrated methods of artificial treatment are needed.

Sedimentation, usually preceded by screening is the simplest primary treatment. By sedimentation is meant the separation of suspended solids from the liquid. These insoluble solids are kept in suspension due to the velocity of the sewage and to make them settle, a period of quiescence is necessary. This is accomplished by admitting the sewage into large tanks of various designs.

These tanks are sometimes of a circular type with a bottom sloping towards the center. To keep the settled sludge in the center a scraper is located in the bottom which constantly scrapes the sludge towards the central outlet. Others are built rectangular in section with an endless chain scraping the bottom and thus drawing sludge all to one end. Another common type of design
provides for intermittent removal of sludge by draining the tank and removing sludge by hand. These generally have bottoms whose slope is of such a degree that the sludge will be concentrated at one end.

These sedimentation tanks may be of either the horizontal or vertical flow type. The horizontal flow is most commonly used in which the inlet is near the top and the sewage is spread out by peripheral flow or through several inlets. In the circular Dorrco type the sewage is admitted at the center and allowed to flow out in all directions. In the vertical flow type the inlet is near the bottom and the sewage percolates upward. This may also permit the use of agitation and subsequent mixture of sludge with incoming sewage for further classification.

The time of settling is of prime importance in these tanks depending, of course, on the nature of the influent. Hazen has developed a theory as to the amount of material removed under varying conditions. A detention period of from 1 to 3 hours is generally sufficient, but may have to be lengthened in some chemical precipitation tanks. This detention period regulates the size and number of tanks required for a plant. The circular tanks can vary from 20 ft. in diameter to 150 feet and from 9 to 15 feet deep. Rectangular tanks are generally built from 6 to 10 feet deep with a ratio of width to length of 1:2 to 1:6. It is desirable to keep the width small in comparison to the length in order to permit uniformity of distribution. Longitudinal baffles are sometimes used to obtain this distribution. The area is an important factor in sedimentation and Imhoff suggests 1 sq. ft. for each 600 gallons daily.
Weirs are sometimes used for the inlet to provide for uniform distribution but are undesirable because of sedimentation in the inlet channel. They are, however, used for the outlet. The best method seems to be with the use of several large inlets, baffled to prevent too much agitation.

Scumboards are also provided to scrape off the floating solids and the scum forming on top. Oil traps are an essential part of some installations.

These tanks are usually preceded by screens which take out the large floating materials such as twigs, rags, etc., but are rapidly being displaced by comminutors, a machine which through mechanical action, shreds these materials to a size where they do no damage to the pumps. Grit chambers are also installed ahead of sedimentation tanks. These are smaller than other tanks and reduce the velocity only to such a point that sand, dirt and other rapidly settling inert solids are removed.

Some installations provide for sludge digestion in conjunction with the sedimentation and these are called septic tanks. In the single-story septic tank relatively large sludge storage is provided so that the sludge will have ample time to digest and stabilize itself. The sewage is admitted horizontally and solids allowed to settle to the bottom where they remain and are digested by anaerobic bacteria. Gases are formed and they sometimes cause the sludge to be broken up and float, forming a scum at the top. Floating matter also collects in this top scum and limits the amount of gas that can escape. The effluent is generally septic and has a high oxygen demand. Odors from the tank are quite rank and the job of cleaning one of these tanks is quite a problem so
this type of treatment is falling into disuse except for small, usually private, installation.

The two-story septic tank was designed to provide for separation of the incoming sewage from the sludge. These are of two types, the Imhoff and Travis tanks. The essential difference between the two lies in the more rigid separation of sludge from sewage in Imhoff tanks. Travis admitted some fresh sewage, about 1/8 of the volume, to the sludge on the theory that it would admit new bacteria and wash out undesirable enzymes and toxic products of bacterial growth. Travis also used vertical splats or splines called colloiders which were for the purpose of collecting fine suspended matter on their surface.

Imhoff tanks are constructed so that only the sewage passes through the sedimentation tanks which are so designed as to permit the sludge to slide down the inclined bottom and fall into the sludge digestion chamber below. The slot is trapped so that the gases will not pass through it and into the sewage. The gases which are evolved arise through the portion of the sludge chamber which is extended above the top of the tank and are taken off here. Scum forms here the same as in single-story septic tanks. To give uniform distribution of sludge in the tank the direction of flow is reversed and transverse obstructions are avoided as far as possible. In order to prevent particles of sludge or scum from penetrating into the sedimentation tanks the sludge and scum must be maintained at a distance of at least 18 in. below and above the slots, respectively.

At times so much gas is sometimes produced in Imhoff tanks that the gas vent seems to foam or boil and so much sludge is
brought up that scum overflows the top of the vent. This seems to be due to acid conditions in the digesting sludge. Great care must also be taken to ensure the stagnant condition of the sludge else proper digestion is not obtained.

Separate sludge digestion is rapidly replacing the use of septic tanks. In this type of treatment the sludge is withdrawn from the sedimentation basins and transferred to another tank for storage and digestion. These tanks are usually heated to about 85°F. for best digestion as the bacterial action is best at this temperature. A means of mixing is also provided for. Two tanks are sometimes used in series, the first, or primary tank is mixed constantly while the secondary tank is allowed to remain stagnant. This primary mixing is to ensure complete dispersion of incoming sludge and to forestall the possibility of pocket formations. As the digested solids withdrawn from the tank contain less water than the influent, a provision is made to draw off the supernatant liquor and return it to the raw sewage inlet. A gas dome, sometimes floating on the sludge, is needed to draw off the gas evolved in the digestion which is utilized in gas furnaces and, in some cases, gas motors. Heating coils are put in the secondary digester to provide for constant temperature. At the beginning of sludge digestion it is necessary to seed the tanks with partially digested sludge from some other plant in order to start the cycle. Once started, the process is continuous. The size of the units will depend upon the amount of sludge present and the length of time required for complete digestion of the sludge. This will vary from 15 days to several months. The amount of sludge will vary also, depending upon the preliminary treatment.
Where chemical precipitation is employed the volume of sludge will be of the magnitude of 600 cubic feet per million gallons of sewage. In plain sedimentation it will vary from 100 to 200 cubic feet per million gallons. This sludge is composed of from 85 to 95 per cent water so it is easily handled in pumps. The volume of sludge from septic tanks is somewhat smaller than in plain sedimentation due to the changes in organic matter.

The actual changes that occur in sludge digestion are quite complicated and are not fully understood. However, the three stages have been outlined by Rudolf as follows:

**DIGESTION OF FRESH SEWAGE SOLIDS**
(Neither well-digested sludge nor lime being added)

I. Period of intensive acid production
(A) Materials attacked
   1. Easily available carbohydrates (sugars, soluble starches, cellulose)
   2. Soluble nitrogenous compounds.
(B) Organisms responsible: B. coli group, spore-forming anaerobes.
(C) Characteristics
   1. Increase in acidity
   2. Solids: grey, less than half on top
   3. Odors: putrefactive, H₂S
   4. Liquid: fairly clear to slightly turbid
   5. Slight coagulation of colloidal material with heat and alcohol
   6. Disappearance of protozoa
   7. Increasing B.O.D. values.
(D) Products
   1. Organic acids, H₂S
   2. Gas: comparatively large volume with high percentage of CO₂ and N₂
   3. Acid carbonates.
(E) pH range: 6.8 to 5.1
(F) Results
   1. Reduction of colon organisms
   2. Retardation of proteolysis

II. Period of acid regression or acid digestion
(A) Materials attacked
   1. Organic acids
   2. Nitrogenous compounds.
Organisms responsible: not definitely determined.

Characteristics
1. Prolongation of the low level of pH values followed by a slow rise
2. Solids: gray to yellowish-brown, half to four-fifths at top
3. Odors: H₂S, indol, onion (mercaptans)
4. Liquid: slightly turbid (milky) to yellow
5. Some to considerable coagulation of colloidal material with heat and alcohol
6. High B.O.D. values.

Products
1. Gas: small volume, with decreasing percentage of CO₂ and N₂; hydrogen formed
2. Ammonia compounds (amines, etc.)
3. Acid carbonates.

pH range: 5.1 to 6.6 or 6.8

Results
1. Gradual rise of pH curve
2. Acceleration of digestion
3. Foaming

III. Period of intensive digestion of more resistant materials.

Materials attacked
1. Nitrogenous materials
   (a) Proteins
   (b) Amino-acid, etc.
2. Ligno-cellulose (?)

Organisms responsible: spore-forming anaerobes, and fat-splitting organisms.

Characteristics
1. Decreased acidity
2. Increased alkalinity
3. Slowly rising pH curve
4. Solids: dark brown to black, half to none at top
5. Odors: odor associated with methane; tarry, rubber
6. Liquid: slightly turbid to clear
7. Some to no coagulation with heat, slight to no coagulation with alcohol
8. Reappearance of protozoa

Products
1. Ammonia and other protein degradation products
2. Organic acids
3. Gas: large volume with high percentage of CH₄, low CO₂ and N₂, and no H₂.

pH range: 6.9 to 7.4.

Results: sludge stable enough for disposal.

As shown in the above outline, the rate of reaction depends somewhat on the pH. The optimum condition seems to be at pH 7.2 - 7.3 but any value above 6.8 is quite good. The addition of lime
increases digestion not only by decreasing acidity but also in stimulating the growth of bacterial organisms responsible for digestion. The lime also produces a floc and precipitation of acid colloids. Certain industrial wastes have a marked effect on digestion. Grease decomposes slowly and hinders digestion. Small quantities of iron wastes seem to accelerate digestion, increase sedimentation and reduce odors, hence some plants admit iron in the form of chloride or sulfate to their digestion tanks.

Final disposal of the sludge is by burial, filling lowlands, incineration or sale as fertilizer. In case the sludge is to be burned or sold as fertilizer it must first be dewatered and this is done by filtering through a vacuum filter usually of the Oliver, American or United type. Previous treatment may be given the sludge by the addition of a chemical, as ferric chloride, for further flocculation and concentration. This filtration reduces the amount of water down to about 70-80 per cent and the sludge is then passed to the incinerator, dried by hot air, and fed into the furnace. Very few plants use sludge incineration but where land values are high and large quantities of sludge are dealt with it is advantageous. Minneapolis, Dearborn and Chicago use this method at present. If the sludge is to be sold for fertilizer it must be further dried to a water content of about 5 per cent and ground to pass a -10 mesh screen.

Filtration

Treatment of sewage by filtration is generally considered to be a secondary treatment following sedimentation, for the purpose of further oxidation of putrescible matter. The essential
features are the same as were shown for on-the-surface irrigation, i.e., providing for the distribution of the sewage over a very large surface, on the sand particles, so that oxidation can be more complete.

Filters are made up of three types—intermittent sand filters, contact beds and trickling filters. The intermittent sand filter was an early development in sewage treatment resulting from the use of on-the-surface irrigation. The sewage is applied intermittently to a depth of 2 or 3 inches over the entire bed and is allowed to pass through the sand which strains out the suspended matter in the sewage, oxidizing and stabilizing them. The sand for the beds must be of uniform size else clogging will occur. Finer material then .02 mm clogs rapidly and material coarser than 0.35 mm allows too rapid filtration, too deep penetration of fine solids and makes even distribution of doses over the bed difficult. The depth should be not less than 30 in. but for best results 4 feet is desirable and if coarse sand is used, a depth of 5 feet may have to be resorted to. The underdrain system is usually of vitrified pipe laid with joints about 3/8 in. apart and surrounded with drushed stone or gravel to prevent sand from sifting into it. Next to the pipe is a 3 inch layer of 1-2 inch material and next to this 3 inches of 1/4-1 inch material followed by a layer of gravel less than 1/4 inch material. If presettled sewage is applied to the filters they are capable of treating about 100,000 - 200,000 gallons per acre per day but if raw sewage is applied the allowable rate will be only about 50,000 gallons per acre per day. The beds are usually constructed in rectangular units of 1/4 to 1 acre each. The smaller sizes
are to permit flexibility and adequate rest periods, which must be provided for to keep the filter from becoming septic. For example, a 1 acre bed receiving 100,000 gallons in a single dose should not be used again for 24 hours. At least three beds and preferably four will be needed for proper rotation. Dosing is accomplished by a series of trenches or troughs running longitudinally with transverse troughs to distribute the sewage evenly. As the operation continues, septic conditions may develop and in this case a period of complete rest of at least 2 and preferably 4 weeks is needed. When the top part of the sand becomes clogged it must be removed manually and replaced with new, clean sand as it is not economical to wash the dirty sand. The use of intermittent sand filters results in a very clear effluent which is free from odor, has a low B.O.D. and is quite stable.

Contact beds are made up of broken stone, cinders or similar inert materials (called "Ballast") packed into water tight tanks or basins. The sewage is admitted, slowly, to the tanks, allowed to remain for awhile (2 hours') and is drained out leaving the ballast material exposed to the air. The theory is that when the sewage is applied, organic matter with a large bacterial population coats the ballast material and the bacteria act on the organic matter in the sewage. Then, when the bed is emptied, air penetrates it and permits the aerobic bacteria to decompose the organic matter on the ballast.

The ballast varies in size from 1/8 inch to 2 1/2 inches, the smaller size gives a better effluent but will clog in a few years while the larger size is not so troublesome but does not give the same high quality effluent. The depth of the bed will vary from
2 1/2 to 6 feet with 4 feet as a good average and usually not over 1/2 acre in extent. A 4 foot contact bed will be able to take care of from 400,000 to 600,000 gallons per acre per day while shallower beds should be dosed at a lower rate. The method of dosing is essentially the same as in the intermittent filter. The operation of the beds is quite simple and the only difficulty is in dosing mechanisms and the possibility of the ballast becoming too heavily loaded with humus-like matter in which case it will have to be cleaned.

This type of treatment is not quite so efficient as the intermittent filter but because of the smaller area required, and small pumping costs it was in widespread use for while. It is being superseded now, however, by the trickling filter.

The trickling filter was developed because of the low dosing rates and difficulty with clogging of the other types. The essential difference is that in trickling filters the sewage is sprayed out over the beds by means of nozzles or some other method of uniformly sprinkling the sewage. The nozzles and pipes must be cleaned frequently because of solid matter present even in the settled sewage. The dosage in the case of trickling filters is quite high, a 6 foot bed may take a dosage of 2,000,000 gallons per acre per day. The New Jersey State Health Department gives its requirement for trickling filter based on frequent dosing for short periods as this seems to be better than infrequently for long periods.

The beds are constructed of some inert material such as crushed stone, slag, coke or cinders of 1-2 inches. The depth of bed varies from 5 to 10 feet and sidewalls and the false bottom
(for underdrain) are of concrete. Means should be provided for flooding the bed for a 24 hour period to rid the bed of the Psychoda fly which is very prevalent.

The effluent from a trickling filter is usually quite turbid because of the material unloaded from the ballast. To further increase the efficiency of the plant a final settling basin should be provided for, to remove the sludge which will amount to about 500 gallons, of 90 to 95 per cent water, per million gallons of sewage. This final effluent then will be very clear, non-putrescible, and have a low B.O.D.

**Activated Sludge**

Perhaps one of the most important methods of sewage disposal today is the method using activated-sludge. The method of using aeration of sewage in tanks was investigated as early as 1882 by Dr. Angus Smith, and in 1912 and 1913 Clark and Gage at the Lawrence Experiment Station showed that in aerated sewage growths of organisms could be cultivated which would greatly increase the degree of purification obtained.

The essential principle of activated sludge is the introduction of sludge with the raw sewage in a tank provided with some means of aeration. The aeration is accomplished by blowing air through the sewage; by mechanically mixing the sewage, diffusing atmospheric air into it; or a combination of both methods. The sewage is then passed into a sedimentation basin where the sludge settles out and a part of it (sludge) returned to the aeration chamber, the rest being disposed of by digestion or some other means. As in the case of sludge digestion the process will have to be "seeded" with activated sludge from some other plant other-
wise the period of time to get started will be unduly long. The volume of sludge produced will be generally greater with this type of treatment as very good reduction of settleable solids is obtained and the floc formation is very large. One can expect about 15,000 gallons (98-99 per cent water) of sludge per million gallons of sewage. If the process is properly regulated the sludge can be kept in good condition continuously, on the other hand, if it becomes over- or under-aerated it must be reactivated by removal to separate tanks and aerated there for awhile. Regular reactivation is advantageous in some disposal plants because less air is needed for activation. The efficiency of an activated sludge plant is very high, the effluent has practically no turbidity, no odor and the B.O.D. is reduced up to 98 per cent.

**Chlorination**

Chlorination has only recently been developed as a method of treatment but is finding increased use due to the desirability of protecting water supplies, bathing beaches, shell fish, etc., by its disinfecting power. It has also been used to advantage in controlling odors at treatment works.

Chlorine may be applied in one of two ways—as liquid chlorine or bleaching powder. Chlorine is available in steel cylinders holding 100 to 150 pounds or in drums of 1 ton net under a high pressure. Various methods of controlling the feed are on the market—by pressure drop or pulsating displacement of water by chlorine gas. The gas is very soluble in water and rapidly diffuses throughout the sewage. Another method is that of first dissolving the gas in water and regulating the flow of the known strength solution. Chloride of lime, bleaching powder or calcuim chloro-
hypochlorite (CaClOCl) forms in water calcium hypochlorite \( \text{Ca(OCl)}_2 \) which is the disinfectant. The established usage is to designate the strength of the bleach in terms of "available chlorine" which is the quantity of chlorine liberated on decomposing the hypochlorite with acid. A common value is 33 1/3 per cent. This bleaching powder must first be put into solution before adding to the sewage and this requires from 12 to 24 hours mixing with 4 gallons water for each pound of bleaching powder. This solution is then fed into sewage constantly by means of an orifice feed tank or some other method of regulating feed. Because of the trouble and inconvenience of making solutions, etc., the use of chloride of lime is rapidly being displaced by liquid chlorine.

Much of the chlorine that is added is used up by the unstable organic matter in the sewage so enough must be added to give "residual" chlorine and provide a detention period for the chlorine to disinfect. The reason why chlorine destroys bacterial cells is not known but it is a fact that a detention period of more than 15 minutes is generally needed. Values of .2 to .5 PPM of residual chlorine after 10 to 15 minutes seems to be an adequate amount. This will require an original dosage of from 20 to 25 PPM on raw sewage, 15-20 PPM on settled sewage and 5 to 15 PPM for treated sewage. Another advantage of chlorination is the reduction of the B.O.D. due to the immediate oxidation of the unstable compounds.
SEWAGE TREATMENT AT GRAND FORKS

The sewage at Grand Forks is what can be designated as "Strong" sewage with high turbidity, total solids and B.O.D. The flow is from a city of 18,000 inhabitants varying from 500,000 gallons per day to 1,500,000 gallons per day with an average of approximately 850,000 gallons per day or 50 gallons per capita per day.

Water works sludge is fed into the sewage from the municipal water works plant. This sludge contains free lime, and the hydroxides and carbonates formed from the addition of sodium aluminate and soda ash. The flow of the sludge is kept quite constant during the day and as the flow of sewage varies considerably (see Figure [____]) it can be seen that the ratio of water sludge to sewage is not constant. It is planned to conduct a series of tests to determine the effectiveness of this sludge.

Proportionately large quantities of sludge enter the sewage between the hours of 8 and 9:30 A.M. This is because the sludge flows into the wet pit of the nearby lift station all night long and there is not sufficient sewage flow to fill the wet pit to a point where the pumps start working. Hence in the early morning when sewage starts flowing the first pumpage is composed largely of water works sludge. This gives the sewage a high pH, large flocc formation and a milky appearance.

K. W. Riley (47) gives the following average characteristics of sewage.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Influent</th>
<th>Effluent</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>63</td>
<td>63</td>
<td></td>
</tr>
</tbody>
</table>
Influent | Effluent | % Reduction
---|---|---
Settleable Solids, per cent | 3.2 | .08 | 98
Turbidity (USGS standard) | 1700 PPM | 380 PPM | 74
Suspended solids | 1570 " | 115 " | 93
Dissolved solids | 1400 " | 1225 " | 12
Volatile solids | 582 " | 194 " | 61
Total solids | 3110 " | 1381 " | 57
pH (Coleman Electrometer) | 8.4 | 8.2 |
Alkalinity, Total PPM CaCO₃ | 335 | 321 |
B.O.D. 5-day | 585 PPM | 292 PPM | 50
Dissolved Oxygen | 0 | 0 |
Chlorine Demand | 29 PPM | 19 PPM | 35

The above figures are, of course, average values and as can be expected large deviations are encountered. For instance, in the spring when the flow is increased markedly and again, during the summer months when the University of North Dakota, having about 2000 students, is not in session.

This sewage is collected and transported through mains to 6 lift stations and thence to the main lift station having 3 centrifugal pumps (capacity 1.7 million gallons per day each) from where it is pumped to the sewage treatment plant located 1 1/2 miles northeast of the city. The sewage treatment plant was designed for an average flow of 900,000 gallons per day and a maximum of 2,000,000 gallons per day. It provides for chemical treatment, Sedimentation and separate sludge digestion with facilities for chlorination when needed.

A line diagram of the plant is shown in Figure 2. Sewage enters through an 18 inch main and goes through a recording venturi meter. From here it passes through a bar screen where rubbish is removed and thence through a grit chamber where the heavier, inert, solids are removed. The mixing chamber 16' x 16' x 11' is next and the sewage is retained here for about 30 minutes.
1 - LABORATORY AND CONTROL ROOM
2 - MIXING CHAMBER - AERATION
3 - GRIT CHAMBER
4 - BAR SCREEN
5 - SLUDGE PUMPS

SEWAGE TREATMENT PLANT
GRAND FORKS, N. DAK.

Figure No. 2
Compressed air is used as the mixing medium and a certain degree of aeration is obtained, the immediate oxygen demand being reduced about 30%. When needed, chemicals may be added at this mixing chamber. From this chamber the sewage flows by gravity to two Doroco circular clarifiers (35 feet in diameter, 9 feet deep) run in parallel. This provides for a detention period of about 90 minutes and the sludge is removed intermittently by two sludge pumps (capacity 100 gal. per minute) located in the building proper. The clarified effluent is allowed to run into the Red River of the North.

The sludge is pumped to two sludge digestion tanks operated in series. The tanks are each 40 feet in diameter and 30 feet deep providing a detention period of about 80 days. The first, or primary, tank is provided with a stirrer which keeps the sludge stirred constantly and has a stationary gas collecting dome. The sludge is transferred to the secondary tank intermittently where it is allowed to remain dormant for the duration of the detention period. This tank is equipped with a floating dome in which the gas is collected and carried to a gas fired furnace in the control house which provides heat for the control house and garage as well as hot water for the coils in the primary digester. The primary digester is kept at a constant temperature of 85°F. The supernatant liquor from the secondary digester is returned to the incoming sewage and the settled, digested sludge, containing 45-50% vehicle water is run out onto drying beds, 300 feet by 100 feet, from where it is removed to a more remote district.

The sludge is pumped at the rate of about 10,000 gallons per day. It contains 75% vehicle water, 92% total water, 44% volatile
matter in the solids, 50% ash, and 6% oils and grease. This digestion gives about 10,000 cubic feet of gas per day having a B.t.u. value of approximately 550 providing more than enough heat to heat the buildings and primary digester.

This plant has an excellent laboratory in connection containing standard equipment such as Jackson turbidimeter, Coleman glass electrode, pH meter, Frigidaire 20° incubator, Sargent 37° incubator, centrifuge, autoclave, drying ovens, Bausch and Lomb microscope, staining equipment for bacteriological examination and other equipment, with chemicals, necessary for complete examination of sewage.

This plant was built in 1935-36 with P.W.A. and local funds at a cost of approximately $300,000 and has been operating since February 10, 1937. The total cost of treatment averages $63.16 per million gallons or $2.90 per 1000 population per day. The operating costs average $13.53 per million gallons.

The results obtained from this type of treatment, as can be seen above, are somewhat better than could be obtained with plain sedimentation, due to the use of water works sludge. However, it is felt that too much of the sludge is being used and the digesters are being overloaded, hence an attempt is being made to regulate the addition of this sludge. Although facilities are available for chemical treatment and for chlorination this has not been resorted to as it is felt that sufficient treatment is being given the sewage so as not to grossly pollute the river.
Review of the Literature

As stated previously, the use of chemical precipitation appeared early in the development of sewage treatment. Alum, lime and the iron salts, chloride and sulfate, were used much in the same manner as was prevalent in water treatment. The cost of chemicals and difficulty of disposing of the large volume of sludge together with the rapid progress made in biological methods of treatment combined to cause the decline of this type of treatment. Recently, however, chemical precipitation has begun to find its place in the sewage disposal. According to Steel (9) this has been due largely to: (a) the decrease in cost of chemicals, particularly of the ferric salts which seem to be most efficient, (b) better understanding of floc formation and the factors effecting it, (c) the development of sludge filtration and processing which overcome, in part, the difficulty of greater sludge bulk, and (d) the development of sludge collecting machinery in sedimentation tanks. Potter (10) lists more advantages as: (1) comparatively small odor nuisance permitting building in or near residence district and avoiding the necessity of constructing long and costly lines of sewers, (2) comparatively small area needed for building plant also (3) flexibility of use in caring for variations in amount of sewage as flexible in treating industrial wastes which often get into the sanitary system intermittently and disrupt the operation of biological plants and (4) chemical precipitation is quantitative, i.e., results are proportional to the amount of chemicals added and any degree of purification may be obtained. Hendon (11) reports that chemical precipitation gave results comparable
to intermittent sand filters and were more flexible. This was an added advantage in that complete treatment was necessary only at certain intermittent intervals. If sand filters were used they would have to be constructed of such large size to take care of full load and would be running at only 10-15 per cent capacity at times. Damoose (12) gives rather complete cost data showing economy of chemical precipitation and reports that results comparable to other means of secondary treatment were obtained. He obtained a 50% increase in removal of suspended solids and 40% increase in B.O.D. reduction over the use of plain sedimentation. Chemical precipitation has its limitations, however, and Bach (13) points out that albuminoids and other putrescible organic matter can be destroyed only by biological methods but of course good clarification is obtained and some of the albuminoids are carried down with the floc by adsorption.

Mechanism of chemical precipitation

The process of chemical precipitation depends upon the formation of a large insoluble precipitate, usually the hydroxide of iron or aluminum, which on settling out, carries down with it by sorption and mechanical entrainment, most of the suspended and colloidal substances present in sewage.

The equipment that is necessary for a chemical treatment plant consists of the following: (1) Chemical feed machine—these may be of either the dry feed or set feed types and various methods are on the market for controlling the amount of chemicals added which will vary greatly depending upon the nature of the sewage (2) Mixing chamber—usually a flash mix chamber is provided for where the chemical is thoroughly mixed with the incoming sewage.
This may be followed by a chamber provided with rotating paddles which further mix the floe formed more intimately with the sewage. This mixing may be done by diffused air and Rudolfs (12) states that better results are obtained with this method. The detention period varies with the type and amount of chemical used but a period of 30 minutes will generally suffice. Some authors claim 10-15 minutes while others insist on 1-2 hours mixing. When return sludge is used a longer mixing period is usually employed. Mixing is generally followed by sedimentation, the mechanics of which was explained in the first part of this paper. The effluent from here is usually stable enough to be discharged into the river but further treatment as filtration or chlorination may be necessary.

Since chemical precipitation removes more suspended matter it will produce more sludge than plain sedimentation. The chemical itself forms a floc which is incorporated in the sludge and adds to its bulk. The dry solids in the sludge may therefore be double or more than those of plain sludge. This disadvantage is offset by the smaller amount of water content, say only 90 as compared with 95 per cent for plain raw sludge. The volume of sludge may possibly be as high as 0.5 per cent of the volume of sewage treated.

Effect on sludge digestion—Streander (15) reports that if the sewage is coagulated on the acid side good aid is given to sludge digestion because it is in this range that the anaerobic decomposition is greatest. If, however, the coagulation is in the high pH range then sludge digestion is hindered and other methods such as incineration should be resorted to. The presence
of alum floc does not seem to alter sludge digestion very much but Rudolf's (16) states that the sludge formed with ferric salts digests much better than without the iron. He points out there is a marked increase in gas production if sludge contains ferric chloride. It has been shown by several investigators that iron compounds have a very marked effect on bacterial activity and a definite effect on the enzymes of bacteria. It is contended that under certain conditions certain groups of organisms may be stimulated and others repressed; that the degradation of organic matter may proceed along different lines; and that intermediate decomposition products may react with the chemical added and "locked-up". This locked-up material may be broken down when a new flora has developed. A new flora can be built up or changes in equilibrium made to meet changed conditions. The building up of a new flora can be accomplished by different environmental factors. It becomes clear that the flora can be changed to meet changed conditions in sludge digestion by addition of more and different chemicals.

Kinds of chemicals used.

Alum has not received a very widespread use in sewage treatment but has very recently been receiving considerable attention. Gevett (17) suggests the use of alum for its all-around ability as a sewage coagulant. It can be used alone, without lime, at pH 6.7 and in some cases no pH control is needed, hence the application is simplified greatly. When alum is added to water or sewage containing bicarbonate or CaCO₃ the following reaction takes place:

\[
2\text{Al}_2(\text{SO}_4)_3 + 6\text{Ca}(	ext{HCO}_3)\_2 \rightarrow 6\text{CaSO}_4 + 4\text{Al(OH)}_3 + 12\text{CO}_2.
\]
If insufficient quantities of the bicarbonate are present then calcium oxide (CaO) is added to produce enough of the hydroxyl ion to cause precipitation. One-half grain per gallon of alkalinity, as CaCO₃, is sufficient to react with 1 grain per gallon of alum.

Considerable work has been done on the phenomenon of alum coagulation but most of the work has been confined to water purification. However, since sewage is composed mainly of water, most of the conclusions reached can be applied to sewage treatment.

pH control of the water or sewage is of prime importance in the formation of an alum floc. Theriault and Clark (18) made quite an extensive study on the effect of pH and found the optimum condition for floc formation, measured as being the least time necessary for the first appearance of precipitate, to be at the isoelectric point of pH 5.5. At higher and lower values the hydroxide was dissolved by either the acid or alkali. The pH range of floc formation was found to be wider with increasing dosages of alum and with increasing salt content. They developed an expression for the determination of flocculation time as follows:

\[ t = K_1 e^{K_2 X^2} \]

When \( t \) = flocculation time expressed in minutes.

\( X = \text{deviation of pH value from optimum} = \text{pH} - \text{pH}_0 \) when \( \text{pH}_0 = 5.5 \)

\( K_2 = \text{A constant for given buffer strength} \)

\( K_1 = \text{A constant for a given concentration of alum} \)

\( e = \text{base of naperian Logarithms.} \)

The effect of anions on the alum floc was investigated by Miller (19) and he showed that they have considerable effect on flocculation. The presence of the sulfate and other bivalent
ions widens the range of rapid floc formation. This effect even much more marked than with the univalent chloride ion. This fact was further borne out by Black, Rice, and Bartow (20) who point out that this effect follows, qualitatively, at least, Schultze's law of increasing valency. Miller (19) points out that although the most rapid floc formation, as found by Theriault and Clark (18) is at pH 5.5 it does not follow that this zone should coincide with the formation of floc in presence of a strong anion. It was found that most rapid floc formation occurred at 8.5 in presence of the sulfate ion. At low pH a colloidal suspension is formed which can be flocculated by the addition of sulfate ion. As the pH increases it requires less and less sulfate ion to cause floculation until at pH 9.0 flocculation occurs spontaneously. These experiments were with aluminum chloride forming the alum floc.

Miller (19) further emphasizes the fact that the complex substance called alum floc is not aluminum hydroxide but a complex colloidal material which depends for coagulation on the presence of negative ions. In the case where oxalate was investigated, for example, in passing from lower to higher pH values, the solutions become more and more opalescent, indicating that there is one insoluble substance present in the highly dispersed colloidal state. It is not until the pH rises to a value of 8.8 that flocculation occurs.

The lack of agreement in the literature on the hydrogen ion concentration of best floc formation is undoubtedly due to the variation in quantity and kind of anion present. We know now, for example, that the presence of silica in water has a very marked
effect on coagulation with alum and changes the pH requirements considerably.

Miller (21) has pointed out the similarity between the adsorption by aluminum hydrate and systems in which there are reasons to believe a solid solution system exists. Further, because the reciprocal displacement of negative ions in the alum floc follows the law of distribution between solutions, he considers the adsorption by aluminum hydrate to be a solid solution phenomenon. Rudolfs and Gehm (22) in experiments on the effect of stirring in chemical coagulation state that visual observation leads to the belief that suspended solids removal is by aggregation of finely divided and pseudo-colloidal material because the stirred and settled solids were more free of the readily visible non-settleable solids than the settled samples. This agglomeration was merely physical since removals of turbidity occurred in atmospheres of nitrogen, as well as other gases, which would be inimical to aerobic flocculating activity. However, it is possible that clotting enzymes present in sewage play a role. Carbon dioxide and hydrogen peroxide which are deleterious to aerobic activity did not show greatly different results from nitrogen.

The effect of sodium silicate on alum floc formation will be discussed further on in this paper.

The use of alum, as stated before, is not very general but finds application in some plants. W. A. Hardenbergh (23) describes the use of alum in the sewage disposal plants at Liberty, New York and Ridgewood, New Jersey. The dosage used was about 80 PPM with a raw sewage where BOD varied from 200-250 PPM.
Larger dosages were needed when trade wastes were being added. This dosage resulted in a reduction of 70% on the BOD, entire removal of suspended matter and the effluent was uniformly without turbidity. The alum had no effect on sludge or sludge digestion except to increase its volume. A dry-feed machine was used to feed the alum, the point of application being fairly close to the settling basins as the floc forms rapidly and it is best to allow it to settle without undue agitation. The floc is not very fragile, however, and is not effected much by travel. Good coagulation was obtained in the pH range of 5.4 to 8.9. In higher ranges than this it is suggested that sulfuric acid be used to adjust the pH.

Iron compounds have been used more extensively in chemical treatment because of their lower cost. Copperas (ferrous sulfate) is obtained cheaply from iron mills. Recently, chlorinated copperas has come to be used considerably. In this process the iron is oxidized to the ferric state by solutions of chlorine and much better results are obtained than using the ferrous salt. Ferric chloride can be prepared quite cheaply at the disposal plant by treating scrap or waste iron with a chlorine solution. Yaffe (24) describes a process for preparing ferric chloride in which the problem of removing the fine film of hydrogen bubbles which coat the iron and prevent the chlorine from gaining access to it was released by the mere expedient of introducing alternate layers of used tin cans. This coating of hydrogen over the iron slows up and prevents the action of chlorine, forming ferric chloride, considerably and its removal is necessary.
E. F. Eldridge (25) states that where ferric chloride is added to water in the normal pH range hydrolysis takes place resulting in the formation of hydrates of ferric oxide often wrongly termed ferric hydroxide. There are a number of these hydrates. The one probably predominating in the concentrations used in water treatment is Fe₂O₃·H₂O. Whether or not this flocculates will depend on a number of factors. This colloid carries a positive charge in the acid range and a negative charge in the alkaline. The transition comes at the isoelectric point between the pH range of 6.5 and 8.5. The positive charge is due to the adsorbed hydrogen ion and increases as the hydrogen ion, low pH, increases. Coagulation of this colloid can be accomplished by (1) an adjustment of pH, (2) neutralization of the charge by the addition of a colloid of opposite charge, (3) neutralization of the charge by an ion of strongly opposite charge. He also noted the effect of the anion and different colloidal particles in the water which would affect the floe formation. If negative ions are added the pH range of flocculation is extended towards the acid side and if positive ions are added it is extended towards the alkaline side, and the higher the valency of the ion the more pronounced its effect. In general, it might be said that the action of the iron salts and alum closely parallel each other.

Rudolfs and Gehm (26) made an extensive study of the effect of pH on ferric chloride coagulation of sewages of different strength, septicity, and quantity. They found that there are two general zones of optimum classification—namely, 2.5 to 3.5 and 9.5 to 10.5. These zones are modified or shifted with varia-
tion in septicity, quantity and type of trade waste and quantity of iron used. Weak and rather fresh sewage responded to treat-
ment in the most clear-cut manner. Two optima were found at 3.5 and 10.0 while the minimum remained constant between 6.5 and 7.5. With increase in strength of sewage (but fresh) the pH at which the minimum removal occurred was moved slightly to the acid side while the optima were at somewhat lower and higher pH values than for weakest sewage. With a further increase in strength of sewage (rather stale) the removal between pH values 4.5 to 10.0 was not greatly increased so that the maximum removals occurred only at pH values of 2.5 and 11.0. The type of curve remained, in general, the same. Very stale and strong sewage exhibits the same general curve but the trend gradually changes with increase in strength of sewage until with a very strong sewage, containing much finely divided material, the curve flattens. Best removals were on the acid side between 2.5 and 3.5 but larger amounts of acid cause a peptizing effect and the turbidity increased. The effect varies with the nature of the sewage. The amount of finely divided substances in sewage is an important factor in the percentage removed and there is a medium concentration at which best removal occurs. In addition to this, the soluble portion of the sewage may have a decided effect on the coagulation. Furthermore, such factors as iron salt deficiency in the case of strong sewage, degree of fineness of material in weak sewage, etc., play a role in reduc-
ing the removals of absolute quantities of suspended solids as well as percentages and tend to shift the pH range of optimum clarification to one side or the other.
Ferric sulfate is easily hydrolyzed and Holton and Bean (27) suggest the use of at least one per cent solution to prevent this. They also point out that hydroxyl alkalinity should not be added prior to the addition of the coagulant since the addition of hydroxyl ions tends to stabilize the negatively charged colloids. Since treatment to a high pH produces the true hydrous ferric oxide floc which is dense, quickly settling and not easily broken, if precipitated at low pH the floc is delicate and easily peptized.

The use of iron compounds gives very good results at a low cost. Yaffe (28) reports removal of suspended solids and 64% reduction of BOD as well as a slight reduction of BOD in soluble portion with a dosage of 72 pounds per mg (9 PPM) at a cost of 4 cents per pound for the ferric chloride. Complete cost data of iron salts for sewage and sludge treatment is given by Baumgartner (29).

The use of chemicals in sewage disposal plants brings up the problem of handling them and Hoskins (28) outlines the use of rubber-lined equipment to prevent the corrosion of pipes, tanks, chamber etc. by the chemicals used.

The use of returned sludge is advisable in some chemical treatment plants but Nesmeianoff (30) states that his results indicate that aluminum and iron salts cannot be considered as an effective means for increasing the activity of activated sludge. Rudolfs and Gehm (31) point out the much better clarification obtained when a part of the sludge is returned. Excessive amounts of return sludge do not seem to be particularly beneficial in that only a definite amount of suspended solids can be removed anyway and large quantities have no appreciable effect other than to decrease the
length of time of stirring and sedimentation. Greater amounts of return sludge are needed when dealing with lime-ferric chloride sludge than with alum or plain ferric chloride because (1) of presence of calcium carbonate which is hard to remove and (2) lesser bulk of the sludge and (3) its lower absorptive power. The addition of more coagulant, about 1 to 5 PPM, has about the same effect as returning a part of the sludge.

More Recent Development in Chemical Precipitation

Putnam Process - J. J. McCarthy (32) describes briefly the Putnam process which consists, essentially, of: chemical coagulation using lime, carbon and ferric coagulant, return sludge and mechanical agitation. The settled effluent is filtered through a rapid sand filter. Results claimed are 99% removal of settleable solids and 89% reduction of B.O.D. The sludge is conditioned and vacuum filtered, fed into a heated retort in which it is destructively distilled to yield a gas, (used to fire the retort), a distillate and carbon which is used in the coagulation stage of the process. Total detention period is generally less than an hour and a half and another added advantage is the excess distillate and carbon have by-product values.

Guggenheim Process - Gleason and Loonan (33) claim substantial saving in cost of construction and maintenance of a process developed by Guggenheim Brothers. This process consists of removal of the suspended solids by coagulation with iron compound and settling in the form of sludge. The sludge is filtered and disposed of by incineration. Then the effluent is passed through a specially prepared zeolite bed. In this operation the basic nitrogen, principally
ammonia, is exchanged for the sodium in the zeolite. This gives a high concentration of ammonia in a comparatively small volume and enables the recovery of the ammonia from the brine solution used for regeneration. The attendant group of carbon, hydrogen, sulfur, etc., are also removed to some extent in the zeolite bed. Very good results are claimed for this type of treatment and they show 99% removal of BOD, settleable solids, and Bacteria Count.

Upton and Burwell (34) show that titanium salt alone or with ferric sulfate proved to coagulate better than alum at low temperature. It forms a heavier and bulkier floc more rapidly and coagulates over a wide range than alum. At the present time the cost of the chemical prohibits its use commercially.

Gurham (35) shows further refinements in water coagulation using activated alum and Blockerlum. It is possible that these types of treatment will find use in Sewage treatment so a short description of them will be given.

Standard activated alum is regular alum containing very finely ground siliceous material which aids floc formation producing greater efficiency in many cases. It also contains a small percentage of titanium salts. The floc formed is heavy and settled rapidly due to the siliceous particles in it.

Blackalum is made from standard activated alum and produces desirable refinements to coagulation by the powdered activated carbon in it, acting as nuclei for the formation of the floc. There is also some other phenomena of a physical chemical nature taking place on the surface of the carbon particle when it hits the surface of the water mixed with alum. Perhaps a certain amount of alum dust becomes attached to the highly adsorptive carbon particle.
and when fed into the water in such a manner rapidly dissolves forming momentarily a zone of highly concentrated alumina and acid around the carbon where the aluminum hydrate microcrystal is caused to form first. The speed of floc formation of blackalum is a noticeable attribute and further work is necessary to explain this phenomenon. Blacalum is the only coagulant possessing marked taste and odor removal. Cook (36) Reid (37) and Stuart (38) report on the advantages of Blackalum in giving better taste and odor control and better operation of filter beds.

Bentonite Coagulation
Experimental Procedure

John R. Baylis\textsuperscript{8,9} reported on the aid given to coagulation of water by soluble silicates using alum as the coagulant. The present problem is to apply this type of treatment to sewage noting its effect on B.O.D. reduction, removal of settleable solids, clarification, etc.

Baylis\textsuperscript{8} gives the following instructions for the preparation of active silicate solutions:

"Silicate solutions may be prepared by diluting sodium silicate with water and nearly neutralizing the alkali with sulfuric acid. The most beneficial solutions seem to be those containing 1.0 to 1.5 per cent of $\text{SiO}_2$ at the time of preparation. Such solutions may be diluted after they have reached the stage in which they give maximum aid to coagulation, but to dilute them earlier seems to interfere with their development to the stage where they give maximum aid. The solutions do not become active immediately, but an interval of from a few minutes to several hours is required, depending on conditions, for their helpful properties to develop. Solutions containing less than about 0.5 per cent $\text{SiO}_2$ usually cannot be made very active, or at least the procedure which was used did not produce very active solutions.

"Solutions which will aid coagulation probably can be prepared from most any of the grades of sodium silicate, but as the silica is the substance which gives the aid, a material high in silica probably is the best. A grade of material known as 42° Baume sodium silicate, which contains 9.0 to 9.5 per cent Na\textsubscript{2}O
and 29.0 to 30.0 SiO₂ has worked satisfactorily. The procedure which will be given for preparing solutions of acid-treated sodium silicate applies to the solutions which will aid coagulation when aluminum sulfate is used as the coagulant. The iron compounds also are aided by such solutions, but it is not known if the solutions most suited for aluminum sulfate will give maximum aid to the iron coagulants. This will be investigated more fully at a later date.

The SiO₂ Content of the Sodium Silicate

"Determine the SiO₂ content of the sodium silicate. The manufacturer may be able to furnish the percentage, otherwise a chemical test on the material is essential. Add about 0.7 cc. of the sodium silicate to a weighed platinum dish, and determine the weight. Dilute with distilled water to about 25 cc. and add 4 to 5 cc. of hydrochloric acid. Evaporate to dryness on a water bath then place on a hot plate, or in a drying oven, at 110 to 120 deg. C. for 15 to 20 minutes. Add a little water and several drops of hydrochloric acid, allow to stand a few minutes and transfer the solution and precipitate to a filter paper. Wash the precipitate thoroughly. Add several cc. of hydrochloric acid to the filtrate and again evaporate to dryness. Filter in the same manner as before, using a separate filter paper, and wash the precipitate, if any, thoroughly. Combine the two filter papers in a platinum dish and ignite in a muffle furnace. If great accuracy is not essential, one evaporation to dryness is sufficient. To avoid loss of some of the silica particles in burning the filter paper, the furnace door should not be opened until it is evident all the volatile matter has been driven off."
Cool, weigh, and add sufficient hydrofluoric acid to vola-
tilize the silica. After the excess hydrofluoric acid is driven
off by heating on the hot plate, again ignite in the muffle fur-
nace, cool, and weigh. The loss in weight is the SiO₂. The per-
centage of SiO₂ in the sodium silicate then may be computed.

Dilute Silicate Solution

"Assume that it is desired to produce a solution containing
1.5 per cent of SiO₂, or 0.015 gram of SiO₂ per cc. of solution.
Should the sodium silicate contain 29.0 per cent of SiO₂, 51.72
grams of the material diluted to 1 liter will give a solution
containing 0.015 gram of SiO₂ per cc. As the solution has to be
nearly neutralized with acid it should be made stronger than 1.5
per cent SiO₂ at first. For convenience in measuring and cal-
culating, prepare the solution to contain 0.030 gram SiO₂ per cc.,
which is double strength.

Sulfuric Acid Solution

"Prepare a solution of sulfuric acid of some known normality.
For small amounts of acid-treated sodium silicate, such as would
be prepared for conducting laboratory experiments, a solution of
acid exactly normal is preferred, though stronger solutions may
be used.

Preparation of Acid-Treated Sodium Silicate Solution

"Dilute 50 cc. of the silicate solution containing 0.030
gram per cc. to about 85 cc. with distilled water. Add two drops
of phenolphthalein solution, then add the N/1 sulfuric acid with
the aid of a burette until the pink color of the solution dis-
appears. Add the acid rapidly at first, then drop by drop until
the time required for the pink color to reappear is 10 to 15
seconds. The solution should be agitated during the addition of
the acid. Note the amount of N/l acid used. Dilute the solution
to 100 cc. A 10-cc. portion of this acid-treated sodium silicate
is diluted to 50 cc. with distilled water. Add two or three drops
of methyl orange solution and titrate with N/50 sulfuric acid until
the color begins to turn pink. Titrate to the same shade of color
used in making alkalinity tests on water. Record the total number
of cc. of N/50 acid required.

If the solution is properly acidified, 11 to 13 cc. of the N/50
acid is required to make the 10-cc. portion of the silicate solu-
tion slightly pink to methyl orange. Assume that 15.0 cc. of the
N/50 acid are required, and that it is desired to adjust so that
only 12-cc. are required. This is a difference of 3.0 cc. of the
acid for the 10-cc. portion, or 30 cc. for 100 cc. Thirty cc. of
N/50 acid is equivalent to 0.6 cc. of N/l acid, so 0.6 cc. more of
the N/l acid than was used should bring the solution to the desired
alkalinity. This should be tried on another portion of the sodium
silicate, omitting the addition of the phenolphthalein. If the
solution is still slightly more alkaline than desired, a third
trial should result in the addition of the proper amount of N/l
acid. If the solution is too acid a small amount of sodium silicate
should be added or another solution prepared. Usually the second
solution is so close there is no need to prepare another one. For
one of the 42° Baume sodium silicates used in some of the experiments,
12.6 cc. of N/l sulfuric acid were required to produce a solution
in which 12 cc. of N/50 acid made the 10 cc portion slightly acid
to methyl orange.
"Thought has been given to a term with which to designate the acid-treated solutions. Perhaps they should be known by their alkalinity, expressed in the manner used in designating the alkalinity of water. A solution in which 12 cc. of the N/50 acid is required to make a 10 cc. portion slightly pink to methyl orange should be designated a 1200 alkalinity solution, and one requiring 12.8 cc. a 1280 alkalinity solution. The main reason for using alkalinity is that most water treatment plant operators are familiar with the alkalinity test.

"Efforts have been made to use pH as a measure of the equilibrium of the solution, but the pH value changes. It may be 8.0 to 8.5 a few minutes after the acid is added, and change to a pH of 9.5 to 10.0 several hours afterwards. A relation between the pH and alkalinity may be found which will give better interpretation of the activity of the solution, though this relation has not been studied as yet. One reason why it was difficult to prepare suitable carbonated solutions was that no exact measure of the equilibrium could be made. The alkalinity test is not suitable for a carbonated solution.

"The statement in a previous paragraph that the alkalinity of the solution should be between 1100 and 1300 is not to convey the impression that solutions within this limit are the same. A solution having an alkalinity of 1100 may form a jelly within several hours, whereas a solution having an alkalinity of 1300 probably will stand several weeks before it changes to a jelly. Some of the characteristics of the solutions with various alkalinitles are given in another paragraph."
"When the solution is to be kept for several days, the alkalinity should be between 1250 and 1350. Unfortunately such a solution requires several hours to develop to the condition which gives maximum aid to coagulation. If the solution is to be used the same day it is prepared, the alkalinity should be between 1100 and 1200. This lower alkalinity solution will give excellent aid to coagulation within one to two hours after its preparation."

This procedure was followed quite rigidly. The first tests were run using C.P. Sodium metasilicate, Na$_2$SiO$_3$. 9 H$_2$O or Na$_2$O.1 SiO$_2$ . 9H$_2$O, having a SiO$_2$ content of 21%. The Na$_2$O content of this salt is much higher than the commercial water glass hence more acid was needed than with water glass. About 40 cc. of 0.1 N H$_2$SO$_4$ were needed to give an alkalinity of about 1200 hence the first tests were run using .75% SiO$_2$. The results were not very encouraging, indeed, in some cases deflocculation was the case. However, with solutions of lower alkalinity good results were obtained. Another reason for the use of weaker solutions was because these C.P. metasilicate solutions seemed to jell faster due, perhaps, to the larger proportion of Na$_2$SO$_4$ formed. When the solution was 1.5% SiO$_2$ approximately the same results were obtained as with the subsequent tests with commercial water glass.

The method given by Baylis (8) for determination of the amount of SiO$_2$ in the water glass was used and was found to be 30.0% SiO$_2$ and 9.5% Na$_2$O conforming to the general formula Na$_2$O . 3.25 SiO$_2$. 100 grams of this commercial water glass was diluted to 1 liter giving a 3% solution. This solution was made up every week because the SiO$_2$ seemed to settle out giving a weaker solution.
RELATIONSHIP OF ALKALINITY TO pH
In most cases these tests were run using the pH designation instead of alkalinity, since the alkalinity factor changes just as much as the pH value no advantage could be seen in using it. The correlation between pH and alkalinity is shown in Fig. 3, where pH values are plotted against alkalinity. A Coleman glass electrode pH electrometer was used to determine the value of pH to the closest .05 unit. In passing it might be well to mention the effect of the silicate solution on the glass electrode. A scale is formed after continuous use which seems to slow up the determination as some few minutes are required to reach equilibrium. One should be careful to wash the solution off the electrode immediately after each determination. Another effect was in the formation, in solutions of above pH 8.0, of a jel by the action of the concentrated potassium chloride used for the bridge. This forms a jel in the neck of the sample cup and must be cleaned frequently. Also, the outside of the sample cup becomes covered with a scale, formed by the silicate in presence of air, and this can be cleaned off effectively with a hot, concentrated solution of sodium hydroxide.

In making the coagulation tests a battery of 11 half-gallon mason fruit jars were used as mixing chambers. These were marked off to contain 1500 cc. each. Compressed air was used as the mixing medium being introduced through glass rod, to the ends of which were affixed 1 inch lengths of perforated copper tubing. These rods extended to the bottom and to one side providing quite thorough and uniform mixing. A rapid flash mix of 1 minute was allowed followed by a fairly slow mix of one half hour and a settling period of one hour. This procedure closely followed actual plant practice. As a rough estimate about 10 volumes of air were passed
through per volume of sewage.

Since the addition of water works sludge to the sewage was not constant it was necessary to exercise a good deal of care in collecting a sample so as to get one with not too much of the sludge in it else a good determination could not be made as the untreated sample would sometimes settle out completely giving a very low turbidity. If too little sludge were in the sample lime was added to it. The sample was collected, from the freely flowing sewage, in a 6 gallon pail and the mason jars filled from this, stirring constantly to ensure equal quantities of insoluble matter in each jar. In every case a control using no chemicals and a control using plain alum were run to compare the results.

The efficiency of the coagulation was tested using removal of settleable solids, B.O.D. reduction, turbidity reduction, size of floc formation and time to form a large floc, as a basis for comparison. The first three tests were run following the procedure in standard methods but the last two are essentially comparative tests and have no quantitative measurement. Other more complete tests as removal of total solids, volatile solids, chlorine demand, amount of sludge, etc., were run in a few isolated cases.

The alum used was C.P. \( \text{Al}_2(\text{SO}_4)_3 \) and was made up in solutions containing 15 grams of dry \( \text{Al}_2(\text{SO}_4)_3 \) per liter. 1 cc. of this solution gives 10 PPM when diluted in the 1500 cc. mixing jars. All other solutions such as ferric and ferrous sulfate, Ferric Chloride, bentonite, lime etc. were made up to the same strength.

In the experiments on pH rise of audified sodium silicate solutions the procedure was as follows:
A 50 cc portion of a 3\% solution of $\text{SiO}_2$ was measured into a 250 cc erlenmeyer flask. Into another flask was measured the required, predetermined amount of N sulfuric acid and distilled water. The stop-watch was started and the two solutions poured together and mixed for 30 seconds when the first pH was taken. There was a lag period of a few seconds in every case before the true pH was obtained. pH readings were taken at intervals of one or two minutes for the first few minutes and at irregular intervals thereafter up until the time of jelling. Incidentally, the solution was considered to have jelled immediately on the first appearance of a gel since it was difficult to measure the pH of even partially jelled solutions. A cold water bath was used for those experiments conducted below room temperature and a hot water bath for those above room temperature. The temperature regulation was within 2\°C. The pH meter was adjusted to read at the temperature of the test.

Baylis (8, 9, 39) used the term "active" to indicate those solutions of acidified sodium silicate which would aid coagulation. "Activation", then, is used here to indicate that period of time or process necessary to get the solution into the active state.

Classification of floc.—Baylis' (39) classification was used with some modifications. The floc naturally present in sewage as suspended matter was disregarded in the classification.

Very fine—Particles readily detectable
Fine—Particles probably 0.3 to 0.5 mm in diameter
Large—Particles about 0.5 to 0.8 mm in diameter
Very large—Particles about 0.8 to 1.2 mm in diameter
Exceedingly large—Particles 1.2 to 1.5 mm in diameter
Unusually large—Particles above 1.5 mm. in diameter. This size was used only in the later tests as the size was much larger than noted previously. Particles up to 1/8 inch were noted. This classification is, of course, merely comparative and with a material such as sewage it is hard to state definitely just where one size begins and stops. However care was exercised in its usage and the results are as good as can be expected.

RESULTS

The results obtained in this work are given in Tables 1-6. The results of the plant test are listed in Tables 7, 8, and 9.

Effect of pH of Silicate Solutions.

The effect of the pH of the silicate solutions on the floc formation, when using alum-silicate coagulant, is shown by the data in Table 1.

The pH of the silicate solutions was regulated by addition of varying quantities of N sulfuric acid and was measured about 10 minutes after the addition of the acid. The solutions were then aged for varying periods of time to completely activate them. The time required for activation varies considerably with the pH of the solution and was determined in a separate series of tests that are referred to later in this paper. This permitted a comparison of the solutions at different pH values in their active condition. If the solutions were all aged for the same length of time, those solutions of pH near 7 would have jelled before the other solutions had reached the activated condition.

The effect of pH of the silicate solution was determined by the turbidity of the supernatant liquid and by the physical
Table I -- Effect of pH of silicate solutions on Floe Formation

SO P.P.M. Alum + 10 P.P.M. Silicate

<table>
<thead>
<tr>
<th>Sample</th>
<th>Original pH of Silicate Solution after ageing</th>
<th>Size of Floe</th>
<th>Turbidity of Supernatant Liquid P.P.M.</th>
<th>Time for formation of large size floe minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>No coagulant</td>
<td>None Formed</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Alum Only</td>
<td>Very Fine</td>
<td>90</td>
<td>Remained fine up to 40 minutes</td>
</tr>
<tr>
<td>3</td>
<td>2.3</td>
<td>Very Fine</td>
<td>125</td>
<td>Remained fine up to 40 minutes</td>
</tr>
<tr>
<td>4</td>
<td>5.0</td>
<td>Very Large</td>
<td>60</td>
<td>24</td>
</tr>
<tr>
<td>5</td>
<td>6.0</td>
<td>Exceedingly Large</td>
<td>75</td>
<td>13</td>
</tr>
<tr>
<td>6</td>
<td>7.0</td>
<td>Very Large</td>
<td>60</td>
<td>15</td>
</tr>
<tr>
<td>7</td>
<td>7.8</td>
<td>Large</td>
<td>60</td>
<td>19</td>
</tr>
<tr>
<td>8</td>
<td>8.1</td>
<td>Exceedingly Large</td>
<td>60</td>
<td>5</td>
</tr>
<tr>
<td>9</td>
<td>8.6</td>
<td>Exceedingly Large</td>
<td>50</td>
<td>9</td>
</tr>
<tr>
<td>10</td>
<td>9.0</td>
<td>Exceedingly Large</td>
<td>60</td>
<td>20</td>
</tr>
<tr>
<td>11</td>
<td>9.4</td>
<td>Large</td>
<td>75</td>
<td>24</td>
</tr>
</tbody>
</table>

The data in Table I show that good results were obtained with every one of the samples from No. 3 thru No. 11. Evidently, the original pH of the Silicate Solution had but little influence, in these cases, on the character of the floc and the turbidity of the supernatant liquid. Over this pH range, 4 to 10, the original pH
CHANGE OF PH WITH VARYING AMOUNTS OF ACID

FIGURE NO. 4
has no appreciable influence provided the silicate solutions are properly aged. The time required for proper ageing must necessarily be determined for each solution. In another series of tests it was found that deflocculation resulted in all cases where the original pH of the silicate solution was above 10, even with very long periods of ageing.

Figure 4 shows the change of pH of silicate solutions with varying amounts of $\frac{N}{2}$ sulfuric acid. In obtaining values for this curve a 25 ml. portion of a 3 per cent $SiO_2$ was taken and a predetermined amount of $\frac{N}{2}$ sulfuric acid, diluted to make the final total volume of solution 50 ml., was added to it and the solutions were thoroughly mixed. The pH values were taken 10 minutes after the mixing.

The effect of ageing of the silicate solutions on floc formation is shown in Table 2. A silicate solution of pH 8.6, determined 10 minutes after being prepared, was first prepared and then added to the sewage at periods that varied from two minutes after preparation to 120 minutes. For the 1 day and 3 months tests another solution, but of the same pH was used. No deterioration of the solution, as mentioned by Bayles and Swope$^2$, could be detected even after three months of ageing.
AGEING TIME FOR 3% SILICATE SOLUTION AT 70°F.
Table 2—Ageing effect of Silicate Solutions on Floc Formation.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Age</th>
<th>Final Floc</th>
<th>Turbidity of</th>
<th>Time for Formation of Large Floc</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Minutes</td>
<td>Formation</td>
<td>Supernatant PPM</td>
<td>Minutes</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>No Coagulant</td>
<td>None</td>
<td>250</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>None</td>
<td>Fine</td>
<td>125</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>None</td>
<td>Fine</td>
<td>200</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>None</td>
<td>Fine</td>
<td>200</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>None</td>
<td>Fine</td>
<td>150</td>
</tr>
<tr>
<td>6</td>
<td>20</td>
<td>None</td>
<td>Fine</td>
<td>150</td>
</tr>
<tr>
<td>7</td>
<td>30</td>
<td>None</td>
<td>Fine</td>
<td>125</td>
</tr>
<tr>
<td>8</td>
<td>60</td>
<td>None</td>
<td>Large</td>
<td>60</td>
</tr>
<tr>
<td>9</td>
<td>120</td>
<td>None</td>
<td>Extremely Large</td>
<td>50</td>
</tr>
<tr>
<td>10</td>
<td>1 Day</td>
<td>None</td>
<td>Extremely Large</td>
<td>50</td>
</tr>
<tr>
<td>11</td>
<td>3 Mos.</td>
<td>None</td>
<td>Extremely Large</td>
<td>50</td>
</tr>
</tbody>
</table>

These data give further evidence to the need for proper ageing of the silicate solutions to obtain best results. In every case it was found that the time required for proper ageing varied with the original pH of the solution. This ageing period varies from a few minutes for a solution of pH of 7 to several hours for a solution of pH of 9.

The ageing periods required for silicate solutions of different pH values is shown graphically in Figure 5. It should be noted that the time for these solutions is not absolute because of the difficulty to determine very accurately just when the solution does become active. An active solution, for purposes
particles up to 1/8 inch being noted. These, however, did not settle out well. In every case the floc formed in the acid range settled more rapidly and more completely than those in the alkaline range. The silicate solution widens the effective range of sewage coagulation as Baylis noted in his work on water. The effect of the silicate in the extreme alkaline range could not be verified because of fact that the sewage automatically formed a floc at pH values above 9.3.

The effect of the Temperature of Ageing on the Effect of Silicate Solutions is given in Table 4. The solutions were all made up with the same proportions of acid to silicate and the 70° age was kept at room temperature while the 180° age was kept in a water bath at that temperature. Water works sludge was present in this sewage and the pH was 8.2.

Table 4—Effect of Temperature of Ageing on the Effect of Silicate Solutions. 60 PPM Alum, 10 PPM SiO₂ (pH 8.3 age 1 Hour)

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>pH of Silicate</th>
<th>Time of Ageing : Degrees F</th>
<th>Final Floc Formation</th>
<th>Turbidity of Supernatant : PPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>No SiO₂</td>
<td>---</td>
<td>None</td>
<td>200</td>
</tr>
<tr>
<td>2</td>
<td>8.9</td>
<td>2</td>
<td>Large</td>
<td>30</td>
</tr>
<tr>
<td>3</td>
<td>8.5</td>
<td>2</td>
<td>None</td>
<td>275</td>
</tr>
<tr>
<td>4</td>
<td>9.2</td>
<td>15</td>
<td>Large</td>
<td>75</td>
</tr>
<tr>
<td>5</td>
<td>8.7</td>
<td>15</td>
<td>Small</td>
<td>160</td>
</tr>
<tr>
<td>6</td>
<td>9.3</td>
<td>30</td>
<td>Large</td>
<td>50</td>
</tr>
<tr>
<td>7</td>
<td>8.2</td>
<td>30</td>
<td>Large</td>
<td>100</td>
</tr>
<tr>
<td>8</td>
<td>9.4</td>
<td>60</td>
<td>Large</td>
<td>40</td>
</tr>
<tr>
<td>9</td>
<td>8.9</td>
<td>60</td>
<td>Very Large</td>
<td>30</td>
</tr>
<tr>
<td>10</td>
<td>9.4</td>
<td>180</td>
<td>Small-Large</td>
<td>100</td>
</tr>
<tr>
<td>11</td>
<td>8.9</td>
<td>180</td>
<td>Very Large</td>
<td>30</td>
</tr>
</tbody>
</table>
The effect of dosage on coagulation is shown in Table 5. The silicate solution was at a pH of 8.0 10 minutes after preparation and was used after ageing one hour. In previous experiments it was found that the dosage of 50 PPM alum served to form a very fine floc with fair turbidity reduction hence this amount was used. The mixing period was 30 minutes followed by a settling period of one hour. Water work sludge was present. pH of sewage 8.2.

Table No. 5 - The Effect of Dosage of Silica on Floe Formation

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>PPM SiO₂</th>
<th>Floe Formation</th>
<th>Turbidity of Supernatant</th>
<th>BOD Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Coagulant</td>
<td>50 PPM Alum</td>
<td>None</td>
<td>825</td>
<td>31</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>Fine</td>
<td>150</td>
<td>56</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>Large</td>
<td>75</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>Large</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>15</td>
<td>Large</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>20</td>
<td>Very Large</td>
<td>50</td>
<td>67</td>
</tr>
<tr>
<td>7</td>
<td>30</td>
<td>Very Large</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>50</td>
<td>Large</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>150</td>
<td>Fine</td>
<td>225</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>20</td>
<td>None</td>
<td>800</td>
<td>No Alum here</td>
</tr>
</tbody>
</table>

It is evident from the above data that only a very small amount of silica is necessary to aid coagulation if it is in the active state. It is also evident that the active sodium silicate is not a coagulant. This is in accordance with Baylis' (39) findings in water coagulation. He points out, however, that silica will form a floc with lime above pH 9.0 but says that this is due to the formation of magnesium hydroxide. No additional
floc could be detected here other than that already present in the sewage. As can be seen the use of too much silica say in the ratio of 3 to 1 results in deflocculation. As Baylis (39) states, this is evidently due to the fact that the silica offers too many particles for the aluminum hydrate floc to cover.

The silicate solutions must contain at least one per cent \( \text{SiO}_2 \) before they can be made active. The first series of tests was run using solutions of 0.75 per cent \( \text{SiO}_2 \) and the results were very disappointing. Deflocculation was the result in most cases and only very rarely was any a preciable aid given. Longer periods of ageing are necessary for those solutions weaker than one per cent and the danger of rapid jelling prohibits the use of stronger solutions. This is in accord with the results given by Baylis (8, 9, 39).

BOD determinations were on several of the experimental runs and a typical set of per cent reductions is shown in Table 6.

Table 6 Typical BOD reductions (Comparison of Silica Treatment)

<table>
<thead>
<tr>
<th>Treatment given Sewage</th>
<th>Per Cent Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Chemicals</td>
<td>30.0</td>
</tr>
<tr>
<td>50 PPM Alum</td>
<td>51.2</td>
</tr>
<tr>
<td>50 PPM Alum and 10 PPM ( \text{SiO}_2 ) (pH 8.3 not aged)</td>
<td>52.3</td>
</tr>
<tr>
<td>50 PPM Alum and 10 PPM ( \text{SiO}_2 ) (pH 8.3 age 1 Hour)</td>
<td>73.5</td>
</tr>
</tbody>
</table>

In all cases the mixing period was 30 minutes followed by a settling period of one hour. It can be seen that the silica, in itself, has very little effect on the BOD reduction of the sewage. Its primary use, therefore, is to increase the size and settling properties of the floc formed with the alum.
Sodium silicate can be used to decrease the amount of alum necessary for coagulation of the sewage studied in the present research. The dosage may be decreased from 100 PPM to about 60 PPM by the addition of 10 PPM of $SiO_2^-$. Comparable results were obtained using these dosages. H. Gladys Swop reports that the best dosage at Waukegan, Illinois is 1.5 grains per gallon of alum and 0.2 grains per gallon of $SiO_2^-$, which corresponds to a dosage of 25 PPM alum and 3.4 PPM $SiO_2^-$. The cost of such treatment, at Waukegan, with alum $\not\in$ $1.16 per cwt., sodium silicate $\not\in$ $1.23 per cwt. and sulfuric acid $\not\in$ $2.22 per cwt.$ is given as:

- **Alum** .............. $2.50 per million gallons at 1.5 g/g
- **Sodium silicate** .... $1.08 per million gallons at 0.2 g/g
- **Sulfuric acid** ...... $0.275 per million gallons
- **Total** .............. $3.855 per million gallons.

The higher pH values noted in these solutions kept at 180° are due to the more rapid hydrolysis (see discussion). Crystalline silica settled out much more rapidly in the solutions kept at higher temperatures. Due to the rapid jelling of solutions in the less alkaline range it is impossible to age them at higher temperatures, however for those solutions above pH 8.0 it is possible to decrease the ageing time to practically zero in most cases. A solution that is not "active" can be made so if merely brought to the boiling point provided the pH is below 10.0. Jelling of solutions between pH 7.0 and 8.0 prevents this procedure in those cases. The decrease in time necessary for ageing is dependent upon the temperature used, being longer the lower the temperature. Freezing was attempted in one case and no active solution could be made due to crystallization of the solution.
Activated sodium silicate can be used as an aid to coagulation in conjunction with the other coagulants such as: Ferric Chloride, Ferric Sulfate, Ferrous sulfate and Sodium Aluminate. However, no definite statement can be made as to the exact nature of this aid since extensive experiments were not tried with these coagulants. However it can be said that the aid is not to the same extent with the ferric salts as with alum. Ferrous salts, on the other hand, seem to react much the same as the alum used.

Data—Results of plant test run.

To determine the effect of sodium silicate on alum in the chemical coagulation of sewage, plant test runs were made at the Grand Forks Sewage Treatment Plant. The sodium silicate used was commercial water glass furnished through the courtesy of the Grasselli Chemicals Department of the E. I. duPont de Nemours and Company, St. Paul, Minnesota.

The data obtained from a one day test with alum alone and a one day test with alum and silicate are given in Tables 10 and 9. In these runs the water works sludge, that is ordinarily added in this plant, was cut off completely so that no interference was given and the floc formation was due entirely to the alum or alum and silica.

The alum solution used was quite strong, about 26 per cent available \( \text{Al}_2(\text{SO}_4)_3 \). It was added manually by pouring measured quantities into a funnel which permitted steady application in proportion to the flow. The average rate of application was 35.3 PPM and did not vary by over 7 PPM.

A 1.5 per cent silica solution was prepared from commercial water glass and sulfuric acid. Due to the lack of suitable mixing...
equipment this solution was mixed in portions of 400 pounds each in a 55 gallon barrel and poured into a 1000 gallon plaster-lined tank. This method provided a good check on the nature of each portion and lessened the danger of jelling. The original pH of the solutions (taken 10 minutes after each addition of acid) was 8.8 with an alkalinity of 1500. The alkalinity measurement, however, did not check very well. However, the pH measurements seemed to agree very well with the varying amounts of acid and seems to be a more accurate measurement of the condition of the solution. This solution became active after about six hours and at the end of eight hours it took on a very turbid appearance, due perhaps to some reaction with the plaster of the tank. To lessen the danger of jelling the solution was further diluted to one percent at this time and aged for 20 hours before being used. The pH of the solution at the time of application was 9.6.

The silicate was added ahead of the alum and in the same manner and was mixed thoroughly by means of two baffles placed in the grit chamber of the plant. The alum and silica were mixed with the sewage for an average period of 25 minutes, using compressed air. From the mixing chamber the sewage passed to two radial-flow Dorrco clarifiers, operated in series, where it had a detention period of about two hours. An hourly check was made on the floc formation, turbidity, pH, and amount of settleable solids in the influent, effluent from the mixing chamber and effluent from the clarifiers. A composite sample was taken of the influent and effluent and the BOD, total solids, suspended solids, dissolved solids and volatile solids were determined with these samples using the methods outlined in Standard Methods for the Examination
### Table No. 7 Plant test with Alum only. 8 PM June 20 to 8 PM June 21, 1939

<table>
<thead>
<tr>
<th>Time</th>
<th>Sewage Gallons X1000</th>
<th>Sewage Founds</th>
<th>Alum Pounds</th>
<th>Alum FPM</th>
<th>Comparative pH</th>
<th>Settleable Solids1/2</th>
<th>Inf Eff</th>
<th>Turbidity PPM</th>
<th>pH</th>
<th>Turbidity PPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>8 PM</td>
<td>Started Test</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9 PM</td>
<td>38.3</td>
<td>319.3</td>
<td>9.6</td>
<td>30.0</td>
<td>25</td>
<td>9.1.9</td>
<td>7.1</td>
<td>7.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 PM</td>
<td>31.6</td>
<td>263.7</td>
<td>10.2</td>
<td>39.0</td>
<td>10</td>
<td>10.1.4</td>
<td>7.1</td>
<td>7.0</td>
<td>600</td>
<td>150</td>
</tr>
<tr>
<td>11 PM</td>
<td>35.0</td>
<td>291.5</td>
<td>9.5</td>
<td>32.8</td>
<td>15</td>
<td>9.1.9</td>
<td>6.9</td>
<td>6.8</td>
<td>400</td>
<td>175</td>
</tr>
<tr>
<td>12 Mid.</td>
<td>33.3</td>
<td>277.7</td>
<td>8.9</td>
<td>31.8</td>
<td>25</td>
<td>10.1.1</td>
<td>6.6</td>
<td>6.6</td>
<td>700</td>
<td>200</td>
</tr>
<tr>
<td>1 AM</td>
<td>26.7</td>
<td>222.1</td>
<td>6.4</td>
<td>28.5</td>
<td>10</td>
<td>7.0.1</td>
<td>7.0</td>
<td>7.0</td>
<td>800</td>
<td>200</td>
</tr>
<tr>
<td>2 AM</td>
<td>25.3</td>
<td>194.4</td>
<td>6.9</td>
<td>35.0</td>
<td>20</td>
<td>10.1.3</td>
<td>8.0</td>
<td>8.0</td>
<td>800</td>
<td>200</td>
</tr>
<tr>
<td>3 AM</td>
<td>21.6</td>
<td>180.5</td>
<td>6.1</td>
<td>34.0</td>
<td>20</td>
<td>10.1.3</td>
<td>7.0</td>
<td>7.0</td>
<td>800</td>
<td>200</td>
</tr>
<tr>
<td>4 AM</td>
<td>18.3</td>
<td>152.7</td>
<td>4.4</td>
<td>29.2</td>
<td>20</td>
<td>10.1.3</td>
<td>6.9</td>
<td>6.9</td>
<td>800</td>
<td>200</td>
</tr>
<tr>
<td>5 AM</td>
<td>21.6</td>
<td>180.5</td>
<td>6.1</td>
<td>34.0</td>
<td>20</td>
<td>10.1.3</td>
<td>6.9</td>
<td>6.9</td>
<td>800</td>
<td>200</td>
</tr>
<tr>
<td>6 AM</td>
<td>16.6</td>
<td>138.8</td>
<td>4.4</td>
<td>32.0</td>
<td>10</td>
<td>10.1.3</td>
<td>6.9</td>
<td>6.9</td>
<td>800</td>
<td>200</td>
</tr>
<tr>
<td>7 AM</td>
<td>21.7</td>
<td>180.5</td>
<td>6.1</td>
<td>34.0</td>
<td>10</td>
<td>10.1.3</td>
<td>6.9</td>
<td>6.9</td>
<td>800</td>
<td>200</td>
</tr>
<tr>
<td>8 AM</td>
<td>35.3</td>
<td>277.6</td>
<td>9.5</td>
<td>34.4</td>
<td>15</td>
<td>10.1.9</td>
<td>7.0</td>
<td>6.8</td>
<td>900</td>
<td>150</td>
</tr>
<tr>
<td>9 AM</td>
<td>38.3</td>
<td>319.3</td>
<td>10.9</td>
<td>35.2</td>
<td>20</td>
<td>10.1.5</td>
<td>7.0</td>
<td>6.8</td>
<td>900</td>
<td>150</td>
</tr>
<tr>
<td>10 AM</td>
<td>58.3</td>
<td>486.2</td>
<td>20.4</td>
<td>42.0</td>
<td>25</td>
<td>10.1.8</td>
<td>6.8</td>
<td>6.6</td>
<td>900</td>
<td>200</td>
</tr>
<tr>
<td>11 AM</td>
<td>55.0</td>
<td>458.4</td>
<td>16.0</td>
<td>34.8</td>
<td>20</td>
<td>10.1.2</td>
<td>6.8</td>
<td>6.6</td>
<td>900</td>
<td>200</td>
</tr>
<tr>
<td>12 Noon</td>
<td>70.0</td>
<td>583.5</td>
<td>21.2</td>
<td>36.1</td>
<td>20</td>
<td>10.1.7</td>
<td>6.8</td>
<td>6.6</td>
<td>900</td>
<td>200</td>
</tr>
<tr>
<td>1 PM</td>
<td>55.3</td>
<td>444.5</td>
<td>16.7</td>
<td>37.6</td>
<td>15</td>
<td>10.1.8</td>
<td>7.0</td>
<td>7.0</td>
<td>800</td>
<td>200</td>
</tr>
<tr>
<td>2 PM</td>
<td>76.7</td>
<td>639.0</td>
<td>22.1</td>
<td>34.7</td>
<td>25</td>
<td>10.1.7</td>
<td>7.0</td>
<td>7.0</td>
<td>800</td>
<td>200</td>
</tr>
<tr>
<td>3 PM</td>
<td>36.7</td>
<td>305.4</td>
<td>10.9</td>
<td>35.8</td>
<td>25</td>
<td>10.1.7</td>
<td>7.0</td>
<td>7.0</td>
<td>1000</td>
<td>200</td>
</tr>
<tr>
<td>4 PM</td>
<td>61.7</td>
<td>514.0</td>
<td>18.0</td>
<td>35.2</td>
<td>25</td>
<td>10.1.8</td>
<td>7.2</td>
<td>7.0</td>
<td>900</td>
<td>225</td>
</tr>
<tr>
<td>5 PM</td>
<td>53.3</td>
<td>444.5</td>
<td>16.4</td>
<td>36.8</td>
<td>25</td>
<td>10.1.8</td>
<td>7.3</td>
<td>7.2</td>
<td>1000</td>
<td>250</td>
</tr>
<tr>
<td>6 PM</td>
<td>43.3</td>
<td>360.9</td>
<td>12.9</td>
<td>35.8</td>
<td>25</td>
<td>10.1.8</td>
<td>7.3</td>
<td>7.2</td>
<td>1100</td>
<td>300</td>
</tr>
<tr>
<td>7 PM</td>
<td>36.6</td>
<td>305.4</td>
<td>10.2</td>
<td>33.5</td>
<td>20</td>
<td>10.1.5</td>
<td>6.8</td>
<td>6.9</td>
<td>1200</td>
<td>200</td>
</tr>
<tr>
<td>8 PM</td>
<td>45.0</td>
<td>374.9</td>
<td>11.6</td>
<td>30.8</td>
<td>25</td>
<td>10.1.3</td>
<td>6.8</td>
<td>6.9</td>
<td>900</td>
<td>200</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>949.5</strong></td>
<td><strong>7915.3</strong></td>
<td><strong>275.3</strong></td>
<td><strong>34.8</strong></td>
<td><strong>(Ave)</strong></td>
<td></td>
<td><strong>6.9</strong></td>
<td><strong>6.8</strong></td>
<td><strong>900</strong></td>
<td><strong>200</strong></td>
</tr>
</tbody>
</table>

1/ The column headed "Settleable Solids" refers to the mixing chamber.

2/ Floc formation was on the comparative basis only, hence the numbers have no significance except as a comparison with the later test.
Table No. 8 Plant Test with Alum and Silica. 10 AM June 23 to 10 AM June 24, 1939

<table>
<thead>
<tr>
<th>Time</th>
<th>Sewage Gallons</th>
<th>Sewage Pounds</th>
<th>ALUM Al₂(SO₄)₃/³ Pounds</th>
<th>ALUM Al₂(SO₄)₃ PPM</th>
<th>SILICA SiO₂ Pounds</th>
<th>SILICA SiO₂ PPM</th>
<th>Settleable Solids¹/²</th>
<th>Inf.</th>
<th>Eff.</th>
<th>Mixing %</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 AM</td>
<td>Started Test</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11 AM</td>
<td>81.7</td>
<td>680.7</td>
<td>21.0</td>
<td>31.0</td>
<td>6.25</td>
<td>9.2</td>
<td>0.5</td>
<td>0.0</td>
<td>0.0</td>
<td>2.4</td>
</tr>
<tr>
<td>12 Noon</td>
<td>43.3</td>
<td>361.0</td>
<td>12.9</td>
<td>35.8</td>
<td>3.73</td>
<td>10.3</td>
<td>0.4</td>
<td>0.0</td>
<td>0.0</td>
<td>2.3</td>
</tr>
<tr>
<td>1 PM</td>
<td>51.7</td>
<td>430.6</td>
<td>14.9</td>
<td>35.0</td>
<td>4.12</td>
<td>9.6</td>
<td>0.7</td>
<td>0.0</td>
<td>0.0</td>
<td>2.5</td>
</tr>
<tr>
<td>2 PM</td>
<td>63.3</td>
<td>527.9</td>
<td>18.0</td>
<td>34.0</td>
<td>5.05</td>
<td>9.5</td>
<td>0.5</td>
<td>0.0</td>
<td>0.0</td>
<td>3.0</td>
</tr>
<tr>
<td>3 PM</td>
<td>43.3</td>
<td>361.0</td>
<td>14.2</td>
<td>39.5</td>
<td>3.72</td>
<td>10.3</td>
<td>0.5</td>
<td>0.0</td>
<td>0.0</td>
<td>2.3</td>
</tr>
<tr>
<td>4 PM</td>
<td>58.3</td>
<td>486.2</td>
<td>15.6</td>
<td>32.2</td>
<td>4.12</td>
<td>8.5</td>
<td>0.5</td>
<td>0.0</td>
<td>0.0</td>
<td>2.6</td>
</tr>
<tr>
<td>5 PM</td>
<td>51.7</td>
<td>430.6</td>
<td>15.3</td>
<td>35.5</td>
<td>4.40</td>
<td>10.1</td>
<td>0.5</td>
<td>0.0</td>
<td>0.0</td>
<td>2.0</td>
</tr>
<tr>
<td>6 PM</td>
<td>33.3</td>
<td>277.6</td>
<td>9.9</td>
<td>35.3</td>
<td>2.88</td>
<td>10.3</td>
<td>0.5</td>
<td>0.0</td>
<td>0.0</td>
<td>2.0</td>
</tr>
<tr>
<td>7 PM</td>
<td>35.0</td>
<td>291.5</td>
<td>10.2</td>
<td>35.0</td>
<td>2.88</td>
<td>10.0</td>
<td>0.4</td>
<td>0.0</td>
<td>0.0</td>
<td>1.8</td>
</tr>
<tr>
<td>8 PM</td>
<td>40.0</td>
<td>333.2</td>
<td>11.9</td>
<td>35.8</td>
<td>3.54</td>
<td>10.0</td>
<td>0.5</td>
<td>0.0</td>
<td>0.0</td>
<td>2.8</td>
</tr>
<tr>
<td>9 PM</td>
<td>31.7</td>
<td>263.8</td>
<td>9.9</td>
<td>33.6</td>
<td>2.50</td>
<td>9.5</td>
<td>0.4</td>
<td>0.0</td>
<td>0.0</td>
<td>1.8</td>
</tr>
<tr>
<td>10 PM</td>
<td>26.7</td>
<td>222.1</td>
<td>8.6</td>
<td>38.5</td>
<td>2.40</td>
<td>10.9</td>
<td>0.4</td>
<td>0.0</td>
<td>0.0</td>
<td>2.5</td>
</tr>
<tr>
<td>11 PM</td>
<td>31.7</td>
<td>263.8</td>
<td>9.5</td>
<td>35.8</td>
<td>2.77</td>
<td>10.5</td>
<td>0.4</td>
<td>0.0</td>
<td>0.0</td>
<td>2.2</td>
</tr>
<tr>
<td>12 Mid.</td>
<td>26.7</td>
<td>222.1</td>
<td>7.8</td>
<td>35.0</td>
<td>2.20</td>
<td>10.0</td>
<td>0.3</td>
<td>0.0</td>
<td>0.0</td>
<td>2.3</td>
</tr>
<tr>
<td>1 AM</td>
<td>23.3</td>
<td>194.4</td>
<td>7.8</td>
<td>40.0</td>
<td>2.32</td>
<td>12.0</td>
<td>0.3</td>
<td>0.0</td>
<td>0.0</td>
<td>2.7</td>
</tr>
<tr>
<td>2 AM</td>
<td>21.7</td>
<td>180.5</td>
<td>6.1</td>
<td>35.6</td>
<td>1.75</td>
<td>9.6</td>
<td>0.4</td>
<td>0.0</td>
<td>0.0</td>
<td>2.5</td>
</tr>
<tr>
<td>3 AM</td>
<td>16.6</td>
<td>158.9</td>
<td>4.8</td>
<td>34.2</td>
<td>1.34</td>
<td>9.6</td>
<td>0.6</td>
<td>0.0</td>
<td>0.0</td>
<td>2.8</td>
</tr>
<tr>
<td>4 AM</td>
<td>16.6</td>
<td>158.9</td>
<td>4.1</td>
<td>29.5</td>
<td>1.15</td>
<td>8.3</td>
<td>1.0</td>
<td>0.0</td>
<td>0.0</td>
<td>7.0</td>
</tr>
<tr>
<td>5 AM</td>
<td>21.7</td>
<td>180.5</td>
<td>6.1</td>
<td>34.0</td>
<td>1.72</td>
<td>9.6</td>
<td>0.5</td>
<td>0.0</td>
<td>0.0</td>
<td>3.0</td>
</tr>
<tr>
<td>6 AM</td>
<td>13.3</td>
<td>110.1</td>
<td>5.1</td>
<td>46.6</td>
<td>1.29</td>
<td>11.7</td>
<td>0.2</td>
<td>0.0</td>
<td>0.0</td>
<td>2.4</td>
</tr>
<tr>
<td>7 AM</td>
<td>26.7</td>
<td>222.1</td>
<td>6.8</td>
<td>30.6</td>
<td>1.82</td>
<td>8.2</td>
<td>0.1</td>
<td>0.0</td>
<td>0.0</td>
<td>2.4</td>
</tr>
<tr>
<td>8 AM</td>
<td>26.7</td>
<td>222.1</td>
<td>8.2</td>
<td>35.8</td>
<td>2.30</td>
<td>10.4</td>
<td>0.2</td>
<td>0.0</td>
<td>0.0</td>
<td>2.5</td>
</tr>
<tr>
<td>9 AM</td>
<td>30.0</td>
<td>250.0</td>
<td>8.6</td>
<td>34.8</td>
<td>2.40</td>
<td>9.6</td>
<td>0.4</td>
<td>0.0</td>
<td>0.0</td>
<td>1.7</td>
</tr>
<tr>
<td>10 AM</td>
<td>48.3</td>
<td>402.6</td>
<td>13.6</td>
<td>34.0</td>
<td>3.82</td>
<td>9.5</td>
<td>0.4</td>
<td>0.0</td>
<td>0.0</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Total: 864.3 7202.2 250.2 35.3(Av) 70.25 9.8 (Av)

¹/²Settleable solids were taken after a settling period of only one hour.
Table No. 8 Concluded Plant Test with Alum and Silica. 10 AM June 23 to 10 AM June 24

<table>
<thead>
<tr>
<th>Time</th>
<th>Comparative Size of Flocculation</th>
<th>pH Influent</th>
<th>pH Effluent</th>
<th>pH Mixing</th>
<th>Turbidity Influent</th>
<th>Turbidity Effluent</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 AM</td>
<td>25</td>
<td>7.2</td>
<td>7.0</td>
<td>7.1</td>
<td>6000</td>
<td>60</td>
</tr>
<tr>
<td>11 AM</td>
<td>25</td>
<td>7.1</td>
<td>7.0</td>
<td>7.0</td>
<td>700</td>
<td>50</td>
</tr>
<tr>
<td>12 Noon</td>
<td>50</td>
<td>7.2</td>
<td>7.1</td>
<td>7.1</td>
<td>800</td>
<td>40</td>
</tr>
<tr>
<td>1 PM</td>
<td>80</td>
<td>7.6</td>
<td>7.2</td>
<td>7.3</td>
<td>600</td>
<td>80</td>
</tr>
<tr>
<td>2 PM</td>
<td>70</td>
<td>7.3</td>
<td>7.0</td>
<td>7.1</td>
<td>850</td>
<td>65</td>
</tr>
<tr>
<td>3 PM</td>
<td>80</td>
<td>7.2</td>
<td>7.1</td>
<td>7.2</td>
<td>700</td>
<td>50</td>
</tr>
<tr>
<td>4 PM</td>
<td>100</td>
<td>7.2</td>
<td>7.0</td>
<td>7.1</td>
<td>750</td>
<td>50</td>
</tr>
<tr>
<td>5 PM</td>
<td>100</td>
<td>7.9</td>
<td>7.2</td>
<td>7.3</td>
<td>700</td>
<td>80</td>
</tr>
<tr>
<td>6 PM</td>
<td>100</td>
<td>7.4</td>
<td>7.1</td>
<td>7.1</td>
<td>600</td>
<td>80</td>
</tr>
<tr>
<td>7 PM</td>
<td>70</td>
<td>7.6</td>
<td>7.1</td>
<td>7.3</td>
<td>600</td>
<td>85</td>
</tr>
<tr>
<td>8 PM</td>
<td>70</td>
<td>7.5</td>
<td>7.1</td>
<td>7.1</td>
<td>600</td>
<td>80</td>
</tr>
<tr>
<td>9 PM</td>
<td>80</td>
<td>7.3</td>
<td>7.0</td>
<td>7.1</td>
<td>550</td>
<td>35</td>
</tr>
<tr>
<td>10 PM</td>
<td>80</td>
<td>7.2</td>
<td>7.1</td>
<td>7.1</td>
<td>600</td>
<td>60</td>
</tr>
<tr>
<td>11 PM</td>
<td>80</td>
<td>7.2</td>
<td>7.1</td>
<td>7.1</td>
<td>550</td>
<td>40</td>
</tr>
<tr>
<td>12 Mid.</td>
<td>80</td>
<td>7.2</td>
<td>7.1</td>
<td>7.1</td>
<td>500</td>
<td>50</td>
</tr>
<tr>
<td>1 AM</td>
<td>80</td>
<td>6.9</td>
<td>7.0</td>
<td>7.0</td>
<td>500</td>
<td>50</td>
</tr>
<tr>
<td>2 AM</td>
<td>80</td>
<td>6.7</td>
<td>6.8</td>
<td>6.8</td>
<td>500</td>
<td>60</td>
</tr>
<tr>
<td>3 AM</td>
<td>80</td>
<td>8.0</td>
<td>6.7</td>
<td>7.0</td>
<td>4000</td>
<td>40</td>
</tr>
<tr>
<td>4 AM</td>
<td>50</td>
<td>7.1</td>
<td>7.0</td>
<td>7.2</td>
<td>1000</td>
<td>40</td>
</tr>
<tr>
<td>5 AM</td>
<td>50</td>
<td>6.9</td>
<td>7.0</td>
<td>7.1</td>
<td>600</td>
<td>40</td>
</tr>
<tr>
<td>6 AM</td>
<td>50</td>
<td>6.5</td>
<td>7.0</td>
<td>6.9</td>
<td>550</td>
<td>50</td>
</tr>
<tr>
<td>7 AM</td>
<td>50</td>
<td>6.7</td>
<td>6.9</td>
<td>6.7</td>
<td>550</td>
<td>60</td>
</tr>
<tr>
<td>8 AM</td>
<td>70</td>
<td>6.7</td>
<td>6.8</td>
<td>6.7</td>
<td>500</td>
<td>50</td>
</tr>
<tr>
<td>9 AM</td>
<td>70</td>
<td>7.4</td>
<td>6.8</td>
<td>7.2</td>
<td>300</td>
<td>50</td>
</tr>
<tr>
<td>10 AM</td>
<td>80</td>
<td>6.8</td>
<td>6.9</td>
<td>6.8</td>
<td>300</td>
<td>35</td>
</tr>
</tbody>
</table>

Total: 7.15 (Av.) 7.00 (Av) 7.05 (Av) 650 (Av) 55 (Av)

1/ Floc formation was on a comparative basis only, hence the numbers have no significance except as a comparison with the other test.

Water works sludge was admitted to the lines at 3 AM. This accounts for the high pH, excess of settleable solids and high turbidity at that time.
of Water and Sewage.

A comparison of data in Tables 7 and 8 shows that a much larger floc formation was obtained with the alum-silica mixture. The floc formed was almost twice the size of that obtained with alum alone, and it settled out much faster. The turbidity reduction was increased from 77% to 92% by the use of the silica. Removal of total, dissolved, suspended, and volatile solids was also increased considerably. It seems that, in view of the fact that a high turbidity reduction was obtained, the BOD reduction should have been much higher but the results were checked by two different sources and found to agree. The data do show, however, that better reduction is obtained by the use of the silicate solution. The results obtained are summarized in Table 9.

Table 9. Results of the Plant test runs.

<table>
<thead>
<tr>
<th></th>
<th>ALUM</th>
<th>ALUM &amp; SILICA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Inf.</td>
<td>Eff.</td>
</tr>
<tr>
<td>Turbidity PPM</td>
<td>750</td>
<td>175</td>
</tr>
<tr>
<td>B.O.D. PPM</td>
<td>400</td>
<td>278</td>
</tr>
<tr>
<td>Settleable Solids %</td>
<td>0.5</td>
<td>0.0</td>
</tr>
<tr>
<td>Dissolved Solids PPM</td>
<td>1124</td>
<td>1130</td>
</tr>
<tr>
<td>Suspended Solids PPM</td>
<td>229</td>
<td>96</td>
</tr>
<tr>
<td>Volatile Solids PPM</td>
<td>316</td>
<td>177</td>
</tr>
<tr>
<td>Total Solids PPM</td>
<td>1353</td>
<td>1226</td>
</tr>
</tbody>
</table>

**SUMMARY**

The tests with Grand Forks sewage using activated sodium silicate with alum for coagulation indicate that the silicate solution exerts a beneficial influence. A much better floc formation is obtained by the addition of the silicate. Data obtained
in this research indicate that a reduction of about 40% in the quantity of alum can be made by the addition of as little as 10 PPM of activated silica. In addition to this the turbidity reduction is increased markedly—in this case from 77% with alum alone to 92% with the alum-silicate mixture. The reduction of suspended, dissolved, volatile and total solids was also increased greatly.

In general, a much better effluent is obtained with the silicate treatment used in conjunction with the alum.

Form of Silica that aids Coagulation

Baylis (8) has this to say about the form that aids coagulation, "As the silicates are complex in structure it is not possible to state accurately the form that will aid coagulation. The data show it is a form nearly ready to produce a jelly, and indicate it may be a colloidal suspension of hydrous silica.

Should this be the case, then there is considerable information on the production of this form of silica. When the silicate solution is slightly alkaline, the colloidal silica particles are negatively charged, yet this does not explain why a strongly alkaline sodium silicate solution hinders or retards coagulation."

"Shortly after finding that silica in some form would aid coagulation it was thought that the aid was due to silica in the soluble state. This assumption seemed supported in that a solution prepared from silicon tetrachloride, when added after the aluminum sulfate, aided coagulation, but the fact that it did not offer aid when added prior to adding the coagulant was difficult to explain. Solutions prepared from sodium silicate give best results when applied to the water in advance of the aluminum sulfate.
If the aid is given by a substance in solution, it seems that it would have been nearly as active if applied after the coagulant, but this is not the case in such tests as have been made."

"Some thought has been given to the possibility of there being a slight amount of ionized silica, and that the coagulating properties of a quadrivalent ion are brought into play. Proof that there is ionized silica has not been established. The evidence, in connection with silica added to natural water already containing silica, seems to favor the supposition that the substance which aids coagulation is colloided silica possessing a negative charge. Perhaps the colloidal particles form the nucleus around which the aluminum hydroxide adheres. This, however, does not explain why a partially coagulated solution is greatly aided in forming large floculated particles by the addition of a solution prepared from silicon tetrachloride, but is not aided so greatly by an acid sodium silicate. The investigation has not progressed to the extent that all the factors involved in using silica to aid coagulation, and assumptions now favored may have to be changed or modified after more work has been done."

The difficulties in explaining the action of the silicate can be appreciated if one studies the voluminous literature on this subject but some interesting and pertinent data were found. To begin with, when an acid is added to a solution of sodium silicate, silicic acid is formed according to the equation $\text{Na}_2\text{SiO}_3 + \text{H}_2\text{SO}_4$.
H₂SiO₃ + Na₂SO₄. Then, too, in dilute solution hydrolysis takes place according to Na₂SiO₃ + H₂O NaOH + H₂SiO₃ removal of the NaOH by an acid such as sulfuric will shift the reaction towards the right completing the formation of silicic acid. In very dilute solutions this hydrolysis is almost 100% complete and may explain the form of silicate in natural water, which have been shown by Baylis (8) to coagulate more readily than others.

That the silicic acid, on ageing, is in the colloidal form has been shown by a number of investigators, the reaction being

\[
\text{H}_2\text{SiO}_3 + \text{H}_2\text{O} \rightarrow \text{SiO}_2 \text{(colloidal)}
\]

Mylius and Groschuff (40) believe that at the moment of formation of silicic acid from water glass, it exists in the molecular solution which passes unchanged through a parchment dialyzer. Willstalter and his collaborators proved this definitely to be true by osmotic experiments and that the rate with which colloidal silicic acid is formed from mono-molecular acid depends strongly on the pH of the solution. Colloidal particles then result from polymerization of the simple silicic acid molecules on keeping the solution and this is shown by the increase in molecular weight for many weeks. They designate the initial acid as alpha and show its molecular weight to be about 150. On keeping or warming this alpha acid it is polymerized into the Beta form which has a molecular weight in the magnitude of 50,000. The Beta acid will precipitate albumen from a solution containing the white of an egg. Several other workers (41), (42), (43), (44) have concluded that this ageing process leads to the formation of highly polymerized colloidal particles and finally to crystalline silica. Ghosh and Dhar (45) conclude that since the viscosity and specific conductivity of silicic acid solutions increase con-
tinuously with time, there is a part of the acid in the molecular condition but it polymerizes and passes into the colloidal state with crystalline silica as the ultimate end-point. Schwarz and Leide conclude from the behavior of silica gel when slowly dried at ordinary temperature that the ageing process consists in the condensation of $(SiO_2)_x$ to $(SiO_2)_{2x}$ and that this occurs without any change in the appearance of the gel. From the literature presented and the results found in this study it seems quite reasonable to assume that the silica is in the colloidal state.

There seems to be some question as to the nature of the charge on the silica ion but perusal of the literature reveals the following facts: W. B. Hardy (48) showed that with distilled water, the thoroughly washed hydrogel is iso-electric and with the smallest trace of free alkali in the water, it becomes electronegative. Linder and Picton (49) and Lottermoser (50) also found that dialyzed silicic acid collects on the anode. Blitz (51) and Whitney and Blake (52) made observations on this subject. Losenbech (53) measured the electrical conductivity of silica sols. He found that the conductivity of hydrochloric acid solutions of concentrations up to 1/100 N - HCl is reduced by the presence of silicic acid solutions. The magnitude of the change decreases with time, being at first rapid, and then slows off to a limiting value. The particles of silicic acid are negatively charged, and the charge is steadily reduced by the addition of hydrochloric acid until the iso-electric point is reached. With further addition of the acid the sign of the charge changes, and the charge increases until the positive value is greater than the original negative value. The constant potential of the particles in different concentrations
of the same preparations is dependent on the concentration of the sol, in the sense that the iso-electric point of different sols lies at greater concentration of hydrochloric acid, the greater the concentration of the sol. The observed results are explained by assuming that the silicic acid particles are saturated with hydrochloric acid, like a sponge, and that this acid is taken up slowly. The hydrogen ions are expelled from the sponges with a definite tension, so that the contact potential between particles and solution may be approximately represented by Nernst's formula.

Grudmann (43) studied the electrical properties of sols of silicic acid and showed that the charge in a hydrochloric acid solution changes on keeping, becoming first more negative, reaches a maximum, and then changes in the opposite direction. Colloidal silica in dilute acid and alkaline solution is electronegative, and during electrolysis accumulates about the anode. Billitzer (54) showed that in alkaline and feebly acid solutions—say up to 0.1 N-HCl—the gel is electronegative; with a greater concentration of acid—say 1/2 N HCl—the gel is electropositive; and somewhere in between these limits an iso-electric point occurs where the liquid is electrically neutral. The above work would seem to indicate that the iso-electric point is between a pH of approximately 0.3 and 1.2. Davis and Hay (57), however state that it is in the range of unstable gels which would indicate that it lies between a pH of 5.5 and 8.5. The fact that solutions of pH as low as 4.0 aid in coagulation would appear to substantiate the lower pH values and the fact that solutions of still lower pH values hinder coagulation would then mean that the peptizing effect of strong acids in predominate. More work is needed on this
phase of the work before it can be entirely understood. The results of this work would indicate an iso-electric point of approximately 3.5 since it is here that the solutions fail to aid coagulation. However, as stated above the peptizing effect must be taken into consideration.

These facts have been applied industrially by Scheverin (55) to remove impurities from clays, etc. When solutions of chloride are added to water with the clay in suspension, certain impurities settle rapidly, others remain in suspension. If the added salt also changes the electrical state of certain impurities so that, say, free silica becomes electropositive while the clay remains electronegative, the passage of a current through it will make the electronegative clay to collect about the anode, while the electropositive impurity accumulates about the cathode. Ormandy (56) has discussed the application of this process. Davis and Hay (57) state that with increasing acid concentrations we have first stable alkaline sols of negatively charged silica, then a range of gels, then stable acid sols of positively charged silica, and finally a second series of gels. Perhaps the first series of gels they mention are in the range of feeble charge and surely the iso-electric point is somewhere in between. They also conclude that colloidal silica represents nothing more complicated than a generally hydrophobic material, with some hydrophillic properties, in which the pH of the systems affects the most important variable—the sign and magnitude of the electrokinetic potential.

There are various factors which affect the behavior of silicic acid. The most important of these, perhaps, is the formation of a jel which depends upon a number of variables such as tem-
perature, pH, impurities, etc. The discussion of jel formation is beyond the scope of this paper since it has no particular bearing on the state of silicic acid which aids coagulation. Other factors, however, influence greatly the behavior of the acid. Ghosh and Dhar (45) state that if an alkali is added to a silicic acid sol it will react on the unpolymerized acid molecules readily because of its greater chemical reactivity than that of the polymerized molecules. Hence the amount of polymerized molecules will decrease and more of the unpolymerized molecules will be formed in order to restore the equilibrium. The polymerized molecules of the acid gives out a complex negative ion, which is adsorbed more by silicic acid sol than a simple ion. They have shown (50) that the amount of adsorption is greater for a complex and heavy ion than for a simple one. On the addition of an alkali, the concentration of the complex ions decreases and hence its amount of adsorption by silicic acid sol also decrease. Thus the electrical charge and stability of the sol becomes less in the presence of small quantities of alkali. On the other hand, presence of $H^+$ ions increases the complexity of the anions so that more of anions are now adsorbed by the sol which becomes necessarily stabilized.

L. F. Werner (59) shows that alkalis have a very strong peptizing influence on the hydrosol of silicic acid. The effect is greatest for the medium and low concentrations for the highly ionized bases and in the case of the slightly ionized bases the effect is great in all but the lowest concentrations. He also points out that acids have a strong peptizing effect on silicic acid. In the case of the strong acids, this effect is most marked at a medium concentration. Hurd, Raymond and Miller (61) also remark on the
peptizing effect of alkalies and point out that it is the hydroxyl ion rather than the sodium that is responsible, although Kroger (62) believes the effect is due to the sodium ion in solution.

According to M. Pappada (60) solutions of non-ionized organic substances do not coagulate silica sol, but solutions of ionized salts coagulate negative colloidal silicic acid, and with a given family of salts, the action is all the more marked the greater the atomic weight of the salt and similarly the action is more marked the greater the electrical charge on the ions, thus trivalent ions are more active than bivalent and there in turn more than univalent. Thus W. B. Hardy (48) found aluminum sulfate acted immediately and others of decreasing valency took longer to gelatinize.

Since Baylis (8) and found that some natural waters coagulated better than prepared water and assumed the effect was due to the presence of silica, it might be well to look into the condition of the silica in those waters. Surely in such dilute solutions the silicate is completely hydrolyzed and Jordis, Mylius, Kohlrausch, Linder and Bogue (62) show that in the hydrolysis of the alkali silicates, the silica separates in the colloidal form, and if hydrated sodium metasilicate is treated with water, the first infinitesimal portion dissolved is immediately decomposed with the formation of colloidal silica and the process will go on until some more or less definite end-point is attained. But the presumed equilibrium is in no way determined by the real solubility of sodium silicate itself.

Now we have a fairly accurate picture of the form that aids coagulation of the aluminum hydroxide floc. W. Biltz (63) has shown that colloidal particles of aluminum hydroxide are positively
charged because, if, say, 100 volts be passed through the concentrated sol contained in a U tube, in half an hour the liquid near the negative electrode becomes turbid— anodic cataphoresis— and that near positive electrode becomes clear.

Thus it becomes clear that we are dealing with negatively charged colloidal silica particles and positively charged colloidal aluminum hydroxide particles. As Baylis (8) suggested it would appear that the silica forms a nucleus around which the aluminum hydroxide forms due to the opposite charge on the particle, and then the silica, by ionic attraction, can further conglomerate forming the extremely large floc noticed, and settle out. Since the charge, as pointed out by Loesenbeck (53), Billitzer (54) and Davis and Hay (57), is positive in the more acid range we can see that silicate solutions of low pH, say 3.0 will hinder coagulation since their positive charge will tend only to disperse the aluminum hydroxide floc.

The iso-electric point is evidently on the acid side, say pH 5.0, since it was found that solutions at this pH would give good aid to coagulation and Grundmann (43) found it to be electronegative in dilute HCl. Apparently, the magnitude of the charge has no effect on the coagulation or else the charge reaches a high value immediately on passing the iso-electric point since comparable results are obtained by using solutions of pH from 4.0 to 9.5 if aged properly. On the other hand, Grundmann (43) points out that the charge in hydrochloric acid solution changes on keeping, becoming first more negative, reaches a maximum and then changes in the opposite direction. If this change is more rapid in the lower pH range, 6.5 - 8.0, then it is apparently the electrical charge
on the ion that is responsible for the coagulation aid, if not it would be hard to explain the longer ageing time necessary to obtain an active solution of silicate from the more alkaline solutions. It was found in the study and will be further discussed later that the pH of alkaline silicate solutions rises with time and perhaps the charge on the ion parallels this change since then there would be more of the negative hydroxyl ions to furnish the negative charge. If this charge increases with the alkalinity one would expect very good aid from very alkaline sodium silicate but this is not the case as the peptizing effect of the alkalis noted by Werner (59), Hurd, Raymond and Miller (61) and Kroger (62) evidently serves to keep the particles of silica, coated with aluminum hydroxide, from conglomerating and a very fine suspension of the floc results. The similar effect in the more acid range would serve to help disperse the floc formed even if the charge has no effect on the coagulation. Further, as pointed out by Ghosh and Dhar (45) the presence of large amounts of alkali will prevent the formation of the polymerized molecules leaving the silica in the molecular state which does not aid coagulation. That there is not chemical reaction between the silica and alum has been shown by Foote, Schuler and Langle (64) who prove that aluminum hydroxide precipitated in presence of soluble silica formed a solid solution and no definite compound.

The author has taken into consideration the film of protecting water around colloided particles reported by Mueller (67), the dehydrating power of certain ions reported by Laskin (62) and perhaps these factors have some effect on the "activity" of the silica particles. If the silica particle loses its covering of water then
surely it would have more of a chance to aid coagulation. However, on examination of the data and paying particular attention to the effect of the strong coagulating power of the higher valency ions towards silicic acid it would seem that the charge on the ion has a preponderant influence on aiding coagulation.

An interesting sidelight on the action of acid treated sodium silicate solutions was brought out when an investigation of the pH rise of the solutions was made. Baylis (8) commented on this pH rise but made no measure of it. Batcheler (65) stated that gelation was attended by little or no change in pH in acid sols but a pH rise in the alkaline sols. Hurd and Griffith (66) also noted no change in acid sols but didn't report on alkaline solutions.

Since there is such a rapid rise in the pH of alkaline solutions it was thought to be of value to evaluate the rate of this change so as to be able to determine the pH at any given time provided one knows the pH at any one time and also the temperature. A search of the available literature failed to produce any data on the rate of change of pH although much work was done on the variation of jelling time with pH. The determination of pH of any colloidal solution is, of course, a difficult problem because of the high degree of adsorption on the electrode in any electrometric determination and then, too, the milky turbidity of silicate solution makes any colorimetric method unreliable. In the present work a Coleman glass electrode pH electrometer was used and care was exercised to insure accurate readings.

The procedure followed in making these determinations is given under the chapter on Experimental Procedure.

It was found that the pH of acid treated sodium silicate sol-
VARIATION OF CONSTANT'S WITH pH

KEY:

= 56 F
= 70 F
= 80 F

Figure No. 7
usions varies linearly with the log of time. This relationship is followed very closely up to a certain limiting time value where the pH remains quite constant. At pH values below 6.0 the pH remains quite constant and those values above 9.5 give erratic results.

Figure 6 shows typical curves taken at 70° plotted from data in Table 10. The equation of these curves is \( y = \text{pH}_1 + b \log x \).

where \( y = \) pH at time \( X \)

\( \text{pH}_1 = \) pH at one minute

\( b = \) a constant depending upon pH and temperature.

\( x = \) time in minutes.

The value of \( b \) plotted at different temperatures in Figure 7 varies from 0 at low pH values to 0.4 at the higher values. It was thought, at first, that the value of the constant varied as the temperature and this is true up to a certain point. A number of experiments were conducted at 115°, 150° and 175° F. but the results were not always consistent. The change in pH or hydrolysis of sodium silicate occurs very rapidly in the first minute or two and after that it follows the logarithmic relationship. This first rapid change, of course, reduces the quantity of sodium silicate present and hence will tend to decrease the magnitude of the constant \( b \). It was also found to remain constant over various pH values being about 25 at 115°. Lack of time prevented the further investigation of the pH change at higher temperature hence the values obtained were not plotted with the others in Figure 7. The change in pH of solution at pH 8.8 are shown for various temperatures in Figure 8.

However, in the range of 56° to 80° or 90° the use of the
above equation and curve enables one to determine the pH of any solution at any time provided the time of mixing is known. Further work will be needed before a complete understanding of the change at high temperature may be available.

This rise in pH is, of course, due to the increasing concentration of hydroxyl ions. These hydroxyl ions evidently come from the hydrolysis of the sodium silicate which remains in excess of the acid added. This is according to the reversible equation $\text{Na}_2\text{SiO}_3 + \text{H}_2\text{O} \rightarrow \text{NaOH} + \text{H}_2\text{SiO}_3$. Now we know that the silicic acid polymerizes to colloidal silica and hence is taken out of solution forcing the solution towards the right constantly building up more and more sodium hydroxide until ultimately the hydrolysis constant at this particular concentration is reached. At higher pH values the higher concentration of excess sodium silicate accounts for the more rapid rise in pH tapering off after a few hours. At low pH values all of the sodium silicate has reacted with the sulfuric acid forming sodium sulfate, a neutral salt, leaving no free silicate to hydrolyze, hence the constant pH value noted. Then, too, since we know that the action is more rapid at higher temperatures we can then account for the constant value of the constant $b$ in the equation $y = a + b \log x$ if we assume that the greater part of the reaction takes place almost immediately leaving only a small amount of the silicate left to hydrolyze.
<table>
<thead>
<tr>
<th>Time Min.</th>
<th>pH of 3% Silicate Solutions</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.50 4.90 5.65 6.20 6.90 7.50 8.05 8.50 9.10 9.60 9.90 10.40</td>
</tr>
<tr>
<td>1</td>
<td>3.50 4.95 5.70 6.30 6.95 7.60 8.20 8.60 9.15 9.60 10.00 10.50</td>
</tr>
<tr>
<td>2</td>
<td>3.50 4.95 5.75 6.25 7.00 7.60 8.40 8.70 9.25 9.65 10.05 10.60</td>
</tr>
<tr>
<td>4</td>
<td>3.50 5.00 5.80 6.25 7.10 7.65 8.40 8.80 9.40 9.70 10.10 10.60</td>
</tr>
<tr>
<td>6</td>
<td>3.50 5.00 5.80 6.20 7.20 7.75 8.50 8.80 9.45 9.70 10.20 10.70</td>
</tr>
<tr>
<td>8</td>
<td>3.50 5.00 5.80 6.30 7.20 7.75 8.55 8.95 9.50 9.75 10.20 10.70</td>
</tr>
<tr>
<td>10</td>
<td>3.50 5.00 5.80 6.30 7.20 7.80 8.55 8.95 9.50 9.75 10.20 10.70</td>
</tr>
<tr>
<td>15</td>
<td>3.50 5.00 5.85 6.30 7.80 8.60 9.00 9.55 9.80 10.20 10.70</td>
</tr>
<tr>
<td>20</td>
<td>3.50 5.05 5.85 6.35 7.85 8.60 9.00 9.60 9.80 10.20 10.70</td>
</tr>
<tr>
<td>30</td>
<td>3.50 5.05 5.90 7.80 8.70 9.15 9.60 9.80 10.30 10.70</td>
</tr>
<tr>
<td>45</td>
<td>3.50 5.05 5.90 8.80 9.20 9.60 9.80 10.30 10.70</td>
</tr>
<tr>
<td>60</td>
<td>3.50 5.05 5.90 8.80 9.20 9.70 9.85 10.40 10.70</td>
</tr>
<tr>
<td>90</td>
<td>3.50 5.10 7.80 9.30 9.70 9.90 10.40 10.70</td>
</tr>
<tr>
<td>120</td>
<td>3.50 5.10 8.90 9.40 10.40 10.70</td>
</tr>
<tr>
<td>180</td>
<td>3.50 5.10 8.90 9.40 9.75 9.95 10.40 10.70</td>
</tr>
<tr>
<td>240</td>
<td>3.50 5.15 9.00 10.70</td>
</tr>
<tr>
<td>300</td>
<td>3.50 7.95 9.90 10.00 10.50 10.70</td>
</tr>
<tr>
<td>360</td>
<td>3.50 9.55 9.95 10.10 10.50 10.70</td>
</tr>
<tr>
<td>420</td>
<td>3.50 9.55 9.95 10.00 10.50 10.70</td>
</tr>
<tr>
<td>480</td>
<td>3.50 9.55 9.95 10.10 10.50 10.70</td>
</tr>
<tr>
<td>600</td>
<td>3.50 9.55 9.95 10.00 10.50 10.70</td>
</tr>
<tr>
<td>900</td>
<td>3.50 9.55 9.95 10.10 10.50 10.70</td>
</tr>
</tbody>
</table>
Discussion

As has been pointed out acidified sodium solicate has been found to be a great help in the coagulation of water using alum as the coagulant. This has been found to be true also in the case of sewage treatment. Baylis has stated (39) that silica does not seem especially good in treatment where the water is particularly dirty or has a large amount of color and this would seem to indicate that it would not be of much aid in treating sewage which is, after all, merely very dirty water. However, it has been found in the experiments conducted here that the silica does aid in coagulation very much and silica is a valuable adjunct to alum in sewage treatment. Baylis also states that the amount of alum cannot be decreased where the minimum amount is now being used. It has been found here to allow a decrease in the amount of alum of about forty per cent with only ten PPM of silica as SiO₂. This work was, of course, on sewage and presents a somewhat different problem than the work done on water coagulation.

The use of silica produces a much larger floc which settles more rapidly. This more rapid settling would have the effect of decreasing the size of the settling basins and although no measurement of the settling period needed was made, observations would tend to indicate that one hour would be sufficient in most cases. The floc formation was, in most cases, almost immediate so that no long mixing period nor any flocculators would be needed. The floc formed seemed to be very tough and will not break up if mixed too vigorously. In some cases however, it was noted that when large volumes of air were introduced into the mixing jars and the mixing was very rapid the floc seemed to become saturated with
air and as a consequence floated on top of the sewage. Further slow mixing would dislodge the air and the floc would settle again.

The use of silica also widens appreciably the pH range of effective flocculation with alum. This would mean a decrease in the amount of lime and sulfuric acid or any other chemical used mainly for pH control. Since the effective pH range is so wide this type of treatment would take care of fluctuations in those plants receiving large amounts of industrial trade wastes which ordinarily require constant attention as to pH and its control.

The silica has no other effect on the sludge except as it increases the amount. At any rate there is nothing in the literature that would indicate that there would be any effect on sludge digestion or incineration. The increased bulk presents a problem but it is partly offset by the fact that the material is denser and contains less water than ordinary sludge. Dewatering and filtration of such sludge might present further problems and it is planned to conduct further research on this particular phase of the problem.

The one big disadvantage to the use of silica is, of course, the necessity for careful control in the preparation of the silicate solution. The danger of jelling and subsequent loss of materials is a problem that requires attention and can be lessened only by the use of weak solutions and high pH which mean a longer ageing period. This would necessitate the building of at least two large containers for the solution as well as containers for the silicate and the sulfuric acid. Perhaps there is some other strength solution or some other pH range that will be more effective and require less attention and only further research will
reveal this condition. The use of heat will decrease the ageing time and where cheap heat is available this could be resorted to although the cost, in most cases, will be prohibitive.

The best method of control of silicate solutions appears to be in the measurement of pH and although alkalinity measurements are easy to make by untrained operators, better and easy-to-read equipment is fast coming into use for pH readings as well, so that now there is no great advantage to be had in the use of the alkalinity measurement. In this investigation the author found that pH readings seemed to be much more accurate measure of the condition of the solutions than the alkalinity measurement. The curves for pH rise of silicate solutions enable one to determine more accurately their condition at any time and hence a better comparison at any pH value may be obtained.

The condition of the silica that aids coagulation seems to be colloidal silica possessing a negative charge. As stated previously these particles present a nucleus around which the alum floc can form and then by mutual attraction the silica particles conglomerate and come down together in a large floc. That the silica presents a large number of nuclei is indicated by the fact that when large proportions of silica are used the result is deflocculation—apparently there is too much surface for the aluminum hydroxide to cover. The value of the negative charge is questionable since there is a controversy as to just where the iso-electric point is. If the charge becomes positive it is easy to see that in that range the result will be deflocculation since aluminum hydroxide is also positively charged. The literature would indicate that this positive charge occurs somewhere below a pH of 5.0 and indeed
below this value no aid is given to coagulation. However the peptizing effect of strong acids may be the predominant factor as is the peptizing effect of strong bases in the high pH range above 10.0.
Summary of Results

An investigation of the effect of acidified sodium silicate on alum coagulation of sewage has been made as well as an investigation of the nature of silicic acid. The following facts have been borne out:

1. Sodium silicate must be acidified, as by itself it will cause deflocculation.

2. The pH of the silicate solutions has no appreciable effect on its effectiveness provided the upper and lower limits of 4.0 and 10.0 are not exceeded.

3. An ageing period is required as freshly prepared solutions will tend to cause deflocculation. The length of this period depends upon the pH of the solution varying from a few minutes at pH 7.0 to several hours at pH 9.6. This period may be shortened by the use of higher temperatures.

4. The use of sodium silicate widens the effective range of alum coagulation.

5. Other coagulants, such as the iron salts, are aided by the use of sodium silicate but to a generally lesser extent than alum.

6. The use of sodium silicate permits a reduction of about 40% of the alum necessary. This is with about 10 PPM SiO₂.

7. The form of silica that aids coagulation seems to be colloidal silica particles possessing a negative charge. These particles form a nucleus around which the aluminum hydrate can form. Strongly acid or alkaline solutions cause deflocculation because of their peptizing effect towards silicic acid.

8. The pH rise of acid-treated sodium silicate solutions has been noted and a mathematical investigation has been made.
An equation has been developed to determine the pH of a silicate solution at any time.
BIBLIOGRAPHY


25. E. F. Eldridge, "Notes on Ferric Chloride Coagulation of Sewage". W. W. and Sew 80, 9, 335 (1933).


30. Nesmehanoff, Gesundh, Ing. 58, 471 (1935)


32. J. J. McCarthy, "Fitting Chemicals to Sewage Treatment". Munic. San. 9, 1, 22 (1936).


34. Upton and Bussell, 93rd meeting of the Am. Ch. Soc. Chapel Hill, N. C. April, 1937.


36. Cook, "Results from the Use of Activated Alum at Batavia", N. Y. W. W. and Sew. 81, 2, 47 (1934).


40. Mylius and Groschuff, Ber 39, 116 (1906).


42. Schwarz and Coworkers, Kolloid Z., 28, 77 (1921).


44. Norton and Roth, Jour. Chem. Soc. 19, 832 (1897).


46. R. Schwarz and O. Leide, Ber. 53B, 1508, 1680, (1920).


51. W. Blitz, Ber. 37, 1095 (1904).


55. B. Schwerin, Brit. Pat. Nos. 12431, 1900; 22,301, 1901; and many others.


58. Ghosh and Dhar, Kolloid Zeit, 34, 144 (1924).


69. H. Gladys Swope, private communication.

ACKNOWLEDGEMENT

The author wishes to acknowledge his indebtedness to Dr. Irvin Lavine head of the Chemical Engineering Department for his splendid assistance in this investigation as well as for his help in preparation of this paper. He also acknowledges the assistance of K. W. Riley for his suggestion of the problem as well as aid in analysis and technical advice. He is grateful to the Board of City commissioners of Grand Forks for its consent to use the facilities of the local Sewage Treatment Plant. The splendid cooperation of John B. Kleven, Plant Superintendent, as well as the other plant operators was indispensable in carrying out this work and was appreciated very much. He also wishes to acknowledge the supervision of L. C. Harrington, Dean, College of Engineering, University of North Dakota.