

STATE OF ILLINOIS  
DEPARTMENT OF REGISTRATION AND EDUCATION

DIVISION OF THE  
STATE WATER SURVEY  
A. M. BUSWELL, Chief

BULLETIN NO. 22

**INVESTIGATIONS OF CHEMICAL REACTIONS  
INVOLVED IN WATER PURIFICATION  
1920-1925**



(Printed by Authority of the State of Illinois.)

URBANA, ILLINOIS

PHILLIPS BROS. PRINT.  
SPRINGFIELD, ILLINOIS.



1926  
52183-1500

## CONTENTS.

	Page.
INTRODUCTION AND SUMMARY .....	7
By A. M. BUSWELL	
PART ONE.	
The use of the hydrogen electrode in investigations of chemical reactions involved in water purification .....	15
By R. E. GREENFIELD with A. M. BUSWELL	
PART TWO.	
The relation of hydrogen-ion concentration to the properties of alum .....	47
By G. P. EDWARDS with A. M. BUSWELL	
PART THREE.	
Studies on the precipitation of calcium, magnesium, and aluminum .....	73
By W. U. GALLAHER with A. M. BUSWELL	
PART FOUR.	
Precipitation of alumina in the acid range of hydrogen-ion concentration .....	119
By L. H. MCROBERTS with A. M. BUSWELL	
BIBLIOGRAPHY .....	128

## FIGURES.

	Page
INTRODUCTION—Composite Figure Showing Relation of Residual Alumina and pH Values. . . . .	11
PART ONE.	
1. Titration of carbonates with acid. . . . .	24
2. Precipitation of magnesium as magnesium-hydroxide. . . . .	27
3. Precipitation of calcium as calcium-carbonate. . . . .	29
4. Precipitation of aluminum as aluminum-hydroxide. . . . .	32
PART TWO.	
1. Graphic representation of reactions in coagulating basins. . . . .	50
2. Relation of hydrogen-ion concentration to residual alum in effluents of filter plants in Illinois. . . . .	57
3. Soluble alumina in raw waters sampled on field surveys. . . . .	58
4. Dissolved alumina in water from coagulation basins of filter plants in Illinois. . . . .	59
5. Results of laboratory experiments on residual alum. . . . .	59
PART THREE.	
1. Plan of experimental water-filtration plant. . . . .	SO
2 and 3. Residual alum in effluent from experimental plant (low turbidity). . . . .	82
4 and 5. Residual alum in effluent from experimental plant (high turbidity). . . . .	82
6. Composition of alum floc. . . . .	88
7. Decrease in hardness. . . . .	94
PART FOUR.	
1. Experimental filter. . . . .	123
2. Constant-feed device for mixing tank. . . . .	124

**STATE OF ILLINOIS**  
**DEPARTMENT OF REGISTRATION AND EDUCATION**  
**A. M. SHELTON, Director.**

---

**BOARD OF**  
**NATURAL RESOURCES AND CONSERVATION**  
**ADVISORS.**

**A. M. SHELTON, *Chairman.***

**WILLIAM A. NOYES, Chemistry,**  
*Secretary.*

**JOHN W. ALVORD, Engineering.**

**EDSON S. BASTIN, Geology.**

**HENRY C. COWLES, Forestry.**

**WILLIAM TRELEASE, Biology.**

**C. M. THOMPSON, Representing the**  
**President of the University of**  
**Illinois.**

---

**MEMBERS OF WATER SURVEY DIVISION**  
**SUB-COMMITTEES.**

**A. M. SHELTON.**

**C. M. THOMPSON.**

**WILLIAM A. NOYES.**

**JOHN W. ALVORD.**

---

**WATER SURVEY DIVISION.**

**A. M. BUSWELL, *Chief.***

**LETTER OF TRANSMITTAL.**

---

STATE OF ILLINOIS,

DEPARTMENT OF REGISTRATION AND EDUCATION.

STATE WATER SURVEY DIVISION.

URBANA, ILLINOIS, June 15, 1926.

*A. M. Shelton, Chairman, and Members of the Board of Natural Resources and Conservation Advisors:*

GENTLEMEN: Herewith I submit a report of studies of the chemistry of water purification in Illinois and recommend that it be published as Bulletin No. 22. These studies, based as they are on conditions in Illinois, will find direct application at filter plants in the state.

Since the Directors' report includes a statement of the general activities of all divisions, it has seemed advisable to discontinue the publication of an annual report of this division and to prepare instead summaries of our various investigations as they are completed. **This** policy was adopted with the publication of Bulletin No. 18 in May of 1922, and has been followed since that date.

Respectfully submitted,

A. M. BUSWELL, *Chief.*

# INVESTIGATIONS OF CHEMICAL REACTIONS INVOLVED IN WATER PURIFICATION.

---

## INTRODUCTION AND SUMMARY.

---

The chemical processes that are involved in the operation of filter plants for public water supplies deserve attention both from the point of view of chemists and operators and from the point of view of the general public. The reactions in coagulating basins, in particular, are not as simple as have commonly been supposed. The use of alum as a coagulating and precipitating agent has encouraged many investigators to attempt to determine the most favorable conditions for reactions of this nature, but progress has been retarded by lack of full understanding of the chemistry of aluminum salts.

The question of residual alum in filtered waters has been referred to by writers from various standpoints, some physicians being alarmed by possible physiological effects and some water-works operators being apprehensive of possible waste of chemicals. The term residual alum, as used in such discussions, has not been well defined. Some writers use it without any statement as to the comparative amounts of alumina found in the raw and filtered waters and without any indication as to what may be a safe limit for residual alumina. The chief objections to unprecipitated alumina seem to be the incrustation of sand and of distributing mains and the waste of chemicals. Not only should the alum be precipitated as completely as possible, but it should form a coagulum that will settle with reasonable rapidity and produce maximum clarification. Unprecipitated alum does no work, and the inference is that residual alumina in excess of a certain minimum may be taken as an indication of faulty operation and inefficient clarification.

Until recent years, work such as that of Bartow and Lindgren (5), in which analyses were made of several samples of the same water treated with increasing quantities of reagent, had been the most fruitful means of studying and determining the limitations of such reactions; but the results did not yield all the information that could be desired, for difficulties were usually encountered because of several important conditions peculiar to water purification. In the first place, these reactions are carried out in very dilute solutions, which cannot

be accurately analyzed by ordinary methods. In the second place, although it is essential that they should be carried as nearly to completion as possible, it is not desirable to use a large excess of reagent to force them to completion, for often an excess of reagent would be as harmful as the material which the treatment process is designed to remove. Finally, it has been exceedingly difficult to reproduce in laboratories the conditions under which these reactions take place in filter plants, and it has been still more difficult to maintain adequate control of the experimental conditions.

Hildebrand's paper (48) on the application of the hydrogen electrode to research and teaching had suggested a method which might be applied in studying some of these reactions, since most of them would be expected to take place in such a manner as to cause significant changes in hydrogen-ion concentration. Washburn (123 and 124) had pointed out the importance of the hydrogen-ion concentration in inorganic reactions, and Mason (73) had given directions for the colorimetric determination of hydrogen-ion concentrations in water analysis.

The methods of investigation that had been used with great success by Sorensen in his work on factors determining the course of biological reactions, and by a host of later workers in biochemistry, afforded a promising angle of attack upon many problems in the chemistry of water.\* Morison (81) made the first application of hydrogen-ion concentration as a means of control in water filtration. In this laboratory, Snook (106) had used the hydrogen electrode with some success to study the precipitation of magnesium by means of lime water. His apparatus was, however, rather crude, and the amount of work done was limited; also, as in most of the investigations in this field prior to 1920, the solutions used were much more concentrated than those employed in filter-plant operation.

In 1920, this laboratory undertook a series of investigations of these reactions, giving special attention to hydrogen-ion concentration and using the hydrogen electrode as the principal means of its determination. The investigations were carried out by four workers, each reporting his results in a thesis for an advanced degree in chemistry in the University of Illinois. This bulletin is made up of material from these four theses, each in a separate part, as follows:

---

\* For an extensive list of works on hydrogen-ion concentrations, see Clark (18).



## SCOPE OF THESE INVESTIGATIONS.

### PART ONE.

In 1920 and 1921, R. E. Greenfield used the hydrogen electrode to re-survey a variety of reactions commonly met with in water analysis and purification. He obtained titration curves for several common carbonates and bicarbonates and applied the method of hydrogen-ion determination to the precipitation of magnesium, calcium, and aluminum. In general, his titration curves for aluminum check with those published by Hildebrand (48) and by Blum (12) for more concentrated solutions. The point of maximum precipitation of aluminum appeared to be located between pH 6. and pH 7.5, but there was no definite point of inflection in the precipitation curves. The inference was that pH\* determinations alone did not definitely delimit the zone of optimum conditions, and that the precipitation of alumina deserved to be studied as an individual question for research. Greenfield's work was of value also in suggesting other problems for further investigation and in developing methods of procedure in the application of the hydrogen electrode to water analysis.

### PART TWO.

Following these methods of procedure, G. P. Edwards, in 1922 and 1923, employed the hydrogen electrode to determine the solubilities of aluminum through a wide range of hydrogen-ion concentrations. From gravimetric determinations, the base solubility product of aluminum hydroxide was calculated to be  $3 \times 10^{-14}$ , and the acid solubility product  $1 \times 10^{-13}$ . Under carefully controlled experimental conditions, pH 5.5 and pH 7.8 were found to be the limits of minimum solubility. Edwards also studied the relation of the "isoelectric point" to the optimum conditions for the removal of color from water; he obtained maximum removal of color by alum near pH 6.0 and concluded that the action was one of adsorption rather than chemical combination. In two surveys of various filter plants in Illinois, he collected data showing how the actual decrease in the alkalinity of the water due to the addition of alum differs from the expected decrease as ordinarily calculated, and how residual alumina is related to hydrogen-ion concentration in the effluent. In general, less dissolved alumina was found in the effluents from filter plants than in the raw waters, the amount in the effluent seldom exceeding two parts per million. Least residual alum was found

---

\* For the definition of the symbol pH see Clark (18).

between pH 6.0 and pH 7.8. Both the field work and the laboratory experiments indicate a rather broad pH zone in which the amounts of residual alum are lower than one-tenth of a grain per gallon.

#### PART THREE.

In 1923 and 1924, W. U. Gallaher, using methods, determined the solubility product of magnesium hydroxide and also checked the previous work on alum precipitation by tests made in an experimental filter plant near the laboratory. Samples from filter plants in various parts of the state were analyzed, with special attention to the composition of the alum floc\*. From his data it appears that, where lime is used in connection with alum for coagulation, enough calcium carbonate or magnesium hydroxide precipitates to keep the alkalinity from decreasing at the rate usually calculated; and that in the floc formed at pH 7.4 in actual filter-plant practice there is no basic aluminum sulfate but probably some basic aluminum carbonate. He found that the solubility of alumina in sand-filtered water increases from pH 7.9 to pH 9.8; but, on account of the corrosion of the metal containers and the reaction of the gravel and sand with the water in the experimental plant, he did not get correlated results in the acid range of hydrogen-ion concentrations. In addition, Gallaher studied the effect of heat in a commercial lime-soda softener at the Danville plant of the Illinois Power and Light Corporation, finding that with proper treatment the time required for settling and the final hardness of the water were markedly decreased by increasing the temperature and by using alum.

#### PART FOUR.

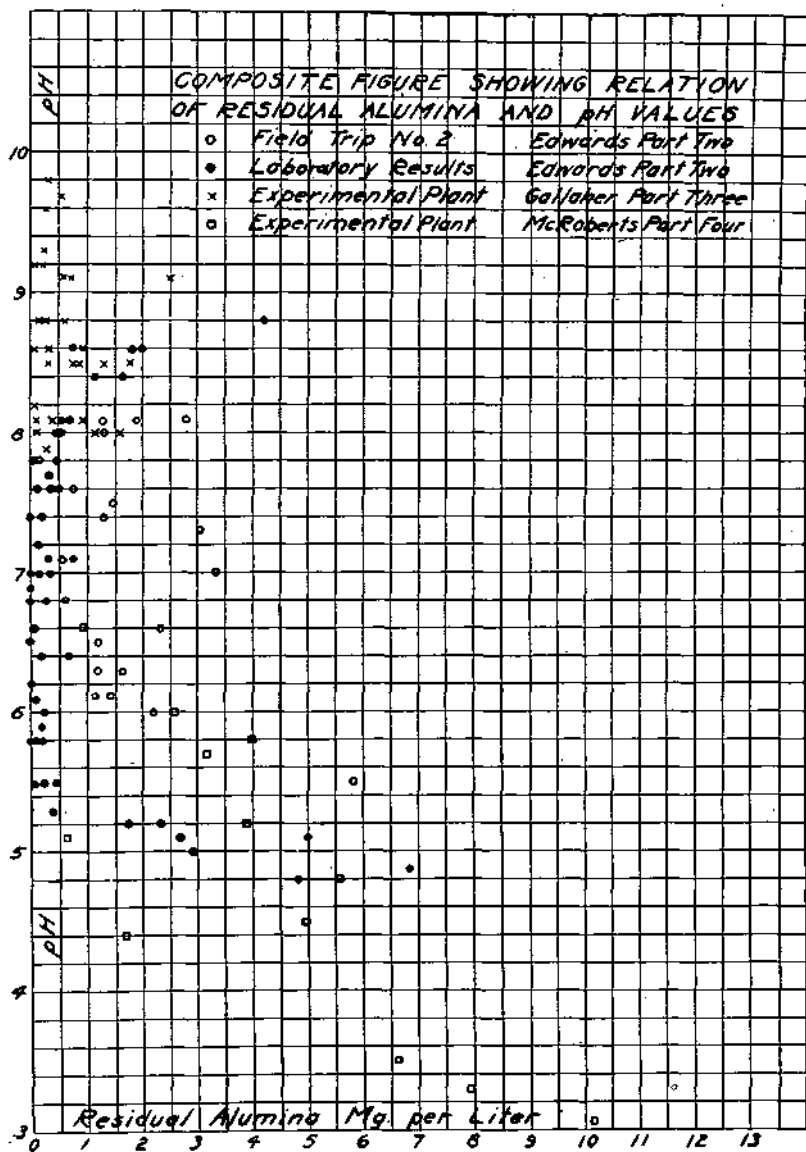
Finally, in 1924 and 1925, L. H. McRoberts modified the experimental plant to eliminate the difficulties formerly encountered at greater hydrogen-ion concentrations and continued the investigation of alum precipitation. He found that residual alumina decreases with decreasing hydrogen-ion concentration from pH 3.2 to pH 7.3, and that the alumina content of the effluent from a plant operated efficiently is considerably less than the alumina content of the raw water.

---

#### \* Editor's Note :-

The literature shows some confusion of terms due to shifting points of view on the nature of the complex mixture of chemical compounds precipitated in coagulating basins. In the present bulletin, the precipitate is generally called "alum floc"—an expression definite enough to be clear without committing a writer to any particular view of the exact composition of the precipitate. Similarly, "residual alum" is here used because it has been widely employed to refer to the aluminum compounds left in solution, although the evidence now seems sufficient to discredit the fears formerly aroused by this unfortunate term.

For convenience in comparison of the results obtained by the several workers, typical data on residual alum have been collected from Parts Two, Three, and Four, and have been plotted on the Composite Figure shown here.



In the preparation of this bulletin, extensive editorial work has been done on these four independent theses. The aim has been to include all the data as originally obtained by each worker with his own interpretation. In some places where the discussion has been abridged to prevent unnecessary repetition of ideas, cross-references are supplied. It is hoped that the bulletin, taken as a whole, thus serves not only to record accurately the point of view of each investigator but also to show fairly the evolution of viewpoint from the beginning of the series of investigations to the present time. All bibliographical references have been collected and arranged alphabetically in an appendix. Credit for this editorial work is due to H. C. Oesterling, of the Department of English in the University, and to S. L. Neave, Chemist, of the Water Survey staff. Acknowledgment is also made of the assistance of G. C. Habermeyer, Engineer on the Survey staff, in the construction and operation of the experimental filtration plant.

#### GENERAL CONCLUSIONS.

It is believed that these investigations, together with those carried on in other laboratories during the last five years, have definitely established several important points:

(1) The amounts of residual alum in filtered water under ordinary conditions are inconsequential and are never sufficient to cause any physiological effect. No economic loss can be inferred from the presence of such slight traces of alum in distribution mains. (The data plotted on the Composite Figure on page 11 bear out this conclusion.)

(2) The saving that results from adjusting the pH to an optimum point is due to the greater efficiency of the alum used rather than to the prevention of unused alum going into the distribution mains. This efficiency consists largely in the formation of better alum floc, which is the first prerequisite in the purification process. It is, therefore, generally desirable to adjust the hydrogen-ion concentration of a natural water to an optimum point.

(3) The optimum point is not the same for all waters and can be determined in any given case only by taking account of all the factors (physical as well as chemical) entering into the purification process and by considering all the circumstances of the case. An operator may find that the optimum point for his plant varies with seasonal changes in temperature, turbidity, hardness and other factors.

(4) The use of pH determinations in the operation of a filter plant affords a guide to more efficient results only when there is no confusion of purposes. For example, other things being equal, pH 5.5

may afford most rapid formation of floc, pH 6.2 may be most effective for removal of color, pH 5.9—6.8 may give least residual alum, and pH 7.1 may be best for removal of turbidity. It is, therefore, unwise to attempt to accomplish too many different purposes at one time. Separate treatment may yield better results.

(5) The great complexity of the reactions involved in water purification is just beginning to be appreciated. Progress requires the utmost cooperation of engineers, chemists, and operators in the handling of problems of design and dosage. Great economies are yet to be effected. Continued research, looking toward solutions of these problems, is indispensable from the point of view of the general public.

A. M. BUSWELL.

AUGUST, 1925.

**PART ONE.**

**THE USE OF THE HYDROGEN ELECTRODE IN INVESTIGATIONS OF CHEMICAL REACTIONS INVOLVED IN WATER PURIFICATION.**

By R. E. GREENFIELD with A. M. BUSWELL

**CONTENTS.**

	Page.
Introduction . . . . .	17
Apparatus, chemicals and calculations. . . . .	18
Titration of carbonate solutions. . . . .	23
Precipitation of magnesium as the hydroxide. . . . .	26
Precipitation of calcium as the carbonate. . . . .	28
Precipitation of aluminum as the hydroxide. . . . .	30
Summary. . . . .	33
Suggestions for further study. . . . .	34

## THE USE OF THE HYDROGEN ELECTRODE IN INVESTIGATIONS OF CHEMICAL REACTIONS INVOLVED IN WATER PURIFICATION\*.

### INTRODUCTION.

Water purification involves some chemical reactions on which it has been difficult to obtain definite and direct data. Ordinary titration of the alkalinity of calcium carbonate or magnesium carbonate solutions assumes that the end-points are the same as those obtained when titrating sodium carbonate solutions. Little is known concerning the velocities of the precipitation reactions of calcium, magnesium and aluminum and concerning the conditions for complete precipitation. The use of the hydrogen electrode for following the courses of these reactions seemed to promise a method for obtaining more exact data both as to the end-points in alkalinity titrations and as to the optimum conditions for precipitation.

Using the hydrogen electrode, Hildebrand (48) had plotted titration curves of aluminum hydroxide which showed that precipitation began in solutions as acid as pH 4.0 and was practically complete between pH 6.5 and 7.5. He had also titrated sodium carbonate with a strong acid using the hydrogen electrode but had not titrated calcium carbonate or magnesium carbonate.

Blum (12) had published electrometric titration curves for the precipitation of aluminum hydroxide which were similar to those of Hildebrand. He had also determined the optimum limits of hydrogen-ion concentration for the precipitation of aluminum hydroxide in rock analysis. These determinations were made by adjusting the reaction of his solution to a certain value of the hydrogen-ion concentration and then boiling; when less than 0.1 mg. was found in 100 cc. of the supernatant liquid after boiling, the precipitation was considered complete. While furnishing valuable data for analytical procedure, Blum's paper unfortunately does not enable us to decide upon the best conditions for precipitation of aluminum hydroxide in the cold. The solutions used by Hildebrand were so much more concentrated than those

---

\* From a thesis submitted July, 1921, by E. E. Greenfield in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry in the Graduate School of the University of Illinois.

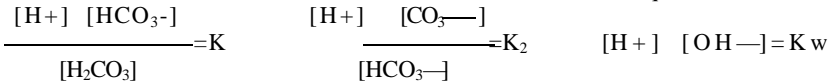
An abridged account of this work was printed in the Journal of the American Chemical Society, Vol. XLIV, No. 7, pp. 1435-42, July, 1922.



dealt with in water analysis and purification, that it seemed advisable to repeat his work using more dilute solutions and a more sensitive apparatus. The other reactions here studied have not, as far as we can learn, been investigated with reference to hydrogen-ion changes during their course.

#### APPARATUS, CHEMICALS AND CALCULATIONS.

It has been shown by Tillmans (113), Prideaux (91), McClendon (70), Greenfield and Baker (38), and others, that the hydrogen-ion concentration of natural waters is to a considerable extent determined by the carbonate and carbon dioxide content of the water. The mass law equations:



are valid in the case of any carbonate or carbon dioxide solution. If we know the value of the constants, and fairly accurate evaluations of these constants have been made (47, 48, 55, 56, 57), and if it is possible to determine experimentally any two of the four unknowns in the first two equations, it will be possible to calculate the others.

In the light of the discussion on this point in the papers referred to, an attempt was made to design an apparatus in which a given volume of hydrogen, one liter, would be brought into equilibrium with a carbonate solution contained in a hydrogen electrode vessel. If equilibrium were reached, by determining the hydrogen-ion concentration of the carbonate solution and the carbon dioxide content of the hydrogen, valuable data would be obtained for calculating the equilibrium conditions in carbonate solutions. McCoy (71) has reported experiments in which mixtures of carbonates and bicarbonates were shaken for some time with air, the air removed in such a manner as not to change the pressure, and the carbon dioxide content determined. This gave direct experimental data as to the partial pressure of carbon dioxide over carbonate solution containing various percentages of bicarbonate. If a successful apparatus had been designed, it would have been possible to repeat this work of McCoy's and at the same time find the hydrogen-ion concentrations in the same solutions upon which the partial pressure of carbon dioxide had been measured.

The apparatus tried consisted of a vessel (100 cc. capacity) provided with a side tube to make liquid contact with the salt bridge, a mercury-seal glass stopper carrying two platinized electrodes, and inlet and outlet tubes to introduce hydrogen at the bottom under the surface of the liquid and take the hydrogen off at the top. The vessel to hold the required volume of hydrogen was a special liter flask with an inlet tube sealed into the neck and passing to the bottom of the flask, and an outlet tube also sealed into the neck. A small mercury pump with mercury valves was designed to draw hydrogen from the containing flask, pass it through the hydrogen electrode and return it to the containing flask. Stopcocks were so arranged as to make easy the filling of the entire system with pure hydrogen. The containing flask could be disconnected and removed and the carbon dioxide content determined by regular methods. The entire apparatus could be placed in a constant-temperature waterbath. No rubber stoppers were used, the

only stopper in the system being a mercury-sealed glass stopper. All stopcocks were of the best quality obtainable, well ground and carefully greased. Where two glass tubes had to be joined with rubber connections, the ends of the glass were pushed close together, the connecting rubber tube was soaked in paraffin, and each joint was carefully tied with wire. In spite of these precautions no satisfactory results were obtained. The hydrogen electrodes gave check results only when the hydrogen atmosphere was first placed in the system; after a few hours of rotation by means of the mercury pump, the results became erratic. This was probably due to contamination of the hydrogen with oxygen. Work with the apparatus was finally given up as unsuccessful. McClendon (70) has attacked the problem from a different angle with somewhat more success. It would be desirable, however, to obtain results with a little higher degree of accuracy.

The potentiometer used was a Leeds & Northrup, Type K. The working current was furnished by a small ten ampere-hour lead-plate storage battery. This was left continually in the circuit, as the working current was found to be much more uniform when used in that way than when the battery was taken out of the circuit each night. The null-point indicator was a Leeds & Northrup galvanometer, Catalogue No. 2500-e, with a sensitivity of 396 megohms, a period of 3.4 seconds, and a coil resistance of 1800 ohms. The galvanometer was read by means of a lamp-and-scale device placed for convenience three meters from the instrument. (This distance was greater than was necessary to give the indicated sensitivity.) The standard cadmium cell, used in adjusting the potentiometer, was of the unsaturated type manufactured by Eppley. It was compared with another cell manufactured by the same firm and certified by the United States Bureau of Standards.

No attempt was made at shielding. High-voltage connections used on motors, etc., were well insulated and kept from crossing the potentiometer circuits as much as possible. Very little trouble from current leaks was experienced. The hydrogen and calomel electrodes were connected to the potentiometer through double-throw single-knife switches as recommended by Clark (17) one pole of each switch being connected to the negative pole of the potentiometer, and the other pole of each switch connected to the positive. The electrodes were connected to the knife of the switch. With a bank of such switches the rapid reading of several electrodes is made quite easy.

Saturated calomel half elements were used throughout the entire course of the work. The values for these elements given by Fales and Mudge (32) have been taken as the most reliable and have been used in the calculation of all results reported. The electrode vessel described by Fales and Vosburgh (31) was used. The mercury used was purified by placing it in an ordinary gas-washing bottle along with dilute nitric acid and stirring with a vigorous stream of air for 30-60 minutes. The nitric acid was changed once. The mercury, after purification, was dried by passing through a pin hole in filter paper and was finally distilled under reduced pressure with a small current of air. The ordinary grade of C. P. potassium chloride was purified by recrystallization from water three times and drying at 120° C. for two days. The calomel was prepared by the solution of some of the purified mercury in C. P. nitric acid, diluting the concentrated acid solution with redistilled water before all the mercury had dissolved, and precipitating the calomel with vigorous stirring, by a slow addition of C. P. hydrochloric acid. The

resultant calomel mixed with some free mercury was washed by decantation several times with redistilled water and then with potassium chloride solution of the strength to be used in the electrodes. The washed calomel was placed in potassium chloride solution of the desired strength and allowed to stand for several days with frequent shaking. The resultant mixture was used in the preparation of the electrodes.

Saturated electrodes made from this mixture, with an excess of solid potassium chloride resting on the surface of the mercury, were reproducible within one-tenth of a millivolt or better after they were twenty-four hours old. The electrodes that were in use daily, and had fresh stock solution added to make up the loss that always occurred due to flushing and leakage, could be depended upon to keep their original value within 0.1—0.2 millivolts for a month or two. The electrodes that were made up and left standing out of use changed sometimes as much as 0.5 millivolts in less than a month. They could be restored almost to the original value, but never completely, by taking out the old potassium chloride solution and adding fresh. The best practice seemed to be to make fresh electrodes frequently to check the ones in use.

Tenth-normal electrodes were prepared and compared with the saturated. The difference in potential agreed with the values given by Fales and Mudge. The tenth-normal electrodes were also used in making some comparisons of hydrogen electrode measurements. In every case tried, the results from a saturated electrode and a tenth-normal electrode differed from each other by the same amount as the difference in potential between the two when directly compared. The tenth-normal electrodes, because of lower conductivity, made the entire set-up much less sensitive. They were quickly spoiled by diffusion from the saturated salt bridge, even when cotton plugs, as recommended by Fales and Mudge, were used in the connecting tubes; and individuals made from the same material differed from each other more often and to a greater extent than did the saturated electrodes.

One of the most important necessities in the successful operation of hydrogen electrodes is an abundant source of pure hydrogen. During the first part of this work, an attempt was made to use hydrogen from a cylinder, purified by passing through alkaline pyrogallic acid and then through water. Only by frequently renewing the alkaline pyrogallic acid, which was rapidly exhausted by the considerable quantities of oxygen in the hydrogen, could this source be satisfactorily used. For the latter part of the work, hydrogen was generated by the electrolysis of sodium hydroxide and purified by washing through water to remove sodium hydroxide spray, and by passing through a quartz tube filled with platinized asbestos and maintained at a dull-red heat in a small electric furnace to remove the oxygen. The gas was finally passed through a second wash bottle containing either water or some of the solution under examination. The hydrogen generator was constructed by placing a large adapter, large end down, in a battery jar. The nickel gauze cathode was placed on the inside, running from top to bottom of the adapter and the anode, and on the outside near the top of the battery jar. The hydrogen was taken off from the small end of the adapter. Three such cells connected in series, using a current of from three to seven amperes, produced ample hydrogen with a satisfactory head for any of the electrodes used.

The hydrogen electrodes first used were made by welding a small square

of platinum foil (6 mm. on the side) to a short length of platinum wire which was fused into a glass tube. The electrical connection was made by means of mercury in the glass tube. The electrodes were blacked by electrolyzing in a 1% solution of platinum chloride acidified with hydrochloric acid, using a four-volt storage battery as recommended by Clark (17). Later it was found that better results were obtained by cutting the potential difference down, by means of a sliding resistance, to about 2.5 volts. This was enough to give a vigorous but not a violent evolution of gas in a dilute sulfuric acid solution. Even with this modification it was found to be very difficult to get a uniform or adherent coating of the black, and almost as difficult to remove an unsatisfactory coating. The black could be removed by electrolyzing in concentrated hydrochloric acid with the electrode as the anode, but this was a slow process which badly pitted the electrode and eventually rendered it useless. Gold-plating the electrodes was tried, but the successful gold-plating of an electrode was a long and tedious process, and the gold plate all came off with the platinum black when an attempt was made to clean up an imperfect electrode. Lead acetate was not used, as it had been found unsatisfactory by Clark (17), Ellis (28), and others.

Palladium chloride in a 1% solution acidified with hydrochloric acid was then tried. This proved to be much better than the platinum. The deposits were smoother and more adherent and were easily removed by electrolysis without any material damage to the platinum electrode.

It was also found that short lengths (about 1 cm.) of a fairly large platinum wire (about 1.6 mm. in diameter), sealed into glass tubes, made more satisfactory electrodes than did the platinum foil. The coating of black seemed to be more uniform and more adherent when placed on the wire form. The electrodes were thoroughly cleaned in hot "cleaning mixture", electrolyzed for a few minutes with the electrode as the cathode in dilute sulfuric acid, and then in the palladium chloride solution at a potential of about two and one-half volts until a uniform velvety black coating was formed (usually from five to ten minutes). An electrode was considered satisfactory if, when again electrolyzed in the dilute sulfuric acid, it formed only small bubbles of hydrogen uniformly distributed over the entire surface. Large bubbles or bubbles unevenly distributed indicate an uneven and unsatisfactory coating of black. It was found<sup>1</sup> necessary to remove the coating and reblack the electrodes at intervals of from two days to two months, depending to some extent upon the solutions upon which the determinations were being made. Most of the results in this paper represent check readings using two electrodes.

Two types of electrode vessels were used, the first as designed by Clark (17) and the second a larger vessel. Clark's cell was found very useful when the hydrogen-ion concentrations of a large number of different solutions were to be measured. Because of its small size it was of no use when the hydrogen-ion concentration of the same solution was to be measured after each addition of reagent, as in the titration of an alkali with acid. For this latter purpose a larger electrode vessel was designed which would hold about 160 cc. This had a stopcock, such as is used on Clark's cell, at one end on the lower side, which when turned one way connected with the saturated salt bridge, and when turned the other way drained the vessel. On the upper side at each end there was a tabulation which would take a No. 2 rubber stopper; one

stopper carried two platinum electrodes, and a tube for introduction of hydrogen, the other a burette for introducing the standard solution and a tube for exit of hydrogen. The exit for hydrogen was left open only long enough to flush the cell thoroughly; after it was closed, the titration was finished under a constant pressure. This electrode vessel was mounted on a rocking device and connected to the salt bridge vessel in the same manner as the Clark vessel.

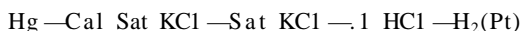
For ordinary titrations the readings may be made with the stopcock closed, sufficient contact being obtained around the ungreased plug of the stopcock. If, however, extremely accurate hydrogen-ion determinations are to be made, the contact must be made as is done in the Clark cell; by squeezing the rubber tube connecting the salt bridge and the electrode in order to expel a few drops of salt solution, then turning the stopcock to connect with the electrode and releasing the rubber tube. This makes a sharp but broad contact in the tube below the stopcock. There must be another stopcock farther back in the tube leading to the salt bridge which must be kept closed to prevent filling the cell with potassium chloride solution. Carrying on a titration and making the contact by this latter method interferes slightly with the accuracy of the titration from a volumetric standpoint, for a small portion of the solution being titrated is lost each time the contact is made. The results in this paper were obtained by the latter method, however, since it was more important to obtain the exact position of the curve than to locate the exact end-point of each reaction.

The water used for all solution was prepared by redistillation of the ordinary grade of distilled water after the addition of alkaline permanganate, the distillate being rejected until it failed to give a test for ammonia with Nessler's reagent. The water so prepared was stored in pyrex flasks. All chemicals used, other than those especially described elsewhere, were C. P. of the highest grade obtainable. The standard sodium hydroxide was standardized with benzoic acid obtained from the U. S. Bureau of Standards, and fused immediately before using. The hydrochloric acid solution was standardized against the sodium hydroxide. All volumetric ware used had been certified by the U. S. Bureau of Standards, and the weights used were carefully checked against a set calibrated by the same bureau.

The measurements reported were all made on the system



With the exception of the titrations with acid and the reactions involving the precipitation of calcium as the carbonate, the over-all E. M. F. of this system was measured with sufficient accuracy to give check results within  $\pm 0002$  volts. In order to calculate the hydrogen-ion concentrations from these measurements, accurate values must be obtained for the E. M. F. between the mercury and the saturated KCl calomel solution as well as values for the potentials at the various liquid contacts and a standard value for the normal hydrogen electrode. The value 5266 volts, as determined by Fales and Mudge (32), was accepted for the value of the saturated calomel element at 25° C., and the temperature coefficient .0002 volts per degree was used in calculating the value of this electrode at other temperatures. From the value 2165 volts given by Fales and Mudge for the system



and from the activity of .1 N HCl of .843 given by Ellis (28), the value .2800

volts was obtained for the normal hydrogen electrode, which is slightly lower than the value (.2817 volts) calculated from data given by Fales and Vosburg (31). However, since the value of Fales and Miudge for the saturated calomel electrode was being used, the latter value (.2817 volts) for the hydrogen electrode was also used. The difference between the E. M. F. of the normal hydrogen electrode and that of the saturated calomel electrode will give, therefore, the value of the saturated calomel electrode referred to the normal hydrogen electrode as zero. This is .2466 volts at 25° C. and is referred to as ECAL.

There are doubtless potential differences set up at the contacts between the unknown solution and the saturated salt bridge. Estimation of values for these potentials from a consideration of ion mobilities was not possible in such complex solutions as dealt with in this paper; neither did the nature of the work permit the use of the compensation method of Bjerrum (10). Although such contact potentials are known to amount at times to as much as .0005 volts, they have been considered as zero in all the calculations in this work. While this assumption is not entirely justified in view of the accuracy with which the over-all E. M. F. was measured, the neglect of these quantities probably does not introduce very serious errors.

The over-all E. M. F. values were corrected to one atmosphere pressure of hydrogen by means of the equation:

$$E_{BAR} = \frac{RT}{2F} \ln \frac{1}{P} \quad \text{or} \quad E_{BAR} = \frac{0.00019837 T}{2} \text{Log} \frac{1}{P}$$

in which  $E_{BAR}$  is a quantity which is added to the total over-all E. M. F. measured;  $T$  is the absolute temperature; and  $P$  is the barometric pressure in atmospheres corrected for vapor pressure of the unknown solution and whatever back pressure may be imposed upon the system.

Using the above values and corrections, the hydrogenion concentration (reported in all cases in Sorensen's (107) pH numbers, i. e., negative log of the hydrogen-ion concentration) has been calculated by means of the following equation:

$$\frac{E. M. F. + E_{BAR} - ECAL}{0.00019837 T} = pH$$

E. M. F. is the total over-all potential measured, and the other terms have the significance defined above. The values used at the various temperatures are as follows:

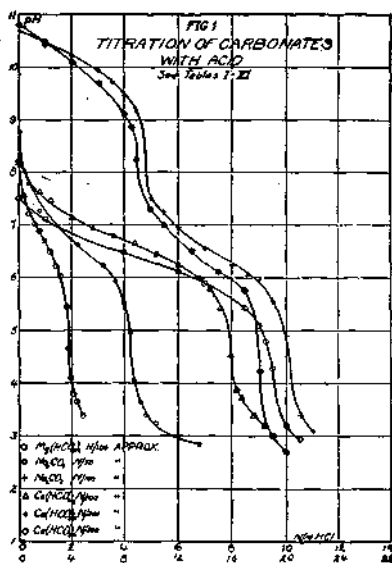
Temp.	°C.	ECAL	0.00019837 T
	20	.2456	.0581
	21	.2456	.0583
	22	.2460	.0585
	23	.2462	.0587
	24	.2464	.0589
	25	.2466	.0591
	26	.2468	.0593
	27	.2470	.0595
	28	.2472	.0597
	29	.2474	.0599
	30	.2476	.0601

#### TITRATION OF CARBONATE SOLUTIONS.

One of the most common methods of estimating the normal carbonate content of a solution is to "titrate with a standard acid until the solution is neutral to phenolphthalein", and in the same manner the

total carbonate and bicarbonate content may be estimated if methyl orange is used in place of phenolphthalein. If the hydrogen-ion concentration is determined at various steps in the titration and plotted against the quantity of acid used, a curve is obtained which shows two inflection points, the first inflection occurring when acid equivalent to one-half the normal carbonate has been added and the second when acid equivalent to all the carbonate has been added. These curves are useful in confirming the suitability of the indicators used, for an indicator of the highest accuracy should show its end-point color at a hydrogen-ion concentration corresponding to the inflection point of the curve. Such data as have already been published show that the above-mentioned indicators are about as satisfactory for the purpose as could be expected.

In order to confirm these findings more fully, a study was made of reactions of a strong acid with dilute solutions of the carbonates of sodium, calcium and magnesium. Small quantities of standard acid were added to dilute carbonate solutions, and after each addition the hydrogen-ion concentration was determined electrometrically by means of the familiar gas chain. Each titration was continued until acid had been added in excess of the quantity necessary to react with all the carbonates present. In order to avoid most of the errors due to change in carbon dioxide content referred to by Tillmans (113), Johnston (56) and Kolthoff (62), the rocking electrode vessel described on page 21 was used for these titrations.



The results are shown in Tables I—VI and in Fig. 1. In order to make the scale of the curves uniform, the results for the calcium bicarbonate have been recalculated so that each abscissa represents cubic centimeters of 0.1 N acid used per 100 cc. of solution titrated; for the same reason, each abscissa in the case of the 0.02 N sodium carbonate has twice the value of an abscissa in all the other cases. The sodium carbonate solutions (being normal carbonate) show two inflection points while the others show only one.

The position of the inflection point, while not materially affected by the nature of the metal ion, is to a considerable extent affected by the concentration of the solution, as would be expected, from a consideration of the mass-law equations involved. This effect, however, is not sufficient to necessitate the changing of the indicators commonly used. If extreme accuracy is desired, a color comparison standard could be used corresponding to the particular pH value desired. For the first, or carbonate, inflection point, which is near pH 8.2, phenolphthalein, or any other indicator showing a good end-point color at this value, is satisfactory. The second inflection point occurs near pH 4.5, for which methyl orange is an indicator. Here, however, it would be an advantage. (39) in most cases if an indicator were selected showing its end-point color slightly below pH 4.5; for Acree and Brunei (2) have shown that sodium chloride, which is so often present in natural waters, tends to raise the hydrogen-ion concentration of the methyl orange end-point. The error due to the hydrolysis of aluminum salts (which, when present, constitute a portion of the alkalinity)\* may be partly offset by the use of an indicator changing color at a lower hydrogen-ion concentration; this is a special case, however, and one in which the most accurate results cannot be obtained.

\* This point is to be discussed in a paper now in preparation. (Part II.) It is, however, apparent that during the titration of a solution having an original pH value on the alkaline side of the methyl orange end-point and containing aluminum salts, some hydrogen ions will have been used up in reversing the hydrolysis of the aluminum salts by the time the end-point (pH 4.2) is reached. Fig. 4 may be made to represent such a titration by considering the units of alkali on the X-axis as negative quantities of acid. Suppose then that in this figure a line be dropped perpendicular to the X-axis from a point on any one of the three curves representing the hydrogen-ion concentration at the beginning of a titration, e. g., pH 5.5, and a line be similarly drawn from a point on the same curve corresponding to pH 4.2, the distance intercepted on the axis between these two lines will represent the acid required to cause the change from pH 5.5 to pH 4.2. Since the "alkalinity" of a water is its acid capacity up to the methyl orange end-point, it is seen that partially neutralized aluminum salts constitute a part of the alkalinity.



## THE PRECIPITATION OF MAGNESIUM AS THE HYDROXIDE.

The problem of removing magnesium from a very dilute solution divides itself into two parts: (1) to determine when sufficient reagent (hydroxide) has been added to throw as much of the magnesium out of solution as possible; (2) to treat the precipitate in such a way as to cause it to coagulate and settle properly. We may hope to throw light on the first part by means of various chemical determinations and by means of hydrogen electrode measurements. The second part, dealing with the behavior of colloids, would require different methods of study; here physical factors also, such as rate and character of stirring and changes of temperature, exert considerable influence. Also, the excess of reagent and the amounts and kinds of other salts in solution doubtless affect coagulation.\*

Bartow and Lindgren (5) have shown that, in treating a magnesium solution with lime water, the minimum content of magnesium is not reached until the alkalinity with phenolphthalein is somewhat greater than one-half that with methyl orange, or until some free hydroxide is present in the solution. This would correspond approximately to an alkalinity represented by pH 11, that is, a slightly higher hydroxylion concentration than that of a dilute carbonate solution. This approximate figure could also be deduced from a consideration of the solubility product of magnesium hydroxide ( $1.2 \times 10^{-11}$ , the value most nearly correct according to Johnston (55) ), and can be verified from a rather small scale curve obtained by Hildebrand (48) for the titration of magnesium.

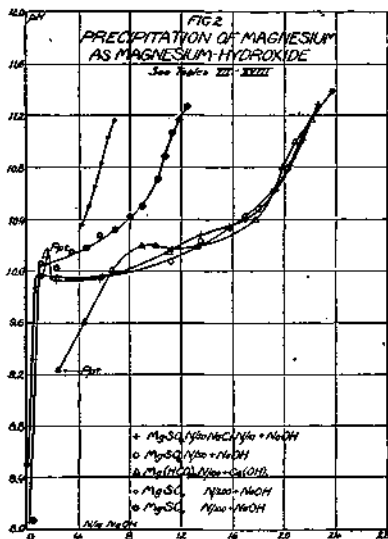
In view of the meagerness of the data available, it was considered advisable to prepare titration curves using standard sodium hydroxide and various concentrations of several magnesium salts. It was found by preliminary experiments that addition of an alkali to an excess of magnesium in solution caused the hydrogen-ion concentration first to decrease sharply and then to rise gradually for several hours. This was taken to indicate that the precipitation of magnesium as the hydroxide was a rather slow reaction requiring a long time to reach completion. The slowness of reaction was more marked, the more dilute the solution, as was to be expected. Since it would have been extremely difficult to keep a hydrogen electrode in working order long enough to complete a titration allowing time for equilibrium to be reached after each addition, it was decided to carry on the reaction in a large number of bottles (250 cc.) containing equal amounts of magnesium solution.

A small amount of hydroxide solution was added to the first bottle, more to the second, and so on to the last bottle, to which more alkali was added than would be equivalent to the magnesium present. The bottles were allowed to stand with frequent shaking for 24 hours or more, after which the hydrogen-ion concentration was determined on each. To prevent contamina-

---

\*Editor's Note :—See below, pp. 75-79.

tion with carbon dioxide from the atmosphere during addition of the chemical and withdrawal of sample, the bottles were fitted with stoppers carrying an arrangement of tubes similar to that of an ordinary wash bottle. During the time allowed for the reaction to take place, the tubes were closed by means of rubber tubing and pinchcocks.



Experiments were run using solutions of magnesium sulfate (0.02, 0.01 and 0.005 normal) with sodium hydroxide, and magnesium bicarbonate solution (0.01 normal) with lime water. In two experiments with 0.02 normal magnesium sulfate, sodium chloride was added until the solution was 0.1 N with respect to this salt. The complete results are given in Tables VII-XVIII, and in Fig. 2 typical examples of these experiments are given graphically, each abscissa representing cc. of 0.1 N alkali added to 100 cc. of solution. Since neither the sodium hydroxide nor the lime water was exactly tenth-normal, it was necessary to multiply the actual number of cc. used by the proper factor to get the values for making the graphs.

The results show that the inflection point of the curve falls at practically the same pH value regardless of the concentration of the solution or the nature of the salt. This value is in the neighborhood of pH 10.6 and corresponds to a hydroxyl-ion concentration slightly lower than would be expected from consideration of the solubility product  $1.2 \times 10^{-11}$ . This deviation from the calculated value supports Johnston's (55) opinion that all previously reported values of the solubility product are too large.

The presence of sodium chloride in concentrations as high as 0.1 N does not materially affect the position or shape of the curve. It is especially noticeable that the curve for the titration of magnesium bicarbonate solution with lime water passes a maximum in the neighborhood of pH 10. Since the reactions are somewhat complicated at this point, it is difficult to assign an explanation. The solution is undoubtedly depositing both calcium carbonate and magnesium hydroxide, and probably also magnesium carbonate. One explanation that might be offered is that one of the precipitates changes its physical state; that is, if one of the precipitates were colloiddally dispersed, it would probably have a solubility somewhat greater than the same substance would have in a non-colloiddal state. If a certain hydroxyl-ion concentration should cause coagulation, there might result a decrease in solubility and a corresponding decrease in hydroxyl-ion concentration.

The assumption that the coagulated precipitate is not peptized by a decrease in hydroxyl-ion concentration is justified in view of the fact that these colloiddal reactions are often not reversible in the strictest sense of the word. This explanation of the peculiarity in the curve is, however, by no means the only one that could be advanced. It is also true that, while the formation of a maximum in the neighborhood of pH 10 is more noticeable in the magnesium bicarbonate curve, it can be detected to some extent in some of the others. The other curves are quite steep at this part, and the points are rather few, making the exact shape of each curve hard to follow.

In a few experiments the phenolphthalein alkalinity and the alkalinity to brom phenol blue were determined on the same bottles on which the hydrogen-ion concentration determinations were made. The results with brom phenol blue are the same as would be obtained with methyl orange (39). The inflection point of the pH curve occurs at about the point where the phenolphthalein alkalinity is equal to or slightly in excess of one-half of the brom phenol blue alkalinity. This is what would be predicted from the work of Bartow and Lindgren (5).

The titrations also show that, although some precautions were taken against contamination by the carbon dioxide of the atmosphere, some carbonates were present. This was to be expected because the standard sodium hydroxide was prepared from a saturated sodium hydroxide solution diluted with carbon dioxide-free water, a method which gives a solution that is fairly free from carbonates but not completely so. It would seem, however, that such small amounts of carbonate would not seriously affect the results obtained, and it is believed that the solutions used more nearly represent those encountered in actual water-softening than would those more nearly free from carbonates.

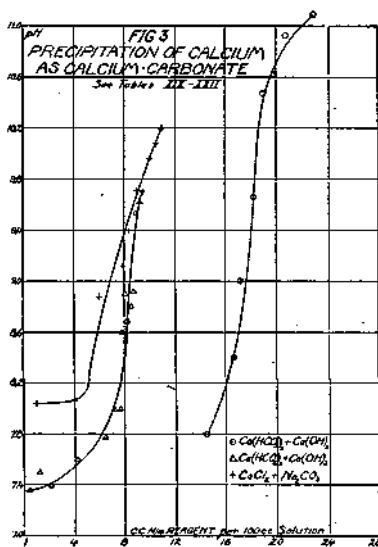
#### **PRECIPITATION OF CALCIUM AS THE CARBONATE.**

The precipitation of calcium carbonate is dependent, primarily, upon the concentration of the carbonate ion and, secondarily, upon, the hydrogen-ion concentration, since at higher hydrogen-ion concentrations the soluble calcium bicarbonate is formed. The subject of the solubility of this salt and the various factors influencing it has been very completely discussed by Johnston and Williamson (57). They

show that the minimum solubility (about 16 parts per million) occurs at a partial pressure of carbon dioxide of about  $3.73 \times 10^{-7}$  atmospheres and a hydroxyl-ion concentration of  $0.787 \times 10^{-4}$ . This corresponds to approximately pH 10. If, however, the partial pressure of carbon dioxide is more nearly that of the atmosphere, the solubility is 60 parts per million and the hydroxyl-ion concentration is lower, corresponding to approximately pH 8.

Experiments were carried out on the precipitation of calcium from a calcium chloride solution using sodium carbonate and from a bicarbonate solution using lime water, with the same methods as outlined for magnesium.

In these experiments the high partial pressure of carbon dioxide introduced serious errors. The liquid, when it was transferred to the electrode, would give up carbon dioxide to the hydrogen in the electrode and would become more alkaline, i. e., have a lower hydrogen-ion concentration. This trouble was overcome to some extent by introducing a portion of the liquid into the cell and shaking to cause it to come into equilibrium with the hydrogen, then passing in fresh liquid and allowing the original to run out but retaining the same hydrogen in the cell. This was repeated until addition of fresh liquid did not change the potential of the electrode. On the other hand, the dilution of the hydrogen by the carbon dioxide would cause the results to be in error in the opposite direction, but this error can be shown by calculation to be practically negligible in all measurements in this series. In spite of all precautions, the results of these experiments are very erratic, giving irregular curves, and are not as reproducible as those of the precipitation of magnesium or aluminum.



The results are given in Tables XIX-XXII, and three representative runs are shown graphically in Fig. 3. The results show that calcium carbonate begins to precipitate in solutions slightly more alkaline than pH 7 and that the inflection point of the curve is reached near pH 9.5. This figure supports Johnston's calculated value fairly well. In view of the extreme difficulty of sufficiently protecting these solutions from the carbon dioxide of the air, it is probable that the minimum solubility calculated by Johnston was not attained. Moreover, the difference in temperature between these experiments and those for which his results were calculated would render impossible too close comparison.

#### PRECIPITATION OF ALUMINUM AS THE HYDROXIDE.

Most natural waters, as has been stated before, contain bicarbonates; under ordinary conditions these bicarbonates hydrolyze, furnishing hydroxyl ions sufficient to cause the precipitation of aluminum salts as the hydroxide. This using up of the hydroxyl-ions by the aluminum causes hydrolysis to proceed farther, so that the net result of the precipitation is that bicarbonates equivalent to the alum precipitated are decomposed, and free carbon dioxide, or carbonic acid, is formed. This results, of course, in increasing the hydrogen-ion concentration. If the bicarbonates present are not sufficient to react with all of the alum added, some free aluminum ions will be left in the solution. The solution will be quite acid, due both to the free carbonic acid resulting from the decomposition of what bicarbonates were present, and to the hydrolysis of the aluminum salt itself. Although it is true that a certain degree of alkalinity is necessary for the complete precipitation of aluminum, it is also well known that aluminum does not precipitate completely in solutions that are strongly alkaline, i. e., have a low hydrogen-ion concentration, and that the precipitated aluminum hydroxide can be completely dissolved by the action of a sufficiently strong alkali.

There has been considerable controversy as to whether this re-solution is merely a change in physical state, such as peptization of the colloidal aluminum hydroxide, or whether it results from variations in chemical combination. Hildebrand (48) believed that there was an aluminate formation because of a second inflection point in the precipitation curve as determined by means of the hydrogen electrode, the second inflection occurring at the point where sufficient sodium hydroxide had been added to form an aluminate of the empirical formula  $\text{NaAlO}_2$ . He was unable, moreover, to detect colloidal particles in the alkaline solution by means of the ultramicroscope. Mahin (72) and his co-workers, in support of the opposite view, reported that the heat of solution of aluminum hydroxide in sodium hydroxide was too

small to be accounted for by the formation of a salt. It was pointed out by Blum (11) that there is possibly a negative heat of solution of the hydrated aluminum oxide in water that may well counterbalance a rather large heat of reaction between the two hydroxides. Mahin also based conclusions upon the amount of aluminum hydroxide precipitated from an alkaline solution by the action of ammonium nitrate, assuming that ammonium hydroxide was not sufficiently alkaline to dissolve aluminum hydroxide of itself; but Blum (12) showed that aluminum hydroxide is soluble in ammonia to some extent. Chatterji and Dhar (16) argued that there was no aluminate formation because there was not much change in the resistance of a sodium hydroxide solution when aluminum hydroxide was dissolved in it. On the other hand, Goudriaan (37) reported a stable compound of the formula  $\text{NaO}_3\text{—Al}_2\text{O}_3\text{—H}_2\text{O}$  as well as other aluminates with different formulae. While the proof seems, to be unsatisfactory on both sides, it would seem at present that the preponderance of evidence is for the formation of aluminates. It is sufficient for the purpose of this paper, however, to note that at fairly high hydrogen-ion concentrations the aluminum hydroxide dissolves, that at lower hydrogen-ion concentrations the aluminum is precipitated as the hydroxide, and at still lower hydrogen-ion concentrations the aluminum hydroxide redissolves.

The titration curves of Hildebrand (48) and those of Blum (11, 12), along with the analytical work of Blum (12), indicate that the point of minimum solubility is between pH 6.5 and 7.5. Most natural waters have hydrogen-ion concentrations somewhat lower than this optimum. It might, therefore, be expected that incomplete precipitation of aluminum would often result, not from a lack of sufficient bicarbonate alkalinity to react with all the aluminum salt added, but from the formation of the aluminate, due to too great a concentration of hydroxyl-ions.

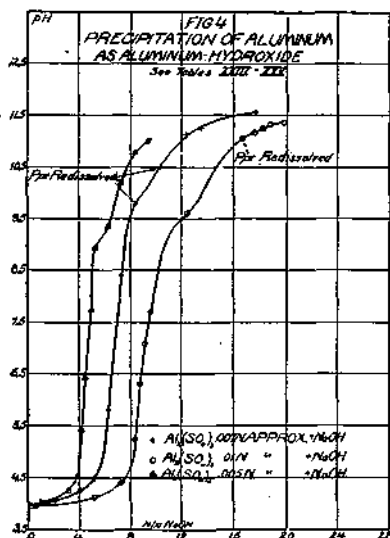
The results of several investigations indicate that this actually happens. Morison (81), by adding various amounts of alum to a certain water, found that optimum conditions for clarification were obtained when sufficient alum was added to neutralize one-half the alkalinity of the raw water. With doses of alum either greater or less than this optimum amount, the hemotoxylin test showed the presence of aluminum in the effluent. Howard and Hannan (54), also using hemotoxylin, found small amounts of alumina in water from rapid-sand filter plants and concluded that rapid-sand filters could not completely remove aluminum hydroxide. They were working with water at pH 8, from which aluminum was most completely precipitated if a small amount of acid was added before the alum. Addition of still more acid brought the water to such a hydrogen-ion concentration that the precipitation was again incomplete. It may, however, be noted that, if the bicarbonates in the water were sufficient, probably the same effects would have been obtained by addition of more alum; for the addition of aluminum salts to bicarbonate tends to increase the acidity of the solution.

Although Wolman and Hannan (127) reported the most satisfactory flocculation in samples that showed least residual alum, it does not necessarily follow that the point of minimum solubility always corresponds to the

point of maximum flocculation, for the latter is influenced by several physical factors. Smith (104), using alum in the coagulation of silicic acid, reported optimum precipitation at pH 8.2. This is much higher than other values reported, but the points on Smith's curve are so far apart that his value may be misplaced. Langelier (63) reported the best coagulation in certain laboratory stirring tests, other things being equal, at pH 7. He and many others,\* in both laboratory and large-scale experiments, have investigated the part played by physical conditions such as stirring, period of detention, method of applying the alum, and nature of the suspended turbidity.

In an attempt to fix the zone of maximum precipitation somewhat more closely, experiments were run similar to those on magnesium, using the same methods and apparatus. Solutions of aluminum sulfate approximately 0.01 N and 0.005 N were used. The results‡ are given in Tables XXIII-XXV and shown graphically in Fig. 4, where the abscissae are pH values and the ordinates cubic centimeters of 0.1 N sodium hydroxide solution per 100 cc. of alum solution.

In spite of the fact that a more dilute solution and a more sensitive apparatus were used, the optimum precipitation zone was not fixed within any narrower limits than previously. The results of these ex-



periments are very similar to those presented by Hildebrand and by Blum. Aluminum hydroxide starts precipitating in solutions that are as acid as pH 4.0, and the precipitation is practically complete in the range

\*Editor's Note:—Cf. Pirnie (89), Hatfield (43), Jordan (58), Catlett (14, 15), Hopkins (52), Baylis (7), Cox (20), Howard (51), Veatch (117) Delaporte and Burn (23).

‡ Editor's Note:—Subsequent experimental work by Theriault and Clark (112) checked these results.

pH 6.5—7.5. At higher pH values the precipitate partly re-dissolves, and the re-resolution is complete at a point between pH 10 and 11.

From these curves it can be seen that, in determining the bicarbonate alkalinity of waters treated with alum, if an indicator is to indicate successfully the point at which sufficient alum has been added to give an appreciable excess of aluminum in solution, the indicator must show an acid reaction at a point not much below pH 6. However, the results of experiments described above on the reaction between carbonates and acids show that an indicator giving an end point at such a high pH value would not always be the most satisfactory for this titration. With fairly high bicarbonate concentration this point would fall where the buffer action of the bicarbonate was marked; the color change would be gradual and would be reached before acid had been added equivalent to all of the bicarbonates present. If the bicarbonate concentration were low, the end-point color change would be more satisfactory and would more nearly represent the total bicarbonates present. Since it is only in waters of low bicarbonate alkalinity that there is danger of adding alum in excess of the amount that the bicarbonate could successfully precipitate, such an indicator could be used fairly accurately on the treated water. It would also show when the water had been so overtreated with alum that excess alum was present in solution. Of the common indicators, methyl red most nearly fulfills these conditions, although brom cresol purple would also seem to be satisfactory for the purpose. Experience has shown that methyl red actually does give satisfactory results when used on such alum-treated waters.

#### SUMMARY.

Hydrogen electrode titration curves have been run with carbonates of sodium, magnesium and calcium, using a strong acid. The shape and position of these curves are unaffected by the metal ion, but the inflection point occurs at slightly lower hydrogen-ion concentrations in dilute solutions than in the more concentrated solutions.

Curves of the precipitation of magnesium as the hydroxide show that the precipitation commences at pH 9.0 and is complete at approximately pH 10.6. The concentration of the solution has practically no effect upon the position of the inflection point.

Curves of the precipitation of calcium as the carbonate, while not as regular as those obtained for the precipitation of magnesium, indicate that the reaction is complete at pH 9.5.

Aluminum hydroxide starts precipitating in solutions as acid as pH 4 and is completely precipitated from pH 6.5 to 7.5. At hydroxyl-



ion concentrations much higher than this, re-resolution commences and is complete between pH 10 and 11.

These precipitation reactions are not instantaneous but take several hours to reach an equilibrium. This was more noticeable, the more dilute the solution.

### **SUGGESTIONS FOR FURTHER STUDY.**

The speed of reaction of all of the precipitation reactions investigated should be more carefully studied. Preliminary experiments indicate that, especially in dilute solutions, considerable time elapses before equilibrium is reached. This may be due to a slowness in precipitating, the solution being supersaturated for some time after the reagent is added; or it may be due to a recrystallization or coagulation of fine or colloidal particles; or it may be a combination of the two effects. In one experiment with aluminum sulfate, to which had been added sufficient sodium hydroxide to partly redissolve the precipitated aluminum hydroxide, the hydrogen electrode showed that the solution for several hours gradually became more alkaline. This lowering of the hydrogen-ion concentration was probably due to a slow hydrolysis of the sodium aluminate. Such a slow hydrolysis has previously been reported by Heyrovsky (47). The hydrogen electrode would seem to offer a new means of studying such phenomena.

The speed of reaction and coagulation in these reactions is not only of interest scientifically but is also of utmost importance in the proper design of plants for softening and purifying water. Little work which has yielded results of any great value has been done on this subject, the design of such plants being for the most part worked out from experience with previously constructed plants.

The determinations of hydrogen-ion concentrations in the various steps of coagulation and water softening would be of interest, first, to see if the results obtained on small-scale experiments such as are reported in this paper are similar to those obtained in large operations, and, secondly, to see if the use of such determinations does not offer a simple and accurate means of controlling such processes.

The effect of other salts on the reactions reported should be more fully studied. Some of the reactions should be repeated, making careful determinations of the dissolved salts as well as of the hydrogen-ion concentrations at various stages of completion.

TABLE I.

**TITRATION OF MAGNESIUM BICARBONATE.**  
Using 100 cc.  $\text{Mg}(\text{HCO}_3)_2$  Solution Approximately 0.01 N.

0.1 N HCl	Obs. E. M. F.	Temp.	pH
cc.	volts	°C.	
0	.6946	27	7.52
1	.6695	27	7.12
4	.6313	27	6.47
6	.6102	27	6.12
7	.5985	27	5.92
8.5	.5696	28	5.43
9.0	.5509	28	5.12
9.25	.5329	28	4.82
9.5	.5010	28	4.29
9.75	.4523	28	3.47
10.0	.4372	28	3.22
10.5	.4196	28	2.96

TABLE II.

**TITRATION OF SODIUM CARBONATE.**  
Using 100 cc.  $\text{Na}_2\text{CO}_3$  Solution Approximately 0.02 N.

0.1 N HCl	Obs. E. M. P.	Temp.	pH
cc.	volts	° c.	
<b>0</b>	.8873	25.6	10.8
<b>2</b>	.8638	25.6	10.5
<b>4</b>	.8432	25.6	10.10
<b>6</b>	.8198	25.6	9.70
<b>8</b>	.7828	25.6	9.10
8.5	.7701	25.6	8.86
<b>9.0</b>	.7334	25.5	8.25
10.0	.6780	25.6	7.31
11.0	.6589	25.7	7.00
13.0	.6312	25.7	6.52
15.0	.6074	25.7	6.12
17.0	.5725	25.7	5.52
18.0	.4959	25.7	4.23
19.0	.4245	25.7	3.02
20.0	.4058	.25.7	<b>2.70</b>

TABLE III.

## TITRATION OF SODIUM CARBONATE.

Using 100 cc.  $\text{Na}_2\text{CO}_3$  Solution Approximately 0.01 N.

0.1 N HCl	Obs. E. M. P.	Temp.	pH
cc.	volts	$^{\circ}\text{C}$ .	
0	.8802	25.8	10.7
1	.8640	25.8	10.4
2	.8491	25.8	10.2
3	.8306	25.8	9.89
3.5	.8199	25.8	9.70
4.0	.8052	25.8	9.45
4.5	.7823	25.8	9.20
5.0	.7195	25.9	7.50
5.5	.6741	25.9	7.25
6.0	.6576	25.9	6.95
7.0	.6344	25.9	6.57
8.0	.6146	25.9	6.24
8.5	.6045	25.9	6.07
9.0	.5913	25.9	6.02
9.5	.5758	25.9	5.57
10.0	.5367	26.0	4.92
10.5	.4493	26.0	3.44
11.0	.4292	26.0	3.11

TABLE IV.

## TITRATION OF CALCIUM BICARBONATE.

Using 50 cc.  $\text{Ca}(\text{HCO}_3)_2$ .

0.02 N $\text{H}_2\text{SO}_4$	Obs. E. M. F.	pH
cc.	volts	
0	.7288	8.19
1	.7067	7.82
2	.6982	7.67
3	.6872	7.47
5	.6665	7.14
7	.6544	6.94
9	.6472	6.82
11	.6375	6.65
13	.6253	6.45
15	.6130	6.24
17	.5977	6.02
18	.5845	5.75
19	.5669	5.46
20	.5131	4.55
20.5	.4744	3.88
21	.4671	3.76
22	.4472	3.42
23	.4357	3.23

**TABLE V.**  
**TITRATION OF CALCIUM BICARBONATE.**  
 Using 50 cc.  $\text{Ca}(\text{HCO}_3)_2$ .

0.02 N $\text{H}_2\text{SO}_4$	Obs.-E. M. F.	pH
cc.	volts	
0	.7605	8.74
2	.6745	7.26
4	.6557	6.95
6	.6359	6.62
8	.6129	6.24
9	.5951	5.94
10	.5713	5.53
10.5	.5367	4.94
11	.4846	4.05
11.5	.4625	3.68
12	.4512	3.40
13	.4372	3.25
15	.4224	3.00
17.0	.4136	2.85

**TABLE VI.**  
**TITRATION OF CALCIUM BICARBONATE.**  
 Using 50 cc.  $\text{Ca}(\text{HCO}_3)_2$ .

0.02 N	$\text{H}_2\text{SO}_4$	Obs. E. M. F.	pH
cc.		volts	
0.0		.7447	8.46
0.5		.6900	7.54
1.0		.6691	7.18
1.5		.6597	7.02
2.0		.6523	6.88
2.5		.6404	6.69
3.0		.6290	6.50
3.5		.6133	6.23
4.0		.6015	6.04
4.5		.5659	5.44
4.75		.5205	4.66
5.0		.4877	4.12
5.25		.4703	3.81
5.5		.4614	3.66
6.0		.4487	3.42

**TABLE VII.**  
**TITRATION OF MAGNESIUM SULFATE.**  
**Using 100 cc. MgSO<sub>4</sub> Solution Containing 24.4 mg. of Mg.**  
**Temperature 25°C.**

0.1127 N NaOH cc.	Obs. E. M. F. volts	pH	Alkalinity as CaCO <sub>3</sub>	
			Phenolph- thalein ppm.	Brom phenol blue ppm.
0	.7440	8.501	0	12
1	.8308	9.949	12	40
2	.8305	9.944	16	40
5	.8301	9.940	16	40
10	.8382	10.077	14	38
12	.8480	10.237	18	44
14	.8529	10.327	18	52
15	.8581	10.417	22	52
16	.8618	10.477	24	54
17	.8705	10.617	32	56
18	.8812	10.797	46	72
19	.8965	11.067	78	98
20	.9095	11.287	124	162
21	.9164	11.397		

**TABLE VIII.**  
**TITRATION OF MAGNESIUM SULFATE.**  
**Using 100 cc. MgSO<sub>4</sub> Solution Containing 24.9 mg. of Mg.**  
**Barometric pressure 749 mm.**

0.1038 N NaOH cc.	Obs. E. M. F. volts	Temp. °C.	pH
1	.8215	25.5	9.793
4	.8330	24.2	9.988
8	.8359	25.6	10.027
10	.8384	24.8	10.077
12	.8421	24.9	10.147
14	.8424	25.1	10.147
15	.8457	25.0	10.197
17	.8531	25.0	10.327
18	.8576	25.0	10.407
19	.8681	25.0	10.577
20	.8835	25.0	10.837
21	.8988	25.0	11.107

TABLE IX.

## TITRATION OF MAGNESIUM SULFATE.

Using 100 cc. MgSO<sub>4</sub> Solution Containing 24.7 mg. of Mg.  
0.1 N to NaCl. Temp. 27° C.

0.1127 N. NaOH	Obs. E. M. F.	pH
cc.	volts	
1	.8327	9.910
10	.8393	10.020
12	.8425	10.077
14	.8438	10.097
15	.8547	10.277
16	.8583	10.377
17	.8675	10.497
18	.8782	10.667
19	.8913	10.887
20	.9043	11.117

TABLE X.

## TITRATION OF MAGNESIUM SULFATE.

Using 100 cc. MgSO<sub>4</sub> Solution Containing 24.6 mg. of Mg.  
0.1 N to NaCl.

0.1127 N. NaOH	Obs. E. M. P.	pH	Alkalinity as CaCO <sub>3</sub>	
			Phenolphthalein ppm.	Brom phenol blue ppm.
	volts			
2	.8230	9.929	12	28
5	.8238	9.940	12	28
10	.8365	10.167	12	28
12	.8437	10.287	16	32
14	.8480	10.357	20	38
15	.8501	10.387	22	40
16	.8560	10.497	24	40
17	.8633	10.617	24	42
18	.8748	10.807	46	68
19	.8904	11.077	74	83
20	.9029	11.297	116	134

**TABLE XI.**  
**TITRATION OF MAGNESIUM SULFATE.**  
**Using 100 cc. MgSO<sub>4</sub> Solution Containing 12.2 mg. of Mg.**  
**Temperature 24° C.**

0.1127 N NaOH	Obs. E. M. F.	PH	Alkalinity as CaCO <sub>3</sub>	
			Phenolph- thalein	Brom phenol blue
cc.	volts		ppm.	ppm.
0	.6816	7.445		
<b>1</b>	.8346	10.047		60
2	.8325	10.018	20	54
3	.8405	10.157	20	54
4	.8418	10.177	22	54
5	.8479	10.277	22	56
<b>6</b>	.8504	10.317	24	56
7	.8551	10.417	28	60
8	.8615	10.507	30	72
9	.8728	10.707	42	80
9.5	.8837	10.887	54	98
<b>10.0</b>	.8941	11.067	7S	112
10.5	.9008	11.167	106	136
11.0	.9067	11.277	124	164

**TABLE XII.**  
**TITRATION OF MAGNESIUM SULFATE.**  
**Using 100 cc. MgSO<sub>4</sub> Solution Containing 12.2 mg of Mg.**  
**Barometric Pressure 746 mm.**

0.1127 N NaOH	E. M. F.	Temp.	Alkalinity as CaCO <sub>3</sub>		
			Phenolph- thalein	Blue Brom Phenol	
cc.	volts	°C.	ppm.	ppm.	
<b>0</b>	.6795	23.7	7.419		
<b>1</b>	.8324	23.7	10.015	10	40
4	.8404	23.7	10.157	12	32
5	.8451	23.7	10.237	14	42
<b>6</b>	.8478	23.7	10.277	10	32
<b>7</b>	.8543	23.7	10.288	12	30
<b>7.5</b>	.8592	23.7	10.467	16	30
8.0	.8633	23.7	10.547	20	40
8.5	.8690	21.2	10.757	22	42
9.0	.8755	21.2	10.857	30	48
<b>9.5</b>	.8863	21.2	11.057	44	60
<b>10.0</b>	.8971	21.2	11.227	62	81
10.5	.9042	21.2	11.357	88	106

TABLE XIII.

**TITRATION OF MAGNESIUM SULFATE,**  
**Using 100 cc. MgSO<sub>4</sub> Solution Containing 12.4 mg. of Mg.**  
**Barometric pressure 753 mm.**

0.1038 N NaOH	B. M. F.	Temp.	pH
cc.	volts	° C.	
.5	.7351	26	8.295
2.0	.8234	26	9.784
4.0	.8367	26.5	9.990
8.0	.8513	26.8	10.227
8.5	.8999	26.8	10.367
9.0	.8458	28	10.097
9.5	.8648	28	10.417
10.0	.8757	28	10.587
10.5	.8848	28	10.747
11.0	.8942	28	10.897
11.5	.9011	28	11.017
12.0	.9078	28	11.127

TABLE XIV.

**TITRATION OF MAGNESIUM SULFATE.**  
**Using 100 cc. of MgSO<sub>4</sub> Solution Containing 12.5 mg. to Mg.**  
**Barometric Pressure 753 mm.**

0.1038 N NaOH	E. M. F.	Temp.	pH
cc.	volts	° C.	
7.0	.8496	25.0	10.267
7.5	.8505	25.0	10.287
8.0	.8506	25.1	10.287
8.5	.8559	25.5	10.377
9.0	.8608	25.1	10.457
9.5	.8665	25.4	10.557
10.0	.8767	25.0	10.727
10.5	.8858	24.9	10.877
11.0	.8868	25.1	10.877

TABLE XV.

**TITRATION OF MAGNESIUM SULFATE.**  
**Using 100 cc. MgSO<sub>4</sub> Solution Containing 6.26 mg. of Mg.**

0.1038 N NaOH	E. M. F.	Temp.	pH
cc.	volts	° C.	
4.0	.8548	25	10.357
4.5	.8639	25	10.507
5.0	.8721	25.2	10.647
5.5	.8832	25.0	10.837
6.0	.8952	25.2	11.037
6.5	.9023	25.2	11.167



TABLE XVI.

## TITRATION OF MAGNESIUM BICARBONATE.

Using 100 cc.  $\text{Mg}(\text{HCO}_3)_2$ . Barometric Pressure 750 mm.100 cc.  $\text{Mg}(\text{HCO}_3)_2 = 10.0$  cc. 0.1N acid (B. P. B. indicator)100 cc.  $\text{Mg}(\text{HCO}_3)_2 = 1.6$  cc. 0.17N acid (Phenolphthalein)

1 cc. Lime Water = 0.425 cc. 0.1N alkali.

Lime Water cc.	E. M. P. volts	Temp. ° C.	pH
5	.8084	30.5	9.398
10	.8245	30.0	9.667
15	.8361	30.0	9.863
20	.8475	30.0	10.047
23.5	.8439	29.0	10.027
25	.8406	28.0	10.006
30	.8433	28.0	10.047
40	.8696	31.2	10.427
45	.8866	31.2	10.667
47	.8961	31.2	10.817
49	.9037	31.2	10.937
51	.9092	31.2	11.037

TABLE XVII.

## TITRATION OF MAGNESIUM BICARBONATE.

Using 100 cc.  $\text{Mg}(\text{HCO}_3)_2$ . Barometric Pressure 750 mm.100 cc.  $\text{Mg}(\text{HCO}_3)_2 = 9.9$  cc. 0.1N acid (B. P. B. indicator)100 cc.  $\text{Mg}(\text{HCO}_3)_2 = 1.3$  cc. 0.1N acid (Phenolphthalein)

1 cc. Lime Water = 0.413 cc. 0.1N alkali.

Lime Water cc.	E. M. F. volts	Temp. ° C.	pH
5	.8068	31.5	9.306
15	.8382	31.5	9.824
18	.8424	31.5	9.895
20	.8464	31.5	9.960
22	.8480	31.5	9.986
24	.8447	31.7	9.931
26	.8473	31.7	9.974
28	.8470	31.8	9.969
30	.8487	31.3	10.037
40	.8683	31.3	10.357
43	.8775	30.3	10.547
45	.8881	30.3	10.727
48	.9029	28.7	11.007
51	.9110	28.7	11.147

TABLE XVIII.

## TITRATION OF MAGNESIUM BICARBONATE.

Using 100 cc.  $\text{Mg}(\text{HCO}_3)_2$ . Barometric Pressure 751 mm.100 cc.  $\text{Mg}(\text{HCO}_3)_2 = 10.0$  cc. 0.1N acid (B. P. B. indicator).

1 cc. Lime Water = 0.443 cc. 0.1N alkali.

Lime Water	E. M. F.	Temp.	pH
cc.	volts	° C.	
5	.7923	27	9.231
10	.8151	27	9.609
15	.8383	27	10.004
20	.8500	27	10.197
22.6	.8500	27.5	10.197
25	.8486	28.0	10.137
30	.8517	28.5	10.187
40	.8640	28.5	10.397
45	.8888	28.5	10.807
47	.9009	28.5	11.007
50	.9100	28.5	11.167

TABLE XIX.

## TITRATION OF CALCIUM BICARBONATE.

Using 100 cc  $\text{Mg}(\text{HCO}_3)_2$ . Barometric Pressure 750 mm.100 cc.  $\text{Ca}(\text{HCO}_3)_2 = 11.9$  cc. 0.1N acid (B. P. B. Indicator).100 cc.  $\text{Ca}(\text{HCO}_3)_2 = 17.3$  cc. 0.1N acid when titrated with sodium hydroxide and barium chloride.

1 cc. Lime Water = 0.415 cc. 0.1N alkali.

Lime Water	E. M. F.	Temp.	pH
cc.	volts	° C.	
35	.7090	28	7.800
40	.7439	28	8.389
41.7	.7805	28	9.000
44	.8202	28	9.665
46	.8689	28	10.477
48	.8780	28	10.627
50	.8969	28	10.937
55	.9078	28	11.127

TABLE XX.

## TITRATION OF CALCIUM BICARBONATE.

Using 100 cc.  $\text{Mg}(\text{HCO}_3)_2$ . Barometric Pressure 750 mm.100 cc.  $\text{Ca}(\text{HCO}_3)_2 = 5.3$  cc. 0.1N acid (B.P. B. Indicator).100 cc.  $\text{Ca}(\text{HCO}_3)_2 = 8.8$  cc. 0.1N acid when titrated with sodium hydroxide and barium chloride.

1 cc. Lime Water = 0.424 cc. 0.1N alkali.

Lime Water cc.	E. volts	M. F.	Temp. ° C.	pH
1	.6868		31	7.348
3	.6960		31	7.501
5	.6890		31	7.385
10	.7023		31	7.605
15	.7127		31	7.779
17	.7255		31	7.991
18	.7278		31	8.009
18.5	.7610		30	8.607
19	.7795		30	8.917
19.5	.7654		30	8.683
20	.7728		30	8.807
20.5	.7797		30	8.721
21	.8173		30	9.546
22	.8220		30	9.625

TABLE XXI.

## TITRATION OF CALCIUM CHLORIDE.

Using 100 cc.  $\text{CaCl}_2$  Solution Containing 16.9 mg. of Ca.

0.1N $\text{Na}_2\text{CO}_3$ cc.	E. M. F. volts	Temp. ° C.	pH
1	.7197	26	8.040
4	.7211	26	8.062
6	.7690	26	8.670
8	.7842	26	9.126
8.5	.8002	26	9.396
9.0	.8188	26	9.710
9.5	.8224	28	9.701
10.0	.8383	28	9.967
10.5	.8447	28	10.077
11.0	.8582	28	10.307

TABLE XXII.

TITRATION OF CALCIUM CHLORIDE.  
Using 100 cc.  $\text{CaCl}_2$  Solution Containing 17.2 mg. of Ca.  
Temperature 31.5°C.

0.1N $\text{Na}_2\text{CO}_3$	E. M. F.	
cc.	volts	pH
7.5	.7861	8.981
8.0	.7790	8.862
8.25	.7971	9.164
8.5	.7986	9.187
8.75	.8070	9.328
9.0	.8125	9.418
9.25	.8557	9.637
9.5	.8325	9.758
10.0	.8381	9.842
11.0	.8495	10.027

TABLE XXIII.

TITRATION OF POTASSIUM ALUM.  
Using 100 cc. Solution Approximately 0.01 N.  
Barometric Pressure 745 mm.

0.1038 N NaOH	E. M. F.	Temp.	
cc.	volts	° C.	pH
0.5	.4727	31.2	3.977
5.0	.4921	31.2	4.134
7.0	.5097	31.2	4.437
8.0	.5601	31.2	5.264
8.5	.6256	31.5	6.355
8.75	.6705	31.6	7.101
9.0	.6869	31.7	7.374
9.25	.7078	31.8	7.722
10.0	.8240	31.3	9.654
16.0*	.9093	31.8	11.077
17.0	.9158	30.3	11.177
17.5	.9200	30.0	11.257
18.0	.9236	28.7	11.307
19.0	.9276	28.7	11.377

\* Ppt. in all bottles to 16 cc. At 16 cc. ppt. doubtful. Above 16 cc. no ppt.

**TABLE XXIV.**  
**TITRATION OF POTASSIUM ALUM.**  
**Using 100 cc. Solution Approximately 0.007 N.**  
**Barometric Pressure 745 mm.**

0.1038 N NaOH cc.	E. M. F. volts	Temp. ° C.	pH
2	.4873	28	4.073
4	.4979	28	4.251
5	.5124	27	4.530
6	.5920	27	5.865
7	.7450	27.5	8.415
8*	.8292	28	9.799
10	.8744	28	10.557
12	.9096	28	11.157
13	.9179	28	11.257
14	.9242	28	11.387
17	.9356	28	11.577

\* Ppt. present up to and including 8.

**TABLE XXV.**  
**TITRATION OF POTASSIUM ALUM.**  
**Using 100 cc. Solution Approximately 0.005 N.**  
**Barometric Pressure 745 mm.**

0.1038 N NaOH cc.	E. M. F. volts	Temp. ° C.	pH
0.0	.4780	29	3.920
0.25	.4840	31.8	3.970
1.0	.4872	31.8	4.022
3.0	.5017	31.8	4.262
3.75	.5217	31.8	4.592
4.0	.5731	31.2	5.464
4.25	.6317	31.2	6.436
4.75	.7129	31.2	7.783
5.0	.7851	31.2	8.979
6.0*	.8061	31.0	9.328
7.0	.8608	30.5	10.237
8.0	.8939	30.0	10.817
9.0	.9067	30.0	11.027

\* Ppt. up to 6.

**PART TWO.**

**THE RELATION OF HYDROGEN-ION CONCENTRATION TO  
THE PROPERTIES OF ALUM FLOC.**

By G. P. EDWARDS with A. M. BUSWELL

**CONTENTS.**

	Page.
Introduction . . . . .	49
Reactions in coagulating basins. . . . .	49
Historical items. . . . .	52
Methods of analysis. . . . .	53
Results of field surveys. . . . .	56
Results of laboratory experiments. . . . .	59
Summary. . . . .	63

## THE RELATION OF HYDROGEN-ION CONCENTRATION TO THE PROPERTIES OF ALUM FLOC\*.

### INTRODUCTION.

In view of the results of the preceding investigation (40) of the chemical reactions involved in water purification, it was considered advisable to determine more completely and more accurately the optimum conditions for the precipitation of aluminum as the hydroxide. Although pH determinations show a zone of optimum conditions, the zone is not definitely delimited by those determinations alone. A somewhat different laboratory method was therefore adopted, the plan being (1) to determine under carefully controlled conditions the solubilities of aluminum hydroxide through a wide range of hydrogen-ion concentrations, and (2) to discover the optimum conditions for color removal and their relation to the "isoelectric point."

Since this procedure was one which would involve considerable labor, a field survey of various filter plants in the State of Illinois was first made, with special attention to residual alum, in order to estimate the possible practical value of more exact information concerning the optimum conditions for formation of alum floc. On completion of the laboratory experiments, another field survey was made to obtain a second set of data under different weather conditions.

### REACTIONS IN COAGULATING BASINS.

The chemical reactions taking place during coagulation have from time to time been represented in textbooks and technical journals by various styles of chemical equations. All of these show, in the main, that 8 parts per million of alkalinity (as  $\text{CaCO}_3$ ) will react with 1 grain per gallon of filter alum, forming aluminum hydroxide, although it is very well known that none of these reactions go to completion, for most of them are reversible, each depending for its final equilibrium upon all the others.

---

\* From a thesis submitted July, 1923, by Gail Philips Edwards in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry in the Graduate School of the University of Illinois. Part of this work was reported under the title of "Some Facts about Residual Alum in Filtered Water," in *Chem. Met. Eng.* Vol. 26, No. 18, May 3, 1922. A report of the complete results was read before the Water, Sewage, and Sanitation Section of the American Chemical Society, Milwaukee, Sept., 1923.



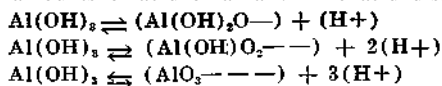


thus cause a net decrease in the alkalinity due to this same precipitation of  $\text{CaCO}_3$ . On the other hand, the formation of colloidal aluminum hydroxide\* instead of the precipitate would tend to offset the decrease in alkalinity.

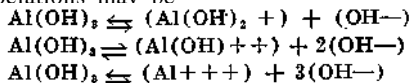
It will be observed that the substances  $\text{H}^+$ ,  $\text{AlO}_3\text{H}_2^-$ ,  $\text{Al}(\text{OH})_3$ ,  $\text{Al}^{+++}$  and  $\text{OH}^-$  form a cycle. The reactions may be made to take place in either direction around this cycle, depending upon the concentrations employed. Suppose, starting with these substances in equilibrium, we decrease the hydrogen-ion concentration; more water will be ionized by the reaction from  $\text{H}_2\text{O}$  in the direction of the light arrow, and this will increase the amount of  $\text{OH}^-$  present, thereby causing the reaction to go in the direction of  $\text{Al}(\text{OH})_3$  and removing some of the  $\text{Al}^{+++}$  from the solution. If the hydrogen-ion concentration is depressed low enough, reaction will take place to an appreciable extent counter-clockwise, in the direction of the light arrow from  $\text{Al}(\text{OH})_3$ , forming some aluminate ion,  $\text{AlO}_3\text{H}_2^-$ , with the side reaction forming some  $\text{Ca}(\text{AlO}_3\text{H}_2)_2$ , calcium aluminate written in the hydrated form. If the hydrogen-ion concentration is now increased, the reaction will be turned in a clockwise direction, and aluminum will be precipitated; if, however, the hydrogen-ion concentration is raised high enough, the aluminum will be redissolved as  $\text{Al}^{+++}$  from  $\text{Al}(\text{OH})_3$ .

In addition to the factors already mentioned, the alkalinity may be decreased by (a) removal of colloidal iron and aluminum hydroxide and carbonates, (b) removal of alkaline turbidity, (c) titration error caused by absorption of acid on colloids during titration (see Pirnie (88)) or (d) use of excessively acid alum. On the other hand, the decrease in alkalinity may be counteracted by (a) use of basic alum, (b) precipitation of basic aluminum sulfate instead of aluminum hydroxide, or (c) re-solution of  $\text{CaCO}_3$  previously deposited on the sand.\*

These are six ways in which  $\text{Al}(\text{OH})_3$  may ionize, depending upon the presence of various amounts of acid or alkali. The acid dissociation may be



The basic dissociations may be



It is possible for any of these ions to be in solution. It is apparent, however, that between the action of acids and bases producing these two types of dissociation, there must be a hydrogen-ion concentration where there is a minimum of ionization. This hydrogen-ion concentration may be called the "isoelectric point". Here probably two of the above equilibria would express

\* Editor's Note :—"Aluminum hydroxide" is here used according to the practice current at the time this part of the work was done. The formation of basic aluminum sulfate and possibly other compounds in the course of alum precipitation was then only suspected. Experiments with alum as an aid in the operation of a water-softening plant (see page 95) indicate that there is some colloidal  $\text{CaCO}_3$  formed. The graph should be revised, then, by inserting colloidal  $\text{CaCO}_3$  between the calcium ion and the precipitated calcium carbonate. If basic aluminum carbonate is formed, the equilibrium diagram should be still further altered.

\* Editor's Note:—Baylis (8) has pointed out that badly incrustated sand grains may show a base exchange comparable to the action of zeolites.

the conditions present in the solution. Under present methods of analysis there is no way of calculating the amount or kind of aluminum ion in solution at that point.

These complications have been the cause of much difficulty in investigations of the solubility of aluminum hydroxide.

### HISTORICAL ITEMS.

In 1908, Wood (129) found that when powdered aluminum was added to a solution of sodium hydroxide, sodium metaluminate was formed together with a little aluminum hydroxide. On heating, this sodium metaluminate decomposed much more rapidly until equilibrium was established, the molar ratio of sodium hydroxide to aluminum hydroxide left in solution having increased from 2.28 to 3.63. Considering the solubility of aluminum hydroxide to be too small to permit direct determination, Wood equated the results of two equilibrium experiments and thus obtained a theoretical value for the solubility of metaluminic acid; from that, he calculated the value of the acid dissociation constant to be 0.0188 and the value of the acid solubility product to be  $6.3 \times 10^{-13}$ . Recalculating Wood's data, Slade (102) found the solubility product to be  $0.37 \times 10^{-14}$ , which was very near the value ( $0.11 \times 10^{-14}$ ) that Slade obtained from data of Russ (96).

Heyrovsky (47), from the results of experiments in which he gradually neutralized sodium hydroxide by the addition of weighed amounts of aluminum sulfate, calculated the solubility product as  $35 \times 10^{-14}$  at 25° C.

Mortensen (82) attempted the determination of the "isoelectric point" by settling experiments. He placed solutions of aluminum sulfate in Imhoff cones, precipitated them with various kinds and amounts of alkali, and allowed them to settle. His results showed that the point at which he obtained maximum volume of precipitate varied with the alkali used. He claimed precipitation was complete for lime at pH 6.6, NaOH at pH 6.8, and  $\text{Na}_2\text{CO}_3$  at pH 7.4.

The "isoelectric point" was determined as pH 7.0 to 7.1 by Ellms and Marshall (30). They concluded that the amount of aluminum sulfate necessary to bring about the optimum conditions for precipitation was considerably in excess of the amount required to effect good clarification and, consequently, entailed an expense not warranted by the results obtained in their experimental work. Even a higher hydrogen-ion concentration has been calculated by Theriault and Clark (112). From known acidic and basic dissociation constants of aluminum hydroxide, they obtained an "isoelectric point" corresponding to pH 5.49. This value was checked by results of their experiments on the period of time required for the first appearance of the floc. The floc which formed most quickly in any series was invariably the best as far as appearance, rapid settling, and abundance were concerned. Optimum conditions for formation of floc were found within a narrow zone of hydrogen-ion concentrations centered for dilute solutions at pH 5.5. The less total salts in solution and the less alum added, the narrower became their pH zone.\*

---

\* Editor's Note:—Cf. Miller (79).

Baylis (6) found best clarification at pH 5.5. A series of gravimetric determinations showed a minimum amount of residual alumina from pH 5.7 to 6.5. He reported that at the Montebello Filters, Baltimore, sulfuric acid was added to the water to increase the hydrogen-ion concentration to a point favorable to the precipitation of alum. The addition of acid permitted a decrease in the amount of alum needed, which would mean a net saving of \$55 per 100 million gallons of water treated, or \$12,000 for 6½ months.

Hatfield (45) reported the results on a series of experiments in many ways very similar to those of Theriault and Clark. He determined the time required for appearance of floc in water from Lake St. Clairie, Michigan. The results showed an apparent "isoelectric point" at pH 6.1. Gravimetric determinations of residual alumina showed that the effluents were practically free from all the aluminum added as alum between pH 5.0 and 7.5. Earlier experiments by Hatfield (43) had indicated most complete precipitation at pH 7.2--7.3.

Two articles have recently appeared by Wolman and Hannan (127 and 128) which furnish a very complete review of the current scientific literature having a bearing on the alum-precipitation question. These authors in their experimental part confirmed the statements of Blum (11), Mahin (72) and others to the effect that aluminum hydroxide is appreciably soluble at a pH value of 8 or more, probably existing as the acid ion. They further showed that, by acidifying their reaction mixture as Blum did to a pH value of about 7, a more complete precipitation was effected. Pirnie (88) has discussed the colloid chemistry of water purification and the relation between alkalinity and coagulation, and Eddy (26) has presented the possible applications of hydrogen-ion determinations to filter-plant control.

The data described in the following pages were collected from two field surveys and a program of laboratory work to determine the solubility of aluminum hydroxide through a wide range of hydrogen-ion concentrations and to discover the optimum conditions for color removal and their relation to the "isoelectric point."

#### METHODS OF ANALYSIS.

During the field surveys, the determinations of alkalinity, free carbon dioxide, and hydrogen-ion concentration were made at the various plants; and samples were shipped to the laboratory for the determination of aluminum and iron. The determination of alkalinity and free carbon dioxide were made according to Standard Methods of Water Analysis (109). Hydrogen-ion concentrations were determined by the use of Clark's indicators and buffers (18).

The aluminum determination was made gravimetrically. A two-liter sample was evaporated to dryness, and the residue was taken up in hydrochloric acid, separated from silica by filtration, and precipitated with ammonium hydroxide according to Blum's method (12). All evaporations were made in palau or platinum dishes. The silica was ignited and volatilized with hydrofluoric acid. To prevent the loss of

any alumina which might have been filtered off with silica, the precipitate obtained with ammonium hydroxide was added to the non-volatile residue. The ignited precipitate was considered as  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{P}_2\text{O}_5$ .<sup>\*</sup> Iron was determined colorimetrically according to Standard Methods, and phosphate was estimated colorimetrically by a method given by Deniges (24), which is briefly as follows: If an acid solution of stannous chloride and an acid solution of ammonium molybdate are added to water containing small amounts of phosphate, a blue color is produced, the intensity of which varies with the amount of phosphate present. These colors may be compared with colors produced with standard phosphate solutions. Aluminum was then calculated by subtracting the iron and phosphate from the total residue.

The use of hematoxylin as an indicator changing color with the hydrogen concentration is described by Abderhalden (1), Richter (94), Prideaux (91), and others. Its use in the determination of aluminum is possible only in a buffered solution. Buffering may be accomplished in a measure by blowing breath ( $\text{CO}_2$ ) into the solution or by acidifying with acetic acid as recommended by Richards (93). However, hematoxylin gives various colors with most of the heavy metals. Using it, Morison (81) found that "a red color was given by the raw water and by a water completely clarified by a dose of alum just sufficient;" and Wolman and Hannan (127) state that treated water "showed the usual alumina blue changing to brown with acetic acid." Richards states, moreover, that the test may be made only in an acid solution in order to avoid the color produced by the alkaline earths. In view of these discrepancies in the literature, the hematoxylin test was not used.<sup>\*</sup>

Since aluminum sulfate is not easily purified by crystallization from water, it was decided to use one of the alum's for the laboratory experiments on residual alumina. Potassium alum ( $\text{Al}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$ ) was tried first. A quantity of it was recrystallized three times from distilled water. Solutions of the purified potassium alum were treated with varying amounts of tenth-normal sodium hydroxide and allowed to stand two days. The precipitates were then filtered, ignited and weighed. The results, however, were not consistent, probably on account of the amounts of sodium and potassium sulfates adsorbed.

To eliminate the error due to absorption, it seemed best to use materials which upon ignition would give only  $\text{Al}_2\text{O}_3$ . A quantity of ammonium alum ( $\text{Al}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$ ) was purified by three crystallizations to take the place of the potassium alum. Freshly distilled diethylamine was used to replace the sodium hydroxide. Even with larger volumes of sample, the

---

<sup>\*</sup> Editor's Note:—The symbol  $\text{P}_2\text{O}_5$  is here used arbitrarily as the most convenient way to represent the phosphorous compound which is one of the constituents of this total residue. For further discussion of the method of Deniges, see below pp. 82-85.

---

<sup>\*</sup> Editor's Note:—Subsequent work by Hatfield (44) overcomes some of these objections, but it was done on one plant under uniform conditions which permitted the determination of *relative* values of residual alum. For the determination of *absolute* values, under varying conditions of plant operation, a gravimetric method is obviously to be preferred. See below, pp. 83-85.

results were still too high, although the precipitates were heated in palau crucibles on a blast lamp for two hours, to make sure that all volatile matter had been driven off.

Since satisfactory results could not be obtained from weights of the precipitated alumina, possibly because of the formation of basic salts, the alternative was to work with the supernatant liquids. Solutions of the purified ammonium alum were precipitated with varying amounts of ammonium carbonate, ammonium hydroxide and acetic acid. After standing two days, the liquids were passed through a Berkefeld filter. The aluminum hydroxide in the filtrate was precipitated according to Blum's method. The amounts of alumina obtained were unreasonably high and inconsistent. For such determinations as this, filtration is at best a rather uncertain thing, for the filters tend to absorb substances from solution, thus changing the hydrogen-ion concentration, and usually the size of the pore is not definitely known.

If any method of filtration were suitable for this work, the ultra-filter would seem to show the most promise of success, since the pores in the membranes can be fairly closely regulated and measured. As an alternate, the Sharpies Laboratory centrifuge was considered a possible means of separating completely the solid phase from the liquid. To make a comparison between results obtainable from the centrifuge and from the ultra-filter, two liters of ammonium alum solution in concentration of about ten grains per gallon was precipitated and allowed to stand two days. The pH value was found to be 6.2. The sample was divided and one liter was passed through the centrifuge twice while it was rotating at a speed of 26,000 to 30,000 revolutions per minute. The other liter was passed through the ultra-filter with about fifty pounds air pressure. The membrane for the filter was made by immersing a filter paper in 7% collodion solution. The effluent from the centrifuge appeared to show a heavier Tyndall cone effect, although actually the amount of alumina found to be present was slightly less than that found in the sample which passed through the ultra-filter. There was .56 milligrams per liter of  $Al_2O_3$  found in the effluent from the centrifuge and 68 milligrams per liter found in the ultra-filter effluent. Neither of these methods proved very satisfactory.

Settling experiments seemed more promising. Solutions of ammonium alum were precipitated with diethylamine, pyridine or ammonium carbonate. These were stirred for various periods of time and allowed to settle. Samples precipitated with pyridine and diethylamine settled neither as rapidly nor as completely as those precipitated with ammonium carbonate. The organic compounds seemed to make the floc light and feathery. The addition of silica to the samples before precipitating did not increase the rapidity with which they settled.

The most satisfactory method was found to be as follows: Solutions of ammonium alum in concentration of about ten grains per gallon were placed in a good grade of flint-glass bottles with glass stoppers. The aluminum was precipitated by adjusting the hydrogen-ion concentration with various amounts of ammonium carbonate and acetic acid. The solutions were shaken two hours and allowed to stand four weeks. This period of time assured establishment of equilibrium and produced

a supernatant liquid which was free from any Tyndall cone effect. Two-liter samples were siphoned off, great care being taken not to disturb the precipitate. Determinations of hydrogen-ion concentrations were made by means of a Leeds and Northrup simplified potentiometer. The residue from the two-liter samples was taken up in hydrochloric acid and filtered to remove silica dissolved from the glass. The aluminum was precipitated with ammonium hydroxide. After a preliminary ignition, the precipitate was treated with hydrofluoric acid to remove any silica present, as recommended by Hillebrand (49). The residue was ignited and weighed as  $Al_2O_3$ . The data will be discussed in connection with Table III.

### RESULTS OF FIELD SURVEYS.

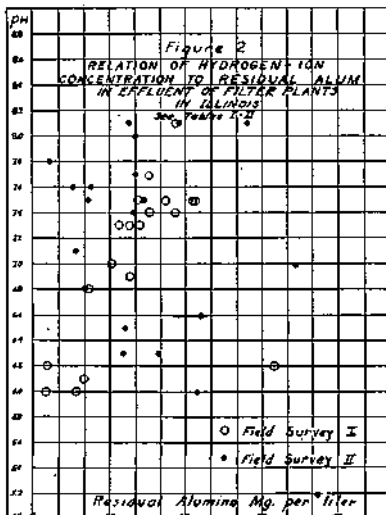
The preliminary field survey, made during the summer and early autumn of 1921, in order to estimate the practical value of the problem, included visits to more than twenty filter plants in different parts of Illinois. In the spring of 1923, after the bulk of the laboratory experiments had been completed, it seemed advisable to make another field survey to get data under different weather conditions. Plants not visited in the previous work were included in this second survey. Improvements in technic probably make the latter results the more reliable. On account of irregularities in operation at the time of visit, a few of the results of both series had to be discarded; it is believed, however, that the data may be taken as truly representative of operating conditions throughout the state.

Towns visited are listed in Tables I and II in the order of decreasing pH values in the effluents. Columns at the right in these tables show how the observed decrease in alkalinity due to the addition of alum differs from that calculated. In the first survey (Table I), four of the nineteen plants studied (2, 10, 13, 14) showed a decrease in alkalinity of 8 ppm. for each grain of alum used per gallon of water, which is the decrease usually expected. At nine plants (1, 7, 9, 12, 15, 17, 18, 19, 20) the decrease in alkalinity was greater than that calculated; this group includes, as would be anticipated, the three plants at which lime as well as alum was added. At six plants the decrease was less than calculated. In this second survey (Table II), of the twenty-two plants visited, three (3, 5, 22) showed the theoretical decrease, twelve (1, 2, 8, 9, 10, 11, 13, 15, 17, 18, 19, 20) showed a decrease greater than theoretical, and seven (4, 6, 7, 12, 14, 16, 21) showed a decrease less than theoretical. The factors tending to produce deviations from theoretical values have already been discussed (see above,

p. 51). Further investigation would be required in order to account quantitatively!}' for the part played by each factor.

Tables I and II also show the extent to which alumina is present in the effluents of filter plants visited. In addition to the description of method given above, it should be stated that in all cases except No. 2 in Table I, the raw water was filtered through Whatman No. 50 filter paper before making the aluminum determination. Since a comparison was to be made of the aluminum in solution or in a fine colloidal state in the raw and treated waters, it seemed best to exclude the filterable turbidity. The data on No. 2 in Table I indicate what results might have been without the adoption of this procedure. Nos. 12 and 17 of Table I and Nos. 1, 16, and 28 of Table II are excluded from consideration since they showed turbidities over 20 in the filtered waters. Only in seven cases, four of which have been explained, does the alumina in the effluent exceed 2.22 mg. per liter (approximately of a grain per gallon) ; furthermore, in more than half the cases, the alumina is distinctly less in the effluent than in the raw water. It should also be noted that, although a fairly wide range of pH value is exhibited by these waters, in no case does the alumina in the effluent reach zero. From our knowledge of the individual plants and their operators, we feel that these traces of residual alum cannot be attributed to faulty operation.

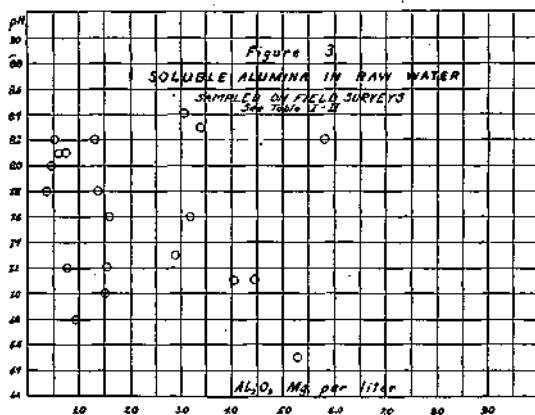
From the above data it appears that, with reasonably good operation, the amounts of residual alum occurring in filter-plant effluents in Illinois are not such as to be cause for alarm. Whether or not the con-





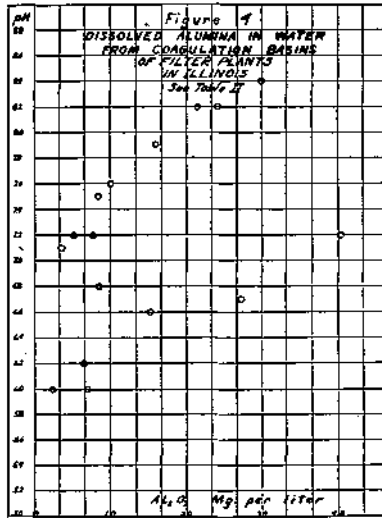
condition of the residual alum is such that it is more subject to subsequent deposition or adsorption, is a question for further study.

The residual alum values and the pH values are plotted as coordinates of points in Fig. 2. Although the points for the first field survey do not lie in a smooth curve, they show a distinct trend toward a minimum of residual alum at a point near pH 6. This is considerably more acid than any value previously reported; it is however, the first value to be determined gravimetrically under operating conditions. The values obtained from the second field survey are more consistent, possibly on account of improvements in technique. They show minimum residual alum between pH 6.0 and 7.8 as is easily seen from Fig. 2. The values fall into a fairly smooth curve, as smooth as could be expected considering the fact that samples were collected under widely varying condition. Difference in chemical composition of the raw water and even only temporary faulty operation would influence the results. Moreover, it is probable that a filter just before washing would yield results different from those just after washing. Data collected from one plant operated uniformly for a long period of time should give still more consistent results. A glance at Fig. 3 will show that points repre-



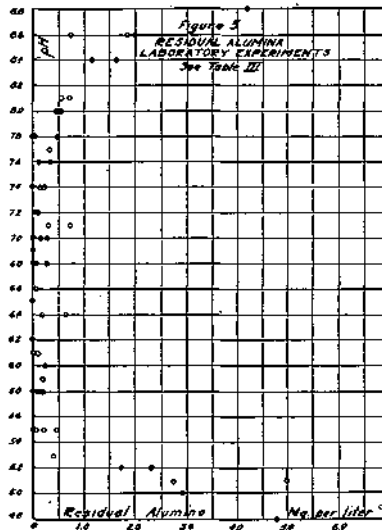
senting the alumina in raw waters are not arranged in any definite order with respect to pH values but are distributed very widely.

In addition to the raw and filtered samples, waters which had been coagulated but not filtered were collected from 19 of the plants visited on the second survey. These samples were also filtered through Whatman No. 50 filter paper before making the alumina determinations. The results (Fig. 4) show minimum  $Al_2O_3$  between pH 6.0 and 7.9.



### RESULTS OF LABORATORY EXPERIMENTS.

In order to obtain more exact data as to the solubility of aluminum hydroxide, laboratory experiments were conducted under conditions which could be more easily controlled and duplicated. The amounts of



alumina left in solution from pH 4.8 to 8.8, determined by the method explained above, are shown in Table III. From Fig. 5 it is clear that

under laboratory conditions there is a broad zone (pH 5.5 to 7.8) in which amounts of residual alumina are very small.

Some high results are inevitable as long as the liquid is separated from the solid phase in the manner used. In siphoning, a few very small particles of floc could be carried over without detection. Generally, however, the separation was quite complete, and the results are fairly consistent. Although the amounts of residual alumina in Fig. 5 are slightly lower than those in Fig. 2, it is to be noted that the pH zone of maximum precipitation under experimental conditions includes the zone of minimum values for residual alum obtained in the two field surveys. These zones also coincide generally with the values reported by Hatfield (45) and by Baylis (6) for plant operation.

Table IV is made up of data selected from Table III for the calculation of the base solubility product  $K_{bs} = [Al(OH)_2^+] \times [OH^-]$ . A value of approximately  $3 \times 10^{-14}$  is thus obtained for  $K_{bs}$ . This is a much higher value than that obtained by Heyrovsky,  $1 \times 10^{-33}$ , when working with aluminum chloride at pH 3.0—4.0 and assuming the aluminum ion ( $Al^{+++}$ ) to be present (47). Being based upon more probable ionizations and calculated from gravimetric determinations of alumina within the zone of minimum solubility, this new value is believed to be more nearly correct than that of Heyrovsky, which was obtained by indirect methods.

Table V, similarly, is made up of data selected from Table III for the calculation of the acid solubility product according to the equation  $K_{as} = [Al(OH)_2O^-] \times [H^+]$ . The results lie between the value given by Heyrovsky ( $35 \times 10^{-14}$ ) and that given by Slade ( $0.37 \times 10^{-14}$ ) (102). The average of these results gives approximately  $1 \times 10^{-13}$  for the value of  $K_{as}$ . It should be noted that these calculations are based upon the assumption of the primary ionization of aluminum hydroxide. Secondary and tertiary ionizations are also possible, as was pointed out above (see page 51).

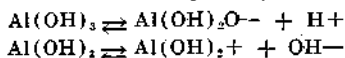
In calculating a provisional pH value for the "isoelectric point", Theriault and Clark (112) used the equation  $[H^+] = \frac{\sqrt{K_{as}K_w^a}}{\sqrt{3K_{bs}}}$  where  $K_{as}$  = the acid solubility product of  $Al(OH)_3$ , and  $K_{bs}$  = the base solubility product of  $Al(OH)_3$ .

Their calculations were based upon the assumptions made by Heyrovsky that  $Al(OH)_3$  ionized to give  $Al(OH)_2O^-$  and  $Al^{+++}$  at the "isoelectric point," and that  $[Al(OH)_2O^-] = 3[Al^{+++}]$ . His assumptions can hardly be adopted in this case, however, for he worked with aluminum chloride in acid solutions (pH 3—4), determined the chloride ion and not the aluminate ion, and neglected the hydrolysis, as it did not exceed 3.8%. Theriault and Clark were working with aluminum hydroxide at considerably lower hydrogen-ion concentrations (pH 5—6), where hydrolysis should be nearly complete. It is doubtful if all their assumptions are consistent with the definition of the "isoelectric point". Moreover, the applicability of the solubility product in such calculations is open to question.

It is also possible that Heyrovsky had basic aluminum chloride or something other than aluminum hydroxide. Recently, Clark and Miller (19)

have found that the precipitate formed at pH 5.6 contained basic aluminum sulfate. This is in agreement with qualitative tests of our own showing considerable amounts of phosphate and silicate in the floc precipitated when alkali is added to solutions of aluminum salts containing sulfate or silicate anion. The fact that the precipitate is not at all properly represented by  $\text{Al}(\text{OH})_3$  but is probably a mixture of aluminum hydroxide and various basic salts, renders all calculations of the "isoelectric point" useless.

If we were justified in assuming  $\text{Al}(\text{OH})_3$  as the composition of the alum floc, we could obtain other expressions for the value of  $[\text{H}^+]$  depending upon the ionization assumed. If the primary ionization took place:



then at the "isoelectric point" the following equation would be fulfilled:

$$[\text{Al}(\text{OH})_2\text{O}^-] = [\text{Al}(\text{OH})_2^+]$$

Using Theriault and Clark's method of calculation, we would have

$$[\text{H}^+] = \sqrt{\frac{\text{KasKw}}{\text{Kbs}}}$$

Substituting in this expression the value  $\text{Kbs} = 2.9 \times 10^{-14}$  (from Table IV) and the value  $\text{Kas} = 10.4 \times 10^{-1}$  (from Table V) would give  $\text{pH} = 6.72$  for the "isoelectric point." This is approximately in the middle of the zone of minimum solubility as defined by our experimental data (see Fig. 5). However, we attach no importance to this agreement, for it is undoubtedly a coincidence. Assuming other possible ionizations, we would get eight other expressions by Theriault and Clark's method of calculation, which would give eight different pH values for the "isoelectric point." The ionizations from which these expressions may be calculated are all possible, and some are even more probable than those assumed by Theriault and Clark. But such calculations are useless, in view of the improbability that the concept of the "isoelectric point" is applicable in the case of alum floc.

### COLOR REMOVAL.

Recognition of the importance of colloids in water purification began when Biltz and Krohnke (9) showed that part of the organic matter in water was negatively charged colloidal matter. S. Rideal and E. K. Rideal (95) described the general properties of colloids in relation to water, and Catlett (13) and Saville (98) intensively investigated the colloidal nature of the color in certain waters. Catlett carried on experiments at Wilmington, N. C., where the water supply is obtained just below the junction of two rivers, one of high color and the other of high turbidity. He demonstrated that some colloids are precipitated by other colloids of opposite charge and by soluble crystalloids, such as aluminum sulfate, which yield ions of opposite charge. Thus positively charged particles of "color" are precipitated by negatively charged particles of "turbidity".

Loeb (66, 67) compared the behavior of aluminum hydroxide and that of the amphoteric colloid gelatin. According to his theory and considering alum floc to be  $\text{Al}(\text{OH})_3$ , if the "isoelectric point" of a dye should correspond to that of aluminum hydroxide, and if the ionization constants of the one were about equal to those of the other, there could be no action between them at any hydrogen-ion concentration; because they would always be similarly charged. Suppose, however, that the isoelectric point of a dye is

pH 4.5 and that the "isoelectric point" of  $\text{Al}(\text{OH})_3$  is pH 6.0; then, from pH 4.5 to 6.0 there would be color removal, but below pH 4.5 and above pH 6.0 the dye and the  $\text{Al}(\text{OH})_3$  would not react, for both would have the same charge. This argument, of course, rests on the belief that alum floc has a positive charge, and this charge is accounted for by: (1) positive ionization of aluminum aluminate, which may be one of the forms in which alumina is found in water; (2) hydration of gel form, splitting off an  $(\text{OH}-)$  and leaving a positive residue; (3) absorption of  $(\text{Al}^{+++})$  or  $(\text{H}^+)$  on the floc.

In an attempt to determine the optimum pH for color removal, experiments were carried out in the following manner: Tubes were set up containing dilute solutions (approximately 0.1%) of ammonium alum buffered with ammonium carbonate and acetic acid so as to give a pH range of 5-8. Equal amounts of a dye solution or a colored infusion were then added to these tubes. After being thoroughly shaken, the tubes were centrifuged to remove the precipitate. The pH values were determined potentiometrically. The amount of dye remaining in the supernatant liquid was estimated by matching the color against tubes containing known amounts of the dye used; in cases where tea or pine-needle infusions were used, the residual color was matched against the ordinary color standards used in water analysis.

Solutions of malachite green, acid fuchsin, and basic fuchsin were practically unaffected by this treatment. The data on congo red (Table VI) are not consistent enough to be of definite significance. The results for alizarin red S and azolitmin, however, as given in Tables VII and VIII, show marked color removal within a rather wide range of pH values (from pH 5.4 to 8.0). Similarly, infusions of tea leaves and pine needles were decolorized, as shown in Tables IX and X.

It should be remembered in this connection that azolitmin changes color from pH 4.5 to 8.3, and that alizarin red S changes color from pH 5.0 to 6.8. Within these ranges we would expect their "isoelectric points", at which color removal should be impossible according to Loeb's theory. But maximum color removal by alum floc takes place near pH 6.0, which is in the zone of minimum solubility where the "isoelectric point" of aluminum hydroxide is by Loeb's theory assumed to be located. Therefore, it appears that the behavior of aluminum hydroxide is not parallel to that of the amphoteric colloid gelatin. The facts lead to the conclusion that color removal by alum floc is a process of adsorption\*.

---

\* EDITOR'S NOTE :—Recent work by Miller (79 and 79a) throws further light on the properties of alum floc and its role in color removal.

**SUMMARY.**

The chemistry of the alum coagulation process is represented by a diagram which emphasizes both the interdependence of the various equilibria involved and the importance of the hydrogen-ion concentration.

In general, less dissolved alumina is found in the effluent from filter plants than in the raw water. The amount of alumina in the effluent seldom exceeds two milligrams per liter (less than one-eighth a grain per gallon).

Alkalinity changes of water during treatment in filtration plants do not check the theoretical changes as ordinarily calculated. Various reasons for these discrepancies are discussed.

Data from field surveys indicate minimum residual alum between pH 6.0 and 7.8.

Laboratory results indicate minimum solubility of alumina from pH 5.5 to 7.8.

The base solubility product of aluminum hydroxide is calculated to be approximately  $3 \times 10^{-14}$ .

The acid solubility product of aluminum hydroxide is calculated to be approximately  $1 \times 10^{-13}$ .

Maximum removal of color from certain dye solutions and tea infusions by alum floc is obtained within the pH zone of minimum solubility of alumina.

**TABLE I.**  
**SUMMARY OF DATA OBTAINED ON FIRST FIELD SURVEY.**  
**July 22—Sept. 23, 1921.**

Town	Raw Water*					Pre-Treatment		Filtered Water					Decrease					
	PH	CO <sub>2</sub> ppm.	Alk. ppm.	Fe <sub>2</sub> O <sub>8</sub> ppm.	Al <sub>2</sub> O <sub>3</sub> ppm.	Chemicals Gr. per gal.	Time Hrs.	PH	CO <sub>2</sub>	Alk. ppm.	Fe <sub>2</sub> O <sub>3</sub> ppm.	Al A	Turb. ppm.	PH	Alkalinity		Fe <sub>2</sub> O <sub>3</sub> ppm.	Al <sub>2</sub> O <sub>3</sub> ppm.
															Found	Calc.		
1	7.8	2.0	56	0.14	1.36	{ 0.75 alum } { 0.75 lime }	1	8.1	0.0	62	0.14	1.86	5	-0.3	ppm. -6	ppm. -12.0	0.00	-0.50
2	8.3	0.0	116	0.00	20.56	0.7 alum	2	7.7	2.8	110	0.0	1.50	0	0.6	6	5.6	0.00	19.06
3	8.3	0.0	178	0.14	3.19	1.4 alum	3½	7.5	6.8	170	0.0	2.15	3	0.8	8	11.2	0.14	1.04
4	8.0	2.0	192	0.14	1.81	1.0 alum	3	7.5	7.6	186	0.0	2.10	5	0.5	6	8.0	0.14	-0.30
5	7.6	4.8	180	0.14	5.90	1.1 alum	1½	7.5	7.2	176	0.28	1.72	3	0.1	4	8.8	-14	4.18
6	7.5	4.4	79	0.00	1.75	0.37 alum	3	7.5	4.0	84	1.96	(?) 1.39	10	0.0	-5	2.9	-1.96 (?)	0.36
7	8.0	2.0	134	0.14	1.21	1.85 alum	2	7.4	8.8	116	0.14	1.51	10	0.6	18	14.8	-0.00	-0.30
8	...	....	...	....	....	0.7 alum	6	7.4	6.0	124	0.14	1.86	3	...	..	....	....	...
9	7.9	2.4	126	0.00	2.23	{ 2.8 alum } { 1.0 lime }	4½	7.3	7.2	112	0.00	1.25	3	0.6	14	-1.4	0.00	0.98
10	7.9	2.8	130	0.14	1.56	2.8 alum	6-24	7.3	8.8	108	0.28	1.12	0	0.6	22	22.4	-0.14	0.44
11	7.3	12.0	160	0.00	2.95	2.7 alum	4-5	7.2	13.6	154	0.42	1.38	10	0.1	6	21.6	-0.42	1.57
12	7.5	2.4	68	0.28	0.97	0.9 alum	4	7.1	6.4	58	0.00	12.10	30	0.4	10	7.2	0.28	-11.13
13	8.1	0.0	82	0.00	1.60	1.5 alum	½	7.0	9.2	71	0.00	1.35	5	1.1	11	12.0	0.00	0.25
14	7.5	4.0	58	0.14	0.76	0.46 alum	..	6.9	10.4	54	0.14	1.26	20	0.6	4	3.7	0.00'	-0.50
15	7.9	3.6	132	0.28	0.82	3.0 alum	8-24	6.8	15.2	94	0.14	0.71	3	1.1	38	24.0	0.14	0.11
16	7.2	4.0	48	0.85	2.30	2.0 alum	..	6.8	10.0	42	0.14	0.71	3	0.4	6	16.0	0.71	1.59
17	8.4	0.0	54	0.28	0.40	2.0 alum	3½	6.2	23.6	24	0.99	3.16	5	2.2	30	16.0	-0.71	-2.76
18	8.5	0.0	46	0.14	0.71	1.5 alum	4	6.2	19.6	24	0.28	0.17	3	2.3	22	12.0	-0.14	0.54
19	7.2	6.8	60	1.43	3.22	{ 0.4 alum } { 0.5 lime }	3	6.1	33.2	16	0.14	0.66	3	1.1	44	0.8	1.29	2.56
20	6.8	6.8	24	1.68	0.15	2.1 alum	6-7	6.0	23.2	2	0.71	0.55	5	0.8	22	16.8	0.97	-0.40
21	7.3	...	80	....	....	4.5 alum	2	6.0	37.2	6	0.14	0.16	3	1.3	74	36.0	....	...

65

\* NOTE: None of these samples showed phenolphthalein alkalinity except the following: No. 2, 5ppm; No. 3, 16ppm; No. 18, 5ppm.

TABLE  
SUMMARY OF DATA OBTAINED  
April 16—

TUM	Raw Water*					Pre-Treatment		Coagulated Water				
	PH	CO <sub>3</sub>	Alk.	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	Chemicals	Time	pH	CO <sub>2</sub>	Alk.	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>
	ppm.	ppm.	ppm.	ppm.	ppm.	Gr. per gal.	Hrs.		ppm.	ppm.	ppm.	ppm.
1	7.1	2.0	46	1.71	4.45	{ 1.75 alum 1.18 lime }	8.	8.2	0.0	70	.14	2.41
2	7.3	9.0	208	.00	2.91	{ 1.4 alum 4.2 lime }	20.	8.4	0.0	200	.00	2.98
3	7.0	2.0	52	.00	1.53	{ 0.46 alum 0.5 lime }	1.	8.4	0.0	60	.00	5.66
4	8.3	0.0	192	.00	3.38	{ 6.2 alum 0.46 alum }	8.	8.2	2.0	186	.00	2.14
5	8.2	0.0	198	.00	1.31	{ 1.6 alum 1.9 alum }	3.5	...	...	...	...	...
6	8.4	0.0	206	.00	3.09	{ 3.0 alum 1.9 alum }	3.—7	...	...	...	...	...
7	8.2	0.0	214	.00	5.27	{ 3.0 alum 1.2 lime }	3.	7.9	2.0	207	.00	1.59
8	8.2	0.0	106	.14	0.47	{ 1.5 alum 1.0 lime }	4.5	7.2	2.0	92	.14	0.77
9	7.6	2.0	132	.43	3.22	{ 1.0 alum 0.5 lime }	4.—6	7.6	2.5	128	.00	1.01
10	8.1	2.5	183	.00	0.59	{ 1.2 alum 0.7 alum }	1.	7.5	9.0	173	.00	1.17
11	8.0	0.0	170	.00	2.02	{ 3.0 alum 1.2 alum }	4.—20	7.2	7.0	160	.00	4.05
12	7.8	0.0	114	.00	1.39	{ 1.5 alum 1.4 alum }	3.	...	...	...	...	...
13	7.8	6.0	128	.28	0.35	{ 2.3 alum 1.6 alum }	96.	7.2	22.5 (?)	100	.00	0.52
14	7.2	4.0	74	.43	1.55	{ 1.0 alum 2.0 alum }	1.5	7.1	3.0	64	.14	0.38
15	8.1	0.0	100	.00	0.77	{ 6.0 alum 1.4 alum }	6.—18	6.8	8.0	84	.00	0.86
16	7.2	1.0	60	.14	0.77	{ 2.0 alum 1.6 alum }	4.	6.7	10.0	50	.28	2.73
17	7.2	4.0	60	.14	1.25	{ 1.0 alum 2.0 alum }	6.—12	6.6	12.0	38	.14	1.52
18	7.2	4.0	62	1.43	4.05	{ 6.0 alum 1.4 lime }	4.	6.2	17.0	35	.14	0.65
19	6.8	2.0	50	.28	0.94	{ 0.9 alum 3.0 alum }	5.—8	6.0	27.0	20	.14	0.70
20	7.6	1.0	66	.70	1.63	{ 6.0 alum 1.4 lime }	4.	6.0	25.0	15	1.00	0.24
21	6.5	5.0	21	2.00	5.31	{ 0.9 alum 0.9 alum }	24—48	5.0	23.0	6	.43	9.39
22	6.4	2.0	10	4.00	14.17	{ 0.9 alum 0.9 alum }	(?)	5.2	50.0	3	.28	7.29

\*Note—None of these samples showed phenolphthalein alkalinity except the following: No. 5, 8 ppm.; No. 6, 14ppm.; No. 7, 8 ppm.; No. 8, 20 ppm.; and No. 15, 6 ppm.



II.  
ON SECOND FIELD SURVEY  
May 22, 1923

Filtered Water†					Decrease (Raw--Filtered)				
pH	CO <sub>2</sub>	Alk.	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	PH	Alakility		Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>
	ppm.	ppm.	ppm.	ppm.		Found	Calc.		
8.6	0.0	56	1.86	7.96	-1.5	-10	-13.1	-.15	-3.51
8.1	0.0	180	.14	1.24	-0.8	28	-85.4	-.14	1.67
8.1	0.0	60	.00	2.8	-1.1	8	7.9	.00	-1.27
8.1	2.5	184	.00	1.91	0.2	8	50.0	.00	1.47
8.0	3.0	194	.14	1.33	0.2	4	3.7	-.14	-0.02
7.8	3.0	196	.14	0.32	0.6	10	12.8	-.14	2.77
7.7	4.0	204	.28	1.33	0.5	10	15.2	-.28	3.94
7.6	3.0	96	.28	0.52	0.6	10	3.2	-.14	-0.05
7.6	1.5	128	.00	0.79	0.0	4	7.0	.43	2.43
7.5	10.00	172	.00	0.71	0.6	11	3.5	.00	-0.12
7.0	6.0	156	.14	1.44	0.5	14	9.6	.14	0.58
7.4	0.0	112	.28	1.31	0.4	2	5.6	-.28	0.08
7.1	14.0	98	.00	0.55	0.7	30	24.0	.28	-0.17
7.0	3.0	66	.86	3.45	0.2	8	9.6	-.43	-1.90
6.8	7.5	80	.00	0.69	1.3	20	11.2	.00	0.08
6.6	11.0	46	.28	2.22	0.6	14	18.4	-.14	-1.45
6.5	12.0	32	.00	1.20	0.7	28	12.8	.14	0.05
6.3	15.0	36	.86	1.64	0.9	26	8.0	.57	2.41
6.3	12.0	26	.14	1.18	0.5	24	16.0	.14	-0.24
6.0	25.0	16	1.12	2.16	1.6	50	24.0	-.42	-0.53
5.2	14.0	5	.43	3.76	1.3	16	17.8	1.57	1.55
5.0	5.0	3	3.43	23.58	1.4	7	7.2	.57	-9.41

† Note—None of these samples showed phenolphthalein alkalinity except the following: No. 2, 6 ppm.; No. 3, 2 ppm.

**TABLE III.**  
**AMOUNTS OF RESIDUAL ALUMINA IN LABORATORY EXPERIMENTS.**  
 Milligrams per liter.

pH	1	2	3	4	Average
4.8			4.84		4.84
4.9				6.83	6.83
5.0			2.92		2.92
5.1	5.00		2.76		3.88
5.2	2.31		1.75'		2.03
5.3	0.42		0.42		0.42
5.5	0.08	0.21	0.00		0.10
5.6	0.22		0.46		0.34
5.8		0.12	0.16		0.14
5.9				0.19	0.19
6.0	0.25				0.25
6.1	0.35		0.35	0.11	0.27
6.2		0.00			0.00
6.4	0.19		0.66		0.42
6.5	0.00				0.00
6.6		0.00		0.07	0.04
6.8	0.00	0.26	0.00	0.05	0.08
6.9		0.00			0.00
7.0		0.00		0.15	0.08
7.0				0.27	0.27
7.1			0.73	0.29	0.51
7.2		0.08	0.05		0.06
7.4	0.22	0.14	0.01		0.12
7.6		0.115		0.35	0.23
7.7				0.32	0.32
7.8		0.035	0.485		0.26
7.9		0.00			0.00
8.0		0.53	0.46		0.49
8.1		0.70	0.55	2.57	2.54
8.4		1.15	1.63		1.39
8.6	1.85	0.745	1.985		1.19
8.8		4.18			4.18

**TABLE IV.**  
**BASE SOLUBILITY PRODUCT OF Al(OH)<sub>3</sub>.**  
 Calculated from Experimental Data.

pH	Al(OH) <sub>3</sub> mg. per liter	[OH—] concentration		Molar		Solubility Product K <sub>bs</sub> =[Al(OH) <sub>2+</sub> ] X [OH—]
		[OH—]	[Al(OH) <sub>2+</sub> ]	[OH—]	[Al(OH) <sub>2+</sub> ]	
5.0	4.47	1 X 10 <sup>-9</sup>	5.7 X 10 <sup>-5</sup>	1 X 10 <sup>-5</sup>	5.7 X 10 <sup>-14</sup>	5.7 X 10 <sup>-14</sup>
5.2	2.68	1.6 X 10 <sup>-9</sup>	3.4 X 10 <sup>-5</sup>	1 X 10 <sup>-5</sup>	5.44 X 10 <sup>-14</sup>	5.44 X 10 <sup>-14</sup>
5.3	.64	2.0 X 10 <sup>-9</sup>	.82 X 10 <sup>-5</sup>		1.64 X 10 <sup>-14</sup>	1.64 X 10 <sup>-14</sup>
5.5	.34	3.2 X 10 <sup>-9</sup>	.43 X 10 <sup>-5</sup>	10 <sup>-5</sup>	1.38 X 10 <sup>-14</sup>	1.38 X 10 <sup>-14</sup>
5.5	.70	3.2 X 10 <sup>-9</sup>	.9 X 10 <sup>-5</sup>	10 <sup>-5</sup>	2.88 X 10 <sup>-14</sup>	2.88 X 10 <sup>-14</sup>
5.8	.24	6.3 X 10 <sup>-9</sup>	.3 X 10 <sup>-5</sup>	10 <sup>-5</sup>	1.89 X 10 <sup>-14</sup>	1.89 X 10 <sup>-14</sup>
5.8	.18	6.3 X 10 <sup>-9</sup>	.23 X 10 <sup>-5</sup>		1.35 X 10 <sup>-14</sup>	1.35 X 10 <sup>-14</sup>
Average = 2.9 X 10 <sup>-14</sup>						

**TABLE V.**  
**ACID SOLUBILITY PRODUCT OF  $\text{Al}(\text{OH})_3$ .**  
**Calculated from Experimental Data.**

pH	Al(OH) <sub>3</sub> mg. per liter	[H <sup>+</sup> ]	Molar Concentration		Solubility Product K <sub>as</sub> = [Al(OH <sub>2</sub> O—)]X[H <sup>+</sup> ]
			[Al(OH) <sub>2</sub> O—]		
7.7	.49	2.0 X10 <sup>-8</sup>	6.2 X 10 <sup>-6</sup>		12.4 X 10 <sup>-14</sup>
8.0	.81	1.0 X 10 <sup>-8</sup>	10.4 X 10 <sup>-6</sup>		10.4 X 10 <sup>-14</sup>
8.0	.70	1.0 X10 <sup>-8</sup>	8.97 X 10 <sup>-6</sup>		8.97X10 <sup>-14</sup>
8.1	1.07	0.8 X10 <sup>-8</sup>	13.7 X 10 <sup>-6</sup>		10.96X10 <sup>-14</sup>
8.4	1.76	0.4 X 10 <sup>-8</sup>	22.5 X 10 <sup>-6</sup>		9.00X10 <sup>-14</sup>
8.4	2.49	0.4 X10 <sup>-8</sup>	31.9 X 10 <sup>-6</sup>		12.76X10 <sup>-14</sup>
8.6	2.83	0.25X10 <sup>-8</sup>	36.2 X 10 <sup>-6</sup>		9.05X10 <sup>-14</sup>
8.6	3.03	0.25X10 <sup>-8</sup>	38.8 X 10 <sup>-6</sup>		9.70X10 <sup>-14</sup>
Average =					10.4 X10 <sup>-14</sup>

**TABLE VI.**  
**DECOLORIZATION OF 0.002% CONGO RED SOLUTION.**  
**By Ammonia Alum Solution (approximately 0.1%) Buffered With Ammonium**  
**Carbonate and Acetic Acid, Residual Color Being Expressed**  
**in cc. of 0.001% Congo Red Solution.**

pH	1	2	3	4	5
5.8	.30	.5		3.0	10.
5.9		.5	.7	.7	1.0
6.0	.00	1.0			8.0
6.1					
6.2					
6.3					
6.4		2.0	3.0		7.0
6.5	.20	4.0	6.0	5.0	
6.6	2.0	5.0	7.0	8.0	5.0
6.8	1.0	1.0	4.0	4.0	11.0
7.0			6.0	7.0	
7.2	1.5	3.0	6.0		25.
7.4	2.0	2.5		6.0	12
7.6	4.0	5.0		9.0	12
7.8	4.0	4.0	6.0	7.0	15
8.0	4.0	4.0	12.0	30.	35
8.2					
8.4		6.0			

TABLE VII.

DECOLORIZATION OF 0.001% SOLUTION OF ALIZARIN RED S.  
By Ammonia Alum Solution (approximately 0.1%) Buffered With Ammonium  
Carbonate and Acetic Acid, Residual Color Being Expressed  
in cc. of 0.002% Solution of the Dye.

pH	1	2	3	4	5	6
4.8	.25				.5	.25
5.0		.06	.06	.30	.06	.15
5.2	.10	.03	.02	.08	.10	.13
5.4			.01	.03	.001	.07
5.6			.005			
5.8	.01		.01			
6.0		.01	.01	.000	.005	.03
6.2		.01	.01	.01	.01	.07
6.4	.01	.01	.01	.005	.01	.05
6.6	.01	.01		.01		
6.8	.00	.03		.02		
7.0				.05		
7.4		.04			.06	
7.8			.08			.10
8.0	.10		.08			
8.2	.20				.10	
8.4						.20
8.6		.06	.10	1.0		

TABLE VIII.

DECOLORIZATION OF 0.005% AZOLITMIN SOLUTION.  
By Ammonia Alum Solution (approximately 0.1%) Buffered With Ammonium  
Carbonate and Acetic Acid, Residual Color Being Expressed  
in cc. of 0.002% Solution of the Dye.

pH	1	2	3	4
5.0		1.0		
5.2	.06	.50	.07	
5.4		.01	.05	.02
5.6	.01			
6.0	.005	.01		.01
6.2		.02	.01	
6.4	.01		.05	
6.6	.01	.07	.05	.05
6.8	.05	.07	1.0	.15
7.0	.05		1.5	.10
7.2	.10	.10	2.0	.30
7.4	.10		2.0	
8.0	.10			
8.4			1.0	.50
8.6	.40			
8.8	.50	.40		

TABLE IX.

**DECOLORIZATION OF PINE-NEEDLE INFUSION.  
By Ammonia Alum Solution (approximately 0.1%) Buffered With Ammonium  
Carbonate and Acetic Acid, Residual Color Being Expressed  
in Units Used in Water Analysis.**

	Initial Color 100	Initial Color 100	Initial Color 200	Initial Color 150
p H				
4.9	50	55	250	
5.0	20			
5.2	15			
5.4	15			100
5.5	20			
5.6	10	10	25	
5.7		10	25	
6.1				50
6.3				50
6.6	18	20		60
6.8			40	
7.0		30		250
7.2			80	
7.4		35		250
8.2	60			
8.6		90	500	
9.0	80	100	500	

TABLE X.

## DECOLORIZATION OF ORANGE PEKOE TEA INFUSION.

By ammonium alum solution (approximately 0.1%) buffered with ammonium carbonate and acetic acid, residual color being expressed in units of the platinum-cobalt standards.

Initial Color	1000	1000	500	250	500	500	500	250	250	250	500	500	
PH													
4.9	250	150	250	70	150	140		100	150	200	150	150	
5.0				30					70			125	
5.1										100	150	125	
5.2			35		22					40	100	125	
5.3				30		30		300		50	30	100	
5.4				50		30			80	40	30	100	100
5.5			50		20	20	15						
5.6					40		20						
5.7				25				250	35	35		150	
5.9									70		50		
6.0					40						30		
6.1						20			40				
6.2									100			300	
6.3								500			50		
6.4		20			20			250	150				
6.6			200		7				150			300	350
6.8				500		35		350		150			
7.0							500			200			
7.2									200		200		
7.4	800							500					
7.6		800					55						
7.8			1000										
8.0					250								
8.2				600				600					
8.4					500	250							

**PART THREE.**





## STUDIES ON THE PRECIPITATION OF CALCIUM, MAGNESIUM, AND ALUMINUM\*.

### INTRODUCTION.

The installation of an experimental filter plant on the banks of the Boneyard stream in Urbana afforded an opportunity to get data not possible to obtain on a filter plant furnishing potable water. This experimental plant was operated during the fall of 1923 and the spring of 1924. During the winter, when weather conditions prevented operations, such laboratory work was done as would have a bearing on water filtration, including the analysis of samples taken at four filter plants in the State of Illinois. The Illinois Power and Light Corporation allowed the writer to make some tests on the chemical reactions involved in the treatment of water at the plant in Danville, Illinois. This plant which is of the intermittent type and used the hot-process system, afforded an opportunity for studying the effect of heat in a commercial lime-soda softener.

This investigation, therefore, includes three lines of work, each having a bearing on the process of water purification:

(1) The solubility product of magnesium hydroxide has been determined with the aid of the hydrogen electrode. The common error of ignoring carbon dioxide in previous investigations is discussed, and methods are given for its exclusion.

(2) Reactions in coagulating basins are studied with reference to (a) relation of hydrogen-ion concentration to alumina in the effluent, (b) alkalinity changes during filtration, and (c) composition of the floc.

(3) The effect of temperature on the speed of reaction and on the final hardness was determined on a hot-process lime-soda softener. Effect of varying the dosage of chemicals on the speed of reaction at varied temperatures, effect of addition of alum, and effect of filtering are included.

### THE SOLUBILITY PRODUCT OF MAGNESIUM HYDROXIDE.

According to Johnston (55), the values for the solubility of magnesium hydroxide as given by previous investigators (References 25, 46, 61, 69) were much too high because there was always some carbonate present. A sum-

---

\*From a thesis submitted May, 1924, by W. U. Gallaher in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry in the Graduate School of the University of Illinois.



water of hydration of magnesium sulfate is somewhat variable, the standard solution could not be made up to exact strength from weighed salt.

Attempts were made, therefore, to evaporate to dryness portions of a solution of the pure salt in water, in order to weigh the residue, which would be magnesium sulfate. The attempts were not altogether successful. It was found that the temperature during drying must be raised gradually and must not exceed a definite relatively low temperature of about 200° C. If the heating is done too rapidly or the temperature raised too high, the outside of the mass will begin to decompose while the inside will be in the hydrated form. Directions in some of the quantitative textbooks include heating of the salt to a dull red before weighing. This was done but it would not regularly bring the residue to a constant weight. Allowing the top of the bunsen flame to almost touch the bottom of the dish gave better but not reliable results. Heating in a small hot-air oven, about 220° C, also proved unsatisfactory, because it took too long to bring the residue to a constant weight and because the results were sometimes too low before a constant weight was obtained.

The pyrophosphate method was then adopted, which consists in precipitating the magnesium as  $\text{MgNH}_4\text{PO}_4$  with microcosmic salt ( $\text{NaNH}_4\text{HPO}_4$ ) in an ammonical solution and igniting the precipitate to magnesium pyrophosphate. Two procedures were used: the first, after Mellor (76), with two precipitations in the cold; the second, after Schmitz (101), with two precipitations from a hot solution. Preliminary determinations gave slightly higher results with the first procedure than with the second. (Table II.) In the absence of direct evidence as to which results were more nearly correct, the second procedure was preferred because it theoretically involved a smaller probable error.

The procedure finally adopted was to precipitate twice in the hot, the second time adding only a few drops of the phosphate solution and an excess of ammonia. The precipitate was filtered through a Gooch crucible and washed with ammonia water in order to decrease the solubility of magnesium ammonium phosphate; for, according to Mellor, the solubility of  $\text{MgNH}_4\text{PO}_4$  as grams of magnesium per 100 cc, is 0.0115 in pure water (10° C), 0.000031 in 1%  $\text{NH}_3$ , 0.000014 in 2%  $\text{NH}_3$ , and 0.000005 in 3%  $\text{NH}_3$ . Although there may be some slight solubility due to the presence of ammonium salts, this error should be small where only a few drops of hydrochloric acid are used for redissolving the precipitate.

In order to determine how much magnesium was left in solution after precipitation, two methods were tried: (1) determination of the precipitated magnesium to give a basis for calculation of the amount left in solution; (2) direct determination of the amount left in solution by evaporation of a large volume of filtrate.

The first method presented some difficulties. The magnesium hydroxide is hard to filter on account of its gelatinous nature and consequently hard to wash. This difficulty is augmented by the fact that it absorbs large amounts of salts. Although it was found that washing would remove most of the sodium salts, the time required to filter such a gelatinous precipitate was prohibitive, for such long exposure to the air would introduce considerable amounts of carbon dioxide.

It was, therefore, decided to decant two 2-liter samples from a large pyrex bottle, evaporate to a small volume, and precipitate the magnesium with phosphate solution by the method outlined above. The solutions were allowed to stand protected from the atmosphere until they exhibited no Tyndall cone effect. This required about three weeks.

### (c) The Determination of Hydroxyl-ion Concentration.

The hydroxyl-ion concentration was determined from the expression:  $C[OH^-] = \frac{K_w}{C[H^+]}$ . The constant  $K_w$  has been determined by numerous investigators, most recently by Lewis, Brighton and Sebastian (64). For the sake of simplifying calculations, the value  $1 \times 10^{-14}$  was used. The hydrogen-ion concentration was determined electrometrically with the same setup\* as was used by Greenfield and Buswell (40), namely: a small lead-plate storage battery, a Leeds & Northrup type K potentiometer, a Leeds & Northrup No. 2500-e galvanometer, and saturated calomel half-cells (References 31 and 32).

The following formula was used to calculate the negative logarithm of the hydrogen-ion concentration:

$$pH = \frac{E. M. F. + E_{BAR} - E_{CAL}}{0.00019837 T}$$

E. M. F. = observed over-all voltage.

EBAR = correction for barometric pressure.

ECAL = voltage of saturated calomel electrode.

referred to the normal hydrogen electrode as zero.

T = absolute temperature.

## RESULTS.

Experimental data on the solubility of magnesium hydroxide are given in Table III. Column D shows the amounts of pyrophosphate actually in solution after the precipitation of the magnesium as the hydroxide. In order to compare these with the amounts that would be present if the previously accepted solubility product ( $1.2 \times 10^{-11}$ ) were correct, values were calculated as shown in Column E. Column F shows amounts of magnesium determined from values in Column D.

\* Editor's Note:—For fuller description of apparatus, chemicals, and calculations, see above pp. 18-23.

The values of the solubility product, as given in Column G, show an average of  $.5217 \times 10^{-11}$ . The variations from this average are given in Column H, together with, the summation of these variations ( $E_v = 4.9688 \times 10^{-11}$ ). To get the correction to be applied to this average, this summation was used in Bessel's formula (77) :

$$E = \pm 0.6745 \times \sqrt{\frac{E_v^2}{n(n-1)}}$$

giving  $E = \pm 0.1715 \times 10^{-11}$

The probable percentage of error is then about 33. The solubility product is thus calculated to be  $(0.52 \pm 0.17) \times 10^{-11}$ .

The average solubility of magnesium hydroxide would then be  $1.09 \times 10^{-4}$  moles per liter, or .00064 grams per 100 cc.

This value, which is slightly lower than any previously reported, is believed to be more nearly correct because errors due to the presence of carbon dioxide in former determinations have been eliminated. If any further corrections should be made, they would probably be very slight. It is believed that, within the range of temperatures (25-30° C.) under which this work was done, the variations in solubility of  $Mg(OH)_2$  are negligible. Loven (69) and Herz and Muhs (46) have calculated that the solubility should be the same at all temperatures, and there is no accepted experimental data to indicate variations. If there were any variations, they would (by hydrolysis) slightly affect the hydrogen-ion concentration, and for all changes in it due to changes of temperature allowance was made in the calculation of pH values.

#### RESIDUAL ALUM IN AN EXPERIMENTAL FILTER PLANT.

##### (a) Historical Items.

In previous work in this laboratory (40,27), references were made to a number of papers on the precipitation of aluminum as the hydroxide.\* The growing recognition of the importance of a more thorough study of this phase of water purification is shown by the appearance of additional papers in rapid succession.

Catlett (14) reported pH 6.5 to be the optimum for floc formation in a low-color, high-turbidity water and pH 5.7 to 6.5 in a high-color, low-turbidity water. Some highly colored waters may show an optimum as low as pH 4.5. Gammage (33) reported that color was removed better by low alkalinity and high  $CO_2$  than simply by the required alkalinity. Almost in direct opposition to this, Pirnie (89) found that aeration after the addition of chemicals gave a better floc, ascribing these results to the lowering of the acidity by removal of  $CO_2$ . Longley (68), also, had contended that the alkalinity must be low for best coagulation.‡

Daniels (22), working with aluminum sulfate and sodium carbonate, reported maximum flocculation from pH 6.0 to 7.0 and total re-solution at pH

\* Editor's Note:—See above, pp. 30-32 and 52-53.

‡ Editor's Note:—In a recent paper Mortensen (83) has confirmed Longley's findings; in the Cedar Rapids plant an optimum for a highly colored water, was found at pH 5.6 and for a slightly colored water at pH 6.5.



head on the pump as the level on the storage tank was lowered, a barrel "C" was placed in the line, with a float valve on the inlet to maintain a constant level.

The addition of chemicals was accomplished by diverting part of the water as it issued from pump No. 2 to the mixing tank where chemicals such as acid and alum were added in definite amounts. From the mixing tank, the treated water was again sucked into the pump together with the raw water from "A". Taking into account that the pump was 30 gallons per minute capacity and that a constant head was maintained on the filter, the capacity of which was 6 gallons per minute, water was thus re-circulated five times through the pump and mixing tank. Efficient mixing of the water and chemicals was thereby insured.

The coagulation tank was of 2600 gallons capacity and was provided with three baffles to give a detention period of over seven hours. This detention is based on a six gallon per minute capacity for the system. A float valve on the inlet to the tank insured a constant head on the filter, since direct connection was maintained.

The filter was of galvanized iron, two feet in diameter and eight feet in height, with one foot of gravel and two and one-half feet of sand above the strainer. Thus, with a cross-section of 3.1416 sq. ft, and a capacity of 6 gallons per minute, the filter very closely approached the usual rate of filtration in standard plants, that is, 2 gallons per minute per square foot. A funnel six inches in diameter was used for a wash water trough.

A constant level was maintained in the orifice box "G" by means of a float valve, and the orifice was calibrated to give the required flow of 6 gallons per minute.

A wash water tank "E" of 625 gallons capacity was installed above the filter so as to supply city water at sufficient head to back-wash the filter at the usual rate of 2 cu. ft. per minute per square foot, or 24-inch vertical rise per minute.

### **(c) Methods of Analysis.**

Determinations of alkalinity, carbon dioxide, color, and turbidity were made according to methods given in Standard Methods of Water Analysis (110). For determining alumina, two-liter samples of water were evaporated to dryness in platinum dishes. To remove the turbidity the raw water was filtered through No. 50 Whatman paper. A sample of this paper showed no aluminum on analysis. Palau dishes were tried for evaporations, but the nitrates (8.9 ppm.) and nitrites (4.1 ppm.) in the water were found to attack this alloy. Attempts to reduce the nitrates with hydrogen sulfide in an acid solution were not successful.

The silica was removed according to Standard Methods. In order to prevent the loss of any alumina, the non-volatile residue after the treatment of the silica with hydrofluoric and sulfuric acid was fused with potassium bisulfate. The fusion was taken up with water and added to the filtrate from the silica separation.

The aluminum was precipitated as the hydroxide with ammonia water according to the method of Blum (12), filtered, reprecipitated, ignited, and weighed.

Iron was determined colorimetrically according to Standard Methods. Phosphorus, which comes down with the aluminum precipitate, was determined by the colorimetric method of Deniges. (24).

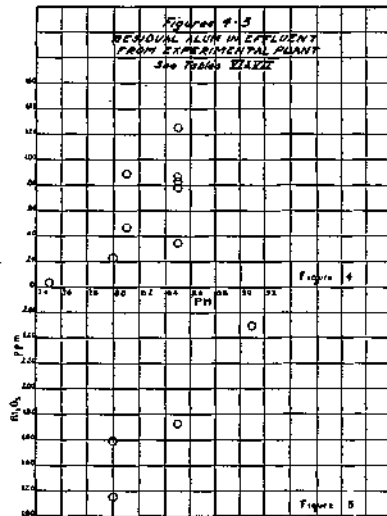
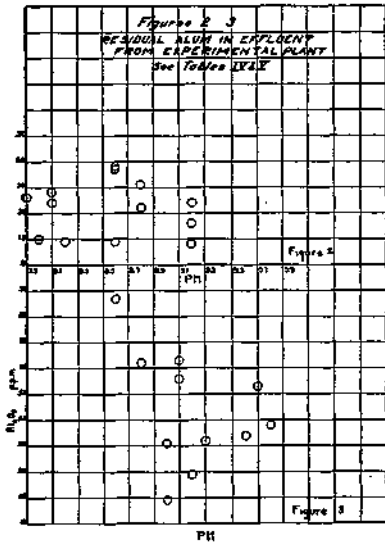
The actual  $Al_2O_3$  present was calculated from the relation:

$$Al_2O_3 = R_2O_3 - Fe_2O_3 - P_2O_5$$

The pH was determined colorimetrically by indicators and Clark's (18) buffers.

The calcium and magnesium were determined by precipitation. A 200 cc. sample was treated with ammonium oxalate in an ammonical solution; after filtering, the residue was ignited and weighed as  $CaO$ . The magnesium was precipitated in the filtrate with microcosmic salt, filtered in a Gooch crucible, ignited, and weighed as the pyrophosphate. This method is similar to that given in Standard Methods with the omission of steps in the purification of the precipitate and with reduction of volume of sample. It is more rapid but, of course, less accurate than the standard method, the accuracy depending on the concentration of the solution. In this case the error is probably within one per cent.

It was found that the sand used in the filters contained considerable limestone which reacted with the water at higher hydrogen-ion concentrations, so that the water going through the filter did not have a constant pH value. This made it impossible to get results on the acid side without radical modification of the plant.\*



\* Editor's Note :—See below, pp. 121-127.



**(d) Results of Experiments on Residual Alum.**

The results of runs on the alkaline side are given in Tables IV, V, VI and VII, and plotted in Figures 2, 3, 4, and 5. These results show that, other things being equal, the solubility of aluminum hydroxide increases with increasing hydroxyl-ion concentration from pH 7.9 to 9.8.

In Table IV, which gives data obtained with water of a low turbidity, the increase in solubility with increase in hydroxyl-ion concentration is slight. However, this increase is greater with higher turbidity, slightly greater in Table V and markedly greater in Table VI.

It will be noticed that in some cases where the points representing residual alumina fall out of line, as Nos. 12 and 13 in Table IV, and Nos. 10 and 11 in Table V, the amount of alumina in the raw water is correspondingly high. In cases where the turbidity is extremely high, as in Table VII, there is shown an extraordinary increase in the residual alumina until at pH 9.1 it is as much as 2.50 ppm.

As was shown by Edwards and Buswell (27)\*\*, the alumina content of the raw water may equal or exceed that of the filtered water. Whatever the nature of the aluminum compounds in the raw water, they will be partly removed during coagulation and filtration, either by precipitation if they are colloidal, or by absorption if they are in true solution. If traces of them are left in the water, they are included in the amounts of residual alumina as determined by gravimetric methods. The residual alumina in each case should be compared, therefore, with the alumina content of the raw water.

In this investigation, the raw water showed a wide range of alumina content, 'due to conditions peculiar to the drainage basin of the Boneyard stream. At times, for example, it carried sludge from a water-softening plant at the university power-house or clay from the Ceramics Building. These unnatural conditions, in addition to changes due to variations in rainfall, made it possible to get data over a range not usually obtainable at one plant.

For work of this kind, gravimetric methods must be taken as the ultimate standard. The hematoxylin test is hardly adequate; for, as ordinarily carried out, it is not necessarily specific. There is a chance for error even under the carefully controlled conditions used by Hatfield (44). Where the aluminum *ion* is the thing to be determined, hematoxylin may be adequate; otherwise, gravimetric methods are to be preferred.

If the point at issue were the amount of actual aluminum hydroxide in solution, instead of the total aluminum content of the water, both the results

---

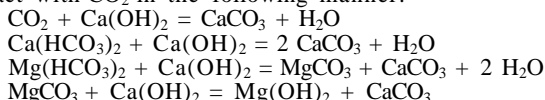
\*\* Editor's Note :—See above, pp. 56-58.

by gravimetric methods and the results by the hemotoxylin test should probably be slightly discounted. The consistently higher results obtained gravimetrically may be accounted for on the basis that the  $Al_2O_3$  determined may not all have been present as  $Al(OH)_3$ ; for the presence of silico-aluminates and other complex aluminum compounds, especially if in colloidal form, would not be indicated by hematoxylin. Every precaution has been taken, however, to remove the silica in the work here reported.

The effect of filtration on the phosphorus content of the water is quite noticeable. Phosphorous is usually present in the raw water but is removed in most cases during filtration.

To follow the change in calcium and magnesium content during treatment with alum and lime, a few determinations were made of these substances, with results as shown in Table VIII. Column  $A_1$  shows the actual decrease (or increase) in alkalinity. Column  $A_2$  shows what the increase in alkalinity would be if there were no precipitation of calcium and magnesium. Column  $A_3$  is figured with consideration for the amount of lime required to precipitate the calcium and magnesium. The calcium and magnesium are expressed as calcium carbonate.

In calculating the decrease of alkalinity due to reaction with alum when lime is used, the practice has been to consider that lime tends to offset decrease in alkalinity. The contrary, however, may be true, since lime will precipitate calcium and magnesium from the bicarbonates of these metals, and also react with  $CO_2$  in the following manner:



Twice as much lime is required to remove the same amount of  $Mg(HCO_3)_2$  alkalinity as is required for  $Ca(HCO_3)_2$  alkalinity. The following method of calculation takes this point into account.

Let  $CaCO_2$  = lime required for  $CO_2$

(This will not be included if there is free  $CO_2$  in the effluent.)

$Ca_1$  = calcium in the raw water

$Ca_2$  = calcium in the effluent

$CaL$  = calcium added as lime

$Mg_1$  = magnesium in the raw water

$Mg_2$  = magnesium in the effluent

$CaCO_2 + 2(Mg_1 - Mg_2)$  = the lime used up in ways not affecting the calcium of the water.

$Ca_1 + CaL - [CaCO_2 + 2(Mg_1 - Mg_2)] - Ca_2$  = amount of calcium precipitated.

Decrease in alkalinity would be

$$A_3 = (Ca_1 - Ca_2) + (Mg_1 - Mg_2) + (\text{alum})$$

assuming .8 ppm. is the alkalinity reduction due to one grain per gallon of alum. This will not affect the total calcium content of the water.

It will be seen from Table VIII that, if the precipitation of calcium and magnesium is taken into account, the actual reduction in alkalinity approximates the theoretical more closely. Discrepancies that still exist may be due to a certain amount of absorption of the different ions, which will throw off the results.

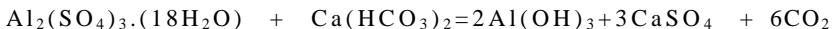
There is, of course, some chance for error in determining the amount of alumina by subtracting the amount of  $\text{Fe}_2\text{O}_3$  and  $\text{P}_2\text{O}_5$  from the total  $\text{R}_2\text{O}_3$  precipitate. The total amount of  $\text{R}_2\text{O}_3$  seldom exceeded one milligram per liter. The relative amounts of  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  (and in the raw water  $\text{P}_2\text{O}_5$ ) were about the same, so that an error in either the  $\text{Fe}_2\text{O}_3$  or the  $\text{P}_2\text{O}_5$  means an error in the  $\text{Al}_2\text{O}_3$  determination. The method of Deniges for the determination of  $\text{P}_2\text{O}_5$  has never been seriously questioned; although it showed a tendency for the color to fade rapidly, it gave check results in this work. Similarly, the  $\text{Fe}_2\text{O}_3$  values are believed to be fairly accurate. All care was taken to insure the reliability of the figures in these crucial determinations. A large number of runs were made in order to determine as accurately as possible the solubility of alumina at a given hydrogen-ion concentration.

There is a possibility of very slight turbidities not visible to the unaided eye. Effluents frequently have a slight Tyndall cone effect, and in a spectrophotometer some waters show that slight turbidity is present although there is not enough to report in the usual analysis.

### COMPOSITION OF THE ALUM FLOC.

#### (a) Historical Items.

Filter plant operators have reported from time to time that the actual decrease in alkalinity does not check the decrease that would be expected from the alum dosage used. The theoretical decrease is ordinarily calculated by the formula:



Edwards and Buswell (27) found many such cases in filter plants in Illinois and presented possible reasons for this discrepancy.\* The only reason common to all plants would be the precipitation of basic aluminum sulfate. If any basic aluminum sulfate is formed, it should be present in the precipitate at the bottom of the coagulating basins. (Formation of what has been called colloidal "aluminum hydroxide" instead of the precipitate would tend to counteract the decrease in alkalinity.)

Some characteristics of the precipitate thrown down by sodium hydroxide have been described by Miller (78). He found under experimental conditions that at pH values below 5.5 the formula  $5(\text{Al}_2\text{O}_3) \cdot 3\text{SO}_3$  is approximated, and that above pH 5.5 the ratio of aluminum to sulfate increases along a definite curve with decreasing hydrogen-ion concentration and becomes infinity at pH 8.9. Grobet (42), on adding a sodium hydroxide solution to a concentrated alum or aluminum sulfate solution, reported that a basic salt  $\text{Al}_2(\text{SO}_4)_3 \cdot 2\text{Al}(\text{OH})_3$  was formed. Similarly, when 2 or 4 moles of NaOH were added to 1 mole of potassium alum  $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ , Williamson (126) obtained a basic salt  $(\text{Al}_2\text{O}_3)_5 (\text{SO}_3)_3 \cdot 15\text{H}_2\text{O}$ .

With the exception of Miller's, these investigations were made in rather concentrated solutions. All used sodium or potassium hydroxides as precipitants because of their great solubility in water. Miller and Williamson used

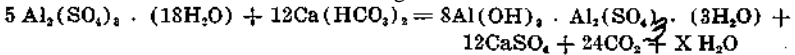
---

\* Editor's Note :—See above, pp. 56ff.

pure potassium alum and sodium hydroxide. This is hardly the same condition as in filter-plant operation, for the potassium alum introduces a higher content of sulfate into solution compared to the aluminum. Also, calcium bases instead of sodium bases usually enter into the reaction in actual practice.

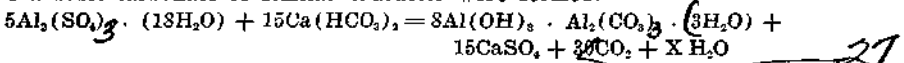
It seemed advisable, therefore, to carry out some experiments following a procedure suggested by Miller but using normal aluminum sulfate instead of potassium alum, and calcium hydroxide and calcium bicarbonate instead of sodium hydroxide.

Another method of attack may be used on this problem. Suppose a basic aluminum sulfate were formed according to Williamson's formula:



Then the theoretical decrease in alkalinity would be ~~8~~ 6.2 ppm.

If a basic carbonate of similar character were formed:



the theoretical decrease in alkalinity would then be 7.7 ppm. This is nearly equal to the theoretical decrease in alkalinity when aluminum hydroxide is assumed to be the only product formed. 27

The fact that the actual decrease in alkalinity is usually more than theoretical furnishes further evidence that a basic aluminum sulfate is not formed, although some basic aluminum carbonate may be formed under ordinary operating conditions, that is, from pH 5.5 to 7. Even in waters of a higher hydrogen-ion concentration it is not probable that basic aluminum sulfate is formed, because such waters show an actual decrease in alkalinity greater than the theoretical, and this is opposite to the condition which would exist if basic aluminum sulfate were formed.

The final test, of course, is the presence of basic aluminum sulfate in filter plant flocs, especially if it be in the same ratio as in the precipitate from the more concentrated solutions which have been used in most laboratory determinations up to the present time. An average dose of one grain per gallon makes a concentration .0000505 molar with respect to aluminum. The use of this concentration in the laboratory necessitates very large volumes of solution in order to yield sufficient precipitates for analysis.

On account of these difficulties, the problem was approached from another angle; samples of sludge were collected from the bottom of coagulating basins at several filtration plants, and were analyzed for sulfate.

**(b) Experimental Methods.**

For the experiments on the decrease of alkalinity, with a view to the analysis of the floc, a good grade of Mallincrodt's aluminum sulfate was selected which had the following composition:

Aluminum sulfate,	$\text{Al}_2(\text{SO}_4)_3$ .....	53.81%
Aluminum oxide,	$\text{Al}_2\text{O}_3$ .....	1.16%
Water, $\text{H}_2\text{O}$ , by difference. . . . .		45.03%

The lime water was prepared from a good grade of marble lime containing the following impurities:

Volatile substances	7.50%
Chlorides	0.01%
Silica	0.10%
Sulfates (SO <sub>4</sub> )	0.21%
Alumina	0.35%

The calcium bicarbonate solution was prepared by bubbling CO<sub>2</sub> into water in the presence of pure calcite.

The procedure consisted, first, in weighing out 3.03 grams of the aluminum sulfate into 3 liter beakers. The salt was dissolved in one liter of distilled water, the solution was then violently agitated by a motor-driven stirrer while saturated lime solution together with enough distilled water was added to make the final volume two liters. At the end of thirty minutes the stirrer was removed, and the precipitate allowed to settle. The clear liquid was decanted after determining the pH colorimetrically. The sludge at the bottom was filtered off, washed several times with distilled water, scraped from the paper, and dried at 110° C. Each sample was then analyzed for aluminum and sulfate ion.

The sludge from the various filter plants was washed with distilled water three times by decantation, then collected on No. 50 Whatman paper, and washed again with four portions of distilled water. It was dried, first, on the steam bath, and then for three hours in an air oven at 110° C.

After cooling, two portions, one for sulfates and one for aluminum, iron, calcium, and magnesium, were weighed out from a glass-stoppered bottle. Each portion was boiled in 15% HCl solution for fifteen minutes, filtered thru a Gooch crucible, and washed with distilled water. The crucible with its contents was dried for six hours at 110° C, and weighed and the percentage of insoluble material was calculated.

The filtrate was twice evaporated to dryness in a platinum dish, with the addition of acid each time, and was filtered through paper. The procedure from this point was the same as given in Standard Methods.

Carbon dioxide was determined gravimetrically by absorbing in KOH, according to the method given by Olsen (86). The gas was released by treating the sludge with H<sub>2</sub>SO<sub>4</sub>, warming slightly at first, and finally boiling for several minutes. The liberated gas was passed first through an air condenser, where most of the water was removed, and then thru calcium chloride. It was swept out at the finish with a current of CO<sub>2</sub>-free air.

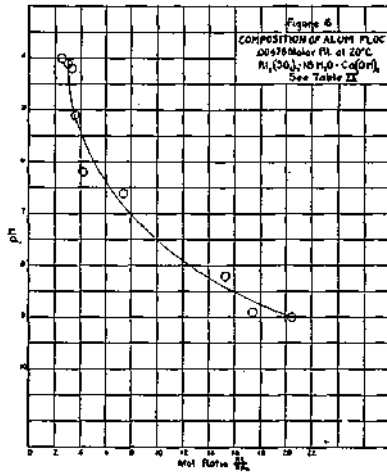
### (c) Results.

The results of analyses of floc produced with aluminum sulfate and calcium hydroxide are given in Table IX, and the data plotted in Figure

Al

6. The molar ratio  $\frac{\text{Al}}{\text{SO}_4}$  increases with increasing hydroxyl-ion concen-

tration. The curve obtained is practically the same as the one obtained by Miller (78), who used a potassium alum solution and sodium hydroxide as his precipitating agent. A definite formula cannot be assigned to the compound formed, because the nature of the curve indicates that the precipitate obtained is variable in composition. However,



as Miller states, below pH 5.5, the formula  $5(Al_2O_3) \cdot 3 SO_4$  is approximated.

The results of a series using calcium bicarbonate are given in Table X. Here on account of the comparatively low solubility of the bicarbonate the final volume of the solution had to be increased to four liters. The difference in quality of the two precipitates is remarkable. Calcium hydroxide threw down a very flocculent precipitate, similar to that formed when sodium hydroxide is used; and this precipitate settled readily, leaving a clear solution. Calcium bicarbonate, on the other hand, formed with alum a finely divided, rather chalky precipitate which settled very slowly. This may indicate that the precipitates have different chemical compositions.

The results of analyses of floc from filter plants, as given in Table XI, bring out several points of interest. First is the high content of iron. Evidently, the iron present in the raw water is precipitated to a great extent during the purification process. This upholds the suggestion made above, that decrease in alkalinity more than theoretical may be due to the precipitation of colloidal iron. The second fact of interest is the lack of appreciable amounts of sulfate. At pH 7.4 the molar

ratio of  $\frac{Al}{SO_4}$  is 9 (see Fig. 6). Neglecting the possibility of a basic sulfate of iron, the amount of sulfate required to combine with the aluminum present in order to form basic aluminum sulfate has been calculated and is given at the foot of each column of Table XI. This is seen to vary from 1.59% to 2.33%. The presence of so large an amount of sulfate could not escape detection.

When the wet sludge was treated directly with HCl there was an evolution of gas, probably carbon dioxide. This may help to account for the 6 to 12 per cent not determined by analysis. Part, of course, is water combined with alumina and iron, part is organic material, and part is probably chlorides. The carbon dioxide content of the dry sludge is rather low, but it is certain that during the drying process some of the carbon dioxide is lost. The analysis of the wet sludge would possibly give a better knowledge of the true compounds precipitated.

Some of the dried material was fused with  $\text{Na}_2\text{CO}_3$ , taken up with water, and tested for sulfates. There were no sulfates present.

There is not enough carbon dioxide to combine with the calcium and magnesium. However, in such a complex mixture the calcium and magnesium may not be present as the carbonates but as the silicates or chlorides.

A complete study of this problem would include an analysis of the raw water as well as the sludge. Only in this way would data be available as to what compounds were introduced by the raw water and what compounds are formed during the purification process.

## EFFECT OF TEMPERATURE IN WWATER SOFTENING.

### (a) Historical Items.

The use of heat as an aid in the lime-soda process of softening a hard water has been adopted to some extent. It is well known that heating the water before softening increases the rate of reaction and shortens the time required for settling. There has been, however, little data published on the subject of the actual effect of temperature on softening.

In 1911, Greth (41) stated that every natural water presented a separate problem, both in rate of reaction and in variation of the amount of chemical used from that required theoretically; that solubilities of salts are greatly affected by one another; that soft waters have a slower reaction rate than hard waters; and that laboratory reactions are often slower than plant reactions.

In 1914, Petit (87) published a paper giving the reactions of some salts in boiling water. His conclusions were: (1)  $\text{Ca}(\text{HCO}_3)_2$  precipitates to a concentration of 0.17 mg CaO or 0.33 mg  $\text{CaCO}_3$  per liter. Precipitation is not affected by mode of heating or condition of walls. (2)  $\text{Mg}(\text{HCO}_3)_2$ , on the other hand, is greatly affected by mode of heating, walls, etc. (3) When both bicarbonates are present, precipitation of calcium is increased; if little magnesium and much calcium is present, magnesium is precipitated as if it were present alone. (4) Sodium chloride decreases directly the precipitation of calcium. (5) Small amounts of NaCl increase the precipitation of magnesium about 10 per cent. This effect becomes less as NaCl increases, and for small amounts of magnesium the precipitation is less than if no NaCl were present. (6) Magnesium sulfate decreases directly the precipitation of calcium bicarbonate. (7) In a mixture of  $\text{CaSO}_4$  and  $\text{Mg}(\text{HCO}_3)_2$ , precipitation of calcium is greater if magnesium is in excess. Magnesium is precipitated in increasing proportions as the initial concentration of calcium is increased, but even a large excess of  $\text{CaSO}_4$  does not precipitate all the magnesium.

In 1917, Wood (130) found that softening with lime alone requires 90 minutes; that the addition of soda reduced the time to 60 minutes; that excess lime reduced the time of softening with lime and soda to 40 minutes; and that raising the temperature 15-20° C. reduced the time of reaction about one-third. According to Gibson (34) reduction in hardness with a 10-minute treatment at 210° F. equals that with a 24-hour treatment at 50° F. The rate of flow can, therefore, be increased greatly at higher temperatures.

The Müller hot-process system has been described by Preu (90). It consists of adding  $\text{Na}_2\text{CO}_3$  to take care of the non-carbonate hardness and heating in the boiler with frequent blow-offs. This method also removes objectionable gases, but it has met with some opposition because there is scale formation in the boiler.

Gleeson and Gleeson (35) made a study of the lime-soda process varying the dosage of chemicals, but they neglected waters containing magnesium compounds. Magnesium-bearing waters had been considered by Bartow and Lindgren (5) in their study of softening Illinois waters. They suggested for some cases a partial treatment that would give a maximum of softening with minimum cost.

In 1923, Hoover (50) reported on the effect of temperature, time, mass action, and addition of alum in water-softening. He believed it necessary to get the floc in crystalline form in order to have it settle easily. High temperatures favor crystalline precipitates, while low temperatures tend to form colloidal precipitates. In tanks in which alum was used, he found that the hardness was more easily reduced than in those in which it was not used. In fact, a softer water with less cost for chemicals was obtained by the use of alum.

Bartow, Flentje, and Gallaher (in a paper read before the American Chemical Society at Birmingham, Alabama, April, 1923) gave laboratory results on the effect of temperature on the rate of reaction, but they did not consider reduction of hardness. Their conclusions were: (1) The rate of reaction in water-softening by the lime-soda ash method increases with increasing amount of lime added, provided sufficient sodium carbonate is added to neutralize the non-carbonate hardness. (2) The rate of reaction increases greatly with rise in temperature, the greatest increase in rapidity occurring probably in the first 18-20° C. rise above normal temperature. (3) The completion of the reaction increases with a rise in temperature, confirming the results of other investigators. (4) With increasing temperature, a small decrease in the lime necessary was shown. (5) Without the addition of chemicals, the bicarbonates of magnesium and calcium do not decompose materially below 65° C.

### **(b) Theoretical Considerations.**

The theoretical relationships between the speed of any reaction and the temperature have been reduced to a formula by Van't Hoff (116) and his collaborators; but, because of the complex system involved, the formula does not serve as a means of predicting the effect of temperature on the series of reactions taking place in water-softening. In general, reaction rate is multiplied 2-4 fold for each rise of 10° C. The exact value of the multiplying factor varies with the nature of the re-



action, approaching unity for very fast reactions and increasing rapidly as the velocity itself decreases. In water-softening, the speed is rather fast, especially on the first addition of chemicals. For this first period, at least, the reaction rate is probably increased somewhat by a slight rise in temperature, but not enough to be detected by simple tests. A second period is very noticeable at low temperatures, where the reaction is slow and takes an indefinite time for completion.

Proper mixing of chemicals with the raw water will do much toward shortening the time of reaction. If the sludge from previous treatments is agitated with the fresh water, the reaction rate is increased.

According to Von Weimarn's theory [see Taylor (111)], there are two rates in the separation of a crystalline solid from a solution. These are: (1) the initial velocity of the condensation, and (2) the velocity of the growth of crystals. The concentration of the salts remaining in a properly softened water is practically constant at any given temperature. In practice this concentration is seldom below 50 ppm. at normal temperatures. The only variable factor affecting the velocity of the first stage is, therefore, the total amount of solute. For a water of low hardness the velocity of the initial condensation will be slower than for a water of high hardness. In actual practice, also, it is found that longer time is required to soften a slightly hard water than a very hard water.

When the sludge from previous treatments is mixed with the raw water, this theory is not applicable. Rise in temperature lowers the solubility of the mineral salts, so that the speed of the initial condensation is increased according to the Noyes-Nernst formula (77). Moreover, even at constant temperature, the velocity of the growth of crystals is affected by several variable factors. The concentration of the dissolved calcium and magnesium salts in the raw water affects the speed of initial condensation. Increasing the temperature also increases the velocity of crystallization.

The effect of the physical properties of the precipitate and the solution of the rate of settling is well brought out by Stokes' formula [see Lewis (65)], which shows that the rate of settling is directly proportional to the difference in density of the liquid and the solid, and inversely proportional to the viscosity of the liquid. A rise in temperature affects the factors that determine the velocity of fall of a precipitated particle. For example, agglomeration of the molecules makes the particles formed in a hot solution larger than those formed in a cold solution, thus increasing the velocity of fall very greatly. A rise in temperature also decreases the viscosity and density of the liquid.

### **(c) Operation of the Water-Softening Plant.**

At the plant of the Illinois Power and Light Corporation, Danville, Illinois, where these observations were carried out, raw water from the Vermilion River is first pumped to the power house and used in large quantities to condense the steam from turbines. It is then run back and down to a sump which continuously overflows into the river. The temperature of the water is raised a few degrees in this use.

From the sump, the water is lifted by a centrifugal pump to the softening plant. If it is to be treated cold, it goes directly to the tanks; if it is to be pre-heated, it passes up and through a tube heater built on the same principle as a surface condenser. Steam is supplied to the heater from the central power plant. The river water is thus not diluted in the heating process.

After passing through the heater, the water goes to one of three wooden tanks, each tank being about 25½ ft. in diameter and 19 ft. deep and having an over-all capacity of approximately 74,000 gallons. As the tanks are never completely filled, nor completely drained between runs, the available capacity of each is reduced to approximately 66,700 gallons.

The tanks are filled through a pipe which enters at the bottom, and are emptied by a pipe which is mounted on a swivel joint at one side of the bottom and supported by a float adjusted to permit only the clear top water to flow out. Samples of the effluent are taken from a tube tapped into the side of the discharge pipe. Compressed air for agitation is furnished through a system of pipes at the bottom. A float-and-bell signal system indicates when the filling or draining has reached the desired point.

When a tank is over half full, the compressed air is turned on, so that the sludge previously deposited is thoroughly mixed with the fresh water. When the tank is almost filled, the solution of chemicals is pumped in. The air agitation is continued until the tank is full, which is about thirty minutes from the commencement of treatment.

The precipitate is allowed to settle for a period varying from four to eight hours depending upon the amount of water the plant is using. From the tanks, the water goes through rapid sand filters at rates varying with the amount of water used daily. It then flows by gravity to the power plant. The filters are back-washed daily by city water and agitated with air during washing.

A special soda is used in this plant, consisting of 45% NaOH and 55% Na<sub>2</sub>CO<sub>3</sub>, which decreases the amount of lime required.

#### **(d) Methods of Analysis.**

Determinations of alkalinity, free carbon dioxide, soap hardness and non-carbonate hardness were made according to Standard Methods. Calcium and magnesium were determined after the method outlined above (page 82). Some determinations of magnesium were attempted by a method sometimes used in rapid work, which consists of neutralizing the alkalinity, boiling off the free CO<sub>2</sub>, adding lime water, filtering, and titrating with 0.02 normal sulfuric acid. This method is based on the complete and exclusive precipitation of the magnesium, the amount present being shown by the difference between the titration of the sample and that of a blank; but it was found to give low results.

In the tables showing the results, the column headed "time from treatment" gives the number of hours and minutes from the commencement of treatment, although the treatment was not completed until approximately 20 minutes later. Filtration of a sample before ti-

tration is indicated by parentheses around the figures for that sample. Turbidity is designated as follows:

V. T. for a very turbid sample.

F. T. for a fairly turbid sample, about 20 by the silica standard.

S. T. for a slightly turbid sample, about 5 or less.

O. T. for a clear sample.

It was thought best to use this approximate method rather than the silica standards because the type of turbidity is hardly the same, the floc formed in the softening process is larger, and the time of complete clarification is the more important consideration.

As these experiments were made in the spring months when the ice was going from the river and snows and rains were frequent, the hardness of the supply varied widely. This made it difficult to adjust the dosage accurately. The usual dosage of the special soda was about 40-45 pounds, weighed to the nearest 5 pounds. A variation from theoretical could thus be expected to be about 6%, and any variation less than 6% was considered to be exact treatment.

The additions of lime and mixed soda were figured to lime and sodium carbonate for the purpose of getting all additions on the same basis. Since one pound of special soda contained 0.45 lb. NaOH and 0.55 lb.  $\text{Na}_2\text{CO}_3$ , it was equivalent to 1.14 lbs.  $\text{Na}_2\text{CO}_3$ .

**(e) Results.**

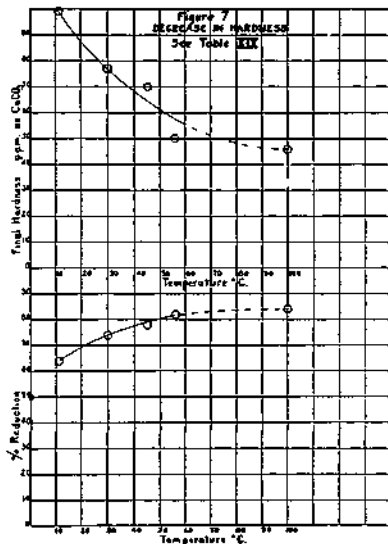
A complete summary of tests made is given in Tables XII-XVIII, which are grouped according to the nature of the treatment:

- A. Table XII. Exact treatment at different temperatures.
- B. Table XIII. Over-treatment lime ; exact treatment soda.
- C. Table XIV. Under-treatment lime; exact treatment soda.
- D. Table XV. Exact treatment lime ; over-treatment soda.
- E. Table XVI. Over-treatment lime; over-treatment soda.
- F. Table XVII. Under-treatment lime ; under-treatment soda.
- G. Table XVIII. Under-treatment lime; over-treatment soda.

Data selected from these results, in order to show more clearly the relations of temperature and alum-treatment to rate of settling, final hardness, and other effects, are shown in Tables XIX-XXII.

It is worth noting that the system of mixing is very thorough and that the chemical reactions are completed very quickly. Although at temperatures near 10° C. there is a slight decrease in alkalinity and in hardness after the first hour, most of the readings are so close to those of the first hour that they are almost within experimental error. Chem-

ical action, therefore, is practically complete within one hour from commencement of treatment, or within half an hour after completion of treatment.



The effect of temperature on the rate of settling, however, is very marked. Six or more hours are required for settling in cold tanks. Tanks in which the temperature of the water is raised 15-20° C. clarify much more rapidly and thoroughly. The convection currents, which are unavoidable in tanks operated on the intermittent system, prevent good settling, especially if the tanks are exposed to the atmosphere. During cold weather, as the top of the tank cools, the warm water rises from the bottom, forming an upward current that opposes the fall of the particles precipitated. Unfortunately, it is during the most severe weather, when settling is most retarded, that the detention period must be shortest. Some practicable method of housing the tanks would, of course, eliminate most of this difficulty.

The effect of temperature on the reduction of hardness is also very marked. Table XIX, of which the values given in group "A" are plotted in Figure 7, shows the hardness remaining at various temperatures. It appears that heating above 60° C to reduce hardness is hardly warranted, as the percentage of reduction (shown by the curve at the bottom of Figure 7), falls off rapidly above that point. The water at 58° C. was slightly under-treated with lime but still shows a marked reduction in hardness compared with water treated with the calculated

amount of chemicals at lower temperatures . The point at 100° C. was found by boiling a sample of the treated water in the laboratory.

The effect of adding alum is shown in Table XX, giving the analyses of two waters treated the same day with the same chemicals with the exception that one received a dose of alum. There is a marked decrease of hardness where alum is used. This is in accord with Hoover's work (50).

The analyses of some waters before and after passing through a sand filter are shown in Table XXI. It is apparent that the filter in this case does not remove hardness to any great extent unless the hardness is due to particles in suspension. The advantage of a filter, then, is for safety and not for any softening effect.

In order to test the time of reaction, two tanks were treated the same day with the same amount of chemicals and at nearly the same temperature. One was agitated with air for thirty minutes, and the other was agitated seventy-five minutes. The results, as shown in Table XXII, indicate that the reactions are complete at the end of thirty-minutes and that continued agitation does not help the reactions.

#### SUMMARY.

The solubility product of magnesium hydroxide has been determined, by the use of the hydrogen electrode, to be  $0.52 \times 10^{-11}$ .

The solubility of alumina in a sand-filtered water increases from pH 7.9 to pH 9.8.

When lime is used in connection with alum for coagulation, enough calcium carbonate or magnesium hydroxide precipitates to prevent the theoretical reduction in alkalinity.

Calcium hydroxide added to a solution .00476 molar with respect to aluminum forms floc of a composition similar to that thrown down by sodium hydroxide, and this floc contains a basic sulfate.

In actual filter-plant practice, floc formed at about pH 7.4 does not contain basic aluminum sulfate, but there is indication that a basic aluminum carbonate may be present.

Observations on the effect of temperature in a water-softening plant show:

- a. Chemical reactions between the calcium and magnesium salts and the softening reagents take place rapidly at all temperatures.
- b. Heating the water agglomerates the particles and decreases the time required for settling. While more than six hours is required below 10° C, less than three hours is required above 30° C.

c. With increase of temperature the final hardness of the softened water decreases along a definite curve which flattens out above 60° C.

d. The addition of alum favors the reduction of hardness, possibly due to the presence of colloidal calcium carbonate or magnesium hydroxide in the softened water.

e. Filtering alone does not decrease the hardness of a softened water but prevents suspended particles entering the boiler.

**TABLE I.**  
**PREVIOUSLY REPORTED VALUES FOR THE SOLUBILITY PRODUCT OF MAGNESIUM HYDROXIDE.**

Bibliog. Number	Temp. Investigator	° C.	Mg(OH) <sub>2</sub> grams per liter	Mg(OH) <sub>2</sub> Moles per liter	Solubility Product [Mg <sup>++</sup> ]X[OH <sup>-</sup> ] <sup>2</sup>
(69)	Loven	10	0.0204	3.5 X 10 <sup>-4</sup>	1.72x 10 <sup>-10</sup>
(46)	Herz&Muhs	29	0.0134	2.2 X 10 <sup>-4</sup>	4.87X 10 <sup>-11</sup>
(61)	Kohlrausch & Rose	18	0.009	1.5 X 10 <sup>-4</sup>	1.35X 10 <sup>-11</sup>
(25)	Duprê & Bialas	18	0.0084	1.44x10 <sup>-4</sup>	1.2 X 10 <sup>-11</sup>

**TABLE II.**  
**DETERMINATION OF MAGNESIUM BY DIFFERENT PROCEDURES.**

No.	Weighed as	Volume cc.	Weight found gms.	MgSO <sub>4</sub> per liter	Magnesium gms. per liter
By drying of salt					
1	MgSO <sub>4</sub>	25	0.0531	2.1240	0.4291
2	MgSO <sub>4</sub>	25	0.0540	2.1600	0.4363
3	MgSO <sub>4</sub>	25	0.0541	2.1640	0.4371
4	MgSO <sub>4</sub>	50	0.1066	2.1320	0.4307
5	MgSO <sub>4</sub>	50	0.1067	2.1340	0.4311
By Method of Mellor (76)					
6	Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	50	0.0988	2.1362	0.4315
7	Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	50	0.0980	2.1190	0.4281
8	Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	50	0.0982	2.1232	0.4289
By Method of Schmitz (101)					
9	Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	50	0.0977	2.1125	0.4267
10	Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	50	0.0978	2.1146	0.4272
11	Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	50	0.0977	2.1125'	0.4267

TABLE III.

SOLUBILITY PRODUCT OF MAGNESIUM HYDROXIDE.

(A)	(B)	(C)	(D)	(E)	(F)	(G)	(H)
No.	pH	AH—	Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> (determined)	Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> (calculated)	Magnesium determined	Solubility Product K = [Mg + ] X [OH] <sup>2</sup>	Variation from average
			gms. per liter	gms. per liter	moles per liter		
1	9.963	10 <sup>-4.037</sup>	0.03075	0.1585	0.00027613	0.233 X 10 <sup>-11</sup>	-.2887 X 10 <sup>-11</sup>
2	10.031	10 <sup>-3.666</sup>	0.0212	0.11585	0.00019037	0.220 X 10 <sup>-11</sup>	-.3017 X 10 <sup>-11</sup>
3	10.058	10 <sup>-3.042</sup>	0.01635	0.1023	0.00014082	0.192 X 10 <sup>-11</sup>	-.3297 X 10 <sup>-11</sup>
4	10.086	10 <sup>-3.914</sup>	0.0191	0.08993	0.00017152	0.255 X 10 <sup>-11</sup>	-.2667 X 10 <sup>-11</sup>
5	10.099	10 <sup>-3.901</sup>	0.03475	0.08471	0.00031205	0.492 X 10 <sup>-11</sup>	-.0297 X 10 <sup>-11</sup>
6	10.251	10 <sup>-3.749</sup>	0.0053	0.04200	0.00004759	0.151 X 10 <sup>-11</sup>	-.3707 X 10 <sup>-11</sup>
7	10.257	10 <sup>-3.743</sup>	0.02715	0.04092	0.00024381	0.796 X 10 <sup>-11</sup>	.2743 X 10 <sup>-11</sup>
8	10.302	10 <sup>-3.698</sup>	0.0208	0.03326	0.00018678	0.750 X 10 <sup>-11</sup>	.2283 X 10 <sup>-11</sup>
9	10.303	10 <sup>-3.697</sup>	0.01125	0.03311	0.00010102	0.408 X 10 <sup>-11</sup>	-.1137 X 10 <sup>-11</sup>
10	10.322	10 <sup>-3.678</sup>	0.01045	0.03033	0.00009384	0.413 X 10 <sup>-11</sup>	-.1087 X 10 <sup>-11</sup>
11	10.359	10 <sup>-3.641</sup>	0.01575	0.02558	0.00014143	0.739 X 10 <sup>-11</sup>	.2173 X 10 <sup>-11</sup>
12	10.370	10 <sup>-3.630</sup>	0.0225	0.02432	0.00020205	1.110 X 10 <sup>-11</sup>	.5883 X 10 <sup>-11</sup>
13	10.389	10 <sup>-3.611</sup>	0.0070	0.02228	0.00006286	0.377 X 10 <sup>-11</sup>	-.1447 X 10 <sup>-11</sup>
14	10.451	10 <sup>-3.549</sup>	0.01035	0.01675	0.00009294	0.742 X 10 <sup>-11</sup>	.2203 X 10 <sup>-11</sup>
15	10.453	10 <sup>-3.547</sup>	0.0053	0.01059	0.00004759	0.383 X 10 <sup>-11</sup>	-.1387 X 10 <sup>-11</sup>
16	10.470	10 <sup>-3.530</sup>	0.0021	0.01534	0.00001886	0.164 X 10 <sup>-11</sup>	-.3577 X 10 <sup>-11</sup>
17	10.486	10 <sup>-3.514</sup>	0.0058	0.01425	0.00005208	0.488 X 10 <sup>-11</sup>	-.0337 X 10 <sup>-11</sup>
18	10.571	10 <sup>-3.420</sup>	0.0046	0.009639	0.00004131	0.573 X 10 <sup>-11</sup>	.0513 X 10 <sup>-11</sup>
19	10.579	10 <sup>-3.421</sup>	0.00525	0.009288	0.00004714	0.678 X 10 <sup>-11</sup>	.1563 X 10 <sup>-11</sup>
20	10.690	10 <sup>-3.310</sup>	0.0059	0.005571	0.00005298	1.270 X 10 <sup>-11</sup>	.7483 X 10 <sup>-11</sup>

Average = 0.5217 X 10<sup>-11</sup> Ev = 4.9688 X 10<sup>-11</sup>

Note: E is used instead of sigma to designate the summation of variations from average.

**TABLE IV.**  
**RESIDUAL ALUM.**  
**pH 7.9—9.2.**

No.	Filtered Water.						(Other Data Expressed in p.p.m.)		Raw Water.							
	Fe <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	AlA	PH	CO <sub>2</sub>	Alkalinity Phenol.	M. O.	Turbidity	FeA	P <sub>2</sub> O <sub>5</sub>	AlA	PH	CO <sub>2</sub>	Alkalinity Phenol.	M. O.	
1	0.09	0.04	0.24	9.2	0	20	110	3	0.09	0.55	1.28	8.0	16	0	268	
2	0.10	0.00	0.08	9.2	0	20	124	2	0.10	0.46	0.00	8.0	17	0	306	
3	0.14	0.00	0.16	9.2	0	24	150	1	0.10	0.23	0.00	8.2	17	0	308	
4	0.14	0.00	0.31	8.8	0	10	166	2	0.10	0.46	0.00	8.0	17	0	306	
5	0.06	0.00	0.22	8.8	0	16	208	2	0.28	0.00	0.00	8.2	13	0	304	
6	0.19	0.00	0.09	8.6	0	12	184	1	0.13	0.00	0.10	8.2	13	0	298	
7	0.01	0.00	0.38	8.6	0	3	216	1	0.13	0.00	0.10	8.2	13	0	298	
8	0.13	0.23	0.37	8.6	0	16	228	2	0.28	0.00	0.00	8.2	13	0	304	
9	0.17	0.02	0.09	8.2	44	0	360	2	0.07	0.09	0.3	8.2	22	0	316	
10	0.10	0.00	0.28	8.1	22	0	302	1	0.09	0.23	0.06	8.3	13	0	316	
11	0.09	0.00	0.24	8.1	19	0	306	7	0.04	0.55	0.06	8.5	7	0	318	
12	0.11	0.23	0.10	8.0	31	0	304	2	0.11	0.32	0.40	8.3	26	0	316	
13	0.13	0.00	0.26	7.9	33	0	302	1	0.10	0.18	0.30	8.1	26	0	330	



TABLE V.  
RESIDUAL ALUM.  
pH 8.6—9.8.

No.	Filtered Water.						(Other Data Expressed In p.p.m.)							Raw Water.			
	Fe <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	Al <sub>2</sub> O <sub>3</sub>	pH	CO <sub>2</sub>	Alkalinity		Turbidity	Fe <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	Al <sub>2</sub> O <sub>3</sub>	pH	CO <sub>2</sub>	Alkalinity			
						Phenol.	M. O.							Phenol.	M. O.		
1	0.29	0.00	0.38	9.8	0	26	62	7	....	....	....	7.8	15	0	298		
2	0.29	0.00	0.53	9.7	0	28	72	15	....	....	....	7.6	10	0	282		
3	0.29	0.00	0.34	9.6	0	34	108	15	....	....	....	7.5	15	0	260		
4	0.40	0.00	0.32	9.3	0	48	162	2	0.10	0.07	0.18	7.6	24	0	330		
5	0.43	0.00	0.19	9.2	0	38	138	5	0.17	0.09	0.16	7.8	10	0	338		
6	0.60	0.00	0.63	9.1	0	50	212	30	0.40	0.08	0.35	7.7	14	0	346		
7	0.43	0.00	0.56	9.1	0	38	192	7	....	....	....	7.5	19	0	276		
8	0.64	0.00	0.14	9.0	0	36	208	20	0.28	0.04	0.32	7.8	13	0	332		
9	0.29	0.00	0.31	9.0	0	40	182	30	....	....	....	7.7	15	0	256		
10	0.28	0.00	0.62	8.8	0	38	262	5	0.43	0.05	0.94	7.8	14	0	336		
11	0.43	0.00	0.87	8.6	0	14	354	5	0.29	0.07	1.67	7.7	14	0	320		

69

TABLE VI.  
RESIDUAL ALUM.  
pH 7.5—8.5.

No.	Filtered Water.						(Other Data Expressed In p.p.m.)							Raw Water.			
	Fe <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	Al <sub>2</sub> O <sub>3</sub>	pH	CO <sub>2</sub>	Alkalinity		Turbidity	Fe <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	Al <sub>2</sub> O <sub>3</sub>	pH	CO <sub>2</sub>	Alkalinity			
						Phenol.	M. O.							Phenol.	M. O.		
1	0.36	0.00	0.35	8.5	6	0	260	15	....	....	....	7.7	14	0	288		
2	0.43	0.00	0.78	8.5	4	0	210	22	....	....	....	7.6	15	0	290		
3	0.31	0.00	0.87	8.5	0	14	232	30	....	....	....	7.5	17	0	244		
4	0.21	0.00	0.83	8.5	1	0	220	17	....	....	....	7.8	14	0	292		
5	0.14	0.00	1.25	8.5	2	0	228	4	....	....	....	7.5	15	0	294		
6	0.29	0.00	0.89	8.1	3	0	258	8	....	....	....	7.8	14	0	280		
7	0.29	0.00	0.47	8.1	7	0	260	9	....	....	....	7.6	16	0	276		
8	0.29	0.00	0.23	8.0	5	0	286	4	....	....	....	7.7	13	0	282		
9	0.24	0.00	0.03	7.5	20	0	268	18	....	....	....	7.8	18	0	282		

**TABLE VII.**  
**RESIDUAL ALUM.**  
**pH 8.0--9.1.**

**Raw Water High in Turbidity.**  
(Other Data in p.p.m.)

No.	Filtered Water.						Raw Water.							
	Fe <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	A <sub>1</sub> A	pH	CO <sub>2</sub>	Alkalinity Phenol. M. O.	Turbidity	FeA	PA	Al <sub>2</sub> O <sub>3</sub>	PH	CO <sub>2</sub>	Alkalinity Phenol. M. O.	
1	0.29	0.05	2.16	9.1	0	10 154	180	0.07	0.14	0.64	7.5	4	0 164	
2	0.14	0.05	1.54	8.5	0	4 192	55	0.07	0.14	0.07	7.6	6	0 218	
3	0.18	0.05	0.92	8.0	5	0 236	40	0.18	0.41	2.08	7.6	8	0 238	
4	0.14	0.11	1.34	8.0	3	0 246	30	0.14	0.37	0.98	7.7	5	0 242	

**TABLE VIII.**  
**THEORETICAL AND ACTUAL REDUCTION IN ALKALINITY.**  
**Experimental Filtration Plant.**

No.	pH value		Alkal. (MO)		Alkal (Ph'th)		Free CO <sub>2</sub>		Ca as CaCO <sub>3</sub>		Mg as CaCO <sub>3</sub>		Lime as Alum		A <sub>1</sub>	A <sub>2</sub>	A <sub>3</sub>
	Raw	Effl.	Raw	Effl.	Raw	Effl.	Raw	Effl.	Raw	Effl.	Raw	Effl.	CaCO <sub>3</sub>	gr. gal.			
1	7.6	8.0	238	236	0	0	8	5	267.1	279.6	184.5	181.8	23.9	1.0	2	—15.9	— 1.8
2	7.7	8.0	242	246	0	0	5	3	272.4	281.3	187.6	184.5	32.8	1.0	— 4	— 24.8	2.2
3	7.7	8.5	246	220	0	10	5	0	262.5	234.9	190.6	185.4	75.1	1.0	26	— 67.1	41.0
4	7.7	8.6	250	270	0	10	8	0	267.1	285.8	180.4	186.3	40.7	1.0	— 20	— 32.7	— 16.6
5	7.7	8.8	250	240	0	10	4	0	271.5	250.0	186.3	182.7	63.9	1.0	10	— 55.9	33.0

TABLE IX.

## COMPOSITION OF FLOC.

Formed When Lime Was Added to a Solution .00476 Molar Al at 20°C.

No.	pH	Equiv. Ca(OH) <sub>2</sub>		Al <sub>2</sub> O <sub>3</sub>	BaSO <sub>4</sub>	Al moles
		per mol. Al				SO <sub>4</sub> moles
				gms.	gms.	
1	4.0	0.370	0.0256	0.0469	2.493	
2	4.1	1.357	0.1309	0.1960	3.051	
3	4.2	1.727	0.1128	0.1574	3.273	
4	5.1	2.240	0.0522	0.0670	3.558	
5	6.2	2.465	0.0767	0.0845	4.146	
6	6.6	2.688	0.0863	0.0529	7.450	
7	8.2	2.913	0.0330	0.0098	15.38	
S	8.9	3.136	0.1195	0.0289	18.89	
9	9.0	3.361	0.0743	0.0166	20.45	

TABLE X.

## COMPOSITION OF FLOC.

Formed When Ca(HCO<sub>3</sub>)<sub>2</sub> Was Added to a Solution 0.00199 Molar Al at 20°C.

No.	PH	Equivs.				Ca(HCO <sub>3</sub> ) <sub>2</sub>
		Al A	BaSO <sub>4</sub>	Al	Equivs.	per Mol.
		gms.	gms.	SO <sub>4</sub>	Ca(HCO <sub>3</sub> ) <sub>2</sub>	Aluminum
1	4.2	0.0820	0.1097	3.415	0.01390	1.396
2	4.2	0.0559	0.0724	3.527	0.02084	2.097
3	4.2	0.0827	0.1058	3.572	0.02316	2.330
4	4.4	0.0615	<b>0.0780</b>	<b>3.603</b>	<b>0.02779</b>	<b>2.796</b>

TABLE XI.

## ANALYSES OF FLOCS FROM FILTER PLANTS.

Town	1a	1b	2	3	4
	near inlet	near outlet			
PH	7.4	7.4	7.3	7.3	7.4
	per cent.	per cent.	per cent.	per cent.	per cent.
insol. in HCl	76.79	69.94	70.44	74.82	73.95
Al <sub>2</sub> O <sub>3</sub>	7.60	11.16	8.20	9.25	10.58
Fe <sub>2</sub> O <sub>3</sub>	2.86	2.86	3.99	3.00	3.46
SO <sub>4</sub>	0.00	0.00	0.00	0.02	0.09
SiO <sub>2</sub>	1.48	2.06	1.97	3.69	4.09
nonvolatile	0.08	0.22	0.58	0.65	0.24
CaO	1.46	1.06	1.51	1.93	0.87
MgO	1.10	1.53	1.10	0.00	0.26
CO <sub>2</sub>				1.31	0.20
Total	91.27	88.83	87.89	94.67	93.74
SO <sub>4</sub> calc.	1.59	2.33	1.71	1.93	2.21

**TABLE XII.**  
**EFFECT OF TEMPERATURE IN WATERING SOFTENING.**  
**Exact Treatment at Different Temperatures.**

RUN 1.

Temperature 10°C.

Treatment from theoretical: lime —3.8%, Na<sub>2</sub>CO<sub>3</sub> —4.2%.

Treated with 115 lbs. lime, 45 lbs. special soda.

No.	Time from treatment	Hardness ppm. as CaCO <sub>3</sub> (Soap)	Alkalinity		Turbidity
			Phenol.	M. O.	
1	1:00	(132)	(62)	(98)	V. T.
2	2:00	136	70	108	S. T.
3	3:00	120	72	102	S. T.
4	4:00	118	70	100	S. T.
Raw		296	0	204	S. T.

Analysis:

Raw water (temp. 6°C.)

Non-carbonate hardness + 92 ppm. as CaCO<sub>3</sub>

Free carbon dioxide 9.2 ppm. as CaCO<sub>3</sub>

Magnesium 118 ppm. as CaCO<sub>3</sub>

Treated water

Non-carbonate hardness + 18 ppm. as CaCO<sub>3</sub>

Magnesium 78 ppm. as CaCO<sub>3</sub>

RUN 2.

Temperature 11°C.

Treatment from theoretical: lime +0.0%, Na<sub>2</sub>CO<sub>3</sub> +6.5%.

Treated with 115 lbs. lime and 47 lbs. special soda.

No.	Time from treatment	Hardness ppm. as CaCO <sub>3</sub>	Alkalinity		Turbidity
			Phenol.	M. O.	
1	0:30	(96)	(74)	(104)	V. T.
2	1:15	94	78	104	S. T.
3	2:30	94	74	104	S. T.
4	3:30	94	74	104	S. T.
5	4:30	96	78	104	O. T.
Raw		285	0	198	O. T.

Analysis:

Raw water (temp. 8°C.)

Non-carbonate hardness + 82 ppm. as CaCO<sub>3</sub>

Free carbon dioxide 7 ppm. as CaCO<sub>3</sub>

Magnesium 114 ppm. as CaCO<sub>3</sub>

Treated water

Non-carbonate hardness — 4 ppm. as CaCO<sub>3</sub>

## RUN 3.

Temperature 13° C.

Treatment from theoretical: lime — 3.1%,  $\text{Na}_2\text{CO}_3$  + 2.5%

Treated with 120 lbs. lime and 50 lbs. special soda.

No.	Time from treatment	Hardness ppm. as $\text{CaCO}_3$	Alkalinity		Turbidity
			Phenol.	M. O.	
1	1:20	84	52	78	S. T.
2	2:20	90	46	76	S. T.
3	3:20	90	44	74	O. T.
4	4:50	90	44	76	O. T.
5	5:50	84	44	74	O. T.
Raw		312	0	214	T.

Analysis.

Raw water (Temp. 6° C.)

Non-carbonate hardness + 98 ppm. as  $\text{CaCO}_3$ Free carbon dioxide 7 ppm. as  $\text{CaCO}_3$ Magnesium 125 ppm. as  $\text{CaCO}_3$ 

Treated water

Non-carbonate hardness + 10 ppm. as  $\text{CaCO}_3$ Magnesium 54 ppm. as  $\text{CaCO}_3$ 

## RUN 4.

Temperature 28° C.

Treatment from theoretical: lime — 5.0%,  $\text{Na}_2\text{CO}_3$  + 1.4%.

Treated with 130 lbs. lime and 55 lbs. special soda.

No.	Time from treatment	Hardness ppm. as $\text{CaCO}_3$	Alkalinity		Turbidity
			Phenol	M. O.	
1	0:50	96	56	90	S. T.
2	2:20	97	56	86	S. T.
3	3:20		50	90	S. T.
4	4:20	86	46	86	O. T.
5	5:20	86	48	82	O. T.
Raw		312	0	214	T.

Analysis:

Raw water (Temp. 6° C.)

Non-carbonate hardness + 98 ppm. as  $\text{CaCO}_3$ Free carbon dioxide 7 ppm. as  $\text{CaCO}_3$ Magnesium 125 ppm. as  $\text{CaCO}_3$ 

Treated water

Non-carbonate hardness 0 ppm. as  $\text{CaCO}_3$  -Magnesium 70 ppm. as  $\text{CaCO}_3$

## RUN 5.

Temperature 29°C.

Treatment from theoretical: lime —6.7%, Na<sub>2</sub>CO<sub>3</sub> 0.07.Treated with 130 lbs. lime and 50 lbs. Na<sub>2</sub>CO<sub>3</sub>.

No.	Time from treatment	Hardness ppm. as CaCO <sub>3</sub>	Alkalinity		Turbidity
			Phenol.	M. O.	
1	0:45	(69)	(44)	(70)	V. T.
2	1:45	71	36	66	S. T.
3	2:45	71	36	66	O. T.
4	3:45	73	34	62	O. T.
5	4:45	77	36	66	O. T.
6	5:45	78	36	66	O. T.
Raw		286	0	202	O. T.

Analysis:

Raw water (Temp. 5°C.)

Non-carbonate hardness + 84 ppm. as CaCO<sub>3</sub>Free CO. 7 ppm. as CaCO<sub>3</sub>Magnesium 114 ppm. as CaCO<sub>3</sub>

Treated water

Non-carbonate hardness + 12 ppm. as CaCO<sub>3</sub>Magnesium 0 ppm. as CaCO<sub>3</sub>

## Run 6.

Temperature 30°C.

Treatment from theoretical: lime +4.2%, Na<sub>2</sub>CO<sub>3</sub> + 5.4%.

Treated with 135 lbs. lime and 54 lbs. special soda.

No.	Time from treatment	Hardness ppm. as CaCO <sub>3</sub>	Alkalinity		Turbidity
			Phenol.	M. O.	
1	1:20	86	50	80	T.
2	2:20	87	48	74	S. T.
3	3:20	81	46	68	S. T.
4	4:20	76	40	70	O. T.
5	5:20	77	42	68	O. T.
Raw		320	0	220	T.

Analysis:

Raw water (Temp. 6°C.)

Noncarbonate hardness + 100 ppm. as CaCO<sub>3</sub>Free carbon dioxide 12 ppm. as CaCO<sub>3</sub>Magnesium 128 ppm. as CaCO<sub>3</sub>

Treated water

Non-carbonate hardness + 8 ppm. as CaCO<sub>3</sub>Magnesium 60 ppm. as CaCO<sub>3</sub>

## RUN 7.

Temperature 30° C.

Treatment from theoretical: lime — 3.7%, Na<sub>2</sub>CO<sub>3</sub> — 4.2%.

Treated with 115 lbs. lime and 45 lbs. special soda.

No.	Time from treatment	Hardness ppm. as CaCO <sub>3</sub>	Alkalinity		Turbidity
			Phenol.	M. O.	
1	1:45	(87)	(36)	(60)	S. T.
2	2:45	74	36	60	S. T.
3	3:45	80	36	64	S. T.
4	4:45	76	36	62	S. T.
Raw		296	0	204	S. T.

Analysis:

Raw water (Temp. 6° C.)		
Non-carbonate hardness		+ 92 ppm. as CaCO <sub>3</sub>
Free carbon dioxide		9 ppm. as CaCO <sub>3</sub>
Magnesium		118 ppm. as CaCO <sub>3</sub>
Treated water		
Non-carbonate hardness		+ 16 ppm. as CaCO <sub>3</sub>
Magnesium		40 ppm. as CaCO <sub>3</sub>

## RUN 8.

Temperature 30° C.

Treatment from theoretical: lime +0.6%, Na<sub>2</sub>O<sub>3</sub> +3.8%.

Treated with 120 lbs. lime, 50 lbs. special soda, and 10 lbs. alum.

No.	Time from treatment	Hardness, ppm. as CaCO <sub>3</sub>	Alkalinity		Turbidity
			Phenol.	M. O.	
1	0:30	77.1	42	72	V. T.
2	,1:30	70	46	68	S. T.
3	2:30	70	42	68	O. T.
4	3:30	71	44	68	O. T.
5	4:30	69	46	68	O. T.
6	5:30	60	46	66	O. T.
Raw		285	0	206	T.

Analysis:

Raw water (Temp. 8° C.)		
Non-carbonate hardness		+ 84 ppm. as CaCO <sub>3</sub>
Free carbon dioxide		7 ppm. as CaCO <sub>3</sub>
Magnesium		114 ppm. as CaCO <sub>3</sub>
Treated water		
Non-carbonate hardness		— 4 ppm. as CaCO <sub>3</sub>
Magnesium		4 ppm. as CaCO <sub>3</sub>

## RUN 9.

Temperature 45° C.

Treatment from theoretical: lime + 4.2%, Na<sub>2</sub>CO<sub>3</sub> + 5.5%.

Treated with 135 lbs. lime and 54 lbs. special soda.

No.	Time from treatment	Hardness ppm. as CaCO <sub>3</sub>	Alkalinity		Turbidity
			Phenol.	M. O.	
1	1:00	93	40	76	S. T.
2	2:00	81	42	74	O. T.
3	3:00	70	44	74	O. T.
4	4:00	70	46	72	O. T.
Raw		320	0	220	T.

Analysis:

Raw water (Temp. 6° C.)

Non-carbonate hardness + 100 ppm. as CaCO<sub>3</sub>

Free carbon dioxide 12 ppm. as CaCO<sub>3</sub>

Magnesium 128 ppm. as CaCO<sub>3</sub>

Treated water

Non-carbonate hardness + 2 ppm. as CaCO<sub>3</sub>

Magnesium 62 ppm. as CaCO<sub>3</sub>

### TABLE XIII.

#### EFFECT OF TEMPERATURE IN WATER SOFTENING.

Over-treatment lime; exact treatment soda (30°C).

Temperature 30° C.

Treatment from theoretical: lime + 11.9%, Na<sub>2</sub>CO<sub>3</sub> + 1.3%.

Treated with 145 lbs. lime and 54 lbs. special soda.

No.	Time from treatment	Hardness ppm. as CaCO <sub>3</sub>	Alkalinity		Turbidity
			Phenol.	M. O.	
1	2:15	86	75	80	S. T.
2	3:15	61	76	88	S. T.
3	4:15	61	75	88	S. T.
4	5:15	64	78	90	O. T.
Raw		326	0	216	S. T.

Analysis:

Raw water (Temp. 7° C.)

Free carbon dioxide 7 ppm. as CaCO<sub>3</sub>

Magnesium 129 ppm. as CaCO<sub>3</sub>

Treated water

Calcium 64 ppm. as CaCO<sub>3</sub>

Magnesium 0 ppm. as CaCO<sub>3</sub>



**TABLE XIV.**  
**EFFECT OF TEMPERATURE IN WATER SOFTENING.**  
**Under-treatment Lime; Exact Treatment Soda.**

RUN 1.

Temperature 33° C.

Treatment from theoretical: lime —14.2%, Na<sub>2</sub>CO<sub>3</sub> + 3.94%.

Treated with 105 lbs. lime and 45 lbs. special soda.

No.	Time from treatment	Hardness ppm. as CaCO <sub>3</sub>	Alkalinity		Turbidity
			Phenol	M. O.	
1	0:40	78.6	(44)	(75)	S. T.
2	1:20		45	73	S. T.
3	1:40	75.7	40	73	O. T.
4	2:40	71.4	41	73	O. T.
5	3:40	72.9	39	68	O. T.
1	0:40	(72.9)	(38)	(68)	T.
2	1:10		(39)	(64)	S. T.
3	1:40	(70)	(36)	(60)	S. T.
4	3:10	70.0	36	63	O. T.
5	4:10	70.0	36	61	O. T.
6	4:55	71.4	34	62	O. T.
Raw		289	0	198	S. T.

Analysis:

Raw water (Temp. 10° C.)

Free carbon dioxide

7 ppm. as CaCO<sub>3</sub>

Magnesium

118 ppm. as CaCO<sub>3</sub>

Treated water

Magnesium

53 ppm. as CaCO<sub>3</sub>

RUN 2.

Temperature 23° C.

Treatment from theoretical: lime —13.9%, Na<sub>2</sub>CO<sub>3</sub> 0.0%.

Treated with 120 lbs. lime and 50 lbs. Na<sub>2</sub>CO<sub>3</sub>.

No.	Time from treatment	Hardness ppm. as CaCO <sub>3</sub>	Alkalinity		Turbidity
			Phenol.	M. O.	
1	0:45	108	54	86	S. T.
2	1:45	102	52	84	O. T.
3	2:45	105	54	84	O. T.
4	3:45		50	86	O. T.
5	4:45'	99	48	84	O. T.
Raw		286	0	202	

Analysis:

Raw water (Temp. 5° C.)

Non-carbonate hardness

+ 84 pmm. as CaCO<sub>3</sub>

Free carbon dioxide

7 ppm. as CaCO<sub>3</sub>

Magnesium

114 ppm. as CaCO<sub>3</sub>

Treated water

Non-carbonate hardness

+ 12 ppm. as CaCO<sub>3</sub>

RUN 3.

Temperature 56° C.

Treatment from theoretical: lime —14.2%,  $\text{Na}_2\text{CO}_3$  +3.94%.Treated with 135 lbs. lime and 60 lbs.  $\text{Na}_2\text{CO}_3$ .

No.	Time from treatment	Hardness ppm. as $\text{CaCO}_3$	Alkalinity		Turbidity
			Phenol	M. O.	
1	1:00	(47.1)	(25)	(50)	V. T.
2	2:00	(45.7)	(24)	(50)	V. T.
3	3:00	(48.6)	(23)	(50)	V. T.
4	4:30	(50.0)	(22)	(49)	S. T.
5	5:30	(50.0)	(22)	(50)	S. T.
6	6:15	(50.0)	(22)	(50)	S. T.
1	0:45	(58.6)	(24)	(50)	V. T.
2	1:15	(52.9)	(25)	(50)	V. T.
3	1:45	(54.3)	(22)	(50)	V. T.
4	2:45	(51.4)	(22)	(49)	S. T.
5	3:45	(50.0)	(23)	(49)	O. T.
6	4:45	(50.0)	(24)	(50)	O. T.
7	5:30	(51.4)	(22)	(54)	O. T.
Raw		289.	0	198	S. T.

Analysis:

Raw water

Free carbon dioxide 7 ppm. as  $\text{CaCO}_3$ Magnesium 118 ppm. as  $\text{CaCO}_3$ 

Treated water

Magnesium 40 ppm. as  $\text{CaCO}_3$ 

**TABLE XV.**  
**EFFECT OF TEMPERATURE IN WATER SOFTENING.**

Exact Treatment Lime; Over-treatment Soda.

RUN 1.

Temperature 26° C.

Treatment from theoretical: lime —2.6%,  $\text{Na}_2\text{CO}_3$  +14.4%.Treated with 135 lbs. lime and 90 lbs.  $\text{Na}_2\text{CO}_3$ .

No.	Time from treatment	Hardness ppm. as $\text{CaCO}_3$	Alkalinity		Turbidity
			Phenol.	M. O.	
1	1:00	77	56	84	S. T.
2	1:30		56	80	S. T.
3	2:00	76	49	80	O. T.
4	2:30	76	52	82	O. T.
5	3:00		51	82	O. T.
6	3:30	75	51	84	O. T.
7	4:15		51	82	O. T.
8	4:45	77	51	81	O. T.
9	5:15		52	80	O. T.
Raw		287	0	198	

Analysis:

Raw water (Temp. 11° C.)

Free carbon dioxide 7 ppm. as  $\text{CaCO}_3$ Magnesium 115 ppm. as  $\text{CaCO}_3$ 

Treated water

Magnesium 53 ppm. as  $\text{CaCO}_3$

## RUN 2.

Temperature 30° C.

Treatment from theoretical: lime + 3.0%, Na<sub>2</sub>CO<sub>3</sub> + 13.8%.

Treated with 120 lbs. lime and 50 lbs. special soda.

No.	Time from treatment	Hardness ppm. as CaCO <sub>3</sub>	Alkalinity		Turbidity
			Phenol.	M. O.	
1	1	81	54	84	S. T.
2	2	81	50	80	O. T.
3	3	84	50	82	O. T.
4	4	84	54	82	O. T.
5	5	84	54	82	O. T.
6	6	82	52	78	O. T.
Raw		285	0	206	T.

Analysis:

Raw water

Non-carbonate hardness + 84 ppm. as CaCO<sub>3</sub>Free carbon dioxide 7 ppm. as CaCO<sub>3</sub>Magnesium 114 ppm. as CaCO<sub>3</sub>

Treated water

Non-carbonate hardness 0 ppm. as CaCO<sub>3</sub>Magnesium 30 ppm. as CaCO<sub>3</sub>

## RUN 3.

Temperature 30° C.

1. Treatment from theoretical: lime — 3.0%, Na<sub>2</sub>CO<sub>3</sub> + 8.0%.Treated with 125 lbs. lime and 65 lbs. Na<sub>2</sub>CO<sub>3</sub>.

Analysis:

Treated water

Hardness 82 ppm. as CaCO<sub>3</sub>

Alkalinity

Phenol. 54 ppm. as CaCO<sub>3</sub>Methyl Orange 94 ppm. as CaCO<sub>3</sub>Non-carbonate hardness — 12 ppm. as CaCO<sub>3</sub>Magnesium 79 ppm. as CaCO<sub>3</sub>2. Treatment from theoretical: lime + 0.9%, Na<sub>2</sub>CO<sub>3</sub> + 16.4%.Treated with 130 lbs. lime and 70 lbs. Na<sub>2</sub>CO<sub>3</sub>

Analysis:

Treated water

Hardness 57 ppm. as CaCO<sub>3</sub>

Alkalinity

Phenol. 60 ppm. as CaCO<sub>3</sub>Methyl Orange 80 ppm. as CaCO<sub>3</sub>Non-carbonate hardness 23 ppm. as CaCO<sub>3</sub>Magnesium 28 ppm. as CaCO<sub>3</sub>

Raw water

Hardness 287 ppm. as CaCO<sub>3</sub>

Alkalinity

Phenol. 0 ppm. as CaCO<sub>3</sub>Methyl Orange 184 ppm. as CaCO<sub>3</sub>Free carbon dioxide 7 ppm. as CaCO<sub>3</sub>Magnesium 113 ppm. as CaCO<sub>3</sub>

**TABLE XVI.**  
**EFFECT OF TEMPERATURE IN WATER SOFTENING.**  
**Over-treatment Lime; Over-treatment Soda.**

RUN 1.

Temperature 25.5°C.

Treatment from theoretical: lime + 6.3%, Na<sub>2</sub>CO<sub>3</sub> + 8.6%.

Treated with 120 lbs. lime and 50 lbs. special soda.

No.	Time from treatment	Hardness ppm. as CaCO <sub>3</sub>	Alkalinity		Turbidity
			Phenol.	M. O.	
1	0:30	73	52	74	V. T.
2	1:30	64	46	68	S. T.
3	2:30	60	54	72	O. T.
4	3:30	60	56	72	O. T.
5	4:30	63	58	74	O. T.
6	5:30	63	56	72	O. T.
Raw		285	0	196	T.

Analysis:

Raw water (Temp. 7° C.)	
Non-carbonate	+ 84 ppm. as CaCO <sub>3</sub>
Free carbon dioxide	7 ppm. as CaCO <sub>3</sub>
Magnesium	114 ppm. as CaCO <sub>3</sub>
Treated water	
Non-carbonate hardness	— 3 ppm. as CaCO <sub>3</sub>
Magnesium	10 ppm. as CaCO <sub>3</sub>

RUN 2.

Temperature 30° C.

Treatment from theoretical: lime + 6.3%, Na<sub>2</sub>CO<sub>3</sub> + 8.6%.

Treated with 120 lbs. lime and 50 lbs. special soda.

No.	Time from treatment	Hardness ppm. as CaCO <sub>3</sub>	Alkalinity		Turbidity
			Phenol.	M. O.	
1	1	63	52	70	S. T.
2	2	53	46	68	S. T.
3	3	51	46	66	O. T.
4	4	50	46	66	O. T.
5	5	51	46	64	O. T.
6	6	51	46	65	O. T.
Raw		285	0	196	F. T.

Analysis:

Raw water (Temp. 7° C.)	
Non-carbonate hardness	+ 84 ppm. as CaCO <sub>3</sub>
Free carbon dioxide	7 ppm. as CaCO <sub>3</sub>
Magnesium	114 ppm. as CaCO <sub>3</sub>
Treated water	
Non-carbonate hardness	— 8 ppm. as CaCO <sub>3</sub>
Magnesium	8 ppm. as CaCO <sub>3</sub>

## RUN 3.

Temperature 30° C.

Treatment from theoretical: lime + 13.2%, Na<sub>2</sub>CO<sub>3</sub> + 17.1%.Treated with 140 lbs. lime and 58 lbs. Na<sub>2</sub>CO<sub>3</sub>

No.	Time from treatment	Hardness ppm. as CaCO <sub>3</sub> ,	Alkalinity		Turbidity
			Phenol.	M. O.	
1	0:30		(38)	(60)	V. T.
2	1:00	51.4	(37)	(58)	F. T.
3	1:30		(38)	(58)	S. T.
4	2:30	54.3	(38)	(57)	S. T.
5	3:30		(35)	(57)	O. T.
6	4:30	54.3	(37)	(57)	O. T.
Raw		260.	0	177	F. T.

Analysis:

Raw Water (Temp. 13° C.)

Free carbon dioxide 7 ppm. as CaCO<sub>3</sub>Magnesium 109 ppm. as CaCO<sub>3</sub>

Treated water

Magnesium 20 ppm. as CaCO<sub>3</sub>

TABLE XVII.

EFFECT OF TEMPERATURE IN WATER SOFTENING.  
Under-treatment Lime; Under-treatment Soda.

## RUN 1.

Temperature 18° C.

Treatment from theoretical: lime — 24.8%, Na<sub>2</sub>CO<sub>3</sub> — 28.8%.Treated with 105 lbs. lime and 40 lbs. Na<sub>2</sub>CO<sub>3</sub>.

No.	Time from treatment	Hardness ppm. as CaCO <sub>3</sub>	Alkalinity		Turbidity
			Phenol.	M. O.	
1	0:45	140	72	115	S. T.
2	1:20	140	70	106	O. T.
3	1:50	140	71	107	O. T.
4	3:05	140	69	106	O. T.
5	3:50	140	67	104	O. T.
Raw		292	0	196	S. T.

Analysis:

Raw water (Temp. 8° C.)

Free carbon dioxide 7 ppm. as CaCO<sub>3</sub>Magnesium 119 ppm. as CaCO<sub>3</sub>

Treated water

Magnesium 91 ppm. as CaCO<sub>3</sub>

## RUN 2.

Temperature 21° C.

Treatment from theoretical: lime —6.60%, Na<sub>2</sub>CO<sub>3</sub> —8.1%.Treated with 145 lbs. lime and 55 lbs. Na<sub>2</sub>CO<sub>3</sub>

No.	Time from treatment	Hardness ppm. as CaCO <sub>3</sub>	Alkalinity		Turbidity
			Phenol.	M.O.	
1	1:25	61	SO	57	S. T.
2	2:40	64	35	60	S. T.
3	3:40	66	34	62	S. T.
4	4:40	63	36	58	S. T.
5	5:40		322	220	

Analysis:

Raw water

Non-carbonate hardness + 102 ppm. as CaCO<sub>3</sub>Free carbon dioxide 9 ppm. as CaCO<sub>3</sub>Magnesium 129 ppm. as CaCO<sub>3</sub>

Treated water

Non-carbonate hardness +8 ppm. as CaCO<sub>3</sub>Magnesium 40 ppm. as CaCO<sub>3</sub>

## RUN 3.

Temperature 30° C.

Treatment from theoretical: lime —12.9%, Na<sub>2</sub>CO<sub>3</sub> — 8.5%.Treated with 115 lbs. lime and 55 lbs. Na<sub>2</sub>CO<sub>3</sub>

No.	Time from treatment	Hardness ppm. as CaCO <sub>3</sub>	Alkalinity-		Turbidity
			Phenol.	M. O.	
1	1:00	79	46	89	S. T.
2	2:00	81	46	84	S. T.
3	3:00	83	47	81	S. T.
4	4:00	82	46	80	O. T.
Raw		286	0	184	

Analysis:

Raw water (Temp. 10° C.)

Non-carbonate hardness + 80 ppm. as CaCO<sub>3</sub>Free carbon dioxide 7 ppm. as CaCO<sub>3</sub>Magnesium 113 ppm. as CaCO<sub>3</sub>

Treated water

Non-carbonate hardness — 8 ppm. as CaCO<sub>3</sub>Magnesium 73 ppm. as CaCO<sub>3</sub>

## RUN 4.

Temperature 32° C.

Treatment from theoretical: lime — 6.6%,  $\text{Na}_2\text{CO}_3$  — 8.1%.Treated with 145 lbs. lime and 551 lbs.  $\text{Na}_2\text{CO}_3$ .

No.	Time from treatment	Hardness ppm. as $\text{CaCO}_3$	Alkalinity		Turbidity
			Phenol.	M. O.	
1	3:00	54	41	58	S. T.
2	3:40	54	39	56	O. T.
3	4:40	53	39	55	O. T.
4	5:40	55	40	52	O. T.
5	6:40	50	40	52	O. T.
Raw		322	0	220	

Analysis:

Raw water

Non-carbonate hardness + 102 ppm. as  $\text{CaCO}_3$ Free carbon dioxide 9 ppm. as  $\text{CaCO}_3$ Magnesium 129 ppm. as  $\text{CaCO}_3$ 

Treated water

Non-carbonate hardness 0 ppm. as  $\text{CaCO}_3$ Magnesium 40 ppm. as  $\text{CaCO}_3$ 

## RUN 5.

Temperature 35° C.

Treatment from theoretical: lime — 9.0%,  $\text{Na}_2\text{CO}_3$ —18.0%.

Treated with 90 lbs. lime and 40 lbs. special soda.

No.	Time from treatment	Hardness ppm. as $\text{CaCO}_3$	Alkalinity		Turbidity
			Phenol	M. O.	
1	0:35	(67.1)	(36)	(62)	F. T.
2	1:05		(35)	(65)	S. T.
3	1:35	65.7	(34)	(64)	S. T.
4	2:35	65.7	37	65	S. T.
5	3:35	64.3	36	65	S. T.
6	4:35	65.7	(33)	(65)	S. T.
Raw		265	0	169	

Analysis:

Raw water (Temp. 11° C.)

Free carbon dioxide 7 ppm. as  $\text{CaCO}_3$ Magnesium 107 ppm. as  $\text{CaCO}_3$ 

Treated water

Magnesium 39 ppm. as  $\text{CaCO}_3$

**TABLE XVIII.**  
**EFFECT OF TEMPERATURE IN WATER SOFTENING.**  
**Under-treatment Lime; Over-treatment Soda.**

RUN 1.

Temperature 12° C.

Treatment from theoretical: lime — 10.5%, Na<sub>2</sub>CO<sub>3</sub> + 6.3%.

Treated with 120 lbs. lime and 60 lbs. Na<sub>2</sub>CO<sub>3</sub>.

No.	Time from treatment	Hardness ppm. as CaCO <sub>3</sub>	Alkalinity		Turbidity
			Phenol.	M. O.	
1	0:20	(87.1)	(82)	(11C)	V. T.
2	0:50		84	118	S. T.
3	1:20	84.3	84.	116	S. T.
4	1:50		78	116	O. T.
5	2:50	81.4	76	114	O. T.
6	3:20		78	114	O. T.
7	3:50	81.4	78	110	O. T.
Raw		287	0	192	

Analysis:

Raw water (Temp. 12° C.)

Non-carbonate hardness + 84 ppm. as CaCO<sub>3</sub>

Free carbon dioxide 7 ppm. as CaCO<sub>3</sub>

Magnesium 114 ppm. as CaCO<sub>3</sub>

Treated water

Non-carbonate hardness — 34 ppm. as CaCO<sub>3</sub>

Magnesium 36 ppm. as CaCO<sub>3</sub>

RUN 2.

Temperature 34° C.

Treatment from theoretical: lime — 7.1%, Na<sub>2</sub>CO<sub>3</sub> + 7.7%.

Treated with 115 lbs. lime and 58 lbs. Na<sub>2</sub>CO<sub>3</sub>.

No.	Time from treatment	Hardness ppm. as CaCO <sub>3</sub>	Alkalinity		Turbidity
			Phenol.	M. O.	
1	0:40	81	(36)	(74)	V. T.
2	1:10		(42)	(76)	S. T.
3	1:40	90	(46)	(85)	S. T.
4	2:40	90	(40)	(87)	S. T.
5	3:40	89	(41)	(84)	S. T.
6	4:40	89	(43)	(87)	S. T.
Raw		269	0	177	

Analysis:

Raw water (Temp. 13° C.)

Free carbon dioxide 7 ppm. as CaCO<sub>3</sub>

Magnesium 108 ppm. as CaCO<sub>3</sub>

Treated water

Magnesium 47 ppm. as CaCO<sub>3</sub>



RUN 3.

Temperature 27° C.

Treatment from theoretical: lime —6.7%,  $\text{Na}_2\text{CO}_3$  +7.1%.Treated with 125 lbs. lime and 58 lbs.  $\text{Na}_2\text{CO}_3$ .

Analysis:

Raw water (Temp. 13° C.)

Hardness 260 ppm. as  $\text{CaCO}_3$ 

Alkalinity

Phenol. 0 ppm. as  $\text{CaCO}_3$ Methyl Orange 177 ppm. as  $\text{CaCO}_3$ Magnesium 109 ppm. as  $\text{CaCO}_3$ Free carbon dioxide 7 ppm. as  $\text{CaCO}_3$ 

Treated water

Hardness 71 ppm. as  $\text{CaCO}_3$ 

Alkalinity

Phenol. 41 ppm. as  $\text{CaCO}_3$ Methyl Orange 74 ppm. as  $\text{CaCO}_3$ Magnesium 45 ppm. as  $\text{CaCO}_3$

TABLE XIX.

## DECREASE IN HARDNESS AT DIFFERENT TEMPERATURES.

Group	No.	Temp. 0° C.	Final Hardness ppm.as	Per Cent from CaCO <sub>3</sub>	Ca(OH) <sub>2</sub>	Theoretical Na <sub>2</sub> CO <sub>3</sub>
A	1	10	116	—3.8	—	4.2
	2	11	96	0.0		6.5
	3	13	84	—3.1		2.5
	4	28	86	—5.9		1.4
	5	29	78	—6.7		0.0
	6	30	77	4.2		5.4
	7	30	76	—3.7		—4.2
	8	30	69	0.6		3.8
	9	45	70	4.2		5.5
B		30	64	11.9		1.3
C	1	23	99	—13.9		0.0
	2	33	72	—14.2		3.9
	3	33	71	—14.2		3.9
	4	56	50'	—14.2		3.9
	5	56	50	—14.2		3.9
D	1	26	77	—2.6		14.4
	2	30	82	3.0		13.8
	3	30	82	—3.0		8.0
	4	30	57	0.9		16.4
E	1	25	63	6.3		8.6
	2	30	51	6.3		8.6
	3	30	54	13.2		17.1
F	1	18	140	—24.8		—28.8
	2	21	63	—6.6		—8.1
	3	30	82	—12.9		—8.5
	4	32	50	—6.6		—8.1
	5	35	65	—9.0		—18.0
G	1	12	81	—10.5		6.4
	2	27	71	—6.7		7.1
	3	32	54	—7.2		13.7
	4	34	89	—7.1		7.7

Note:—For treatment used in each group, see text pp. 93 and 102-114.

**TABLE XX.**  
**EFFECT OF ALUM**  
**As An Aid in the Lime-Soda Process.**

		Hardness as CaCO <sub>3</sub>			Alkalinity as CaCO <sub>3</sub>	
		Ca ppm.	Mg ppm.	Total ppm.	ppm. Ph'th	ppm. M. O.
NOTE—The same amounts of lime (2 lbs. per 1,000 gals.) and soda (0.9 lbs. per 1,000 gals.) were used, and the temperature (29°C) was the same in both runs.						
First Run	Raw Water (Free CO <sub>2</sub> = 8 ppm. as CaCO <sub>3</sub> ).....	192	87	279	0	206
	Treated Water without Alum.....	...	...	84	52	78
	Treated Water with 1.0 gr. per gal. Alum.....	...	...	66	46	66
Second Run	Raw Water (Free CO <sub>2</sub> = 7 ppm. as CaCO <sub>3</sub> ).....	151	109	260	0	177
	Treated Water without Alum.....	26	45	71	41	74
	Treated Water with 0.5 gr. per gal. Alum.....	31.3	4.5	35.8	53	70

**TABLE XXI.**  
**EFFECT OF FILTERING IN WATER SOFTENING.**

No.	Before .					After				
	Alkalinity		Hardness			Alkalinity		Hardness		
	ppm. as CaCO <sub>3</sub>		ppm. as CaCO <sub>3</sub>			ppm. as CaCO <sub>3</sub>		ppm. as CaCO <sub>3</sub>		
	Ph'th	M.O.	Ca.	Mg	Total	Ph'th	M.O.	Ca	Mg	Total
1	34	62	8.9	57.2	61.6	34	56	6.3	54.9	61.2
2	38	66	8.9	44.r	53.0	36	66	7.1	45.5	52.6
3	46	80	5.4	72.9	78.3	38	71	0.9	64.4	65.3
4	36	68	...	....	(78)	36	64	...	....	(61)
5	36	62	...	....	(76)	34	56	...	....	(76)
6	44	74	...	....	(81)	40	68	...	....	(79)
7	40	52	...	....	(50)	40	50	...	....	(46)

Note:—Figures in parenthesis indicate the soap hardness.

**TABLE XXII.**  
**RATE OF REACTION IN WATER SOFTENING.**

Temperature 33° and 35° C.

Treatment from theoretical: Lime —7.0%, Na<sub>2</sub>CO<sub>3</sub> + 17.1%

Treated with 120 lbs. lime and 60 lbs. Na<sub>2</sub>CO<sub>3</sub>.

Time	Hardness	Agitated With Air 30 Min.		Turbidity
		Alkalinity	M. O.	
		Phenol.	M. O.	
1:00	(57.1)	(38)	(68)	S. T.
1:30		(38)	(68)	S. T.
2:00	(57.1)	(38)	(68)	S. T.
2:30		(37)	(70)	S. T.
3:00	60.0	41	74	S. T.
3:45	55.7	36	68	O. T.
4:45	51.4	39	67	O. T.
5:45	52.9	38	68	O. T.
6:45	55	38	66	O. T.
7:45	54.3	38	66	O. T.

Time	Hardness	Agitated with Air 1 Hr. 15 Min.		Turbidity
		Alkalinity	M. O.	
		Phenol.	M. O.	
1:20	(52.9)	(42)	(72)	S. T.
2:20	(51.4)	(41)	(75)	S. T.
2:50		(40)	(70)	S. T.
3:20	(54.3)	(38)	(70)	S. T.
4:20	51.4	42	71	O. T.
5:20	50.0	41	72	O. T.
Raw	271.5	0	188	

Analysis of Raw Water (Temp. 12° C) :

Free carbon dioxide, 5ppm. as CaCO<sub>3</sub>

Magnesium, 106 ppm. as CaCO<sub>3</sub>

PART FOUR.

**PRECIPITATION OF ALUMINA IN THE ACID RANGE OF HYDROGEN-ION CONCENTRATION.**

By L. H. MCROBERTS with A. M. BUSWELL

---

**CONTENTS.**

	Page.
Introduction . . . . .	121
Preparation of the experimental plant . . . . .	122
Details of operation of the plant . . . . .	124
Methods of analysis . . . . .	125
Results. . . . .	126
Summary. . . . .	126

## PRECIPITATION OF ALUMINA IN THE ACID RANGE OF HYDROGEN-ION CONCENTRATION\*.

### INTRODUCTION.

The work here reported is a continuation of a series of experiments begun by this laboratory in 1920. These experiments, which have been concerned, in general, with questions of the rôle of aluminum as a coagulating and precipitating agent, have yielded data on the optimum conditions for the production of an effluent free from undesirable matter. Practically all of these experiments have been conducted in the range of hydrogen-ion concentrations commonly found in filter-plant practice.

The work reported by Gallaher and Buswell (see above, pp. 79ff) included a study of the precipitation of alumina on the alkaline side of true neutrality, that is, above pH 7. Recent investigations in other laboratories (reference numbers 15, 51, 83, 84, and 85) have indicated some advantages to be gained by operation of a filter plant at hydrogen-ion concentrations greater than were formerly considered advisable. For example, alum floc is more satisfactorily formed and color is more easily removed on the acid side; furthermore, the cost of operation may sometimes be reduced by bringing the water in mixing tanks and coagulating basins to a lower pH value.

In practice, however, difficulties are encountered if the water is even slightly acidified, and serious damages to distribution systems are wrought by a markedly acid effluent. While these problems ultimately concern the waterworks engineer, inasmuch as their solution would require certain changes in plant design, they are at present fit subjects for the sanitary chemist to investigate.

Experiments to determine how these advantages are to be secured and these difficulties to be avoided can hardly be conducted satisfactorily in plants furnishing potable water. Present methods of control in most cases preclude such disturbing variations from routine as would be necessary. Some significant work can, of course, be done in laboratories, but the results are not always directly applicable to actual practice. The construction and operation of an experimental water-purifi-

---

\* From a thesis submitted May, 1925, by L. H. McRoberts in partial fulfillment of the requirements for the degree of Master of Science in Chemistry in the Graduate School of the University of Illinois.

cation plant, therefore, seems to be the most promising method of approach.

Such an experimental plant has been provided for purposes of research by the State Water Survey. It permits work to be done on a fairly large scale under a wide range of conditions and is susceptible to as rigid control as is usually possible in the operation of a municipal or industrial treatment plant. A diagram of the layout of the plant was given above by Gallaher and Buswell (see Fig. 1, page 80).

Former attempts to operate the plant in the acid range had resulted in rapid corrosion of the various metal containers, such as the mixing tank for chemicals, the galvanized-iron filter tank, and the orifice tank. It was also found that the gravel and filter sand then in use reacted with the acidified water so that pH determinations made on the effluent could not be correlated with residual alum content.

### PREPARATION OF THE EXPERIMENTAL PLANT.

In order to permit an investigation in the acid range, the plant was modified during the summer of 1924. Corrosion of iron was eliminated, with the exception of surfaces exposed in piping and in the pump, by the application of three coats of asphalt paint ("Turpentine Black Asphaltum", American Asphalt Paint Co., Chicago). A wooden container was used for mixing the water and chemicals.

Rock, gravel, and sand for use in the new filter bed had to be sufficiently inert so that no change of pH was detected as the water passed through the plant. Novaculite\*, a silicious material of 1" to 2" size, was used to cover the strainer. Next was placed a mixture of chert (flint) and quartz gravel. As sufficient chert was not immediately obtainable to complete the filter bed, quartz gravel that had been treated with sulfuric acid was used. The quartz "sand" obtained was of a very good grade and was used in the filter without any previous treatment.

It should be noted here that it is difficult to obtain gravel (even though designated as "quartz gravel") entirely free from material that will react with acid. What was supposed to be a good grade of quartz gravel was purchased for this experiment but was found to be only 93% inert. Before use in the filter it was therefore necessary to digest the gravel in dilute acid (commercial sulfuric). Complete digestion with one application of acid sufficient in quantity to react with the lime present was found to take considerable time; and, since the completion of the filter bed was desired at an early date, it was found necessary to remove the acid at one-week intervals and to wash out the white precipitate that formed (probably calcium sulfate). After three weeks of this treatment the gravel was considered to be sufficiently inert for use in the filter bed. The criterion applied was that of no observable evolution of gas on treatment of a small amount of the gravel (about 50 gms.) with dilute sulfuric acid (1:1). Even if a slight reactivity remained, it was thought that the large body of water in the filter would

---

\* The novaculite and chert were obtained from the Ceramics Department of the University of Illinois.



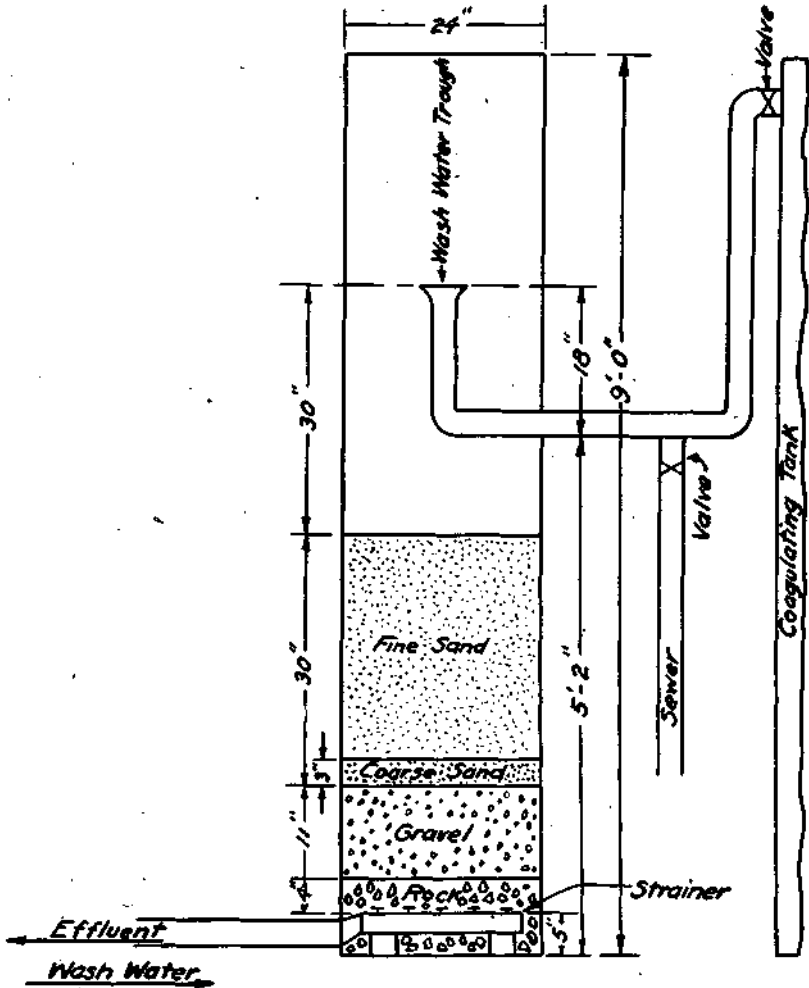


Fig. 1. Cross-Section of Experimental Filter.

buffer itself so that no appreciable change in pH would be caused in passing through the filter bed.

The construction of the filter and filter bed is shown in detail in Fig. 1. The following table gives the amounts of material used and the depth of each layer:

Rock (novaculite) above strainer	4 inches
Gravel (quartz and chert)	
Held on .45 chert sieve	.1 inch
Gravel held on .3 chert sieve	.4 inches
Gravel held on .2 chert sieve	.1 inch
Gravel passing .2 chert sieve	.5 inches
Sand (quartz, coarse)	.3 inches
Sand (quartz, fine)	.27 inches

Total depth of bed before washing . . . . . 45 inches

After the first washing, the depth of the filter bed was fortythree inches, and the top of the filter bed was thirty-two inches from the top of the wash water trough.

The apparatus used for adding chemicals is shown in Fig. 2. The advantages gained by its use were: (1) constant head was maintained at the point of delivery with lowering of level in the chemical tank; (2) rate of feed was regulated by the stop-cock or by the length of the delivery tube below the tank level; (3) clogging was minimized by siphoning so that material floating on the surface was not drawn into the tube. (By the use of a large float the counter weight could be dispensed with).

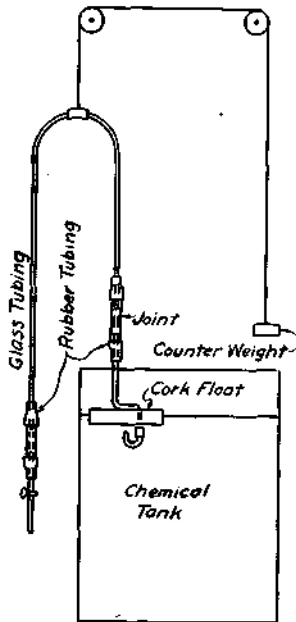


Fig 2. Constant-Feed Device  
For Mixing Tank.

### DETAILS OF OPERATION OF THE EXPERIMENTAL PLANT.

Operation of the plant was begun in September and continued two months. That determinations of residual alum might be comparable throughout the investigation, the alum dosage was kept constant at 2 grains per gallon (approximately 34 ppm.). The alum used was commercial "filter alum". Dilute sulfuric acid was added with the alum in amounts sufficient to give approximately the desired hydrogen-ion concentration. A constant acid dosage was usually maintained for a period of eight hours, after which time the pH value was found to become constant throughout the system; that is, from coagulating tank entrance to filter effluent. (The retention period of the coagulating tank was

7-8 hours). At the end of this time a sample of the effluent was taken for subsequent determination of residual alum. The acid dosage was then either increased or decreased and maintained at the new value for another period of eight hours before again sampling the effluent. The range of hydrogen-ion concentration in the effluent was from pH 3.2 to 7.3. Representative samples of the raw water passing into the system were collected during the usual eight-hour run for comparison with the effluent.

#### METHODS OF ANALYSIS.

At the time of sampling, determinations of alkalinity, free carbon dioxide, and turbidity were made according to Standard Methods of Water Analysis (110). Hydrogen-ion concentrations were determined by indicators according to Gillespie's table of drop ratios. Alumina was determined as in previous investigations (see above, pp. 53-56) on the basis of the following equation:



$R_2O_3$  being the total residue. The exceedingly small quantities of alumina present in the water made it necessary to take all possible precautions for accuracy, some of which are not observed in the mineral analysis as outlined in Standard Methods.

In order to obtain a suitable amount of alumina for analysis and to eliminate certain errors some modifications of the procedure as outlined in Standard Methods were necessary. A comparatively large quantity of water (2 liters) was used in each determination of  $Al_2O_3$ . Fused silica dishes were used for the evaporation. Evaporation to dryness and removal of silica required about five days. As some alumina or ion may be removed with the silica, the nonvolatile residue after the treatment with hydrofluoric acid was fused with potassium acid sulfate and added to the filtrate from the silica separation. The precipitation of the iron and aluminum was made according to the method outlined by Blum (12). The precipitate obtained was dissolved in hydrochloric acid and reprecipitated. It was found that silica was usually present to the extent of 10% of the total weight of residue after ignition, so that a volatilization with hydrofluoric acid was necessary to give the true weight of  $R_2O_8$ .

Iron was determined colorimetrically on the original sample according to Standard Methods. Phosphate was determined colorimetrically according to the method of Deniges (24)\*.

---

\*Editor's Note: See above, pp. 54 and So.

## RESULTS.

Tables I and II show determinations of pH value, alkalinity, and free carbon dioxide made at the time of sampling the effluent and raw water, and determinations of residual alum made subsequently according to the procedure outlined above.

Only on the first six runs, were samples of raw water analyzed for alumina, for the main object of the investigation was to show the relation of alumina in the effluent to the prevailing pH value in the acid range. It had been shown by previous investigations in this laboratory (see above, pp. 56-59) that the alumina content of the effluent was less than the alumina content of the raw water if the plant was operated under the most efficient conditions. This is true in samples No. 1 and 6, which, being taken at pH values of 7.3 and 6.0 respectively, are representative of practical operating conditions.

These data, showing the presence of an increasing amount of alumina with increasing hydrogen-ion concentration will be found plotted on the Composite Figure on page 11. The increase in alumina content from pH 6.6 to 3.5 seems to be fairly regular, but below pH 3.5 a small increase in hydrogen-ion concentration is accompanied by a very large increase in alumina content. As shown by previous investigations, the residual alum content in the zone of minimum solubility is not dependent on the hydrogen-ion concentration alone but is influenced by other conditions. There is a wide variation in residual alum between pH 5 and 7.3. The observation made by Gallaher and Buswell (see above, page 84) that the phosphate content of the raw water was for the most part removed by the purification process, has been here confirmed. The phosphate content of the effluent is either zero or very much lower than that of the raw water.

## SUMMARY.

Residual alum was determined gravimetrically in the effluent of an experimental water-filtration plant operating at various pH values throughout the acid range (pH 3.2 to pH 7.3), and was found to increase with increasing hydrogen-ion concentration.

TABLE I.

No.	ANALYSIS OF EFFLUENT OF EXPERIMENTAL PLANT							Alkalinity	
	A1203 ppm.	R203 ppm.	Fe203 ppm.	P205 ppm.	PH	Free CO, ppm.	M. O.	Phenol	
1	3.05	4.12	1.07		7.3		320	0.0	
2	.94	3.19	2.15	.1	6.6		198	0.0	
3									
4	5.78	23.00	17.16	.06	5.5		46	0.0	
5	3.99	11.90	7.87	.04	5.8		86.	0.0	
6	2.60	6.97	4.29	.08	6.0		152	0.0	
7	1.39	3.15	1.72	.04	6.1		180	0.0	
8	1.19	2.09	.86	.04	6.1	96	196	0.0	
9		1.25	1.57	0.00	5.9	94	170	0.0	
10	3.18	4.04	.86	0.00	5.7	130	100	0.0	
11					3.7	200	0.0	0.0	
12		2.63	7.72	0.00	5.3	180	48	0.0	
13	.63	6.35	5.72	0.00	5.1	250	24	0.0	
14	1.67	9.39	7.72	0.00	4.4	255	0.0	0.0	
15		1.27	3.43	0.00	5.8	146	94	0.0	
16	10.17	14.18	4.00	0.10	3.2	315	0.0	0.0	
17	7.90	12.48	4.58	0.00	3.3	275	0.0	0.0	
18	6.59	12.6	6.01	0.00	3.5	247	0.0	0.0	
19	4.98	8.98	4.00	0.00	4.5	250	14.0	0.0	
20	3.83	6.98	3.15	0.00	5.2	235	20.0	0.0	
21	5.57	7.14	1.57	0.00	4.8	235	18.0	0.0	

TABLE II.

ANALYSIS OF RAW WATER USED IN EXPERIMENTAL PLANT.  
(Free CO<sub>2</sub> Ranged From 8 to 21 p.p.m.)

No.	A1203 ppm.	R203 ppm.	Fe203 ppm.	P205 ppm.	pH	Alkalinity	
						M. O. ppm.	Phenol. ppm.
1	3.31	5.28	1.72	.25	7.5	340	0.0
2		3.90	5.00	.75	7.7	334	0.0
3	0.84	3.87	2.15	.88	7.7	344	0.0
4		4.05	3.58	.63	7.4	294	0.0
5	1.54	3.29	1.00	.75	7.5	332	0.0
6	2.84	4.61	1.14	.63	7.6	336	0.0

## BIBLIOGRAPH.

---

1. Abderhalden, E. (Bestimmung der Löslichkeit) Handbuch der biochemischen Arbeitsmethoden. *1*, 450-58 (1910).
2. Acree, S. F. and Brunei, R. F. On a New Method for the Preparation of Standard Solutions. *Am. Chem. Jour.* 36, 117-23 (1906).
3. Baldwin, F. O. Total Alumina in Water (Modified Atack's Method) Colorimetric Determination. *J. Am. Water Works Assoc.* 12, 439-40 (1924).
4. Banerji, N. L. The Influence of Hydrogen-Ion Concentration on the Dose of Alum and the Mechanism of the Action of Alum in the Clarification of Natural Waters. *Indian J. Med. Research* 11, 695-718 (1924).
5. Bartow, E. and Lindgren, J. M. Laboratory Experiments in Water Treatment. *Illinois State Water Survey Bull.* 6, 33-52 (1907).
6. Baylis, J. R. Use of Acids with Alum in Water Purification and the Importance of Hydrogen-Ion Concentration. *J. Am. Water Works Assoc.* 10, 365-92 (1923).
7. Baylis, J. R. Study of Flocculation Phenomenon with Microscope. *Eng. News-Record* 92, 768-69 (1924).
8. Baylis, J. R. Manganese in Baltimore Water Supply. *J. Am. Water Works Assoc.* 12, 211-233 (1924).
9. Biltz, W. and Krohnke, O. Ueber organische Colloide aus städtischen Abwassern und deren Zustandsaffinität. *Ber.* 37, 1745-54 (1904).
10. Bjerrum, N. Ueber die Elimination des Flüssigkeitspotentials bei Messungen von Elektropodenpotentialen. *Z. Elektrochem.* 17, 389-93 (1911).
11. Blum, W. The Constitution of Aluminates. *J. Am. Chem. Soc.* 35, 1499-1505 (1913).
12. Blum, W. The Determination of Aluminum as the Oxide. *J. Am. Chem. Soc.* 38, 1282-97 (1916).
13. Catlett, G. F. Colloidal Theories, Applied to Colored Water, Reduce Cost of Chemicals. *Eng. Record* 73, 741-42 (1916).
14. Catlett, G. F. Coagulation Control by Hydrogen-Ion Concentration. *J. Am. Water Works Assoc.* 10, 1923; *Eng. Contr.* 60, 281-85 (1924).
15. Catlett, G. F. Optimum Hydrogen-Ion Concentrations for Coagulation of Various Waters. *J. Am. Water Works Assoc.* 11, 887-95 (1924).
16. Chatterji, N. G. and Dhar, N. R. The Physics and Chemistry of Colloids and their Bearing on Industrial Questions. Some Observations on the Peptization and Precipitation. *Chem. News* 121, 253-56 (1920).
17. Clark, W. M. The Determination of Hydrogen Ions. Baltimore, 1920.
18. Clark, W. M. The Determination of Hydrogen Ions. Ed. 2, p. 161 (1922).
19. Clark, W. M. and Miller, L. B. Paper presented at Annual Convention of Am. Water Works Assoc, Detroit, May 1923. (Not printed. See Miller, 1923).

20. Cox, C. R. Alum Agitation Studies at Reading, Pennsylvania. Eng. News-Record 93, 101 (1924).
21. Dallyn, F. A. and Delaporte, A. V. Preparation of Water for Filtration. Can. Eng. 44, 474-76 (1923).
22. Daniels, F. E. Experiments in Water Coagulation with Aluminum Sulfate. Eng. News-Record 91, 93 (1923).
23. Delaporte, A. V. and Burn, G. A. H. Study of Pretreatment of Thames River Water at Chatham. Provincial Board of Health of Ontario, Canada, 42nd Ann. Rept. 151-68 (for 1923).
24. Deniges, G. Reaction de Coloration extrême ment sensible des Phosphates et des Arsé niates. Academie des sciences: Compt. rend. 171, 802-4 (1920); Chem. Abs. 18. 3093 (1924).
25. Dupre, jun. and Bialas, J. Zur Bestimmung der Löslichkeit von Magnesia und Zinkoxyd in Wasser auf Grund des elektrischen Leitvermögens. Z. angew. Chem. 1903, pp. 54-55.
26. Eddy, H. P. The Significance of "Hydrogen-ion Concentration" in Water Purification. Eng. Cont. 56, p. 354-55 (1921).
27. Edwards, G. P. and Buswell, A. M. Some Facts about Residual Alum in Filtered Water. Chem. Met. Eng. 26, 826-29 (1922).
28. Ellis, J. H. The Free Energy of Hydrochloric Acid in Aqueous Solution. J. Am. Chem. Soc. 38, 737-62 (1916).
29. Ellms, J. W. Water Purification. McGraw-Hill Book Co., New York (1917).
30. Ellms, J. W. and Marshall, L. A. Second Annual Report of Ohio Conference on Water Purification, p. 114 (1922).
31. Fales, H. A. and Vosburgh, W. C. Planck's Formula for the Potential Difference between Solutions and the Values of Certain Important Cells. J. Am. Chem. Soc. 40, 1291-1316 (1918).
32. Fales, H. A. and Mudge, W. A. A Study of the Saturated Potassium Chloride Calomel Cell. J. Am. Chem. Soc. 42, 2434-53 (1920).
33. Gammage, A. L. Prechlorination-alum Treatment of Soft Colored Water. Eng. News-Record 50, 291-92 (1922).
34. Gibson, G. H. The Hot-Process Water Softener. Chem. Met. Eng. 22, 899-902 (1920).
35. Gleeson, M. R. and Gleeson, F. M. A Study of the Lime-Soda Ash Water-Softening Process. Chem. Met. Eng. 22, 269 (1920).
36. Gmelin Kraut, Handbuch der anorganischen Chemie, Ed. 7, 2, pt. 2, p. 390 (1909).
37. Goudriaan, F. Aluminates of Sodium. Equilibria in the System  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ . Proc. K. Akad. Wetensch. 23, 129-42 (1900; J. Soc. Chem. Ind. Abstr. 39, 747 (1920).
38. Greenfield, R. E. and Baker, G. C. The Relationship of the Hydrogen-Ion Concentration of Natural Waters to the Carbon Dioxide Content. J. Ind. Eng. Chem. 12, 989-91 (1920).
39. Greenfield, R. E. and Bartow, E. Note of a New Indicator in Water Analysis. Trans. Ill. Acad. Science 13, 326-29 (1920).
40. Greenfield, R. E. and Buswell, A. M. Investigation by Means of the Hydrogen Electrode of the Chemical Reactions. Involved in Water Purification. J. Am. Chem. Soc. 44, 1435-42.(1922).

41. Greth, J. C. W. Time, Temperature and Composition as Factors in Softening Water. *J. Ind. Eng. Chem.* 3, 13-15 (1911).
42. Grobet, E. Sur les Reactions de la Soude Caustique avec les Sels d'Aluminium. *J. chim. phys.* 19, 331-35 (1921).
43. Hatfield, W. D. Relation of Hydrogen-Ion Concentration to Filter-Plant Operation. *J. Ind. Eng. Chem.* 14, 1038-40 (1922).
44. Hatfield, W. D. Soluble Aluminum and the Hematoxylin Test in Filtered Waters. *J. Ind. Eng. Chem.* 10, 233-34 (1924).
45. Hatfield, W. D. Hydrogen-Ion Concentration and Soluble Aluminum in Filter Plant Effluents. *J. Am. Water Works Assoc.* 11, 554-63 (1924).
46. Herz, W. and Muhs, G. Ueber das Gleichgewicht  $Mg(OH)_2 + 2 NH_4Cl \rightleftharpoons MgCl_2 + 2 NH_4OH$ . *Z. anorg. Chem.* 38, 138-41 (1904).
47. (a) Heyrovsky, J. The Electroaffinity of Aluminum. I. The Ionization and Hydrolysis of Aluminium Chloride. *J. Chem. Soc.* 117, 11-26 (1920).
47. (b) Heyrovsky, J. The Electroaffinity of Aluminum. III. The Acidity and Constitution of Aluminic Acid. *J. Chem. Soc.* 117, 1013-25 (1920).
48. Hildebrand, J. H. Some Applications of the Hydrogen Electrode in Analysis, Research, and Teaching. *J. Am. Chem. Soc.* 35, 847-71 (1913).
49. Hillebrand, W. F. The Analysis of Silicate and Carbonate Rocks. *U. S. Geol. Survey Bull.* 700 (1919).
50. Hoover, C. P. Water Softening Can Be Accomplished at Small Cost. *Fire and Water Eng.* 73, 623-24 and 636-39 (1923).
51. Howard, N. J. Recent Progress in Water Purification. *Contr. Record* 38, 1292-94 (1924).
52. Hopkins, E. S. Experiments on Formation of Flocculation. *Eng. News-Record* 90, 204-205 (1923).
53. Hopkins, E. S. Composition of Alum Flocculation in Mixing Basin. *J. Am. Water Works Assoc.* 12, 405-409 (1924).
54. Howard, N. J. and Hannan, F. Alumina Hydrate in Mechanically Filtered Water. *Can. Eng.* 38, 461-62 (1920).
55. Johnston, J. Solubility-Product Constant of Calcium and Magnesium Carbonates. *J. Am. Chem. Soc.* 37, 2001-20 (1915).
56. Johnston, J. The Determination of Carbonic Acid, Combined and Free, in Solution, Particularly in Natural Waters. *J. Am. Chem. Soc.* 38, 947-75 (1916).
57. Johnston, J. and Williamson, E. D. The Complete Solubility Curve of Calcium Carbonate. *J. Am. Chem. Soc.* 38, 975-83 (1916).
58. Jordan, H. E. Fifteen Years Filtration Practice in Indianapolis. *Proceedings Indiana Sanitary and Water Supply Assn. Thirteenth Ann. Convention.* pp. 126-89 (1920).
59. Kendall, J. Solubility of Calcium Carbonate in Water. *Phil. Mag.* 23, 958-76 (1913).
60. Kendall, J. The Specific Conductivity of Pure Water in Equilibrium with Atmospheric Carbon Dioxide. *J. Am. Chem. Soc.* 38, 1480-97 (1916).
61. Kohlrausch, F. and Rose, F. Die Löslichkeit einiger schwer löslicher Körper im Wasser, beurteilt aus der elektrischen Leitungsfähigkeit der Lösungen. *Z. physik. Chem.* 12, 234-43 (1893).



62. Kolthoff, I. M. De Titratie van Koolzuur en zign Zouten. *Chem. Weekblad* 14, 781-93 (1917); *C. A.* 11, 3454 (1917).
63. Langelier, W. F. Coagulation of Water with Alum by Prolonged Agitation. *Eng. News-Record* 86., 924-28 (1921).
64. Lewis, G. N., Brighton, T. B. and Sebastian, R. L. A Study of Hydrogen and Calomel Electrodes. *J. Am. Chem. Soc.* 39, 2245-61 (1917).
65. Lewis, W. C. A System of Physical Chemistry. Ed. 1, Vol. I, p. 28 (1916).
66. Loeb, J. Amphoteric Colloids. *J. General Physiol.* 1, 39-60 (1918-19).
67. Loeb, J. The Proteins and Colloid Chemistry. *Science* 75, 449-56 (1920).
68. Longley, P. F. The Water Supply of Salem and Beverley. *J. New Eng. Water Works Assoc.* 30, 35-45 (1916).
69. Loven, J. M. Chemisches Gleichgewicht in ammoniakalischen Magnesiumsalzlosungen. *Z. anorg. Chem.* 11, 404-15 (1896).
70. McClendon, J. F. The Standardization of a New Colorimetric Method for the Determination of Hydrogen-Ion Concentration, Carbon Dioxide Tension, and Carbon Dioxide and Oxygen Content of Sea Water, of Animal Heat and of Carbon Dioxide of the Air, with a Summary of Similar Data on Bicarbonate Solution in General. *J. Biol. Chem.* 30, 265-88 (1917).
71. McCoy, H. N. Equilibrium in the System Composed of Sodium Carbonate, Sodium Bicarbonate, Carbon Dioxide and Water. *Am. Chem. J.* 29, 437-62 (1903).
72. Mahin, E. G., Ingraham, D. C. and Stewart, O. J. The Constitution of Aluminates. *J. Am. Chem. Soc.* 35, 30-39 (1913).
73. Mason, W. P. Examination of Water, Chemical and Bacteriological. Ed. 5 (1917).
74. Massink, A. and Heyman, J. A. Significance of Hydrogen-Ion Concentration in Drinking Water and Particularly for the Business of Water Supply. *J. Am. Water Works Assoc.* 5, 239-72 (1921).
76. Mellor, J. W. A Treatise on Quantitative Inorganic Analysis pp. 216-18 (1913).
77. Mellor, J. W. Higher Mathematics for Students of Chemistry and Physics. Ed. 4, p. 523 (1913).
78. Miller, L. B. On the Composition of the Precipitate from Partially Alkalinized Alum Solutions. *U. S. Pub. Health Reports* 38, 1995-2004 (1923).
79. Miller, L. B. A Study of the Effects of Anions upon the Properties of Alum Flocc. *U. S. Pub. Health Reports* 40, 351-67 (1925).
79. (a) Miller, L. B. Notes on the Clarification of Colored Waters. *U. S. Pub. Health Reports* 40, 1472-81 (1925).
80. Morey, G. W. Benzoic Acid as an Acidimetric Standard. *U. S. Bureau of Standards. Bull.* 8, 643-50 (1912); *Sci. Paper No.* 183.
81. Morison, J. Dose of Alum for the Clarification of Water by Precipitation. *Indian J. Med. Research* 3, 565-613 (1916).
82. Mortensen, F. C. Hydrogen-Ion Concentration and Water Purification. *Eng. Contr.* 58, 160-2 (1922).
83. Mortensen, F. C. Hydrogen-Ion Concentration and Water Purification At Cedar Rapids, Iowa. *J. Am. Water Works Assoc.* 13, 33-38 (1925).

84. Norcom, G. D. Purification of Colored Water at Wilmington, N. C. *J. Am. Water Works Assoc.* *11*, 96-117 (1924).
85. Norcom, G. D. Efficiency of the Improved Water-Purification Plant at Wilmington, N. C. *J. Am. Water Works Assoc.* *11*, 833-39 (1924).
86. Olsen, J. C. *Quantitative Chemical Analysis* p. 112 Ed. 3 (1908).
87. Petit, P. The Reactions of Some Salts in Boiling Water. *Mon. sci.* (5), *4*, 537-41 (1914); through *C. A.* *9*, 1082-83 (1915).
88. Pirnie, M. Colloid Chemistry and Water Filtration. *Can. Eng.* *41*, Nos. 19 and 20 (1921) *J. Am. Water Works Assoc.* *9*, 247-73 (1922).
89. Pirnie, M. Aeration of Water Immediately after Alum Dose Saves Soda. *Eng. News-Record* *90*, 883-84 (1923).
90. Preu, B. Fortschritte in der Reinigung von Kesselspeisewassern. *A. angew. Chem.* *33*, Aufsatzteil 61-63, 70-72 (1920); Reinigung des Kesselspeisewassers. *Z. angew. Chem.* *34*, Aufsatzteil 67 (1921).
91. Prideaux, E. B. R. The Theory and Use of Indicators, p. 358 (1917).
92. Race, J. Color in Water: Its Nature and Removal. *J. Soc. Chem. Ind.* *40*, 159-62T (1921).
93. Richards, Mrs. Ellen H. A Delicate Test for Alum in Potable Water. *Tech. Quart.* *4*, 194-95 (1891).
94. Richter, V. v. Chemie der Kohlenstoffverbindungen oder organische Chemie. Ed. 11, 2 vol. (1909).
95. Rideal, S. and Rideal, E. K. The Nature of the Colloidal Matter. *Water Supplies*, London, p. 100-102 (1915).
96. Russ, F. Über Tonerhydrat. *Z. anorg. Chem.* *41*, 216-30 (1904).
97. Sand, J. Die Stärke der unterchlorigen Säure. *Z. physik. Chem.* *48*, 610-14 (1904).
98. Saville, T. On the Nature of Color in Water. *J. New Eng. Water Works Assoc.* *31*, 78-103 (1917).
99. Sayler, C. A. and Lloyd, P. V. Studies of the Carbonates. Parts II and III. *J. Chem. Soc.* *111*, 138-58, 994-1001 (1917).
100. Schlumberger, E. Sur quelques Composés aluminiques. *Bull. soc. chim.* (3) *13*, 41-65 (1895).
101. Schmitz, B. Veber die Bestimmung der Phosphorsäure als Magnesiumpyrophosphat. *Z. anal. Chem.* *1,5*, 512-22 (1906).
102. Slade, R. E. Über Natriumaluminatlösungen. *Z. Electrochem.* *17*, 261-65 (1911).
103. Smith, A. Introduction to Inorganic Chemistry, Ed. 3, pp. 372-407, New York, 1917.
104. Smith, O. M. Silicic Acid, Its Influence and Removal in Water Purification. *Illinois State Water Survey, Bull.* *16*, 140-81 (1919).
105. Smith, O. M. The Coagulation of Clay Suspensions and Silicic Acid. *J. Am. Chem. Soc.* *42*, 460-72 (1920).
106. Snook, J. D. and Bartow, E. The Use of Barium Salts in Water Treatment, and the Application of the Hydrogen Electrode to Water Analysis. *University of Illinois Thesis* (1915). (Not printed).
107. Sorensen, S. P. L. Etudes enzymatiques; II. Sur la mesure et l'importance de la concentration des ions hydrogène dans les réactions enzymatiques. *Compt. rend. Lab. Carlsberg*, *S*, 1-168 (1909-1910):
108. Sorensen, S. P. L. and Linderstrom-Lang, K. The Determination and Value of Pro in Electrometric Measurements of Hydrogen-Ion Concen-

- trations. *Compt. rend. trav. ab. Carlsberg 15*, No. 6, 40 pp. (1924); through *C. A. 19*, 21-22 (1925).
109. Standard Methods of Water Analysis. Am. Pub. Health Assoc. Ed. 4 (1920).
  110. Standard Methods of Water Analysis. Am. Pub. Health Assoc. Ed. 5 (1923).
  111. Taylor, W. W. *The Chemistry of Colloids*, p. 171, Ed. 2 (1915).
  112. Theriault, E. J. and Clark, W. M. An Experimental Study of the Relation of Hydrogen-Ion Concentrations to the Formation of Flocc in Alum Solutions. U. S. Pub. Health Reports 35, 181-98 (1923).
  113. Tillmans, J. Uber die quantitative Bestimmung der Reaktion in natürlichen Wassern. *Z. Nahr. Genussm.* 35, 1-16 (1919).
  114. Treadwell, P. P. Zur Nichtfallbarkeit des Magnesiums durch Ammoniak bei Gegenwart von Ammonsalzen. *Z. anorg. Chem.* 37, 326-31 (1903).
  115. Van de Sande Bakhuyzen, W. H. De Waterstofionen-concentratie eener Waterige Oplossing van een Amphoteer Oxyd. *Chem. Weekblad 19*, 41-43 (1922).
  116. Van't Hoff, J. H. *Lectures on Theoretical and Physical Chemistry. I. Chemical Dynamics*, p. 227 (1898).
  117. Veatch, N. T., Jr. Purification Problems of a Turbid Water Supply. *Fire & Water Eng.* 77, 13-4 (1925); *Pub. Health Eng. Abstracts* Mar. 7, 1925.
  118. Veatch, N. T., Jr. Operation Results at the Water-Purification Plant at Topeka, Kansas. *J. Am. Water Works Assoc.* 13, 439-48 (1925).
  119. Wagner, A. and Euslow, L. H. Applied Hydrogen-Ion Concentration—A Study of its Merits in Practical Filter—Plant Operation. *J. Am. Water Works Assoc.* 9, 373-91 (1922).
  120. Walker, J. The State of Carbon Dioxide in Aqueous Solution. *J. Chem. Soc.* 38, 182-84 (1903).
  121. Walker, J. and Cormack, W. The Dissociation Constants of Very Weak Acids. *J. Chem. Soc.* 77, 5-21 (1900).
  122. Walpole, G. S. Gas Electrode for General Use. *Biochem. J.* 7, 410-28 (1913).
  123. Washburn, E. W. The Theory and Practice of the Iodometric Determination of Arsenious Acid. *J. Am. Chem. Soc.* 30, 31-46 (1908).
  124. Washburn, E. W. The Significance of the Term Alkalinity in Water Analysis and the Determination of Alkalinity by Means of Indicators. *Proc. Illinois Water Supply Assoc.* 2, 93-101 (1910).
  125. Wells, R. C. Solubility of Magnesium Carbonate in Natural Waters. *J. Am. Chem. Soc.* 37, 1704-08 (1915).
  126. Williamson, F. S. Basic Aluminum Sulfate. *J. Phys. Chem.* 27, 284-89 (1923).
  127. Wolman, A. and Hannan, F. Residual Aluminum Compounds in Water Filter Effluents. *Chem. Met. Eng.* 24, 728-34 (1921).
  128. Wolman, A. and Hannan, F. Further Observations on pH in Natural Waters. *Chem. Met. Eng.* 25, 502-06 (1921).
  129. Wood, J. K. Amphoteric Metallic Hydroxides. *J. Chem. Soc.* 93, 411-23 (1908).
  150. Wood, J. W. Note upon the Rate of Softening by the Lime-Soda Process. *J. Soc. Chem. Ind.* 36, 1256-58 (1917).