A STUDY OF THE MECHANISM OF WATER SOFTENING WITH LIME

THESIS FOR THE DEGREE OF B. S.

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A Study of the Mechanism of
Water Softening with Lime

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By

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Candidate for the Degree of

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Alfred M. F. Johnson

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MECHANISM OF WATER SOFTENING WITH LIME

Hardness in water is defined as that quality of the water which produces a curd of insoluble material when used with soap and which produces a scale when used in heating and power equipment. It is due to the presence of salts of calcium and magnesium.

It has long been recognized that all water supplies are not of the same quantity of hardness. Some waters are what is called hard and others are known as soft waters. This is only one of many general classifications of water. A further classification, and one which gives a more comprehensive idea of the waters in question, is the grouping of them by the sources of supply, of which the principal ones are as follows:

SOFT WATERS

Rain Water-

Rain water is seldom pure because in its descent through the atmosphere to the earth it takes up soluble gases, carbonic acid, dirt, dust, etc. In manufacturing districts, especially near smelters and chemical plants, the quantity of such materials may be large.

Snow Water-

Snow water is practically the same as rain water, the chief difference being in the temperature at the time of precipitation.

Surface Water-

Surface water is rain water and water condensed from the atmosphere which has run over the surface of the ground and taken up impurities. It may contain some ground water.

River Water-

River water is surface water which has run off from the earth to its natural channel on its way to the ocean. It usually contains ground water. Usually it is contaminated by organic matter such as leaves, coloring matter, etc., as well as soluble mineral matter. The quantity of these materials carried by river water depends upon the location of the stream and its source. Many rivers are used for the disposal of sewage and industrial wastes and may become highly contaminated.

Lake Water-

Lake water is practically the same as river water. It may contain a greater percentage of ground water than the rivers if it be from what is called "a spring-fed lake." Lakes, especially the smaller inland lakes, usually do not receive as much sewage or industrial wastes because there is less movement of the water in a lake than in a river and the use of the lake as a means of disposal would soon create a nuisance, both from the aesthetic and the sanitary viewpoint.

The above water supplies are generally considered as being soft water supplies except where ground water may have become mixed with surface, river, or lake water and caused the resultant water to become hard.

Hard Waters

Ground Water-

Ground water is water which comes out of the earth. It often contains gaseous materials (principally carbon dioxide) given off by decaying vegetable matter. The carbonic acid, which is produced when carbon dioxide dissolves in water, dissolves the limestone in the earth and causes the water to become hard.

Ground water may come from artesian wells and springs or may be pumped from the ground. The source of this water may be either in the surface subsoil or in the underlying rock. Ground waters in general are much harder than surface waters.

Hardness in water is divided into two classes--temporary and permanent;

Temporary Hardness

Temporary hardness is that hardness which is removable by boiling the water. It is caused by the presence of bicarbonate of calcium. Upon boiling the calcium is precipitated from solution in the form of calcium carbonate.

Permanent Hardness

Permanent hardness is that hardness which is not removable by boiling. It is due chiefly to the presence of sulfates and chlorides of calcium and magnesium.

In order that these hardness-causing compounds and their actions may be better understood, a brief discussion of each of the principal ones follows:

Calcium carbonate, ($Ca\ CO_3$), commonly known as limestone, marble, or chalk, does not form a hard scale in boilers and heating equipment but causes much of the soft mud found in the bottoms of these units. In combination with other substances, however, it may form a very hard scale. It is readily soluble in carbonic acid or in water containing carbonic acid gas, (CO_2). Carbonic acid is driven off when the temperature of the water reaches about 200 F. and the calcium carbonate is precipitated.

Magnesium carbonate, ($Mg\ CO_3$), is a toilet preparation, its common form being more soluble in water than calcium carbonate. It is held in solution be carbonic acid and may be precipitated by the use of slaked lime. It precipitates out in boilers as magnesium hydrate and magnesium oxide. The scale formed is a very good non-conductor and is used as an insulating covering for boilers and pipes. This shows the scale to be exceptionally undesirable.

Calcium sulfate (gypsum) forms the hardest form of scale of these encountered in water supplies. It sticks tightly to the walls of the boilers and is also a very poor conductor of heat, causing a tremendous waste of heat in boiler operation.

Magnesium sulfate, ($Mg\ SO4$), or epsom salt, is very easily soluble in cold or warm water. It does not form scale in boilers but when broken up by lime salts, it forms a scale composed of magnesium and calcium sulfate. It has a very corrosive action on boiler iron and fittings.

Calcium chloride ($CaCl_2$) is very soluble in natural water. It is corrosive but does not form a scale unless in combination with $MgSO_4$ when it causes a hard scale to form due to a transfer of acids and in addition forms magnesium chloride which is very corrosive.

Magnesium chloride is very corrosive in boiler water, causing pitting and grooving. It is very soluble in water and is the destructive element in sea water. It is usually found to accompany sodium chloride when the latter is found in a natural water supply.

Carbon dioxide (CO_2) is a gas found in all natural waters. It forms carbonic acid with water which increases the solubility of calcium and magnesium carbonates and is also favorable to pitting and corrosion. It can be completely removed.

The above described compounds are the principal offenders in causing water to be hard. There are other objectionable compounds, as of iron, aluminum, etc. present in water, but they are usually present in such small quantities as to be insignificant from the standpoint of hardness. They are usually objectionable because of coloring the water or because of the staining of fixtures. The process of removing them will not be considered here except to mention that it is possible and is practiced in some cases.

While the chief objection to hard water ariees from the fact that it causes an excessive amount of soap to be used in the ordinary processes of washing in the toilet, kitchen and laundry, there are several conditions in industry where soft, pure water is not only a matter of economy but an actual necessity. A few of the more important of these cases will be mentioned here.

Water for Concrete and Construction Work-

This water, while not required to be soft, should be free from all oil, acids, strong alkalies and vegetable or organic matter. Under certain conditions and within limits the presence of sodium or calcium chloride may be favored as an aid to the curing of concrete in cold weather. The use of such a water is a matter of debate among engineers and in case of its use, it should be thoroughly analyzed before using.

Water in Brewing-

Brewing is a revived industry in this country. Soft water aids in hte preparation of malt and adds to the clearness of beer. For brewing purposes the water should be colorless, odorless, insipid and free from organic material. Mineral salts, in general, are harmful although some help the quality of beer. Sulfates and a very small percentage of salt are generally to be preferred in the water used. Too much salt or carbonates of calcium or magnesium give a bitter taste to beers and ales.

Water in Dyeing and Bleaching-

These industries are especially particular about the quality of the water they use. Certain dyes and dyestuffs require that the water used be of a certain quality and this same water may be absolutely worthless for use with some other dyes and may even cause a complete change of color of the dye. In general, hard water has a tendency with alizarine, direct and basic, dyes to throw down the color itself as an insoluble precipitate and when iron is present, it causes red stains. Hard water used to wash off the loose dyes, and to which no corrective can be applied also has an injurious effect on the fiber and colors of the cloth being treated.

Water in the Tanning Industry-

Quicklime and water are first used to get the roots of the hair out of the leather hide. Water containing calcium carbonate is not good for this purpose, as it prevents the absorption of the tannin, and may also cause brownish stains. Magnesium carbonate acts in a very similar manner. Calcium and magnesium sulfates are very desirable, and in fact, are necessary to the tanning water. Carbonic acid is also very advantageous.

Water in Ice-making-

Ice to be used for cooling and which will eventually be taken internally should be pure bacteriologically. This type of purification is again outside the scope of this work and will only be mentioned at this time. However, it is desirable to have the water used for ice-making colorless and odorless. It is also usually desirable that it contain a moderate amount of air and mineral matter.

Water in Paper-making-

Paper making requires a large amount of high quality water. Fine papers require a water free from suspended or dissolved matter. The Chinese have for centuries prepared their water for paper making by adding alum to coagulate the suspended and colloidal matter. The use of waters containing iron salts results in a brown coloring, and lime and magnesium compounds interfere with the process of sizing the paper. This effect is more noticeable with the vegetable size now used than with the animal size formerly in use.

Water for Heating and Power Equipment-

The effect of hard waters on boilers has been discussed before in this work. It should be noted that in the case of railroad locomotives with clean boilers when using hard water required calking at the end of the third week and also needed thirty-three calkings in seven months, at which time the flues were worn out. After changing to soft water the same locomotives required only six calkings in fifteen and one-half months.

Water in Sugar Refining-

Sugar syrups are filtered through animal charcoal and if calcareous water is used to wash the charcoal filter the charcoal soon loses its good qualities. Magnesium chloride is especially bad in sugar making as hydrochloric acid is liberated which would soon cause trouble.

From the preceding discussion it is evident that "soft" water, either natural, as rain water, or a softened water is essential for best and most economical use in industry and the home.

The supply of natural rain water is quite obviously limited and of both uncertain quality and quantity. Hence, practically all the water used must be a treated, or softened water.

It must be remembered that a hardness of zero p.p.m. (parts per million) of hardness is not as desirable as the foregoing discussion would seem to indicate. Water of zero p.p.m. of hardness is undesirable in many cases because it makes it difficult to rinse soap from the hands or from clothes being laundered. Neither is it economically practical to soften the water supply for a city to zero p.p.m. of hardness, due to the fact that it is quite difficult to remove the last few degrees of hardness. Water having from 50-75 p.p.m. of hardness is usually considered as being soft enough for a public water supply. If the water is of from 75-150 p.p.m. of hardness it would be considered moderately hard but would still not be unduly hard or interfere with its use for most purposes or arouse a demand for softening. Hardness of more than 150 p.p.m. is noticed by nearly everyone and will likely arouse a public demand for softening.

Municipal softening may be done by either of two common methods;

(1) One is zeolite sand softening, in which an exchange of the sodium in the sand and the calcium and magnesium in the water takes place. This method is capable of removing <u>all</u> the calcium and magnesium hardness and it also removes

the iron. It is satisfactory and economical to use for small to medium-sized water supplies.

(2) The other is lime, or lime and soda, softening, which is better adapted to large supplies than is zeolite and hence is more often used for municipal treatment of water supplies.

There is a method of softening by removal of the temporary hardness by heat but it is used only in special cases and, for obvious reasons, only on small supplies. It is used in some boiler installations and under similar circumstances.

DISCUSSION OF THE PROBLEM

For my problem I chose to make a study of the softening of water by the use of lime (as $Ca(OH)_2$) alone, without the addition of soda ash (sodium carbonate) and to observe the results obtained by the different percentages of the theoretical 100 % softening by the lime. In other words, to determine the mechanism of the lime softening reaction.

The equations expressing the reactions occurring when lime is added to remove calcium and magnesium from water are as follows:

(1) $Ca(HCO_3)_2 + Ca(OH)_2 = 2\ CaCO_3 \downarrow + 2\ H_2O$

(2) $Mg(HCO_3)_2 + Ca(OH)_2 = MgCO_3 + CaCO_3 \downarrow + 2\ H_2O$

(3) $MgCO_3 + Ca(OH)_2 = Mg(OH)_2 \downarrow + CaCO_3$

(4) $MgSO_4 + Ca(OH)_2 = Mg(OH)_2 \downarrow + CaSO_4$

(5) $MgCl_2 + Ca(OH)_2 = Mg(OH)_2 \downarrow + CaCl_2$

The first equation shows the reaction of calcium (as calcium bicarbonate) with lime resulting in precipitation of the normal carbonate ($CaCO_3$). The removal is not complete because $CaCO_3$ is soluble to the extent of about 15 p.p.m. The other equations show the removal of magnesium by precipitation as magnesium hydroxide. If insufficient lime is added, $MgCO_3$, a soluble compound, is formed as shown in equation (2). The use of sufficient lime results in the formation and precipitation of $Mg(OH)_2$ as shown in equations (3), (4), and (5). From these equations it will be seen that twice as much lime is needed to remove magnesium bicarbonate as to remove calcium bicarbonate.

The lime also reacts with any free carbon dioxide (CO_2) present as follows:

$$CO_2 + Ca(OH)_2 = CaCO_3\downarrow + H_2O$$

Lime is, therefore, required, (1) to react with all of the bicarbonate present in the water, and (2) to react with the magnesium in any form, and (3) to react with the free CO_2.

To calculate the amount of lime required for the softening reaction it is necessary to make certain chemical tests. The tests needed are (1) free carbon dioxide (CO_2); (2) alkalinity; (3) non-carbonate (incrustant) hardness; (4) calcium; and (5) magnesium. These tests are made as follows:

(1) Free Carbon Dioxide

Fill a 100 ml. Nessler tube to the mark with the freshly taken sample.

Add 10 drops of phenolphthalein indication.

Titrate rapidly with N/44 sodium hydroxide.(NaOH) from a burette, stirring gently, until a slight permanent pink color appears. Record the number of ml. of NaOH used.

$$\text{Ml. of N/44 NaOH} \times 10 = \text{p.p.m. } CO_2$$

This test was not made in the course of this work because of the fact that the sample of water stood for some time in the laboratory. This test for CO_2 should be made at the time the sample is taken because the gas escapes when the water stands for any length of time unless the sample bottle be kept tightly stoppered and at a temperature lower than at which the sample was collected.

(2) Alkalinity

Pipette 100 ml. of the sample into one Erlenmeyer flask and the same quantity of distilled water into another.

Add four drops of phenolphthalein indicator to each.

If the sample becomes pink, add 0.02 N. sulphuric acid from a burette until the pink color just disappears and record the number of ml. of acid used.

Add two drops of methyl orange indicator to each flask.

If the sample becomes yellow, add 0.02N sulphuric acid until the first difference in color is noted when compared with the distilled water. The end point is orange. Record the number of ml. of acid used.

Calculations for alkalinity titrations are made as follows, giving all results in p.p.m. as $CaCO_3$:

Let P = ml. of 0.02 N sulphuric acid used for the titration with phenolphthalein and T = the ml. of the acid used for the total titration (phenolphthalein plus methyl orange).

There are five possible conditions as follows:

1. P = T

   Hydroxide (p.p.m.) = P X 10

2. P greater than ½ T

   Hydroxide (p.p.m.) = (2P - T) X 10

   Normal carbonate (p.p.m.) = 2(T - P) X 10

3. $P = \frac{1}{2} T$

   Normal carbonate (p.p.m.) = T X 10

4. P less than $\frac{1}{2}$ T

   Normal carbonate (p.p.m.) = 2P X 10

   Bicarbonate (p.p.m.) = (T - 2P) X 10

5. P = 0

   Bicarbonate (p.p.m.) = T X 10

(3) Non-Carbonate Hardness

The carbonate and non-carbonate hardness may be calculated from the results of the alkalinity and total hardness determinations.

Calculations-

Carbonate hardness:

Let p.p.m. normal carbonate alkalinity - p.p.m. bicarbonate alkalinity = S.

Case I. Where S is equal to or less than the total hardness, then S = carbonate hardness.

Case II. Where S is greater than the total hardness then the total hardness = the carbonate hardness.

Non-carbonate hardness:

P.p.m. total hardness - p.p.m. carbonate hardness = p.p.m. non-carbonate hardness.

(4) Calcium

Evaporate to dryness, in an evaporating dish on a water bath, 250 ml. of the well mixed sample to which a few drops of concentrated hydrochloric acid have been added. Moisten the residue with a few drops of concentrated hydrochloric acid.

Add 30 ml. of distilled water and heat to boiling.

Filter, rinse the dish and wash the residue on the paper with distilled water, adding the filtered rinsings and washings to the filtrate, but keeping the volume small.

Add a few drops of bromine water to the filtrate and boil gently for 5 minutes.

Add 10 ml. of a 10 % solution of ammonium chloride, make alkaline to litmus with concentrated ammonium hydroxide and boil gently for a few minutes.

Filter, rinse the beaker and wash the precipitate on the paper with small portions of distilled water, adding the filtered rinsings and washings to the filtrate.

Warm the filtrate and add slowly, with constant stirring, 10 ml. of saturated ammonium oxalate.

Allow to stand for 30 minutes in a warm place.

Filter through a quantitative filter paper, rinsing the beaker and paper with small portions of hot distilled water. The filtrate from this filtration is saved for the magnesium determination.

Place the original beaker from which the filtration was made under the funnel and, piercing a hole in the filter paper in the funnel, wash the precipitate into the beaker, using about 30 ml. of 2 % (2 ml. of concentrated acid per 100 ml.) sulphuric acid.

Heat to boiling and add from a burette a standard solution of potassium permanganate until the first permanent pink color is obtained.

Transfer the filter paper to the beaker and continue the titration with potassium permanganate to the first permanent pink color. Record the total ml. of permanganate used.

Ml. of KM_nO_4 X 10 = p.p.m. calcium (Ca).

(5) Magnesium

Use the filtrate which was saved in the calcium determination and continue as follows-

Add an amount of concentrated ammonium hydroxide to the filtrate equal to about 1/9 its volume and then add 10 ml. of a 10 % solution of disodium phosphate. Stir the solution vigorously for five minutes.

Allow to stand at least four hours, and filter the precipitate and several rinsings of the beaker onto a quantitative filter paper, being sure that all of the precipitate is transferred to the paper.

Wash with small portions of dilute ammonia water.

Ignite, cool and weith a weigh a clean crucible.

Transfer the folded filter paper containing the magnesium precipitate to the crucible.

Ignite until almost white, cool in a dessicator and weigh.

Gain in wt. (grams) X 873.6 = p.p.m. Mg.

After making the required analytical tests as described above the next step in the calculation of the lime necessary is to convert the values of the bicarbonate alkalinity and magnesium into a common unit of measure to furthur facilitate computations. It was decided to use the equivalent values as p.p.m. of $CaCO_3$. The alkalinity results were already given as converted to p.p.m. of $CaCO_3$ in the statement of results. Also the molecular weight of $CaCO_3$ is 100.08 amd this makes a very convenient number to use in computations, as will be seen presently.

To convert p.p.m. of Mg (as Mg) to p.p.m. of Mg (as $CaCO_3$) it is necessary to multiply the p.p.m. of Mg (as Mg) by the fraction whose numerator is the molecular wieght of the equivalent compound sought ($Ca\ CO_3$) and whose denominator is the molecular weight of the known material (Mg). The molecular weight of Mg is 24.32. Hence to convert Mg (as Mg) to Mg (as $CaCO_3$) it is necessary to multiply the value obtained in the analysis for Mg by $\frac{100.08}{24.32}$.

After converting the Mg values to equivalent $CaCO_3$, the amounts of $CaCO_3$ for the bicarbonate alkalinity and the Mg are added together. This gives the total value of alkalinity and Mg reacting with the $Ca(OH)$ during the softening reaction.

The quantity of $Ca(OH)_2$ required is computed in a similiar manner as above described for converting the Mg to ~~O~~equivalent $CaCO_3$. The molecular weight of $Ca(OH)_2$ is 74.10 and the conversion fraction here becomes $\frac{74.10}{100.08}$. The result of this computation will be in p.p.m. of <u>pure</u> calcium hydroxide.

Since the $Ca(OH)_2$ obtained commercially is not pure the amount of $Ca(OH)_2$ required by the above calculations should be multiplied by $\frac{100}{\text{per cent } Ca(OH)_2 \text{ in the calcium hydrocide used}}$,

If the above calculations are carried out using p.p.m. of the hardness and the rest of the work is carried out in the metric system, the resultant answer will be the amount (in grams) of commercial calcium hydroxide required to bring about a theoretical 100% lime softening in a one liter sample of water.

Having calculated the amount of $Ca(OH)_2$ required to bring about 100% lime softening, the amounts needed for the following percentages of the 100% treatment were computed,- 15%, 30%, 45%, 60%, 75%, 90%, 100%, 115%, 130% and 150%. This range was selected as giving a sufficiently broad range of treatment to observe the effects of the treatment.

Two samples of water with highly different qualities were selected for this investigation.

The first water selected for this investigation was the College tap water. This water was drawn from the college supply pipes after allowing a sufficient quantity to run to waste in order that the sample would be a representative one. The College water is a ground water of average hardness, having a total hardness of about 300 p.p.m., together with a low chloride content and a low non-carbonate hardness.

The second water was a sample of the river water from Midland, Michigan. This water has a high total hardness, containing nearly 800 p.p.m. of hardness, as well as a very high chloride content and a high non-carbonate hardness. The high chloride content in the water at Midland can be largely attributed to the presence of salt mines and oil wells in that vicinity.

Tests were run throughout the investigation to determine if any reduction in chloride content was obtained during lime softening. This test was made by titrating a 50 ml. sample of the water with a standard silver nitrate solution and potassium chromate as an indicator.

Summary of Data

COLLEGE TAP WATER

Sample No.	Wt. of lime gm/liter	% of theo. 100% Softening	Alkalinity p.p.m. as $CaCO_3$			Ca in p.p.m.	Mg in p.p.m.	Hardness in p.p.m. of $CaCO_3$			Chlorides p.p.m.
			HCO_3	CO_2	OH			Total	Carbonate	non Carbonate	
Original	None	0%	322	0	0	73	25.33	286.6	322		3.0
1	0.0601	15%	255.2	0	0	62.5	27.87	270.73	255.2	15.53	3.1
2	0.1201	30%	221.2	0	0	54.0	24.90	237.29	221.2	16.09	3.0
3	0.1802	45%	166.8	0	0	34.0	27.08	196.33	166.8	29.53	2.8
4	0.2403	60%	111.3	14.4	0	22.0	25.60	160.28	125.7	34.58	3.1
5	0.3003	75%	45.1	50.2	0	17.5	15.11°	105.87°°	95.3	10.57°°	3.0
6	0.3604	90%	20.0	38.0	0	16.0	21.10	126.78	58.0	68.78	3.0
7	0.4005	100%	2.0	60.0	0	13.5	11.97	82.97	62.0	20.97	3.0
8	0.4605	115%	0	42.4	8.8	18.5	5.42	68.49	42.4	26.09	3.3
9	0.5206	130%	0	47.2	54.4	50.0	1.31	130.23	47.2	83.03	3.3
10	0.5807	145%	0	24.2	138.2	74.5	1.31	191.39	24.2	167.19	3.2

°This value is apparently in error.

°°These values are in error due to the error in Mg determination.

Summary of Data

MIDLAND RIVER WATER

Sample No.	Wt. of lime gm/liter	% of theo. 100% Softening	Alkalinity p.p.m. as $CaCO_3$			Ca in p.p.m.	Mg in p.p.m.	Hardness in p.p.m. as $CaCO_3$			Chlorides p.p.m.
			HCO_3	CO_2	OH			Total	Carbonate	non Carbonate	
Original	None	0%	171.0	0	0	221.0	46.21	741.93	171.0	570.93	770
1	0.0503	15%	163.0	0	0	211.5	46.39	718.95	163.0	555.95	754
2	0.1006	30%	99.3	0	0	184.0	45.17	645.27	99.3	545.97	761
3	0.1509	45%	54.7	0	0	167.5	44.55	601.53	54.7	546.83	762
4	0.2012	60%	5.5	16.0	0	164.0	40.80	577.36	21.5	556.86	758
5	0.2516	75%	0	16.6	0.7	181.5	31.97	584.71	30.0	554.71	762
6	0.3017	90%	0	15.6	10.0	197.5	15.20	555.65	15.6	540.05	760
7	0.3353	100%	0	18.0	12.0	215.5	10.92	582.98	18.0	564.98	755
8	0.3856	115%	0	20.0	37.0	234.5	2.71	596.53	20.0	576.53	756
9	0.4358	130%	0	19.4	66.2	251.0	1.92	634.57	19.4	615.17	756
10	0.4861	145%	0	28.60	89.4	212.0°	1.22				760

°Low value - part of sample was lost.

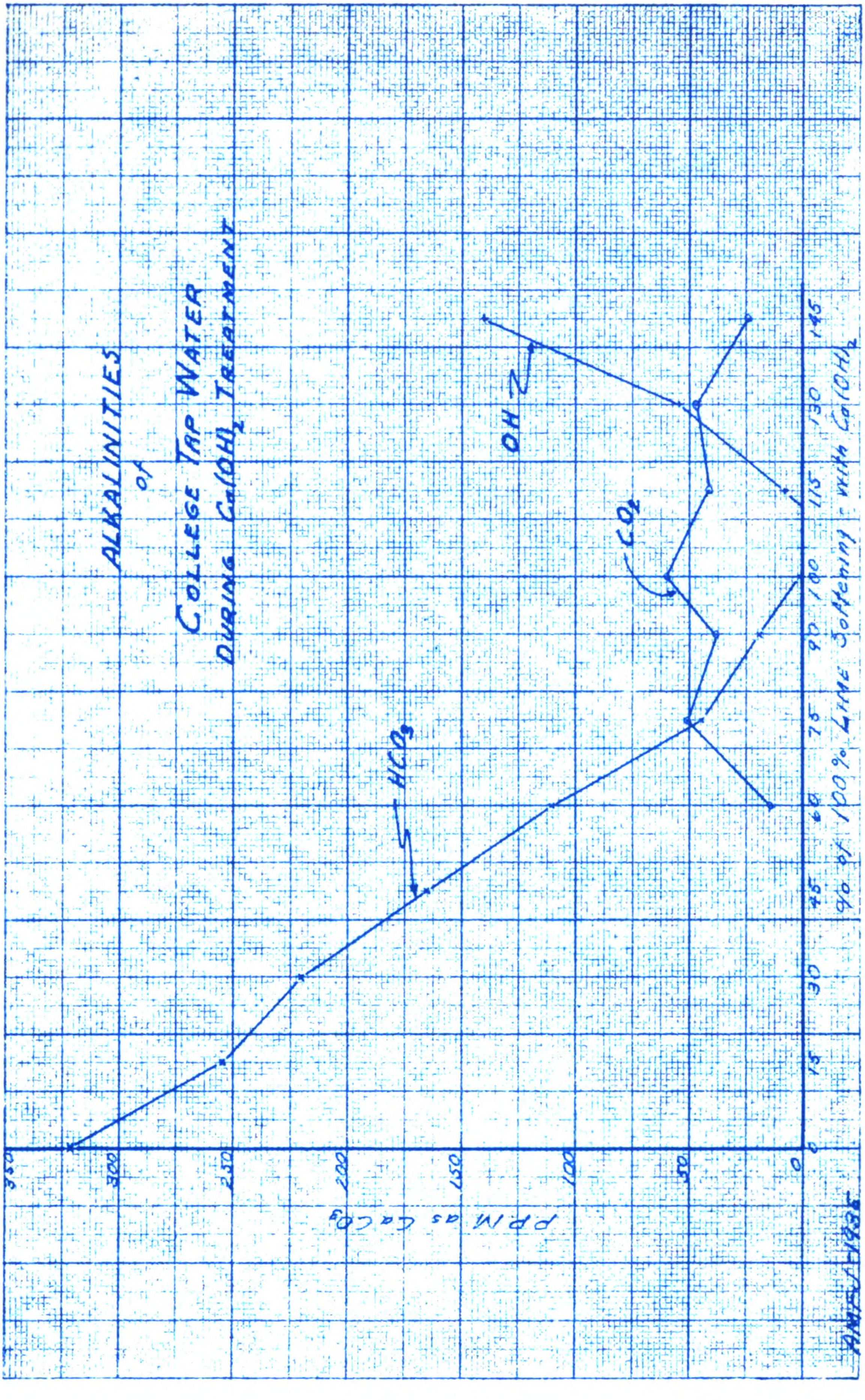

ALKALINITIES
of
COLLEGE TAP WATER
DURING $Ca(OH)_2$ TREATMENT
HCO_3
CO_2
OH
PPM as $CaCO_3$
350
300
250
200
150
100
50
0
0
15
30
45
60
75
90
100
115
130
145
% of 100% Lime Softening - with $Ca(OH)_2$
AMF-J-1935

Fig 1

DISCUSSION OF GRAPHS

Figure 1. Alkalinities of College Tap Water During Lime Treatment.

This graph clearly shows the removal of bicarbonate alkalinity in proportion to the percentage of the calculated theoretical complete lime softening. At the theoretical 100% treatment the bicarbonate alkalinity was practically removed and as the lime treatment was increased to excess treatment the hydroxide alkalinity began to increase in proportion to the increase in lime. This was due to the direct addition of the hydroxide in the form of the lime (calcium hydroxide).

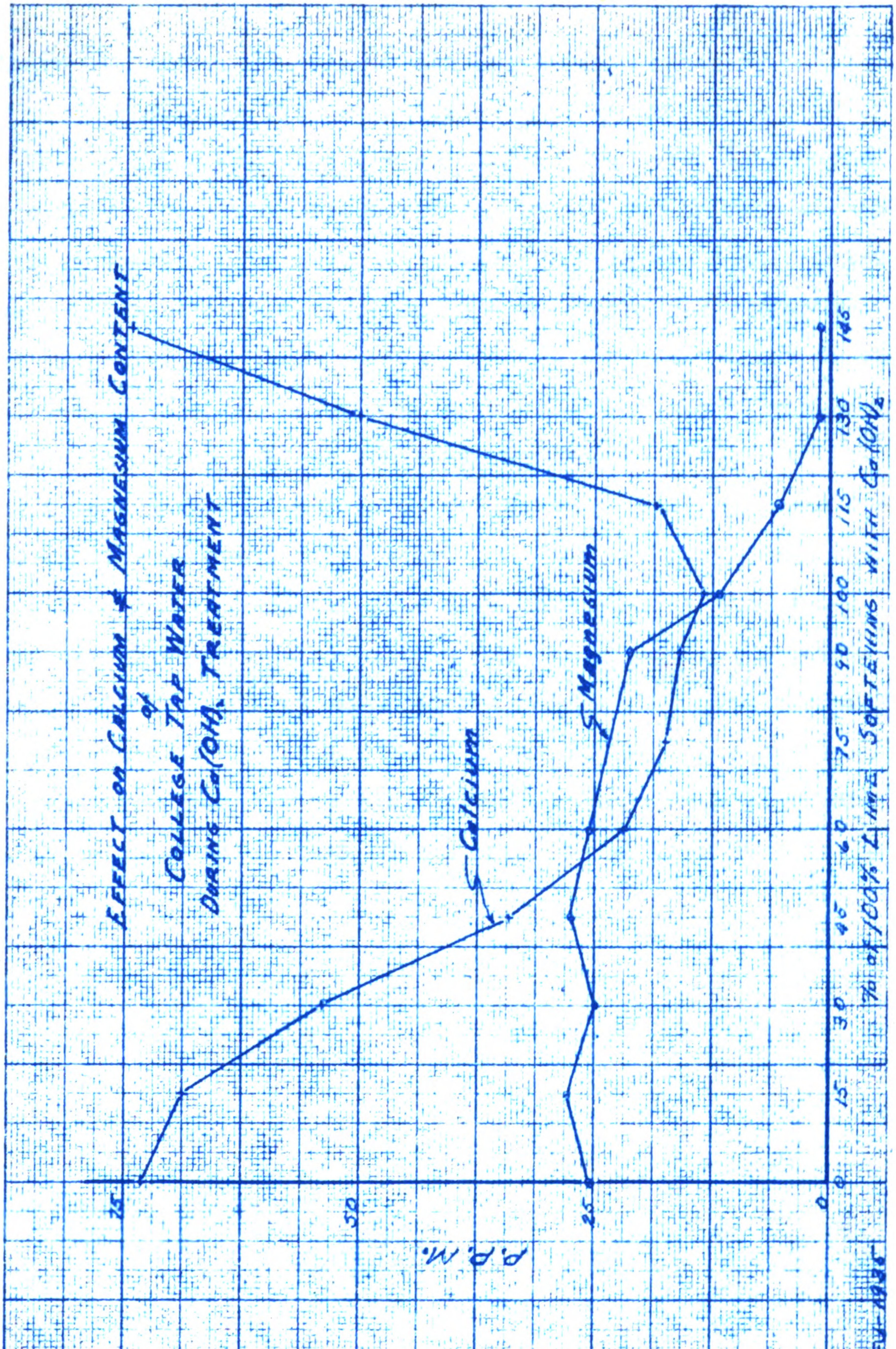

EFFECT ON CALCIUM & MAGNESIUM CONTENT
of
COLLEGE TAP WATER
DURING Ca(OH)2 TREATMENT
Calcium
Magnesium
75
50
25
0
P.P.M.
0
15
30
45
60
75
90
100
115
130
145
% of 100% LIME SOFTENING WITH Ca(OH)2
AMEU-1936

Fig. 2

Figure 2. Effect on Calcium and Magnesium Content of College Tap Water during Lime Treatment.

This graph shows that the calcium in the water is removed at a fairly constant rate until it reached its minimum at the point where the treatment was 100% of the theoretical. After the point mentioned above, the lime treatment was excessive and the calcium content rose rapidly as the lime treatment was increased, due to the introduction of soluble calcium hydroxide

The magnesium content remained practically uniform until the lime treatment began to be in excess of that required for the ~~calcium removal~~ bicarbonate. This shows that the magnesium requires -? more lime for its removal than does calcium. It also shows that magnesium is not removed by lime treatment until practically all the calcium ~~which will be removed by lime treatment~~ in the form of bicarbonate is precipitated out of solution. Upon the addition of sufficient lime practically all the magnesium is removed. This is effected at about 145% of the theoretical treatment.

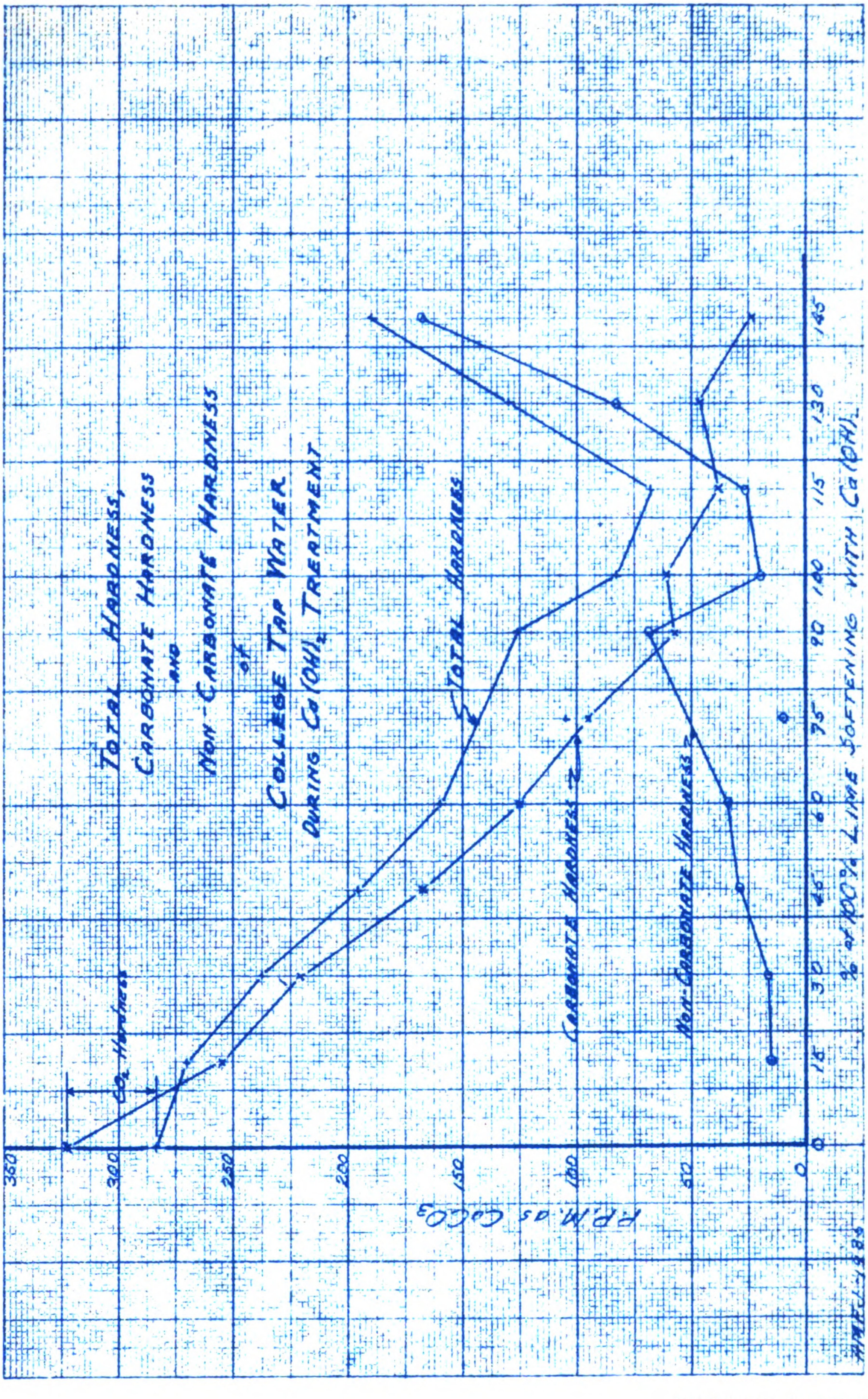

TOTAL HARDNESS,
CARBONATE HARDNESS
and
NON-CARBONATE HARDNESS
of
COLLEGE TAP WATER
DURING Ca(OH)₂ TREATMENT
TOTAL HARDNESS
CARBONATE HARDNESS
NON-CARBONATE HARDNESS
CO₂ Hardness
P.P.M. as CaCO₃
350
300
250
200
150
100
50
0
% of 100% LIME SOFTENING WITH Ca(OH)₂
0
15
30
45
60
75
90
100
115
130
145

Fig. 3

Figure 3. Total Hardness, Carbonate Hardness and Non-Carbonate Hardness of College Tap Water During Lime Treatment.

These graphs show the presence of free CO_2 in the original sample as drawn from the tap and its removal by the lime at the beginning of the lime treatment.

The removal of total hardness and the carbonate hardness go parallel to each other until the total hardness begins to increase due to the increase in calcium as shown in Figure 2. The carbonate hardness continues to decrease due to the beginning of the magnesium removal.

The non- carbonate curve shows a decided increase at the 90% treatment. This is apparently due to some experimental error ? as the curve drops sharply to about where it was before. Then as the hydroxide alkalinity (see Figure 1) increased due to the excess of calcium hydroxide treatment the non-carbonate hardness showed a corresponding increase. This shows the non-carbonate hardness to be due chiefly to hydroxide alkalinity caused by the calcium hydroxide.

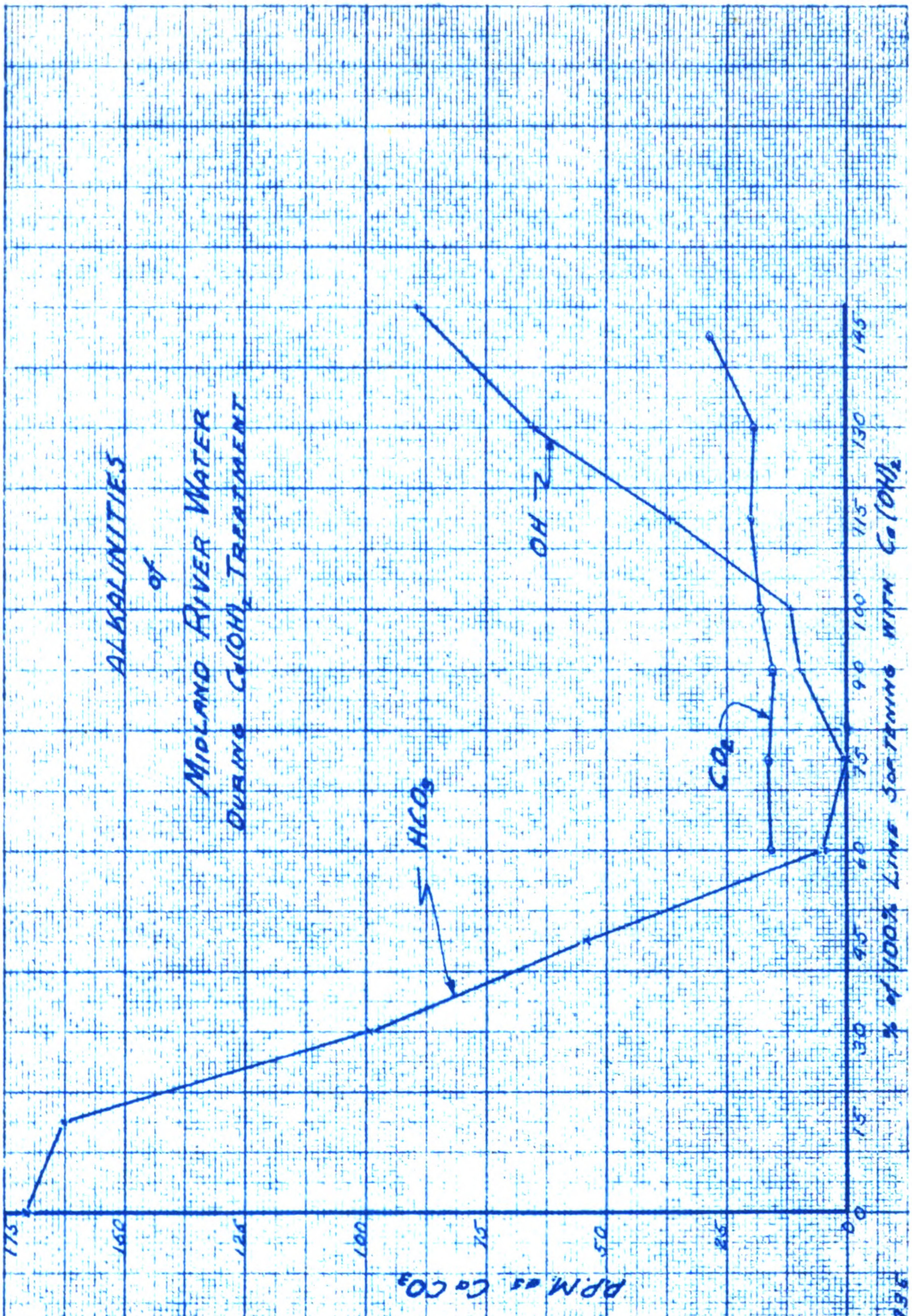
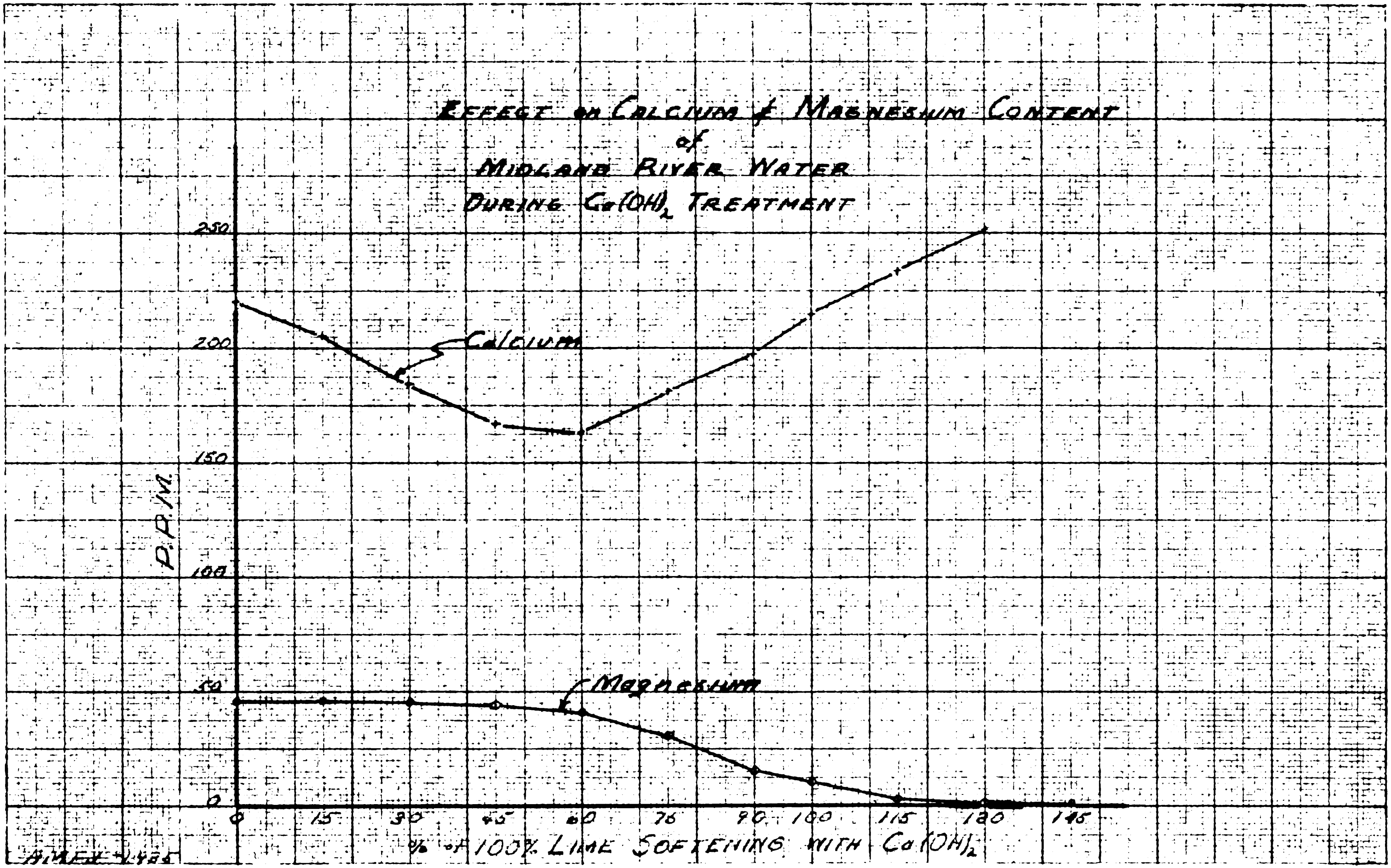

ALKALINITIES
of
MIDLAND RIVER WATER
DURING Ca(OH)2 TREATMENT
HCO3
CO3
OH
P.P.M. as CaCO3
175
150
125
100
75
50
25
0
0
15
30
45
60
75
90
100
115
130
145
% of 100% Lime Softening with Ca(OH)2
AME-1946

Fig. 4

Figure 4. Alkalinities of Midland River Water During Lime Treatment.

This graph is very similiar to Figure 1 showing a rapid reduction in bicarbonate alkalinity until completely removed and immediately following the complete removal of the bicarbonate alkalinity, the hydroxide alkalinity began to increase as the lime dosage increased.

The chief difference between this graph and that shown in Figure 1 is that in the latter the bicarbonate alkalinity was removed at the 100% theoretical lime treatment point for the College water while in Figure 4, the zero for bicarbonate alkalinity occurs at 75% of the theoretical treatment necessary for the Midland water. This may be explained by the fact that in the College water the principal hardness is caused by the bicarbonate alkalinity while in the Midland water the bicarbonate alkalinity is only about half that of the College water, but the calcium is three times as great and the magnesium is twice as great in the Midland water as in the College water.



EFFECT ON CALCIUM & MAGNESIUM CONTENT
of
MIDLAND RIVER WATER
DURING $Ca(OH)_2$ TREATMENT

Fig. 5

Figure 5. Effect on Calcium and Magnesium Content of Midland River Water During Lime Treatment.

These graphs show even better than Figure 2, the order in which the calcium and magnesium are removed in the lime softening process. Here there is no lag in the return of the calcium upon the continued lime treatment. In this case the magnesium is being removed very slowly while the calcium is being precipitated. As soon as the calcium reaches a maximum of removal and begins to increase due to the excess treatment the rate of removal of the magnesium increases and continues until the magnesium is almost entirely removed at 145% treatment point.

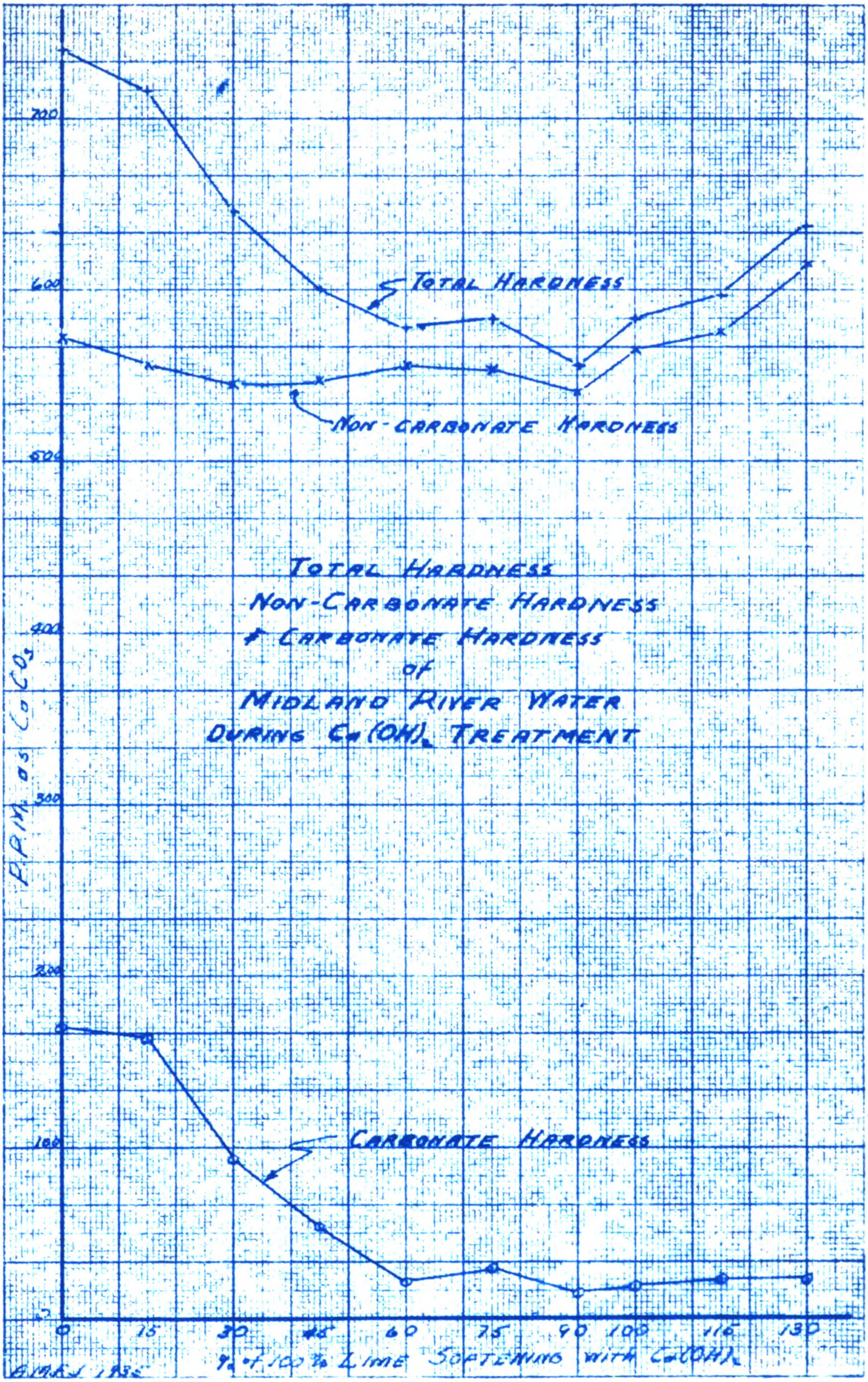

TOTAL HARDNESS
NON-CARBONATE HARDNESS
TOTAL HARDNESS
NON-CARBONATE HARDNESS
& CARBONATE HARDNESS
of
MIDLAND RIVER WATER
DURING Ca(OH)2 TREATMENT
CARBONATE HARDNESS
P.P.M. as CaCO3
700
600
500
400
300
200
100
0
0
15
30
45
60
75
90
100
115
130
% of 100% LIME SOFTENING WITH Ca(OH)2
E.M.K. 1935

Fig. 6

Figure 6. Total Hardness, Non-carbonate Hardness and Carbonate Hardness of Midland River Water During Lime Treatment.

These graphs are comparable with those in Figure 3 and the same explanation holds true here as did in that case. The non-carbonate hardness shows some fluctuation here, but not a sharp increase as it did with the College water in Figure 3. This gives credence to the explanation of its rise there as being due to experimental error rather than some behavior in the softening reaction. Altogether these curves show the paralleling of the hardness relationships during the lime treatment.

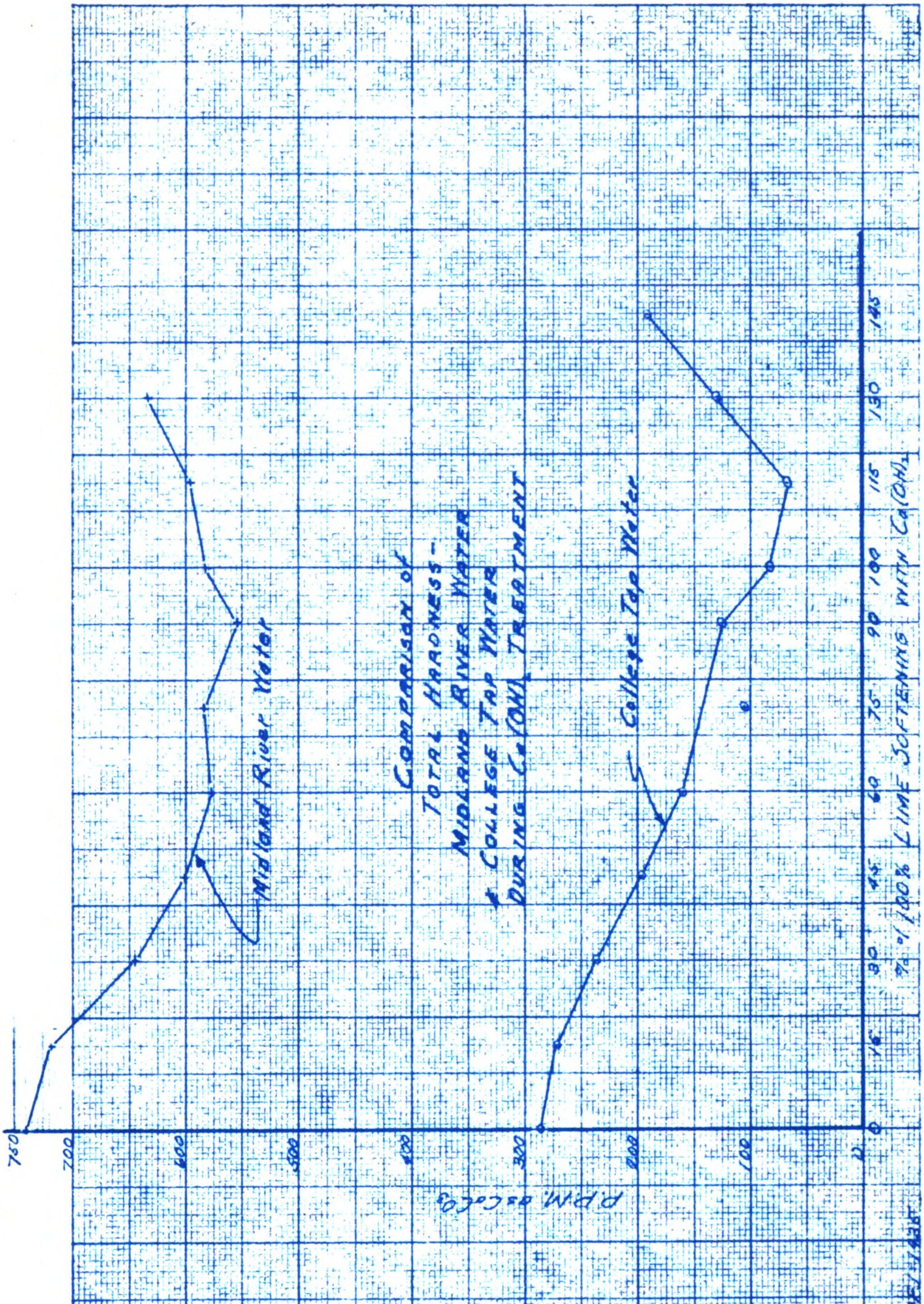

Comparison of
Total Hardness -
Midland River Water
& College Tap Water
During Ca(OH)$_2$ Treatment
Midland River Water
College Tap Water
750
700
600
500
400
300
200
100
0
P.P.M. as CaCO$_3$
0
15
30
45
60
75
90
100
115
130
145
% of 100% Lime Softening with Ca(OH)$_2$

Fig. 7

Figure 7. Comparison of Total Hardness - Midland River Water and College Tap Water During Lime Treatment.

These graphs have no special significance except as they show that in both cases of the treatment of such radically different waters as were used in this investigation the amount of change in the total hardness was about the same, being about 200 p.p.m. In both cases the continued treatment with lime caused an increase in total hardness. This increase has been noted in the previous discussion and will not need to be discussed again here. It should be noted, however, that the lowest amount of total hardness is reached earlier in the Midland water treatment than in the treatment of the College water. This has also been discussed before (see discussion of Figure 4), but is again shown here.

CONCLUSION

From the foregoing discussion and from my results of the treatment of these two different waters with calcium hydroxide I feel that it is possible to draw a few general conclusions.

It must be kept in mind that there is danger in forming too specific a set of conclusions from such a limited number of cases. If time had permitted, I would like to have been able to carry on the investigation of these softening reactions so as to have included a greater number of kinds of water. This would have enabled me to draw a more complete and a truer picture of what actually can be expected of the lime softening process. Time would not permit carrying out the great number of analyses necessary so it was necessary to select a ground water of average (for Michigan) hardness and a river water of a very high degree of hardness for my investigation.

In interpreting the results of these analyses it must also be borne in mind that no matter how carefully one carries out an analysis a certain amount of experimental and personal error is bound to creep into the work. The magnitude of such errors is indeterminate, but based on the laws of probability they may be assumed to be small. Accordingly, small deviations from an average, or an anticipated, value must not be given too much importance.

With the above limitations in mind I have drawn the following conclusions.

1. Lime softening alone does not remove any appreciable amount of iron or aluminum.

2. Lime softening alone does not remove any of the chlorides present in the water. The presence of chlorides apparently (obviously not) does not have any affect upon the softening of the water with lime. This is what would be expected from a study of the chemical equations of the reactions of lime and chlorides. The equations point out the need for the addition of sodium carbonate to effect the removal of chlorides.

3. Calcium is removed from the water by lime softening up to the point where the bicarbonate alkalinity is removed. After this point the calcium content of the water increases with the increased addition of the calcium hydroxide being used for the softening.

4. Magnesium is apparently unaffected until a point is re reached just before the calcium is most completely removed. It then begins to be removed, quite rapidly at first and then more slowly as it approaches the point of complete removal.

5. Carbonate hardness is removed quite rapidly until the calcium content reaches a minimum. After this point the carbonate hardness removal proceeds more slowly. This indicates that the principal carbonate hardness of the waters investigated was that due to calcium bicarbonates.

6. The non-carbonate hardness of the waters investigated did not seem to bear much of a general relation to each other until the treatment with the calcium hydroxide had reached the point where the calcium removal was the greatest. After this point the non-carbonate hardness was the kind of hardness in which the addition of hydroxide alkalinity, by continued treatment with the lime, was indicated. This is shown by the tests for alkalinity.

Perhaps the most significant fact brought out by this investigation as a whole is that it clearly shows that it is impossible to adapt any "cut and dried" treatment to be followed in planning or designing a water softening plant. Each locality has its own pecularities which it imparts to its water supply and each water supply must be individually considered when its treatment is being contemplated.

#

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