TOTAL ALKALINITY CHANGES OCCURRING IN THE EFFLUENT OF A ZEOLITE

SOFTENER, AND AN EXPLANATION OF THEIR OCCURRENCE

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BY

ROY E. KING

Bachelor of Science

Oklahoma Agricultural and Mechanical College

Stillwater, Oklahoma

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APPROVED:

Charles L. Nicholls
In Charge of Thesis

Otto M. Smith
Head of the Department of Chemistry

D. E. McIntosh
Dean of the Graduate School

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ACKNOWLEDGEMENT

TOTAL ALKALINITY CHANGES OCCURRING IN THE EFFLUENT OF A ZEOLITE SOFTENER, AND AN EXPLANATION OF THEIR OCCURRENCE

Zeolites used in the softening of water are usually defined as hydrated double silicates of aluminum and a base which may either be an alkali or an alkaline earth. The formula usually ascribed to the sodium zeolite is as follows: $NaO_xAl_2O_3 \cdot ySiO_2 \cdot zH_2O$.

The bases are interchangeable, and use is made of this property in the softening of water. The base exchange properties of zeolites were first observed by J. Thomas Way in 1850[1], but it was not until about 1910 that commercial use was made of these properties in water treating.

Today the water softening zeolites are broadly designated as green sand zeolites and prepared zeolites. The green sand deposits of commercial importance, in the United States, are located in New Jersey. They require some processing before they are suitable for use in water softeners. The two principal types of manufactured zeolites are: The precipitated zeolites which are formed by the reaction of dilute solutions of sodium aluminate and sodium silicate, and the gel type of zeolite which is prepared by the reaction of solutions of aluminum sulfate and sodium silicate of such concentration that precipitation does not occur, but instead the whole mixture gels. This gel is then dried, washed, crushed, and screened to suitable size.

In the zeolite water softening process the water is softened by passing it through a bed of sodium zeolite, either up flow or down flow. The calcium and magnesium ions present in the raw water are retained in the zeolite bed, and a corresponding quantity of sodium ions

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[1] Way, J. T., J. Roy. Agr. Soc., 11, 313 (1850); 13, 123 (1852).

released. This renders the water soft because the resulting sodium salts are not soap consuming. The process continues until such a quantity of the sodium in the zeolite bed has been replaced with calcium or magnesium that complete exchange is no longer effected, and the softener effluent is no longer of zero hardness. The zeolite is then said to be exhausted, and it becomes necessary to regenerate it; that is, to replace with sodium the calcium and magnesium which are now combined with the zeolites. This is accomplished by passing a sodium chloride brine slowly through the zeolite bed. During this passage of brine through the bed of zeolite an exchange reaction takes place which is the reverse of the softening reaction. After the required quantity of brine has been added, raw water is turned into the softener and the effluent containing the calcium and magnesium chlorides together with the excess sodium chloride is passed to the sewer until tests show the effluent to again be "soft" and the chloride content is nearly that of the influent water.

The reactions occurring during the softening process are represented as follows:

$$Ca(HCO_3)_2 \;+\; Na_2Z \;\longrightarrow\; 2\,NaCHO_3 \;+\; CaZ$$

$$CaSO_4 \;+\; Na_2Z \;\longrightarrow\; Na_2SO_4 \;+\; CaZ$$

$$CaCl_2 \;+\; Na_2Z \;\longrightarrow\; 2\,NaCl \;+\; CaZ$$

$$Ca(NO_3)_2 \;+\; Na_2Z \;\longrightarrow\; 2\,NaNO_3 \;+\; CaZ$$

During the regeneration process the reaction is as follows:

$$CaZ \;+\; excess\ NaCl \;\longrightarrow\; Na_2Z \;+\; CaCl_2 \;+\; NaCl$$

Similar reactions occur in both the softening and regeneration process with magnesium as occur with calcium.

According to the above reactions the only chemical change which

takes place is the exchange of calcium and magnesium for sodium in the softening portion of the cycle and the opposite exchange during the regeneration process. The total alkalinity to methyl orange* should not be affected since the same quantity of bicarbonate ions is represented as being present in the softened water as were present in the raw water. Mr. Frank N. Speller, in referring to the zeolite process of water softening, states,[2] "This treatment does not affect the amount of dissolved carbon dioxide in the water, and the bicarbonates remain in solution as bicarbonate of sodium."

It is the purpose of this paper to show that there is a variable change in the total alkalinity of the softened water, that the quantity of dissolved carbon dioxide is affected, and to present an explanation of these occurrences.

The investigation was begun in 1933 and was continued at intervals, as other work permitted, until the fall of 1937. Test curves and data will be presented in their chronological order to show the steps by which we arrived at our conclusions. For the sake of brevity the results of a series of tests will be shown by one typical curve and data sheet, although a statement concerning the extent of the data will be given with each curve.

The zeolite softeners used were full sized industrial installations having mineral beds of green sand six feet in diameter and about thirty-four inches in depth. In the tests made at Jowett Station of the Panhandle Power and Light Company the water was obtained from wells

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* In the following pages the abbreviation "M. O." is used in lieu of the words "methyl orange".

[2] F. N. Speller, "Corrosion Causes and Prevention", 2nd ed., p. 445. McGraw-Hill (1935).

125 feet in depth and has the following composition. The variation from this analysis is negligible.

The analysis of the untreated water is:

		Parts Per Million	Gr./Gal.	Milli-equivalent
Total Solids at 103° C.		319	18.7	-----
Total hardness as $CaCO_3$		206	12.0	-----
Total alkalinity as $CaCO_3$		180	11.1	-----
Silica	(SiO_2)	24.8	1.45	-----
Fe_2O_3 and Al_2O_3		1.2	.07	-----
Calcium	(Ca)	73.0	4.27	3.650
Magnesium	(Mg)	6.0	.35	0.493
Bicarbonate	(HCO_3)	232.0	13.55	2.800
Carbonate	(CO_3)	-----	-----	-----
Chloride	(Cl)	18.0	1.05	0.508
Sulfate	(SO_4)	33.0	1.93	0.688
Nitrate	(NO_3)	11.7	1.03	0.285
Sodium	(Na) by difference	26.2	1.53	1.138
Free CO_2		15.0	0.88	-----

This water is low in sulfates and high in bicarbonates and if used as boiler make-up after the base exchange method of softening it will yield a water in which the ratio of sodium sulfate to the total alkalinity expressed as sodium carbonate will be far lower than that recommended by the A. S. M. E. for the prevention of "Caustic embrittlement".[3]

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[3] The following is quoted from the 1925 report of the Boiler Code

Because of this low sulfate-carbonate ratio the water intended for boiler feed purposes was treated with 66° Bé sulfuric acid. The acid was added to the water just ahead of the zeolite softener. An automatic acid feeding device was used and was adjusted so that the total alkalinity to methyl orange of the water entering the zeolite softener averaged about 25 p. p. m. as $CaCO_3$, although the alkalinity varied between 20 p. p. m. and 30 p. p. m. as $CaCO_3$.

It was observed that no matter now narrow the range of the variation in the alkalinity of the influent to the softener, there was a wide variation in the total alkalinity of the effluent from the softener. This condition was quite objectionable as we were attempting to recirculate just sufficient boiler concentrate to feed-water heaters to convert the bicarbonate in the softened make-up water entering the heaters into the normal carbonate. The variation in the effluent of the softener made it almost impossible to achieve the desired results.

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[3] Committee of the American Society of Mechanical Engineers: "The attention of the committee has been called to the following exceptional cases in rivet joint cracks described as intercrystalline in character and under water level only:

(a) Boilers in certain localities fed with water containing sodium bicarbonate, but not an appreciable quantity of sodium sulfate. Similar cracking has not been reported in the same localities in boilers fed with surface water free from sodium carbonate, or containing sodium sulfate equal to or exceeding the sodium bicarbonate."

In view of the particular cases of embrittlement cited above and pending further research, the maintenance of not less than the following ratios of sodium sulfate to the methyl orange alkalinity is recommended as a precautionary measure."

Boiler Working Pressure Pounds Gage	Ratio Sodium Carbonate Alkalinity to Sodium Sulfate
0-150	1:1
150-250	1:2
250 and over	1:3

An investigation was therefore made to determine the extent, and if possible, the cause of the variations in the alkalinity of the effluent of the softener. The conditions, results, and conclusions of a series of tests on the total alkalinity of the influent and effluent are shown in "Test Series No. 1".

TEST SERIES NO. 1

Conditions of Test

The softener influent water was treated with 66° Bé sulfuric acid, reducing the total alkalinity from 190 p. p. m. to about 25 p. p. m. as $CaCO_3$. The generated carbon dioxide was not expelled before the water passed to the softener. Raw well water was used for backwashing and for rinsing the softener after regeneration. The rate of flow through the softener was held constant at 40 gallons per minute. Samples of the influent and effluent were taken at intervals of 500 gallons, and the total alkalinity determinations were made in duplicate on each sample. Sampling was started when the softener started delivering "soft" water after regeneration and was continued until water of "zero" hardness was no longer obtained in the effluent.

Alkalinity determinations were made according to "Standard Methods of Water Analysis," using 0.02 N sulfuric acid for titrating and methyl orange as the indicator. Standard A.P.H.A. soap solution was used for determining the starting and ending points of a softening run.

Extent of Data

On an average run of 20,000 gallons about nine consecutive hours were required before regeneration became necessary. During this time approximately forty samples each of influent and effluent were taken.

TABLE I

Total Alkalinity Data on Influent and Effluent Water of Greensand
Zeolite Water Softener. Influent Water Acid Treated. Raw Water Used
for Backwash and Rinse.

Gallons of Water Softened	Total (M. O.) Influent P.P.M.	Alkalinity Effluent P.P.M.
0	30	180
500	30	160
1000	28	140
1500	30	130
2000	34	126
2500	30	116
3000	28	110
3500	28	108
4000	28	104
4500	24	90
5000	22	86
5500	22	84
6000	22	70
6500	24	70
7000	24	60
7500	24	50
8000	22	44
8500	22	44
9000	22	40
9500	22	38
10000	22	36
10500	20	34
11000	20	30
11500	20	28
12000	20	24
12500	24	24
13000	24	22
13500	24	20
14000	24	18
14500	24	18
15000	26	18
15500	24	18
16000	22	18
16500	22	18
17000	24	16
17500	22	16
18000	22	16
18500	20	16
19000	22	16
19500	20	16
20000	22	18

TYPICAL CURVE SHOWING CHANGE IN TOTAL ALKALINITY IN WATER PASSING THROUGH A ZEOLITE SOFTENER. INFLUENT WATER WAS ACID TREATED. UNTREATED WATER USED FOR RINSING SOFTENER.
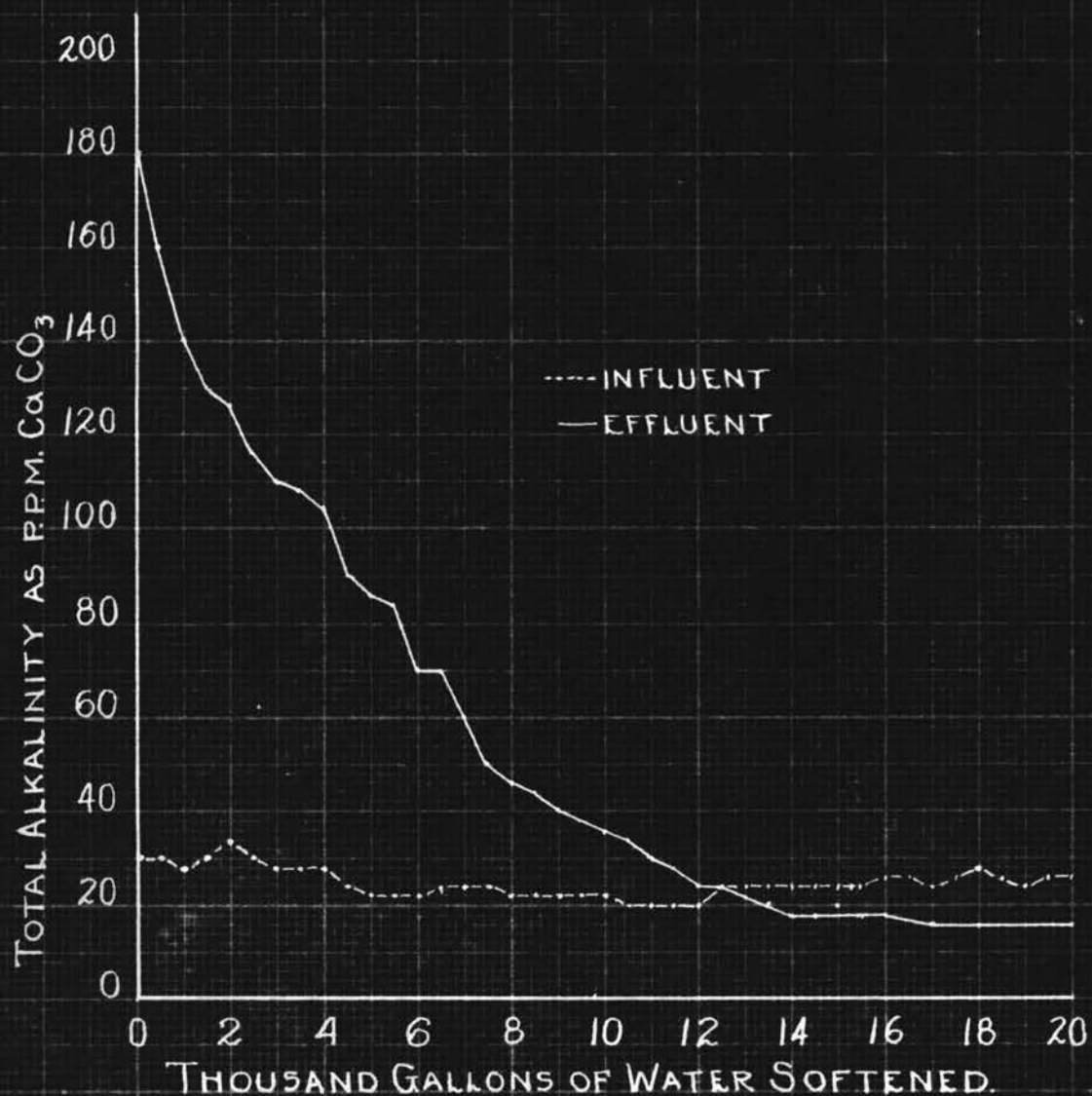
FIG. 1.

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As duplicate checks were made on each sample and five test runs were
made under the conditions outlined above, the data given in Table I and
shown in Figure 1 are supported by about 800 determinations.

Results

The results of a typical test run are given in Table I and shown
in Figure 1. The initial effluent alkalinity of the series of tests
averaged about 185 p. p. m. as $CaCO_3$, although the variation was bet-
ween 170 p. p. m. and 195 p. p. m. The variation shown in the influent
water was typical. In all cases the total alkalinity of the effluent
dropped off rapidly as shown. The rate of decrease in alkalinity was
always greater at the beginning of the run than toward the end. When
about 60% of the run was completed the total alkalinity of the effluent
dropped below that of the influent and remained below it for the re-
mainder of the run.

Conclusions

The variation in the alkalinity was decided to be a characteristic
of the zeolite softening process under the operating conditions encoun-
tered. No satisfactory explanation of the cause of the variation was
reached, although it was suggested that the initial increase in the ef-
fluent over the influent alkalinity might be due to the untreated water
which was held in the zeolite bed after rinsing. It was decided there-
fore to make some test runs in which there would be no raw water in the
softener at the beginning of the run.

TEST SERIES NO. 2

Conditions of Tests

The same conditions apply as were set forth for the previous tests

except that acid treated water was used for rinsing the softener after the backwash with raw water.

Extent of Data

Three test runs were made in which the average number of gallons softened was about 18,000 gallons per run. About 450 alkalinity determinations were made during the course of this series of tests.

Results

Typical results obtained are given in Table II and shown in Figure 2. The curve obtained on plotting the total alkalinity of the influent and effluent water against the total number of gallons passed through the softener is similar in character to that obtained in the previous series of tests. The softening runs were about two thousand gallons shorter than the runs obtained when using raw water. The initial effluent alkalinity, when the softener started delivering soft water was also lower than in the former tests. However, it was observed that if the data obtained on the two series of tests were plotted on the same scale and the curves superimposed so that the end points would coincide then the other portions of the curves would be in close agreement as the curves obtained from two successive tests. In other words, the use of acid treated rinse water only served to reduce the capacity of the softener by about two thousand gallons, and did not in any way affect the character of the curves obtained when the data was plotted.

Conclusions

Since it was concluded that the raw water remaining in the zeolite bed at the beginning of the softening period in the first series of tests was not responsible for the initial increase in alkalinity of the

TABLE II

Typical Total Alkalinity Data on Influent and Effluent Water of
Greensand Zeolite Water Softener. Influent Water Acid Treated. Raw
Water Used for Backwash. Acid Treated Water Used for Rinse After Back-
wash.

Gallons of Water Softened	Total (M.O.) Alkalinity Influent P.P.M.	Effluent P.P.M.
0	22	190
500	22	160
1000	20	136
1500	24	134
2000	24	130
2500	24	124
3000	24	120
3500	24	110
4000	26	98
4500	26	90
5000	26	80
5500	26	74
6000	26	66
6500	28	64
7000	24	62
7500	24	58
8000	28	52
8500	28	48
9000	26	40
9500	24	40
10000	24	40
10500	24	38
11000	26	34
11500	26	34
12000	24	32
12500	24	30
13000	26	24
13500	26	24
14000	26	20
14500	24	20
15000	24	20
15500	24	20
16000	22	18
16500	24	18
17000	24	18
17500	26	18
18000	26	16
18500	26	16
19000	26	16

TYPICAL CURVE SHOWING CHANGE IN TOTAL ALKALINITY IN WATER PASSING THROUGH A ZEOLITE SOFTENER. ACID TREATED WATER USED FOR INFLUENT AND FOR RINSING SOFTENER AFTER BACKWASH.
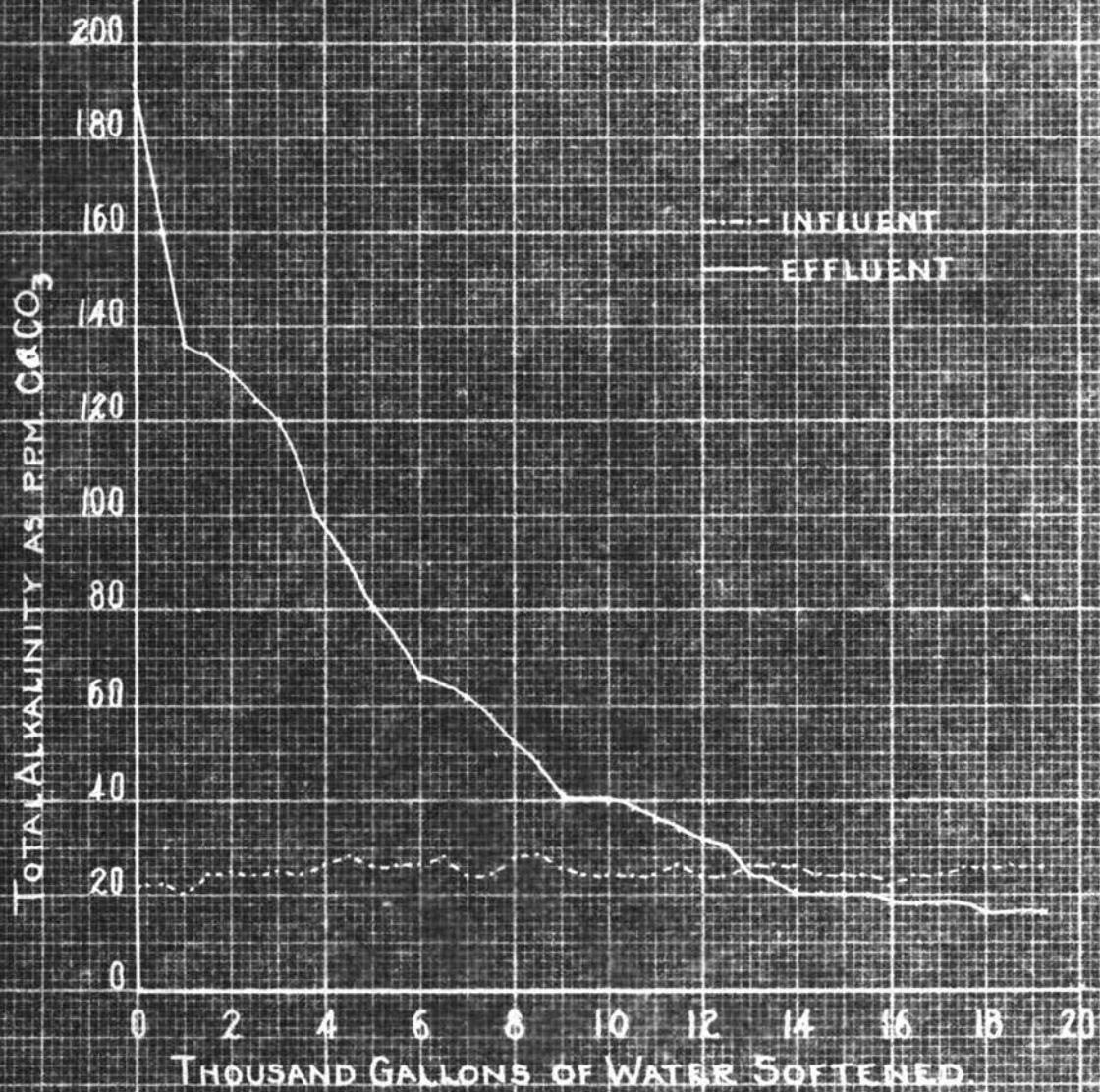
FIG. 2.

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effluent, an explanation of the variable alkalinity of the effluent was not yet known.

As it was now evident that the necessary control of the softener effluent alkalinity could not be obtained by control of the influent alkalinity, the treatment of the softener influent with acid was abandoned.

In order to determine whether the pre-treatment with acid had affected the exchange capacity of the zeolite, and to determine whether the peculiar variation in alkalinity was obtained when using influent water in which the alkalinity had not been lowered by acid treatment, it was decided to make further tests along lines similar to those already described.

TEST SERIES NO. 3

Conditions of Tests

The rate of flow through the softener, the frequency of sampling, and the methods of analysis were the same as in the previous tests. The influent water was not acid treated and had a total alkalinity in terms of $CaCO_3$ of 190 p. p. m. The analysis of this water is shown in Table A. This water was also used for backwashing and rinsing the softener.

Extent of Data

Three test runs were made under the above conditions, and the approximate number of alkalinity determinations made on the effluent was 250. Alkalinity determinations were made on the influent at 1,000 gallon intervals.

Results

TABLE III

Total Alkalinity Data on Influent and Effluent Water of Greensand Zeolite Water Softener. Untreated Deep Well Water Used as Influent and and for Backwashing and Rinsing Softener.

Gallons of Water Softened	Total (M.O.) Alkalinity Influent P.P.M.	Effluent P.P.M.
0	190	230
500	190	228
1000	190	224
1500	190	226
2000	190	220
2500	190	222
3000	190	220
3500	190	220
4000	190	218
4500	190	218
5000	190	214
5500	190	212
6000	190	210
6500	190	208
7000	190	204
7500	190	202
8000	190	202
8500	190	198
9000	190	194
9500	190	190
10000	190	190
10500	190	188
11000	190	186
11500	190	184
12000	190	184
12500	190	182
13000	190	182
13500	190	182
14000	190	180
14500	190	180
15000	190	180
15500	190	178
16000	190	176
16500	190	176
17000	190	172
17500	190	172
18000	190	170
18500	190	170
19000	190	170
19500	190	170
20000	190	170

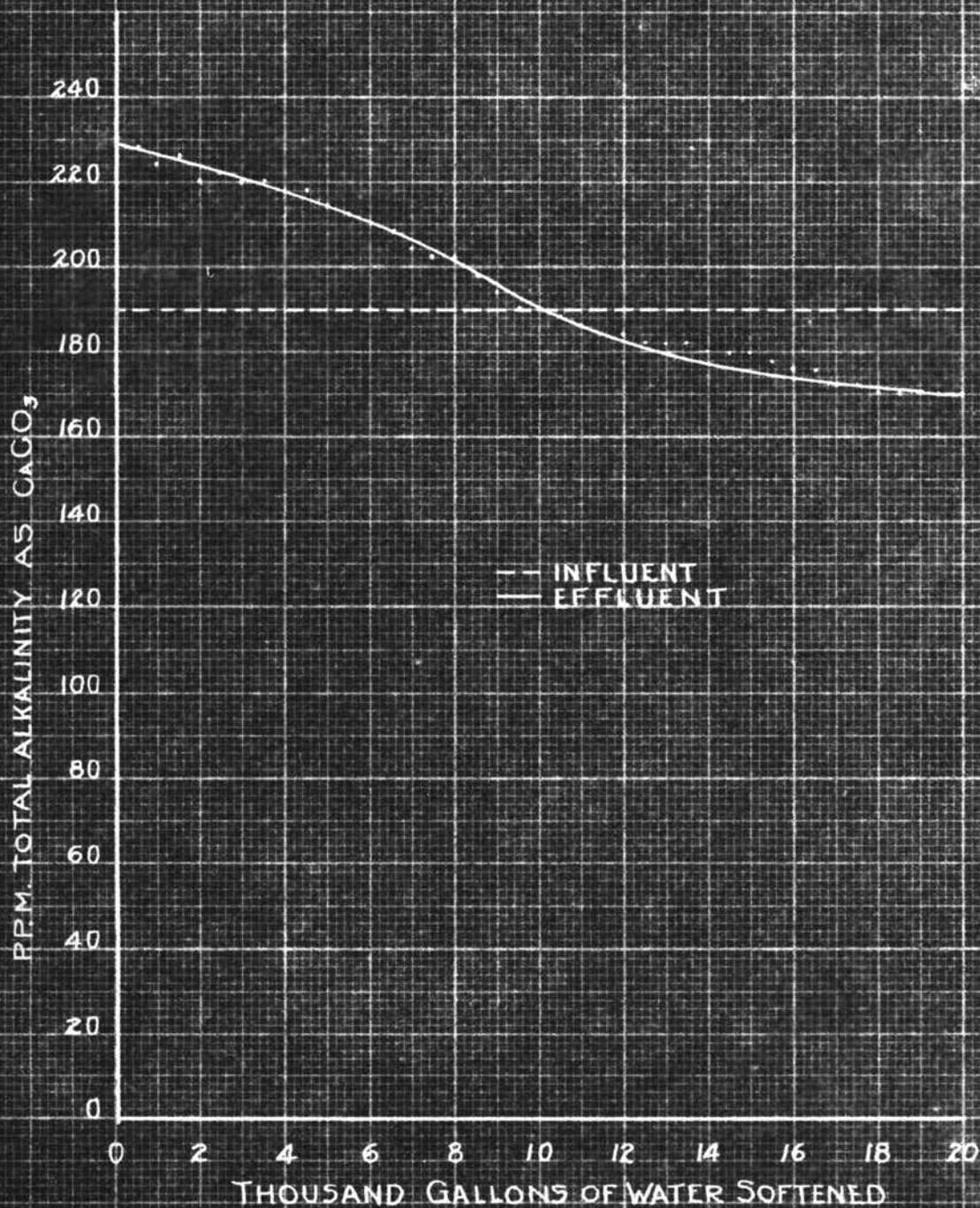TYPICAL CURVE SHOWING CHANGE IN TOTAL ALKALINITY OF WATER PASSING THROUGH A ZEOLITE SOFTENER.

FIG. 3.

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The data were quite similar in character to those obtained from the previous tests. The length of the softening runs was somewhat longer than those formerly obtained, averaging between 20,000 and 21,000 gallons. The rate of decrease in alkalinity of the effluent was less than in the cases where the influent was treated with acid. Typical results are given in Table III and shown in Figure 3.

Conclusions

The capacity of the softener had not been materially affected by the use of acid treated influent. The cause of the change in the alkalinity was not yet known, but it was known that the changes which occurred were typical of zeolite softening regardless of the total alkalinity of the influent water.

The problem was allowed to lie dormant for several months after these tests, although daily tests showed that changes in the alkalinity still occurred as before. In fact it was possible to predict within a few hundred gallons, the number of gallons of water that had passed through the softener on any particular run by making a determination of the alkalinity of the effluent. It was finally observed that immediately after a regeneration the effluent was very slightly alkaline to phenolphthalein. This of course indicated a complete absence of free carbon dioxide in the effluent. Since the quantity of free carbon dioxide in the influent water was known to be 15 p. p. m., it was decided to make further tests, observing the variation of free carbon dioxide as well as the alkalinity of the softener effluent.

TEST SERIES NO. 4

Conditions of Test

The conditions of this test were identical to those in the Series No. 3, with the exception that determinations were made of the free carbon dioxide in the effluent.

Extent of Data

Only two complete tests were made by continuous runs, although numerous random tests made on the softener effluent during the past four years have confirmed the data obtained by these tests.

Results

The data regarding the changes in the total alkalinity were the same as found in all previous tests. The free carbon dioxide content of the effluent was found to be zero for the first few thousand gallons of effluent or for about 20% of the run. Free carbon dioxide then began to appear in the effluent and increased in quantity until the end of the run was reached. As the quantity of free carbon dioxide increased, the total alkalinity decreased, as is given in Table IV and shown in Figure 4. For the first 20% of the softening run the quantity of free CO_2 in the effluent was less than that of the influent water while for the last half of the run it was greater. Changes in alkalinity were just the reverse of this.

Conclusions

Since the changes in the free carbon dioxide content of the effluent were thus linked to the changes in the total alkalinity, it was evident that the CO_2 was entering into the reactions occurring in the zeolite bed. It was suggested that carbonic acid might be reacting with the sodium zeolite forming hydrogen zeolite and sodium bicarbonate. A search of the literature revealed that nothing had been published concerning hydrogen zeolite. (After the thesis was completed it was found

TABLE IV

Data on Influent and Effluent Water of Greensand Zeolite Water Softener.

<u>Influent Data:</u> Total Alkalinity 190 p.p.m. as $CaCO_3$
Free Carbon-dioxide 15 p.p.m.
pH = 7.5

<u>Effluent Data:</u>

Gallons of Water Softened	Total (M.O.) Alkalinity	Free CO_2	pH
0	228	0	7.9
500	228	0	7.9
1000	226	0	7.9
1500	224	0	7.9
2000	222	0	7.9
2500	222	0	7.9
3000	220	0	7.8
3500	220	0	7.8
4000	218	0	7.8
4500	216	0	7.8
5000	214	0	7.8
5500	212	2	7.8
6000	210	3	7.7
6500	208	5	7.7
7000	206	7	7.6
7500	204	10	7.4
8000	202	12	7.3
8500	198	15	7.3
9000	196	18	7.2
9500	194	20	7.2
10000	192	21	7.1
10500	190	22	7.1
11000	188	23	7.0
11500	186	24	7.0
12000	184	24	7.0
12500	182	25	7.0
13000	180	26	6.9
13500	180	28	6.9
14000	180	30	6.9
14500	178	32	6.9
15000	178	33	6.8
15500	176	34	6.8
16000	176	34	6.8
17000	176	35	6.8
17500	174	35	6.7
18000	174	35	6.7
18500	172	36	6.6
19000	170	36	6.6
19500	170	37	6.6
20000	170	36	6.6

TYPICAL CURVE SHOWING VARIATION IN TOTAL ALKALINITY, FREE CO₂, AND pH OF WATER PASSING THROUGH A HIGH CAPACITY SAND ZEOLITE WATER SOFTENER.
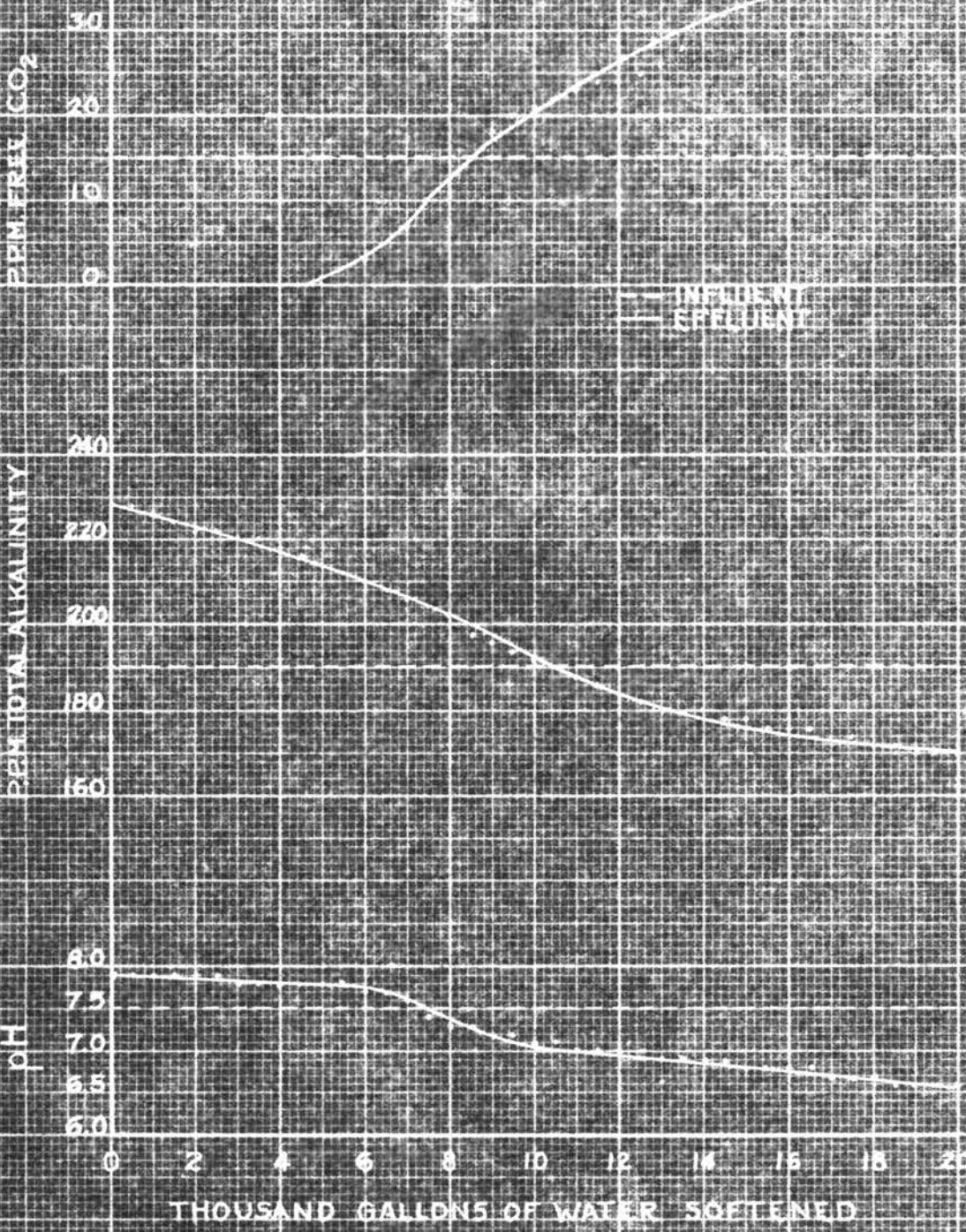
Fig. 4

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that a German patent No. 224,934 was issued to J. D. Reidel, A. G., on a method for removing acid from water by the use of zeolite. He states that sodium bicarbonate is formed by a reaction between the carbonic acid in the water and the alkali of the zeolite.) It was decided to continue the work and if possible find out whether hydrogen zeolite were actually formed.

TEST SERIES NO. 5

While making observations of the free carbon dioxide variations in zeolite softener effluents, several tests were made at Riverview Station of the Panhandle Power and Light Company. The softener used was identical to the one at Jowett Station. The water at Riverview is almost identical to that at Jowett with the exception of the quantity of free carbon dioxide which is only 7.0 p. p. m.

Conditions of Test

The same procedure was used as in the previous tests. Alkalinity and free carbon dioxide determinations were made at 500 gallon intervals.

Results

The typical variation in total alkalinity was observed; however, it was also found that normal sodium carbonate (CO_3^{--} ion) was present in the effluent of the softener for about 50% of the run. It was present in greatest quantity immediately after regeneration and dropped off as the run progressed. Free carbon dioxide, of course, only began to appear after the normal sodium carbonate content had dropped to zero. Typical data are given in Table V and shown in Figure 5.

Conclusions

TABLE **V**

Data on Influent and Effluent Water of a Greensand Zeolite Water Softener.

<u>Influent Data:</u> Total Alkalinity 190 p.p.m. as $CaCO_3$
Free Carbon dioxide 7 p.p.m.

<u>Effluent Data:</u>

Gallons of Water Softened	Total (M.O.) Alkalinity	Normal Na_2CO_3	Free CO_2
0	204	12	0
500	204	12	0
1000	204	12	0
1500	204	12	0
2000	204	12	0
2500	204	10	0
3000	202	10	0
3500	202	10	0
4000	200	10	0
4500	198	8	0
5000	198	8	0
5500	196	6	0
6000	196	6	0
6500	194	4	0
7000	194	4	0
7500	192	4	0
8000	192	4	0
8500	188	2	0
9000	188	2	0
9500	188	2	0
10000	188	2	0
10500	188	2	0
11000	188	0	0
11500	186	0	0
12000	186	0	0
12500	186	0	1
13000	184	0	1
13500	184	0	2
14000	184	0	2
14500	182	0	3
15000	182	0	4
15500	178	0	8
16000	178	0	8
16500	178	0	8
17000	176	0	14
17500	174	0	18
18000	174	0	18
18500	172	0	20
19000	172	0	20
19500	168	0	22
20000	166	0	22
20500	166	0	22

TYPICAL CURVE SHOWING FORMATION OF NORMAL SODIUM
CARBONATE AND VARIATION OF TOTAL ALKALINITY AND
FREE CO₂ IN THE EFFLUENT OF A ZEOLITE SOFTENER.
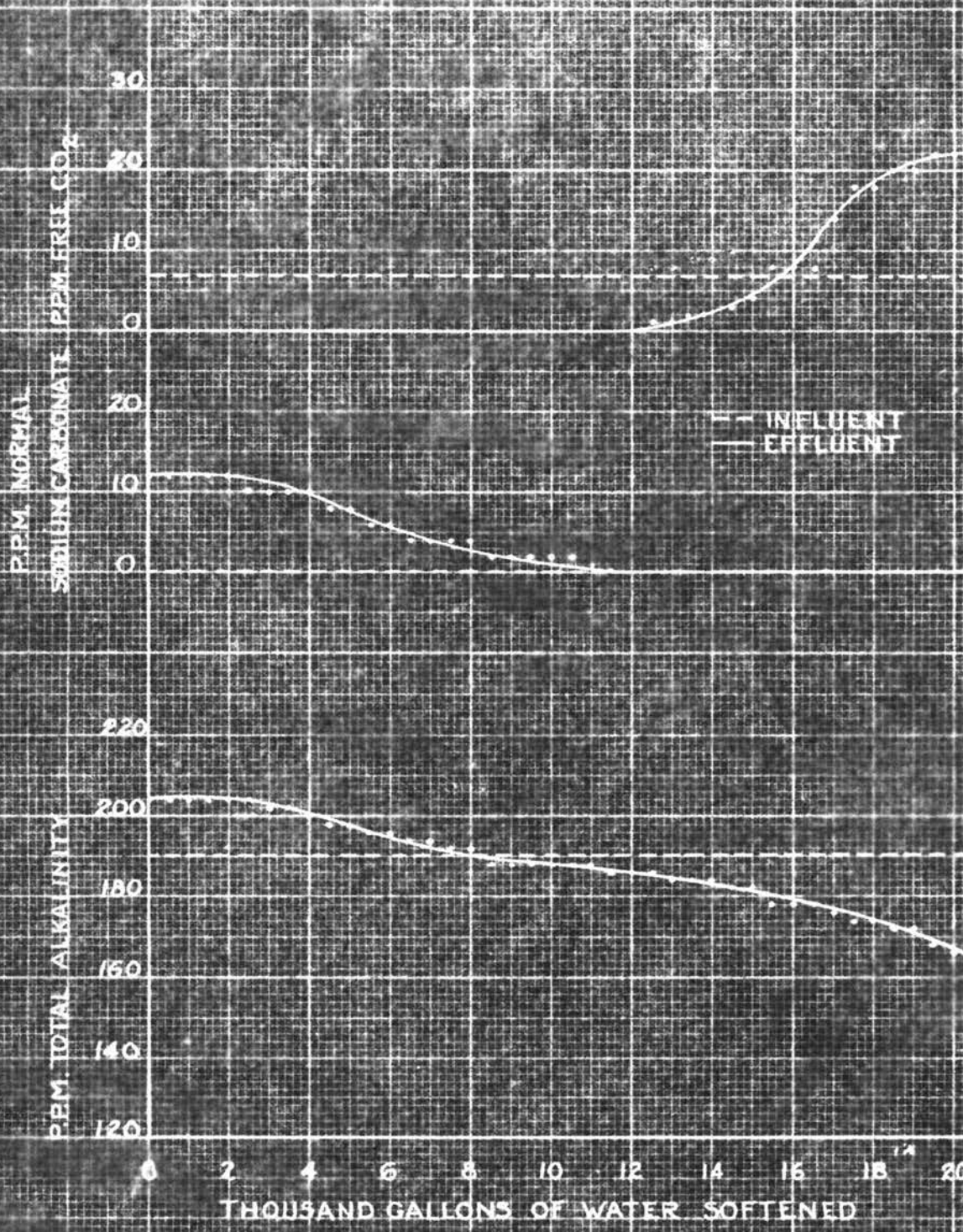
Fig. 5

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From the data we now had, the assumption of the formation of hydrogen zeolite seemed quite logical because of the way its formation and reactions would fit into the known facts. It is believed that the reaction between sodium zeolite and carbonic acid is as follows:

$$H_2CO_3 + Na_2Z \longrightarrow H_2Z + Na_2CO_3$$

However, if the free carbon dioxide content of the influent to the zeolite softener is about 15 p. p. m. or higher the normal sodium carbonate is converted to the bicarbonate and never appears in the effluent as normal sodium carbonate. If the free carbon dioxide content of the influent water is lower than 15 p. p. m. the normal sodium carbonate does appear in the effluent.

The assumption of the formation of hydrogen zeolite, and its subsequent reaction also explains the decrease in the total alkalinity of the effluent to a value below that of the influent water during the latter part of the softening run, and explains the increase in quantity of the free carbon dioxide in the effluent during this latter stage.

As the softening run progresses the quantity of sodium zeolite in the bed decreases and there is a corresponding increase in the quantity of calcium, magnesium and hydrogen zeolite. Finally a point is reached where the ability of the sodium zeolite to exchange completely with the H_2CO_3 is exceeded. As still more sodium is replaced by calcium and magnesium a point is reached where an exchange reaction occurs between the hydrogen zeolite and the calcium and magnesium salts entering the softener. This reaction would of course give an acid and either calcium or magnesium zeolite. The mineral acids so formed would react with the sodium bicarbonate, thus lowering the total alkalinity and causing the observed increase in the free carbon dioxide.

Behrman and Gustafson[5] while studying the effect of low pH waters on zeolites, also observed the pH change which occurs throughout the softening run. They found shorter runs were obtained when using influent water that had been treated with sulfuric acid, than were obtained when the water was not so treated.

On the assumption that H_2CO_3 does react with sodium zeolite forming hydrogen zeolite and sodium carbonate, then the softening run should be shorter when using influent water that had been treated with acid. The hardness of the water as far as the zeolite is concerned will be materially increased, if the carbonic acid formed is not removed from the treated water prior to the time it entered the softener.

The following experiments were made to determine whether the assumption that the hydrogen zeolite was formed by a reaction with the dissolved carbon dioxide in the influent water.

Carbon dioxide gas was passed through distilled water until the pH of the water was 6.8. The water was then allowed to percolate through a small quantity of sodium zeolite (greensand). After passing through the zeolite bed the pH of the water was 9.0, and a titration revealed that there were 21 p. p. m. of normal sodium carbonate present, and that there was no bicarbonate alkalinity. Next, carbon dioxide was passed through distilled water until the pH was lowered to 4.9. When this water was allowed to percolate through the zeolite bed the pH of the water after passing through the bed was 7.9. The alkalinity was due entirely to bicarbonates, no normal carbonate being present. Titration showed the total alkalinity to be 100 p. p. m. as Na_2CO_3.

When sufficient carbonated distilled water had been poured through

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[5] Behrman, A. S. and Gustafson, H., Ind. Eng. Chem., 28:1279-83 (1936)

the bed so that there was no change in alkalinity upon its passage,
tap water of pH 7.5 and a total alkalinity of 190 p. p. m. was passed
through the zeolite bed. The effluent water had a pH of 4.4 after it
had been boiled to drive off any carbonic acid.

This definitely proved that carbon dioxide dissolved in water is
responsible for the observed changes which occur in the pH, total alka-
linity, and dissolved carbon dioxide content, of the effluent of a ze-
olite softener. Of course any acid could form hydrogen zeolite by re-
action with the sodium zeolite, but under normal operating conditions,
the formation of hydrogen zeolite is dependent upon the presence of
carbon dioxide in the influent water.

The explanations of the corrosive character of many zeolite sof-
tened waters have been many and varied, but it is believed by the auth-
or that the effluent water during the latter stages of a softening run
is the water that is responsible for the corrosive characteristics. A
water containing an appreciable quantity of free carbon dioxide should
by all means be aerated before being softened by the base exchange
method using any of the sodium zeolites.

SUMMARY

This study brings to light some reactions which occur during the base exchange method of water softening which have not been previously mentioned in the literature.

When a water containing calcium and magnesium salts and dissolved carbon dioxide is passed through a freshly regenerated bed of sodium zeolite the total alkalinity of the effluent shows a marked increase above the total alkalinity of the influent. As the softening run progresses the total alkalinity of the effluent gradually decreases until, before the end of the run is reached, it drops below that of the influent. The effluent will contain no free carbon dioxide at the beginning of a softening run; however, before the run is finished the effluent will contain free carbon dioxide in excess of that present in the influent.

The formation and reaction of hydrogen zeolite is responsible for these changes. Hydrogen zeolite is formed by the reaction of carbonic acid with the sodium zeolite. The resulting normal sodium carbonate causes the increase in alkalinity which is observed at the beginning of a softening run. If the influent water is high in free carbon dioxide, then normal sodium carbonate does not appear in the effluent, but instead sodium bicarbonate is found.

As the quantity of sodium zeolite remaining in the bed becomes smaller the hydrogen zeolite, formed during the first part of the run, begins to react with the calcium and magnesium ions forming calcium and magnesium zeolite and an acid. The acid thus formed reacts with the sodium bicarbonate reducing the total alkalinity and pH, and forming

carbonic acid. This accounts for the observed decrease in total alkalinity and pH, and the increase in the quantity of free carbon dioxide during the latter stage of the softening run.

If a water to be softened by the base exchange method is found to contain a considerable amount of dissolved carbon dioxide, it would be desirable practice to expel the gas before softening the water. Otherwise a water of a corrosive nature would be obtained during the latter part of each softening run.

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AUTOBIOGRAPHY

I, Roy Edwin King was born near Enid, Oklahoma, June 9, 1906.
I attended the public schools there, and was graduated from High School
in the Spring of 1924.

I received a B. S. Degree in Chemical Engineering from Oklahoma
A. and M. College in 1929. I was a student member of the American
Chemical Society, and a charter member of Alpha Delta chapter of Phi
Lambda Upsilon.

During the first year after graduation, I was employed in the sales,
service, and supervision of installation of water treating equipment, in
Oklahoma and adjacent states.

In June, 1930 I married Miss Cornelia Shell, who was graduated from
Oklahoma A. and M. College in 1929, with a B. S. Degree in Home Economics.
We have a six year old son.

I returned to Oklahoma A. and M. College in 1931 and did graduate
work in chemistry and engineering.

Since August, 1932, I have been employed by the Panhandle Power
and Light Company, Borger, Texas. I have been in charge of the chemical
control of this company's plants in the Texas Panhandle.

Typed By:

Marvin D. Livingood