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Theoretical Limits of the Lime-Soda Method of Water Softening

T. E. LARSON AND A. M. BUSWELL
Illinois State Water Survey, Urbana, Ill.

Revised calculations involving the activity coefficients of the Debye-Hiickel theory and common ion effect show that under specific conditions lime-soda softening may produce a water of hardness as low as 10 to 15 p. p. m.

The beneficial effect of the use of sodium aluminate in water softening is due to an increase in caustic alkalinity and colloidal coagulating action rather than to the formation of insoluble aluminates. The presence of small amounts of colloidal silica is beneficial to coagulation.

SEVERAL reports in the literature (3) have indicated exceptionally low residual hardness on auxiliary treatment in softening with sodium aluminate. Although it has been reported *(6, 10)* that the presence of aluminate induces the precipitation of a highly insoluble magnesium aluminate, no experimental proof was presented to verify this assumption.

A careful consideration of the solubilities of calcium carbonate and magnesium hydroxide will show the variations that may be expected from lime-soda softening, with or without the presence of sodium aluminate.

The solubility products for calcium carbonate and magnesium hydroxide as commonly used give the expected residual hardness as 24.2 p. p. m. (as calcium carbonate).

Using the activity product data of Johnston (7) and Kline *(8)* and the activity coefficients derived from the Br0nsted-LaMer modification of the Debye-Hiickel equation for waters of various ionic strengths (μ), and using sodium sulfate as the typical nonincrusting salt, the following data are indicated (in parts per million):

Na_2SO_4	0	100	500
$\mu^{1/2}$	0.026	0.053	0.106
Ca(as $CaCO_3$)	7.9	8.9	11.4
Mg(as $CaCO_2$)	11.4	12.2	14.1
Total (as $CaCO_2$)	19.3	21.1	25.5

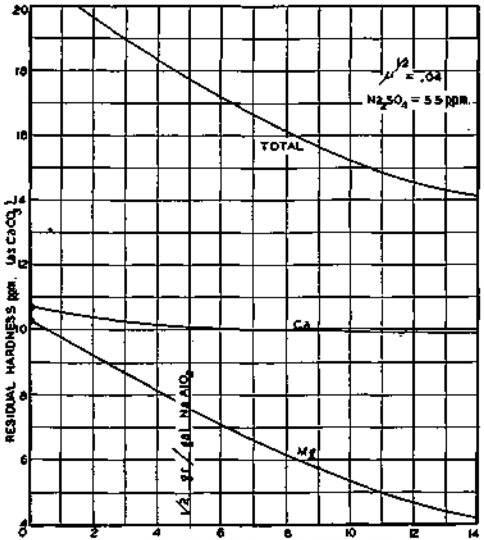


FIGURE 1. EFFECT OF ADDITION OF SODIUM ALUMINATE ON HARDNESS

However, the calcium carbonate hydrolyzes:

$$2CaCO_3 + H_2O \rightleftharpoons 2Ca^{++} + x\,CO^{--} + y\,OH^- + y\,HCO_3^-$$
$$\text{where } x + y = 2$$
$$\text{and } (Ca^{++})_{total} = (CO_3^{--}) + {}^1/_2(OH^-) + {}^1/_2(HCO_3^-) \qquad (1)$$

Only the CO_3^{--} of the alkalinity present can be used in the solubility product calculations. However, any excess of either *y* or *x* will decrease the calcium solubility. Magnesium hydroxide is ionized to give excess hydroxyl ions. It can also be shown that with residual alkalinities less than 100 p. p. m. (as calcium carbonate), the maximum CO_3^{--} concentration is obtained at a pH of 10.4.

Lime-soda softening alone at normal temperatures (15° to 25° C.) should give the following approximate residual hardness (calculated with the mutual effect of presence of excess hydroxyl ion from calcium carbonate and magnesium hydroxide hydrolysis, in parts per million):

$\mu^{1/2}$	0.026	0.106
Ca	10.0	14.8
Mg	10.0	12.6
Total	20.0	27.4

These calculations and data presuppose final equilibrium and cannot be valid otherwise since the constants and equations are all on the basis of final equilibrium. The data, therefore, do not give values to be expected in softening practice but give those that may be approached under proper regulation.

Since the rate of reaction doubles with approximately every 10° C. rise in temperature, and since carbon dioxide is expelled and leaves excess hydroxide as the soluble calcium hydroxide, precipitation and coagulation should be more complete at elevated temperature. This is the basis for hot water softening. As the result of such treatment the values given will be less for magnesium and may be more for calcium.

Should a compound such as sodium aluminate be added to the extent of 0.5 gram per gallon, complete hydrolysis to aluminum hydroxide should give excess hydroxyl ion to the extent of 5 p. p. m. (as calcium carbonate), which should reduce the calcium plus magnesium hardness by 3.4 p. p. m. (Figure 1). Actual tests showed that the hardness reduction by addition of sodium aluminate were greater than calculated values for excess hydroxyl ion, particularly for magnesium.

Clark and Price *(5)* gave four reasons why low final hardness due to the formation of very insoluble magnesium aluminate is probably untrue. To these may be added the fact that if this were so, magnesium aluminate would be the first to precipitate, leaving the excess magnesium to obey the solubility or "activity" product equation for magnesium hydroxide, since the magnesium concentration is always greater than the aluminate concentration.

SAMPLES of magnesium chloride, ⅔ e. p. m. (equivalents per million equivalents of water) or 33 p. p. m. (as calcium carbonate) samples were treated with varying amounts of sodium aluminate (92 per cent). The results of analyses (gravimetric) showed that the magnesium was precipitated not according to the aluminate concentration but according to the hydroxyl-ion concentration. The aluminate precipitated was far less than that which would be expected to be removed per equivalent of magnesium removed.

Samples of tap water (hardness 275 p. p. m., alkalinity 340 p. p. m., total mineral content 365 p. p. m.) were treated with sulfuric acid to give a noncarbonate water. These and unaltered 2-liter samples were thoroughly aerated to remove carbon dioxide and treated in 3.5-liter battery jars with varying amounts (not greatly different from theoretical requirements) of lime and soda ash or lime alone.

Since tests showed that calcium carbonate did not form or settle out as readily as magnesium hydroxide unless sufficient stirring was employed, a 2-hour stirring period and a 1-hour settling period were used in all tests. Samples were collected from the supernatant liquor and analyzed according to Standard Methods of Water Analysis *(1)* without filtration.

Tests *C* and *D* (Table I, Figure 2), typical of eight series, show the effect of the addition of 0.5 grain per gallon of sodium aluminate. In these tests, as in the others, the effect of the presence of hydroxyl ion (due to hydrolysis of sodium aluminate) is clearly evident. The residual calcium as well as magnesium is decreased. The decrease is more than can be accounted for by calculation, which shows that the action of aluminate and the hydrous alumina aid in coagulating the colloidal magnesium hydroxide and calcium carbonate. The residual hardness was in no case less than the theoretical limit calculated for final equilibrium.

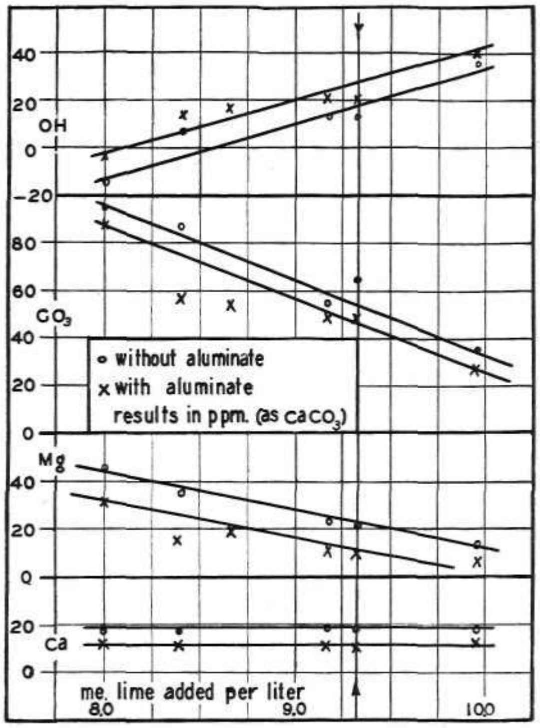
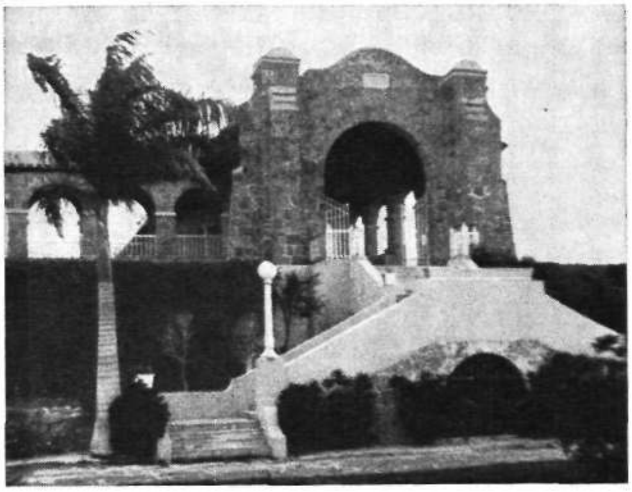


FIGURE 2. EFFECT OF ADDING 0.5 GRAIN PER GALLON OF SODIUM ALUMINATE



Courtesy, Alvord, Burdick & Howson, Chicago, Ill.

ENTRANCE TO THE OPERATING GALLERY OF THE MIAMI, FLA., SOFTENING PLANT WITH A CAPACITY OF 40 MILLION GALLONS A DAY

TABLE I. EFFECT OF ADDING 0.5 GRAIN PEB GALLON OF SODIUM ALUMINATE

	M. E.[a] Added/Liter		Residual P. P. M./Liter (as $CaCO_2$)				
Test	CaO $NaCO_2$	$NaAlO_2$	OH	CO_2	Ca	Mg	Total
			C. 2-Hour Stirring				
Original soln.	9.32[b]	...	−345.0	...	155.0	121.0	276.0
1	8.00	...	− 14.1	94.6	16.1	45.3	61.4
2	8.00	0.10[c]	− 12.1	98.8	14.1	47.1	61.2
3	9.33	...	13.1	64.5	17.2	21.6	48.8
4	8.00	0.10	− 3.0	86.6	10.4	31.4	41.8
5	9.33	0.10	20.2	48.4	9.9	9.0	18.9
6	8.66	0.10	17.2	54.4	12.5	18.0	30.5
			D. 4-Hour Stirring				
1	8.40	0.10	14.1	56.4	9.9	15.3	25.2
2	8.40	...	7.0	86.6	17.2	35.1	52.3
3	9.18	0.10	21.2	48.4	10.4	11.3	21.7
4	9.18	...	13.1	54.4	17.2	23.4	40.6
5	9.96	0.10	40.3	26.2	11.5	5.8	17.3
6	9.96	...	36.2	36.2	16.7	13.5	30.2

[a] Milliequivalents.
[b] Theoretical requirement.
[c] NaOH equivalent to $NaAlO_2$

SINCE sodium aluminate has been found very effective in the removal of large quantities of soluble silica (4, *11)*, it was decided to investigate the possible effect of soluble silica in water softening.

Synthetic samples of tap water were made with controlled amounts of silica present. Experiments indicated that the presence of some silica (6 p. p. m.) even with high excess hydroxyl-ion concentration and aluminate was necessary for good coagulation. Also if high silica (30 p. p. m.) was present but no sodium aluminate, the solution remained very turbid and did not settle out. Natural waters nearly always contain 5 to 20 p. p. m. soluble silica; therefore from the tests cited little more than theoretical value can be derived. Also, since the stock solution was of diluted water glass from a 40 per cent commercial brand, there was also about an equal quantity of insoluble silica present due to hydrolysis. Colloidal silica itself is an aid to coagulation, and it is probable that this is the effective agent in these tests rather than the soluble silica. Baylis (*2*) also reported that the presence of silica in some form has an effect on coagulation. Since colloidal silica is negatively charged in alkaline solution, its action should be similar to colloidal alumina. On the addition of sodium aluminate anhydrous aluminosilicate may be formed which should have action similar to the clays described by Mattson (*9*).

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WATER SOFTENING

Sign of the Charge on Colloidal Particles of Hydrous Alumina, Hydrous Magnesium, and Calcium Carbonate

T. E. LARSON AND A. M. BUSWELL
Illinois State Water Survey, Urbana, Ill.

Colloidal hydrous alumina is negatively charged above, and positively charged below, a pH of 8.2. As the pH changes on aging, a flocculation zone is approached in which basic aluminum sulfate of variable composition constitutes the solid phase. Colloidal calcium carbonate is shown to be negatively charged and magnesium hydroxide positively charged throughout the pH range of water softening.

THE relation between electrical charge and certain coagulation effects met with in water purification is not clear in several instances. This is partly due to the earlier notion that hydrous alumina was positively charged throughout the pH range encountered and partly due to a lack of information concerning the charge on other precipitating substances.

Various optimum pH zones of coagulation for alum floc have been reported in the literature *(1,2, 3, 8, 9)*. Investigations have shown that these zones are dependent to a certain extent upon the type and concentration of ions in the water to be coagulated *(2, 8, 9)*. The purpose of this paper is to present data on the charge on colloidal calcium carbonate and magnesium hydroxide, and to indicate the change undergone by hydrous alumina in connection with coagulation and softening.

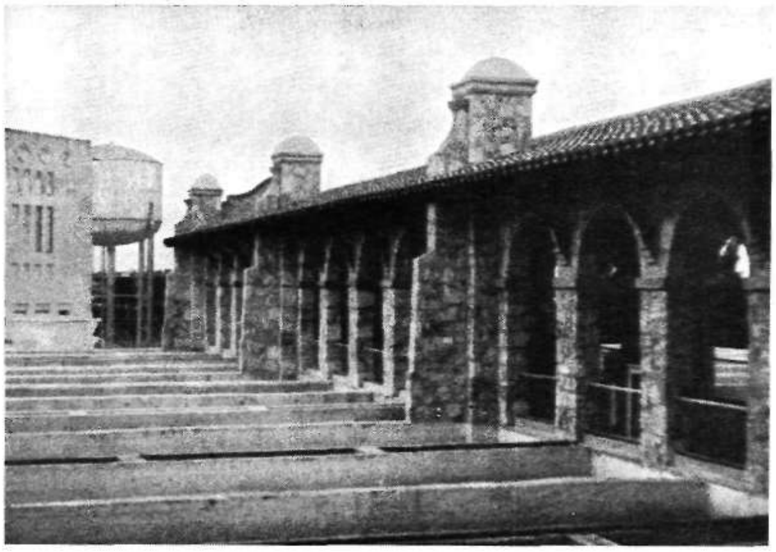
Electrophoresis determinations were made on hydrous alumina at various pH values by means of the ultramicroscope with the cylindrical cell of Mattson *(5)*. Corrections for light beam deviation *(4)* were used to obtain focus at the correct depth. The pH was determined potentiometrically with a glass electrode.

The hydrous alumina was prepared by adding aluminum chloride and aluminum sulfate, respectively, to various concentrations of sodium hydroxide. Continued stirring showed a steady change in the pH of the solution. When aluminum chloride was used, if the initial pH on addition of the coagulant was greater than 8.2 the colloidal particles were negatively charged and the pH decreased with time. If the initial pH was less than 8.2, the particles were of positive charge and the pH increased with time.

When aluminum sulfate was used, the behavior was similar to that of aluminum chloride when the initial pH was greater than 8.2. When the initial pH was less than 8.2, an increase with stirring was noted, but if the final pH became as great as 7.6 to 8.2, flocculation occurred. Colloidal particles were positively charged below 7.6 and negatively charged above 8.2. As the pH changed, particles of opposite charge appeared in the solution, and when flocculation occurred, particles of either charge were equally apparent. Typical data are shown in Figure 1 for 2 grains of $A1_2SO_4.16H_2O$ per gallon.

The fact that aluminum hydroxide is not the only compound in the solid phase when polyvalent negative ions are present accounts for the variation in isoelectric point when other than monovalent ions are present. Miller *(8)* has shown the existence of a basic aluminum sulfate of composition varying with pH (or hydroxyl-ion concentration), and aluminum concentration. Each of these compositions of basic aluminum sulfates should have a particular isoelectric point, which explains the zone of precipitation found when sulfate is present. Mattson *(6)* checked Miller's work with phosphate present and varied the phosphate concentration to obtain basic aluminum phosphates, each having a particular isoelectric pH for the particular phosphate concentration within the zone of insolubility. Likewise aluminosilicates were shown to have isoelectric points varying with the relative concentration of aluminum and silicate present *(7)*.

Magnesium hydroxide was found to be positively charged at all pH values as high as 12, beyond which no determinations were considered necessary. Calcium carbonate was found to have a negative charge in the presence of calcium bicarbonate as well as in the presence of calcium hydroxide.



Courtesy, Alvord, Burdick & Howaon, Chicago, Ill.

THE MILD CLIMATE AT MIAMI MAKES IT PRACTICABLE TO OMIT THE CUSTOMARY BUILDING OVER THE FILTERS OF THE SOFTENING PLANT

The relatively slow approach to equilibrium is shown by the change of pH with prolonged stirring, which is substantially equivalent to aging. Proper mixing and sufficient detention period are primary prerequisites for efficient softening and coagulation. The resulting formations of precipitates of variable composition of mixtures of various insoluble compounds are significant in many phases of water treatment. Although no definite stoichiometric relations can be shown, it is seen that color, turbidity, and bacteria removal are all dependent on pH of flocculation of the agent which, in turn, is dependent on the relative concentration of polyvalent ions present. Each particular water should have a particular isoelectric pH for each concentration of aluminum added, and this pH will also vary according to whether the aluminum is added as potassium alum, filter alum, aluminum chloride, or sodium aluminate. This pH will depend slightly on the form and amount of colloidal matter (color, turbidity, and bacteria) and more definitely on the highly charged, greater concentrations of polyvalent ions such as sulfate, carbonate, silicate, and iron.

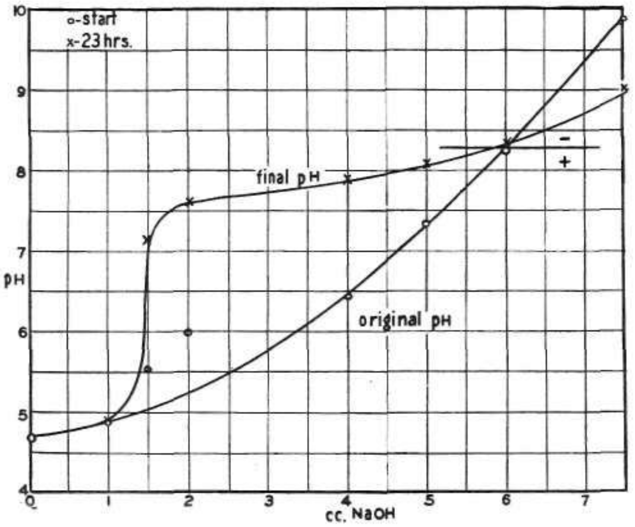


FIGURE 1. DATA FOR ALUMINUM SULFATE

Likewise, the addition of an aluminum floc in treatment should not be so effective as the addition of aluminum in solution or in the solid or colloidal state since in that event, two consecutive reactions must take place instead of one. These steps are solutions of ions combined with aluminum to maintain equilibrium with those in solution, and then adsorption of ions from solution to maintain another solid-to-solution equilibrium. This does not mean that the use of a floc would be totally ineffective, whether it be freshly prepared or obtained from a previous coagulation.

With reference to water softening where the pH is high, most of the aluminum should exist as soluble aluminate. In the presence of considerable excess magnesium hydroxide (positively charged), definite adsorption of and coagulation by the negatively charged aluminate ions and alumina particles should take place. Colloidal particles are coagulated by oppositely charged particles as well as by ions, and the resulting hydrous oxides act as catalysts or reservoirs for hydrogen and hydroxyl ions adjacent to the magnesium and aluminum hydroxides as the relatively slow formation of calcium carbonate takes place and thereby hastens the approach to equilibrium.

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Effect of Carbonate-Ion Concentration in Water Softening

T. E. LARSON
State Water Survey, Urbana, Ill.

This paper and one published previously (4) present revised calculations that indicate the cosolubility of calcium carbonate and magnesium hydroxide to be 20 p. p. m. (as calcium carbonate) at 25° C. The presence of nonincrustant salts increases the solubility. Excess of hydroxyl or carbonate ion decreases the solubility. The known beneficial effect of sodium aluminate is shown to be due to the excess hydroxyl ion formed on hydrolysis and the coagulating power of hydrous alumina.

The solubility of both may be decreased considerably by treatment with excess reagent. The curves derived from the constants and equations presented give a basis for determining the relative limits of softening with excess treatment by the lime-soda method. The solubility data indicate that at 25° C, 7 to 20 p. p. m. excess may be added before the total mineral content is increased.

A RECENT publication (4) indicated the related solubility of calcium carbonate and magnesium hydroxide as calculated from solubility products, activity coefficients, and common ion effect. This paper indicated the theoretical effect of softening with excess hydroxyl ion from lime, sodium hydroxide, or sodium aluminate.

It is appropriate to complete the picture on these limits of softening by indicating the theoretical effect of excess soda ash as practiced in many municipal and industrial plants. The results of the calculations are shown in curves (Figure 1) in which the following constants or equations were used:

$$K_{CaCO_3} = 0.48 \times 10^{-8} \quad (1) \qquad \text{(A)}$$

$$K_{Mg(OH)_2} = 5.0 \times 10^{-12} \quad (2) \qquad \text{(B)}$$

$$K_{2(HCO_3)} = 5.59 \times 10^{-11} \quad (5) \qquad \text{(C)}$$

$$\mu = 0.000025 \text{ total mineral content, in p. p. m.} \quad (3) \qquad \text{(D)}$$

$$pK'_{2(HCO_3^-)} = pK_2 - 1.2\,\mu^{1/2} \quad (6) \qquad \text{(E)}$$

$$-\log \gamma_i = 0.4\, z_i^2 \mu^{1/2} \qquad \text{(F)}$$

$$pH = -\log(\gamma_1 H^+) \qquad \text{(G)}$$

$$K_w = 10^{-14} \qquad \text{(H)}$$

$$pH = 14 - \log \frac{50{,}000}{(OH^-)} - 0.4\,\mu^{1/2} \qquad \text{(I)}$$

where (OH^-) = concn. in p. p. m. (as $CaCO_3$)

$$(\text{Alk.}) = 10^6\left(\frac{K_2K_w}{\gamma_2(\gamma_1H^+)^2} + \frac{K_w}{\gamma_1(\gamma_1H^+)}\right) \qquad \text{(J)}$$

where (Alk.) = Na_2CO_3 = concn., in p. p. m. (as $CaCO_3$)

$$p(Ca^{++}) = (pK_s - pK_2) - p[(\text{Alk.}) - (OH^-)] - 3.6\,\mu^{1/2} - \log[(2\gamma_1K_2 + \gamma_2(\gamma_1H^+)] \qquad \text{(K)}$$

where (Ca^{++}) = concn., in moles/liter
(Alk.) = total alkalinity = $(HCO_3^-) + (CO_3^{--}) + (OH^-)$ = concn., in equivalents/liter
$(OH^-) = \dfrac{10^{-14}}{\gamma_1(\gamma_1H^+)}$ = concn., in equivalents/liter

$$p(Mg^{++}) = 2pH - 2pK_w + pK_{Mg(OH)_2} - 1.6\mu^{1/2} \qquad \text{(L)}$$

where Mg^{++} = concn., in moles/liter

The pH of hydroxyl-carbonate mixtures was obtained graphically from data from Equations I and J. The value of 0.4 was arbitrarily chosen in Equation F, contrary to the common value of 0.5, since it appears to be a closer approach to actual data for mixed electrolytes. Complete reaction to equilibrium at 25° C. is presupposed. Nonincrustants are considered as salts having no effect on calcium carbonate or magnesium hydroxide solubilities other than their effect on the ionic strength of the water.

Consideration of the action of precipitation in connection with the common theory on the activity of ions leads to the conclusion that efficient precipitation induces more efficient precipitation by decreasing the ionic strength and resulting

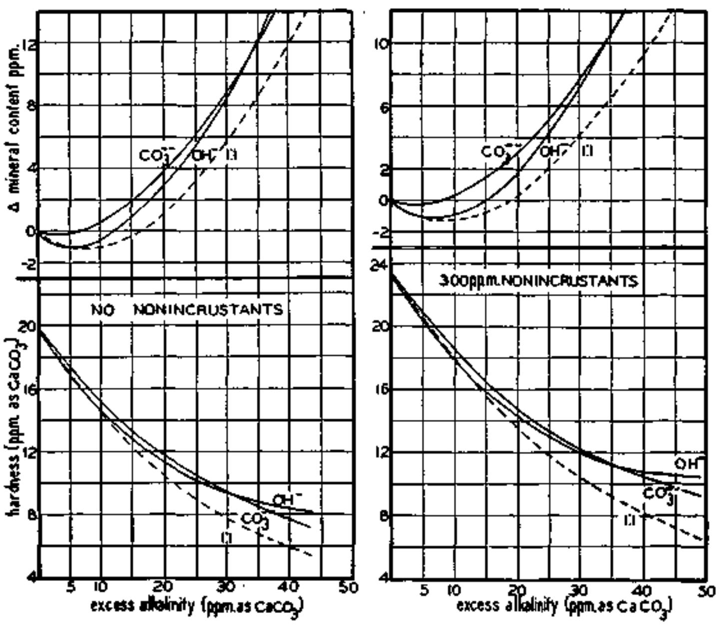

FIGURE 1. THEORETICAL EFFECT OF EXCESS SODA ASH

in increased ionic activity. However, this is counteracted by the decrease in reaction rate since fewer ions are involved as precipitation proceeds. Modern treatment methods involve the use of coagulants to combat slow rates of reaction and resultant colloidal solutions.

The calculated solubilities do not indicate appreciable differences in solubilities at equivalent amounts of different types or mixtures of types of alkalinity. The effect of treatment with excess soda ash on the residual hardness is similar to that obtained by treatment with an equivalent of sodium hydroxide. The effect of either is limited by the concentration of the other.

It would appear that excess treatment with equal parts of carbonate and hydroxyl ($2Na_2CO_3$:lCaO) would be more effective than treatment with either alone. However, from the theoretical data and the current cost of lime and soda ash, such treatment would not be economically effective unless an excess of more than 0.75 e. p. m. (equivalents per million parts of water) carbonate alkalinity were added.

From the standpoint of residual mineral content, excess treatment increases the mineral content only after a limited concentration, of excess has been added. At 25° C. the figures indicate that excess treatment may be from 0.15 to 0.4 e. p. m. before the mineral content becomes greater than the theoretical limit without excess treatment.

As previously stated *(4)*, the data presented do not give values to be expected in softening practice but indicate the limits that may be approached under proper regulation. More complete data on the constants involved would permit further desirable calculations to indicate higher solubility limits at 18° and lesser limits at 60° C.

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