

Water Softening and Conditioning Problems

SOLUTION BY CHEMICAL EQUILIBRIUM METHODS

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IN RECENT years, the equilibrium methods of physical chemistry have found increasing application in the solution of problems of applied chemistry encountered in the conditioning of water supplies. Largely through the efforts of McKinney (8) and Langelier (3), inconsistencies resulting from the use of older methods have been pointed out and new methods based on equilibrium considerations have been developed.

An important recent development is the stability diagram published by Langelier (4). Prior to the introduction of this diagram, calculation of the concentration of residual ions in solution resulting from the addition of conditioning chemicals was limited by the complexity of the mathematics involved. The stability diagram permits the rapid determination of the calcium carbonate saturation index and provides a basis for the calculation of the quantity of chemical involved in water conditioning for scale control and in lime soda softening. For problems of the latter type, calculations are difficult and time consuming, even with the aid of the stability diagram.

The construction and use of a diagram designed to simplify equilibrium calculations as applied primarily to water softening is described in this paper. Use of the diagram enables the determination of equilibrium concentrations of calcium, magnesium, total alkalinity, and pH as related to the dosage of any of the commonly used conditioning chemicals. Because the diagram is equally applicable to other water conditioning problems, it is termed a "water conditioning diagram."

Two diagrams are given for waters at two temperatures—25° and 100° C. In the following discussion the construction and use of the diagrams are described and examples are given illustrating their application to typical problems and correlation of graphical and experimental results is discussed.

CONSTRUCTION OF WATER CONDITIONING DIAGRAM

In the construction of the conditioning diagrams, the following steps were taken:

- A. Equations were derived giving quantitative changes in calcium, alkalinity, and pH occurring in a saturated calcium carbonate solution after the addition of each of the various conditioning chemicals.
- B. The equations were arranged as axes on a rectangular coordinate diagram.
- C. Equilibrium equations were then derived giving the calcium, alkalinity, and pH in terms of the coordinate axes.
- D. Using the equations developed in C, three families of lines were plotted on the rectangular coordinate diagram giving equilibrium values for calcium, alkalinity, and pH.
- E. Equations were developed to indicate that the axes of the diagram may also be used to measure the chemical dosage.
- F. The relationship between magnesium and pH was added as a separate scale.

ADDITION OF CONDITIONING CHEMICALS TO A SATURATED CALCIUM CARBONATE SOLUTION. The conditioning chemicals considered are: calcium hydroxide, sodium carbonate, sodium hydroxide, sodium bicarbonate, carbon dioxide, hydrogen ion, and calcium chloride or sulfate. Derivation of equations giving quantitative changes in calcium, pH, and the various forms of alkalinity can be illustrated by an example involving the addition of calcium hydroxide to a saturated calcium carbonate solution. In this and subsequent developments it is assumed that the solution is in equilibrium with solid calcium carbonate at all times.

When calcium hydroxide is added to a saturated solution of calcium carbonate and bicarbonate ions, calcium carbonate will be precipitated. The decrease in calcium plus the calcium added will equal the decrease in total carbonate—i.e., the decrease in the sum of the equivalent carbon dioxide, bicarbonate, and carbonate. This reaction may be expressed as follows:

$$\Delta(\text{Ca}^{++}) + (\text{Ca}^{++}) \text{ added} = \Delta(\text{CO}_2) + 2\Delta(\text{HCO}_3^-) + \Delta(\text{CO}_3^{--}) \quad (1)$$

where Δ represents a decrease in concentration and $()$ denotes concentrations expressed in gram equivalents per liter.

Since the hydroxide from the added calcium hydroxide is available to react with both the carbon dioxide and the bicarbonate or to increase the hydroxide concentration, the calcium added may be expressed as follows:

$$(\text{Ca}^{++}) \text{ added} = \Delta(\text{CO}_2) + \Delta(\text{HCO}_3^-) - \Delta(\text{OH}^-) \quad (2)$$

Substituting Equation 2 in Equation 1

$$\Delta(\text{Ca}^{++}) = \Delta(\text{HCO}_3^-) + \Delta(\text{CO}_3^{--}) + \Delta(\text{OH}^-) \quad (3)$$

Since

$$(\text{alky.}) + (\text{H}^+) = (\text{HCO}_3^-) + (\text{CO}_3^{--}) + (\text{OH}^-)$$

Equation 3 may be written as follows:

$$\Delta(\text{Ca}^{++}) = \Delta(\text{alky.}) + \Delta(\text{H}^+) \quad (4)$$

Equation 4 shows that when calcium hydroxide is added to a saturated solution of calcium carbonate, thereby precipitating solid calcium carbonate, the change in calcium must equal the change in alkalinity plus hydrogen. For this case then, the following equilibrium equation may be written:

$$(\text{Ca}^{++}) - (\text{alky.}) - (\text{H}^+) = C \quad (5)$$

where C is an arbitrary constant.

For the addition of sodium carbonate, the change in calcium must equal the change in total carbonate plus the carbonate added.

Hence

$$\Delta(\text{Ca}^{++}) = \Delta(\text{CO}_2) + 2\Delta(\text{HCO}_3^-) + \Delta(\text{CO}_3^{--}) + (\text{CO}_3^{--}) \text{ added} \quad (6)$$

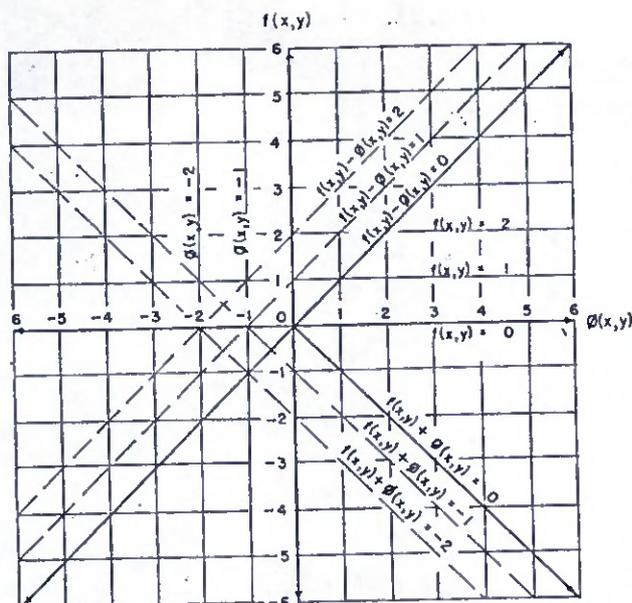


Figure 1. Rectangular Coordinate Diagram Showing General Relationship between Two Variables

Since the carbonate added may react with carbon dioxide to produce bicarbonate, hydrolyze to produce hydroxide, or be consumed in precipitating calcium, the following equation may be written:

$$(CO_3^{++}) \text{ added} = -\Delta(HCO_3^-) - \Delta(CO_3^{--}) - \frac{\Delta(OH^-)}{\Delta(Ca^{++})} \quad (7)$$

Substituting Equation 7 in Equation 6

$$\Delta(HCO_3^-) + \Delta(CO_2) - \Delta(OH^-) = 0 \quad (8)$$

or

$$(HCO_3^-) + (CO_2) - (OH^-) = C \quad (9)$$

Equations for other conditioning chemicals have been worked out in a similar manner with the following results:

Sodium hydroxide

$$2(HCO_3^-) + (CO_3^{--}) + (CO_2) - (Ca^{++}) = C \quad (10)$$

Sodium bicarbonate

$$(Ca^{++}) - (CO_3^{--}) + 2(H^+) - 2(OH^-) + (CO_2) = C \quad (11)$$

Carbon dioxide

$$(alky.) + (H^+) - (Ca^{++}) = C \quad (12)$$

Acid (except carbonic or phosphoric) and magnesium salt

$$(Ca^{++}) - 2(HCO_3^-) - (CO_3^{--}) - (CO_2) = C \quad (13)$$

Calcium chloride or sulfate

$$(OH^-) - (HCO_3^-) - (CO_2) = C \quad (14)$$

SELECTION OF AXES OF CONDITIONING DIAGRAM. Two equations of the forms $f(x,y) = C_1$ and $\phi(x,y) = C_2$ can be illustrated graphically as two families of parallel straight lines intersecting at an arbitrary angle. If the angle of intersection is taken as 90°, the plotted equations, when each constant is zero, become the axes of a rectangular coordinate system as illustrated in Figure 1. The general equation of all lines making an angle of 45° with the coordinate axes and having a positive slope is $f(x,y) - \phi(x,y) = C_1 - C_2$, while the equation for similar lines with a negative slope is $f(x,y) + \phi(x,y) = C_1 + C_2$.

An analysis of the equations developed shows that by letting the equation $f(x,y) = C_1$ represent the equation for sodium carbonate, and the equation $\phi(x,y) = C_2$ represent the equation for calcium hydroxide, the equations for sodium hydroxide and sodium bicarbonate can be represented by $f(x,y) - \phi(x,y) =$

$C_1 - C_2$ and $f(x,y) + \phi(x,y) = C_1 + C_2$, respectively. The equation for carbon dioxide is the negative of the equation for calcium hydroxide; calcium chloride is the negative of sodium carbonate; and acid or magnesium salt is the negative of sodium hydroxide. Substituting the equations for the general functions, the diagram appears as shown in Figure 2. The scale of the vertical axis is in terms of $f(x,y)$, while the scale of the horizontal axis is in terms of $\phi(x,y)$.

EQUILIBRIUM EQUATIONS FOR CALCIUM, ALKALINITY, AND pH. Figure 2 represents a rectangular coordinate system in two functions, $f(x,y) = (HCO_3^-) + (CO_2) - (OH^-) = C_1$ and $\phi(x,y) = (Ca^{++}) - (alky.) - (H^+) = C_2$. Each function includes all or some of the following variables: (OH^-) , (HCO_3^-) , (CO_2) , (H^+) , (Ca^{++}) , and $(alky.)$, hence every point on the diagram is a function of these variables. In order to use the diagram for the purposes intended it is necessary to locate three additional families of lines representing constant values of calcium, alkalinity, and pH. This can be done in several ways, the most direct of which would be to develop equations for the desired variable in terms of the coordinate axes.

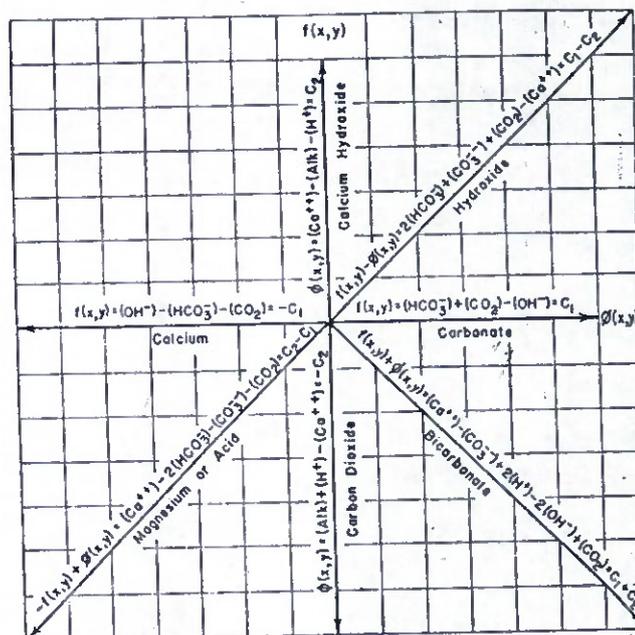


Figure 2. Rectangular Coordinate Diagram for Water Showing Relationship among the Variables (OH^-) , (HCO_3^-) , (CO_2) , (H^+) , (Ca^{++}) , and $(alky.)$

In order to accomplish this, it is necessary to have additional equations relating calcium with the various forms of alkalinity and pH.

These may be obtained from the following mass law equations

$$(Ca^{++}) (CO_3^{--}) = K_{CaCO_3} = K_4 \quad (15)$$

$$(H^+) (OH^-) = K_w \quad (16)$$

$$\frac{(H^+) (HCO_3^-)}{(H_2CO_3)} = K_1 \quad (17)$$

$$\frac{(H^+) (CO_3^{--})}{(HCO_3^-)} = K_2 \quad (18)$$

Using the above equations in conjunction with the equations of the diagram axes, the relationships shown in Equations 19 to 21 are developed.

In plotting the constant lines defined by the three equations, a value was first assigned to the variable in question, and the equation solved for values of one axis in terms of various assigned

pH lines

$$C_2 = \left\{ \frac{K_2}{\left[\frac{K_2(\text{OH}^-)}{K_w} \right]} \left[\frac{(\text{OH}^-) + C_1}{1 + \frac{K_2}{K_1(\text{OH}^-)}} \right] \right\} - \left\{ \frac{K_2(\text{OH}^-)}{K_w} \left[\frac{(\text{OH}^-) + C_1}{1 + \frac{K_2}{K_1(\text{OH}^-)}} \right] \right\} - \left\{ \frac{(\text{OH}^-) + C_1}{1 + \frac{K_2}{K_1(\text{OH}^-)}} \right\} - (\text{OH}^-) \quad (19)$$

Calcium lines

$$C_1 = (\text{Ca}^{++}) - \frac{K_2}{(\text{Ca}^{++})} + C_2 - \frac{-2 + \sqrt{4 - 4 \frac{K_2(\text{Ca}^{++})}{K_1 K_2} \left[-(\text{Ca}^{++}) + \frac{K_2}{(\text{Ca}^{++})} - C_2 \right]}}{2 \frac{K_2(\text{Ca}^{++})}{K_1 K_2}}$$

$$\frac{K_2 K_2}{K_2(\text{Ca}^{++})} \frac{-2 + \sqrt{4 - 4 \frac{K_2(\text{Ca}^{++})}{K_1 K_2} \left[-(\text{Ca}^{++}) + \frac{K_2}{(\text{Ca}^{++})} - C_2 \right]}}{2 \frac{K_2(\text{Ca}^{++})}{K_1 K_2}} \quad (20)$$

Alkalinity lines

$$C_1 = \frac{K_2}{C_2 + \text{alky.}} - \text{alky.} - \left[K_2 - C_2 - \frac{K_2}{C_2 + \text{alky.}} \pm \sqrt{\left(\text{alky.} - \frac{K_2}{C_2 + \text{alky.}} \right)^2 - \frac{4K_2 K_2}{K_2(C_2 + \text{alky.})}} \right] +$$

$$\frac{K_2(C_2 + \text{alky.})}{4 K_1 K_2} \left\{ \left[K_2 - C_2 - \frac{K_2}{C_2 + \text{alky.}} \right] \pm \sqrt{\left(\text{alky.} - \frac{K_2}{C_2 + \text{alky.}} \right)^2 - \frac{4K_2 K_2}{K_2(C_2 + \text{alky.})}} \right\}^2 \quad (21)$$

values of the other axis, using the equilibrium constants given in Table I. For example, a value of pH was selected, the corresponding (OH⁻) calculated and inserted in the equation which was then solved for $f(x,y) = C_1$ in terms of assigned values of $\phi(x,y) = C_2$. The completed diagrams are presented in Figures 3 and 4.

TABLE I. EQUILIBRIUM CONSTANTS USED IN CONSTRUCTING WATER CONDITIONING DIAGRAM

(Ionic strength, $\mu = 0.01 \approx 400$ p.p.m. dissolved solids)

Equilibrium Constants	Concn. at 25° C.		Concn. at 100° C.	
	Gram moles/liter	P.p.m. equiv. CaCO ₃	Gram moles/liter	P.P.M. equiv. CaCO ₃
(H ⁺) (HCO ₃ ⁻) = K ₁	10 ^{-6.3}	10 ^{-4.90}	10 ^{-6.36}	10 ^{-4.94}
(H ⁺) (CO ₃ ⁻) = K ₂	10 ^{-10.33}	10 ^{-8.15}	10 ^{-10.39}	10 ^{-8.69}
(H ⁺) (OH ⁻) = K _w	10 ^{-14.01}	10 ^{-14.01}	10 ^{-13.21}	10 ^{-12.81}
(Ca ⁺⁺) (CO ₃ ⁻) = K _{CaCO₃}	10 ^{-8.00}	10 ^{3.00}	10 ^{-7.5}	10 ^{3.10}
(Mg ⁺⁺) (OH ⁻) ² = K _(MgOH₂)	10 ^{-16.24}	10 ^{4.14}	10 ^{-15.47}	10 ^{3.53}

DOSAGE SCALES FOR CONDITIONING CHEMICALS. Up to this point, no provision has been made for measuring the quantity of conditioning chemical involved in moving from one point to another on the diagram. For this purpose it is necessary to consider only two distinct ions, hydroxide and carbonate. This is because, as far as their effect on the solubility of calcium carbonate is concerned, all conditioning chemicals are made up of these two ions, their chemical opposites, or combinations of the ions and opposites. The term "chemical opposites" is used to describe two chemical compounds which are chemically incompatible—i.e., which react with each other quantitatively. For example, calcium ion is chemically opposite to carbonate ion, and calcium hydroxide is a combination of calcium and hydroxide; carbon dioxide is chemically opposite to calcium hydroxide, and sodium bicarbonate is a combination of carbon dioxide and sodium carbonate. Magnesium ion reacts as an acid if it is precipitated as magnesium hydroxide.

These conclusions may be checked graphically by referring to

Figure 2. In this figure, for example, the direction of the calcium chloride line is opposite to that of sodium carbonate—i.e., the effect of adding calcium chloride is the reverse of adding sodium carbonate; hence the dosage of calcium ion may be measured in terms of a negative carbonate dose. This same reasoning also applies to the addition of the other chemicals listed, the dosages of which may all be measured in terms of equivalent carbonate or hydroxide ion.

To obtain the equations for chemical dosage of carbonate and hydroxide, it is necessary to consider the effect of adding each to a water solution saturated with calcium carbonate. For the addition of hydroxide a reaction can occur with carbon dioxide and bicarbonate to form carbonate, and free hydroxide can be produced; hence the equation may be written as follows:

$$\text{OH dosage} = \Delta(\text{CO}_2) + \Delta(\text{HCO}_3^-) - \Delta(\text{OH}^-) \quad (22)$$

In the addition of carbonate, a reaction can occur with carbon dioxide to form bicarbonate, some can hydrolyze to form bicarbonate and hydroxide, and free carbonate can be produced. Some of the carbonate, however, may be removed in precipitating calcium; hence the following equation may be written:

$$\text{CO}_2 \text{ dosage} = \Delta(\text{Ca}^{++}) - \Delta(\text{HCO}_3^-) - \Delta(\text{CO}_3^{--}) - \Delta(\text{OH}^-) \quad (23)$$

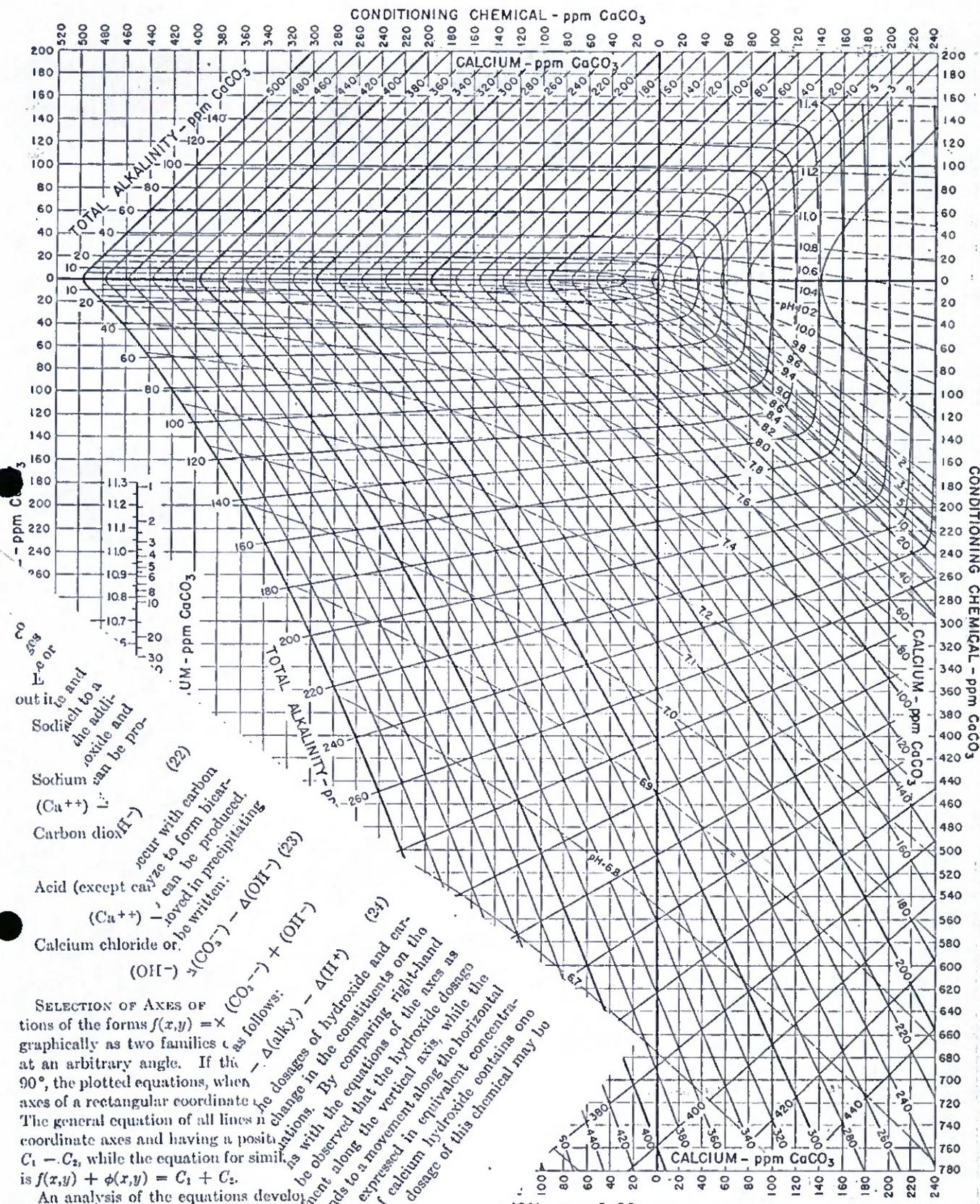
Since

$$(\text{alky.}) + (\text{H}^+) = (\text{HCO}_3^-) + (\text{CO}_3^{--}) + (\text{OH}^-)$$

the equation also can be expressed as follows:

$$\text{CO}_2 \text{ dosage} = \Delta(\text{Ca}^{++}) - \Delta(\text{alky.}) - \Delta(\text{H}^+) \quad (24)$$

Equations 22 and 24 give the dosages of hydroxide and carbonate in terms of the total change in the constituents on the right-hand side of the equations. By comparing right-hand members of those equations with the equations of the axes as given in Figure 2, it will be observed that the hydroxide dosage corresponds to a movement along the vertical axis, while the carbonate dosage corresponds to a movement along the horizontal axis, all constituents being expressed in equivalent concentration. Since one equivalent of calcium hydroxide contains one equivalent of hydroxide ion, the dosage of this chemical may be



Water Conditioning Diagram

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SELECTION OF AXES OF
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 $C_1 - C_2$, while the equation for simi-
is $f(x,y) + \phi(x,y) = C_1 + C_2$.

An analysis of the equations develop-
the equation $f(x,y) = C_1$ represent
carbonate, and the equation $\phi(x,y) = C_2$
for calcium hydroxide, the equations for
sodium bicarbonate can be represented

as follows:
 $\Delta(\text{alky}) - \Delta(\text{H}^+)$ (24)
The dosage of hydroxide and cur-
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is observed that the hydroxide dosage
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of calcium hydroxide contains one
oxide ion, the dosage of this chemical may be

CONDITIONING CHEMICAL - ppm CaCO₃

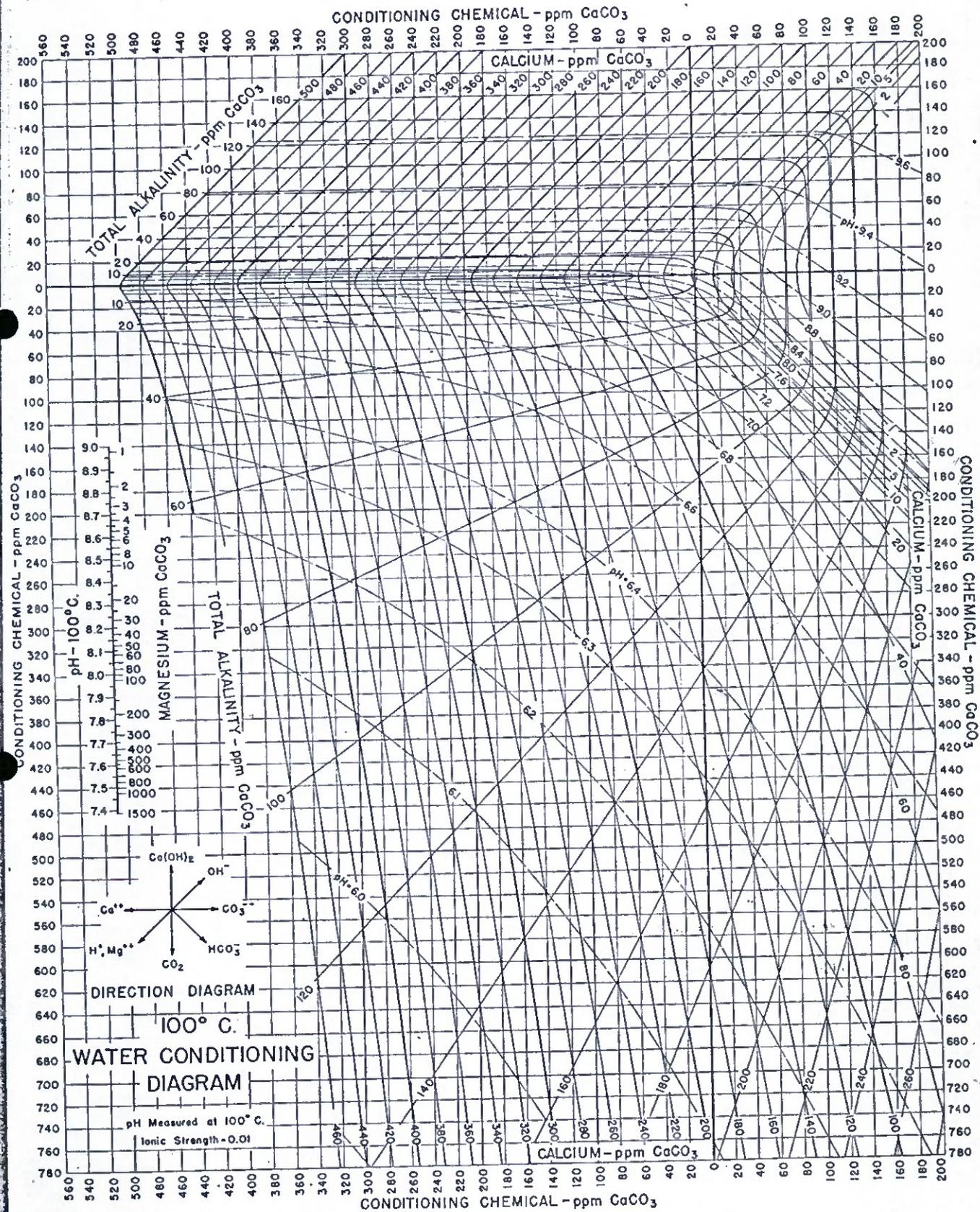


Figure 4. 100° C. Water Conditioning Diagram

TABLE II. CONVERSION OF pH, 25° C. to pH, 100° C. (5)

pH, 25° C.	pH, 100° C.					
	Alky. = 10	Alky. = 25	Alky. = 50	Alky. = 100	Alky. = 200	Alky. = 400
7.2	Subtract 0.08 from 25° C. value					
7.4	7.20	7.22	7.26	7.30	7.32	7.32
7.6	7.26	7.32	7.38	7.42	7.46	7.50
7.8	7.30	7.40	7.46	7.54	7.60	7.68
8.0	7.34	7.46	7.54	7.64	7.72	7.82
8.2	7.36	7.52	7.62	7.72	7.82	7.96
8.4	7.42	7.58	7.72	7.84	7.94	8.08
8.6	7.48	7.68	7.82	7.96	8.08	8.22
8.8	7.56	7.77	7.93	8.06	8.22	8.37
9.0	7.66	7.88	8.06	8.20	8.38	8.54
9.2	7.78	8.00	8.18	8.34	8.52	8.70
9.4	7.92	8.14	8.32	8.50	8.68	8.86
9.6	8.06	8.30	8.46	8.66	8.84	9.02
9.8	8.20	8.42	8.60	8.80	9.00	9.18
10.0	8.36	8.56	8.74	8.94	9.14	9.32
10.2	8.52	8.70	8.88	9.08	9.26	9.46
10.4	..	8.84	9.00	9.20	9.38	9.57
10.6	..	8.96	9.12	9.30	9.48	9.66
10.8	9.22	9.38	9.57	9.74
11.0	9.30	9.43	9.60	9.78

measured along either the vertical or horizontal axis. Moreover, since the result of measuring the hydroxide or acid dosage along the horizontal axis is numerically the same as if measured along the vertical axis, either axis may be used with equal validity.

In order to facilitate use of the diagram, the scales of the axes which measure the chemical dosage have been placed around the outside and have been labeled "conditioning chemical," as shown in Figures 3 and 4. The intersection of the vertical and horizontal zero axes corresponds to the chemical content of a solution which would be obtained by dissolving pure calcium carbonate in water containing neither carbon dioxide nor alkalinity. It represents the minimum value of the sum of the calcium and total alkalinity obtainable by any of the precipitation methods of water conditioning.

MAGNESIUM EQUILIBRIUM. Magnesium equilibrium can be illustrated by a simple relationship with pH in accordance with the equation

$$pMg - 2pH = pK_1 - 2pK_2 \quad (25)$$

where pK_1 and pK_2 are the negative logarithms of the ionization constant for water and the solubility product for magnesium hydroxide, respectively.

The relationship is not included in the main part of the water conditioning diagram but is shown on the left by a separate straight-line scale. In using Equation 25 to obtain this scale, the values of pK_1 at 25° and 100° C. and an ionic strength of 0.01 were taken to be the same as used by Langelier (4), namely, 13.91 and 12.21, and the value of pK_2 at 25° C. and 0.01 ionic strength was taken from the work of Näsänen (9) who gives a value of 10.26. The value of pK_2 at 100° C. and 0.01 ionic strength was taken as 11.47 from the work of Travers and Nouvel (11) after correction for ionic strength.

The axes of the conditioning diagram represent additions of chemicals in the same manner and in the same order as the Arbatsky (1) chart described by Langelier and Ludwig (6). The conditioning diagram, however, differs from the Arbatsky chart in the method of plotting the initial analysis and in the interpretation of the results obtained.

USE OF CONDITIONING DIAGRAM

Softening problems involving treatment with both lime and soda ash or with sodium hydroxide to produce a finished water having given residual hardness characteristics can be solved directly on the diagram. Problems involving treatment with lime are slightly more difficult to solve when magnesium as well as calcium hardness is to be removed. Both types will be illustrated by examples, the solutions of which may be divided into three steps:

1. Determine the equilibrium concentrations of calcium, alkalinity, and pH in accordance with one of the methods described.

2. Compute the quantity of chemical required to react with the difference between the initial and final magnesium concentrations. The final magnesium concentration is determined from the magnesium scale using the final pH to calculate the final magnesium. The magnesium to be removed is then plotted on the diagram by starting at the initial equilibration point, step 1, and moving across the diagram in the direction of magnesium addition—i.e., downward and to the left. The distance to be moved is such that its projection on either the horizontal or vertical dosage scale will equal the magnesium to be removed. This gives a second point below and to the left of the initial point. The calcium, alkalinity, and pH values represented by this second point have no particular significance, but the point must be established as a step in the solution of the problem.

3. Determine the kind and quantity of chemical necessary to reduce the calcium hardness to the given final residual. This is accomplished by starting from the second point, step 2, and moving in the direction or directions indicated in the direction diagram for the softening chemicals required to reach the proscribed final point. The total chemical dosage for softening may be read directly from the vertical or horizontal dosage scale.

Figure 5 illustrates the equilibration of water initially not saturated with calcium carbonate as specified in step 1. The two solutions shown are for undersaturation and supersaturation and represent the results obtained when water is equilibrated by contact with powdered calcium carbonate. In water softening problems this is the only equilibrating chemical involved since it is always present in solid form at some time during treatment. However, in other cases where only enough softening chemical such as lime or soda ash is added to bring the water into initial equilibrium with calcium carbonate, different graphical solutions are required. These are illustrated in the subsequent discussion of the graphical solution of problems of calcium carbonate stability control.

The following examples demonstrate the method of use of the 25° C. diagram. Use of the 100° C. diagram is similar in all respects, except that pH values indicated are for 100° C. They may be converted to 25° C. values by means of Table II taken from the work of Langelier (5). All concentrations except pH are expressed in parts per million (p.p.m.) of equivalent calcium carbonate.

EXAMPLE 1 (See Figure 6)

Given: Ca, 380; Mg, 120; alky., 260; pH, 7.0

Find: Lime and soda ash requirement to produce a water in which the alkalinity is a minimum and the calcium hardness is 40 p.p.m.

Solution: The final point lies on the horizontal zero axis where the alkalinity is 10 p.p.m. when the calcium hardness is 40 p.p.m. At this point, the pH is 9.8 and the equilibrium magnesium is 900 p.p.m.

Step 1. Since the water is supersaturated with calcium carbonate, it must be equilibrated in accordance with the example in Figure 5 pertaining to supersaturated water. After equilibration, the analysis will be Ca, 364; alky., 244; and pH, 6.90.

Step 2. The equilibrium magnesium concentration at the final point is 900 p.p.m., hence no magnesium will be precipitated.

Step 3. Starting from Ca 364 and alky. 244 on the diagram, proceed vertically upward to the horizontal line passing through the desired final point. This requires a lime dosage of 365 p.p.m. Proceed horizontally to the final point giving a soda ash dosage of 90 p.p.m. It is immaterial which chemical is added first. Analysis of the water at the final point is as follows: magnesium hardness, 120; calcium hardness, 40; alkalinity, 10; pH, 9.8.

It is interesting to compare the dosages of lime and soda ash as determined from the diagram with the stoichiometric values which are:

$$\begin{aligned} \text{Lime} &= \text{carbon dioxide} + \text{alkalinity} \\ &= 105 + 260 = 365 \text{ p.p.m. CaCO}_3 \\ \text{Soda ash} &= \text{calcium} - \text{alkalinity} - \text{residual calcium} \\ &= 380 - 260 - 40 = 80 \text{ p.p.m. CaCO}_3 \end{aligned}$$

The lime dosage is the same for both methods of calculation, while the soda ash dosage is 10 p.p.m. less when computed stoichiometrically.

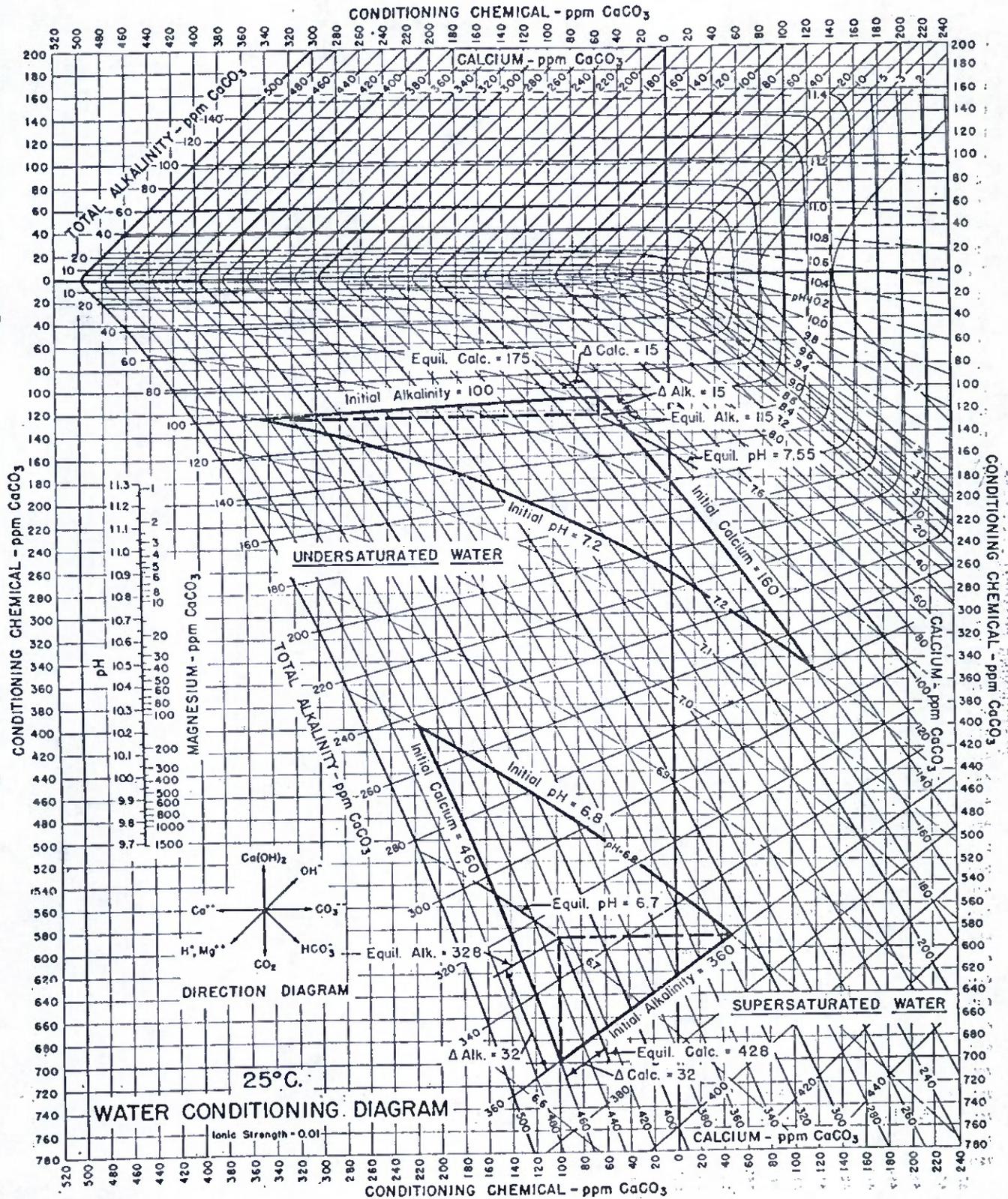


Figure 5. Graphical Solution of Problems of Calcium Carbonate Stabilization

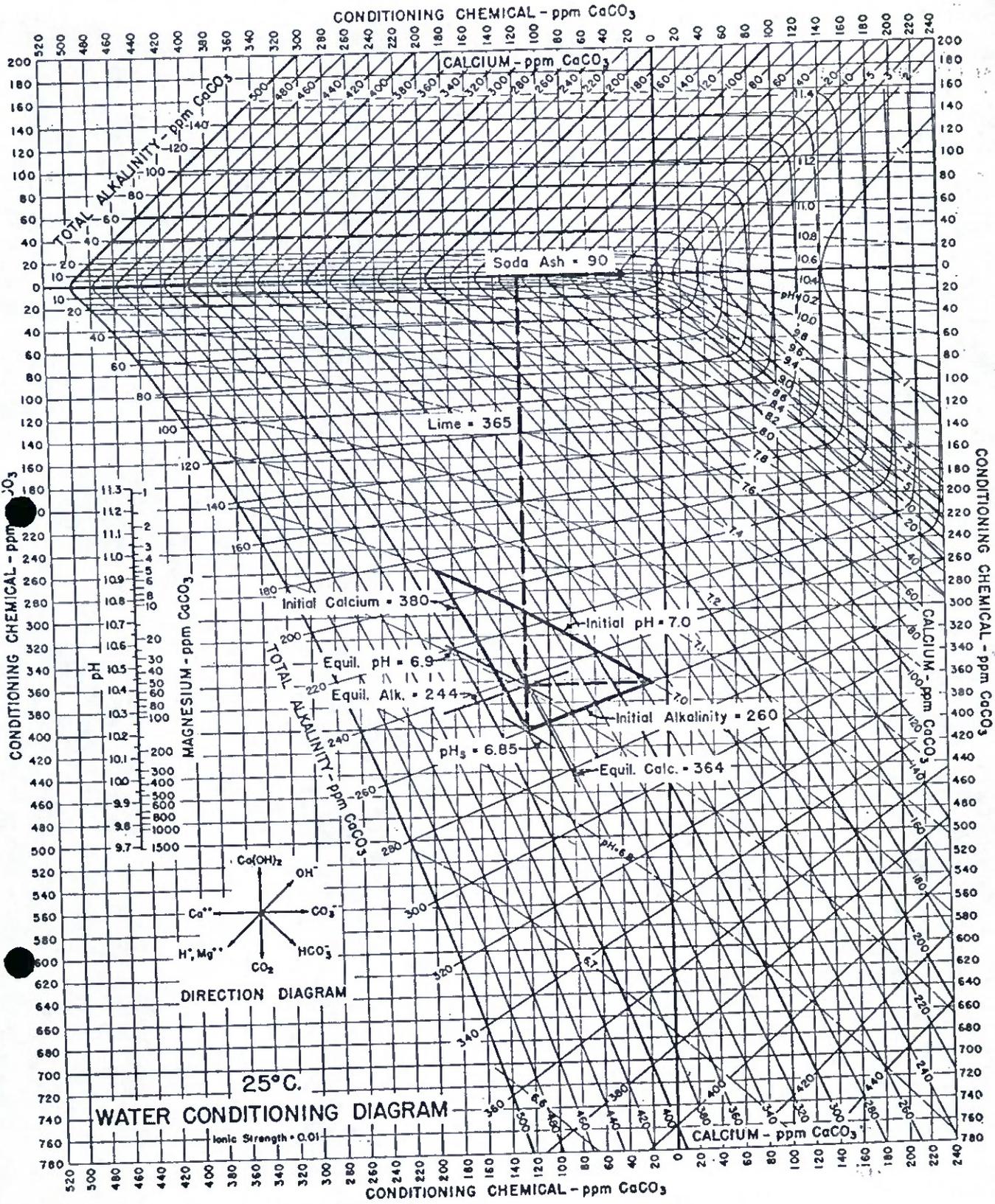


Figure 6. Graphical Solution of Lime Soda Softening Problem

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chiometrically. Either method would have given the same result if the final point coincided with the zero of coordinates. The farther the final point is away from the zero point, the more difference will be noted between the results of the two methods.

EXAMPLE 2 (See Figure 3)

Given: Ca, 87; Mg, 110; alky., 160; pH, 7.32

Find: Lime required to produce a water of minimum alkalinity

Solution: An examination of the diagram shows that irrespective of the initial water analysis, when lime alone is used the point of minimum alkalinity will fall on the horizontal zero axis. With this consideration in mind, the steps in the solution are as follows:

Steps 1 to 3. The water is undersaturated with calcium carbonate so that the first step is to equilibrate the water in accordance with Figure 5. The analysis at the point of equilibrium is found to be Ca, 103; alky., 176; and pH, 7.6. In order to compute the calcium added to the solution when lime precipitates magnesium it is necessary to know the final pH controlling the magnesium removal. In the present case, the final pH must be determined by approximations, as follows: Proceed vertically upward from the initial point to a second point such that by moving downward and to the left, a distance corresponding to the estimated magnesium removed, the final point will lie on the horizontal zero axis. Since the exact quantity of magnesium removed is unknown until the final point has been determined, two or more trials usually are necessary to locate the final point. Following this procedure, the final analysis is found to be Ca, 4; Mg, 90; alky., 55; and pH, 10.30. The lime dosage for softening is found to be 210 p.p.m.

Other examples will suggest themselves to the reader for trial. The method to be used in all problems is the same as has been described in the two examples cited and no difficulty should be encountered in problems involving the addition of other chemicals.

A use of the diagram involving all of the steps in the above examples relates to the investigation of the effect of various combinations of chemicals on the residual hardness, alkalinity, and pH of a treated water. A study such as this can best be represented by suitable graphs showing the effect on these variables of increasing dosages of each treating chemical. For practical application, the theoretical results obtained from the graphs can be checked by a few laboratory experiments and conclusions drawn as to the most economical or most efficient treatment considering all variables.

To illustrate this use of the diagram, the following problem has been solved and the results illustrated graphically in Figure 7.

EXAMPLE 3 (See Figure 7)

Given: Ca, 160; Mg, 100; alky., 100; pH, 7.65

Find: Investigate the effect of softening this water with lime alone, lime and soda ash, and sodium hydroxide alone.

Solution: Figure 7, a, indicates the effect of increasing doses of lime on the residual hardness, alkalinity, and pH. The minimum calcium hardness and the minimum alkalinity both occur at the same lime dosage. Figure 7, b and c, shows the effects of adding increasing amounts of lime with a constant sodium carbonate dosage. Sodium carbonate dosage used in constructing Figure 7, b, is the ideal—i.e., the dosage designed to produce minimum alkalinity plus calcium. This minimum is $16 + 16 = 32$ p.p.m., which would be the value obtained for any water regardless of initial characteristics. Calcium hardness in the minimum range is not affected appreciably by slight variations in lime dosage.

Figure 7, c, is similar to Figure 7, a, except that sodium hydroxide was used instead of calcium hydroxide. For the particular water under consideration, the characteristics of the final softened water are better using sodium hydroxide than those using calcium hydroxide, because sodium hydroxide combines the softening characteristics of lime and soda ash. Other considerations, however, may make it more desirable to use lime and soda ash in place of sodium hydroxide.

CALCIUM CARBONATE STABILITY CONTROL PROBLEMS

The discussion thus far has dealt with problems of water treatment in which continuous equilibrium with solid calcium carbonate is maintained. A closely related subject is concerned with the calculation of the amount of chemical involved when the water is not in equilibrium with solid calcium carbonate. Because natural waters have a strong tendency to become supersaturated,

the equilibration process may involve either the solution or deposition of this salt. Also, since calcium carbonate solubility is controlled by the variables calcium, alkalinity, and pH, an added chemical which changes any one of these variables will also affect the calcium carbonate equilibrium. Thus, the addition of a sufficient quantity of sodium carbonate to a water which is initially undersaturated with calcium carbonate will bring about equilibrium. Likewise, a supersaturated water may be equilibrated by the addition of acid or carbon dioxide. In such cases, it is desirable to be able to calculate the quantity of chemical involved in equilibrating the water as well as the final equilibrium values of calcium, alkalinity, and pH.

Problems of this nature fall into two general classifications, namely, those related to undersaturated waters and those related to supersaturated waters. Both classes can be solved on the stability diagram as demonstrated by Langelier (4) and by Lawrence (7). While the solutions given by these authors are complete and sufficient for use in softening calculations, the conditioning diagram can also be used for this purpose and permits the solution of both classes of problems without resorting to auxiliary diagrams.

SUPERSATURATED WATER. Equilibration can be effected for this class of water by the autogenous precipitation of calcium carbonate induced by agitation of the solution in the presence of added solid calcium carbonate or by the addition of an acid or acid-reacting salt. Possible additive chemicals are acids, carbon dioxide, sodium bicarbonate under some conditions, and magnesium chloride or sulfate in sufficient quantity to precipitate magnesium hydroxide.

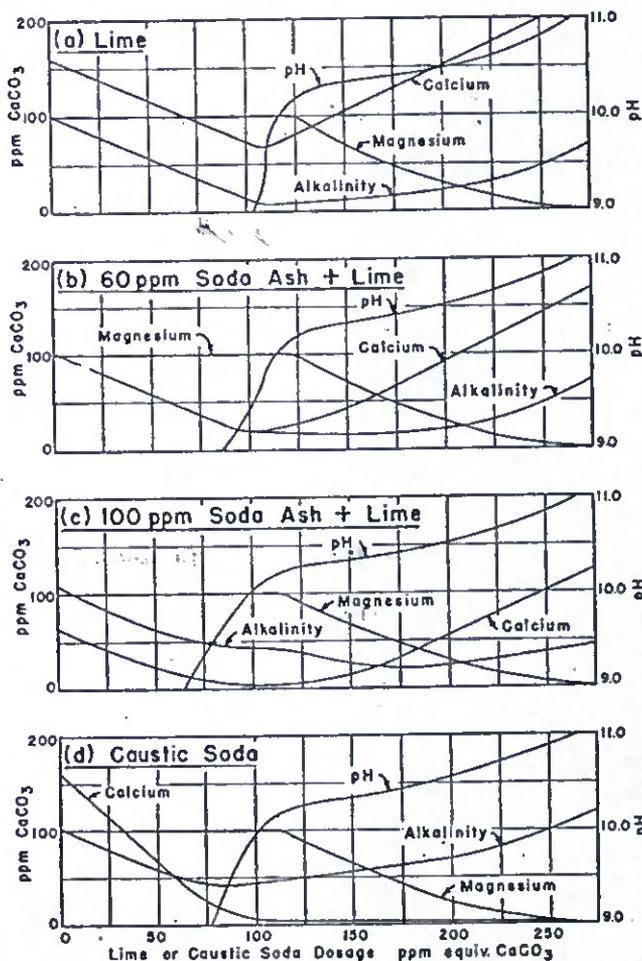


Figure 7. Effect of Chemicals on Hardness, Alkalinity, and pH As Determined by Use of Conditioning Diagram

TABLE III. DETERMINATION OF CHEMICAL CHARACTERISTICS OF LIME SOFTENED AND STABILIZED MERAMEC RIVER WATER

Lime Dosage		Analytical Results (2)				Graphical Results 25° C. Diagram					
92% CaO, g./gal.	P.p.m. CaCO ₃	Total alk., P.p.m. CaCO ₃	Hardness, p.p.m. CaCO ₃			Total alk., P.p.m. CaCO ₃	Hardness, p.p.m. CaCO ₃				
			CaH	MgH	Total	pH	CaH	MgH	Total	pH	
0	0	175	103	97	199	8.4	
Equilibrated	93	96	189	...	160	85	97	182	7.7
2	56	...	56	91	147	...	105	49	97	137	8.2
4	112	...	21	86	107	...	79	6	97	103	9.4
6	168	...	10	75	85	...	72	2	95	97	10.2
6.3	177	...	10	70	80	...	66	3	87	90	10.3
8	224	...	18	52	70	...	36	7	54	61	10.4
10	281	...	40	21	61	...	32	40	17	57	10.6
12	337	...	80	8	88	...	67	88	3	91	11.0
0	0	104	62	58	120	8.2
Equilibrated	61	58	119	8.1	102	61	58	119	8.1
2	56	...	32	51	83	8.5	55	16	53	74	9.0
4	112	...	15	41	56	9.6	42	5	37	62	10.4
6	168	...	20	22	42	10.3	32	31	19	50	10.6
8	224	...	58	9	67	10.9	64	79	3	82	11.0
10	281	...	101	2	103	11.4	117	133	1	134	11.2

Graphical solutions for acids and carbon dioxide have been worked out on the conditioning diagram and are shown diagrammatically in Figure 8. Autogenous precipitation of calcium carbonate is illustrated in Figure 5. In solving a particular problem, the construction shown in the appropriate diagram of Figure 5 or Figure 8 is utilized in conjunction with the conditioning diagram and the equilibrium calcium, alkalinity, and pH are read directly from the final point.

UNDERSATURATED WATERS. This class of water can be equilibrated with any of the following chemicals: calcium carbonate, calcium hydroxide, sodium carbonate, sodium bicarbonate under certain conditions, sodium hydroxide, and calcium chloride or sulfate.

Graphical solutions for calcium hydroxide and sodium carbonate have been worked out on the conditioning diagram and are shown diagrammatically in Figure 9. The figure also shows the method of computing the quantity of chemical required for equilibration. Equilibration with calcium carbonate is shown in Figure 5. After using the appropriate diagram of Figure 5 or Figure 9 in the solution of a particular problem the equilibrium calcium, alkalinity, and pH are read directly from the final point.

In water conditioning it is sometimes desired to add a chemical such as calcium hydroxide in sufficient amount to produce a supersaturated water of given saturation index. Likewise, recarbonation or acid addition may be carried to the point where a slight negative saturation index is produced. Calculation of the final water analysis, as well as the quantity of chemical involved, can be carried out in a manner similar to the methods already described. For this purpose, the appropriate graphical construction corresponding to the chemical being added as shown in Figure 8 or 9 is used, but instead of stopping the dotted construction lines at their intersection, which is the equilibrium point, they are carried beyond to produce the desired final saturation conditions. Figure 10 indicates the method of calculating chemical dosages during the conditioning of an undersaturated water with calcium hydroxide to produce a supersaturated water with an index of 0.85. Other conditioning chemicals may be substituted for lime by using the appropriate graphical construction given in Figures 8 and 9.

DEPOSITION OF CALCIUM CARBONATE DUE TO CHANGE IN TEMPERATURE. The two diagrams may be used together to determine the quantity of calcium carbonate deposited due to a change in temperature from 25° to 100° C. To accomplish this, the water is first put into equilibrium with respect to calcium carbonate on the 25° C. diagram using an appropriate chemical. The equilibrium values of calcium and alkalinity thus determined, together with the 100° C. pH determined from Table II are plotted on the 100° C. diagram and the equilibration process repeated. The saturation index may either increase or decrease,

or the water may remain in equilibrium due to a change in temperature. In general, the index decreases if the initial equilibrium point lies above the horizontal zero axis of the 25° C. diagram and increases if the point lies below the zero axis.

GRAPHICAL AND EXPERIMENTAL RESULTS

The fundamental principles upon which the conditioning diagram is based have long been used in chemical technology. Although their validity may be accepted generally, their application to water softening problems should be considered as open to

question because there is a lack of conclusive proof of the chemical composition of the precipitates. For example, in the development of the diagram it was assumed that calcium would precipitate as calcium carbonate and magnesium as magnesium hydroxide, while possibility of the formation of other compounds such as magnesium basic carbonate or magnesium aluminate was not considered.

It is generally conceded that equilibrium equations for calcium carbonate solubility are sufficiently precise to be applied to water softening reactions, although all laboratory and field tests designed to test their validity are hampered by the tendency of the salt to form metastable supersaturated solutions. On the other hand, magnesium hydroxide solubility as applied to water softening has not been investigated exhaustively and there is considerable variation in the values of the equilibrium constant found by different investigators. The work of Näsänen (9) is considered to be most precise, and his constant has been used in the 25° C. conditioning diagram. The 100° C. constant was taken from the work of Travers and Nouvel (11) after correction for ionic strength. These values, however, are subject to some question, principally from the standpoint that compounds other than magnesium hydroxide may be formed. Graphical results should therefore be checked in practical cases wherever possible.

In this connection, the literature affords few reports of tests of softening operations wherein sufficient information is given

TABLE IV. DETERMINATION OF CHEMICAL CHARACTERISTICS OF LIME SODA SOFTENED WELL WATER

Test Series 2, Test No. 7, Dec. 21, 1942	Analytical Results (10)		Graphical Results	
	Raw water	Accelerator effluent	Raw water equilibrated	Accelerator effluent
Calcium hardness	353	25	317	2
Magnesium hardness	178	170	178	178
Total hardness	531	195	495	180
Total alkalinity	333	135	296	112
pH	7.05	10.2	6.9	10.2
Test Series 3, Test No. 6, Dec. 28, 1942				
Calcium hardness	349	51	310	5
Magnesium hardness	161	165	161	161
Total hardness	510	216	471	166
Total alkalinity	333	104	295	100
pH	7.09	9.67	6.9	9.2
Data on Chemical Dosage				
	92% CaO		98% Na ₂ CO ₃	
	Lb./1000 gal.	P.p.m. CaCO ₃	Lb./1000 gal.	P.p.m. CaCO ₃
Test Series 2, Test No. 7	2.18	431	1.20	133
Test Series 3, Test No. 6	1.85	386	1.00	111

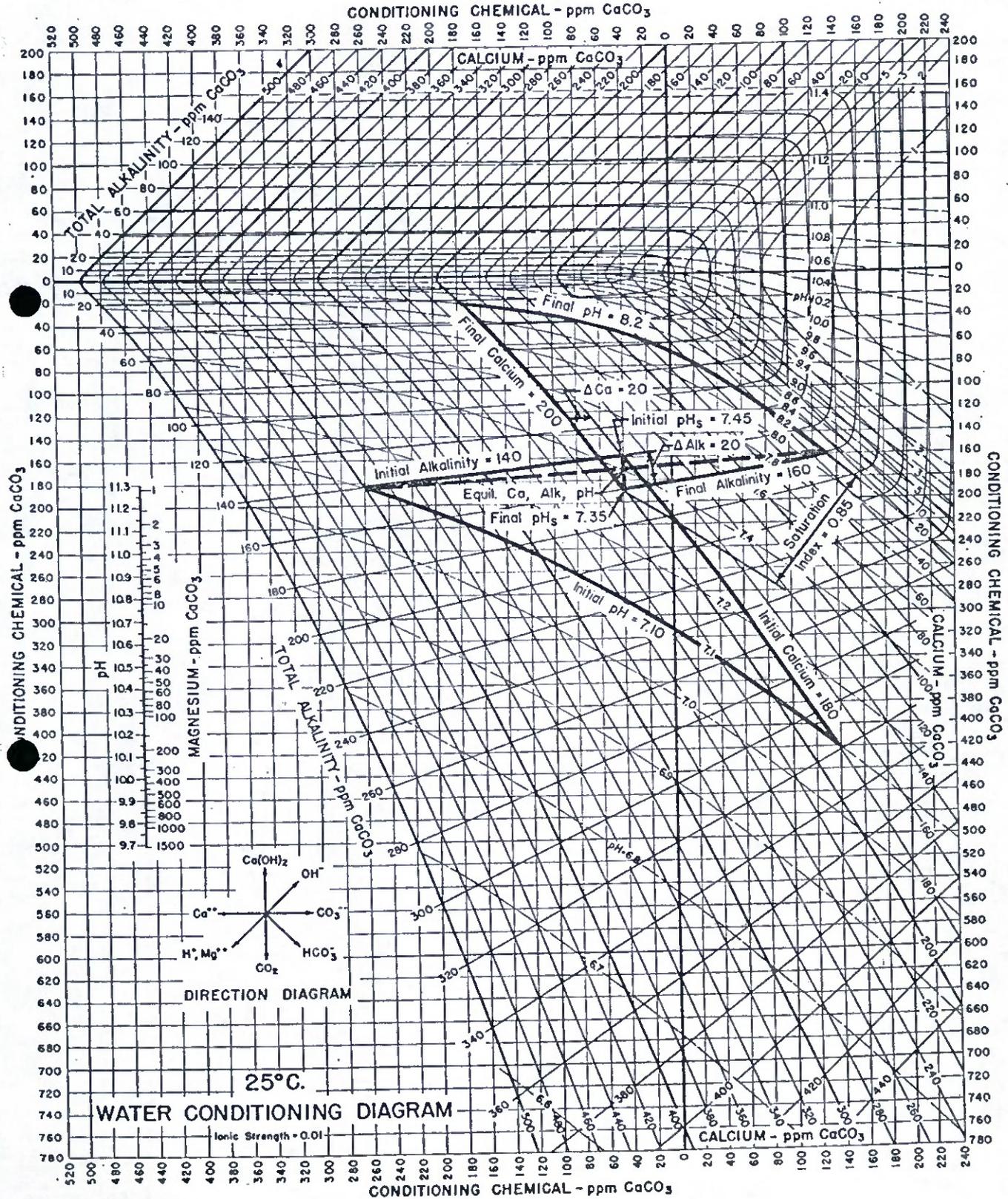


Figure 10. Graphical Solution of Problem of Production of a Treated Water with Positive Saturation Index

to allow a comparison with graphical results. Among those suitable for use are a report of laboratory work by Hartung (2) and a report of plant scale tests by Sheen and Woodruff (10). Hartung treated a series of water samples with increasing quantities of 92% calcium oxide. After a reaction period, each sample was filtered and equilibrated with calcium carbonate. Results of tests for total, calcium, and magnesium hardness, and pH (where available) are given in Table III for two different waters. The table also gives values of total, calcium, and magnesium hardness, pH, and alkalinity as determined graphically from the 25° C. diagram. Agreement between the experimental and computed hardness values is reasonably good. In general, the computed values of calcium hardness are higher than the experimental, indicating incomplete stability at larger lime dosages. This may be due to incomplete solution of the lime during the experiments. Magnesium started to precipitate before the theoretical solubility product for magnesium hydroxide was exceeded. This resulted in less lime being used for calcium precipitation than is indicated by the diagram. The computed total hardness values, however, agree well with the experimental except for large lime dosages.

Sheen and Woodruff (10) reported upon the results of a series of tests of Softening Plant No. 2 at the Wright Aeronautical Corp., Cincinnati, Ohio. This plant employs an Accelerator and analytical determinations during the test periods were exceptionally complete. Table IV presents significant analytical

results of the raw water and of the Accelerator effluent for two typical tests. The table also gives the corresponding graphical results determined from the conditioning diagram. Both of these tests were aimed at removing as much calcium as possible without reduction in magnesium. As pointed out by the authors, the Accelerator effluent is not completely stable but is supersaturated with calcium carbonate. It is apparent from Table IV that the actual excess of calcium carbonate in solution is 23 p.p.m. in the first test and 43 p.p.m. in the second.

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Elements in Coal Ash and Their Industrial Significance

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THE ash produced by combustion of the coal mined in West Virginia amounts to some 10,000,000 tons of ash each year. Since West Virginia produces some 28% of the bituminous coal consumed in the United States, a large tonnage of coal ash is available.

This paper is a resume of the analyses of 596 spot samples for 38 elements from 16 coal seams, representing the major coal producing area in West Virginia. The study was undertaken to supply fundamental data on the composition of coal ash. These data have an industrial significance indicated below.

Coal ash is made up of the elements sodium, potassium, calcium, aluminum, silicon, iron, and titanium in concentrations greater than 1% when calculated as the oxide; lithium, rubidium, strontium, barium, magnesium, arsenic, beryllium, boron, chromium, cobalt, copper, gallium, germanium, mercury, lanthanum, manganese, molybdenum, nickel, phosphorus, lead, tin, vanadium, tungsten, zinc, and zirconium in concentrations between 1 and 0.01% calculated as oxide; silver, bismuth, and antimony in concentrations between 0.01 and 0.001% as oxide; and a number of other elements not reported in this paper, such as sulfur, halogens, nitrogen, and rare earths. Gibson and Selvig (1) give a review of the minor elements in coal ash.

The minerals that make up coal ash are either inherent in the organic matter which makes up the coal or are in joints and partings, extraneous from or outside of the organic matter. The over-all composition of the two types is similar; however, spot samples may be quite unlike because of the presence of localized concentrations of calcite or pyrite. The compounds making up these two types of ash, however, may not be the same.

SAMPLING AND TESTING SOLID COLUMNS OF COAL

Samples were obtained by sawing a 3-inch square column of coal from the full height of the seam and bringing this column intact into the laboratory for further sampling. One-inch cubes were cut from the column every 3 inches beginning at the top. Apparent specific gravity and porosity of these cubes were determined. The cube was then ground to 60-mesh. The pyritic, sulfate, organic and total sulfur, and ash content were determined on each sample.

The ash determination was made by spreading the coal in a flat porcelain dish, placing in a cold muffle furnace, and heating to 740° C. maximum. One-gram samples of coals having more than 5% ash were burned; if the coals had less than 5% ash, 2 grams were ashed. The ash from these determinations was ground to 200 mesh and analyzed quantitatively for 38 elements with a large Littrow spectrograph (4). The quantity of the element reported in these ash analyses is not necessarily the total amount present in the raw coal sample. The burning operation may volatilize some of these elements similar to the manner in which sulfur is removed. Analyses of coal and its ash indicate that considerable beryllium and possibly aluminum are volatilized in the laboratory ashing process. Most of the halogens probably volatilize in the ashing process as volatile metal halides.

ANALYTICAL PROCEDURE

The basic method was proposed by Slavina (5) and further developed in this laboratory (4) for the analysis of coal and coal ash. Only the major improvements since that report was written are presented here.

The standard employed for these analyses was the ash of a West Virginia coal identified as C-5 (4). To this ash was added a mixture of 20 oxides of elements, six of which were not in the