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Stabilization of Magnesium Hydroxide in Solids-Contact Process

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IN any industry, a quality product and efficient service are the keys to producing satisfied customers. Everyone is aware of the annoyance caused by a red water or a staining water, especially when obtained from a new water plant designed to soften the water and provide a quality product for which the customer is ready and willing to pay.

When a plant produces a water that still plugs hot-water lines, or scales hot-water tanks, or even causes excessive pressure losses or corrosion in transmission from plant to the household tap, the consumer has a perfect right to be unhappy and to think seriously before docilely accepting a needed increase in water rates.

Figure 1 shows some of the results of improperly softened water. The scale in each pipe was found to be composed of magnesium hydroxide, usually with some calcium carbonate and silica. In a number of places, so much scale formed on hot-water tank heating coils within a few weeks that it was impossible to provide the desired temperature.

The causes of this phenomenon were shown by the author in 1951 (*1*) and data were provided indicating the maximum pH and magnesium concentrations that would prevent magnesium scale problems.
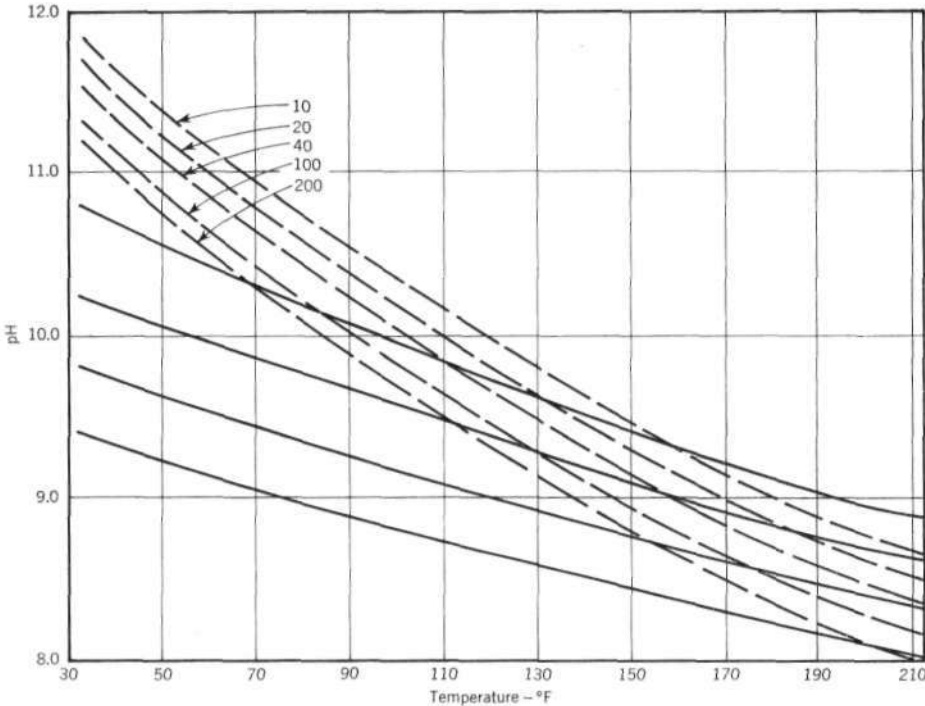
Magnesium Solubility

Magnesium solubility is highly sensitive to pH and temperature. Based on the solubility product constant of Travers and Nouvel (*2*) the influence of temperature on the solubility of magnesium in a water of 50 ppm alkalinity is shown in Fig. 2. Changes in temperature affect the equilibrium constants, K_w and K_2, as well as $K_{Mg(OH)_2}$. Very few investigators agree on the solubility product for magnesium hydroxide, but the data selected were in the range of the various determinations near 25°C and were also the only data that indicated the determination of $K_{Mg(OH)_2}$ over a range of temperature.

The sensitivity of magnesium solubility to pH and to temperature is shown in Fig. 2. Particular attention is directed to the 32°-77°F range, which indicates that for precipitation a higher pH is needed with cold water than with warm water. The sensitivity of pH to temperature is also indicated. The effect of carbonate alkalinity is not shown. If the total alkalinity were 25 ppm, the pH at 167°F would be 0.14 lower; with a total alkalinity of 100 ppm, the pH
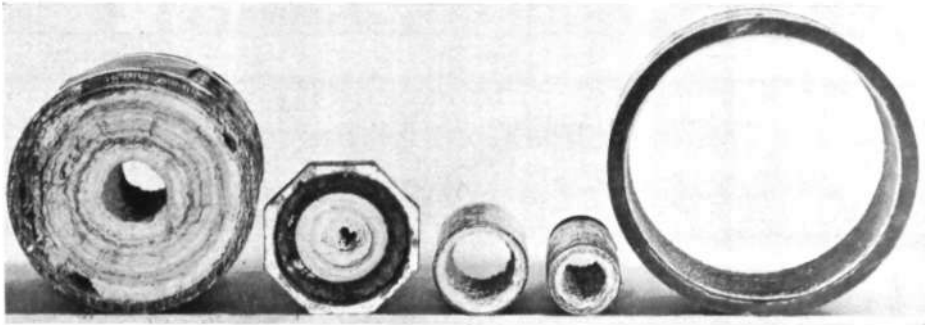
Fig. 1. Results of Improperly Softened Water

The pipe specimens shown above are (*left to right*) : *hot-water line after 35 years in a state hospital; hot-water line in a hotel; hot-water line in a city hospital; hot-water line in a state hospital; cold-water main in a city distribution system* (*the Hazen-Williams coefficient was reduced from 125 to 100*).

Fig. 2. **Influence of Temperature on Magnesium Solubility**

The dashed curves represent magnesium solubility (*as* $CaCO_3$) *and the solid curves represent pH variation. The solubility curves are based on the solubility product constants of Travers and Nouvel* (1).

at 167°F would be 0.16 pH units higher (*3*).

Figure 2 also does not show the effect of dissolved minerals on the solubility of magnesium. The data shown are for water with 200 ppm total dissolved minerals. According to the data of Naesaenen (*4*), the solubility would be increased by about 30 per cent if the total mineral content were 600 ppm. It should be recognized that, because controlled laboratory conditions do not prevail in plant operation, a degree of discrepancy between theory and practice must be expected.

Figure 3, based on field data collected in 1951, indicates *recommended* maximum pH and magnesium concentrations for treated water. The data on which these recommendations are based (*1*) were obtained from plants where magnesium hydroxide problems were experienced in hot-water tanks and hot-water lines as well as from plants where no problems occurred. As a general rule, a plant effluent at 75°F should have a pH of less than 9.0 and a magnesium hardness of less than 40 ppm; for the same magnesium hardness in cold water, a pH of 9.5 may be permissible; a 55°F well water may have a pH of 9.2. These limits are 0.5-0.7 pH units lower than predicted by theory, because the actual operating temperature of a hot-water tank is always considerably lower than at the heating surface, and because these data were obtained from waters containing less than 200 ppm dissolved minerals.

For those who prefer to use an equation to provide a numerical index to possible magnesium hydroxide problems, the following equation may be used for waters of approximately 50 ppm alkalinity and 200 ppm dissolved solids:

$$I = 2 \ pH + \log \ Mg + 0.02 \ t - 21.2$$

in which I is the magnesium index and t is the temperature (in degrees Fahrenheit) of the effluent. Magnesium is expressed as parts per million $CaCO_3$. When the index is such that $I \quad 0$, no magnesium hydroxide scale problems are likely; if I is 0.1-0.3 there may be isolated problems over long operation; 0.4-0.7 indicates that a significant number of difficulties are likely; if $I \quad 0.7$, problems will almost certainly be numerous after several months of continuous operation, their
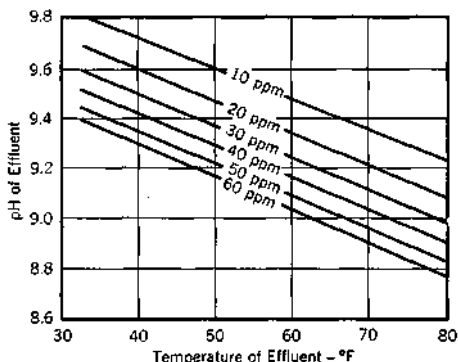
Fig. 3. Maximum Recommended Magnesium Hardness at Various Recorded Temperatures and pH Values

Hardness concentrations are expressed as $CaCO_3$.

number and severity depending, of course, on the temperature of the heating surface and the quantities of water used.

Quality Product

There is a need to set some standard for water quality. The usual objective in public water supplies is to reduce hardness to 75-100 ppm. This has been fairly standard practice for many years. Were it not for red-water problems, water could be softened to zero hardness; in fact, that is done at a few ion-exchange plants.

but the practice is limited to certain noncorrosive waters.

It has long been recognized that the maintenance of calcium carbonate stability is the most effective method for
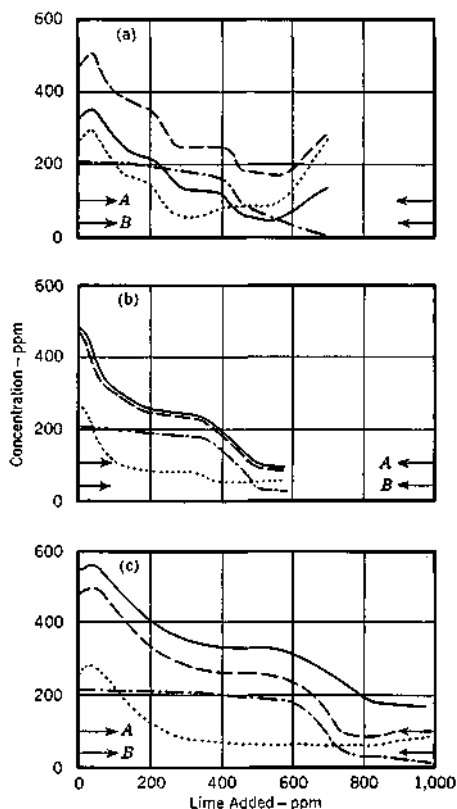

Fig. 4. **Reduction of Magnesium Hardness Under Various Conditions of Alkalinity and Total Hardness**

Solid, dashed, dashed and dotted, and dotted curves represent alkalinity, total hardness, magnesium hardness, and calcium hardness, respectively. Parts a, b, and c represent the following conditions: Part a—total hardness exceeds alkalinity; Part b—total hardness and alkalinity are equal; Part c—alkalinity exceeds total hardness. Levels A and B represent desired total-hardness and magnesium hardness levels, respectively. All concentrations are expressed as CaCO₃.

preventing red water; the effectiveness is enhanced if the maximum possible calcium concentration is maintained (*12*). It has also been shown (*1*) that an alkalinity of less than 50 ppm results in a decrease in the saturation index at hot-water tank temperature.

It has also been long established (*5*) that in waters with a pH greater than 9.5 there is a greater tendency to dissolve zinc from galvanized pipe or hot-water tanks. This tendency is also decreased when calcium carbonate stability is maintained because the formation of a protective zinc carbonate coating is dependent on the same factors as govern calcium carbonate stability.

The hazards of excessive magnesium were recognized as long ago as 1919 by Sperry (*6*) and again by Hoover in 1942 (*7*). Lime softening plants should therefore regulate their treatment process to provide an alkalinity near a minimum of 500 ppm, a calcium hardness of at least 50 ppm, and a magnesium concentration of not more than 40 ppm; pH should be adjusted to a satisfactory level above the saturation pH of the water at the temperature of the plant effluent. Thus, a saturation pH of 8.5 is necessary for a 77°F plant effluent, and a pH of 9.0 is needed for a 33°F effluent. These limits may be considered arbitrary, but they are designed to insure the quality of the product delivered to the consumer's tap.

Chemistry of Softening

The earliest method used to soften water consisted of adding hydrated lime to react with calcium bicarbonate to form insoluble calcium carbonate. This reaction is stoichiometric at equilibrium conditions and limited only by the solubility constant for calcium carbonate.

The reaction described above, however, is only one of at least a dozen or so interrelated reactions that occur simultaneously when hydrated lime is added to a hard water containing calcium, magnesium, and carbonate alkalinity. The reactions proceed to a point of equilibrium, which is dependent on time, the proportions of natural components, and the amount of added lime. The reactions are predictable if time and aids to the approach to equilibrium are permitted.

Perhaps the simplest way to learn what will result from the addition of lime to a given water is to set up a series of ten, fifteen, or twenty 1-qt or
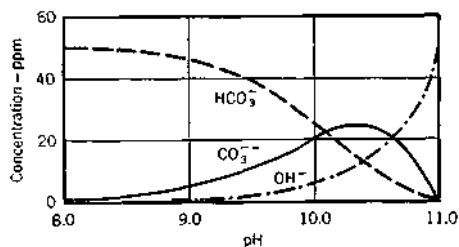
Fig. 5. Proportions of Various Forms of Alkalinity at pH 8.0-11.0 and Total Alkalinity of 50 ppm

Concentrations are expressed as CaCO$_3$.

1-gal bottles. With the temperature maintained at that of the plant water, the operator can add increasing quantities of lime to the bottles, shake them well periodically, allow them to stand overnight, and then perform analyses of the clear supernatants for hardness, calcium, alkalinity, and pH.

The results of such tests will depend on the relative proportions of alkalinity to hardness of the raw water. This is illustrated diagrammatically in Fig. 4. The numerical values in Fig. 4 are roughly representative of room temperature reaction after 6 hr. From the upper illustration, it

can be seen that the hardness could not be reduced to the desired level without the aid of soda ash. With the addition of soda ash (middle illustration), an alkalinity equal to the hardness was obtained, and little difficulty was experienced. With the third type of water (lower illustration), it can be seen that the excess bicarbonate alkalinity required the use of more lime. It will be noted that the addition of lime reduces the calcium hardness first, before any appreciable amount of magnesium is removed; and until this point is reached the alkalinity and calcium curves are parallel. Addition of more lime causes the calcium content to increase or decrease with magnesium precipitation. Under either condition the magnesium is eventually reduced to a low concentration. In each example, a longer reaction time or contact with a slurry of calcium carbonate and magnesium hydroxide would provide a clear approach to equilibrium conditions.

In Fig. 5 the proportions of the various forms of alkalinity are shown for the pH range of 8.0-11.0 with an alkalinity of 50 ppm.
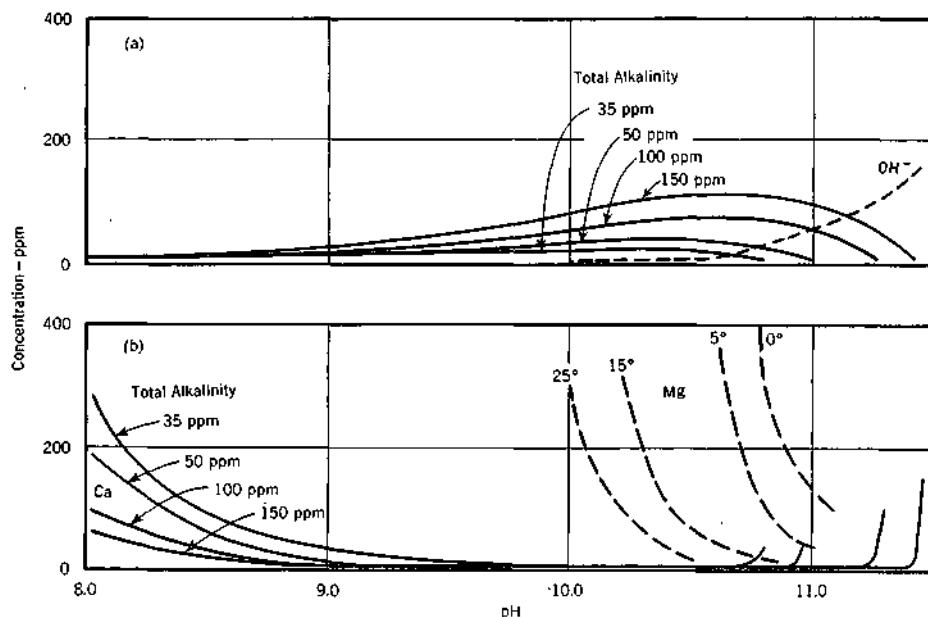
In Fig. 6 the calculated solubility limits are shown for various pH values and alkalinity concentrations. The much lower theoretical values indicate that equilibrium conditions had not been attained in the jar tests in the previous figure. Hartung (*8*) and Calise (*9*) recently showed the benefits of using slurry circulation to approach the equilibrium conditions.

At the equilibrium obtained thereby, however, a dilemma exists: although saturation with respect to magnesium hydroxide is not desirable, saturation with respect to calcium carbonate is. If magnesium saturation were corrected by reducing the pH, calcium carbonate saturation would be de-

stroyed, unless excess calcium hydroxide were present.

In usual practice, equilibrium conditions are rarely obtained even under optimum conditions of contact time and slurry circulation. Supersaturation may, however, be a blessing in disguise, because it provides greater flexibility in control. As previously shown, the pH must be reduced to

tion procedures for separate determination of calcium and magnesium hardness. Also, the possible problems with magnesium hydroxide were not fully recognized. The only control tests were for total hardness (H), phenolphthalein (P) and methyl orange (M) tests for alkalinity. Such tests sufficed as long as the only criterion of a satisfactory product was the

**Fig. 6.   Calculated Solubility Limits at Various pH Values and
Alkalinity Concentrations**

Part a shozvs relative concentrations of CO_3^{--} and OH^-; Part b shows Ca solubility at various concentrations of alkalinity at 15°C, and Mg solubility at 0°, 5°, 15°, and 25°C (total dissolved minerals, 200 ppm).   Concentrations are expressed as $CaCO_3$.

avoid precipitation of magnesium hydroxide; supersaturation permits pH adjustment to a point where calcium carbonate saturation can be attained without the use of excessive amounts of calcium hydroxide.

Control Tests

.   When lime-soda softening was first introduced, there were no simple titra-

total hardness of the effluent. This is no longer true, however. The inadequacies of *P, M,* and *H* control are insufficient magnesium removal, excessive use of lime, and consequent excessive demands on recarbonation.

The *P* and *M* determinations must be made with great care if they are used to indicate hydroxyl ion concentrations (for lime dosage). The cor-

rections associated with temperature and total mineral content, as indicated by Dye (*10*), should also be applied.

With the advent of the EDTA procedure for calcium hardness and total hardness, the old control criteria became outmoded. For 10 years, quick, simple titration procedures have been available for the separate determination of calcium, and for magnesium by difference from the total hardness. There is, therefore, no reason to retain the outdated *P, M,* and *H* control tests when a quality product is desired.

It is a logical step to base lime dosage on the residual magnesium hardness, the second step in the softening chemistry, as even an accurate $(2P - M)$ determination is only an indirect indication, by means of the hydroxyl-ion concentration, of possible magnesium hardness. The magnesium determination, however, is a direct indication of the quality of the end product, regardless of the plant temperature, because calcium reduction is insured by prescribed adjustment of the lime dosage and by precalculation of the soda ash requirement.

Magnesium hardness is the difference between the total hardness and the calcium hardness. With practice, an analyst can determine calcium hardness on the same sample used for the alkalinity determination. After the usual *P* and *M* alkalinity titrations, the calcium hardness buffer solution and indicator are added and titration is continued with EDTA. The pink color associated with phenolphthalein is observed to change rather suddenly to a wine color at the calcium endpoint.

Recarbonation

With proper magnesium hardness in the effluent, recarbonation is necessary to reduce the pH to the level of calcium carbonate stability.

At one 1.5-mgd solids-contact plant, 40 ppm carbon dioxide is required to reduce the pH of the treated water to 8.5-9.0. The fuel oil (No. 2) used costs $2.34 for 1 mil gal of water. Another plant of 0.4-mgd capacity requires similar carbon dioxide treatment. Propane provides carbon dioxide at a cost of $4.30 for 1 mil gal. Much less maintenance has been required for the propane equipment than for fuel oil equipment. For 40 ppm carbon dioxide, the equivalent cost of alum for this purpose would be $18.25 for 1 mil gal.

If, on the other hand, alum is added with lime and soda ash, it must be neutralized with additional lime and soda ash to maintain the alkalinity desired in the end product and the pH necessary for magnesium precipitation. The effectiveness of alum for magnesium removal appears to be limited at higher temperatures (70°-80°F) but more effective at lower temperatures (35°-50°F). The difficulty of reducing magnesium hardness to its calculated solubility is indicated by the recorded use of alum dosages of 50-85 ppm during winter months and 17-35 ppm during the summer months. Such use of alum *does not* eliminate the need for recarbonation.

It has been indicated that soda ash is required in waters with excessive noncarbonate hardness to precipitate calcium and provide sufficient residual alkalinity for calcium carbonate stability. The usual quantity required may be calculated from the total hardness and alkalinity of the raw water.

$$H - M - (25 \text{ to } 50)$$
$$= \text{ppm } Na_2CO_3 \text{ (as } CaCO_3)$$

This dosage is designed for an effluent alkalinity of 50 ppm and a hardness of 75-100 ppm; it may be desirable to add a portion of it after filtration if

excessive lime buildup on the sand filters indicates a need for recarbonation to a subsaturation pH.

Lime dosage may be determined by the following method of calculation:

$$2.3 \; CO_2 + \text{Alkalinity} + Mg + \text{excess} = \text{ppm } CaO \; (\text{as } CaCO_3)$$

Control tests for magnesium will show a need for more lime if the magnesium hardness is greater than 40 ppm or for less lime if it is less than 20 ppm.

An additional control test concerns the circulation of the slurry. In the plants used for this study, it was not possible to maintain as high slurry concentrations in the draft tubes as were obtained by Hartung (*11*). Because solids-contact units are. designed ostensibly to take advantage of the clarifying effects of suspended solids, however, every effort should be made to maintain the maximum possible slurry concentration without excessive carryover to the filters. The permissible concentration was found to be different for each plant, and inconsistencies in the methods for determining suspended solids caused further complications.

On the basis of a limited number of gravimetric determinations, little or no consistent relation involving specific gravity or sludge volume was found for 5-min settling periods at three plants. It would thus appear that each plant must experimentally determine empirical limits of suspended solids for optimum operation. It is probable that the quantity and type of turbidity in the raw water, temperature, and hardness may be variables that seriously limit the effectiveness of any general rules for suspended solids.

The frequently unrecognized problems caused by magnesium hydroxide can be overcome in lime softening by proper control tests and recognition of the dependence of magnesium hydroxide solubility on pH and temperature. In order to maintain a defined desirable quality for softening plant effluent, the use of the magnesium determination as a control test is recommended.

References

1. LARSON, T. E. The Ideal Lime-Softened Water. *Jour. AWWA,* **43**:649 (Aug. 1951).
2. TRAVERS, A. & NOUVEL. On the Solubility of Magnesium Hydroxide at High Temperatures. *Compt. Rend.* (Fr.), **188**:499 (1929).
3. LANGELIER, W. F. Effect of Temperature on the pH of Natural Waters. *Jour. AWWA,* **38**:179 (Feb. 1946).
4. NAESAENEN, R. The Potentiometric Determination of the Solubility Product of Magnesium Hydroxide. *Z. physik. Chem.* (Ger.), **188A**:272 (1941).
5. BRITTON, S. C. Resistence of Galvanized Iron to Corrosion by Domestic Water Supplies. *J. Soc. Chem. Ind.,* **55**:19T (1936).
6. SPERRY, W. A. The Lime Softening of Water and the Use of Sludges as an Aid Thereto. *Jour. AWWA,* **6**:215 (Mar. 1919).
7. HOOVER; C. P. Stabilization of Lime-Softened Water. *Jour. AWWA,* **34**:1425 (Sep. 1942).
8. HARTUNG, H. O. Calcium Carbonate Stabilization of Lime Softened Water. *Jour. AWWA,* **48**:1523 (Dec. 1956).
9. CALISE, V. J.; DUFF, J.; & DVORIN, R. Chemical Reactions in Hot and Cold Treatment Units. *Jour. AWWA,* **47**:665 (Jul. 1955).
10. DYE, J. F. Correlation of the Two Principal Methods of Calculating the Three Kinds of Alkalinity. *Jour. AWWA,* **50**:800 (Jun. 1958).
11. HARTUNG, H. O. Treatment Plant Innovations in St. Louis County, Missouri. *Jour. AWWA,* **50**:965 (Jul. 1958).
12. RYZNAR, J. W. A New Index for Determining Amount of Calcium Carbonate Scale Formed by a Water. *Jour. AWWA,* **36**:472 (Apr. 1944).