

to settle the agreement (18 years is the period of time remaining) with the subdivider would be calculated as follows:

Amount advanced	\$53,910
Amount refunded to date	5,130
Balance due	\$48,780

Equal annual payments of the unfunded balance of \$48,780 for 18 years would be:

$$\frac{\$48,780}{18} = \$2,710$$

The present worth of an annuity of \$1.00 per year for 18 years computed at 6 per cent interest is 10.827603 (Table 3). Multiplying the annual payment by this annuity factor results in the total payment of:

$$10.827603 \times \$2,710 = \$29,343$$

The procedure may be simplified by the use of Table 3, which contains percentages to be applied to unfunded amounts. The percentage in the case described could be computed as follows:

$$0.60153350 \times \$48,780 = \$29,343$$

The factor used was derived in the construction of the table by dividing

the present worth of an annuity of \$1.00, or 10.827603, by the remaining years of the agreement, or 18 years. The difference between the unfunded amount and the lump sum payment to the subdivider would be accounted for in the utility's books as a donation:

Amount unfunded	\$48,780
Less payment to subdivider	29,343
To donations account	\$19,437

Conclusion

No one would have the temerity to conclude the new extension rule is the answer to all the financial problems of utility extensions. Undoubtedly, problems will arise in the application of the new rule, which will, however, be considerably less burdensome to the regulated water utilities of California than the old rules, which have proved to be inequitable for all concerned except the applicant. The new rule will certainly have to be reviewed in several years to analyze the financial impact it has had on the water utilities operating under its provisions.

Reference

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Accelerating Calcium Carbonate Precipitation in Softening Plants

Robert F. McCauley and Rolf Eliassen

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RADIOACTIVE strontium presents one of the greatest problems among the radioisotopes which may find their ways into water supplies as a result of the use of nuclear weapons or nuclear power (1). Extensive studies on the removal of this element from contaminated waters have been conducted in the Sedgwick Labs. of Sanitary Science at Massachusetts Institute of Technology, Cambridge, Mass., under a contract with the US Atomic Energy Commission (No. AT(30-1)-621). Previous papers and reports (2-5) have presented some of the procedures and results of these studies.

Because strontium is an element which occupies a position in the periodic table of elements similar to calcium, the removal of strontium ions from water supplies could be accomplished by the processes utilized for calcium removal (1). Reduction of calcium hardness to a low level is imperative for a high degree of removal of strontium. The authors found that more basic information was needed on the mechanism of calcium carbonate precipitation in lime softening processes in order to assure maximum precipitation of strontium. This paper presents some of the results obtained in the calcium carbonate studies and

establishes the background needed for an understanding of the paper in this issue (see p. 494) covering studies on the removal of radiostrontium from water supplies.

Reaction Rate

The precipitation of calcium carbonate in a water-softening process is a chemical reaction which does not proceed to equilibrium at a rapid rate. The importance of reaction time is demonstrated by Fig. 1, which shows the time-hardness relationship obtained when calcium carbonate was precipitated in five different chemical reactions. The treated waters were stirred throughout the entire period, and a constant-temperature water bath was used. These experiments showed that, after 5 min of reaction time, 325-380 ppm of hardness remained in each sample. This value decreased to 100 ppm or less within 80 min after the reacting chemical had been added, and to 30-50 ppm after about 3 hr of stirring. Thus, after 3 hr of reaction, the solutions had not reached the theoretical equilibrium value of about 15 ppm hardness. It was observed that the addition of calcium carbonate crystals, or other crystalline material, combined with rapid stirring, accelerated the reaction to a marked degree. The

addition of 5 per cent of preformed crystals to the waters after a 3-hr reaction time, together with rapid stirring, reduced the hardness to the theoretical value within 5 min.

hardness, and noting, at the same, the changes in pH. Figure 1 indicates that, when no preformed crystals were present, a wide variation was to be found between the titration curve and

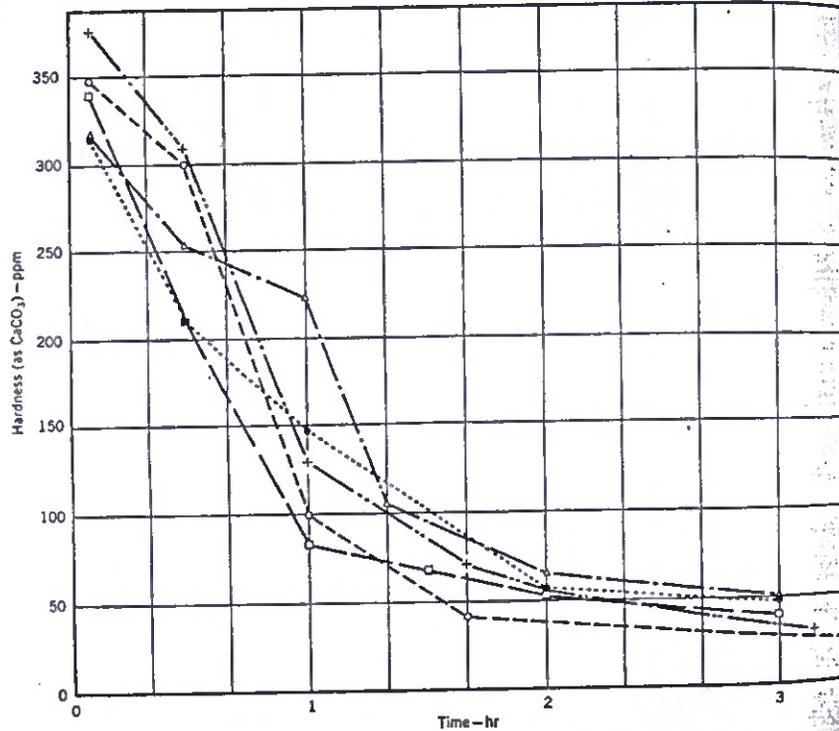


Fig. 1. Time-Hardness Relationship in Lime Softening

O— $\text{Ca}(\text{HCO}_3)_2$ in solution, $\text{Ca}(\text{OH})_2$ added; +— $\text{Ca}(\text{HCO}_3)_2$ plus 700 ppm NaCl in solution, $\text{Ca}(\text{OH})_2$ added; Δ — CaCl_2 in solution, Na_2CO_3 added; \square — CaCl_2 + $\text{Na}(\text{HCO}_3)$, NaOH added; \bullet — Na_2CO_3 , CaCl_2 added. Various chemical reactions precipitate the CaCO_3 .

A measure of the effect of the preformed crystals upon the reaction rate may be obtained from Fig. 2a and 2b by comparing the separation between the equilibrium condition curve to the curves obtained by adding lime to water containing calcium bicarbonate

the equilibrium condition curve. With increasing percentages of preformed crystals, the after-1-min curve approached the equilibrium condition curve. Thus, the presence of 8 per cent of preformed crystals, by weight, accelerated the softening reaction to

such a degree that an equilibrium condition was approached during the first 1-min period when saturated lime water was being added, and an equilibrium state was reached during the 1-min period of rapid stirring.

Pilot Plant Studies

The practical significance of the results of the experiments described is strikingly illustrated by the data obtained from a small-scale pilot plant (see Fig. 3) designed to soften water under carefully controlled conditions. A reaction basin having an average retention time of 20 min was provided with a propeller mixing device. This was followed by a solids-contact process ("upflow") basin having a retention time of only 2 min at an overflow rate of 5 gpm per square foot. The short settling time and high overflow rate were made possible by the use of sizable quantities of rapidly settling crystals in the reaction tank. Calcium carbonate hardness was removed in the form of substantial growths of crystals rather than as a fine crystalline precipitate. The settling characteristics and accelerating action of the crystals permitted water to be softened to near equilibrium at almost any level of hardness desired. The effluent was remarkably clear.

An integral part of the softening plant was a pH meter which served as the control device for plant operation. Lime was fed to maintain the desired pH level and never on a concentration basis. It was necessary to analyze alkalinity and hardness only when the raw waters contained noncarbonate hardness. Determinations were then required to compute the soda ash required to soften to the theoretical limit. The value of pH control of plant operation is shown in Fig. 4 by the rela-

tionship of pH to final effluent hardness. This curve was determined by operating the pilot plant at various pH levels while softening with lime a water which contained only calcium bicarbonate hardness. Preformed crystals were present to the extent of 3 per cent by weight. The pH level was adjusted to give the various points on the curve by increasing the lime concentration in the feed line. Under conditions approaching equilibrium it was possible to obtain an optimum removal of calcium hardness by feeding lime to maintain the pH level which plant experience had shown to be most satisfactory. This operational procedure was successful because the 20-min stirring period carried the lime-calcium bicarbonate reaction virtually to completion by the mass action effect of 3 per cent of preformed crystals.

When part of the calcium hardness was in the noncarbonate form, soda ash was required to obtain optimum calcium precipitation. The soda ash was added upon a concentration basis, as it could not be fed in terms of pH level. When soda ash was added in the necessary concentration, or in a slight excess, lime was fed to maintain the desired pH level. Effluent hardness again ranged from 15 to 25 ppm.

Discussion of Results

The results of these experiments on the mechanism of the lime-soda water softening process have indicated that the rate of the softening reaction may be accelerated in the presence of preformed calcium carbonate crystals and by using pH as the principal criterion of plant control. The reaction proceeds quickly to a state approximating equilibrium, yielding an extremely stable effluent without the necessity for long periods of mixing and flocculation.

When a water is lime-soda softened in the presence of copious quantities of calcium carbonate crystals, a relationship may be established between residual calcium hardness and pH level. If the requisite concentration of soda ash is added to react with noncarbonate hardness, a value of 15-25 ppm of cal-

state close to equilibrium. Shorter reaction periods may be used with higher concentrations of preformed crystals. This suggests that the methods mentioned are directly applicable to the softening of waters containing 60 ppm or less of magnesium hardness. Some magnesium removal may then be noted

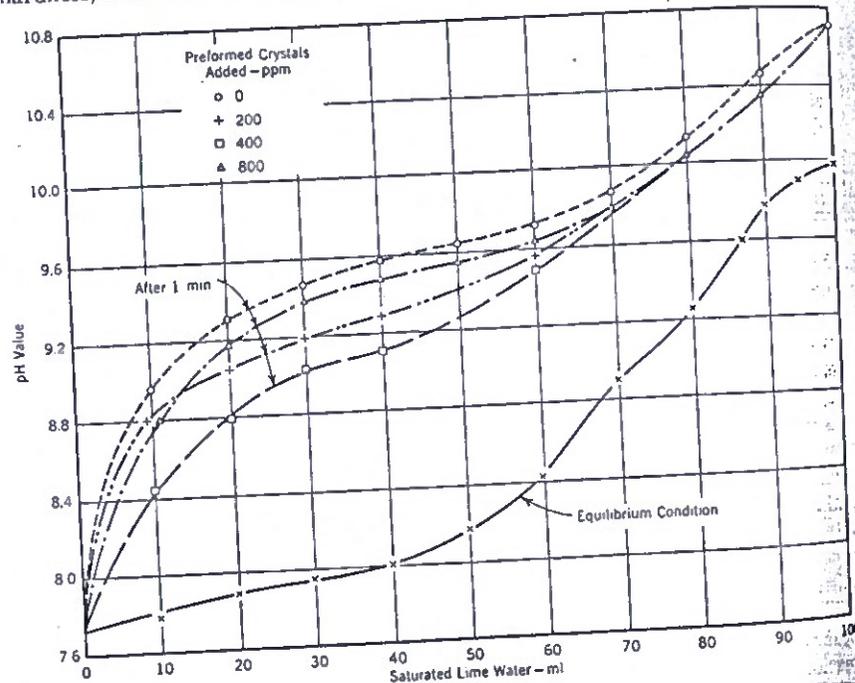


Fig. 2a. Effect of Preformed Crystals

Water containing calcium bicarbonate is titrated at 25°C with lime water. (Compare Fig. 2b.)

cium hardness should be obtained easily. This is accomplished by reacting the raw water with lime and soda ash and stirring rapidly in the presence of 3-5 per cent preformed calcium carbonate crystals at a pH of about 9.8-10.2. Under such circumstances about 20 min is required to cause the chemical reaction to reach a

and calcium hardness may be reduced to a level of 25 ppm or less, to provide an effluent hardness of 85 ppm or lower.

These procedures are applicable to both upflow and conventional plants. No change in upflow plants is necessary. In conventional lime-soda plants with separate coagulation and settling

tanks, provision must be made for 5-20 min of thorough mixing with 3 per cent or more of preformed crystals by returning sludge from the settling tanks. The basic suggestion here is that the pH meter is the proper instrument for plant control when preformed crystals are added to the mixing basin in

of lime, based on chemical analyses of the raw water. Thus, quantity of lime rather than pH is the criterion of control. This leaves no direct measure of undertreatment or overtreatment and does not provide for a determination of the rate of the softening reaction in the plant. Further, the degree to

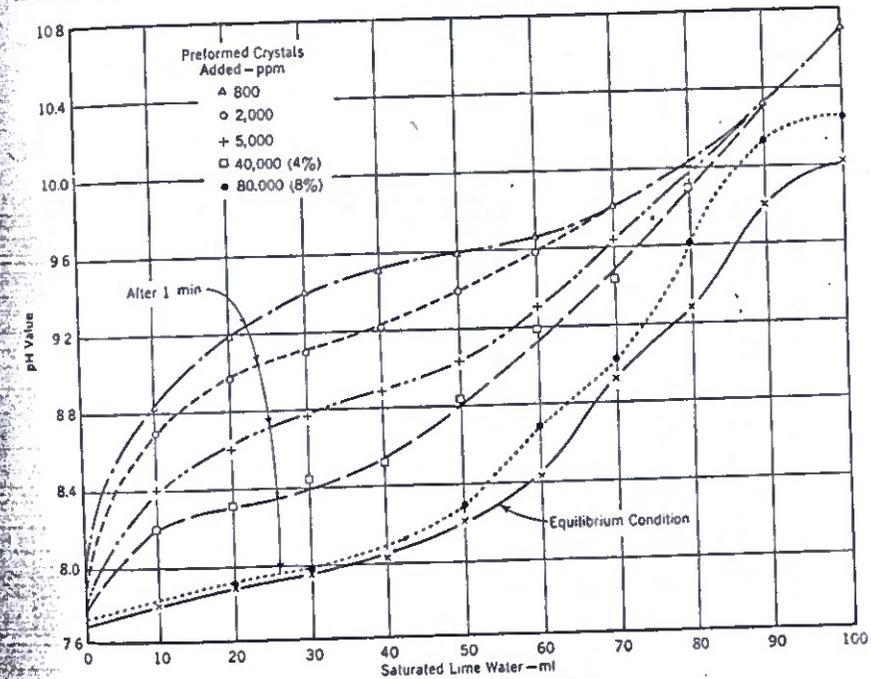


Fig. 2b. Effect of Preformed Crystals

Water containing calcium bicarbonate is titrated at 25°C with lime water. (Compare Fig. 2a.)

such concentration as to cause softening to proceed quickly to completion. If lime feed is controlled directly in terms of the desired pH level, the feeding of an almost exactly chemically equivalent quantity will result.

Many plants control operations by setting chemical feeders to dose the water with a predetermined quantity

which the reaction has proceeded at various points in the plant is not readily observed. With a limited time in the mixing, coagulation, and settling basins or compartments, the rate of reaction becomes all-important. Plant control by pH measurement and return of preformed calcium carbonate crystals to the influent will assure rapid

rates of reaction and the lowest possible hardness of the effluent.

When waters contain more than 60 ppm of magnesium hardness, excessive lime treatment is required to remove magnesium hydroxide at a pH of 10.5 or higher. If this reaction is made to take place in the presence of preformed calcium carbonate crystals, while adding enough soda ash to react with non-carbonate hardness, the calcium level

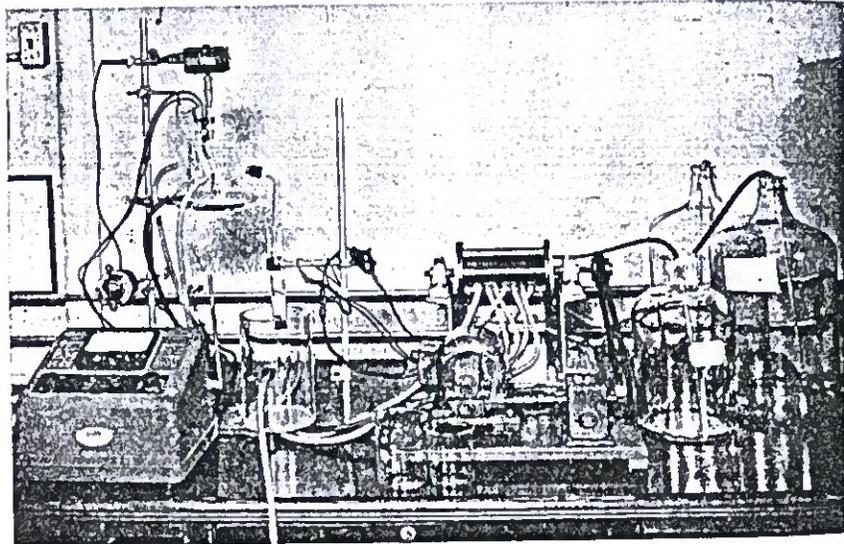


Fig. 3. Small-Scale Pilot Plant

Small amounts of water are softened under carefully controlled conditions.

of the water should be 30–50 ppm (as CaCO_3), and the total hardness 40–80 ppm.

If this treated water is settled, the pH may then be lowered by the addition of CO_2 (recarbonation) or by mixing with raw water (split treatment). Particles of magnesium hydroxide carried over from the settling basin may tend to redissolve because

of lowered pH and thus increase the hardness. If recarbonation or split treatment is carried out in the presence of preformed crystals, however, the decrease in calcium hardness will be greater than the increase in magnesium hardness. When recarbonation or split treatment is carried out at a pH level of 9.8–10.2, a very considerable reduction in the hardness of the settled water or mixture of settled and raw water

will be noted. Such reduction in hardness may be large enough to permit the feeding of soda ash to be greatly reduced, or even abandoned entirely, with a considerable saving in cost of chemicals.

Sand filtration of water which has undergone recarbonation or split treatment causes calcium carbonate growth upon the sand grains unless the water

is stabilized before filtration. The authors have shown on a pilot plant scale (5) that this stabilization may be accomplished by stirring the water with preformed crystals in the manner just described in order to drive the reaction between unreacted lime and CO_2 or raw water to completion.

Conclusions

1. Lime-soda softening reaction is a "rate process" which takes place

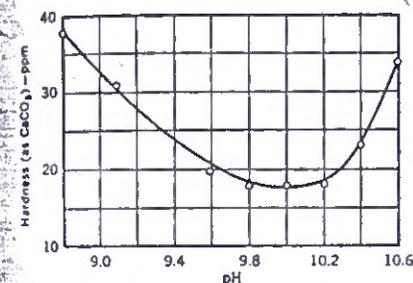


Fig. 4. Effect of pH on Effluent Hardness

A pilot plant was operated at various pH levels. Raw water hardness was 120 ppm (as CaCO_3); reaction time was 20 min; and preformed crystals were 3 per cent by weight.

quickly at high concentrations of reacting substances but proceeds slowly as the reaction approaches equilibrium. 2. Rapid mixing with preformed crystals accelerates the reaction. This effect explains the value of solids-contact units.

3. When a water containing only calcium bicarbonate hardness is softened with lime in the presence of enough preformed crystals to approximate equilibrium conditions, a relationship can be shown between calcium

hardness and pH level. If calcium noncarbonate hardness is present, the same relationship can be obtained by adding soda ash in a chemically equivalent quantity which will react with the noncarbonate hardness.

4. Lime-soda removal of calcium in the presence of preformed calcium carbonate crystals occurs through the growth of the crystals. These settle rapidly and produce an effluent of high quality.

5. Stirring treated waters with preformed crystals is of value in producing a stable, low-calcium water after recarbonation or split treatment.

6. A minimum calcium level of 15–25 ppm (as CaCO_3) can be obtained by stirring lime-soda softened or recarbonated water with copious quantities of calcium carbonate crystals at an equilibrium pH of about 9.8–10.2.

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