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Project Summary

Limestone Bed Contactors for Control of Corrosion at Small Water Utilities

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A study was conducted to investigate the use of limestone contactors for mitigating corrosion in small water supply systems that use dilute acidic (corrosive) water. As water is transported through a packed bed of crushed limestone, calcium carbonate dissolves and the pH, calcium concentration, and alkalinity increase.

A mathematical model was derived for use in contactor design. The model is based on the interfacial transport of calcium ion and relates the depth of limestone required in the contactor to the desired effluent water chemistry, influent water chemistry, limestone particle size and shape, limestone bed porosity, water temperature, and superficial velocity. The model was calibrated and tested using laboratory column experiments.

In a field contactor monitored for 2.5 years, the water quality following treatment (except for the initial few months) was essentially constant. No gradual, long-term degradation in performance was noted. After several months of operation, however, the rate of $CaCO_3$ dissolution was not as high as that observed in the laboratory using fresh limestone. The rate of dissolution was possibly reduced by an alumino-silicate residue that remained after the $CaCO_3$ was dissolved from the limestone matrix. A microbiological film may also have been a limiting factor.

Field studies indicated that limestone contactors can effectively reduce the tendency of water to take up corrosion byproducts (copper, lead, and zinc) from surfaces in piping systems. First-flush samples of cottage tap water receiving untreated spring water showed copper and lead concentrations that were significantly higher than those in contactor-treated cottage tap water (1.9 ± 0.31 mg Cu/L and 0.046 ± 0.004 mg Pb/L as opposed to 0.030 ± 0.037 mg Cu/L and 0.0084 ± 0.0084 mg Pb/L, respectively).

This Project Summary was developed by EPA's Water Engineering Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

In many areas of the United States, homeowners and small public and private water supply systems use water that is potentially corrosive to metallic materials used in the distribution system. Corrosion is a concern to the owners and users of small water supply systems because of the potential health problems associated with the ingestion of corrosion byproducts, the degradation of the aesthetic quality of the water, and the significant economic consequences of piping system deterioration.

Corrosion and contamination of the water by corrosion byproducts may be caused by the use of dilute (low-ionic-strength) acidic waters that generally have low pH, alkalinity, and concentrations of dissolved solids. Dilute acidic groundwaters and surface waters are found in a number of regions of the country, particularly in regions underlain by siliceous bedrock. The waters naturally have low buffering capacity and are corrosive. They are also prone to acidification by atmospheric deposition of strong acids (acid precipitation) or other factors such as changes in

land use. In some areas (for example, the Adirondack region of New York State); it is possible that the corrosivity of water has been increased by acid precipitation. In any event, until recent concern developed about acid precipitation and the resulting deterioration of water quality, residents and visitors tolerated or ignored the problems caused by corrosive water. Now this indifference has changed to a significant concern, and many home and resort owners as well as those responsible for village water supplies have begun to adopt techniques designed to mitigate drinking water corrosivity.

Low cost is a very important criterion in establishing the feasibility of any corrosion mitigation technique for a small water supply system. Also, the maintenance required should be minimal, and the technique should present a low potential for public health hazard resulting from improper construction, installation, or maintenance. Limestone contactors are water treatment devices that generally meet these requirements.

In a limestone contactor, water is closed to the atmosphere and flows through and dissolves a packed bed of crushed limestone. The chemistry of the water is altered as the limestone dissolves. Sources of $CaCO_3$ other than high-calcium limestone (e.g., seashells) are sometimes used. Limestone contactors are simple but effective devices with low capital cost and minimum maintenance requirements. They have been used to neutralize acid mine drainage, acidic industrial wastes, and dilute acidic surface waters.

The overall objective of this project was to investigate the use of limestone contactors for mitigating corrosion in small water supply systems that use dilute acidic water. The research plan included the development and testing of a rational method for contactor design and the evaluation of the field operation of a contactor with respect to corrosion control and operation and maintenance problems. The study had the following specific objectives:

(1) to derive and test a mathematical model for limestone contactor design, using laboratory, column-type reactors,
(2) to develop design objectives by experimentally determining the relationship between contactor-treated water quality and metal release from pipes, and
(3) to evaluate the practical application of the design equations and objectives by monitoring the field performance of full-scale contactors and to determine the feasibility of long-term operation and the type and frequency of maintenance required.

Results

As dilute acidic water is transported through a packed bed of crushed limestone, calcium carbonate in the limestone dissolves, the pH, calcium ion concentration, and alkalinity increase, and these characteristics generally tend to mitigate the dissolution of corrosion byproducts from surfaces in piping systems.

A laboratory study was conducted using packed-column contactors (Figures 1 and 2). Results were used to develop and test a numerical model for contactor design.

The design equations are based on the interfacial transport of calcium ion. Limited axial dispersion was also considered. According to the model, the depth of limestone, L, required to achieve a given level of treatment is given by

$$L = \frac{\ln[(C_{eq} - C_{bL})/(C_{eq} - C_{bo})]}{\frac{K_o\, a\, \varepsilon}{U_s} - 2\,\bar{d}\left[\frac{K_o\, a\, \varepsilon}{U_s}\right]^2}$$

where a is the interfacial area of limestone per unit volume of interstitial water, ε is the bed porosity, U_s is the superficial velocity, $\bar{d}$ is the effective diameter of the limestone particles, and K_o is the overall $CaCO_3$ dissolution rate constant. C_{bo} is the in-

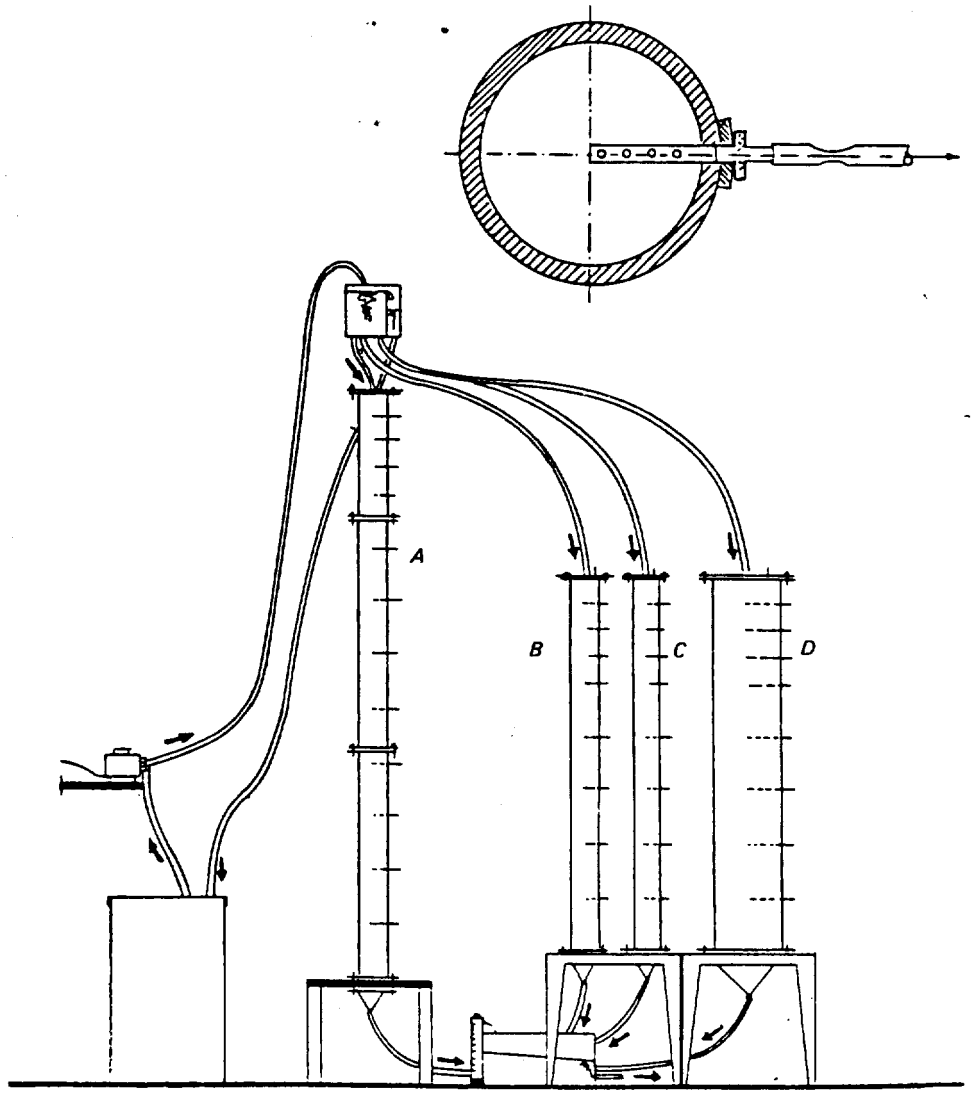

Figure 1. Laboratory columns with water supply and flow control system. Insert is a drawing of a typical through-the-wall sampling tube.

fluent calcium concentration. The quantity a is calculated using $\bar{d}$ and the particle sphericity.

The results of this study indicate that K_o can be estimated using a correlation of dimensionless mass transfer parameters.

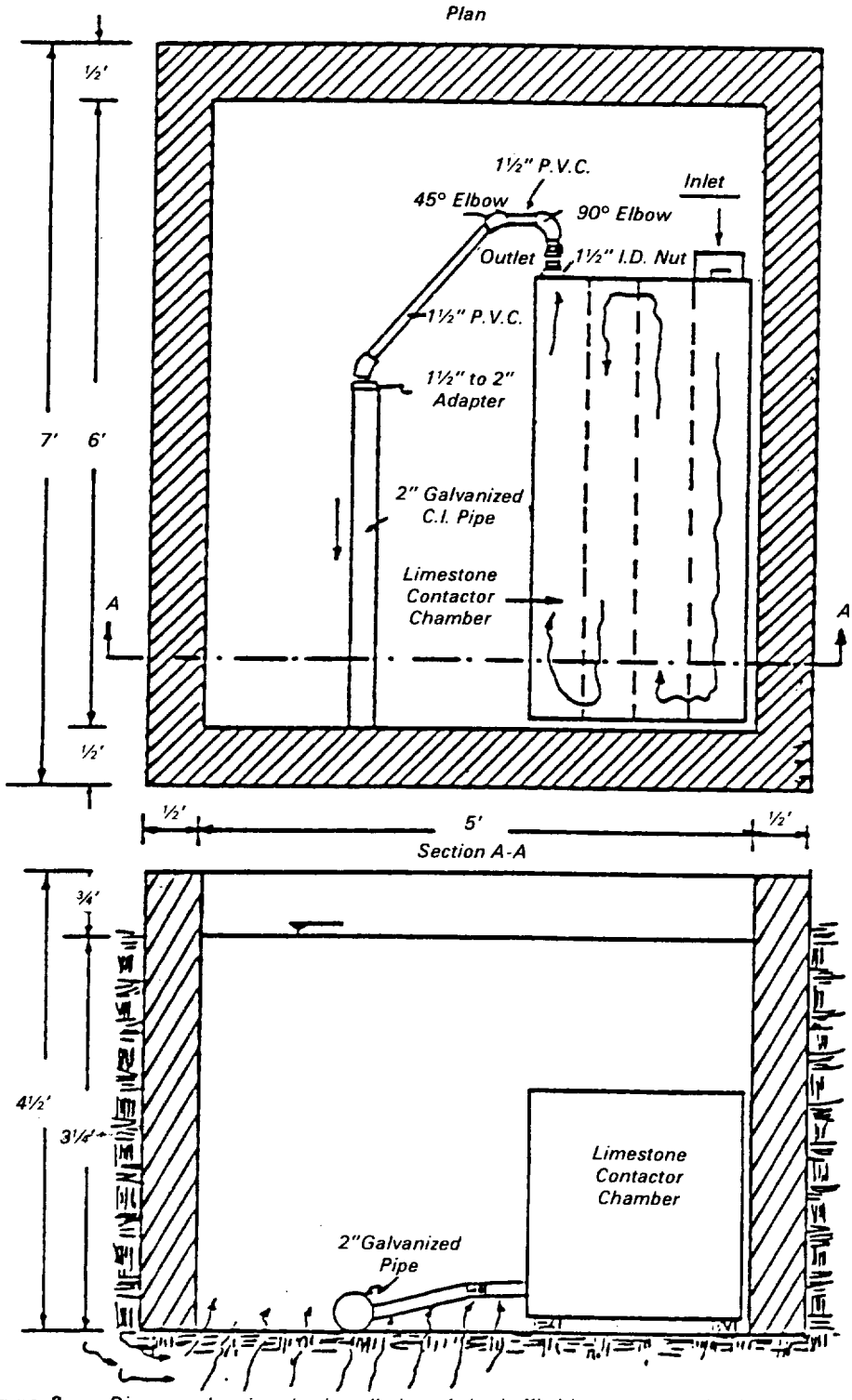

Figure 2. Diagram showing the installation of the baffled-box contactor in the spring at Covewood.

For low values of a modified Reynolds number (1< MRe < 30)

$$K_o = 5.70\ (MRe)^{-0.78}\ (U_s)\ (\nu/D)^{-0.67}$$

where $MRe = dU_s/[\nu\ (1-\varepsilon)]$, ν is the kinematic viscosity, and D is the diffusivity of calcium ion (1.2×10^{-5} cm²/s at 20 °C). For 30<MRe< 10,000

$$K_o = 1.77\ (MRe)^{-0.44}(U_s)(\nu/D)^{-0.67}$$

is appropriate.

The equilibrium and effluent calcium concentrations, C_{eq} and C_{bL}, can be determined using a chemical equilibrium model. The magnitudes of these concentrations are a function of the characteristics of the influent solution, particularly the temperature, pH, and calcium and dissolved inorganic carbon (DIC) concentrations. A conditional $CaCO_3$ solubility product of $10^{-8.71}$ (20 °C) was determined by batch experiments and used to model the dissolution of the calcite from the limestone matrix.

As the influent calcium or DIC concentration increases, the maximum pH (pH_{eq}) that can be attained in a contactor decreases, and the depth of limestone required to reach a given effluent pH (< pH_{eq}) increases. The depth of limestone required to achieve a given level of treatment also increases with decreasing influent pH, increasing superficial velocity, and increasing limestone particle size.

An evaluation of a limestone contactor in the field suggests that except for the initial few months, water quality following treatment was constant throughout the 2.5-year study period. There was no evidence of a gradual, long-term reduction in performance. However, after 3 or 4 months of continuous operation, the rate of $CaCO_3$ dissolution was not as high as that predicted by the laboratory results obtained with fresh limestone. Analysis of the limestone surfaces by x-ray energy spectrometry indicated that prolonged operation altered the surface of the limestone; the relative abundance of calcium on the surface decreased, and aluminum and silicon increased. Apparently, aluminosilicate impurities in the limestone remained as a thin residue after the $CaCO_3$ was leached from the limestone surface matrix. This residue may have slowed the dissolution rate. It is also possible that the dissolution process was adversely affected by a microbiological film on the limestone.

The model derived for contactor design assumes that the water flows through the limestone under a condition that is closed to gaseous carbon dioxide. Equilibration of the column effluent with atmospheric car-

bon dioxide can have a significant effect on the pH of the solution and hence on the tendency of the water to dissolve corrosion byproducts. When the influent DIC is high (e.g., greater than 10 mg C/L), equilibration of the effluent with the atmosphere causes the pH to increase. When the influent DIC concentration is less than several mg C/L, the pH tends to decrease.

Results of the study suggest that dilute acidic waters facilitate the release of elevated concentrations of trace metals from metal piping systems. Passivation films of most significance include $Cu_2(OH)_2CO_3$ and $Cu(OH)_2$ for copper; $PbCO_3$, $Pb_3(OH)_2(CO_3)_2$, or $Pb(OH)_2$ for lead; and $Zn_5(OH)_6(CO_3)_2$ for zinc. Because the solubility of these minerals depends on pH and inorganic carbon, metal corrosion can generally be mitigated by increases in pH and DIC concentrations. However, elevated inorganic carbon concentrations coupled with high pH values can facilitate the solubilization of trace metals through the formation of soluble metal carbonate complexes. This problem is most significant for lead, as copper and zinc do not form strong aqueous complexes with carbonate.

Laboratory pipe-section experiments using copper pipe with lead-tin solder indicate that limestone contactor treatment reduces copper and (to a smaller extent) lead leaching. Theoretical thermodynamic calculations were consistent with measured copper concentrations in the neutral pH range (pH 6.5 to 7.5). However, copper concentrations in acidic waters ($pH \leq 6.0$) were substantially undersaturated with respect to theoretical metal solubility. Lead derived from lead-tin solder in pipe section experiments was highly undersaturated with respect to the solubility of lead passivation films.

Field and laboratory observations of trace metal concentrations were generally consistent. Spring and lake waters with and without limestone contactor treatment were corrosive. Elevated metal concentrations were observed in first-flush tap water from both treated and untreated cottages. Running the tap water for 3 minutes significantly reduced copper, lead, and zinc concentrations. Although treated waters were generally corrosive, trace metal concentrations were significantly reduced in both treated spring and lake water relative to untreated water. For example first-flush copper and lead concentrations in cottage tap water receiving untreated spring water were considerably higher than in those receiving treated water, as follows:

	mg/L
Cu in untreated water	1.9±0.31
Cu in treated water	0.030±0.037
Pb in untreated water	0.0046±0.004
Pb in treated water	0.0084±0.0084

The probability of tap water copper concentrations exceeding the secondary MCL of 1.0 mg Cu/L was reduced from greater than 75% to less than 15% by limestone treatment. The probability of consuming elevated lead concentrations in first-flush tap water was also reduced by $CaCO_3$ treatment.

Measured trace metal concentrations from first-flush tap water were compared with theoretical calculations from the chemical equilibrium model. Untreated lake water was generally highly acidic (ph 4.6), and measured copper concentrations were highly undersaturated with respect to the theoretical solubility of $Cu_2(OH)_2CO_3$. Following treatment, however, measured copper values agreed closely with thermodynamic predictions. Concentrations of lead largely derived from lead-tin solder were highly undersaturated with respect to the solubility of lead passivation films.

Conclusions

Limestone contactors can effectively mitigate the dissolution of corrosion byproducts from surfaces in piping systems. A numerical model was derived to predict the effect of contactor design and operational parameters on the chemistry of the contactor effluent. Chemical equilibrium models may be useful in predicting the concentration of metal ions released from solution as a function of the level of contactor treatment.

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***Gary Logsdon** is the EPA Project Officer, see below.*
The complete report, entitled "Limestone Bed Contactors for Control of Corrosion at Small Water Utilities," (Order No. PB 87-112 058/AS; Cost: $24.95, subject to change) will be available only from:
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