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December 1997



# **The Effect of Temperature on Corrosion Control**



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### **This Publication Contains the Following Documents:**

Colling, J.H., Croll, B.T., Whincup, P.A.E., and Harward, C. June 1992. Plumbosolvency Effects and Control in Hard Waters. *J IWEM*, 6(3):259-268.

Dodrill, D.M., and Edwards, M. July 1995. Corrosion Control on the Basis of Utility Experience. *Journal AWWA*, 74-85.

Edwards, M., Schock, M.R., and Meyer, T.E. March 1996. Alkalinity, pH, and Copper Corrosion By-Products Release. *Journal AWWA*, 81-94.

Rezania, L.W. and Anderl, W.H. 1996. Copper Corrosion and Iron Removal Plants. Conference Paper. Section of Drinking Water Protection, Minnesota Department of Health.

U.S. Environmental Protection Agency. An Evaluation of the Secondary Effects of Enhanced Coagulation, With Emphasis on Corrosion Control. Conference Paper prepared by D.A. Lytle, M.R. Schock, and R.J. Miltner, Treatment and Technology Evaluation Branch, Water Supply and Water Resources Division, National Risk Management Research Laboratory.

U.S. Environmental Protection Agency. December 19, 1996. Memo from Michael R. Schock, Treatment and Technology Branch, Water Supply and Water Resources Division, National Risk Management Research Laboratory, to Jeffrey B. Kempic of the Office of Ground Water and Drinking Water, entitled: Seasonal Monitoring Revision. December 19, 1996. (Note: References 5, 6, and 7 cited in the memo are not provided for public review and comment. The Agency is not factoring the data contained in these studies into its decision making.)

Wagner, I. June 18-22, 1988. Effects of Inhibitors on Corrosion Rate and Metal Uptake. Proceedings of American Water Works Conference. Memo from Michael R. Schock to Judith M. Lebowich, February 13, 1997, regarding Requested References.

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## Plumbosolvency Effects and Control in Hard Waters

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### ABSTRACT

A laboratory lead-pipe rig has been used to support Anglian Water's successful orthophosphate dosing programme to reduce plumbosolvency. The hard waters in the region generally fall into low or high plumbosolvency categories according to the types of crystalline deposit formed. To improve the cost-effectiveness of plumbosolvency control, the effects of temperature, phosphate doses, blending and alternation of these waters were investigated.

Initial phosphate concentrations must be above 0.6 mg P/l (as phosphorus) to establish plumbosolvency control. Subsequently, phosphate doses may be reduced, provided that dosing is continuous and sufficient phosphate reaches the extremities of the distribution system. When high and low plumbosolvency waters are blended before distribution, both (or the mixture) must be phosphate dosed. However, where waters alternate in distribution, laboratory studies have shown that low plumbosolvency deposits are more stable, resulting in low lead concentrations. The high plumbosolvency of some hard waters may be due to the presence of low concentrations of humic substances.

**Key words:** Hard water; lead; phosphate; plumbosolvency; treatment; water.

### INTRODUCTION

Up to the mid-1970s hard waters, such as exist in the Anglian Water region, were not normally considered to be plumbosolvent, the problem normally being seen as one of soft waters. The increased water supply monitoring in the Anglian region following the reorganization of the water industry in 1974 showed that some hard waters were plumbosolvent, although not to the same degree as soft waters. This information was confirmed by the survey organized by the Department of the Environment (DoE) from 1979 to 1981<sup>(1)</sup> which identified priority areas for action to reduce lead concentrations at the tap.

This paper is an updated version of a paper presented to the Institution's Scientific Section Symposium on *Lead in Water* held in London on 12 April 1989.

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Concurrent with the DoE survey, experimental work at the Water Research Centre (WRC) identified that the addition of orthophosphate to waters at a concentration of approximately 1.0 mg P/l (as phosphorus) was able to reduce lead solvency in hard waters<sup>(2)</sup>. This treatment was successfully installed in two trial areas in Anglian Water (Boston and Sleaford)<sup>(3)</sup> and was subsequently recommended for plumbosolvency control in hard waters by the WRC<sup>(4)</sup> and DoE<sup>(5)</sup>.

The 1979-81 survey identified those areas where the incidence of lead solvency was highest, based on the proportion of random samples giving elevated lead concentrations. Therefore, if an area had very few lead pipes but a plumbosolvent water, it was possible that it would not be designated high priority. The former Anglian Water Authority decided that the small number of customers in such areas should be protected against high lead concentrations, and therefore adopted a policy of treating all high plumbosolvency waters, unless it could be demonstrated that lead pipes were absent in the distribution system.

In order to classify its waters, a contract was placed with Humberside College of High Education (now Humberside Polytechnic) to develop a test to classify waters as high-plumbosolvency or low-plumbosolvency and subsequently to test all Anglian Water treated waters<sup>(6)</sup>. On the basis of this work, phosphate dosing to control plumbosolvency has been successfully installed at 85 water-treatment works in Anglian Water.

Following the survey performed by Humberside College, further information on the topics listed below was required in order to ensure cost-effective control of plumbosolvency:

- (a) Effects of temperature on lead solubility;
- (b) The minimization of phosphate dose to establish and maintain plumbosolvency control;
- (c) The effects of breaks in phosphate dosing;
- (d) The mixing of waters in distribution; and
- (e) The effect of using exhumed old lead pipes in the test apparatus.

During the experimental programme on the above topics, it was discovered that low concentrations of organic compounds, probably naturally occurring, can influence plumbosolvency. This work is also described later in this paper.

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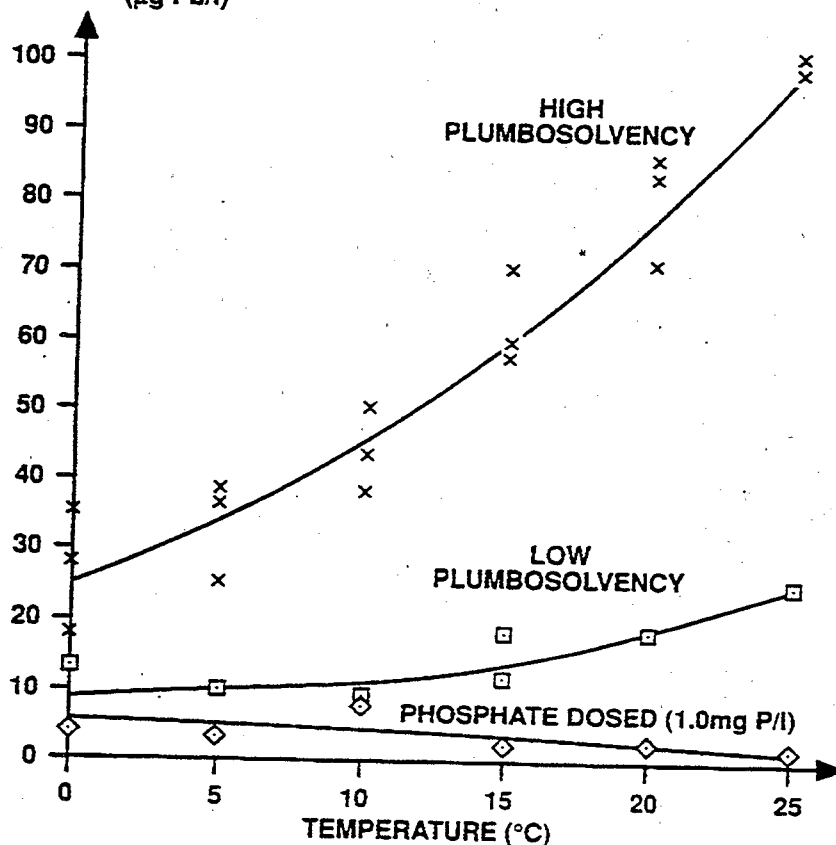
LEAD CONCENTRATION  
( $\mu\text{g Pb/l}$ )

Fig. 1. Effects of temperature on lead solvency

## PLUMBOSOLVENCY TESTING EXPERIMENTS

Full details of the standard test have been published<sup>(6)</sup>. The test water is continuously pumped at 30 ml/h through 150 mm sections of new 12 mm lead pipe at 25 $^{\circ}\text{C}$  for up to 25 days. The measured lead concentrations in the exit water from each pipe normally begin to be stable after 7–10 days. The stable lead concentration is quoted as the test result. Most waters give a 'high plumbosolvency' result ( $100 \pm 20 \mu\text{g/l}$ ), or a 'low plumbosolvency' result ( $30 \pm 10 \mu\text{g/l}$ ).

These differences are thought to be due to the formation of either the more soluble basic lead carbonate or the less soluble normal lead carbonate, as the corrosion product on the lead surface<sup>(2)</sup>. This is despite the prediction that normal lead carbonate should be the thermodynamically stable product over the pH and alkalinity range involved<sup>(2,7)</sup>. Scanning electron microscopy (SEM) reveals characteristic differences in the crystal deposits formed in pipes during the test. Thin hexagonal plates are formed from high plumbosolvency waters, and

relatively smooth solid surfaces from low plumbosolvency waters. Typical micrographs have been published earlier<sup>(6)</sup>.

It should be noted that distinct crystals cannot be identified in old pipes. Pipes that have been in service are generally coated with relatively thick, stratified and contaminated deposits. However, the presence of basic lead carbonate in some such deposits has been confirmed by x-ray diffraction and infra-red absorption spectroscopy<sup>(2)</sup>.

## PHOSPHATE-DOSED RESULTS AND SEM

Waters dosed with other phosphates (1.0 mg P/l) give low lead levels, frequently less than 10  $\mu\text{g/l}$ . With continued running, lead values as low as 3  $\mu\text{g/l}$  can be obtained. The lead phosphate compound formed is clearly of extremely low solubility, and its exact composition is not known. It has a very characteristic appearance by SEM (rounded granules and surface features, as evident in the

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Fig.

published photograph<sup>(6)</sup>, and the presence of phosphorus and some calcium can be detected by energy-dispersive x-ray spectroscopy (EDS).

### EFFECT OF TEMPERATURE ON LEAD SOLUBILITY

The monitoring results from the high plumbosolvency Boston distribution system showed higher lead concentrations in summer than in winter in both untreated and phosphate-dosed waters<sup>(6)</sup>. This effect was thought to be due to the differences in water temperature. In order to confirm and more accurately quantify the effect, typical high and low plumbosolvency waters, and the high plumbosolvency water dosed to 1.0 mg P/l with orthophosphate, were examined at 0°C, 5°C, 10°C, 15°C, 20°C and 25°C (in random order); the mean lead results are plotted against temperature in Fig. 1. Despite the different lead concentrations, the undosed waters follow a similar relationship, and, as would be expected for simple solubility effects, plots of log (Pb) versus 1/Temp (°K) are effectively linear.

Deposits on a selection of pipes were also examined by SEM. At the lower temperatures the crystals are generally similar to those described for

25°C<sup>(6)</sup>, although smaller in size. These examinations therefore support the water lead concentration results in indicating that the temperature effects in undosed waters are largely due to crystal solubility. Since no change in mechanism is involved, it is clear that the accelerated results obtained at 25°C in the standard test are also representative of effects at lower temperatures.

The phosphate-dosed high plumbosolvency water is different, showing little temperature dependence, and apparently a small decrease in lead level with increasing temperature. However, all these lead values are low, and the results may simply reflect a more rapid approach to ultimate coverage of phosphated deposit at the higher temperatures. SEM/EDS examinations show the expected round nodules containing phosphorus and calcium.

### INITIAL PHOSPHATE CONCENTRATION

The WRc investigations suggested that for high alkalinity waters phosphate concentrations of 0.7–1.0 mg P/l<sup>(4)</sup> would be effective in establishing plumbosolvency control within a distribution system. In order to optimize the phosphate concentration required for a particular high plumbo-

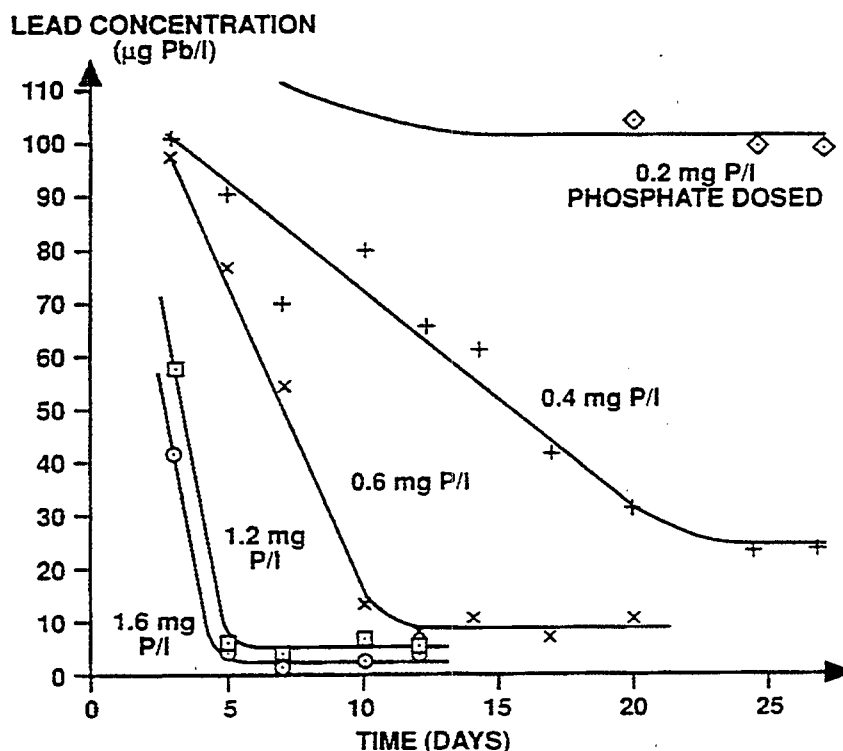


Fig. 2. Effects of initial orthophosphate concentration on high plumbosolvency water at 25°C

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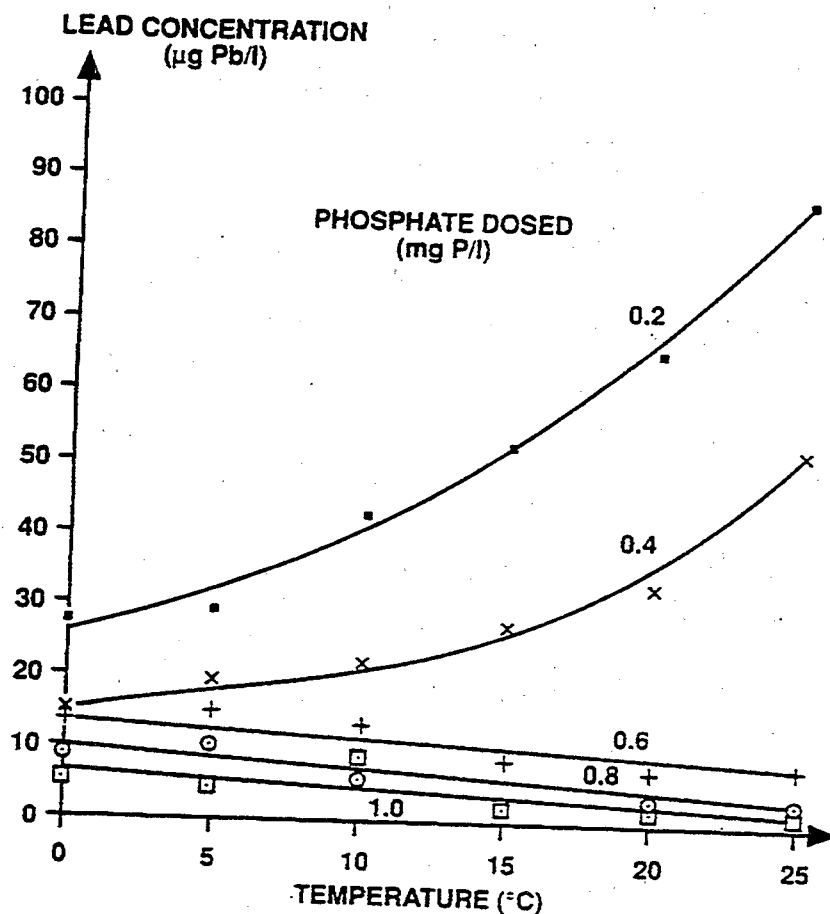


Fig. 3. Effects of temperature at different initial orthophosphate concentrations in high plumbosolvency water

solvency water. experiments were performed in concentrations of 0.2–1.6 mg P/l. The results are shown in Fig. 2. They demonstrate that the phosphate dose affects not only the final lead concentration, but also the rate at which the phosphate is effective. It is clear that 0.2 mg/l has little effect. For the water tested, 0.4 mg/l has some effect, but at a slow rate, and this dose is less effective with some other waters. It is only at doses of 0.6 mg/l and above that the major effect of phosphate dosing is apparent. However, the faster rate of establishment of control at 1.0 mg P/l and above is significant, particularly when distribution system conditions are considered.

Theoretically, as noted by staff of the WRC<sup>(7)</sup>, phosphate dose requirements should be lower at lower calcium concentrations. This was confirmed by similar experiments using water containing 50 mg/l of calcium compared with about 150 mg/l for the water used in Fig. 2. The effect, however, appeared to be relatively small, the final lead value

for a dose of 0.4 mg/l being 18 µg/l compared to 25 µg/l.

The effect of a range of initial phosphate concentrations was also examined at a series of different temperatures (0–25°C). The results (Fig. 3) indicate that the 0.2 and 0.4 mg P/l waters behave similarly to undosed waters, whilst the concentrations of 0.6 mg P/l and above behave as phosphate-dosed waters.

The above results indicate that an initial phosphate dose of 0.6 mg P/l or above is necessary to establish control of plumbosolvency in these waters. The higher the phosphate concentration above 0.6 mg P/l, the more rapidly is control established.

#### BREAKS IN PHOSPHATE DOSING

The effect of breaks in phosphate dosing is important for two reasons. (i) to assess the impact of equipment failure at the treatment works, and (ii) to investigate intermittent dosing as a means of achiev-

ing cost-effective experiments in winter than in a given lead policy of summer.

In order to phosphate doses were established weeks with low plumbosolvent stopped and a period. Meaning the change

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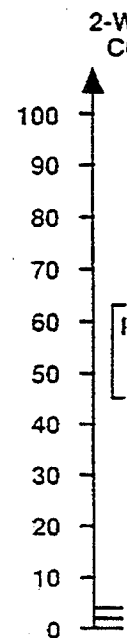


Fig. 4

## PLUMBOSOLVENCY EFFECTS AND CONTROL IN HARD WATERS

ing cost-effective control. The temperature dependence experiments indicated that lead concentrations in untreated waters were much lower in winter than summer, and therefore control to below a given lead concentration might be achieved by a policy of summer-only phosphate dosing.

In order to investigate the effect of breaks in phosphate dosing, appreciable phosphated deposits were established in pipes run continuously for 33 weeks with doses of 1.0 mg P/l on typical high and low plumbosolvency waters. Dosing was then stopped and undosed water run for a further lengthy period. Mean results from two-week periods following the change are presented in Fig. 4.

It is clear that the two types of water behave very differently. For the high plumbosolvency water there was a slow but steady increase in lead concentration, eventually reaching the normal undosed lead level about 30 weeks after the cessation of dosing. With the low plumbosolvency water however, there was a relatively rapid effect, and lead values *higher* than normal undosed water occurred within four weeks. Subsequently there was a slow decrease to typical low plumbosolvency values.

The pipes were then examined by SEM. The final lead values were similar to those normally obtained from the relevant waters indicative of the presence of basic and normal lead carbonates respectively.

However, both the surfaces consisted of small smooth round 'phosphate-type' granules, and by EDS analysis, phosphorus and calcium were still present. The well-phosphated surface, which has very low solubility, had apparently not been destroyed on cessation of phosphate dosing but must have been encapsulated within a carbonate coating.

The results in Fig. 4 illustrate that short breaks in phosphate dosing of, say, a few days are unlikely to cause large increases in plumbosolvency. It appears that the phosphated pipe deposits are reasonably stable over short periods, resulting in only small rises in lead concentrations. Over longer periods (several weeks) the pipe deposits gradually change. The rate of increase in lead concentrations can vary between different pipes, and the prospects for plumbosolvency control by summer-only phosphate dosing appear unpromising.

## LONGER-TERM REDUCTION IN PHOSPHATE DOSE

Although phosphate concentrations of at least 0.6 mg P/l are necessary to establish plumbosolvency control it is possible that once established it will be maintained by low or continuous phosphate doses. In order to test this hypothesis, pipes which had been exposed to high plumbosolvency water dosed

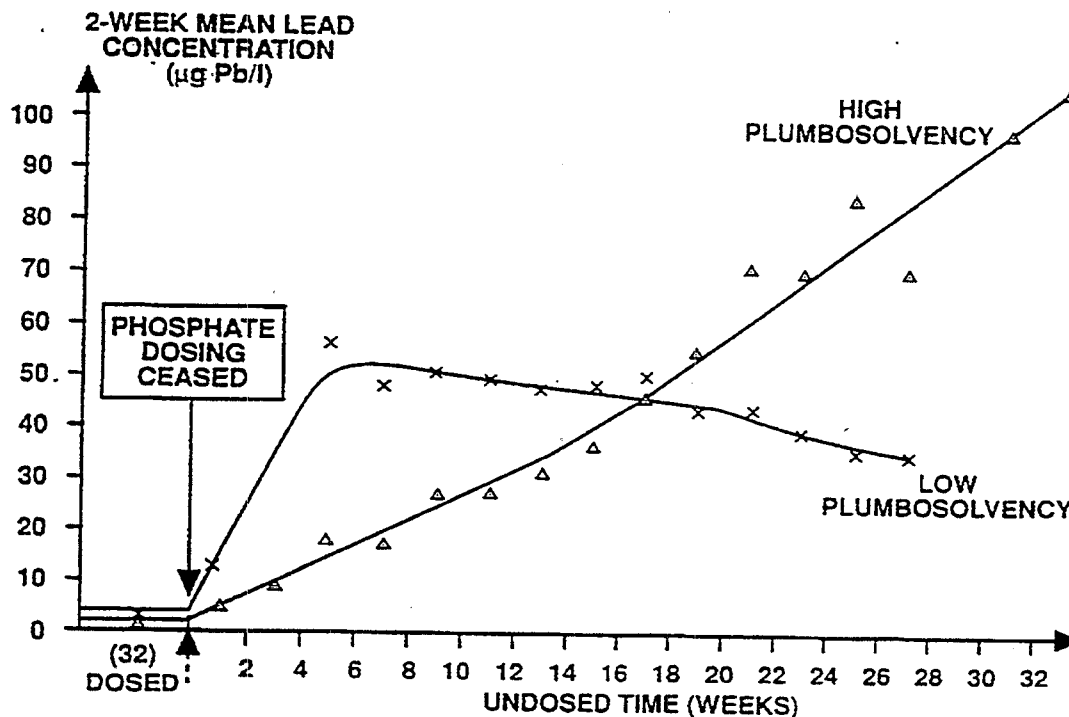


Fig. 4. Effect of cessation of orthophosphate dosing (after 33 weeks at 1.0 mg P/l)



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at 0.8 and 1.0 mg P/l for eight weeks, and which had established steady lead concentrations in the water from the test rig, were exposed to reduced phosphate concentrations of either 0.2 or 0.4 mg P/l. The reduced phosphate concentrations were run for a total period of 44 weeks at various temperatures finishing at 25°C. During this period lead concentrations remained low and stable.

The phosphate concentration in two of the pipes was then reduced to 0.1 mg P/l. After several weeks' operation the lead concentrations from these pipes became more variable and slightly higher than those operating at 0.2 and 0.4 mg P/l. However, the lead concentrations remained low and similar to those from the other pipes.

Subsequently, the phosphate dosing to all the pipes was ceased. Unlike the pattern of the pipe in high plumbosolvency water dosed at 1.0 mg P/l shown in Fig. 4, the lead concentrations from all the pipes increased rapidly, reaching typical high plumbosolvency values within two weeks.

These results illustrate that plumbosolvency control can be maintained by phosphate doses of 0.4 mg P/l or less, but that breaks in dosing are then more important, presumably due to the less robust nature of the pipe deposits.

## MIXING AND ALTERNATION OF WATERS IN DISTRIBUTION

### BLENDED UNDOSED WATERS

The effects of mixing waters, equivalent to blending them before distribution, have been previously published<sup>(6)</sup>. It was shown that only 5-10% of a high plumbosolvency water mixed with a low plumbosolvency water was sufficient to impart a high plumbosolvency to the mixture. Further mixtures have since been tested, confirming the original conclusion.

### ALTERNATING UNDOSED WATERS

A more usual situation in distribution is that part of a distribution zone will be exposed to different waters for periods determined by demand and pumping regimes, i.e. alternating exposure to different waters. In order to investigate the effect of alternating high and low plumbosolvency waters, various periods of alternation were investigated on the pipe rig. Several pairs of waters were alternated daily for a number of weeks in new lead pipes with some commencing the experiment on high plumbosolvency waters and some on low. In all cases only low plumbosolvency results were recorded.

After weekly alternation in new lead pipes, low plumbosolvency results were obtained after one week on the pipes beginning with low plumbosolvency water (as expected), and after two weeks on the pipes beginning with high plumbosolvency

water. Subsequently, stable, low plumbosolvency results were obtained from both sets of pipes.

In practice, waters may be alternated after long periods of pipe exposure to one type of water where pipe deposits are well-established. In order to investigate this situation, pipes were exposed to high or low plumbosolvency waters for a period of eight weeks in order to establish longer-term pipe deposits. At the end of this period lead concentrations were typical of the waters used. The waters in some of the pipes were then alternated weekly. Within two weeks of alternation only low plumbosolvency results were obtained. In other pipes the waters were alternated on a 6 day/1 day basis, with the same result.

In order to investigate even longer-term changes, pipe deposits from low and high plumbosolvency waters were established over 33 weeks and then the waters interchanged in some of the pipes. In the pipes originally exposed to high plumbosolvency, low plumbosolvency results were obtained within two weeks. Contrastingly, the pipes originally exposed to low plumbosolvency water showed only slight increases in lead concentrations over the 27-week period of the experiment.

It can therefore be concluded that low plumbosolvency pipe deposits are much more stable than high plumbosolvency pipe deposits, and that in areas where high and low plumbosolvency waters alternate only low plumbosolvency lead concentrations can be expected.

### MIXING AND ALTERNATION OF PHOSPHATE DOSED AND UNDOSED WATERS

When a high plumbosolvency water dosed with phosphate is blended with an undosed low plumbosolvency water before distribution, the phosphate is diluted and the concentration may drop below that necessary to establish phosphated pipe deposits<sup>(6)</sup>. Due to the dominance of high plumbosolvency in mixtures, control may not be established in such a situation and it will be necessary also to dose the low plumbosolvency water to raise the phosphate concentration in the mixture to above 0.6 mg P/l in order to effect control.

When such waters were alternated weekly, stable lead values were not obtained quickly, only steadying after about 16 weeks. Lead concentrations remained low and, on average, decreased throughout the experiment. However, each time that the water was changed to an undosed low plumbosolvency water, the lead concentrations became erratic and early in the experiment showed some values higher than those normally obtained for low plumbosolvency waters. This effect reduced with continued running. It should therefore be possible to alternate phosphate-dosed high plumbosolvency and undosed low plumbosolvency waters in distribution and still obtain low plumbosolvency results.

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## PLUMBOSOLVENCY EFFECTS AND CONTROL IN HARD WATERS

TABLE I. EFFECT OF ION-EXCHANGE NITRATE REMOVAL ON ISLEHAM WATER

Water	Nitrate (mg/l NO <sub>3</sub> )	Sulphate (mg/l)	Chloride (mg/l)	Plumbosolvency test results (µg/l Pb)
Combined raw	97	87	68	108, 102 : HIGH
Raw - added chloride	97	87	177	100, 97 : HIGH
IX treated water (mean mix)	20	8	177	28, 31 : LOW
IX treated water with added nitrate	97	8	177	28, 29 : LOW
IX treated water with added sulphate	20	87	177	31, 31 : LOW
IX treated water with both additions	97	87	177	27, 29 : LOW
IX treated water (end of run)	35	58	121	38, 33 : LOW

However, the experiments indicate that this should be carefully investigated to ensure that good control is maintained.

### OLD LEAD PIPES

The experiments described in the preceding sections were performed using new lead pipe. It is possible that the old lead pipes in distribution will behave differently, due to the more heterogeneous nature of their old surface deposits which may include extraneous and organic matter. Several of the experiments were therefore repeated using carefully exhumed old lead pipes which were subjected to minimum disturbance and kept filled with the relevant water. From the results of these experiments it can be concluded that the final lead concentrations obtained on various waters using old lead pipes are not significantly different from those using new lead pipes. However, the time taken to reach stable values is generally much longer, up to twenty times as long. With old pipes the effect of phosphate-dosing can continue to increase for several years.

### SURFACE WATERS

The results illustrated in this paper were obtained using underground waters. All the surface-derived potable waters in the Anglian Water region have high plumbosolvency. The final test results from the phosphate dosing of surface-derived waters are essentially the same as those derived from high plumbosolvency underground water. However, the time taken to reach similar lead levels is longer.

### INFLUENCE OF ORGANIC MATTER ON PLUMBOSOLVENCY

As part of the commissioning procedure for a new process, water from the Anglian Water ion-exchange nitrate-removal plant at Isleham was tested for plumbosolvency. The untreated water at Isleham has high plumbosolvency and is phosphate-dosed after nitrate removal. The water from the ion-

exchange vessels, at the beginning of the service cycle, is high in chloride and low in alkalinity. Such an extreme composition had not previously been tested and it was suspected that it might be more plumbosolvent than the untreated water. Surprisingly it was shown to have a low plumbosolvency.

By appropriate additions to either the untreated or ion-exchange treated waters, it was demonstrated that the main ions added (chloride) or removed (nitrate, sulphate, bicarbonate) during the treatment were not influencing plumbosolvency (Table I). This view was reinforced by testing the plumbosolvency of water towards the end of the operating cycle of the ion-exchange resin bed, when the water composition is closer to the untreated water. This water also showed low plumbosolvency. As previously experienced, mixtures (about 1:1) of untreated and ion-exchange treated water, as supplied to the customer, showed high plumbosolvency requiring continued addition of phosphate at the works.

The strongly basic ion-exchange resins used to remove nitrate from water are known to also remove humic acids<sup>(8)</sup>. As humic acids are known to complex metals and hold them in solution, it was suspected that their removal might be the reason for the reduced plumbosolvency of ion-exchange treated waters, despite the generally low total organic carbon (TOC) content of groundwaters. The reduced TOC of the ion-exchange treated water (0.5 mg C/l) compared to the untreated water (1.5 mg C/l) was significant. The failure to find a correlation between inorganic water composition and plumbosolvency by multivariate analysis during the Anglian Water plumbosolvency survey<sup>(9)</sup> reinforced the suspicion that organic matter was causing the effects observed.

In order to test this hypothesis, experiments were performed with both addition of humic material to low plumbosolvency waters, and removal of organic matter from high plumbosolvency waters.

### ADDITION OF HUMIC MATERIAL TO LOW PLUMBOSOLVENCY WATER

A solution of humic substances was prepared by filtering a slurry of peat in low plumbosolvency

## PLUMBOSOLVENCY EFFECTS AND CONTROL IN HARD WATERS

**TABLE III. EFFECT OF REMOVAL OF ORGANICS FROM HIGH PLUMBOSOLVENCY WATERS WITH FRESH GRANULAR ACTIVATED CARBON**

High plumbosolvency water	TOC (mg C/l)		Test result (µg/l Pb)	
	Untreated	GAC filtered	Untreated	GAC filtered
Isleham (raw)	1.5	0.3	105	38
Typical groundwater	1.2	0.2	107	30
Typical surface water	4.2	0.3	118	28

a real inverse relationship. Results at Boston over a much longer period indicated higher summer lead concentrations (20 µg/l compared to 10 µg/l in the winter).

Short breaks in phosphate dosing do not lead to significantly increased lead concentrations in waters dosed at 1.0 mg P/l; however, long breaks lead to a re-establishment of plumbosolvent pipe deposits. Waters dosed at concentrations lower than 1.0 mg P/l show a more rapid return to plumbosolvent conditions.

Once phosphated pipe deposits have been established, they can be maintained in the pipe rig by phosphate concentrations as low as 0.1 mg P/l. However, breaks in phosphate dosing at these lower maintenance concentrations result in a rapid rise in lead solvency, returning to the original high plumbosolvency results within two weeks. Thus if maintenance dosing is adopted, it becomes important to ensure that interruptions to dosing are not longer than a day or two. Longer periods will lead to a return to plumbosolvent conditions necessitating at least a one-year period of dosing to 1.0 mg P/l to re-establish phosphated deposits before maintenance dosing can be reintroduced. Phosphate doses as low as 0.1 to 0.2 mg P/l may not penetrate to the ends of a distribution system, leading to loss of control at the system extremities. In practice, therefore, it is expected that in the longer term phosphate doses may be reduced by up to 50%, thereby lowering costs whilst maintaining effective plumbosolvency control. Lower doses may be possible in some systems. However, care must be taken to maintain an adequate phosphate concentration at the extremities of the distribution system and to avoid breaks in phosphate dosing.

Where high and low plumbosolvency waters are blended before distribution, even a small proportion of high plumbosolvency water will give a plumbosolvent mixture. It will therefore normally be necessary to phosphate dose both waters (or the mixture) in these circumstances. In the more normal situation of waters mixing in distribution in an undefined manner and some parts of the system receiving alternating waters, it has been shown that when high and low plumbosolvency waters alternate the low plumbosolvency pipe deposits are the more stable. In such a situation low plumbosolvency results are obtained whichever water is present. These results explain why some parts of certain

distribution systems give low plumbosolvency results, even though they more often contain high plumbosolvency water than low. In practice, however, there will always be part of the system exclusively supplied by high plumbosolvency water and therefore this water will be phosphate dosed. Alternation of this water with the low plumbosolvency water may give erratic initial lead concentrations but should enable control to be maintained in the long term.

The general introduction of phosphate into plumbosolvent zones in Anglian Water has given successful control of lead solvency. The mean reductions (thirty-minute stagnation lead levels) at fixed points are entirely consistent with the trials and experimental data, 45% for 3-6 months dosing, increasing to 63% for 9-12 months. The lead concentrations now achieved easily comply with the requirements of the EC drinking water Directive<sup>(9)</sup> and the more stringent requirements of the Water Supply (Water Quality) Regulations 1989<sup>(10)</sup>.

Experimental evidence from high plumbosolvency waters, where passage through ion exchange or GAC columns gave low plumbosolvency, and from the addition of peat extract to low plumbosolvency waters, making them highly plumbosolvent, indicates that low concentrations of humic acids may be the cause of high plumbosolvency in hard waters. In practice this finding is unlikely to alter plumbosolvency control measures in Anglian Water in the foreseeable future as phosphate dosing is much less expensive, at present, than the removal of organic compounds.

### CONCLUSIONS

1. In order to establish effective plumbosolvency control, initial doses of phosphate of at least 0.6 mg P/l (as phosphorus) are required.
2. Lower continuous phosphate doses can maintain control.
3. Short breaks in phosphate dosing of 1 or 2 days should not affect plumbosolvency control.
4. The effects of longer breaks in phosphate dosing depend on the phosphate dose. High plumbosolvency conditions can return within two weeks at low phosphate doses.
5. Where high and low plumbosolvency water are blended before distribution both waters, or the mixture, must be phosphate dosed.

## COLLING, CROLL, WHINCUP AND HARWARD ON

water. Increasing quantities of this extract were added to 25 l of low plumbosolvency water and the resulting solutions tested for their plumbosolvency. It will be seen that addition of sufficient quantities of the peat extract gave higher plumbosolvency. During these experiments the TOC of the water tested ranged from 0.6 mg C/l in the control water to 1.7 mg C/l in the water with 1000 ml of peat-extract added. Addition of the peat extract to the ion-exchange treated water from Isleham gave high plumbosolvency results (Table II).

TABLE II. EFFECT OF ORGANIC ADDITIONS TO LOW PLUMBO SOLVENCY WATERS USING A STANDARD PEAT EXTRACT

Addition to 25 l low plumbosolvency water	Plumbosolvency test result ( $\mu\text{g Pb/l}$ )
no addition	30
+ 10 ml peat water	26
+ 50 ml peat water	51
+ 75 ml peat water	82
+ 100 ml peat water	97
+ 250 ml peat water	114
+ 1000 ml peat water	102
Isleham IEX treated water	29 LOW
+ 100 ml peat water	82 HIGH

## REMOVAL OF ORGANIC COMPOUNDS FROM HIGH PLUMBO SOLVENCY WATER

The organic content of three typical high plumbosolvency waters was reduced by passage at a slow rate (1 l/h) through a column (500 mm  $\times$  400 mm dia.) of fresh granular activated carbon (GAC). TOC analysis confirmed that a substantial proportion of the organics present had been removed. The results of testing these waters for plumbosolvency are shown in Table III. It will be seen that in all cases the high plumbosolvency waters had been reduced to low plumbosolvency. Thus two different methods of removing organic compounds from water have been shown to reduce plumbosolvency. If humic matter contains the factor promising high plumbosolvency, it would be expected that GAC columns would have a short lifetime for plumbosolvency reduction, as they have only a short lifetime for the removal of humic material. Continued use of the GAC column confirmed that its capacity for plumbosolvency reduction was rapidly exhausted.

Although the above initial experiments are not conclusive, and further experiments to investigate the influence of organic compounds on plumbosolvency are being carried out, they give a strong indication that the main factor causing high plumbosolvency in hard waters is their content of humic substances.

## SURVEY OF ANGLIAN WATER POTABLE WATERS

The TOC content of Anglian Water potable waters was compared with their plumbosolvency. It was found that waters with the highest TOC concentrations ( $>3$  mg C/l) were all plumbosolvent. This category includes all the Anglian Water surface-derived water supplies. Waters with very low TOC ( $<0.6$  mg C/l) were mostly of low plumbosolvency. However, for the majority of Anglian Water supplies TOC content is not a reliable indicator of plumbosolvency. This is not surprising if humic substances or some fraction or component of them are responsible for the effect, as the contribution of humic matter to the TOC will vary with the water source.

## DISCUSSION

The plumbosolvency of hard waters is determined by the type of crystalline deposit formed on the inside of the lead pipe. These deposits can be identified using electron microscopy. The solubility of the deposits is temperature dependent. The addition of orthophosphate to high plumbosolvency waters causes a phosphated pipe deposit of low solubility to be formed. In order to form an effective deposit, it has been shown that phosphate concentrations of at least 0.6 mg/l are required. The higher the phosphate concentration (up to 1.6 mg P/l) the more rapidly the deposits are formed.

Old lead pipes contain thick surface deposits which have been shown to change more slowly than the younger deposit in the new lead pipes normally used in the pipe rig tests; however, the long-term effects of treatment are the same. Thus in a distribution system where the phosphate takes some time to penetrate to the ends of the system and only old lead pipes are present, it is expected that initial phosphate concentrations of at least 1.0 mg P/l will need to be maintained in order to establish plumbosolvency control within a reasonably short period of time. Indeed in most distribution systems, where phosphate may be reduced by adsorption or absorption on deposits in non-lead pipes, it may not be possible to achieve the 0.6 mg P/l, the lowest concentration required to establish plumbosolvency control, at the ends of the system unless phosphate concentrations above this value are dosed.

The minimum period to establish control in the field will depend upon the situation, but experience at Boston and Sleaford<sup>(1)</sup> indicates that a year is not unreasonable. In subsequent years further small reductions in lead solvency will be achieved. In test-rig results, lead concentrations from phosphated lead pipes appeared to decrease with increasing temperature. This apparent effect was thought to be due to the more rapid establishment of highly phosphated deposits at the higher temperatures in the limited time-scale of the experiments rather than

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## PLUMBOSOLVENCY EFFECTS AND CONTROL IN HARD WATERS

6. Where high and low plumbosolvency waters alternate in distribution, low plumbosolvency results are obtained.
7. Where phosphate-dosed high plumbosolvency and low plumbosolvency waters alternate in distribution, low plumbosolvency results are obtained after a short period of erratic behaviour.
8. Initial results indicate that humic substances (at low concentrations) may be the cause of high plumbosolvency in hard waters.

## ACKNOWLEDGEMENTS

The authors wish to thank the Director of Quality of Anglian Water for permission to publish this paper. Grateful thanks are also expressed to Mr C. R. Hayes, Mr D. N. Harris and all the other Anglian Water and former Anglian Water staff who provided assistance, to Mr R. Gregory of the WRc and to Mr J. G. Watson of SCM Chemicals Limited for scanning electron microscopy.

## DISCLAIMER

The views expressed in this paper are those of the authors and do not necessarily represent the views of Anglian Water Services Ltd.

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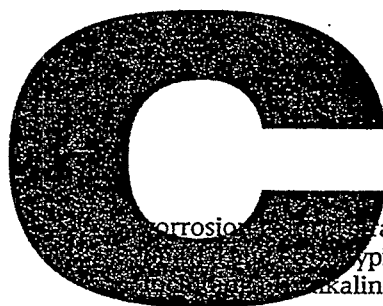
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# Corrosion control on the basis of utility experience

*Although selection of corrosion control optimization strategies is more art than science, utility experiences can provide a basis for rational decision-making.*

**Donna M. Dodrill  
and Marc Edwards**

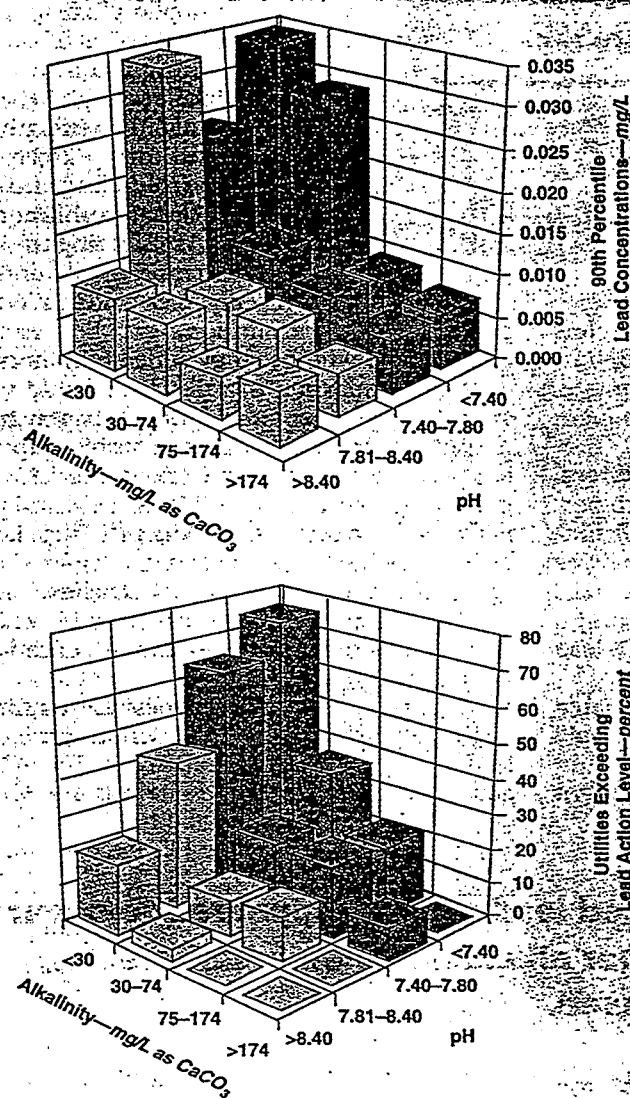


Utility experience under the Lead and Copper Rule was examined to provide improved insight into corrosion control. Average 90th percentile lead concentrations were highest in very-low-alkalinity waters (<30 mg/L as  $\text{CaCO}_3$ ) at utilities that did not use inhibitors; lead release was significantly reduced at higher alkalinities. Average lead releases were 20–90 percent lower for utilities using phosphate inhibitors (orthophosphates, polyphosphates, and blended phosphates) in very-low-alkalinity waters than for utilities not using inhibitors. At alkalinities of 30–74 mg/L as  $\text{CaCO}_3$  and at pH values > 7.40, it appeared that polyphosphate inhibitors had adverse effects on average lead release. Utilities with pH < 7.40 and high-alkalinity waters had the highest copper concentrations. Phosphate inhibitors were usually beneficial in mitigating copper release; however, most benefits were at utilities with pH < 7.80 and alkalinity > 90 mg/L as  $\text{CaCO}_3$ . Inhibitors appeared to adversely affect average copper release in some pH and alkalinity categories.

Conventional lead and copper corrosion control strategies have been based largely on pH adjustment, alkalinity adjustment, addition of corrosion inhibitors, or both. Because regulations were less stringent in the past, this approach proved adequate if not optimal. With enactment of the Lead and Copper Rule in 1991, water suppliers needed a more refined understanding of corrosion control. This article examines data originally compiled during a 1992 AWWA survey in an attempt to provide practical insight into lead and copper corrosion problems.<sup>1</sup>

The effects of distribution water pH and alkalinity on 90th percentile lead and copper were

**Average 90th percentile lead release and percentage of utilities exceeding the lead action level for utilities not adding phosphate inhibitors**



considered by assigning the utilities to specific pH and alkalinity categories. pH was divided into four ranges: (1) pH < 7.40, (2) pH 7.40–7.80, (3) pH 7.81–8.40, and (4) pH > 8.40. Utilities in each pH category were further subdivided according to alkalinity: (1) < 30, (2) 30–74, (3) 75–174, and (4) > 174 mg/L as CaCO<sub>3</sub>. These divisions maintained an approximately even distribution of the data, ensured an ample number of points within most pH–alkalinity categories, and allowed for qualitative classifications of potable water according to pH and alkalinity (i.e., very low, low, moderate, and high).

After sorting the data according to these categories, average 90th percentile lead and copper concentrations were calculated using data from all util-

ities in each category. In addition, the percentage of utilities in each pH and alkalinity category that exceeded the lead or copper action level (i.e., 0.015 mg/L Pb or 1.3 mg/L Cu) was also examined. Parametric statistics were used to rigorously evaluate the significance of observed trends for selected data at the 95, 90, and 85 percent confidence levels (i.e., the 5, 10, and 15 percent significance levels, respectively) using a standard comparison of means test.<sup>2</sup> Given the lognormal distribution of the data, it was first necessary to normalize the data using the log-transformation of Benjamin and Cornell.<sup>3</sup> Details of the statistical analysis are provided elsewhere.<sup>4</sup>

It is important to qualify the work by noting several points.

- Given that this analysis compares aggregate data of utilities with differing water qualities, results will not apply quantitatively to a specific utility. Indeed, even the qualitative trends must be viewed with caution when viewed from the perspective of a single utility.

- Terms such as “increase” and “decrease” refer to comparative changes in the pH and alkalinity categories for the aggregate data. For example, the phrase “increasing the pH from 7.0–7.4 to pH > 8.4” does not mean that a given utility or utilities made such changes and observed the cited effect. Rather, it is a comparison of averaged corrosion by-product release for utilities having pH values of 7.0–7.4 with those utilities having pH values > 8.4. The cited trends might apply if a given utility did make such changes, but such conclusions cannot be made from this work unambiguously.

- pH and alkalinity values are six-month averages calculated from water released to the distribution system. Some utilities reported pH and alkalinity data averaged from a number of distribution

sites or point-of-entry (POE) values. In some instances, pH and alkalinity values were derived from samples collected over several months or days. Regardless of how the data were taken, variations in pH and alkalinity are expected in any distribution system water, and this analysis cannot account for these effects.

#### Lead corrosion

Of the 397 total survey respondents, 365 utilities reported their first-round 90th percentile lead concentrations. The effects of pH, alkalinity, inhibitors, calcium, and temperature on 90th percentile lead values are based on their responses. Use of phosphate inhibitors was given special consider-

Percent reduction in lead release as a result of the indicated increase in alkalinity for utilities not adding phosphate inhibitors

pH	Alkalinity Change—mg/L as CaCO <sub>3</sub>		
	<30 to 30-74	30-74 to 75-174	75-174 to >174
Reduction in Lead Release—percent			
<7.40	21*	67	21
7.40-7.80	51*	18	26
7.81-8.40	74*	9	26
>8.40	8	31	-15

\*Significant at the 95 percent confidence interval

ation in this analysis—the term “inhibitors” refers only to phosphate-based inhibitors (e.g., orthophosphate, zinc orthophosphate, hexametaphosphate, polyphosphates, and various blends) in subsequent discussion.

#### Utilities not using phosphate-based inhibitors.

For utilities not adding inhibitors, average 90th percentile lead levels were highest in very-low-alkalinity (< 30 mg/L as CaCO<sub>3</sub>) waters (Figure 1). Raising pH to < 8.40 did not appear to strongly affect lead release in very-low-alkalinity waters, although increasing pH above 8.40 did appear to reduce lead release.

Lower lead levels (at a given pH) were associated with higher alkalinities in each pH category with only one exception (Table 1). Differences in lead levels in each category were represented by calculating percent reductions. In this study, percent reduction was defined as [(Initial Pb – Final Pb)/Initial Pb × 100 percent]. Thus, in Table 1, the initial Pb was the lower of the two alkalinity categories being compared in a given alkalinity change. As shown in Figure 1, increased alkalinity of 30–74 mg/L as CaCO<sub>3</sub> (as compared with alkalinity < 30 mg/L as CaCO<sub>3</sub>) yielded statistically significant lower lead release at the 95 percent confidence level when pH was < 8.4 (Table 1).

For utilities that did not add inhibitors, the percentage exceeding the lead action level seemed to be correlated with differences in both alkalinity and pH (Figure 1). In the lowest pH and alkalinity category, utilities had an 80 percent likelihood of exceeding the lead action level. This likelihood was less in higher-alkalinity or higher-pH categories almost without exception. As observed for lead release, a large reduction in the percentage of utilities exceeding the lead action level was realized at the transition from < 30 to 30–74 mg/L as CaCO<sub>3</sub>.

#### Utilities adding phosphate-based inhibitors.

The use of phosphate inhibitors may reduce lead concentrations in drinking waters.<sup>5-9</sup> The initial analysis of the data did not distinguish between the vari-

ous types of phosphate inhibitors or doses used. That is, all utilities that added orthophosphate, blended orthophosphate, or polyphosphate were classified as “adding inhibitors.” In the 1992 survey, 116 utilities reported using phosphate inhibitors; 261 utilities reported they did not use phosphate inhibitors. Without considering the effects of either pH or alkalinity, differences between average 90th

percentile lead were insignificant between utilities regardless of whether they added inhibitors.

Any comparison of utilities that add inhibitors with those that do not add inhibitors may be subject to systematic biases that are impossible to quantify. At one extreme, most utilities might be adding phosphate-based corrosion inhibitors to control problems with iron corrosion. Consequently, the data might be overweighted in pH-alkalinity categories that propagate red water problems. Nonetheless, there is no reason to suspect that this bias would invalidate use of the database for the examination of lead and copper corrosion problems.

At another extreme, utilities that add inhibitors might be doing so to mitigate serious problems with lead or copper corrosion. In this case, the utilities that add inhibitors might represent only the most prob-

### Increased lead release appeared to occur at higher alkalinity when inhibitors were used.

lematic waters with respect to lead and copper corrosion. Given the relative lack of concern regarding lead and copper corrosion by-product release at the tap before enactment of the Lead and Copper Rule, however, there is no strong reason to suspect this bias exists in the data set used from the first round of sampling. Also, the database cannot quantify the effect of time on the development of passivating films or decreasing lead leaching (by physical depletion).

Keeping these potential problems in mind, it is still illustrative to make comparisons between utilities that currently add inhibitors and those that do not. Particular attention was paid to identifying pH-alkalinity regimes in which inhibitors appeared to have beneficial, detrimental, or no effect on lead and copper corrosion by-product release. The comparison is used to highlight water qualities for subsequent laboratory confirmation studies that unambiguously test these identified trends in inhibitor performance. Trends in the data were also examined for consis-



tency with theoretical predictions that guide inhibitor use.<sup>5,7,10</sup>

For utilities that added inhibitors between pH 7.40 and 8.40, lead release was adversely affected by increasing alkalinity from < 30 to 30–74 mg/L as CaCO<sub>3</sub> (Figure 2; Table 2, negative numbers). These trends were statistically significant at the 85 percent confidence interval. In contrast, at pH < 7.40 increasing alkalinity from < 30 to 30–74 mg/L as CaCO<sub>3</sub> had the opposite effect, leading to a 53 percent reduction in lead release. This observation was not supported at the 85 percent confidence level, however, given the high standard deviation of the data in this category.

Trends in the percentage of utilities exceeding the lead action level were complicated by inhibitor addition. For instance, the highest percentage of utilities (47 percent) exceeded the lead action level at 30–74 mg/L as CaCO<sub>3</sub> and at pH 7.40–7.80 (Figure 2). Lead concentrations did not exceed the action level in systems using inhibitors at very low alkalinities (<30 mg/L as CaCO<sub>3</sub>) above pH 7.80, and the use of inhibitors generally reduced lead leaching throughout the low-alkalinity range.

**Inhibitor effectiveness.** An examination of the difference between systems with and without inhibitors is instructive, as shown by the following equation:

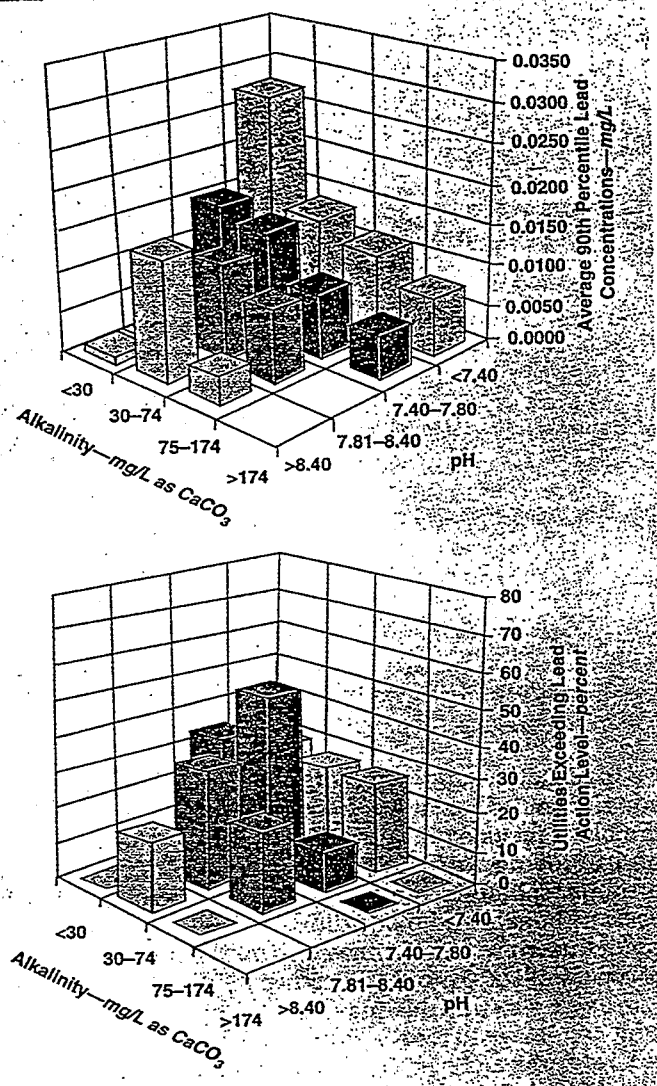
$$\text{Reduction in lead release associated with inhibitors} = \text{Average lead release without inhibitors} - \text{Average lead release with inhibitors}$$

In this equation a positive number means an improvement (reduced lead release), whereas a negative number means an adverse effect (increased lead release) associated with inhibitors. This general formula was used to evaluate the effect of phosphate-based inhibitors on average 90th percentile lead release as well as on the percentage of utilities exceeding the lead action level.

Beneficial effects of inhibitors were observed only in the lowest alkalinity category (<30 mg/L as CaCO<sub>3</sub>) at all pH values (Figure 3). Conversely, in several instances in the 30–74 mg/L as CaCO<sub>3</sub> alkalinity category and at pH > 7.40, total lead release and the percentage of utilities exceeding the lead action level were apparently higher. Differences between systems that add inhibitors and those that do not add inhibitors were inconsequential at alkalinities > 74 mg/L as CaCO<sub>3</sub>.

In the lowest alkalinity category (<30 mg/L as CaCO<sub>3</sub>) average lead release was 20–90 percent lower

**FIGURE 2** Average 90th percentile lead release and percentage of utilities exceeding the lead action level for utilities adding phosphate inhibitors



for utilities using inhibitors compared with those not using inhibitors (Table 3). These results were all significant at the 95 percent confidence interval, indicating that addition of inhibitors may be very effective in reducing lead release in very-low-alkalinity waters regardless of pH (Table 3). Inhibitors did not produce a statistically significant reduction in lead release (at the 95 percent confidence level) in any other pH-alkalinity category tested. In fact, in the alkalinity range of 30–74 mg/L as CaCO<sub>3</sub> and at pH > 7.40, inhibitors had higher average lead release (negative numbers in Table 3). These increases were all significant at either the 95 or 85 percent confidence interval. Thus, the indication is that inhibitors exacerbate 90th percentile lead release when used in waters with pH > 7.40 and alkalinity 30–74 mg/L as CaCO<sub>3</sub>.

**TABLE 2** Percent reduction in lead release as a result of the indicated increase in alkalinity for utilities that add phosphate inhibitors

pH	Alkalinity Change—mg/L as CaCO <sub>3</sub>		
	<30 to 30-74	30-74 to 75-174	75-174 to >174
<7.40	53	19	33
7.40-7.80	-5*	50	31
7.81-8.40	-77*	29	ND†
>8.40	ND	76	ND

\*Significant at the 85 percent confidence interval

†ND—no data or insufficient data in the category

**TABLE 3** Percent reduction in lead release for utilities adding phosphate inhibitors compared with those not adding phosphate inhibitors

pH	Alkalinity—mg/L as CaCO <sub>3</sub>			
	<30	30-74	75-174	>174
<7.40	20*	52	-17†	0
7.40-7.80	39*	-29	21	27
7.81-8.40	81*	-28	0	ND†
>8.40	90*	-91	34	ND

\*Significant at the 95 percent confidence interval

†Significance for negative results are not reflected in the table.

‡No data or insufficient data in the category

Explanations for increasing lead levels at moderate alkalinities for utilities adding phosphate-based inhibitors include the possibility of inadequate phosphate dosing to form protective films. That is, orthophosphate is known to inhibit the growth of basic carbonate and oxide films on copper pipe.<sup>11</sup> It is not known whether it may also inhibit the growth of cerussite (PbCO<sub>3</sub>) or hydrocerussite [Pb<sub>3</sub>(CO<sub>3</sub>)<sub>2</sub>OH]. For example, utilities may not have the optimal inhibitor dosage to form a protective layer of hydroxypyromorphite [Pb<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>OH] or lead phosphate [Pb<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>]. Phosphate may also be interfering with other film formation.

**Detailed examination of inhibitor use.** Of the 116 utilities using phosphate inhibitors, there was an approximately even split between utilities using orthophosphate and those using polyphosphates. Few utilities added blended phosphates or did not specify the type of inhibitor added (Table 4). For the inhibitor effects cited as statistically significant for lead in the preceding section, the types of inhibitors used in each identified pH and alkalinity category were then carefully scrutinized. That is, the information on inhibitor types was used to clarify whether beneficial or adverse inhibitor effects could be attributed to orthophosphate alone, polyphosphates alone, or both in combination.

**Copper release is reduced by higher pH in the presence and absence of inhibitors.**

CaCO<sub>3</sub> when inhibitors increased average lead release by 91 percent (Table 3), all 13 utilities used polyphosphate inhibitors. Thus, it seems reasonable to attribute the significant adverse effects observed for inhibitors in this category to polyphosphate exclusively. The finding that utilities are using polyphosphate chemicals above pH 8 apparently contradicts the notion

Phosphate-based inhibitors had significant effects only in the two lowest alkalinity categories (<30 and 30-74 mg/L as CaCO<sub>3</sub>). In the lowest pH region (<7.40), average 90th percentile lead release for utilities with alkalinities <30 mg/L as CaCO<sub>3</sub> and using polyphosphates was more than double that for utilities applying orthophosphate alone (Figure 4). For polyphosphates, average lead release was even higher than was observed for utilities not adding inhibitors. Thus, in this pH-alkalinity category at least, it seems reasonable to attribute beneficial effects of inhibitors to orthophosphates and either no or adverse effects to polyphosphates.

Interestingly, in the same alkalinity category but at pH 7.4-7.8, the opposite effect was observed (Figure 4); utilities using polyphosphates had an average corrosion by-product release about three to four times lower than utilities

using orthophosphates. However, the average lead release was lower at utilities using either type of inhibitor than at utilities not using inhibitors. For utilities with alkalinities of 30-74 mg/L as CaCO<sub>3</sub> at pH 7.4-7.8, there did not appear to be a significant difference between the two types of inhibitors in performance (but inhibitors did have a statistically significant adverse effect in this pH-alkalinity category).

In the two highest pH categories (7.81-8.40 and >8.40) there was either insufficient data or a highly uneven division between inhibitor types, so an inhibitor-to-inhibitor comparison is not possible. Nevertheless, this overweighting is still noteworthy. For instance, at pH >8.40 and alkalinity 30-74 mg/L as

that phosphate inhibitors are used only near neutral pH.<sup>12</sup>

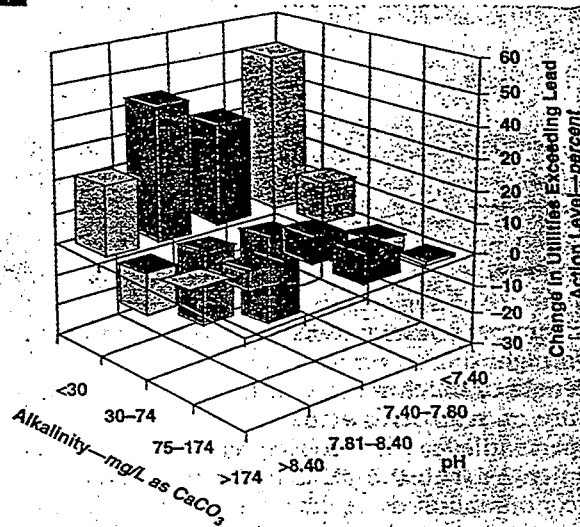
In the lowest alkalinity range (<30 mg/L as CaCO<sub>3</sub>) and pH values > 7.81, where significant beneficial effects of inhibitor were observed, all of the utilities used polyphosphate inhibitors. Lead release was significantly lower for utilities in these two pH categories; however, only three utilities used phosphate chemicals (two in the pH 7.81–8.40 region and one in the pH > 8.40 region). In the alkalinity category 30–74 mg/L as CaCO<sub>3</sub> at pH 7.81–8.40 in which lead release was increased by inhibitors, five utilities used orthophosphate and only one utility used polyphosphate.

Potentially adverse effects of polyphosphate addition on lead release have been noted by others. Holm and Schock, using a discrete two-ligand model, predicted the effects of polyphosphate addition at pH 8.0 and 40 mg/L Ca as a function of alkalinity.<sup>13</sup> The authors modeled solutions in equilibrium with either hydrocerussite or hydroxypyromorphite. In both situations, waters treated with a proprietary liquid formulation of polyphosphate (consisting of 40 percent orthophosphate) dosed at 1 mg P/L were predicted to have significantly higher plumbosolvency than untreated waters (or waters dosed with 0.4 mg/L orthophosphate in the case of hydroxypyromorphite precipitation). Similarly, Sheiham and Jackson demonstrated that lead release was higher in new and old lead pipes (at pH 6.5 and 7.5, respectively) for two polyphosphate chemicals than for orthophosphate.<sup>8</sup> All three inhibitors were dosed at 1 mg/L in a low-alkalinity (< 10 mg/L as CaCO<sub>3</sub>) water.

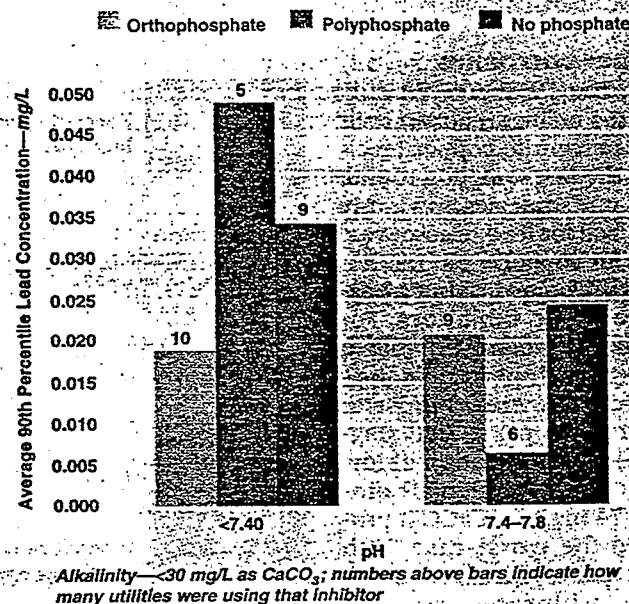
Although the preceding discussion considerably clarifies matters with respect to the practical effects of inhibitors, inherent shortcomings of using the results to guide phosphate inhibitor use remain. Nevertheless, in the absence of systematic laboratory studies to confirm trends, the preceding discussion provides a good starting point for bench or pipe-loop investigations at individual utilities. Future work and experimentation should examine the inhibitor question in greater detail.

**Effects of temperature.** Average 90th percentile lead as a function of alkalinity and cold (<15°C) or warm (> 15°C) water was calculated in the presence and absence of inhibitors (Figure 5). Temperature was taken by utilities at several distribution system water quality sampling locations (data were collected between January and June 1992). In general, lead

**Improvement in percentage of utilities exceeding the lead action level as a result of adding phosphate inhibitors**



**FIGURE 4 Comparison of average 90th percentile lead release for utilities adding orthophosphate and polyphosphate and utilities not adding inhibitors**



levels decreased with increasing alkalinity for both cold and warm distribution waters regardless of inhibitor use. In contrast to the conventional wisdom, warm waters did not appear to induce higher lead release than did cold waters at a given alkalinity.<sup>14–16</sup> If anything, the opposite effect was observed in the lowest alkalinity category. In retrospect this trend probably should have been expected, given that at-the-tap monitoring precludes wide variations

#### Utilities using specified type of phosphate inhibitor

Type of Phosphate Inhibitor	Number of Large* Utilities
Orthophosphate†	51
Polyphosphate†	53
Blended phosphate	5
Other or unspecified	7
Total	116

\*Large is defined as utilities serving 50,000 people  
†Includes Na Zn Ortho-P, Zn Ortho-P, and Ortho-P  
‡Includes Na Poly-P, Na Zn Poly-P, Zn Poly-P, and Poly-P

in temperature (either seasonal or geographical) after an overnight stagnation period.

**Effects of calcium.** Similar to the effect of temperature on lead release, the effect of calcium on 90th percentile lead was considered as a function of alkalinity. As with the pH and alkalinity data, calcium concentrations were determined either at point-of-entry locations or in the distribution systems. Two divisions for calcium content, low (<50 mg/L as Ca) and high (>50 mg/L as Ca) were made (data not shown). Overall, there was not a strong trend between lead release and calcium concentration in any system studied.

#### Copper corrosion

In the 1992 AWWA survey, 361 utilities reported their 90th percentile copper levels from the first sampling round. The same strategies previously described for lead release were used for copper.

**Utilities not using phosphate-based inhibitors.** For utilities not adding inhibitors, average 90th percentile copper levels were highest in waters with pH < 7.40 (Figure 6). A combination of low pH (<7.80) and high alkalinity (>74 mg/L as CaCO<sub>3</sub>) produced the worst-case 90th percentile copper levels. This agrees with recent research hypotheses that Cu(OH)<sub>2</sub> solids control copper solubility under some circumstances in distribution systems.<sup>10,17-19</sup>

In the absence of inhibitors, average 90th percentile copper release clearly tended to decrease at higher pH (Figure 6). Percent reductions ranged from 1 to 100 percent with only one exception (Table 5). In waters with alka-

linity < 74 mg/L as CaCO<sub>3</sub>, raising pH from < 7.40 to 7.40–7.80 resulted in a 43–68 percent reduction in average 90th percentile copper release—changes that are significant at the 95 percent confidence level. Raising pH from 7.81–8.40 to >8.40 always led to significant reductions in copper release without regard to alkalinity, whereas increasing pH from 7.40–7.80 to 7.81–8.40 significantly decreased copper release only if alkalinity was >75 mg/L as CaCO<sub>3</sub>.

The described trends are magnified when viewed in the context of the percentage of utilities exceeding the copper action level in each pH and alkalinity category (Figure 6). No utilities with pH > 7.80 exceeded the copper action level (Figure 7). The highest percentage of utilities exceeding the action level was at pH < 7.40 and alkalinity <30 mg/L as CaCO<sub>3</sub>. However, all utilities exceeding the copper action level in the very-low-alkalinity category also had pH < 7.0. Excluding those utilities with pH < 7.0, all other utilities exceeding the copper action level had alkalinity > 75 mg/L as CaCO<sub>3</sub> and pH < 7.80. A closer examination of that data (not shown) demonstrated that all utilities exceeding the action level had alkalinity > 90 mg/L as CaCO<sub>3</sub> and many had pH > 7.0. Copper corrosion by-product release is likely worse at higher alkalinity as a result of the formation of soluble cupric-bicarbonate complexes.<sup>18,19</sup>

TABLE 5 Percent reduction in copper release as a result of the indicated increase in pH for utilities not adding phosphate inhibitors

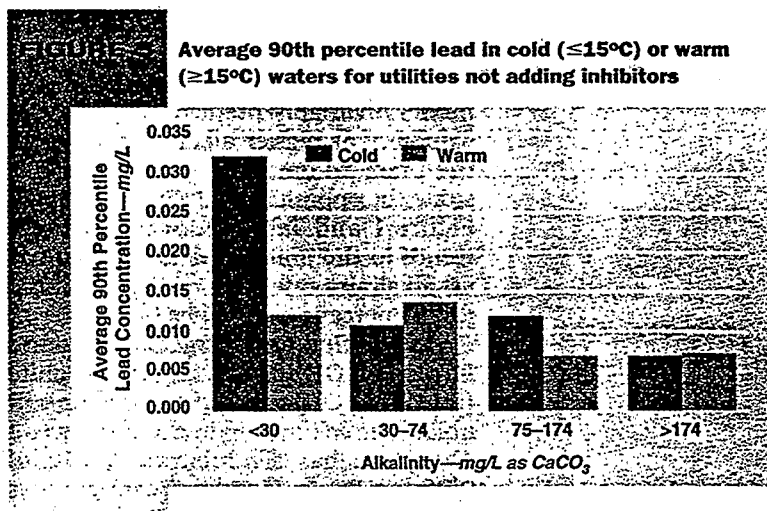
Alkalinity mg/L as CaCO <sub>3</sub>	pH Change		
	<7.4 to 7.40–7.80	7.40–7.80 to 7.81–8.40	7.81–8.40 to >8.40
<30	68*	1	75*
30–74	43*	30	45*
75–174	39	51*	47†
>174	–1	53†	100*

\*Significant at the 95 percent confidence interval  
†Significant at the 85 percent confidence interval  
‡Significant at the 90 percent confidence interval

TABLE 6 Percent reduction in copper release for utilities adding phosphate inhibitors compared with those not adding phosphate inhibitors

Alkalinity mg/L as CaCO <sub>3</sub>	pH Change			
	<7.4	7.40–7.80	7.81–8.40	>8.40
<30	56*	13	47	26
30–74	11	–2	–45	–5
75–174	51	34†	–34	50†
>174	23	4	NDS	ND

\*Significant at the 95 percent confidence interval  
†Significant at the 90 percent confidence interval  
‡Significant at the 85 percent confidence interval  
§No data or insufficient data for the category



**Inhibitor effectiveness.** As was observed for lead corrosion, when the effects of pH and alkalinity were ignored, overall differences in copper release attributable to inhibitor addition were not significant. Thus, performance of inhibitors is clearly dependent (at a minimum) on the pH and alkalinity of the specific system.

Although few systematic studies have evaluated the effects of phosphate inhibitors on copper release, most work completed to date demonstrates improvements to copper corrosion at higher pH values (7.0–8.0) and no effects at lower pH ( $< 7.0$ ). For instance, Reiber found that corrosion rates were reduced by a factor of 3–5 for utilities having waters at pH 7.5 dosed with 1–5 mg/L orthophosphate compared with utilities having waters at the same pH that did not add inhibitors.<sup>20</sup> In another study, weight loss of copper pipes in the presence of 1 or 5 mg/L orthophosphate was dramatically reduced by orthophosphate addition at pH 8.0.<sup>21</sup> However, at pH  $< 6.0$ , orthophosphate inhibitors did not affect corrosion rates in the Reiber study. Similarly, when dosed with 3.2–4.5 mg/L of zinc orthophosphate, Boston water at pH 6.7 exhibited no change in copper release when compared with the same water without inhibitors.<sup>15</sup>

As was the case for utilities that did not add inhibitors, copper release decreased with increasing pH for utilities that added inhibitors (data not shown). Percent reductions as a result of increasing pH category ranged from 0 to 80 percent with two exceptions. Interestingly, the apparent benefits of inhibitor addition are mostly confined to the lower pH ranges for the copper release data (Figure 7), although the percentage of utilities exceeding the copper action level was reduced by inhibitors in all pH and alkalinity categories (Figure 7).

At pH  $< 7.80$  utilities using inhibitors generally had lower average 90th percentile copper release

when compared with utilities that did not add inhibitors, with percentage improvements as high as 56 percent (Table 6). However, only two of these trends were significant at greater than 90 percent confidence. Above pH 7.80, addition of inhibitors had disparate effects on copper release, depending on the specific alkalinity category, with percentage increases attributable to inhibitors (negative numbers in table) as high as 45 percent. The result at pH  $> 8.40$  and alkalinity  $< 30$  mg/L as  $\text{CaCO}_3$  was significant at the 95 percent confidence interval, suggesting that inhibitors can have adverse effects for copper corrosion, at least under some circumstances. No other adverse effects were significant at or above 85 percent confidence.

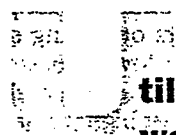
On the basis of this analysis, it seems safe to state that the effects of inhibitor use above pH 7.80 are highly variable for copper corrosion.

**Effects of temperature.** Average 90th percentile copper as a function of pH and cold or warm water was quantified in both the presence and absence of inhibitors. In general, copper levels decrease with increasing pH for both cold and warm waters whether or not the utilities added inhibitors (data not shown). There does not appear to be a significant trend in terms of temperature (i.e., copper concentration is dependent on pH and other water quality parameters and not on whether the water is warm or cold). In addition, inhibitors are most effective in reducing average 90th percentile copper at pH below 7.80 and did not seem affected by temperature.

**Effects of calcium.** Similar to the trend with temperature, calcium content did not have much of an effect on average 90th percentile copper release.

#### Comparison to solubility modeling theory

It is instructive to compare the trends described earlier to current frameworks of corrosion control based on solubility modeling.

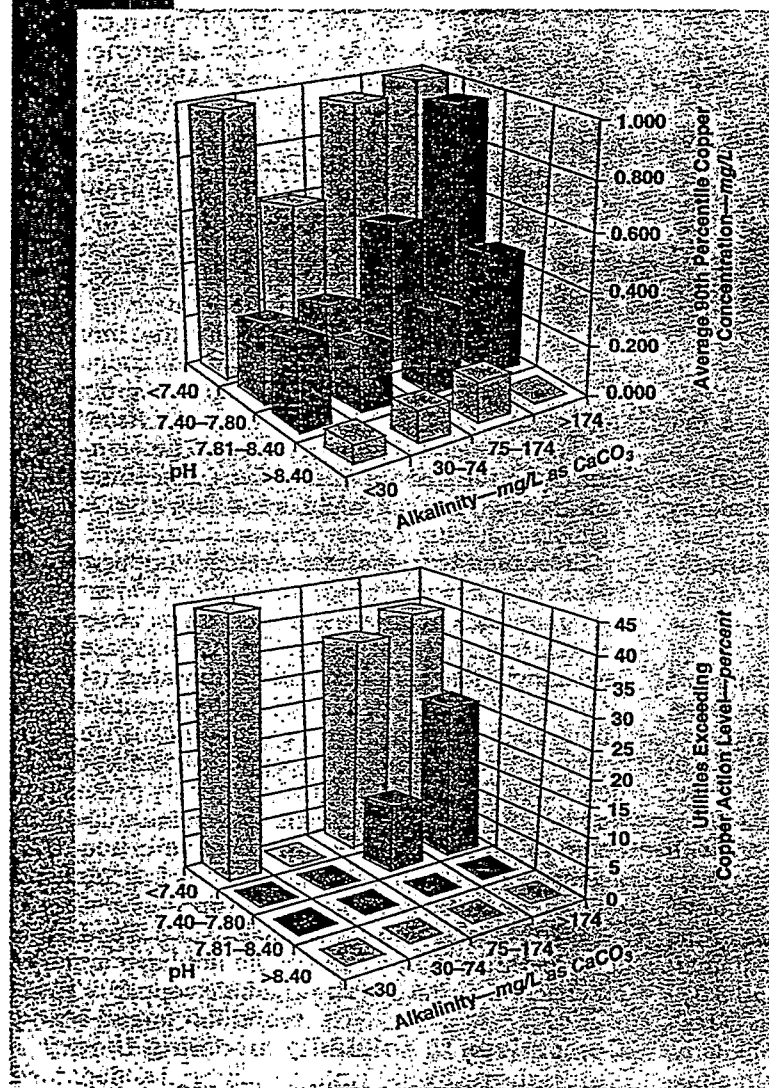


**Utilities with pH  $< 7.40$  and high-alkalinity waters had the highest copper concentrations.**

**Lead.** The chemical equilibrium modeling program MINEQL+ (version 3.01)<sup>22</sup> and associated database were used to make equilibrium predictions of lead solubility using various models. The basis for the prediction was to model the approximate midpoint of the pH-alkalinity categories used previously in segregating the practical utility data. That is, pH 7.0, 7.6, 8.1, and 8.8 were modeled at



Average 90th percentile copper release for utilities not adding phosphate inhibitors



alkalinities of 15, 50, 75, and 175 mg/L as CaCO<sub>3</sub>. The different modeling approaches are based on distinct assumptions as to solids that control lead solubility—in this work solids considered included cerussite (PbCO<sub>3</sub>), hydrocerussite [Pb<sub>3</sub>(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub>], and both in combination.

The best agreement between the utility data and solubility models was observed when both cerussite and hydrocerussite formation were considered. In this model lead levels are predicted to decrease with higher alkalinity at pH ≤ 7.6 (Figure 8). This prediction is consistent with the significant trends in the utility data (Figure 1 and Table 1). The solubility models also predict nearly insignificant reductions in lead solubility at alkalinity > 50 mg/L as CaCO<sub>3</sub> at pH < 7.6, results that are again consistent with significant trends in the practical data (Table 1).

At pH ≥ 8.1 there was general lack of agreement between the solubility models and the practical data. That is, the model invariably predicted higher lead solubility at higher alkalinity, whereas the practical data very clearly demonstrate the opposite trend (Figure 8 versus Figure 1 and Table 1). Some of these trends in the practical data (at the lowest alkalinity category) are significant at the 95 percent confidence level.

In addition to the solids PbCO<sub>3</sub> and Pb<sub>3</sub>(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub>, hydroxypyromorphite [Pb<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>OH] was included in the solubility model for lead in the presence of phosphate-based inhibitors. A dose of 0.95 mg PO<sub>4</sub><sup>3-</sup>/L orthophosphate was used in the model. In general, lead release showed some qualitative agreement between solubility modeling and the practical data. For instance, in the lowest alkalinity category, formation of Pb<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>OH is predicted to greatly reduce lead solubility regardless of pH, a trend observed in the practical data as discussed previously (Figure 2 and Table 3). Predicted lead release approximately doubled when alkalinity increased from 15 to 50 mg/L as CaCO<sub>3</sub> in the presence of orthophosphate at all pH values tested (Figure 8). Once again, this trend is qualitatively consistent with some of the practical observations defined in Figure 2.

Despite the noted agreements between the model and practical data, in general the solubility models tended to overpredict beneficial effects of inhibitors at higher alkalinities. That is, in the presence of orthophosphate inhibitors, lead levels are predicted to be reduced in nearly all pH-alkalinity categories (Figure 8). This was not observed in the utility data. Much of this disagreement is

because utilities were probably dosing polyphosphate inhibitors or dosing orthophosphate at concentrations too low to observe significant effects. Nevertheless, some observable beneficial effects would be expected at higher alkalinity if the model was perfectly accurate. There are also many reasons why predictions based on solubility models are not expected to agree with the observed trends in the practical first-draw lead data, as discussed by Schock.<sup>5</sup> This work does not provide any additional basis for speculation as to which of those effects is dominant in the practical data collected for this work.

**Copper.** There is good correlation between Cu(OH)<sub>2</sub> solubility models<sup>10,17-19</sup> and the previously described utility database (utilities without inhibitors). As pH increases, copper solubility decreases for both theory and practical data. In addition, high copper

release is observed at high alkalinities when pH is below about 7.8–8.

Comparisons between theory and practice for copper release with inhibitor addition are problematic because it has been difficult to determine which copper-phosphate solids are controlling copper solubility. Recently, assuming the formation of  $\text{Cu}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  solid, Schock<sup>18</sup> predicted the effects of orthophosphate on  $\text{Cu}(\text{OH})_2$  solubility. Below pH 8.0, orthophosphate addition reduces copper release according to these predictions, whereas above pH 8.0 copper release does not decrease when orthophosphate is added. Although solubility modeling cannot currently predict adverse effects attributable to inhibitor addition (because there are no complexation constants for polyphosphates and because interference with the formation of protective oxide, hydroxide, or hydroxycarbonate scale cannot be predicted), the general trend of the solubility model provides insight into the disparate effects of phosphate inhibitors at pH above 7.8.

### Recommendations to utilities

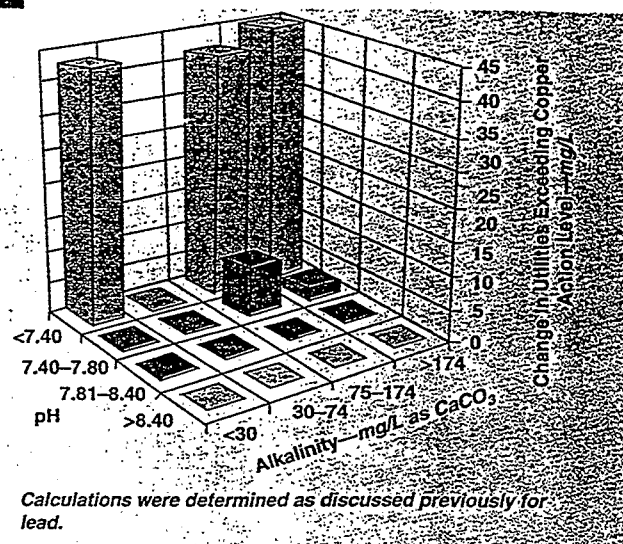
Although other water quality parameters (e.g., dissolved oxygen, temperature, calcium, sulfate, and chloride) can influence lead and copper corrosion, this treatment indicates these factors are of secondary importance when compared with pH and alkalinity. That is, if any other water quality factor was of primary importance in lead or copper corrosion con-

**Phosphate inhibitors were usually beneficial in mitigating copper release; however, most benefits were at utilities with pH < 7.80.**

trol, no significant trends would have been observed when this data set was sorted on the basis of pH and alkalinity. Trends in by-product release, when viewed in the context of pH and alkalinity categories, were highly significant in some cases.

On the basis of the graphical and statistical findings, a variety of simple measures have been identified that utilities may follow to mitigate high lead or copper release. Given the variation in corrosion phenomena from system to system, however, these predictions may not be universally applicable. Further research is needed to better define the types of inhibitors and chemical dosages that are effective in specific water quality types, and more information is needed regarding desirable

**Figure 1**  
Improvement in percentage of utilities exceeding the copper action level as a result of adding phosphate inhibitors



target pH values or alkalinities. Laboratory experiments performed thus far are encouraging in that they generally support the trends identified in this work regarding lead and copper release as a function of pH, alkalinity, and phosphate inhibitor addition.<sup>23</sup>

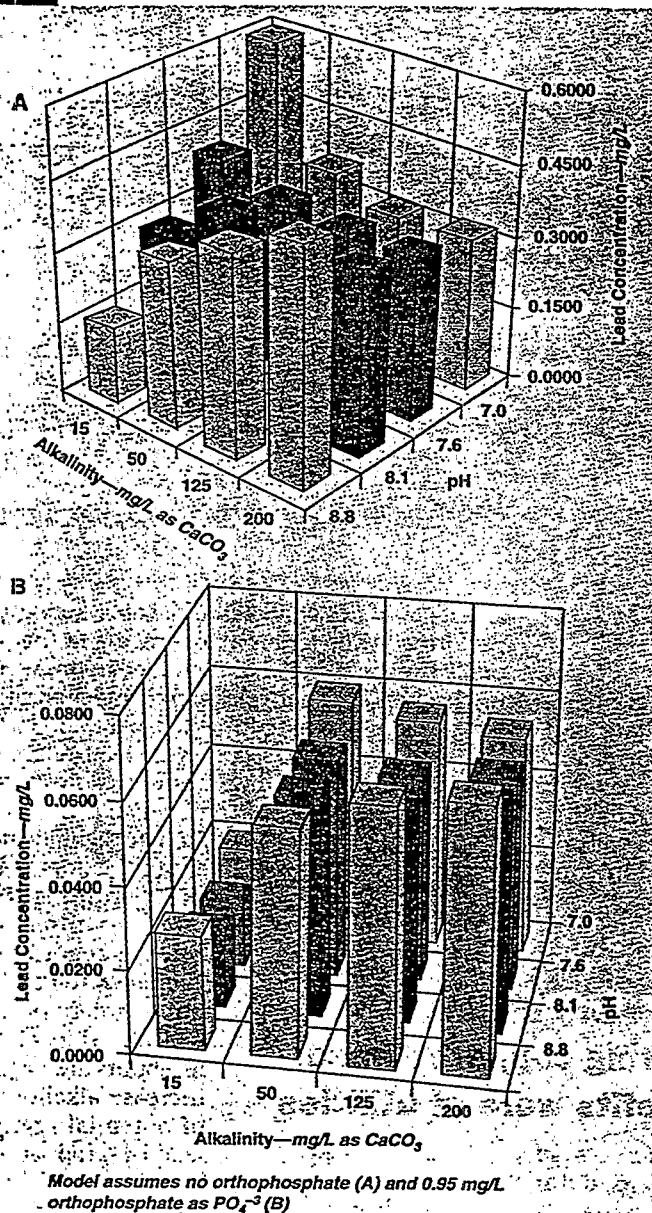
**Lead.** Most problems with lead release were in low-alkalinity (< 30 mg/L as  $\text{CaCO}_3$ ) waters. In such waters, if pH is < 8.40, increasing the alkalinity to 30–74 mg/L as  $\text{CaCO}_3$  is likely to significantly reduce lead release. Likewise, adding inhibitors to low-alka-

linity waters may also be effective in reducing lead release regardless of pH. Utilities with very-low-alkalinity waters (<30 mg/L as  $\text{CaCO}_3$ ) that already add inhibitors are not advised to increase alkalinity because of potential aggravation of lead by-product release.

Whether considering alkalinity–pH adjustment or addition of orthophosphate inhibitors, maintaining pH is absolutely critical for corrosion control in poorly buffered waters. For example, adding acidic orthophosphate formulations (most commercial zinc orthophosphate liquids are pH 1 or 2) can inadvertently lower the pH below the optimal level. Utilities must ascertain and maintain the proper pH.

For utilities in all other pH–alkalinity categories not adding inhibitors, either increasing alkalinity, pH, or both is predicted to reduce lead release and the likelihood of exceeding the lead action level. Inhibitors were generally not useful in reducing lead release in waters with alkalinity > 30 mg/L as  $\text{CaCO}_3$ , although, once again, it would be useful to test such conditions if

**Figure 1**  
Model-predicted lead solubilities in the absence of orthophosphate (A) and in the presence of orthophosphate (B)



inhibitor use was desired at a given utility. At pH > 7.40 and alkalinity of 30–74 mg/L as CaCO<sub>3</sub>, adding inhibitors can apparently increase lead release. Many of these adverse effects of inhibitors appeared attributable to polyphosphates, so stopping polyphosphate dosing if it is used for sequestering might be a viable optimization strategy to be tested further at affected utilities.

In high-alkalinity waters near or exceeding the action level, pH adjustment often is not feasible because of possible calcite precipitation. Orthophosphate or blended phosphate chemicals are probably

the only viable alternatives in these waters, and they may have to be added at high dosages. Overall, the use of phosphate inhibitors alone did not significantly correlate with low lead release. The qualitative effect observed depends, at a minimum, on the specific pH and alkalinity of the water of interest.

**Copper.** The following strategies are suggested as effective for control of copper corrosion. At alkalinities < 90 mg/L as CaCO<sub>3</sub>, no utilities exceeded the copper action level unless pH was < 7.0. Thus, increasing pH to > 7.0 would seem to be an effective and simple mitigation strategy for utilities in the low-pH and very-low-alkalinity regime. At alkalinities > 90 mg/L as CaCO<sub>3</sub>, two strategies seem viable. Because utilities with pH > 7.80 in this category did not exceed the copper action level, increasing pH seems to be promising.

For utilities with high-alkalinity and high-calcium waters that cannot increase pH above 7.80 because of concerns regarding calcite precipitation, any increase in pH would likely improve matters substantially. Many small systems using groundwater supplies are likely to have such waters. Some trends in the data suggest that inhibitors were successful in mitigating copper release in such systems; however, these trends were variable and not of high significance. Above pH 7.80 there is some evidence indicating that inhibitors can adversely affect copper corrosion by-product release. In general, inhibitors caused highly variable effects above pH 7.80.

## Conclusions

The following conclusions were reached regarding lead.

- For utilities not dosing inhibitors at pH < 8.4, lead release was significantly lower if alkalinity was 30–74 mg/L compared with alkalinity < 30 mg/L CaCO<sub>3</sub>.

- For utilities dosing inhibitors at alkalinity < 30 mg/L as CaCO<sub>3</sub>, inhibitors

appeared to improve lead corrosion by-product release compared with utilities not dosing inhibitors. At pH < 7.4 these benefits were attributable to orthophosphate and not polyphosphates. No significant improvement in lead release attributable to inhibitors was observed at other pH-alkalinity categories, although this might be the result of improper inhibitor dosing with respect to corrosion control.

- At alkalinities 30–74 mg/L as CaCO<sub>3</sub> and at pH > 7.40, inhibitors seemed to adversely affect lead release. Many of these effects were directly attrib-



uted to polyphosphates and not orthophosphates. Increased lead release seemed to be significantly correlated with higher alkalinity (<30 to 30–74 mg/L as  $\text{CaCO}_3$ ) when inhibitors were used.

The following conclusions were reached regarding copper.

- Copper release is reduced by higher pH in the presence and absence of inhibitors.
- Problems with meeting the copper action level are confined to two water quality regimes: (1) pH < 7.0 at alkalinity < 30 mg/L as  $\text{CaCO}_3$  and (2) pH < 7.8 at alkalinity > 90 mg/L as  $\text{CaCO}_3$ .
- The optimal inhibitor dosages are probably dependent on pH. Inhibitors appear to reduce average 90th percentile copper release at pH < 7.80. Above pH 7.80, inhibitors had highly variable and some adverse effects on copper corrosion by-product release.

### Acknowledgment

This work was supported by a grant from the AWWA Research Foundation (AWWARF). The authors appreciate the constructive criticism provided by their project advisory committee members: Joel Catlin, Leonard Graham, Preston Luitweiler, and Tiffany Tran. The insightful comments provided by Michael Schock and Steve Reiber were of immeasurable value to this work. Special thanks to all utility personnel and project participants in the 1992 AWWA Lead and Copper Survey—without their effort this work would not have been possible.

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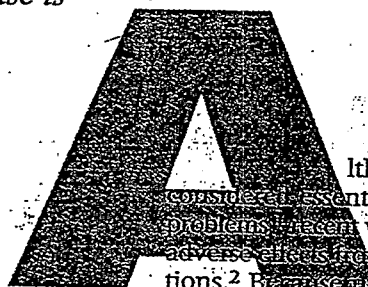
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# Alkalinity, pH, and copper corrosion by-product release

*The conventional Langelier index or Larson's ratio approach to controlling copper corrosion by-product release is demonstrably inaccurate.*

**Marc Edwards,  
Michael R. Schock,  
and Travis E. Meyer**

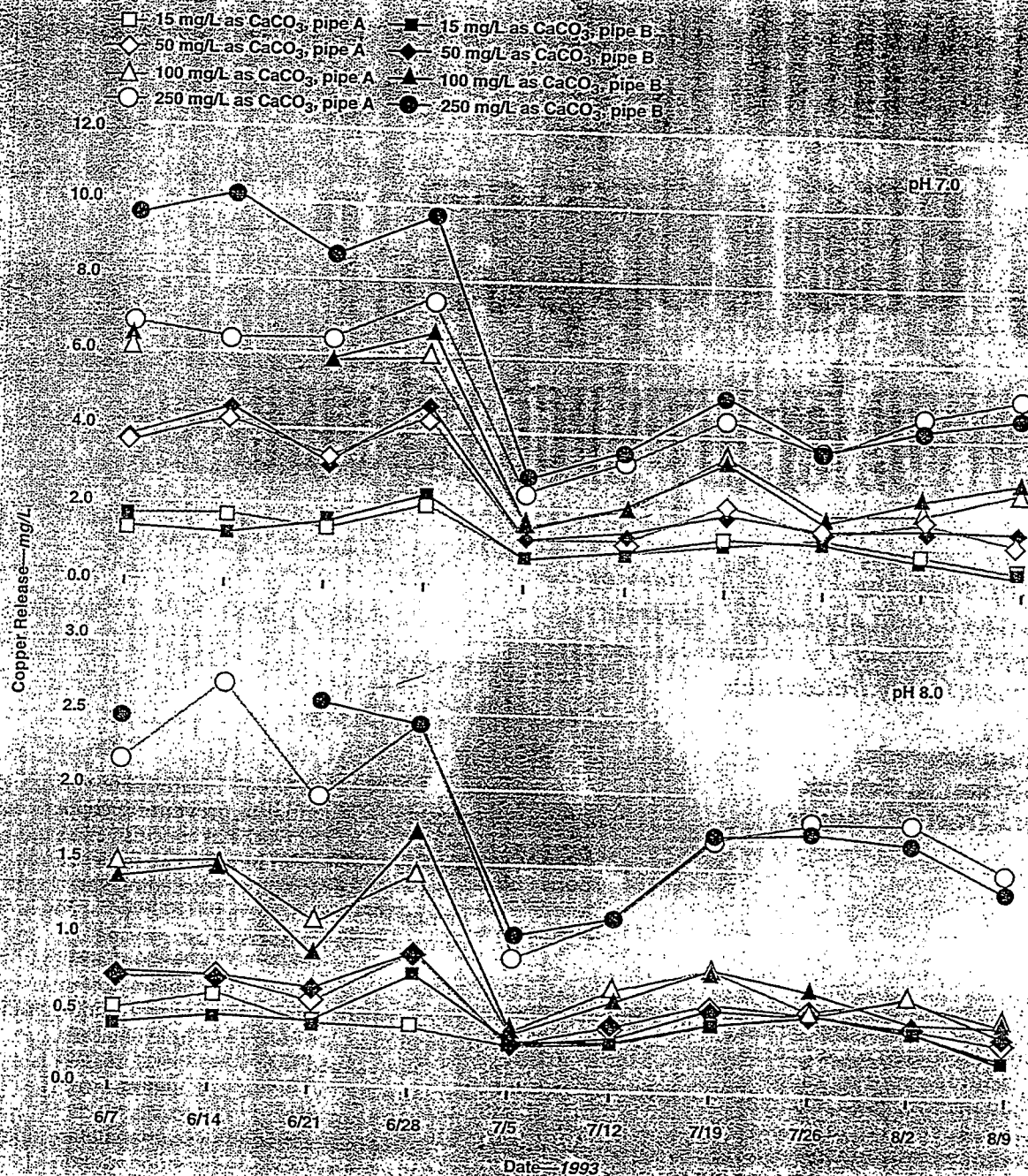


Although bicarbonate was previously considered essential to preventing copper corrosion problems, recent work has conclusively demonstrated adverse effects from bicarbonate under certain conditions.<sup>2</sup> Because utilities exceeding the US Environmental Protection Agency (USEPA) "action limits" for corrosion by-products must consider pH and bicarbonate (alkalinity) adjustments to optimize corrosion,<sup>3</sup> understanding the role of bicarbonate in copper corrosion is of critical importance. That is, if the basic effects of pH and bicarbonate are not understood, utilities that follow recommended mitigation strategies may unwittingly aggravate copper corrosion problems.

Contrary to expectations, higher bicarbonate concentrations exacerbate copper corrosion rates and by-product release. In fact, as illustrated by monitoring experiences of large utilities and by laboratory data, the concentration of copper corrosion by-products in drinking water increases linearly with bicarbonate concentration at constant pH. This relationship implicates cupric hydroxide solubility in control of copper release from relatively new (less than a few years old) copper plumbing. Decision-making guidance from a traditional Larson's ratio or Langelier index approach can aggravate copper corrosion problems; consequently, their use should be discontinued for copper corrosion mitigation. In contrast, aeration-CO<sub>2</sub> stripping is a particularly attractive strategy because benefits from higher pH are realized without adverse effects from higher alkalinity.

This work was designed to provide practical insight into the effects of bicarbonate on copper

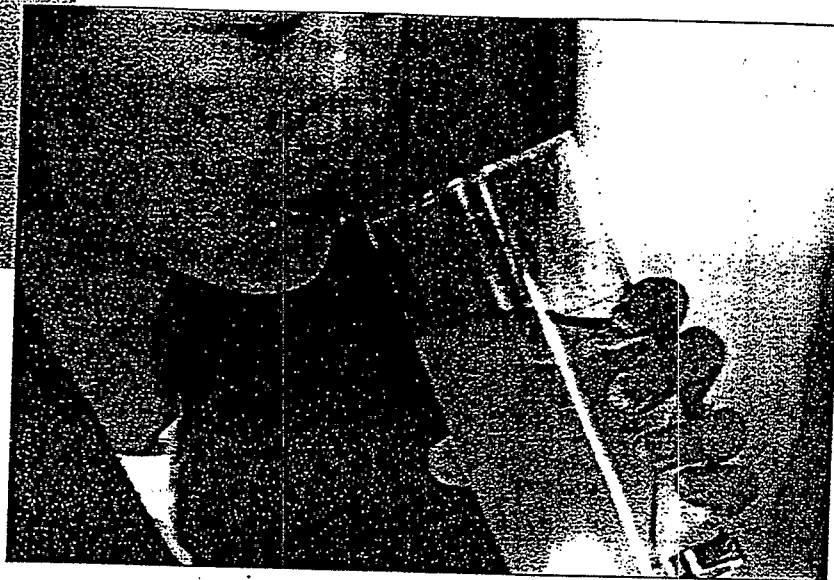
**FIGURE 1** Copper corrosion by-product release from pipe rigs



Pipe A started 5/19/93 and B started 5/31/93; temperature in July ranged from 22 to 28°C

*"Blue" water is the result of excessive concentrations of copper corrosion by-products being released from indoor plumbing.*

corrosion and, if possible, to unambiguously establish the mechanism by which bicarbonate acts. An in-depth analysis of monitoring data from large utilities, basic solubility experiments, and pipe-rig testing allowed rigorous evaluation of accepted corrosion mitigation strategies. A special focus of this investigation was the range of pH 7.0–8.5, over which a critical transition in bicarbonate effects was observed in previous research.<sup>2</sup>



## Materials and methods

**Tap water test solutions.** Because combined lime- $\text{CO}_2$  processes are the least expensive methods of pH and alkalinity adjustment for many utilities, experiments were conducted on tap water from Boulder, Colo., modified with lime and  $\text{CO}_2$ . During these experiments, unaltered Boulder tap water had an average pH of 7.2 and alkalinity of 15 mg/L as  $\text{CaCO}_3$  (Table 1).  $\text{CO}_2$  was always bubbled to the solution before the addition of lime to prevent precipitation of  $\text{CaCO}_3$ .

**Although bicarbonate was previously considered essential to preventing copper corrosion problems, recent work has conclusively demonstrated adverse effects from bicarbonate under certain conditions.**

To precisely maintain pH during experiments without altering the ionic composition of the solution, acid solutions constituted from Boulder tap water bubbled with  $\text{CO}_2$  to pH 4.0 were dosed with a pH controller. This effectively controlled alkalinity and pH within  $\pm 0.2$  units and  $\pm 3$  mg/L as  $\text{CaCO}_3$  of their desired values, respectively. pH was increased (if necessary) without altering alkalinity by bubbling  $\text{CO}_2$ -free air through the solution to strip  $\text{CO}_2$ . Ionic strength differed in these tests, thereby simulating practical application of lime- $\text{CO}_2$  corrosion control strategies.

**Synthetic test solutions.** A few experiments required precise control over other inorganic con-

stituents in addition to pH and alkalinity. Thus, these tests were conducted with "synthetic waters" constituted in the laboratory. Copper solubility was examined in 1-L solutions at a predetermined alkalinity and pH in the presence of a 0.01-M  $\text{NaClO}_4$  swamping electrolyte. A  $4 \times 4$  experimental matrix was evaluated, including alkalinities of 10, 50, 100, and 250 mg/L as  $\text{CaCO}_3$  at levels of pH including 7.0, 7.5, 8.0 and 8.5. Experiments examining bicarbonate and chloride interactions also utilized synthetic solutions. In these experiments alkalinity and pH were adjusted

to the target value using an appropriate combination of  $\text{CO}_2$  and  $\text{NaHCO}_3$ . Thereafter, if desired, 1 mM of  $\text{NaCl}$  was added. Finally, solution ionic strength was adjusted to 0.01 M by addition of  $\text{NaClO}_4$  (an inert electrolyte).

**Soluble and total copper.** Soluble copper was measured at 20°C after membrane filtration (0.2- $\mu\text{m}$ -pore-size cellulose acetate). The filter apparatus

consisted of a 60-mL syringe, a 25-mm-diameter filter, and a polycarbonate support. Approximately 25 mL of sample were filtered for each analysis, and no significant sorption or leaching of copper occurred using the filter apparatus.

Total copper was quantified in unfiltered samples after acidification to pH 2.0 for inductively coupled plasma-emission spectroscopy (ICP-ES)\* analysis or by a colorimetric bicinchoninate method† as per standard method 3500-Cu.<sup>4</sup> The metal detection limit was 0.0001 mg/L on the ICP-ES and was 0.005 mg/L

\*TOPCON Co., Paramus, N.J.  
†Hach Co., Loveland, Colo.

**TABLE 1** Typical base water quality during testing period

Parameter	Value	Units
pH	7.2	pH
Alkalinity	12-18	meq/L as CaCO <sub>3</sub>
	2.3-3.5	meq/L DIC
	0.24-0.36	meq/L Ca <sup>2+</sup>
Orthophosphate	0.05	mg/L
Silica	5-5	mg/L
Calcium	25	meq/L as CaCO <sub>3</sub>
Chloride	6	meq/L
Copper	0.01	mg/L
Fluoride	4.1	mg/L
Total hardness	32	meq/L as CaCO <sub>3</sub>
Iron	1.01	mg/L
Lead	0.02	mg/L
Magnesium	4.6	meq/L
Specific conductance	64	µmhos/cm
Sulfate	6	meq/L
Total organic carbon	1.26	mg/L

using the colorimetric test. For all waters in which the colorimetric test was used, possible matrix interferences were evaluated by comparison with ICP-ES in 10 percent of the samples. The two analytical methods always agreed to within  $\pm 5$  percent for these split samples.

**Scanning Electron Microscope (SEM) analysis.** Samples were prepared for SEM analysis by cutting the pipes lengthwise. The pipe surfaces were not coated because the conductivity of the copper itself was sufficient, thereby guaranteeing that surfaces would be unaffected by a coating procedure. The samples were examined in a vacuum at 30 kV on an electron microscope.\*

**Pipe-rig tests.** Copper corrosion by-product release was examined in standardized "pipe rigs." Type M copper pipe measuring 24 in. (609 mm)  $\times$   $\frac{3}{4}$  in. (19 mm) was purchased from a local hardware store and was washed in 0.1 M NaOH for 2 min to remove organic deposits. Thereafter, pipes were rinsed five times with deionized water before immediate exposure to target solutions. Pipes were filled with the target solutions three times a week (Monday, Wednesday, Friday) and maintained in a horizontal position at all other times. A rubber stopper tightly sealed each end.

Filtered and unfiltered samples were taken weekly to determine soluble and total copper concentrations after 72 h of exposure (Friday to Monday stagnation). After three months of exposure, representative coupons were cut from each pipe for electrochemical and SEM examination. Prior to the electrochemical analysis, pipe coupons were exposed to the target solutions at a flow rate of 0.2 gpm (0.013 L/s) for 30 min. Each water quality was tested using replicate pipe rigs. The only difference between replicates was that exposure to test solutions was initiated

12 days apart. This provided insight into short-term effects of aging time on copper corrosion by-product release.

**Electrochemical corrosion rate measurement and accelerated aging procedure.** Specifics of standard electrochemical tests and the apparatus have been reported previously.<sup>2,5</sup>  $I_{corr}$ , the key parameter derived from electrochemical testing, is the total corrosion current divided by the exposed macroscopic surface area of the corroding metal; i.e., the instantaneous corrosion rate of the sample.  $I_{corr}$  was determined using an electroanalysis system.<sup>†</sup> This article reports averaged  $I_{corr}$  results from duplicate analysis because these determinations were quantitatively consistent ( $\pm 0.15 \mu\text{A}/\text{cm}^2$ ).<sup>6</sup>

For accelerated aging tests, the general goal was to produce scales on copper pipe representative of those formed after years of conventional exposure. Copper was exposed to the solution of interest for three days while a corrosion-accelerating potential ( $E = E_{corr} + 120 \text{ mV}$ ) was applied. At the end of this "aging" period, the applied potential was removed, and the target solution was replaced. Each coupon was exposed for 24 h before corrosion rates were determined electrochemically on the aged copper surfaces, as reported in the previous section. The flow rate (0.5 gpm [0.031 L/s]  $\pm$  0.02 gpm [0.0013 L/s]), pH ( $\pm 0.03$  pH units), and alkalinity ( $\pm 3 \text{ mg/L CaCO}_3$ ) were rigidly controlled during experiments.

**C**  $\text{O}_2$  concentrations are a surrogate for copper carbonate complexation capacity in many waters.

**Monitoring experience of large utilities.** Data collected during a national survey of 435 large utilities were used in this investigation.<sup>7</sup> The analysis of that database proceeded as follows.

- Because inhibitor additions might hopelessly complicate the role of pH and alkalinity in copper corrosion, any utilities using corrosion control other than pH, alkalinity adjustment, or both were deleted from the database.

- Any utility not reporting essential information including pH, alkalinity, or 90th percentile copper release was also deleted.

The 151 remaining utilities were sorted into pH and alkalinity categories for analysis. pH and alkalinity values in the database, typically six-month averages for water released to the distribution system, did not account for possible variations within the distribution system or between different sources.

\*Model SX30, International Scientific Instrument Co.  
†Gamry Instruments, Langhorne, Pa.



**Bicarbonate, alkalinity, and dissolved inorganic carbon.** Over the pH range of most natural waters (pH 5.3–8.7) and at alkalinities >10 mg/L as  $\text{CaCO}_3$ , bicarbonate concentrations are directly proportional to alkalinity within  $\pm 3$  percent error (i.e., 50 mg/L alkalinity as  $\text{CaCO}_3 = 1 \text{ mM HCO}_3^-$ ). Accordingly, this work will apply the terms alkalinity and bicarbonate interchangeably according to utility convention. Approximate units of dissolved inorganic carbon (DIC) are provided for reader convenience using the equation  $\text{DIC (mg C/L)} \approx 0.24 [\text{alkalinity (mg/L as CaCO}_3)]$ . At pH values between 7.5 and 8.7 this approximation is valid to within  $\pm 5$  percent, but the approximation underpredicts actual DIC by 17 percent at pH 7.0.

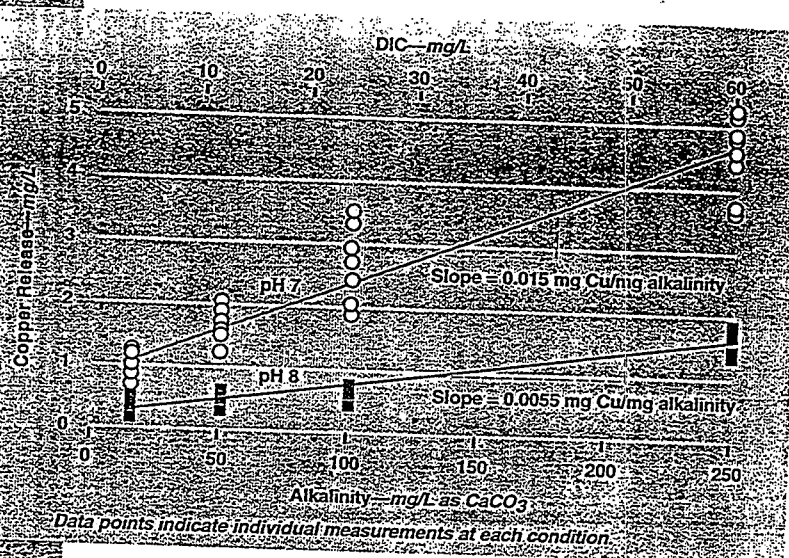
### Experimental results

The experimental results are divided into three sections, with the first two addressing the effect of bicarbonate on copper corrosion by-product release and solubility. Thereafter, the combined effects of bicarbonate and chloride are examined in detail.

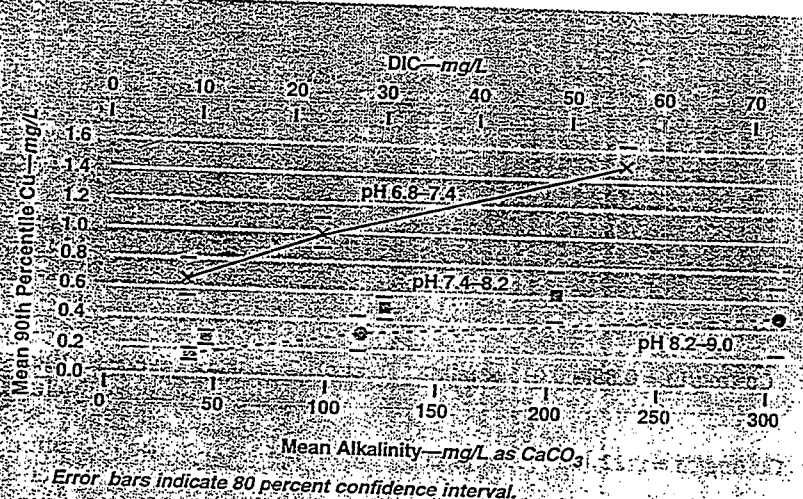
**Effect of bicarbonate on by-product release and solubility.** Bicarbonate and by-product release from pipe rigs. Copper corrosion by-product release was more dependent on water quality than on time of exposure (Figure 1). That is, although the exposure of replicate pipes was initiated 12 days apart, copper concentrations were nearly identical when plotted versus calendar date rather than versus time of exposure. This was particularly evident on July 5, 1993, when each pipe exhibited a dramatic reduction in copper release. If differences in exposure time caused the observed decrease, only the pipe exposed for the extra 12-day time period would have exhibited this drop. Interestingly, the decrease in by-product release corresponded to a period of high stormwater runoff.<sup>8</sup>

Copper release was fairly constant at each condition over the last four weeks of exposure (Figure 1), with

**FIGURE 2** Linear relationship between copper release and alkalinity during last four weeks of exposure



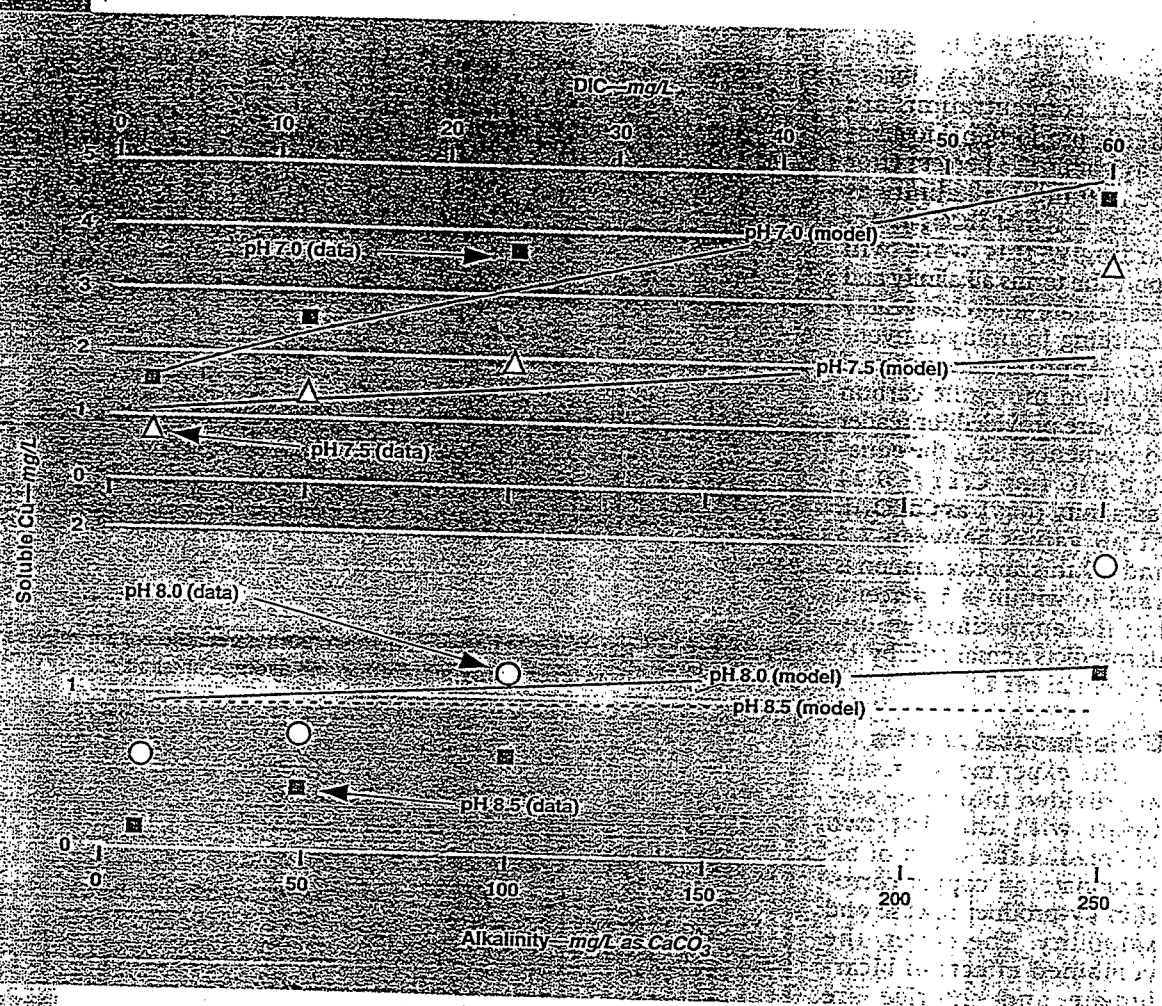
**FIGURE 3** Relationship between average 90th percentile copper release from large utility monitoring and average alkalinity



average data differing less than 0.1 mg/L for replicates at each water quality. Over this time period, in which reproducibility was very good, average copper corrosion by-product release was a linear function (Figure 2) of alkalinity (bicarbonate concentration). The regression coefficient ( $R^2$ ) was 0.89 and 0.90 for the averaged data at pH 7 and 8, respectively. Because more than 95 percent of the copper in the samples passed through a 0.2- $\mu\text{m}$ -pore-size filter, this copper was operationally defined as soluble and not particulate.

The best-fit linear regression yielded the following equations for soluble Cu:

**FIGURE 4** Measured soluble copper after solubility experiments and predicted soluble copper based on  $\text{Cu}(\text{OH})_2$  solubility



$$\text{Cu (mg/L)} = 0.88 + 0.015 \times [\text{alk}] \quad \text{at pH 7} \quad (1)$$

$$\text{Cu (mg/L)} = 0.22 + 0.0055 \times [\text{alk}] \quad \text{at pH 8.0} \quad (2)$$

in which alkalinity (alk) is mg/L as  $\text{CaCO}_3$ . Based on the slope of the regression equation, copper release was 270 percent more sensitive to alkalinity at pH 7.0 than at pH 8.0. In other words, a given level of alkalinity was 2.7 times more effective in mobilizing copper at pH 7.0 than at pH 8.0.

**Copper corrosion by-product release based on utility monitoring.** Given that the previously described results were contrary to expectations, it was imperative to determine their relevance to practical utility experience and at-the-tap monitoring data. To accomplish this, 90th percentile copper concentrations from 151 large utilities not using corrosion inhibitors were compiled. These data were sorted into three categories, including pH 6.8–7.49, 7.5–8.19, and 8.2–9.0. Within each pH category, data

were further subdivided according to alkalinity category, including 0–75, 76–175, and 176–358 mg/L alkalinity as  $\text{CaCO}_3$ , yielding nine categories. With the exception of the highest pH and alkalinity category, which contained only two utilities, all categories had monitoring data from at least six utilities. The mean 90th percentile copper release was then calculated to represent the average 90th percentile copper release for utilities in that category.

Plotting the mean 90th percentile copper versus average alkalinity in each category clearly illustrates the adverse effects of bicarbonate on copper release noted in the preceding experiments (Figure 3). These adverse effects are approximately linear and become more significant at lower pH. Specifically, slopes were about 0.0040, 0.0020, and 0.001 mg copper/mg alkalinity in the low-, moderate-, and high-pH ranges, respectively.

**Copper solubility: theory versus practice.** To elucidate the factors controlling copper solubility in greater detail, simple solubility experiments were

conducted. In these experiments soluble cupric ion was added to solutions at fixed pH, ionic strength, and alkalinity. After allowing 20 min for precipitation to occur, soluble copper was then measured in filtered samples. Consistent with previous trends, soluble copper was approximately a linear function of alkalinity (Figure 4). The experimentally observed slope at pH 7.0 and 7.5 was about 0.0116 mg soluble copper/mg alkalinity, whereas the slope at pH 8.0 and 8.5 was about 0.004 mg soluble copper/mg alkalinity. Thus, at pH 7.0–7.5 soluble copper was about 2.9 times more sensitive to the presence of alkalinity than at pH 8.0–8.5. This was fairly consistent with the 2.0–2.7-fold slope differential in the by-product release data (Figure 2) and utility monitoring data (Figure 3).

Given the previous experimental findings, various candidate solids that might be controlling copper solubility were evaluated using MINEQL+.<sup>9</sup> Constants in

**TABLE 2** Model constants from MINEQL+ database<sup>12-16</sup>

Formation Reaction	Name of Solid	log (K)	$\Delta H^\circ$ kcal/m
<b>Solids</b>			
$4\text{Cu}^{2+} + 6\text{H}_2\text{O} + \text{SO}_4^{2-} \rightarrow \text{Cu}_4(\text{OH})_6(\text{SO}_4)$	Bronchantite	-15.2	40
$\text{Cu}^{2+} + 2\text{H}_2\text{O} \rightarrow \text{Cu}(\text{OH})_2$	Cupric hydroxide	-8.64	15.25
$\text{Cu}^{2+} + 2\text{H}_2\text{O} \rightarrow \text{Cu}(\text{O})$	Tenorite	-7.62	15.24
$2\text{Cu}^{2+} + 2\text{H}_2\text{O} + \text{CO}_3^{2-} \rightarrow \text{Cu}_2(\text{OH})_2\text{CO}_3$	Malachite	-5.18	15.61
<b>Complexes</b>			
$2\text{Cu}^{2+} + 2\text{H}_2\text{O} + 2\text{H}^+ \rightarrow \text{Cu}_2(\text{OH})_2^{2+}$		-10.36	
$\text{Cu}^{2+} + \text{H}_2\text{O} + \text{H}^+ \rightarrow \text{Cu}(\text{OH})^+$		-8.0	
$\text{Cu}^{2+} + 2\text{H}_2\text{O} + 2\text{H}^+ \rightarrow \text{Cu}(\text{OH})_2$		-13.63	
$\text{Cu}^{2+} + 3\text{H}_2\text{O} + 3\text{H}^+ \rightarrow \text{Cu}(\text{OH})_3^-$		-26.9	
$\text{Cu}^{2+} + 4\text{H}_2\text{O} + 4\text{H}^+ \rightarrow \text{Cu}(\text{OH})_4^{2-}$		-39.6	
$\text{Cu}^{2+} + \text{HCO}_3^- \rightarrow \text{Cu}(\text{HCO}_3)^+$		-13.00	
$\text{Cu}^{2+} + \text{CO}_3^{2-} \rightarrow \text{Cu}(\text{CO}_3)$		-16.73	
$\text{Cu}^{2+} + 2\text{CO}_3^{2-} \rightarrow \text{Cu}(\text{CO}_3)_2$		-9.83	

complexes at higher pH, because the  $\text{Cu}(\text{OH})_2$  model predicts a weak dependency on alkalinity whereas the solubility data (Figure 4), by-product release experiments (Figure 2), and utility data (Figure 3) indicate a much stronger dependence on alkalinity.

By comparison, predictions of soluble copper based on tenorite and malachite solubility were low by about one order of magnitude over the tested

pH and alkalinity ranges, whereas that based on bronchantite overpredicted copper solubility by a factor of three to four. Moreover, malachite solubility predicts less soluble copper at higher alkalities if pH was >7.4, a tendency that was obviously inconsistent with the described experimental

results. A similar conclusion regarding the importance of cupric hydroxide has recently been put forward by Schock et al<sup>10</sup> using data from USEPA pipe rigs.

**Effect of alkalinity on corrosion rates and scale morphology.** *Corrosion rates of copper in pipe-rig tests.* At the end of the by-product release experiments, coupons were cut from the pipes, and instantaneous corrosion rates were determined electrochemically under flow conditions. Although the trends in corrosion rate are not a linear function of alkalinity, the copper corrosion rates did increase consistently with higher alkalinity at both pH 7.0 and 8.0 (Figure 5).

The corrosion rate,  $I_{\text{corr}}$ , represents total copper oxidized at the pipe surface per unit of time. This oxidized copper may either be incorporated into solids on the pipe surface, forming a scale, or be released to solution as a corrosion by-product. Assuming that corrosion proceeds through a one- $e^-$  transfer, the following conversion was derived relating corrosion rate to copper mass corroded:

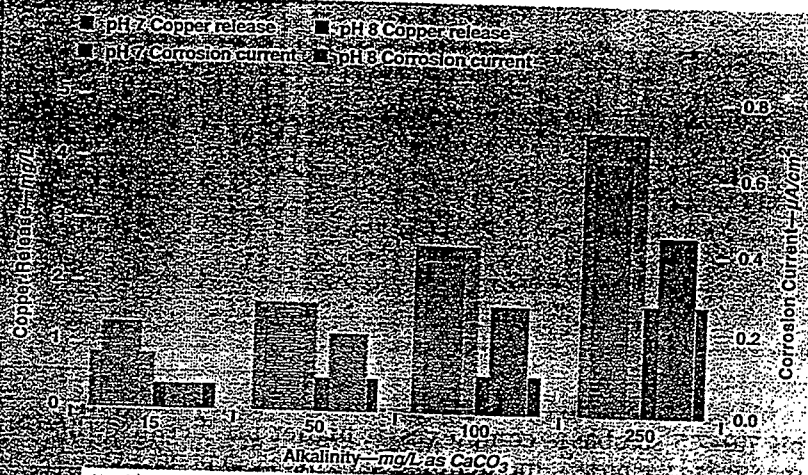
**O**ver the pH range of about 7.0–8.0, adverse effects from bicarbonate are significantly reduced by even small increases in pH.

the MINEQL database were used without any critical evaluation, though an internally consistent critique has been presented elsewhere.<sup>10</sup> Four cupric solids known to form on copper pipe were examined for consistency with experimental data including tenorite  $[\text{CuO}]$ , cupric hydroxide  $[\text{Cu}(\text{OH})_2]$ , malachite  $[\text{Cu}_2(\text{OH})_2\text{CO}_3]$ , and bronchantite  $[\text{Cu}_4(\text{OH})_6(\text{SO}_4)]$ .<sup>11</sup> The model prediction was based on the assumption that soluble copper was controlled by equilibrium with one of these solid phases (Table 2).

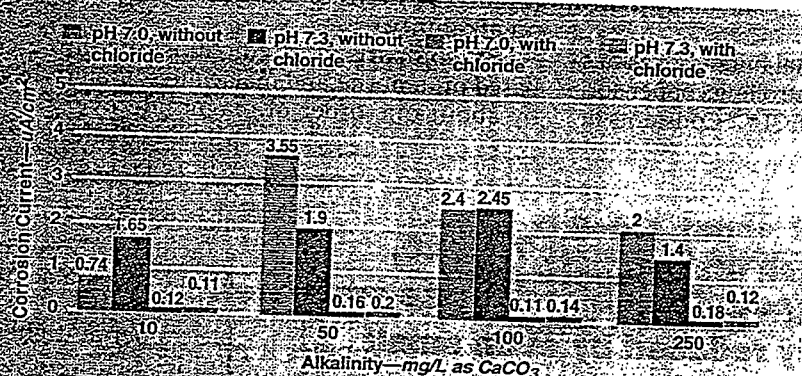
Predictions of soluble copper based on cupric hydroxide solubility were both qualitatively and quantitatively consistent with the previous data (Figure 4). Quantitative predictions always agreed to within 1.5 mg/L copper, a very reasonable result given uncertainties in the required equilibrium constants. The agreement between the  $\text{Cu}(\text{OH})_2$  model and observed solubility was excellent at pH 7.0, with weaker predictive capability at the higher pH values. The discrepancy between the model prediction and the experimental data appears to be due to an underestimate in copper carbonate



**FIGURE 5** Average copper release and measured corrosion current in naturally aged samples showing the same trend



**FIGURE 6** Corrosion currents in the presence and absence of 1 mM chloride



$$\frac{1 \mu\text{A}}{\text{cm}^2} \times \frac{1\text{A}}{10^6 \mu\text{A}} \times \frac{20 \text{ cm}^2}{\text{coupon}} \times \frac{1 \text{ C/s}}{\text{A}} \times \frac{1\text{e}^-}{1.6 \times 10^{-19} \text{ C}} \quad (3)$$

$$\times \frac{1 \text{ Cu}^+}{\text{e}^-} \times \frac{1 \text{ mmol Cu}}{6.02 \times 10^{20} \text{ Cu}^+} \times \frac{86,000 \text{ s}}{\text{day}} = 0.018 \frac{\text{mmol Cu}}{\text{day}}$$

Two major factors might contribute to differences in corrosion-rate estimates based on copper mass lost to solution (i.e., the by-product release data) versus the direct electrochemical measurement. The first factor was that by-product release measurements were made under stagnant conditions, whereas corrosion rates were determined under flow conditions. This difference would tend to increase the corrosion rate during flow versus stagnation because of improved mass transport. The second factor was that much of the oxidized copper could be incorporated into a growing scale layer and not released to solution. Any copper incorporated into scale will not be quantified by measurement of released corrosion by-products, thereby

reducing the estimate of corrosion rate based on by-product measurement.

Despite these difficulties, it was instructive to examine the actual measured corrosion rate and compare it with that estimated on the basis of by-product release to stagnant waters. Assuming that corrosion rate was not influenced by differences in flow, calculations indicate that about 3 percent of copper that was corroded was actually released to solution; in this case, about 97 percent of the corroded copper must have been incorporated into scale formed on the pipe surface. At another extreme, if it was assumed that all the corroded copper was actually released to solution as a corrosion by-product and none was incorporated into scale, the corrosion rates under conditions of stagnation must have been more than 33 times slower during stagnation than under conditions of flow. Reality probably reflects a compromise between these two extreme assumptions.

**Dual ion interactions: chloride and bicarbonate.** Although the previous experiments clearly isolated the effects of pH and bicarbonate

on copper corrosion rates, other water quality constituents such as natural organic matter, chloride, and sulfate can also strongly influence copper corrosion.<sup>5,11</sup> Because both chloride and bicarbonate appear to be critical to controlling copper corrosion rates, their combined effect was examined.

The accelerated aging technique was used to examine copper corrosion in well-defined synthetic waters at pH 7.0 and 7.3 and constant ionic strength. At a given level of alkalinity, solutions were constituted with or without the addition of 1 mM chloride at all alkalinity values (Figure 6). Chloride addition decreased corrosion rates between 84 and 95 percent in all cases. Thus, from this perspective at least, the presence of chloride can counter adverse effects of bicarbonate.

A comparison of scales formed in the presence and absence of chloride verified the dominant effect of chloride on scale appearance. Chloride supported formation of a reddish scale that was nearly identical to that observed at pH 7.0 in the presence of chloride only.<sup>6</sup> In contrast, scales formed in the absence of

chloride were quite smooth in appearance under the SEM, giving the surface a nonporous appearance. Thus, chloride induced very significant visual and electrochemical changes to copper corrosion.

### Synthesis: role of bicarbonate in copper corrosion

This section critically evaluates key results of this investigation in light of previous research. The effects of bicarbonate on corrosion by-products and corrosion rates are discussed separately. The section concludes with a short discussion of copper carbonate complexation versus dissolved  $\text{CO}_2$  as a source of copper corrosion problems.

**Effect of bicarbonate on copper corrosion by-product release.** Evidence from the pipe-rig experiments and the monitoring experience of large utilities is clear and unambiguous: soluble copper corrosion by-product release increases as a linear function of alkalinity. Because these trends were con-

using conventional units with copper in mg/L,  $\text{H}^+$  as pH, and alkalinity ( $= \text{HCO}_3^-$ ) in mg/L as  $\text{CaCO}_3$ . At constant pH of 7.0 and 8.0, this equation simplifies to a linear form:

$$\text{Soluble Cu (mg/L)} = 0.83 + 0.015 [\text{alk}] \text{ at pH 7.0} \quad (7)$$

$$\text{Soluble Cu (mg/L)} = 0.58 + 0.0013 [\text{alk}] \text{ at pH 8.0} \quad (8)$$

Qualitatively, this predicted linear relationship between soluble copper and alkalinity (at constant pH) is in excellent agreement with the experimental results. The quantitative agreement is also quite good, especially at lower pH values. Indeed, a comparison of Eqs 1 and 7 demonstrates remarkable agreement between the model at pH 7.0 and the actual by-product release data, consistent with the excellent predictive capability of the model at the lower pH for the solubility data (Figure 4). A comparison of Eqs 2

and 8 reiterates the fact that the model underpredicts sensitivity of copper release attributable to alkalinity at the higher pH.

The slope of the equation, equal to the increase in soluble copper (mg/L) per incremental increase in alkalinity (mg/L as  $\text{CaCO}_3$ ), increases at lower

pH (Figure 7). The slope is directly related to the likelihood of forming soluble copper-carbonate complexes, with a higher slope indicating a greater tendency to form carbonate complexes. Decreasing the pH by 0.5 units (i.e., from 8.5 to 8.0 or from 8.0 to 7.5) increases the slope by about a factor of three, indicating a threefold increase in copper carbonate complexes at the lower pH.

If enthalpy values for the  $\text{Cu}(\text{OH})_2$  solid in the MINEQL+ database are considered (Figure 7), copper-carbonate complexation is predicted to be a strong function of temperature, with each  $10^\circ\text{C}$  increase halving the slope. In other words, because  $\text{Cu}(\text{OH})_2$  dissolution is exothermic, a given concentration of bicarbonate (alkalinity) is predicted to complex about twice as much copper at  $5^\circ\text{C}$  as it would at  $15^\circ\text{C}$ . Interestingly, this predicted temperature dependency can explain recent findings that copper corrosion by-product release is lower in household hot-water taps than it is in cold-water taps.<sup>8</sup> This temperature dependency also calls into question recent proposals to require utilities to monitor only in the summer because the presumption of higher copper release at higher temperature is at odds with predictions based on solubility and is not supported by utility monitoring data.<sup>17</sup>

The  $\text{Cu}(\text{OH})_2$  model is also consistent with empirical linear relationships developed at KTW to predict the maximum concentration of copper released to water during stagnation:<sup>18,19</sup>

**Without considering inhibitor dosing on temperature, the best advice is to raise pH.**

sistent with measurements of copper solubility in simple laboratory experiments, it appears that solubility is a key control over copper corrosion by-product release. Of the available solids known to form in copper pipe, only solubility predictions based on  $\text{Cu}(\text{OH})_2$  (solid) were quantitatively and qualitatively consistent with the available data.

In this model, the predominant soluble copper species over the pH range 7.0–8.5 include  $\text{Cu}^{+2}$ ,  $\text{Cu}(\text{OH})_2(\text{aq})$ ,  $\text{CuCO}_3(\text{aq})$ , and  $\text{CuHCO}_3^+$ . Thus, the concentration of soluble Cu can be calculated as:

$$\text{Cu} = [\text{Cu}^{+2}] + [\text{Cu}(\text{OH})_2(\text{aq})] + [\text{CuCO}_3(\text{aq})] + [\text{CuHCO}_3^+] \quad (4)$$

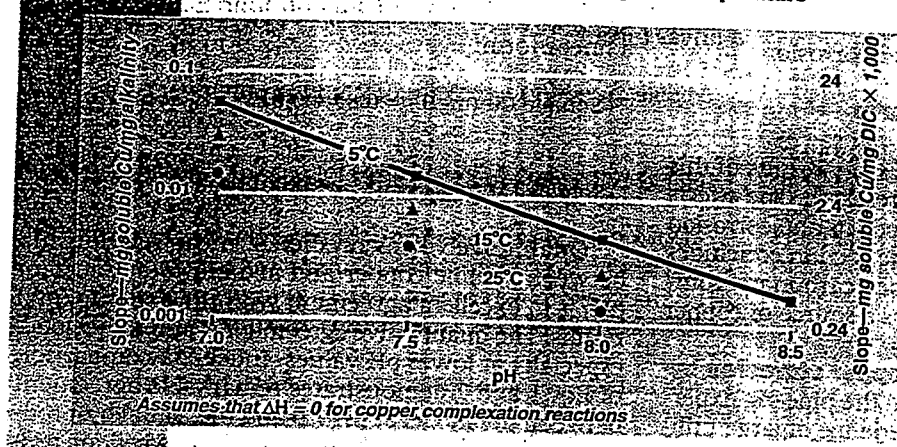
$$\text{Cu} = K_{sp} K_w^{-2} [\text{H}^+]^2 + K_1 K_{sp} + K_2 K_4 K_{sp} [\text{HCO}_3^-] K_w^{-2} [\text{H}^+] + K_3 K_{sp} K_w^{-2} [\text{H}^+]^2 [\text{HCO}_3^-] \quad (5)$$

in which  $K_1 = [\text{Cu}(\text{OH})_2(\text{aq})]/[\text{Cu}^{+2}] [\text{OH}^-]^2$ ,  $K_2 = [\text{CuCO}_3(\text{aq})]/[\text{Cu}^{+2}] [\text{CO}_3^{2-}]$ ,  $K_3 = [\text{CuHCO}_3^+]/[\text{Cu}^{+2}] [\text{HCO}_3^-]$ ,  $K_4 = [\text{CO}_3^{2-}] [\text{H}^+]/[\text{HCO}_3^-]$ ,  $K_{sp} = [\text{Cu}^{+2}] [\text{OH}^-]^2$ ,  $K_w = [\text{OH}^-] [\text{H}^+]$ , and Cu is in mol/L.

Because  $K_1$ ,  $K_2$ ,  $K_3$ ,  $K_4$ , and  $K_{sp}$  are constant, calculating results at  $25^\circ\text{C}$  without activity corrections yields:

$$\text{Soluble Cu (mg/L)} = 10^{(13.4-2\text{pH})} + 0.58 + 10^{(5.1-\text{pH})} [\text{alk}] + 10^{(11.4-2\text{pH})} [\text{alk}] \quad (6)$$

**FIGURE 7** Sensitivity of copper solubility to alkalinity and temperature



Old pipe:  $Cu_{\text{maximum}} \text{ (mg/L)} = 0.0110 [\text{Alkalinity}] - 1.37 \text{ pH} + 0.021 [\text{SO}_4^{-2}] + 10.2$

New pipe:  $Cu_{\text{maximum}} \text{ (mg/L)} = 0.0104 [\text{Alkalinity}] - 2.26 \text{ pH} + 18.1$

in which alkalinity is in mg/L as  $\text{CaCO}_3$  and  $\text{SO}_4^{-2}$  is in mg/L (units have been changed for consistency with US utility convention). The empirically determined slope of 0.0104–0.0110 mg Cu/mg alkalinity is within the range of those determined in this work, corresponding approximately to the slope predicted at pH 7.3 at 15°C by the  $\text{Cu}(\text{OH})_2$  model (Figure 7).

Predictions based on the  $\text{Cu}(\text{OH})_2$  model, even if  $\text{Cu}(\text{OH})_2$  solids do control solubility in a given system, will only predict monitoring data if equilibrium is attained. Kinetic limitations, inaccuracies in model constants, and significant concentrations of particulate copper not removed by a 0.45- $\mu\text{m}$ -pore-size filter would also cause discrepancies between model prediction and actual experience. Nevertheless, it is encouraging that trends in the experimental data and the  $\text{Cu}(\text{OH})_2$  predictive model are consistent with those observed in aggregated monitoring data of large utilities.

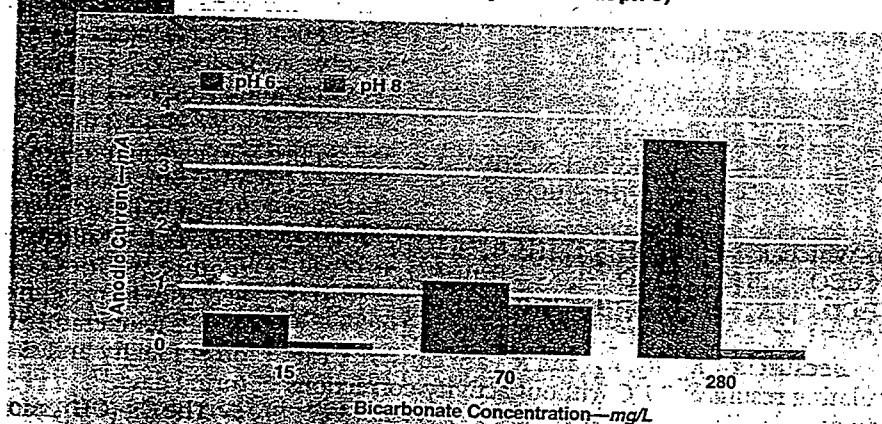
**Effect of bicarbonate on copper corrosion rates and scale morphology.** At first glance, findings that bicarbonate has an adverse effect on corrosion rates appear contrary to results of previous researchers. The authors' previous work, however,<sup>6</sup> dem-

onstrated that bicarbonate has a dual nature dependent on the solution pH. Above about pH 8.1, the presence of bicarbonate tends to passivate copper surfaces and decrease corrosion rates.<sup>6</sup> However, below about pH 8.1, bicarbonate is increasingly aggressive at higher alkalinities ( $\geq 100$  mg/L as  $\text{CaCO}_3$ ). A closer look at the literature reveals an interesting trend; i.e., the solution pH is greater than 7.7 in nearly all cases in which bicarbonate is reported to have beneficial effects.<sup>20–22</sup>

In cases in which the current findings seem to be contradictory to the conclusions of previous research, a closer look reveals just the opposite. For instance, bicarbonate was studied at pH 6 and pH 8 by Mattsson and Fredriksson.<sup>23</sup> Though the authors conclude that bicarbonate forms passivating scales, the data showed that at pH 6 anodic corrosion currents did increase with bicarbonate concentration and a very large increase was observed at the highest alkalinity tested (Figure 8). At pH 8, however, the currents and adverse effects of bicarbonate were greatly reduced.<sup>23</sup>

Cohen and Myers<sup>24</sup> examined treatment alternatives for an outbreak of copper pitting in Fort Shawnee, Ohio. Prior to treatment, the water had an alkalinity of 296 mg/L as  $\text{CaCO}_3$  and an average pH of 7.3. This water is well within the aggressive pH range for bicarbonate.<sup>6</sup> Soda ash was subsequently added to raise and maintain the pH at 8.4, also increasing the alkalinity to 360 mg/L as  $\text{CaCO}_3$ . After

**FIGURE 8** Increase in corrosion currents at pH 6 with higher bicarbonate concentrations (effects greatly reduced at pH 8)



six months, the copper pitting problems had virtually disappeared. Results from the current work indicate that the beneficial effect of adding soda ash should be attributed to the critical change in pH from 7.3 to 8.4, and not to the slight (20 percent) increase in alkalinity in this system.

Moss and Potter<sup>25</sup> investigated 18 waters in New Zealand and, although they also conclude that bicarbonate forms passivating scales, two of the three most aggressive waters had 411- and 178-mg/L bicarbonate concentrations at pH 7.3 and 7.1, respectively.<sup>25</sup> Both of these waters are within the aggressive region for bicarbonate defined in recent work done by the authors of this article. In addition, the beneficial effects attributed to bicarbonate in Moss and Potter's work was partly based on anodic polarization experiments, and the cathodic oxygen reduction reaction was ignored. Thus, these investigators would not have observed an increase in the cathodic oxygen reduction reaction rate as was observed in previous work.<sup>2,5</sup>

The similar trends observed between copper solubility and corrosion rates prompt the question "Why does this agreement exist?" The authors speculate that this is because soluble copper-bicarbonate and

excellent surrogate for copper carbonate complexation capacity. That is, the concentration of copper complexed with carbonate species (CCCu) is defined as

$$\text{CCCu (mg/L)} = [\text{CuCO}_3] + [\text{CuHCO}_3^+]$$

which may be rewritten as

$$\text{CCCu (mg/L)} = [\text{CO}_2 \text{ (mol/L)}] \times [3.09 \times 10^3 + 10^{-\text{pH}} [5.79 \times 10^3]]$$

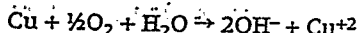
using equations and constants described previously. In the preceding expression carbonate-complexed copper is estimated based on equilibrium with  $\text{Cu(OH)}_2$  solid at 25°C, ignoring ionic strength corrections. As the expression indicates, the concentration of copper tied up with carbonate species is linearly related to dissolved  $\text{CO}_2$  (mol/L) or, equivalently, dissolved  $\text{H}_2\text{CO}_3$  (mol/L). At pH values above about 6.3, the concentration of  $\text{CuCO}_3$  becomes dominant compared with  $\text{CuHCO}_3^+$ , yielding a simplified approximation:

$$\text{CCCu (mg/L)} \approx [\text{CuCO}_3] = 3.09 \times 10^3 [\text{CO}_2]$$

which is linear at any pH. Even in a nonequilibrium condition, the preceding expression would define the maximum concentration of carbonate complexes that would form or, in other words, the tendency of a given solution to form carbonate complexes. Future research should revisit hypothesized direct roles for  $\text{CO}_2$  in copper corrosion, because correlations between copper corrosion problems and  $\text{CO}_2$  may be an artifact of copper-carbonate complex formation.

## The described benefits of aeration are expected to apply to many high-alkalinity, low-pH waters.

copper-carbonate complexes become increasingly important at higher alkalinity, tending to reduce the free copper ( $\text{Cu}^{+2}$ ) activity in solution. At a fixed pH and dissolved oxygen concentration, the driving force for the anodic corrosion reaction increases as free copper activity decreases:



Thus, the presence of complexing-carbonate species could reduce the free copper concentration, thereby increasing the corrosion rate. Alternatively, an adverse influence of bicarbonate on scale porosity has been observed,<sup>6</sup> which might induce formation of a less protective scale that increases corrosion rates at higher alkalinity. In that case, the agreement in trends for effects of alkalinity on solubility and corrosion rates would be fortuitous.

**Copper carbonate complexation versus dissolved carbon dioxide ( $\text{CO}_2$ ).** Dissolved  $\text{CO}_2$  has been correlated to many types of copper corrosion problems including pitting tendencies, corrosion rates, and by-product release.<sup>1</sup> Such correlations have been thought to indicate a direct mechanistic role for  $\text{CO}_2$  in copper corrosion. It is possible, however, that the concentration of dissolved  $\text{CO}_2$  simply serves as an

## Implications for utilities

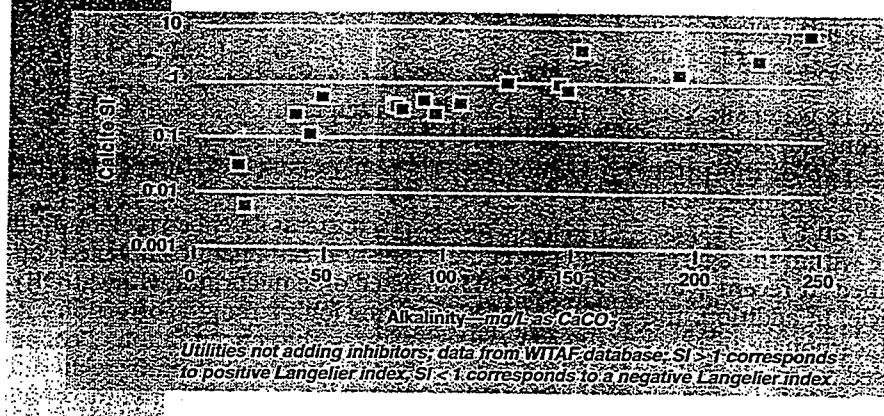
Important implications of this research fall into two broad categories: corrosion control strategies to avoid and recommended strategies. Given the regulatory framework of the Lead and Copper Rule, these strategies apply specifically to mitigation of copper (i.e., not lead) corrosion by-product release.

**Corrosion control strategies to avoid.** Utilities examining copper corrosion mitigation strategies often find it simple and attractive to use a Langelier, Larson's, or other corrosion index. Indeed, the Langelier approach is currently recommended by several state regulatory agencies<sup>26</sup> and is supported by user-friendly corrosion optimization software sold through AWWA.<sup>27</sup> This work demonstrates that not only are these indexes without basis, but that under certain conditions they provide the advice most likely to exacerbate copper corrosion by-product release.

For example, the Langelier index (LI) approach is based on the notion that the interior of a copper pipe must be coated by a calcite scale in order to be protected. According to this model, higher degrees of

# FIGURE 9

At a given pH, calcite saturation indexes tend to increase at higher alkalinity (data shown for pH 7.2-7.4)



calcite supersaturation are correlated with reduced corrosivity.<sup>28</sup>

$$\text{Calcite saturation index (SI)} = [\text{Ca}^{+2}][\text{CO}_3^{-2}]/K$$

in which  $[\text{Ca}^{+2}]$  = calcium concentration,  $[\text{CO}_3^{-2}]$  = carbonate concentration, and  $K$  = calcite solubility product.

To connect the SI expression with the traditional LI approaches, a positive LI corresponds to SI values above 1.0, whereas a negative LI corresponds to SI values below 1.0. The SI and LI both increase as  $\text{Ca}^{+2}$  and  $\text{CO}_3^{-2}$  concentrations increase. Thus, in the simplest test of this model's validity, at constant pH copper corrosion problems should decrease as  $\text{Ca}^{+2}$  and  $\text{CO}_3^{-2}$  increase.

The work described here directly repudiates this hypothesis. In experiments in which both  $\text{Ca}^{+2}$  and  $\text{CO}_3^{-2}$  were increased at pH 7.0 or 8.0 (Figure 2), leading to a higher SI and presumably a better condition for copper according to Langelier theory, problems with copper corrosion by-product release worsened. Similarly, as evidenced by the costly experience of large utilities under the Lead and Copper Rule (Figure 3), in a given pH category copper corrosion by-product release increases at higher alkalinity. Because higher-alkalinity waters have much higher calcite SI values at a given pH (Figure 9), the LI predicts reduced problems with copper by-product release at higher alkalinity. In sum, both findings are completely inconsistent with the Langelier approach but are consistent with the  $\text{Cu}(\text{OH})_2$  model developed by Schock et al and in this work.<sup>10,29</sup>

With respect to Larson's ratio (LR):<sup>30</sup>

$$\text{LR} = [\text{Cl}^-]/[\text{HCO}_3^-]$$

the higher the LR ratio, the higher the corrosivity of the water supply. With respect to copper corrosion, this work and others have demonstrated that chloride has long-term beneficial effects (on copper corrosion rates), whereas bicarbonate has adverse effects on both by-product release and corrosion rates.<sup>6</sup> Thus, if

anything, the exact opposite of Larson's prediction is likely to be valid for copper.

The preceding discussion should not be interpreted as a criticism of the index originators. They, more than those who followed, understood the limitations of their work. For instance, the Larson's index was not derived for copper, it was derived for steel and cast iron. Likewise, with respect to the Langelier theory, it has long been known that calcite does not actually precipitate on pipes in most distribution systems; thus, the theory might actually work

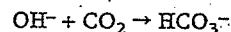
quite well for the few cases in which precipitative calcite scales do form.

The question arises, however, as to why the Langelier model has gained such widespread and apparently misguided acceptance. The answer, in the authors' opinion, is that it provides an easy-to-use guide to solving a complex problem. Moreover, because the LI is typically applied to answer the question "How high should we raise the pH?", it will work quite well under some circumstances. Because higher pH typically reduces copper corrosion by-product release, the index occasionally works by accident. Thus, when used in the context of calculating the maximum pH allowable in a given system to avoid problems with calcite precipitation, the LI still has considerable value.

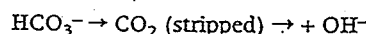
## Recommended corrosion control strategies.

Without considering inhibitor dosing (viable but beyond the scope of this work) or temperature (which is uncontrollable), the best advice is to raise pH. In particular, over the pH range of about 7.0-8.0, adverse effects from bicarbonate are significantly reduced by even small (+ 0.2 pH units) increases in pH.

Interestingly, the authors' analysis indicates that the method of increasing pH is important. Consider three different options including NaOH (caustic),  $\text{Ca}(\text{OH})_2$  (lime), or aeration- $\text{CO}_2$  stripping. For the caustic and the lime up to a pH of about 8.5, the  $\text{OH}^-$  added will increase alkalinity:



In contrast, raising pH by stripping  $\text{CO}_2$  increases pH but does not alter alkalinity, because the reaction producing  $\text{OH}^-$  consumes bicarbonate (which is subsequently regenerated):



The significance of this effect on predicted copper solubility depends on the initial alkalinity and pH of the water. Consider a hypothetical water with initial



alkalinity of 250 mg/L as  $\text{CaCO}_3$ , initial calcium hardness of 100 mg/L as  $\text{CaCO}_3$ , and temperature of 25°C. If the final pH is raised to 7.2 with lime or caustic, soluble copper is predicted to be 3.8 and 3.4 mg/L if the initial pH is 6.5 or 6.7, respectively (Figure 10). If pH is raised to 7.2 using aeration, soluble copper is predicted to be only 2.8 mg/L regardless of initial pH (because alkalinity does not change upon aeration). This represents a 17–26 percent enhancement in copper corrosion control (at a given final pH) using aeration compared with lime or caustic.

More important, however, is that pH may be increased to higher values without precipitating calcite if aeration is used. In the waters modeled in Figure 10 and for lime addition, calcite is supersaturated at only pH 7.2 or 7.3, depending on the initial pH. If pH is raised using aeration, calcite is not supersaturated until pH 7.6. Thus, aeration provides flexibility to raise pH to higher values without precipitating calcite.

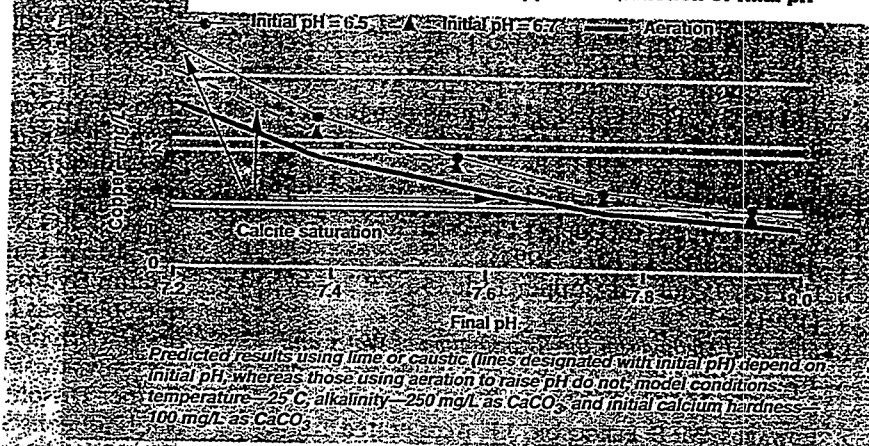
Quantitatively, increasing pH to the point of calcite supersaturation (pH 7.6) using aeration is predicted to yield soluble copper of 1.3 mg/L (Figure 10). If pH is also raised to the point of calcite supersaturation using lime, soluble copper is predicted to be 3.9 and 2.8 mg/L at an initial pH of 6.5 and 6.7, respectively. Therefore, aeration offers a predicted improvement of 53–66 percent compared with lime if pH is raised to the point of calcite saturation. This improvement may be attributed to the higher possible pH as well as the lower final alkalinity. Because the use of caustic would increase alkalinity without concomitant increases in calcium (as with lime dosing), the pH at which calcite becomes saturated using caustic is between that observed for lime (lowest pH) and aeration (highest pH).

Although the described benefits of aeration are expected to apply to many high-alkalinity, low-pH waters, they will probably not apply to all waters. For example, in waters without any initial dissolved oxygen, measurable copper corrosion may not be occurring, and aeration (leading to higher dissolved oxygen) might induce a worsened condition.<sup>10,29,31</sup> Also, some waters are substantially undersaturated with respect to atmospheric  $\text{CO}_2$ , in which case aeration will actually reduce pH and thereby worsen copper corrosion problems. Nevertheless, aeration is an attractive, low-cost option deserving of testing at many utilities.

## Conclusions

- At constant pH, soluble copper corrosion by-product release in relatively new copper plumbing

**FIGURE 10** Predicted equilibrium soluble copper as a function of final pH



Predicted results using lime or caustic (lines designated with initial pH) depend on initial pH, whereas those using aeration to raise pH do not; model conditions: temperature = 25°C, alkalinity = 250 mg/L as  $\text{CaCO}_3$ , and initial calcium hardness = 100 mg/L as  $\text{CaCO}_3$ .

is a linear function of bicarbonate concentration (alkalinity).

- Qualitative and quantitative trends in soluble copper corrosion by-product release are consistent with predictions based on  $\text{Cu}(\text{OH})_2$  equilibrium.
- The sensitivity of copper solubility to alkalinity (bicarbonate), expressed as mg additional soluble copper/mg alkalinity as  $\text{CaCO}_3$  added, depends on pH and temperature. Copper carbonate complexes are most significant in cold and low-pH waters.
- $\text{CO}_2$  concentrations are a surrogate for copper-carbonate complexation capacity in many waters, providing a possible mechanistic basis to correlations between dissolved  $\text{CO}_2$  and copper corrosion problems.
- The conventional Langelier index or Larson's ratio approach to controlling copper corrosion by-product release is demonstrably inaccurate.
- Compared with lime or caustic addition, raising pH by aeration ( $\text{CO}_2$  stripping) has inherent advantages for copper corrosion control in low-pH, high-alkalinity waters. These advantages are attributed to lower final alkalinity and a reduced likelihood of calcite precipitation.

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# **Copper Corrosion and Iron Removal Plants**

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## **ABSTRACT**

Since July 1992, more than 140 Community Public Water Systems in Minnesota have been coping with a copper problem. This paper gives an overview of the copper corrosion problems encountered in Minnesota and summarizes the corrosion control treatment experiences of three iron removal Treatment plants. Phosphate inhibitor treatment is suggested be the most prominent copper control alternative for iron removal plants in Minnesota.

## **INTRODUCTION**

Groundwater, conventionally considered as non-corrosive, usually having a pH above seven and a positive Langlier Index (LI) is now defined as corrosive, due to a lead or copper exceedance under the Lead and Copper Rule. Public water systems with a lead/copper exceedance are required to conduct a corrosion control treatment study and ultimately install an optimal corrosion control treatment for lead and/or copper. Iron removal systems make up two-third of the total copper exceedances in Minnesota. Corrosion control treatment studies conducted by the medium-size water systems show that these iron removal systems are facing a bigger challenge controlling copper than controlling lead.

## **COPPER CORROSION IN MINNESOTA**

All copper exceedances in Minnesota came from groundwater systems. Groundwater in Minnesota characteristically has pH between 7 and 8, high in total dissolved solids, dissolved inorganic carbon, hardness, alkalinity, and rich in iron and manganese. In the southwest corner of Minnesota, groundwater also contains high level of sulfate.



## Scaling Water

Langlier Index (LI) and calcium carbonate precipitation potential (CCPP) are two indexes commonly used to predict the scaling tendency or corrosivity of a water. Scaling water conceptually is non-corrosive, unfortunately, it is not so in Minnesota as far as copper corrosion is concerned. Seventy-five percent of the water systems with a copper exceedance are having a positive CCPP in their treated waters.

## High Dissolved Inorganic Carbon

Dissolved inorganic carbon (DIC) and pH are the two key parameters associated with cuprosolvency. The high dissolved inorganic carbon content in finished water, is blamed for causing the copper exceedances in Minnesota. Theoretical dissolved inorganic carbon contents ranging from 200 mg/L to 900 mg/L as  $\text{CaCO}_3$  were predicted for all systems using the Rothberg, Tamburini & Winsor (RTW) Model. The majority of them have DIC between 500 and 800 mg/L as  $\text{CaCO}_3$  or between 60 mg C/L and 95 mg C/L in their treated water.

## Iron Removal Treatment Plants

Iron removal treatment is used across the State of Minnesota by about one-third of the municipal public water systems in Minnesota. In most cases, the treatment process consists of aeration/oxidation, filtration, chlorination, and fluoridation. It is notable that among those 142 public water systems exceeding the copper action level, 83% of the medium-size (Figure 1) and 57% of the small-size systems (Figure 2) are iron removal plants. It is believed that the aeration/oxidation step in the iron/manganese removal process results in a more corrosive finished water, due to the higher dissolved oxygen levels and/or the content of oxidizing agents such as potassium permanganate, and chlorine in the water.

## IRON REMOVAL PLANTS D.O. STUDY

A study on copper corrosion of iron removal treatment systems in Minnesota was conducted in summer 1993, by the Public Water Supply Unit. Nineteen (19) iron removal filtration plants were studied for their finished water dissolved oxygen levels associated with the aeration/oxidation process they use and their reported 90th percentile copper values. This study focused on the way oxygen is introduced into the water and demonstrated a strong association of 90th percentile copper levels with the dissolved oxygen levels (figure 3).

## Gravity Plants

Gravity iron removal filtration plants are the ones with copper problems. Most gravity filtration systems use a combination of steps such as tray aerator, spray aerator, gravity drop, flow splatter or splitter to aerate the water. Some also use oxidizing agents such as Chlorine and  $\text{KMnO}_4$  oxidizing agents in this iron/manganese oxidation step and followed by a gravity filtration process to remove the oxidized precipitates. Finished water dissolved oxygen levels of gravity iron removal plants are generally at or near the D.O. saturation point.

In winter 1993, eight more systems were added to the study. This study concluded that gravity systems are most susceptible to copper corrosion. The average finished water dissolved oxygen level from fourteen (14) gravity plants was 6.5 mg/L and the average 90th percentile copper level was 2.35 mg/L. The average dissolved inorganic carbon was 71 mg C/L. The average dissolved oxygen level, 90th percentile copper levels, and dissolved inorganic carbon level from thirteen (13) pressure plants are 1.52, 0.74, and 76 mg C/L, respectively.

## Pressure Plants

Pressure systems use compressed air and/or oxidizing agent(s) to precipitate iron and manganese and a pressure filtration process to remove the precipitates. Dissolved oxygen levels in the finished water from pressure plants normally do not exceed 2.0 mg/L. It is noted that among the 27 iron removal plants studied, the five compressed air aerated plants resulted with the highest average dissolved inorganic carbon level of 87 mg C/L, this may be contributed to carbon dioxide in the injected air. The eight non-aerated pressure plants on the other hand have the lowest average DIC of 65 mg C/L. Average 90th percentile copper value for these two groups are .88 mg/L and 0.60 mg/L, respectively.

## Phosphate Treatment Survey

Approximately 20% of the iron removal systems in Minnesota also treat with phosphate inhibitor for corrosion and scale control. In 1994, a phosphate treatment survey study conducted by the Public Water Supply Unit confirmed that iron removal systems are susceptible to copper corrosion even with the presence of phosphate inhibitors. This survey study found the only exceptions are systems with finished water pH above 8 and those using zinc-orthophosphate for corrosion control treatment.

## SEASONAL VARIATION IN COPPER LEVEL

In winter 1994, 35 water systems with no first round problems exceeded the copper action level. Higher copper tap levels were tested in a significant number of homes. A number of them experienced increases from a less than detection limit ( $<0.05$  mg/L) in the first round monitoring to a greater than the 1.3 mg/L copper action level in the second testing. Winter heating has been blamed for causing the elevated copper levels. The Minnesota Department of Health, Public Water Supply Unit, has investigated the seasonal variation issue in following efforts.

### Demonstration Tests

First-draw taps were collected seasonally and analyzed for copper concentrations from 11 homes for an eighteen months period. This testing program found six homes exhibited a clear seasonal pattern in tap copper levels, peak in midwinter and big drops for the rest of the year with the lowest levels tested in summer and fall. Four sites demonstrated the only elevated copper level tested was the second round monitoring sample, collected in January and February 1994. One site shows the peaks occurred in summer months. These tests strongly demonstrate the highly variable copper levels in the first draw taps during heating season and raised concerns of the corrosion control treatment issue for water systems caught up with a copper exceedance due to this seasonal phenomenon.

### Copper Tap Level Reproducibility

The lead/copper monitoring results of 5311 sites were analyzed for their copper tap level reproducibility. Sites were selected out of the Lead/Copper Monitoring Database, by matching up each location with the 1st and 2nd samples taken approximately six months apart, so that a well-defined "season" can be referred to, and the seasonal variation issue can be examined.

Three data sets were produced and analyzed as presented in Table 1. The average copper levels were higher in the second round testing. About 8.5% of the sites experienced a change in copper level greater than 0.5 mg/L in the two tests, with extremes showing copper levels less than detection limits at one sampling and up to 7 mg/L at the other. This percentage (8.5%) is significant due to its potential to cause a copper exceedance, since 10% is used as the trigger in the Lead and Copper Rule.

Data Set	1st Round Monitoring		2nd Round Monitoring	
No. of Sites	Sampled in	Ave. Cu	Sampled in	Ave. Cu
2603 Sites	Jul/Aug 93	.18 mg/L	Jan/Feb 94	.21 mg/L
2652 sites	Sep/Oct 93	.29 mg/L	Mar/Apr 94	.35 mg/L
55 sites	Nov/Dec 93	.21 mg/L	May/Jun 94	.28 mg/L
Overall Reproducibility in Two Tests:				
$ Cu1 - Cu2  \leq 0.1 \text{ mg/L} \dots\dots\dots 61.3\%$ $0.1 \text{ mg/L} <  Cu1 - Cu2  \leq 0.5 \text{ mg/L} \dots\dots\dots 30.2\%$ $ Cu1 - Cu2  > 0.5 \text{ mg/L} \dots\dots\dots 8.5\%$				

Table 1

## TREATMENT EVALUATION

The Lead and Copper Rule suggested that four treatment approaches be evaluated by every public water system exceeding an action level. Evaluations, based on the treated water characteristics for systems with a copper exceedance using both the EPA guidance and the AWWA's RTW Model, show that phosphate inhibitor is the most prominent alternative for copper corrosion control in Minnesota.

### Carbonate Passivation

Optimal water characteristics for employing this treatment approach for lead control are low dissolved inorganic carbon (DIC) and high pH. This treatment application is limited to few lime softening water systems for lead control.

### Calcium Carbonate Precipitation

The RTW Model was used to obtain the LI, DIC, and the CCPP values. These values were used to assist public water systems in the evaluation of the suggested corrosion control treatment alternatives required by the lead and copper rule. The calcium carbonate precipitation corrosion control treatment approach was eliminated by the majority of water systems due to the exhibited high CCPP values.

Although increasing the treated water pH appears to be beneficial for copper corrosion control, however, due to the high alkalinity (to resist the change in water pH) and high hardness (risk of excessive scaling) in the water, this approach needs to be carefully evaluated and closely monitored when implemented.

### **Silicate Inhibitor**

There are only 3 or 4 non-iron removal water systems in Minnesota using sodium silicate for iron/manganese and scale control. This treatment option has not been explored in Minnesota for the lead/copper corrosion control treatment purpose.

### **Phosphate Inhibitor**

Phosphate treatment is well received by most of the public water systems and communities in Minnesota due to its historical use for iron/manganese and scale control. A survey conducted in 1994 with small water systems using phosphate products found 85% of them were using a polyphosphate for red water and scale control. There were 9% using blended phosphate and 6% using orthophosphate for a corrosion control purpose. With the lead/copper monitoring results, the survey study concluded that the conventional polyphosphate treatment in Minnesota had provided some protection toward lead leaching due to the low lead exceedances among them, but it had not helped in the copper corrosion control.

The lead and copper exceedances have caused a shift from using polyphosphate to using blended phosphate and zinc-orthophosphate treatment in Minnesota. Treatment recommendations submitted by the medium-size public water systems show that 73% of them selected phosphate inhibitor treatment for optimal corrosion control for lead and copper (Figure 4).

## **TREATMENT EXPERIENCE FROM IRON REMOVAL PLANTS**

Followings are copper corrosion treatment experiences of three iron removal systems in Minnesota.

### **Utility #1 - Treatment With Poly-Orthophosphate Blend**

Population Served: 7,500

90th Percentile Copper Level: 2.25 mg/L

Water Treatment Used: induced aeration, gravity filtration, fluoridation, chlorination

Treatment Modification After Exceeding Cu A.L.: blended phosphate treatment

Corrosion Control Treatment: using a blended phosphate inhibitor with a poly/ortho ratio of 1 at 1.5 - 2.0 mg/L as total phosphates; phosphate feed rate is constrained by costs and local wastewater discharge limits

Treatment Outcome (Figure 5): immediate reduction in tap copper levels was appreciated, the effectiveness started to level off after achieving 50% to 65% reduction.

#### Water Quality Data:

<u>Parameters</u>	<u>Finished Water</u>
pH	7.6 - 7.9
Calcium as $\text{CaCO}_3$	150 - 180 mg/L
Alkalinity as $\text{CaCO}_3$	320 - 340 mg/L
Dissolved Solids	350 mg/L
Orthophosphate as $\text{PO}_4$	0.8 - 0.9 mg/L

Utility #1 demonstrates corrosion control treatment experience of the majority of the iron removal systems in Minnesota who have started or switched to feeding blended phosphates for corrosion control purposes. Copper tap level reduction of 50% or more can be easily achieved by feeding phosphate at 1 to 2 mg/L as total phosphate (orthophosphate ranging from 0.7 to 1.0 mg/L). However, the reduced copper levels remain at 1.0 to 1.5 mg/L, indicating the likelihood of exceeding copper action level in future monitoring effort.

#### Utility #2 - Calcium Carbonate Precipitation

Population Served: 22,000

90th Percentile Copper Level: 4.08 mg/L

Water Treatment Used Prior to Pb/Cu Monitoring: chlorination and fluoridation

Water Treatment After Exceeding Cu A.L.: two new pressure iron removal plants have been installed, treatment involving strip aeration, pre-chlorination, pressure filtration, and fluoridation

Corrosion Control Treatment: practicing calcium carbonate precipitation treatment approach; as a result of the aeration, water pH has increased from 7.5 to 8.1;

theoretical CCPP for treated waters are 40 mg/L and 80 mg/L as  $\text{CaCO}_3$ .

Treatment Outcome (Figure 6): copper reduction above 50% has been achieved contributing to the higher finished water pHs and CCPP values produced by the new treatment plants; system remains to face the challenge in meeting the 1.3 mg/L copper action level

#### Water Quality Data:

<u>Parameters</u>	<u>Plant #1</u>	<u>Plant #2</u>
Raw Water pH:	7.5	7.7
Finished Water pH:	8.1	8.1
Alkalinity as $\text{CaCO}_3$ :	430 mg/L	390 mg/L
Calcium as $\text{CaCO}_3$ :	260 mg/L	150 mg/L
Dissolved Solids:	630 mg/L	490 mg/L
Free Ammonia mg/L as N:	2.8 mg/L	3.0 mg/L

Utility #2 demonstrates that regardless of the positive (high) calcium carbonate precipitation potentials exhibited in the finished water, copper levels remain above the action level. The appreciated copper reduction can be credited to the aeration used that has increased pH from 7.5 to 8.1. This utility also demonstrated a very rare case in that copper remains as a concern at pH of 8.1. The high ammonia concentrations in the treated water may be the reason for their continuing copper problem.

#### Utility #3 - Treatment With Zinc-Orthophosphate

Population Served: 49,000

90th Percentile Copper Level: 3.36 mg/L

Water Treatment Used: utility has one pressure plant and one gravity plant; copper problems are located in areas supplied by the gravity plant; the treatment involves cascade aeration followed by gravity filtration, chlorination and fluoridation; potassium permanganate and chlorine are added as oxidizing agent

Treatment Modification After Exceeding Cu A.L.: zinc-orthophosphate treatment

Corrosion Control Treatment: zinc-orthophosphate at 0.8 - 1.3 mg/L as ortho- $\text{PO}_4$

Treatment Outcome (Figure 7): treatment successfully reduced copper levels to below 1.0 mg/L at four test sites, achieved greater than 70% reduction in copper tap levels showing promise in meeting the copper action level in future monitoring



### Water Quality Data:

<u>Parameters</u>	<u>Gravity Plant</u>	<u>Pressure Plant</u>
Finished Water pH	7.1 - 7.5	6.8 - 7.0
Finished Water D.O.	8.2 mg/L	0.8 mg/L
Alkalinity as CaCO <sub>3</sub>	270 - 380 mg/L	200 - 310 mg/L
Calcium as CaCO <sub>3</sub>	190 - 240 mg/L	170 - 200 mg/L
Ortho-phosphate as PO <sub>4</sub>	0.8 - 1.3 mg/L	None
DIC as C	87 mg/L	77 mg/L

Utility #3 demonstrate a successful copper corrosion control treatment experience using zinc-orthophosphate, achieved by a gravity iron removal system. Copper tap levels were reduced below 1.0 mg/L at a relatively low orthophosphate feed rate (0.8 - 1.3 mg/L) with respect to the high level of dissolved inorganic carbon and dissolved oxygen in the finished water. This study echoed the conclusion from the small systems phosphate treatment survey study that orthophosphate treatment is the most prominent corrosion control treatment option for Minnesota's iron removal systems.

## SUMMARY AND CONCLUSIONS

1. High dissolved inorganic carbons in groundwater sources and high dissolved oxygen in treated water from iron removal plants are causes for copper exceedances in Minnesota.
2. Iron removal plants using gravity filtration are most susceptible to copper corrosion due to the high levels of dissolved oxygen introduced by aeration.
3. Calcium carbonate precipitation appears to be ineffective for copper corrosion control. This treatment approach has very limited application in Minnesota due to the high hardness and alkalinity in groundwater.
4. Seasonal variation in tap copper levels was demonstrated in Minnesota, raising concerns of requiring corrosion control treatment for systems exceeding the copper action level due to this seasonal phenomenon.
5. The common experience using blended phosphates in Minnesota is that a 50% reduction in copper levels can be easily achieved. However, the lowered copper levels remain near the 1.3 mg/L copper action level, leaving water systems with continuing challenge of meeting the copper action level.

6. Ortho-phosphate levels at 0.8 - 2.0 mg/L have successfully reduced copper tap level below 1.0 mg/L for five gravity iron removal systems. A minimum ortho-phosphate level of 1.0 mg/L is recommended to be maintained throughout the distribution for iron removal systems treating with a phosphate inhibitor for copper corrosion control.

## REFERENCES

1. "Copper Corrosion Study of Iron Removal Treatment Systems in Minnesota", Minnesota Department of Health, Section of Drinking Water Protection, Public Water Supply Unit, November 1993.
2. "Corrosion Control Treatment Survey for Small-Size Community Public Water Systems - Summary and Conclusion", Minnesota Department of Health, Section of Drinking Water Protection, Public Water Supply Unit, June 1994.
3. Rezanian, L.W. & Anderl, W.H., "Copper Corrosion and Iron Removal Plants, the Minnesota Experience", Proc. of AWWA WQTC, 1995, New Orleans, LA

# Treatment Process Used Medium Systems with Copper Exceedance

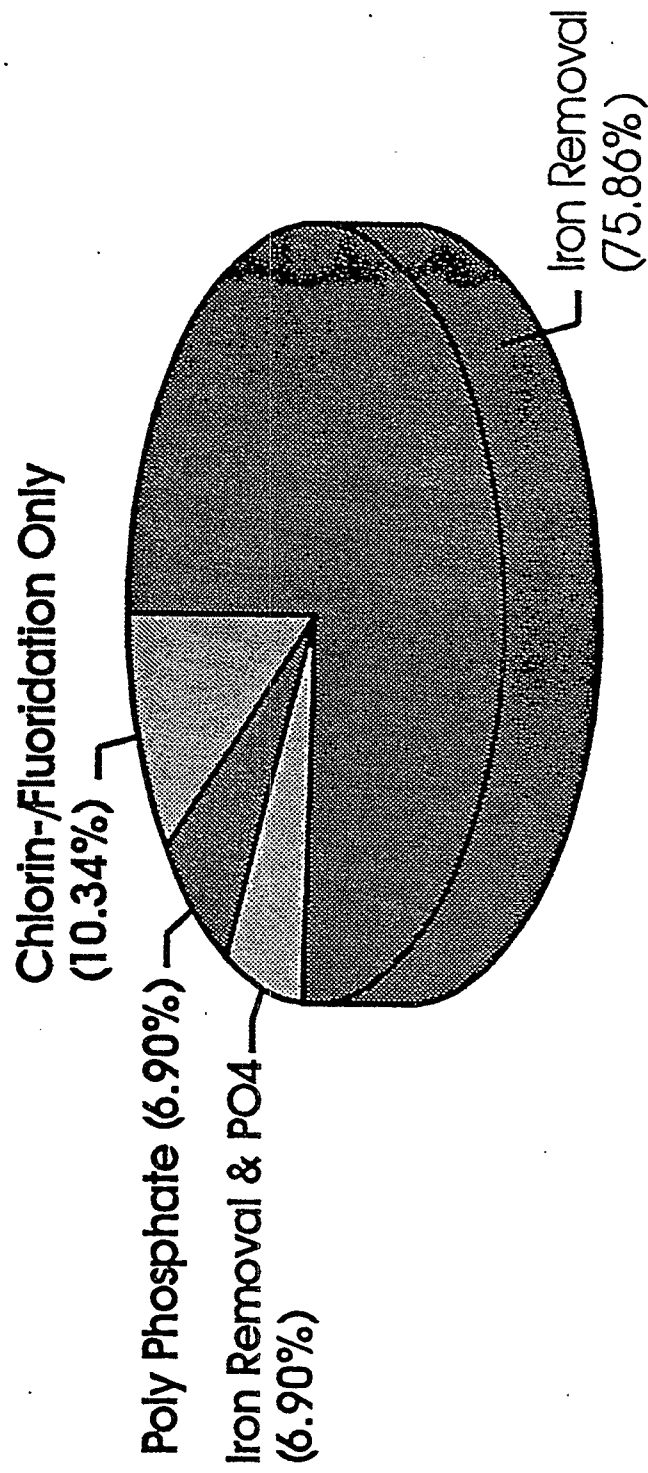


Figure 1

# Treatment Process Used Small Systems with Copper Exceedance

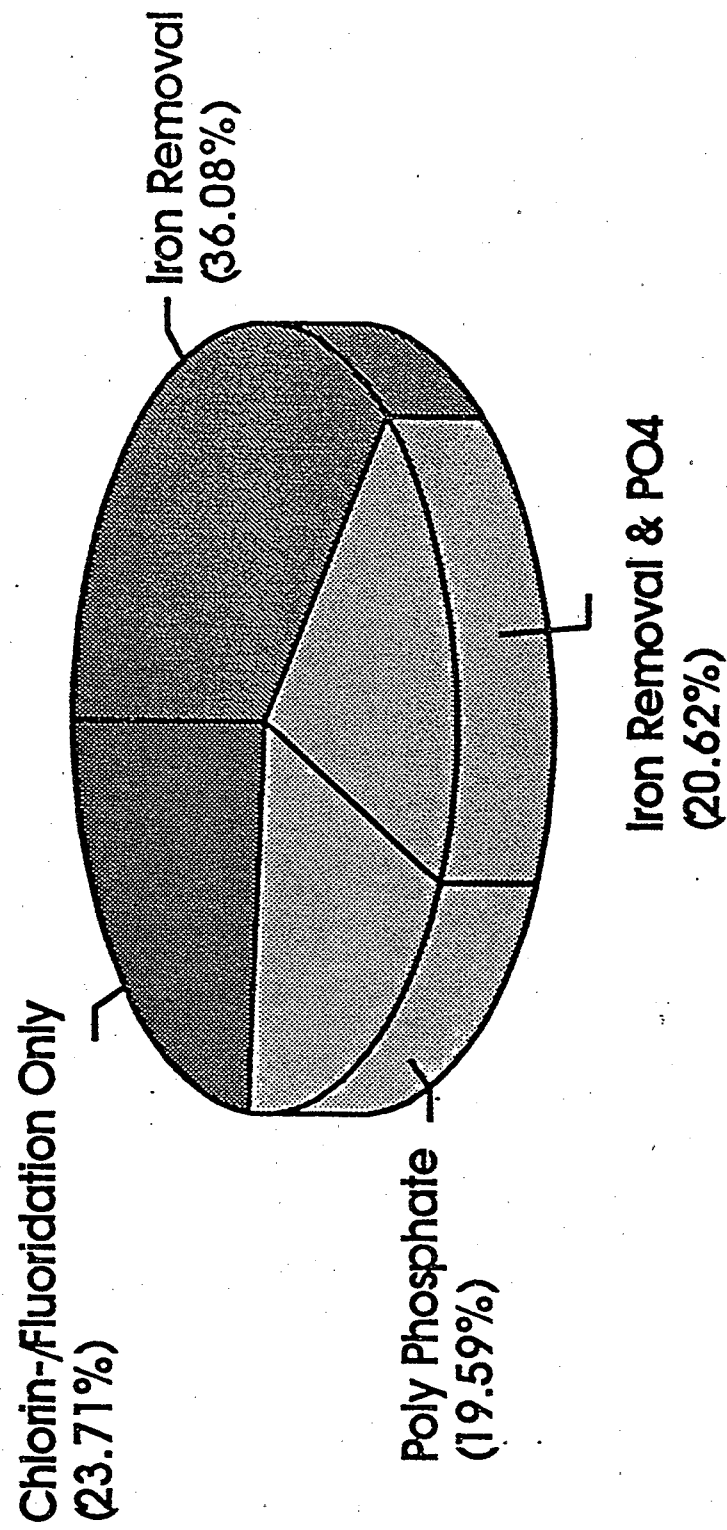


Figure 2

# Treatment Study 1 Blended Phosphate Inhibitor

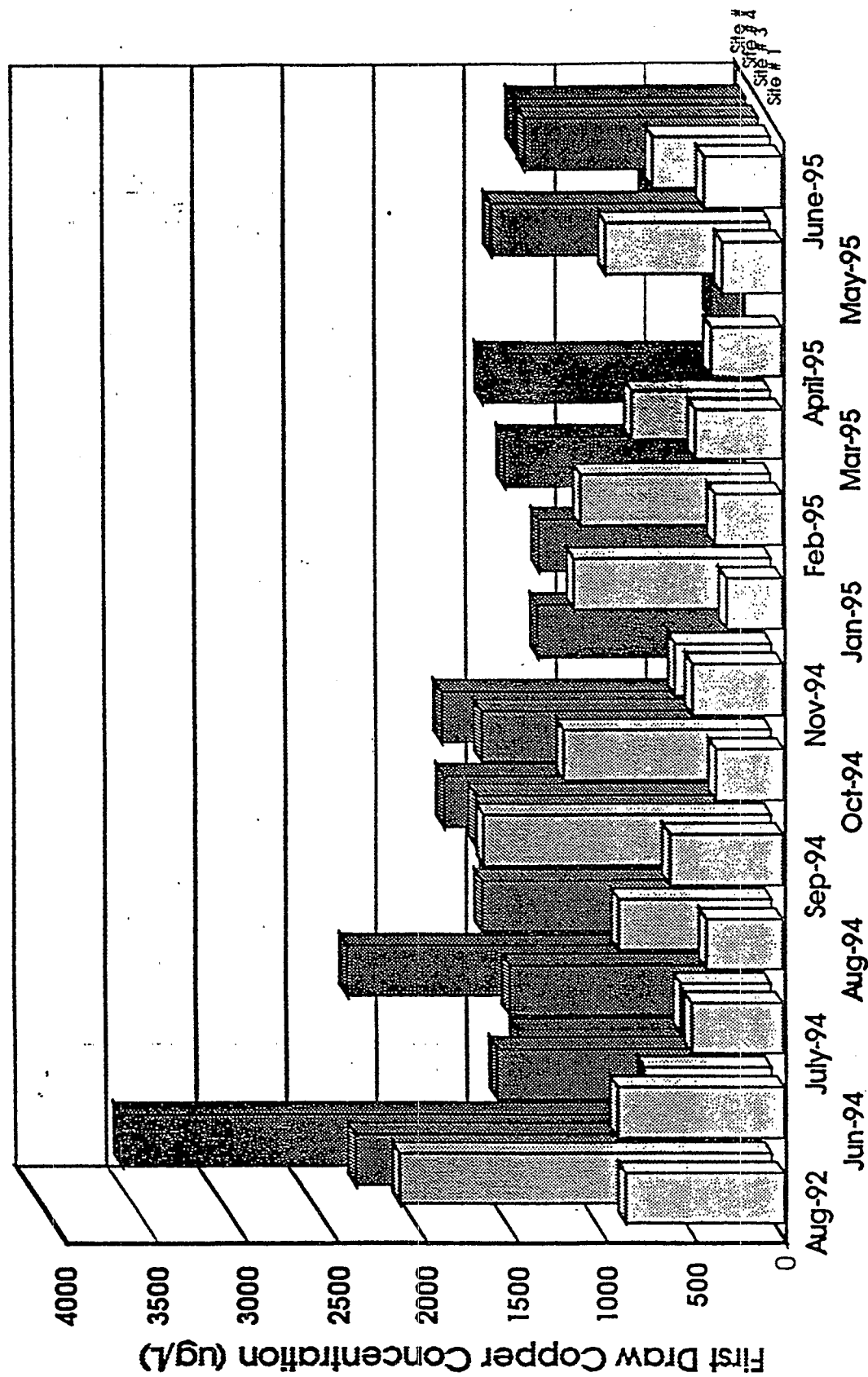


Figure 5

# Treatment Study 2

## Calcium Carbonate Precipitation

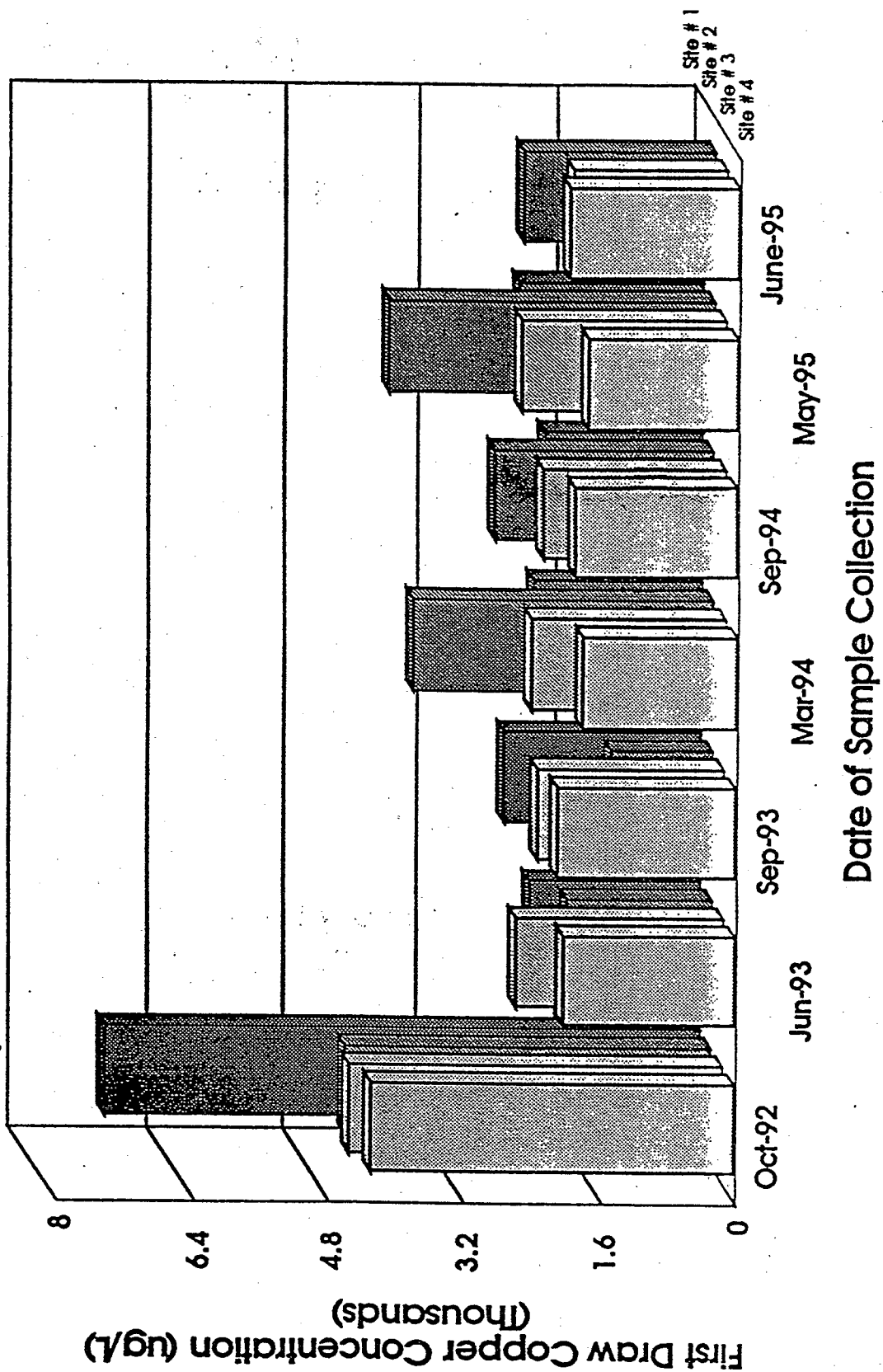
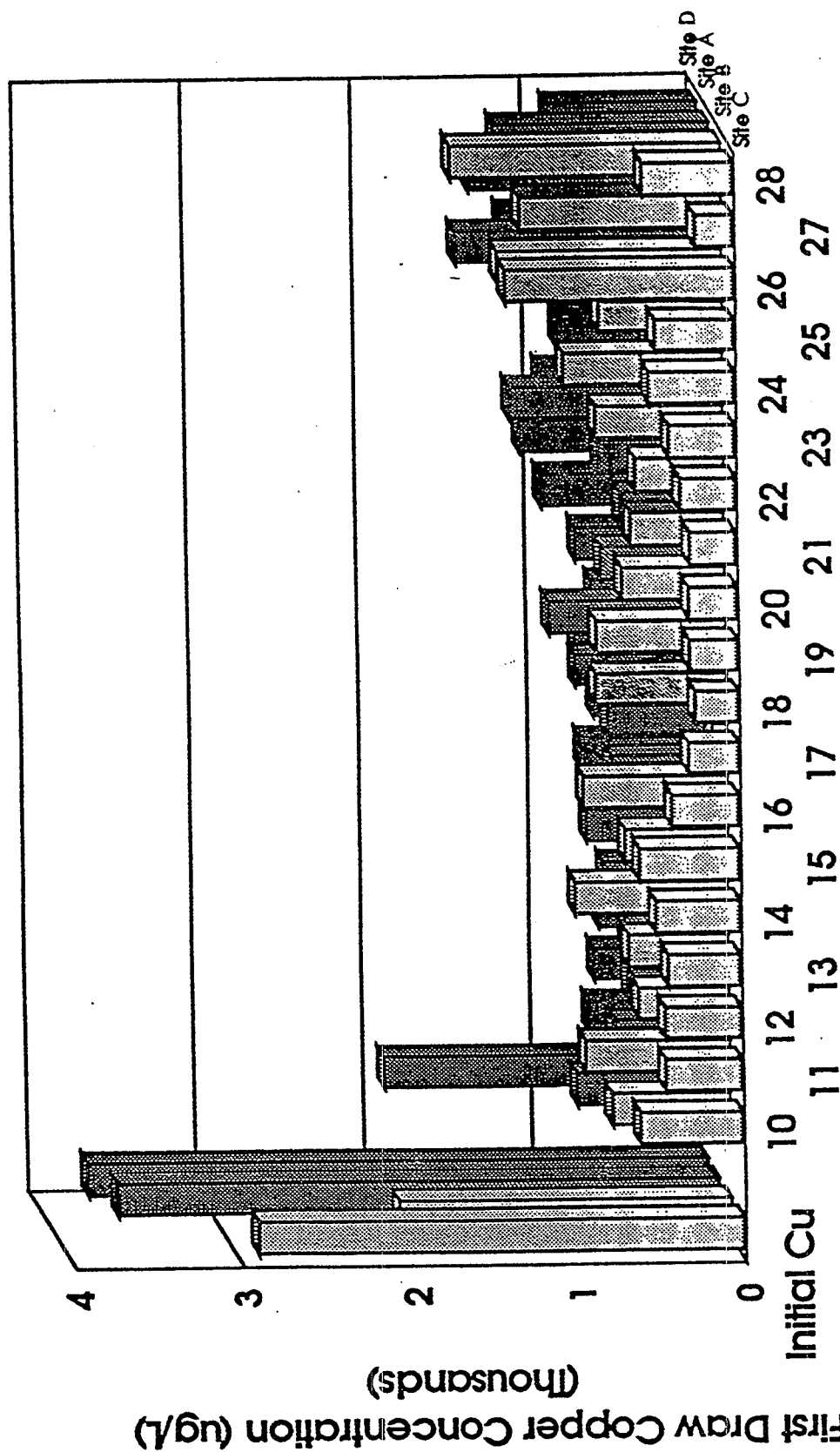


Figure 6

# Treatment Study 3 Zinc-Orthophosphate Inhibitor



Weeks After Treatment Was Initiated

Figure 7



# **An Evaluation of the Secondary Effects of Enhanced Coagulation, With Emphasis on Corrosion Control**

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## **Abstract**

The proposed Disinfectant-Disinfection By-product (D-DBP) Rule will require many water purveyors to meet enhanced coagulation or softening objectives for total organic carbon (TOC) removal as a means of controlling DBP precursors. Enhanced coagulation can be achieved by performing chemical coagulation at lower pH values by increasing the coagulant dose, adding acid, or a combination of the two. Pilot studies using enhanced alum coagulation revealed a number of secondary effects, many of which directly impact lead and copper corrosion. Aluminum, sulfate, pH, and dissolved inorganic carbon were significantly altered during enhanced coagulation. These parameters can directly affect metal solubility and surficial pipe film stability.

## **Introduction**

Under the proposed Disinfectant-Disinfection By-product (D-DBP) Rule, many utilities will be required to meet enhanced coagulation or softening objectives for total organic carbon (TOC) removal as a means of controlling DBP precursors.<sup>1</sup> A recent survey found that 64 percent of responding coagulation plants would comply with the specified TOC removal requirements of the proposed rule.<sup>2</sup> Several researchers have investigated natural organic matter (NOM) control by coagulation and discussed the importance of pH in removal efficiency. Qasim et al.<sup>3</sup> found that TOC removal in natural waters by coagulation and softening was strongly pH dependent and Randtke<sup>4</sup> found that removal of NOM by coagulation was optimum at pH 5.0 to 6.0.

Most coagulation plants that will be required to meet TOC removal requirements under the proposed D-DBP Rule will likely do so by either increasing coagulant dosage, lowering the pH by acidification during coagulation, or a combination of the two. Enhanced coagulation will provide improved removal of DBP precursor material, as well as secondary benefits such as lower chlorine demand, increased disinfectant stability in the distribution system, lower color, and reduced substrate for microbiological growth.<sup>3</sup> However, negative secondary impacts of enhanced treatment must also be addressed to insure that other water quality parameters and treatment plant operations are not compromised. Some of the secondary impacts that must be considered include sludge production, filter run time, inorganic water quality changes, turbidity and particulate removal efficiency, and distribution system corrosion and corrosion control.

The U.S. Environmental Protection Agency's (USEPA's) National Risk Management Research Laboratory (NRMRL), in Cincinnati, Ohio, in conjunction with the University of Cincinnati, conducted bench- and pilot-scale tests to evaluate enhanced coagulation for optimal NOM or DBP precursor removal from a surface water using aluminum sulfate, more commonly referred to as "alum". Results of those studies directly related to the goals of the D-DBP Rule have been previously discussed.<sup>5,6</sup> This paper explores several secondary impacts relative to corrosion control of enhanced alum coagulation based on observed water parameter changes

during pilot-scale studies. Specifically, the effect of pH, dissolved inorganic carbon (DIC) and alkalinity, sulfate and chloride (during ferric chloride coagulation), total organic carbon (TOC), and aluminum on the corrosion and corrosion control will be discussed.

## Experimental

Based on preliminary jar tests studies<sup>6</sup>, East Fork Lake water (Cincinnati, Ohio) was selected for pilot testing. Two parallel pilot-scale treatment plants consisting of rapid mix, flocculation, and sedimentation basins were used to compare conventional and enhanced coagulation as shown in Figure 1. Settled water was chlorinated and sand filtered. The adjustment of pH for corrosion control was made after filtration in the conventional plant. The enhanced plant was split into two parallel filters where pH was adjusted before one filter and after the other. Final pH in all cases was adjusted to approximately 8 using NaOH. Chlorine was fed as NaOCl. A number of water quality parameters were monitored at a variety of locations throughout the plant and are given in Table 1. Operational data including chemical doses, temperature, head loss development and filter run time were also regularly monitored. The sampling described in Table 1 took place on six days between September 7 and September 13, 1994. East Fork Lake water was trucked to the USEPA research facility daily during pilot plant operation.

## Results

Because the results of the pilot study have been presented elsewhere<sup>5,6</sup> and page constraints, data will not be presented or analyzed in great detail. A number of secondary impacts (both positive and negative) beyond the corrosion impacts addressed in this report have also been previously identified in some detail.<sup>7</sup> Positive secondary impacts of enhanced coagulation included: reduction in turbidity, particle counts, coliform and heterotrophic bacterial densities, and chlorine residual. Increased cost and sludge production, and potential future regulatory conflicts such as the proposed sulfate standard were identified among negative secondary impacts. This document lists the differences in water quality between conventional and enhanced coagulation treatment modes that are considered important in lead and copper corrosion control.

Table 2 shows the major average water quality parameter measurements throughout the treatment trains. It should be pointed out that in the case of East Fork Lake water, only 35 percent TOC removal would be required given the TOC (4.8 mg/L) and alkalinity (99 mg CaCO<sub>3</sub>/L) of this water.<sup>8</sup> It is important to note that in these pilot studies, conventional coagulation (29 percent removal of TOC) was compared to optimum coagulation (54 percent removal of TOC). Enhanced coagulation in the regulatory sense (35 percent removal of TOC) was not studied. Thus, findings regarding secondary effects must be viewed as examining the extreme shift from conventional to optimum coagulation rather than the expected shift from conventional to enhanced coagulation.

Alum doses were 44 mg/L (3.7 mg/L as aluminum) and 152 mg/L (13.3 mg/L as aluminum) for conventional and optimized coagulation, respectively, as shown in Table 2. Aluminum concentrations in settled waters were lower after optimized coagulation than after conventional coagulation (0.47 mg/L versus 0.65 mg/L) despite the higher alum dose. This observation follows the established pH-aluminum hydroxide solubility relationship.<sup>9-13</sup> The location of pH adjustment was clearly the most important factor impacting aluminum residuals after the filters, as shown in Figure 2. When pH adjustment was practiced following filtration

(filters F1 and F2), the lowest clearwell aluminum residuals were observed. This results from the lower solubility of aluminum at lower pH values, and retention of unsettled residual alum floc by the filters. However, when the pH was raised to 7.95 prior to filtration (filter F3), aluminum solubility was increased, enabling the passage of more dissolved aluminum into the clearwell. The trade off was that filter run times were shorter in the lower pH waters.

Aluminum levels were the lowest (less than 0.025 mg/L) following optimized coagulation, filtration, and pH adjustment in clearwell 2. This can be explained by the fact that the pH of settled water entering filter 2 was 6.90, which is closest to the minimum solubility of aluminum hydroxide. The highest aluminum levels were observed following optimized coagulation, pH adjustment, and filtration because the pH of the water (pH=7.95) was the highest, resulting in the most soluble aluminum entering the filters. Aluminum concentrations in filter effluents were used to develop the empirical pH-aluminum solubility relationship shown by Figure 3. This diagram clearly follows the known pH-soluble aluminum chemistry of aluminum and trends observed by others.<sup>9-13</sup>

Sulfate increased after both coagulation approaches as a result of the addition of alum as seen in Table 2. Optimally coagulated water contained at least 40 mg  $\text{SO}_4^{2-}$ /L more than conventionally treated water. The point of pH adjustment had no significant impact on sulfate concentration.

In this study, the pH needed to meet optimum enhanced coagulation conditions was 0.7 pH units lower than the pH during conventional coagulation. Without pH readjustment, the drop in pH would result in increased lead and copper solubility and destabilization of existing pipe surface films in the distribution system. Thus, pilot plant finished water pH values were adjusted to near 8 to represent reasonable conditions under the Lead and Copper Rule and to drive DBP reactions under representative conditions.

In addition to the effect of the location of pH adjustment to aluminum residual, another important consideration is the impact of the pH adjustment chemical on finished water quality. Besides chemical costs, chemical feed system costs, and related chemical storage and handling issues, pH adjustment chemicals such as caustic soda (NaOH) or soda ash ( $\text{Na}_2\text{CO}_3$ ) will contribute sodium to the finished water. Although lime was not used in this study for pH adjustment, lime will increase calcium hardness and may contribute aluminum as a result of chemical impurities.

Total inorganic carbon (TIC) was not affected by conventional coagulation; however, TIC decreased significantly from optimized coagulation (see Table 2). The amount of TIC decrease observed (approximately 4 to 5 mg C/L) is clearly far beyond analytical uncertainty for the coulometric method employed.<sup>14</sup>

### Corrosion impacts

**The effect of pH and DIC on lead and copper corrosion.** DIC has been shown to have both a positive and negative impact on corrosion control.<sup>15-17</sup> DIC serves to control the buffer intensity in most water systems, and therefore, sufficient DIC is necessary to provide a stable pH throughout the distribution system for corrosion control of copper and lead.<sup>17-19</sup> However, larger amounts can result in increased lead and copper solubility.<sup>17-20</sup>

The importance of pH to lead and copper solubility is well-established. Therefore, the reduction of pH during enhanced coagulation will likely have to be counteracted by pH adjustment following treatment to maintain corrosion control objectives outlined under the Lead and Copper

Rule<sup>21-23</sup> or state or local wastewater discharge requirements for copper. Without pH readjustment, the drop in pH from coagulation would result in increased lead and copper solubility and destabilization of existing pipe surface films in the distribution system, if corrosion control is currently being practiced through pH/DIC adjustment. Even the effective use of orthophosphate or blended phosphate chemicals for lead or copper control may require a higher pH than that achieved during enhanced coagulation.<sup>15-17</sup>

Considerable research has been devoted to the study of the aqueous speciation of copper in natural waters and seawater, in which the role of carbonate species was extremely important.<sup>24-30</sup> The concept of the significance of carbonate complexation was then applied to drinking waters with indications that high DIC levels would aggravate cuprosolvency.<sup>31,32</sup> Recently, a variety of new research has helped define the complicated interrelationships of pH, DIC, orthophosphate, the formation of metastable solids, and plumbing material age on cuprosolvency and observed copper levels in drinking waters.<sup>19,20,33-40</sup>

Figure 4 illustrates the effect of DIC and pH on cupric hydroxide solubility, as would be the case with relatively young plumbing systems. An increase in copper solubility with lower pH and higher DIC is evident from the figure. Above a pH of approximately 9.5, an upturn in solubility is predicted, caused by carbonate and hydroxide complexes increasing  $\text{Cu}(\text{OH})_2(\text{s})$  solubility. In the pH range of approximately 6.5 to 9, significant increases in copper solubility are predicted from the addition of even small amounts of carbonate, although maximum solubility remains less than about 0.3 mg/L.

Figure 5 shows a solubility diagram for copper(II), corresponding to equilibrium with either  $\text{Cu}_2(\text{OH})_2\text{CO}_3(\text{s})$  (malachite) or  $\text{CuO}(\text{s})$  (tenorite), whichever is thermodynamically stable at a given pH/DIC point. This kind of situation represents the case with aged plumbing, though the number of years of exposure needed to achieve these stable solids likely depends greatly on the water chemistry of the system.<sup>19,34</sup> Several important contrasts in cuprosolvency behavior between the case represented by Figure 4 as opposed to the assumptions behind Figure 5 should be noted. If  $\text{Cu}_2(\text{OH})_2\text{CO}_3$  (malachite) is present and capable of forming, below a pH of about 6.5 the addition of DIC is predicted to decrease cuprosolvency, but increase cuprosolvency above about pH 7. There is a small transition zone between these values where the first approximately 5 mg/L of DIC should slightly reduce copper solubility, but additional carbonate would decrease it or have essentially no effect. In an aged system, below a pH of about 8, cuprosolvency becomes essentially insensitive to DIC above approximately 30 mg C/L. Malachite formation would enable attainment of 1.3 mg/L after stagnation below approximately pH 6.5 for all DIC levels. This is in stark contrast to the effect of pH and DIC when only cupric hydroxide is formed, where a pH of over 7 would be necessary to stay under 1.3 mg/L for long stagnation times at very low DIC levels, and over 7.5 for systems with high DIC.

In a simple system of metallic lead immersed in water containing dissolved carbonate species, the solubility will be controlled by either the simple lead carbonate ( $\text{PbCO}_3$ , cerussite) or one of the two basic lead carbonates,  $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$  (hydrocerussite) or  $\text{Pb}_{10}(\text{CO}_3)_6(\text{OH})_6\text{O}$  (plumbonacrite). Above approximately pH 12.5, lead hydroxide ( $\text{Pb}(\text{OH})_2$ ) may form. The conventional solubility constants for lead hydroxide reported in the literature vary over about five orders of magnitude ( $\log K_{sp}$  from -19.85 to -14.9). Samples of deposits from potable water systems and accompanying dissolved lead concentrations do not indicate either lead oxide ( $\text{PbO}$ , massicot or litharge) or lead hydroxide to be active in governing lead solubility, though  $\text{PbO}$  is frequently found in underlayers of surface films. Under very oxidizing conditions, the lead(IV)

solid  $\text{PbO}_2$  may form, and it has occasionally been found in pipe deposits.  $\text{PbO}_2$  is less soluble than any of the  $\text{Pb(II)}$  carbonates or hydroxycarbonates.

When only pH and carbonate concentration effects are considered, lead solubility is shown by Figure 6. Detailed computations show that the minimum lead solubility is at a pH of approximately 9.8, with a DIC concentration of between 3.6 and 4.8 mg C/L (0.0003 to 0.0004 M).<sup>15,17,31</sup> Above approximately pH 8, the closeness of the lines and steepness of the slopes represent the high sensitivity to both pH and DIC. These properties, plus the reversal of solubility trends above about 5 mg C/L DIC result from the stability of the solid  $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$  (hydrocerussite) plus strong hydroxide and carbonate complexation. The downward-trending lines for pH 6 and 7 are caused by the formation of  $\text{PbCO}_3$  (cerussite), and an absence of carbonate complexation. In the lead carbonate stability region, below approximately pH 8 and above approximately 25 mg C/L, lead solubility is not very sensitive to either pH or DIC, although the trend is toward slightly lower levels as DIC is increased below about pH 7.5. Detailed discussions of lead solubility controls for drinking water are readily available elsewhere.<sup>15,17,18,31,41,42</sup>

**The effect of chloride, sulfate, and aluminum on lead and copper corrosion.** The effect of chloride, sulfate and aluminum on copper corrosion has recently come under renewed investigation, as a result of the interest in controlling cuprosolvency for drinking water or waste water regulations. Interesting results were obtained from X-Ray diffraction and Energy-Dispersive X-Ray (EDXA) analyses of the deposits formed on experimental pipes used in DWRD pipe loop studies.<sup>19,34</sup> Significant diffraction peaks for  $\text{Cu}_4(\text{OH})_6\text{SO}_4 \cdot \text{H}_2\text{O}$  (posnjakite) were found in pipes from experiments at pH 8 and pH 9 with 5 mg C/L DIC, even though sulfate levels were only approximately 30 mg/L. This mineral has also been reported in some copper pipes in a German study of pipe corrosion in a hospital.<sup>43</sup> Diffraction peaks likely corresponding to the solid  $\text{Cu}(\text{Cl},\text{OH})_2 \cdot 2\text{H}_2\text{O}$  (calumetite) were found, particularly at pH 8 and 7. Qualitative elemental analysis confirmed the presence of S, Cl and also Al on the pipe surfaces. A large peak and a secondary peak apparently consistent with the solid  $\text{CuAl}_4\text{SO}_4(\text{OH})_{12} \cdot 3\text{H}_2\text{O}$  (chalcoalumite) were found on the pH 7 specimen, but only a corresponding minor peak was found on the pH 8 sample. Additional peaks for  $\text{Cu}_2(\text{OH})_2\text{CO}_3$ ,  $\text{CuO}$ , and  $\text{Cu}_2\text{O}$  were also identified. From the qualitative elemental analysis, the Al concentration on the pipe appeared higher at pH 7, consistent with the general trend in solubility of many aluminum minerals, and a statistically-significant decrease in aluminum in the water during the pH 7 experiment. The presence of aluminum on the pipe is also noteworthy because of the low Al concentration in the water in all three experimental systems ( $< 0.1$  mg/L), which suggests possibly a strong role for aluminum in the formation of natural diffusion barriers in plumbing and distribution systems.

Examination of copper leaching results from DWRD studies at pH's  $> 8$  show the copper levels were consistently above the solubility of copper predicted by cupric hydroxide or oxide models when elevated levels of sulfate ( $> 30$  mg  $\text{SO}_4^{2-}$ /L) were present.<sup>19,34</sup> An example of this effect is shown in Figure 7, representing data from 72-hour stagnation samples from pH-adjusted Cincinnati tap water containing approximately 70-120 mg/L of sulfate.<sup>19,34</sup> A detailed literature investigation suggested that above some threshold combination of pH and sulfate concentration, metastable hydroxysulfate solids may form, rather than the more protective cupric hydroxide or tenorite.<sup>19,34</sup> Edwards, et al.<sup>33,40</sup> showed that sulfate increased copper corrosion rates in water. Rehling and Edwards<sup>44</sup> attributed higher copper corrosion rates in enhanced coagulated waters to additional sulfate carryover from the alum coagulant and also showed lower copper corrosion rates from chloride carryover from ferric chloride enhanced coagulation. The effect of sulfate on

copper corrosion is significant; however, the degree sulfate enhances copper solubility and effects copper action level exceedences is not fully known. The greatest negative impact of sulfate on cuprosolvency seems to be for waters with a pH over 8, based on early USEPA experiments at low DIC. Increases in copper solubility resulting from increased sulfate levels may more likely be a concern for wastewater discharge exceedences of copper.

To add to the confusion about sulfate effects, equilibrium chemical modeling shows that there is some potential that the same cupric hydroxysulfate solids that cause increased cuprosolvency above pH 8 may actually reduce cuprosolvency below approximately pH 7, relative to the solubility of cupric hydroxide on young plumbing.<sup>19</sup> This hypothesis needs experimental verification.

Several researchers have considered possible effects on lead solubility of simple anions, such as nitrate, chloride, and sulfate. Beccaria et al.<sup>45</sup> used a variety of electrochemical and x-ray techniques to study the corrosion of lead in seawater, which provided an extreme case for effects of chloride and sulfate. During the initial passivation stage,  $\text{Pb(OH)Cl(s)}$  and  $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2(\text{s})$  were found to be constituents in the deposit. After long immersion periods,  $\text{PbCO}_3 \cdot \text{PbCl}_2(\text{s})$ ,  $\text{Pb}_2\text{O}_3(\text{s})$ ,  $\text{PbO(s)}$ , and  $\text{PbCl}_2(\text{s})$  were also found. The presence of sulfate ions did not interfere with the film formation, and sulfate ions did not precipitate to form a lead sulfate solid on the surface. In solutions with extremely high sulfate concentrations, some basic lead sulfate solids were found, notably  $\text{Pb}_3(\text{SO}_4)_2(\text{OH})_2$  and an unidentified compound with a 1:1 oxide:sulfate ratio.

Lead(II) forms somewhat weaker complexes with sulfate and chloride than with carbonate, either of which might occasionally be found in water supplies at a sufficiently high level to impact lead solubility. The greatest impact, if it happened, would be at relatively low pH and low DIC levels, where less lead is complexed by hydroxide and carbonate species. Calculations were performed for chloride, sulfate, and for both sulfate and chloride at DIC levels of 3-30. The ionic strength of the waters for these modeling calculations was set to 0.05 mol/L, to allow higher chloride and sulfate concentrations more plausibly. However, there appears to be no significant impact of practical proportions is decided based on solubility.

Ironically, reducing aluminum residuals could cause the destabilization of Al-containing films built up in domestic plumbing over many years of normal plant operation. These films have been suggested as having been beneficial to lead and copper leaching from plumbing.<sup>17,42,46,47</sup> One study has observed an increase in lead mobilization apparently resulting from sloughing-off of Al-based pipe scales.<sup>47</sup>

Considerable recent evidence for a corrosion-reducing aluminum or aluminosilicate film has been described in a study conducted by the Denver Water Department, where significant precipitated coatings were inhibiting lead and copper release from corrosion control pipe loop study test rigs.<sup>46</sup> For utilities adding sodium silicate as a corrosion inhibitor, residual aluminum from conventional coagulation may enable additional protective films to form. The solubility and complexation chemistry of aluminosilicates is highly complex and somewhat controversial in its details.<sup>48-52</sup> However, aluminosilicate minerals clearly are important naturally-forming solids, and are geochemically plausible for many drinking waters with a near-neutral to slightly acidic pH.

An adverse affect of aluminum on copper piping in hot water lines was reported by Tunturi,<sup>53</sup> who found pitting failures associated with deposition of aluminum hydroxide from a drinking water with 0.3 to 0.7 mg/L.

As described earlier, aluminum has a tendency to form several highly-insoluble orthophosphate compounds under certain chemistry conditions. Whether or not the formation of

such solids would occur in the distribution system if a water system was dosing orthophosphate is not known, and requires more investigation. Depending upon the surface interaction properties of any of these solids formed, the result could be an increased protection from additional surface film formed, increased turbidity in hot or cold water, or depletion of orthophosphate dosed and consequent lessening of passivation of lead or copper.

**The effects of NOM on lead and copper corrosion.** A goal of the D-DBP Rule is lower TOC concentrations prior to chlorination, so that lower DBP concentrations of regulated and unregulated DBPs will result.<sup>1</sup> The impact of TOC on lead and copper solubility and in the structure of protective films, however, may be significant.

Many investigators have looked at interactions between  $\text{Cu}^{2+}$  and dissolved natural organic matter. Some studies suggest that while copper can form complexes with NOM ligands (sometimes called DOM for "dissolved organic matter"), at concentrations of copper typical of drinking waters, copper speciation is more likely dominated by hydrolysis or carbonate complexes.<sup>54-56</sup>

$\text{Cu}^{2+}$  ion may also bind with adsorbed organic material containing appropriate functional groups. The binding with adsorbed organic matter seems to be stronger than direct binding with surface sites on several materials tested.<sup>57</sup> Copper present as an organic complex may bind preferentially with adsorbed organic material.<sup>57,58</sup> These studies suggest that some reduction in copper concentration may be caused by adsorbed organic material acting as either a diffusion barrier, or as a less-soluble corrosion film.

Some other studies suggest, however, that NOM may play a major role in the aqueous speciation of cupric ion, particularly when carbonate concentrations are low.<sup>59,60</sup> Organic ligands produced by marine diatoms and during diatom blooms have been shown to strongly complex copper, though usually at low copper concentration.<sup>61,62</sup> Unsaturated organic ligands were also shown in experiments at pH's generally lower than drinking water to increase the dissolution rate of copper metal in the presence of cupric ion, by a complicated interaction affecting the electron transfer rate between  $\text{Cu(s)}$  and  $\text{Cu}^{2+}$ , and by stabilizing the  $\text{Cu(I)}$  state by complexation.<sup>63</sup>

The significance of NOM to cuprosolvency relative to drinking water concentrations of copper and competing non-metals and ligands has not been conclusively determined, though it is an area under active investigation by some research groups in the United States. Research into copper plumbing pitting has indicated that some NOM may actually alleviate the propensity of a water to cause pitting attack, and possibly alter some scale formation characteristics of uniform copper corrosion.<sup>64</sup> Any effect on cuprosolvency will likely be stronger in untreated surface water supplies than in ground waters having very low TOC, or historically coagulated and filtered surface waters.<sup>65,66</sup>

In many potable water systems, the behavior of lead is complicated by its interaction with organic ligands, or colloidal material, or both.<sup>67</sup> Some other studies have found lead associated with flakes of nonadherent corrosion products related to iron and organic material.<sup>68</sup>

Samuels and Meranger<sup>69</sup> found concentrated "fulvic acid" solutions of pH 6.2 to be aggressive toward lead in solder and brass, and Thresh<sup>70</sup> believed that organic material in the water could prevent the deposition of films on lead surfaces by enhancing the solubility of lead. Miles found that the organic content of moorland waters appeared to accelerate the initial attack on the lead surface.<sup>71</sup> Harrison and Laxen<sup>67</sup> analyzed water from three localities in the United Kingdom and found that significant quantities of dissolved lead (over 50 percent) in some samples appeared to be found in organic complexes. Therefore, simple solubility computations that



include only inorganic species may underestimate the levels of dissolved lead attainable in a distribution system. Including the problem with associations with colloids or nonadherent scales, even though the inorganic *dissolved* lead equilibria may be accurately predicted given enough information, the accurate prediction of observed levels of *total* lead may not be possible.

In contrast to NOM species that may enhance metal solubility, organic material that can adsorb or otherwise adhere to the inside surfaces of the pipe could serve to decrease lead solubility. Theoretical interpretations are hindered by the lack of characterization of the numerous types of organic materials involved. Some simple experiments by Sheiham and Jackson<sup>41</sup> on two waters with varying degrees of natural color suggested that only highly colored waters might have a significant impact on lead corrosion. They emphasized that this conclusion must be treated with extreme caution because only two waters were tested and because the organic component characteristics might vary from place to place. Campbell has unambiguously expressed the opinion that at least some NOM species provide an effective natural inhibitor for copper dissolution,<sup>65,66</sup> and that flocculation can remove the protective substance.<sup>72</sup>

In drinking water systems, the presence of extensive amounts of metal piping as a source creates a considerably different environment than natural water or aquifer systems where NOM/copper complexation has been studied most extensively. In addition to pH and ionic strength, which have been widely acknowledged to be important in complexation studies with NOM, consideration must also be given to the considerable competitive role that cupric carbonate, hydroxide, and hydroxide/carbonate complexes must play, particularly as the pH increases above 7. Further, depending on source water and disinfection conditions, the redox potential of drinking waters can vary over a wider range than natural systems, and a variety and quantity of solids may exist that are also not present in ground waters, lakes and sea water.

The behavior of organic ligands can be modified by their association with or adsorption on particle surfaces, and some natural ligands, such as fulvic acid, may enhance metal removal by precipitation.<sup>73,74</sup> NOM species interactions with surfaces and dissolved metal ions are greatly affected by the concentrations of other metals and ligands in the ionic medium, with their own competitive complexation and surface-binding effects, and the relative rates of reactions of the NOM ligand species with trace metals as opposed to major ions such as calcium.<sup>74,75</sup> Aluminum in conjunction with sulfate may be an important agent in assisting particle formation and possible surface adsorption of NOM.<sup>76</sup> Adsorption films on actual pipe surfaces may take dozens of years to form, so they are not amenable to laboratory study. Studies are further complicated by the fact that the natural ligand or adsorbing molecules are difficult to identify and quantify, and may be altered by isolation from their natural water chemistry matrix.

## Conclusions

A number potential secondary impacts on lead and copper corrosion have been identified. Specific negative impacts on lead and copper corrosion include: (1) Possibly reduced protection from NOM and Al-containing diffusion barrier or passivation films, (2) Increased corrosion control costs from additional pH adjustment and possible need for corrosion inhibitor additions, and (3) Increased sulfate levels causing increased cuprosolvency under some pH/DIC conditions.

In this study, the use of ferric chloride or other iron-based coagulants was not investigated in similar detail to alum. A general prediction about its effect is that chloride effects on copper(II) or lead(II) corrosion, at the likely chloride levels, should be insignificant.

The removal of NOM and absence of aluminum will cause the potential for passivation or

diffusion barrier film destabilization as noted above. The long-term practical impact of this potential is unknown, as it depends on the unknown tendency for reversibility of the different existing pipe deposits in the distribution systems.

In contrast to the generally negative anticipated impacts of enhanced coagulation there are two anticipated benefits. First, if a water supply has particular NOM species that are effective complexants for lead and copper, reduced metal levels might ultimately result after complete implementation of the combination of coagulation changes and corrosion control. Second, there may be reduced aluminum residuals in the distribution system, if those levels are of concern for reasons of health, turbidity control, or possible hot water pitting enhancement.

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### Disclaimers

Mention of commercial names does not constitute endorsement or recommendation by the agency. The views expressed in this paper are those of the authors, and do not necessarily reflect USEPA policy.

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Table 1. Sample parameters and sampling sites.

Location #	Location Description	Metals <sup>a</sup>	Wet <sup>b</sup> Chemistry	pH	Alkalinity	TIC	UV/TOC	DBPs <sup>c</sup>	Turbidity	Particle Counts	Micro. <sup>d</sup> Chlorine
1	Raw water	X	X	X	X	X	X	X	X	X	X
2	Conventional mixing	X									
3	Conventional flocculated										
4	Conventional settled	X	X	X	X	X	X	X	X	X	X
5	Conventional filtered	X	X	X	X	X	X	X	X	X	X
6	Conventional clearwell	X	X	X	X	X	X	X	X	X	X
7	Optimized mixed	X		X							
8	Optimized flocculated										
9	Optimized settled	X	X	X	X	X	X	X	X	X	X
10	Optimized filtered, pH adj. after filter	X	X	X	X	X	X	X	X	X	X
11	Optimized clearwell, pH adj. after filter	X	X	X	X	X	X	X	X	X	X
12	Optimized filtered, pH adj. before filter	X	X	X	X	X	X	X	X	X	X
13	Optimized clearwell, pH adj. before filter	X	X	X	X	X	X	X	X	X	X

<sup>a</sup> Includes Al, Ca, Cu, Fe, Mg, Mn, Na, Pb, Si, Sn, Zn

<sup>b</sup> Includes chloride, silicate, sulfate

<sup>c</sup> THMs, HAAs, and TOX

<sup>d</sup> Total coliforms, and heterotrophic plate count bacteria using R2A media.

Table 2. Average water quality at stages of conventional and optimized pilot plant operations using East Fork Lake water.

Analyte, mg/L	Raw	Conventional Treatment				Optimized treatment					
		Mixing	Settled	Filter 1*	CW 1	Mixing	Settled	Filter 2*	CW 2	Filter 3**	CW 3
Aluminum	0.081	3.699	0.648	0.080	0.089	13.286	0.472	<0.025	<0.025	0.291	0.288
Calcium	31.8	31.6	31.5	32.6	32.4	31.4	31.4	34.1	33.8	31.1	31.1
Iron	0.071	0.077	0.009	<0.002	<0.002	0.084	0.005	0.004	0.002	<0.002	0.002
Magnesium	10.4	10.4	10.4	10.4	10.5	10.4	10.4	10.6	10.5	10.3	10.4
Sodium	6.25	6.21	6.33	11.79	14.83	6.36	6.32	10.29	25.57	29.83	29.40
Alkalinity, as CaCO <sub>3</sub>	99	NA	81	92	90	NA	35	40	74	67	69
Chlorine dose, mg/L		NA	NA	4.81	NA	NA	NA	3.99	NA	4.07	NA
Chloride	13.34	NA	13.38	NA	19.20	NA	13.38	NA	18.29	NA	17.69
Silicate, as SiO <sub>2</sub>	1.03	NA	1.02	NA	1.29	NA	1.00	NA	1.02	NA	1.00
Sulfate, as SO <sub>4</sub>	25.0	NA	43.6	NA	42.6	NA	88.0	NA	86.5	NA	85.5
TTC, as C	20.5	NA	20.5	20.4	20.6	NA	15.4	14.7	16.8	16.2	16.3
pH	8.16	NA	7.37	7.49	7.99	NA	6.68	6.90	7.80	7.95	8.06
Turbidity, NTU	3.37	NA	0.99	0.24	0.21	NA	0.73	0.17	0.15	0.18	0.13
Alum dose, mg/L		44	NA	NA	NA	152	NA	NA	NA	NA	NA

NA - Not analyzed

TIC - Total inorganic carbon

CW - Clearwell

\* pH adjusted after filter

\*\* pH adjusted before filter

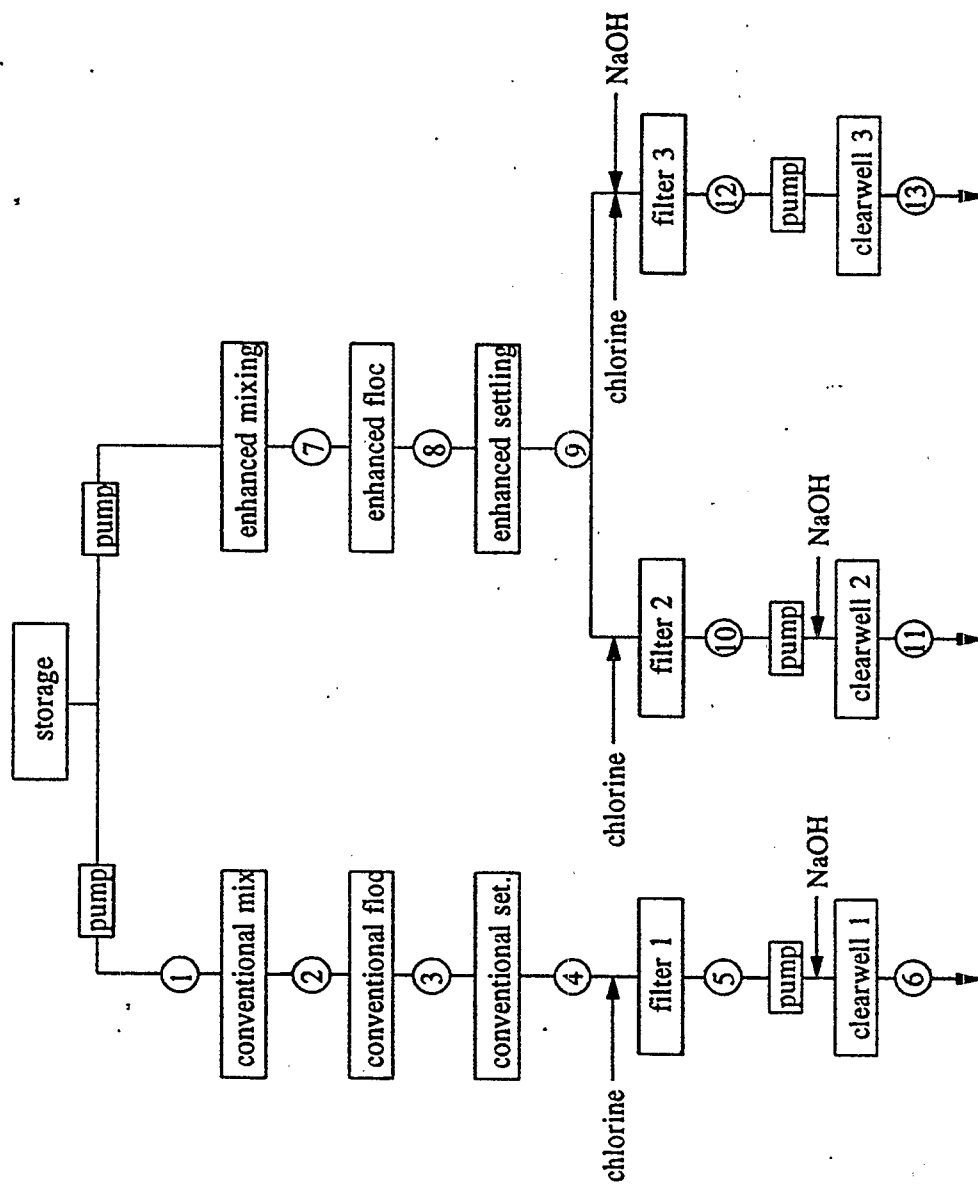


Figure 1. Pilot plant schematic diagram.

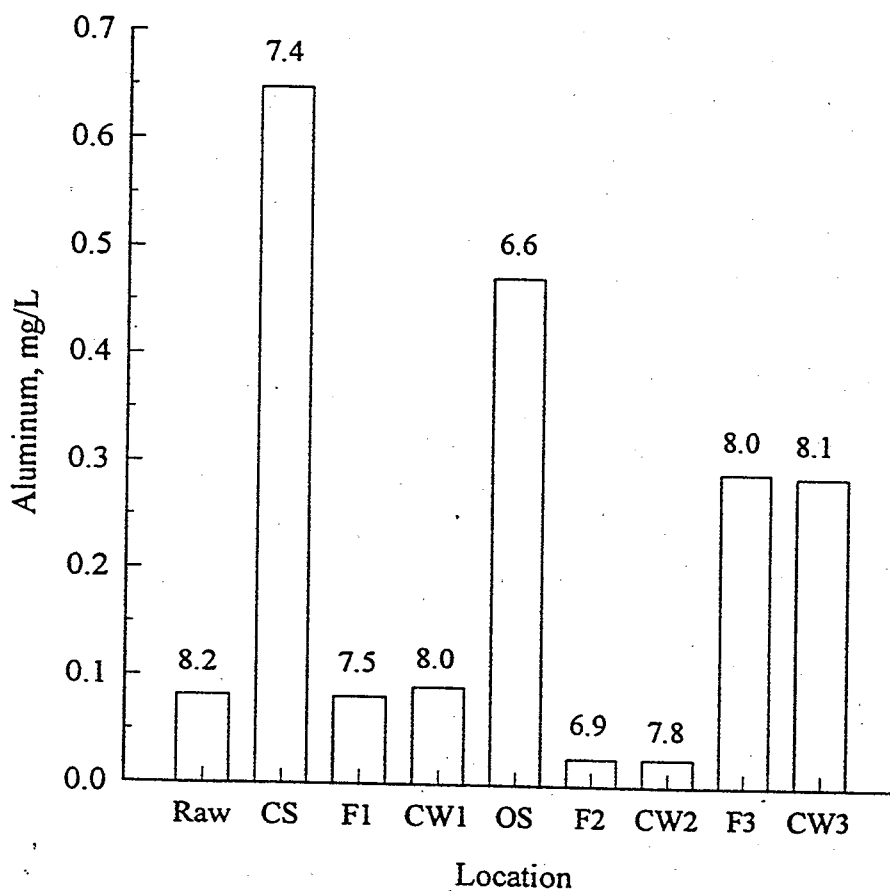


Figure 2. Aluminum residual at stages of pilot plant operation using East Fork Lake water (CS- conventional settled, CW- clearwell, OS- optimized settled, F- filter). The average pH values are shown above bar.

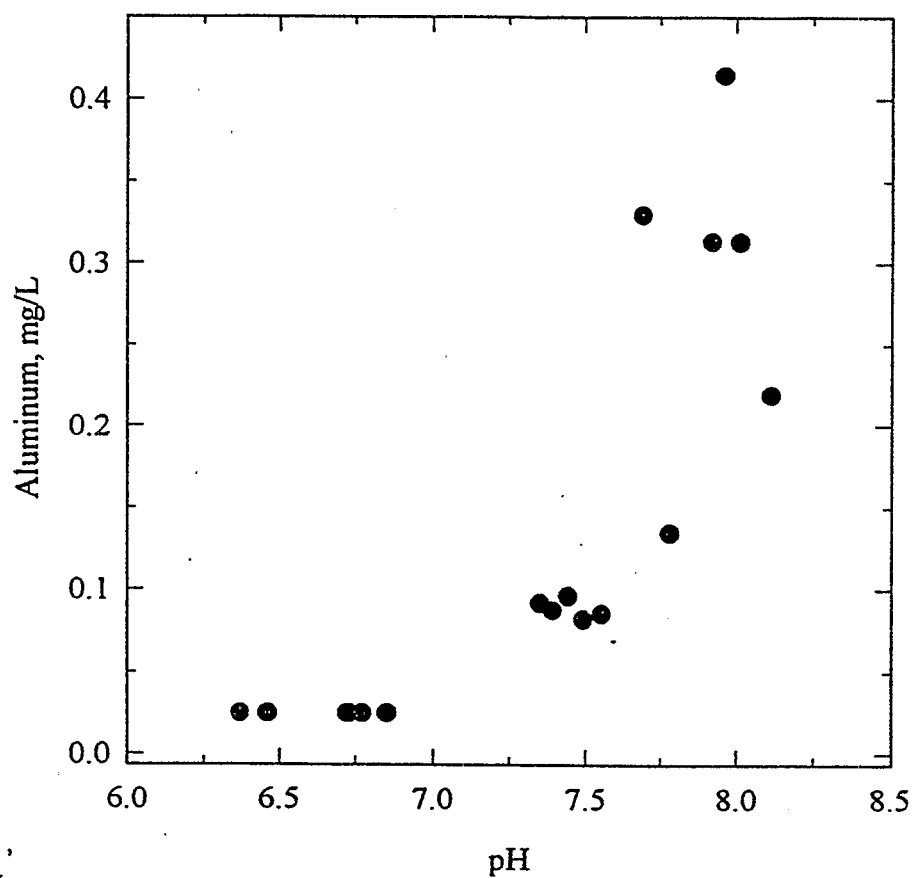


Figure 3. Residual aluminum after filtration as a function of pH in the filter influent. Aluminum concentrations represent all filters.

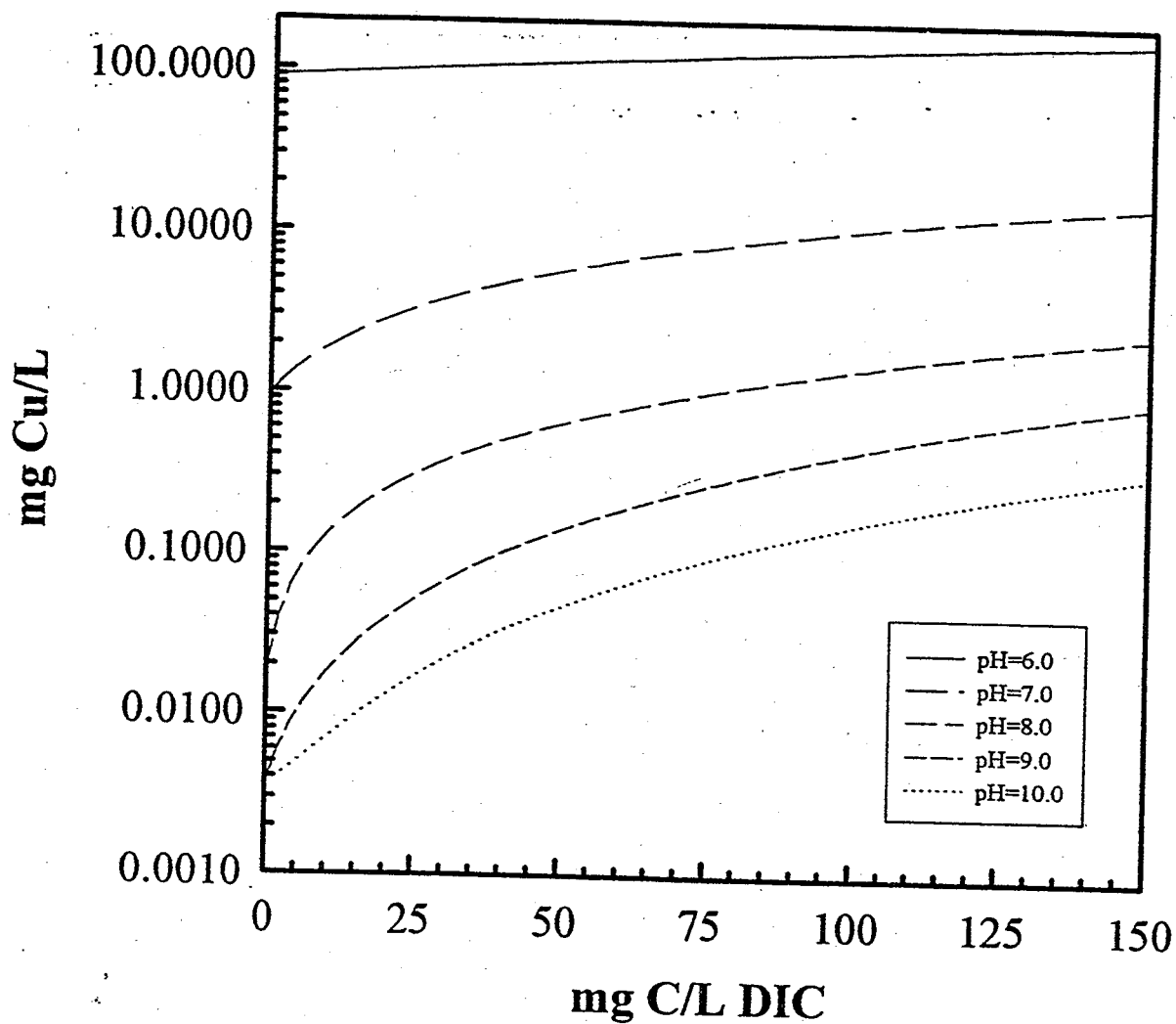


Figure 4. Solubility of copper(II) in response to pH and DIC, assuming equilibrium with  $\text{Cu}(\text{OH})_2$  solid at 25° C and  $I=0.02$ .

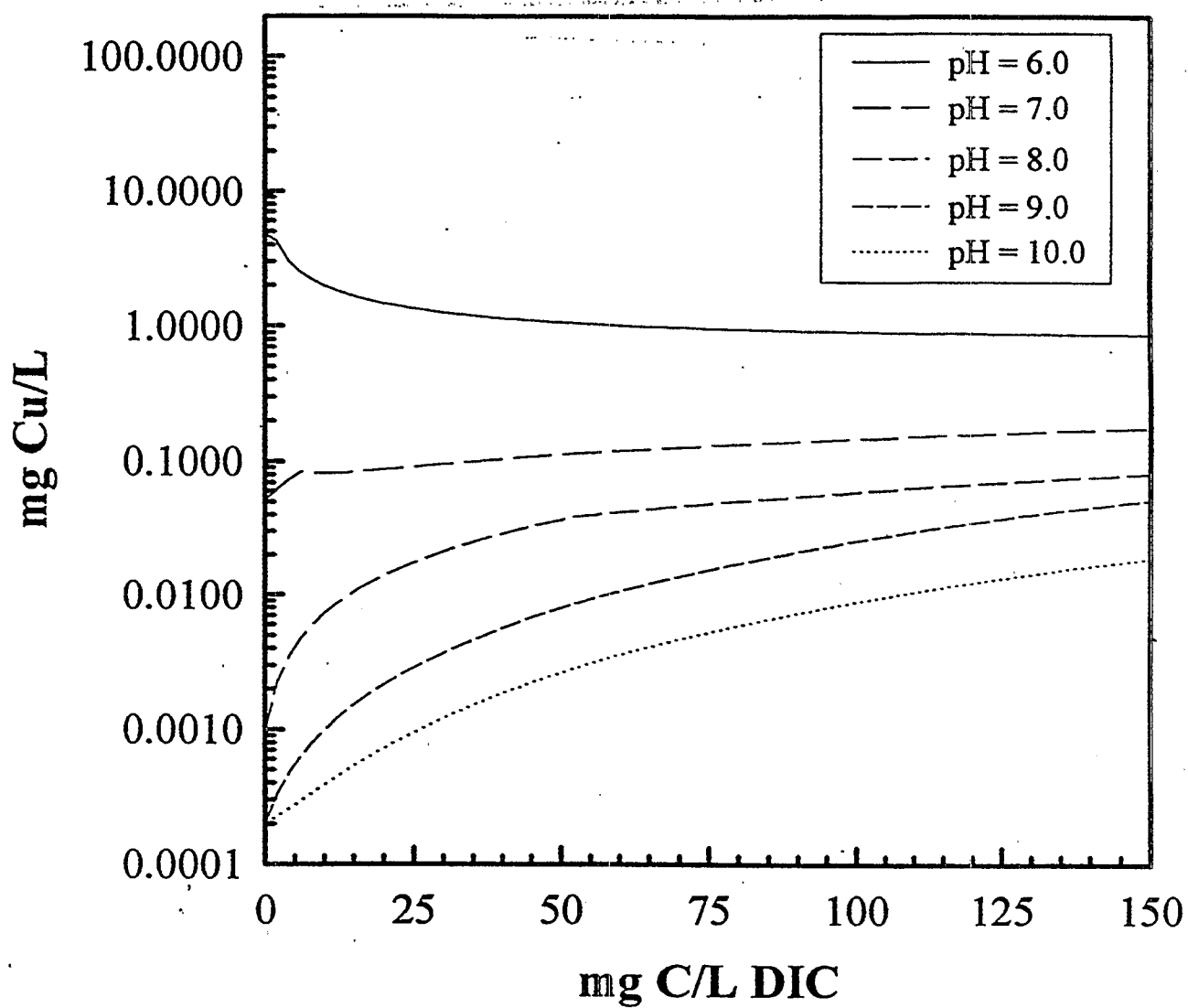


Figure 5. Solubility of copper(II) in response to pH and DIC, assuming equilibrium with  $\text{Cu}_2(\text{OH})_2\text{CO}_3$  and  $\text{CuO}$  solid at  $25^\circ\text{C}$  and  $I=0.02$ . This would represent a case of aged plumbing.



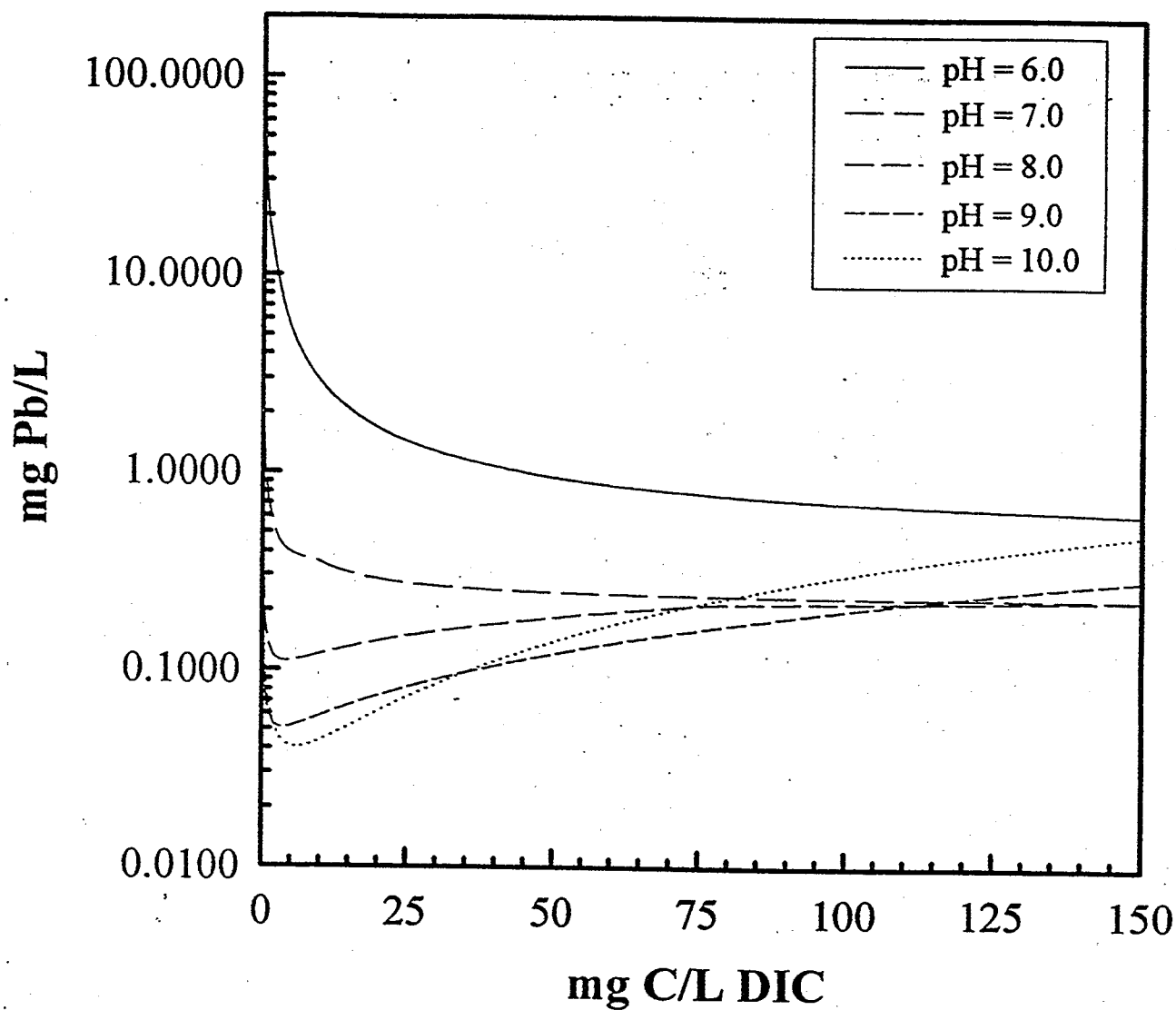


Figure 6. Solubility of lead(II) in response to pH and DIC, assuming equilibrium with  $\text{PbCO}_3$  or  $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$  solids at  $25^\circ\text{C}$  and  $I=0.02$ .

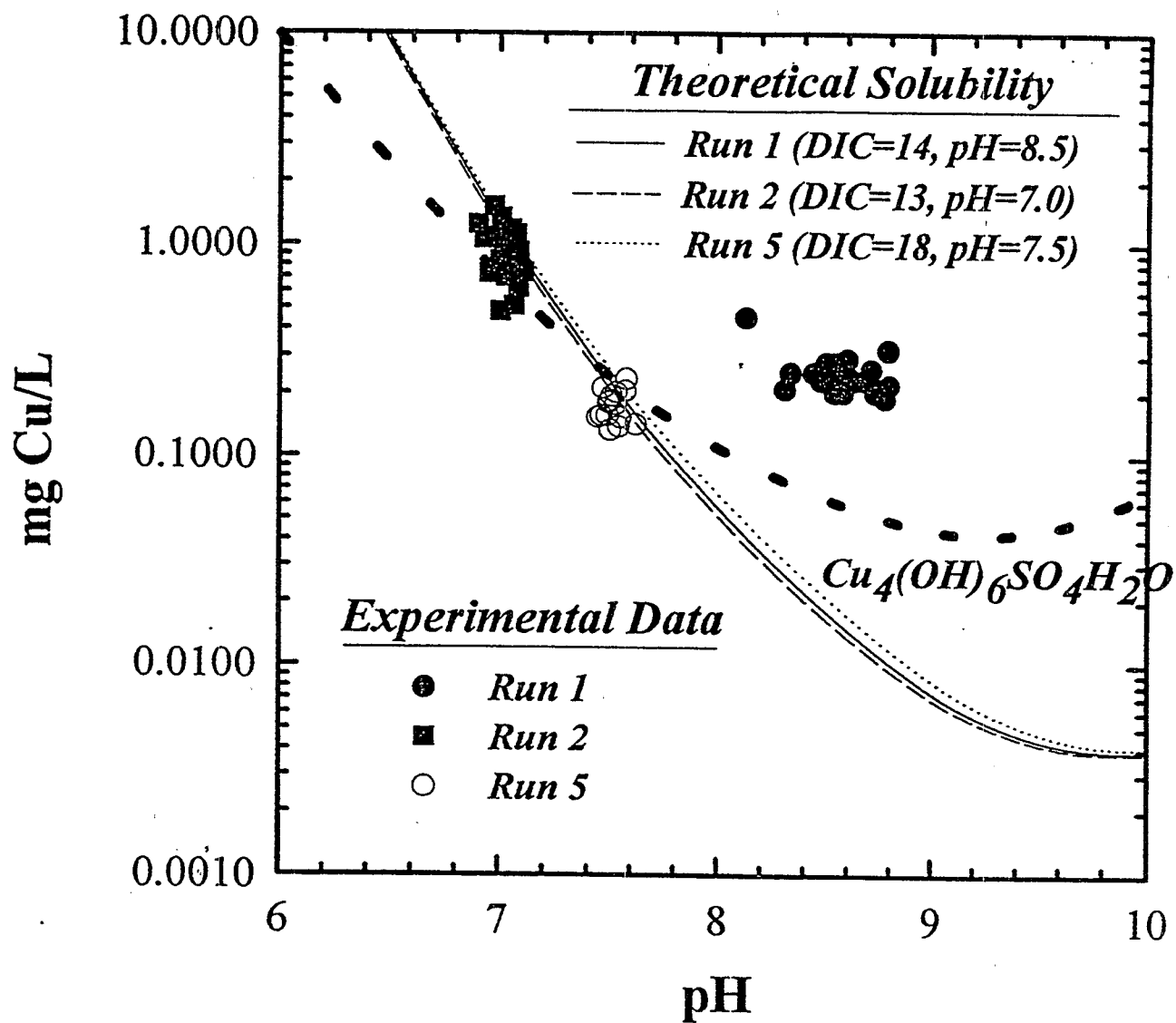


Figure 7. Comparison of equilibrium theoretical and observed 24-hour stagnation copper levels for coupon study, showing large deviation from expected value for system with high pH and high sulfate. Thick line is predicted "langite" solubility.

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## EFFECT OF INHIBITORS ON CORROSION RATE AND METAL UPTAKE IN DRINKING WATER SYSTEMS

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### Introduction

Drinking water distribution systems in Germany, mainly the older one, are often made from steel, cast iron or ductile iron without a sufficient internal corrosion protection. Despite that, damages caused by internal corrosion attack which leads to a perforation of the pipes are rarely occurring and can be linked directly, if it happens, to unqualified pipe-laying with residues inside the pipes, no sufficient flushing or unfavourable operation conditions.

On the other hand, red water problems, often arise from such systems and are the reason for complaints of the customers (1-3). Beside that, iron content in drinking water is limited in Germany to 0,2 ppm Fe. In these cases, where problems arise, the use of inhibitors can be helpful to reduce or even resolve the problems in a short time range while relining or replacement are long term measures.

The use of inhibitor chemicals is restricted to sodium and potassium salts of phosphoric acid and silica and is additionally limited to 2,2 ppm P and 19 ppm Si. In many cases an optimization of the total necessary quantity of dosage chemicals is wishable with regard to the treatment costs and a minimization of phosphorus quality is proposed to reduce ecological impact, mainly concerning the pollution of lakes and rivers.

Because of the lack of sufficient basic informations on the connections between different water qualities and the corrosion inhibition effects of the dosage chemicals, field tests have to be carried out to obtain the needed data for optimization.

### Test methods

To obtain correct data, tests have to be performed on site where the original water quality is available. Test pipes ( $\frac{3}{4}$ ") and pipe coupons are installed and operated usually as a throughflow system with the original water and the inhibitor dosage at a flow velocity of minimum 0,2 m/s (turbulent flow) for several months.

During the test period, the test pipes are taken out from the pipe ris at different times and installed in a closed loop to obtain data on the momentarian corrosion rate and iron uptake rate. Corrosion rate is determined by oxygen depletion and iron uptake rate by automatized monitoring of the increase of iron concentration in the closed loop.

Wagner



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December 19, 1996

OFFICE OF  
RESEARCH AND DEVELOPMENT

MEMORANDUM

SUBJECT: Seasonal Monitoring Revision

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TO: Jeffrey B. Kempic, Environmental Engineer  
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Pursuant to our prior correspondence and discussion about removing requirements that samples be collected in "warmest" months, I have collected a small set of papers for your information and justification of the change. I agree that in some water systems the highest lead, copper, or both levels could be highest in the warmest months. However, I do not think that the presumption that it is always the case is supportable by scientific evidence. There are many cases where exactly the opposite is true, as evidenced by both fundamental chemistry arguments as well as data from experiments and water distribution system sampling. Therefore, when possible, I believe that the Lead and Copper Rule should be revised to allow sampling flexibility to account for this phenomenon. Of course, for water systems required to collect two or more rounds of monitoring data that can encompass "seasonality," there is no reason to make any change in requirements.

Language changes may be required in some places to modify statements that would imply guidance towards biasing of collection times to the "warmest" months. In such cases, phrases could simply be amended to suggest biasing towards seasons or months "where the highest levels are most likely to occur."

For seasonally-operated water systems, a secondary supplemental argument is that the intent of the Rule was to reduce major exposures of sensitive populations to lead and copper. Therefore, sampling is most appropriate when the systems are actually being used. The question then becomes when to sample if operation encompasses a range of months covering a

range of temperatures. There is no definitive argument on this, because currently we can rarely predict beforehand whether a given water chemistry coupled with physical factors, will cause the highest values at a particular time. Therefore, I do not think we should attempt to be too precise in proscribing exactly when to take the samples in a confining regulatory structure.

As noted previously, I think the strongest line of argument we should use is to say that the uncertainty of the time of "worst" metal levels causes EPA to refrain from specifying particular months for sampling across the country. If monitoring data from similar systems or prior monitoring or survey experience in that particular system is available to the States, and if the States wish to use that information to make particular time requirements for the systems, then I think that would be reasonable.

There are several plausible "theories" about why metal levels could frequently be higher in the "winter" months, each or some combination of which could operate in a given water system. Some of these are:

- The intrinsic net solubility of many minerals, especially carbonates, goes up as the temperature goes down.
- Corrosion inhibitors, especially orthophosphate, may react more slowly at lower temperature, so passivating film formation is less effective in colder water.
- Corrosion inhibitors and other treatment chemicals may be more viscous at lower temperatures. Therefore, the chemical feed rates may be lower when cold.
- Many pipes are near heating systems, and in the winter the operation of the heating systems causes the pipes to be hotter. Plus, the change in temperature could also disrupt the existing protective films in the pipes built up over the earlier months of more stable temperatures (this is an argument advanced by several staff members of Minnesota DOH).
- Dissolved oxygen levels are often higher in colder waters, resulting in enhanced concentrations of primary oxidants in the water (when added to chlorine species). This causes more rapid increases in metal levels through enhanced oxidation during short standing times (6-16 hours).

The information I have attached is as follows, with brief descriptions of their significance.

- ✓1. Colling, et. al. *Jour. IWEM* (1992) paper showing field data where lower lead levels are obtained at higher temperatures in some orthophosphate-dosed hard water systems in the UK (page 262, Fig. 3).
- ✓2. Edwards/Schock/Meyer *Jour. AWWA* (1996) paper showing theoretical arguments why copper levels should be higher at lower temperatures in many cases. This paper cites some data from Boulder (not published) and utility data (see next one).
- ✓3. Dodrill/Edwards *Jour. AWWA* (1995) paper (pp. 79-80) showing temperature trends not readily apparent in major utility monitoring data. There was a suggestion of a trend of lower levels at higher temperatures especially for lower alkalinities. This paper brings up another interesting point that because of the different structures of houses and where the first-draw liter of water resides in the plumbing, major temperature trends should not be expected. Some unpublished work Chet Neff and I did many years ago (which could be reproduced with the assistance of some standard heat-transfer equations) suggested that waters in lead and copper pipes quickly (minutes to only an hour or two) take on the temperatures of their surroundings.
- ✓4. Rezania/Anderl conference paper (1996) on observations of higher Cu levels in winter in Minnesota sampling (page 4). They have several arguments to explain this, with some in the paper, and some noted above in my discussion.
5. Some supplemental laboratory test data by doctoral student Loay Hidmi, University of Colorado, Dept. of Civil Engineering. This shows higher copper release at pH 7 for lower temperature in water of same alkalinity. Compare Cu level at most times from Chart 1 to Chart 4. This may not be citeable.
6. Some data from a couple of water systems in MN collected by U. Colorado. Note highest Cu levels are usually associated with "winter" month sampling. (Probably not citeable)
7. Some other experimental data from Marc Edwards' group at U. Colorado (currently confidential but possibly citeable with permission from Marc) showing soluble copper being higher in cold water loops than in hot water loops.

Interestingly, a review of the original preamble (Page 26524-26525) shows that EPA had information showing field data was equivocal about any particular month or period having higher or lower metal levels. The choice was apparently made to essentially "weight" the evidence from some unspecified studies more highly than others, and the proposal to use July through September was kept (after adding June). I believe, therefore,



that this proposal is not really particularly new, but does help argue that the increased inconvenience of requiring sampling in specific months does not pay off in tangible public health protection. It also provides an option for States that have good reason to believe a particular time period would be preferable for sampling to use their discretion to designate such a time constraint.

If you need additional research to find other articles, or if you would like me to help with some preamble language, let me know.

Attachments

cc: Judy Lebowich