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ABSTRACT

In order to properly evaluate the corrosiveness of water supplies to asbestos-cement (A/C) pipe, several different analytical methodologies are being compared with regard to their cost, ease of use, type and amount of information gathered and accuracy in describing the pipe condition under field and laboratory conditions. Reported here are experiences gathered thus far from the use of water chemical analyses coupled with computer-assisted calculation of aqueous and solid speciation, reflected-light optical microscopy, scanning and transmission electron microscopy and energy-dispersive x-ray spectroscopy. References are made to more detailed theoretical interpretations of results of experimental and field studies, and compilations of the experiments.

INTRODUCTION

Because of concern about the possible problem of asbestos fibers being released from the walls of asbestos-cement (A/C) pipe, the American Water Works Association Research Foundation reviewed the problem and in September, 1974⁽¹⁾ suggested several research needs in this area. As a response to this call for research, several projects were designed by the Drinking Water Research Division (DWRD), U.S. Environmental Protection Agency, to determine whether A/C pipe would be attacked and asbestos fibers would be released from the pipe under various conditions of water quality. In general, this research has been divided into four general phases. The phases are: a field evaluation of 10 public water supply systems that used A/C pipe, an A/C pipe loop system operated under controlled conditions, numerous pilot plant tests of A/C

'pipe coupons," and research projects that are attempting to rehabilitate deteriorated pipe in place. Buelow et al⁽²⁾ presented results from the first three phases of the research, and Schock and Buelow⁽³⁾ presented additional detail on the laboratory experimentation, and proposed a theoretical chemical framework upon which a more accurate assessment of A/C pipe behavior in drinking water can be based. Presently, as an adjunct to several studies focusing on exposure assessment and investigation of possible human health effects,^(4,5) more field chemical data is being gathered to correlate with the chemical model of naturally-occurring and synthetic corrosion inhibitory factors. Additionally, DWRD has recently begun investigation and evaluation of various methods for quantitatively and qualitatively describing A/C pipe surficial condition, and this paper reports some of the experience gathered thus far with those techniques.

CHEMICAL EVALUATION OF A/C PIPE CONDITION

Limitations of the "Aggressiveness Index"

Classically, the tendency of a water to deteriorate the structure of asbestos cement pipe has been described by the "Aggressiveness Index" (AI)^(6,7) given as

$$AI = pH + \log (AH)$$

where

$$pH = -\log aH^+ \text{ (-log of the hydrogen ion activity)}$$

$$A = \text{total alkalinity in mg/L as CaCO}_3$$

$$H = \text{calcium concentration in mg/L as CaCO}_3$$

Waters possessing an AI equal to or in excess of 12.0 are considered to be "nonaggressive;" those where $AI < 10.0$ are said to be "highly aggressive," and those with an AI between 10 and 12 are "moderately aggressive." The AI is derived⁽⁶⁾ from a simplified form of the Langelier Index of calcite saturation^(8,9) with factors introduced to compensate for the temperature dependency of the solubility product constant (K_{s0}) of calcite and for the ionic strength^(10,11) of the solution.

The use of the AI as a predictor of the condition of the interior surface of the pipe in contact with the drinking water and its tendency to retain or release asbestos fibers has come about in spite of the fact that the original intention of the index was to outline water conditions that might cause

structural failure of the pipe.⁽¹²⁾ The difference in application is very significant.

Substantial field and pilot plant data, combined with a comprehensive evaluation of many of the important chemical complexation and precipitation reactions occurring in a drinking water, give compelling evidence that the AI has immense shortcomings with regard to use as a predictor of fiber release and interior surficial pipe condition that enjoin against its use under most circumstances. Schock and Buelow have discussed many limitations in detail,⁽³⁾ and they may be briefly summarized as follows:

1. The temperature dependence of the solubility constant for calcite used appears to be in substantial error. The original experimental work did not account for the existence of ion pairs of calcium and carbonate species. It is also not clear that the first-precipitated calcium carbonate solid phase can be accurately characterized by the solubility product constant of calcite.
2. There is no a priori reason to expect the dissolution of a primarily silicious material, such as portland cement, to be accurately represented by calcite (or any calcium carbonate solid, for that matter) solubility.
3. The AI does not include any provision for the consideration of complexation reactions (such as with polyphosphate additives) that can limit the free ion activities of calcium and carbonate ions, and either inhibit calcium carbonate precipitation or enhance the pipe dissolution rate.
4. The AI does not consider the formation of protective precipitates of ferric iron, manganese, zinc or silica that have been observed to be the corrosion inhibiting agents in field and laboratory studies. Other, less common constituents such as copper, ferrous iron and orthophosphate also can form protective coatings under the proper chemical conditions.
5. Certain coatings formed on the A/C pipe tend to allow some continued dissolution or alteration or both, of the pipe surface below, although the coating is tenacious enough to continue to bind the asbestos fibers against release into the water. Ferric oxyhydroxide coatings seem to operate in this manner in many instances. Therefore, there should be a differentiation in the effectiveness of a coating with regard to fiber retention and structural protection.

In most cases the dependence upon the AI has resulted in more pessimistic projections of the deteriorative nature of the water than actually exist, so the human exposure to released fibers and the number of utilities encountering

large-scale pipe degradation is less than it otherwise might be. However, the concern over the health implications of ingested fibers has lead to numerous instances of strong public reaction to the presence of A/C pipe in water systems possessing a "low" AI (less than 10), though the water in fact may not be aggressive in the true sense. By considering the trace metal equilibria and redox potential of the water, along with the calcium and carbonate speciation, a much more reliable estimation of the pipe condition and potential for asbestos fiber release can be obtained,⁽³⁾ and a later section will correlate the refined water chemistry-based interpretation with other methods of pipe condition assessment.

Chemical Monitoring of Pipe Dissolution

Attack upon A/C pipe by drinking water may generate two quite different problems. Dissolution of the pipe matrix material will lead to structural deterioration, which causes economic and service problems for the water utility. Additionally, deterioration of the interfacial fraction of the interior pipe surface will lead to the release of asbestos fibers, over which there is considerable concern for possible human health effects. As will be discussed later, it has been shown that it is possible to form adherent coatings on the pipe that will prevent fiber release, but which may or may not totally prevent some surficial softening.

The cement matrix of asbestos cement pipe is a very complicated combination of compounds and phases, some of which are poorly identified or are of indefinite composition. Over 100 compounds and phases important to the chemistry of portland and related cements have been described and identified,⁽¹³⁾ and because of solid solution possibilities, probably many more exist. The state of knowledge of the solubilities in water of the individual predominant compounds of the cement lags far behind that of minerals and related man-made compounds important to drinking water chemistry. Until more research is done, only some qualitative generalizations can be made.

The corrosion of A/C pipe is governed virtually completely by solubility considerations, and therefore, the dissolution and coating processes of the pipe can largely be described and predicted by bulk-solution chemical parameters and straightforward solid solubility reactions.

The effects of pipe dissolution on the distribution system water quality, in addition to fiber release, are several.

The "free lime" component of the pipe (essentially equivalent to the solid portlandite) can dissolve, which would increase the pH, titration alkalinity and the calcium content of the water during its passage through the pipe (and, therefore, the AI). The pH increase would enhance the ability of the water to absorb and hydrate any CO₂ gas present. Subsequently, the reaction of any absorbed CO₂ with the hydroxyl ions present would lead to the

formation of bicarbonate ions, a step that would favor increased dissolution of $\text{Ca}(\text{OH})_2$ (s) by the mass-action effect. In the present commercial autoclaved type II A/C pipe, the free lime phase is regulated to be $\leq 1.0\%$ by weight.⁽⁷⁾

Three of the predominant phases of the matrix of A/C pipe are tricalcium silicate (nominally Ca_3SiO_5) dicalcium silicate (nominally Ca_2SiO_4) and tricalcium aluminate ($\text{Ca}_3\text{Al}_2\text{O}_6$).^(13,4)

An estimate of the solubility constants for Ca_3SiO_5 and Ca_2SiO_4 has been made,⁽³⁾ utilizing an internally-consistent set of Gibbs free energy of formation data, and the calculations indicate a very high solubility.

Dissolution would produce three major effects. First, the levels of calcium, aluminum, and silicon species (as well as any substitutional elements) will increase with time upon standing, or with distance of passage through a pipe line, unless threshold conditions are met for saturation and precipitation of another less soluble phase.

Second, the pH of the system would tend to increase because of several dissolution reactions and the two dissociations of silicic acid. The dissolution of calcium hydroxide would provide hydroxyl ions directly, and it could be a strong influence by virtue of its high solubility. The presence of carbonate, as in a drinking water, could lower the magnitude of pH increase possible resulting from calcium hydroxide dissolution by pH buffering or if calcium carbonate saturation were attained. The overall solution pH may also be increased by dissolution of the asbestos fibers themselves, though the impact of this factor would be quite small except for small water volumes and stagnant flow conditions.

One would not ordinarily expect large pH gradients between the pipe surface and the bulk solution. The water in a distribution main would have minimal periods of suspended flow, such as in a household system during overnight standing, except at dead ends. Also, the buffer capacities of most, even "aggressive," water should be sufficient to substantially moderate a pH rise, especially when combined with constant water flow. Additionally, a very large local rise in pH would often cause CaCO_3 deposition and subsequent protection. This would tend to conflict with the observation of continual Ca^{2+} leaching in field and laboratory tests discussed by Buelow et al.⁽²⁾ and Schock and Buelow.⁽³⁾

Third, the alkalinity of the system may also show an increase. Considering that alkalinity is a charge-neutralizing capacity, the only newly-formed directly-contributing entities would be OH^- , $\text{SiO}(\text{OH})_3^-$ and $\text{SiO}_2(\text{OH})_2^{2-}$. However, a pH increase favors the production of HCO_3^- and CO_3^{2-} , which are the significant contributors to alkalinity in most drinking waters of pH less than approximately 9 to 10. It must be emphasized that the alkalinity increases observed in field studies⁽²⁾ do not necessarily indicate input

of dissolved carbonate from pipe materials. That possibility may be checked by carefully obtained, analyzed and preserved samples for potentiometric total alkalinity, pH, temperature and major constituents.

Precipitation reactions in a field situation may obscure some of the three major dissolution indicators, though pH and calcium increases with increasing distance of travel (or recirculation in a closed loop) are generally good evidence of pipe softening. Decreases in the total concentrations of various constituents (such as calcium, zinc, manganese, iron, silica or orthophosphate) with travel through a system tend to indicate the formation of a pipe coating, provided that the analytical procedures are sufficiently precise to accurately find those trends. Some constituents such as iron and manganese that may exist as colloidal or particulate species in many cases frequently show large analytical variability because of the inhomogeneity of the samples.

Laboratory Experimentation

The apparatus and experimental procedure utilized in DWRD coupon tests has been given in detail by Buelow⁽¹⁵⁾ and Buelow et al.⁽²⁾ Table 1 presents a summary of the major constituent water qualities of the DWRD small-scale pipe loop studies, along with the concentrations of additional primary corrosion-control constituents (zinc, orthophosphate, and silica). Table 2 gives qualitative information on the physical conditions of the coupons at the end of the experiments. The test periods were of approximately six months duration (11 months for experiment 22), and more detailed analytical information has been provided by Schock and Buelow.⁽³⁾ Earlier, larger-scale tests have been described by Buelow et al.⁽²⁾

The Solubility Modeling Approach

Just as calcium carbonate may precipitate and adhere to a pipe surface to form a protective coating, so too could any other reasonably dense solid. Few combinations of cations and anions are present in drinking water in sufficient quantity to provide enough mass for precipitation and effective pipe coating. Four elements that can be useful in this regard are iron, zinc, manganese and silicon.

In order to form a generalized chemical model that can take into account the many chemical reactions in a drinking water, the computer program REDEQL.EPAK^(16,17) was used. Two types of diagrams have been prepared, primarily to explain and predict conditions under which A/C pipe will become protected by zinc or iron compounds.^(3,18) The "Saturation Index" (SI) diagrams are a plot of the saturation indices of solids of interest defined as the common logarithm of the quotients of the stoichiometric ion activity products (IAP) and the thermodynamic solubility constants (K_{so}), versus pH for a system of a given composition. If a solid at equilibrium is oversaturated,

SI > 0. If the solid is undersaturated SI < 0, and if the solid is exactly at saturation, SI = 0. Figures 1 - 4 show example SI diagrams for the system compositions given in Table 3.

By examining the areas where the curves are above the SI = 0 line, a domain of pH is given where pipe protection can be predicted. SI diagrams can often be prepared for general classes of waters, and a relatively small number of diagrams can be used to cover a wide range of concentration extremes that would likely be encountered, and therefore they can yield a large amount of semi-quantitative information on the occurrence and identity of pipe coatings.

Precipitation diagrams were calculated by the same computer program, by "allowing" supersaturated solid phases to precipitate to their saturation levels.⁽³⁾ While it is just as easy to plot the concentration of each solid phase versus pH, a plot of total dissolved constituent concentration(s) versus pH was selected. Figures 5 - 8 illustrate the Precipitation diagrams corresponding to the previously given SI diagrams. The selection of dissolved total constituent concentration as the variable to plot versus pH was made because it is representative of the practical situation of the addition of known concentrations of soluble corrosion-control compounds. The minimum dosage level is easily estimable, by observing the dissolved concentration of the constituent of interest (zinc or ferric iron, in this case) in the pH region where precipitation would be taking place.

The relationship of effective zinc coating on A/C pipe to pH and carbonate levels in a water have been extensively studied by DWRD using these types of diagrams, and the results have been reported by Schock and Buelow, along with the thermochemical data used.⁽³⁾

The aqueous and solid species included in the DWRD chemical model calculations are listed in Tables 4 and 5. Subsequent to the completion of the modeling calculations previously reported, the observation was made that the projected zinc solubility in systems of much greater carbonate concentration (approximately 0.08 M) is much lower than that observed in precipitation experiments by Patterson et al.⁽²⁰⁾ The addition of a dicarbonate complex of zinc ($\text{Zn}(\text{CO}_3)_2^{2-}$) and the adoption of the formation constants suggested by Mattigod and Sposito⁽²⁰⁾ lead to still worse agreement, but this time by overestimating the zinc solubility. A careful examination of the published stability constant data of Bilinski et al.⁽²¹⁾ originally used in the modeling revealed that their polarographic data could alternatively be explained by the formation of ZnCO_3 and $\text{Zn}(\text{CO}_3)_2^{2-}$ complexes. A graphical extrapolation yielded $\log B_{11} = 5.2$ and $\log B_{12} = 7.5$ (corrected for ionic strength). Until the formation constant issue is decided, the latter values have been incorporated into the model, and excellent agreement is obtained in comparison with both the precipitation data⁽¹⁹⁾ and the DWRD coupon studies.⁽³⁾ Inclusion of the ZnHCO^+ complex suggested by Zirino and Yamamoto⁽²²⁾ would have mostly minor impact³ throughout the carbonate range examined.

Evaluation Using Field Chemical Data

Some of the interactions observed to provide either total corrosion inhibition or fiber retention by a soft surficial deposit are summarized in Table 6. The levels in the table are mutually related, so the numbers are semi-quantitative at best. Other interactions such as calcium and zinc with silica, or silica with iron and organic material are not covered here, but some aspects have been covered elsewhere.⁽³⁾

In order to interpret the chemical data in a more quantitative manner, the saturation states of several solids that can have an inhibiting effect on A/C pipe deterioration can be used. Unfortunately, the use of the AI (and Langelier Index) as the dominant indicators of corrosivity toward A/C pipe has lead to the recording of data for only a few chemical parameters (mainly pH, alkalinity and calcium hardness). Therefore, complete enough information is rarely available that one could use to compare fiber counts with the saturation indices and assess the accuracy of the multiple-SI method of estimating corrosivity.

Table 7 shows how various saturation indices can be used to predict protection or deterioration of pipe. It is necessary to either know or estimate the redox potential of the water in order to determine the saturation states of solids possessing more than one stable valence state in drinking water. A value of the redox potential representing moderately oxidizing conditions was chosen in Table 7, for all waters that were chlorinated. The interrelationship of the redox potential, pH and the domain of water stability to chlorination species is shown in Figure 9.

It is important to select solids that represent precipitation reactions that are not inhibited under drinking water conditions.⁽¹⁸⁾ For example, spontaneous precipitation of amorphous silica probably would not be achieved in water distribution systems. Therefore, quartz was chosen to represent observed behavior of silica in the hardening of A/C pipe, though the role of the dissolved silica in pipe protection is not yet understood in detail.⁽³⁾ On the basis of the observation that the MnO₂ phase birnessite is common in stream deposits, it is chosen as the representative manganese solid.⁽²³⁾ Figure 10 shows the thermodynamic potential-pH relations of manganese species in water.⁽³⁾ Although the MnO₂ solid used in the calculation of the diagram was pyrolousite, the boundary between solid and dissolved species is little changed by the identity of the solids chosen.⁽²⁴⁾ The calculated saturation state of MnO₂ is extremely sensitive to the redox potential of the water, and it is therefore very imprecise without precise and accurate analytical redox potential measurements.

Note that the system with the highest AI (least aggressive) also contained the highest fiber count, whereas systems with high SI values for quartz, MnO₂ and amorphous Fe(OH)₃ generally show fiber counts near or below detectable levels. Some calcium leaching in systems M and N is evident, but there is also the suggestion of iron and manganese deposition, perhaps binding the fibers. The increased iron level in system P could be the result of corrosion of iron or steel piping, and the increased iron hydroxide saturation could actually be removing some fibers from the water as well as providing a coating on the A/C pipe.

Obviously, the sample number is too few, and the documentation is not sufficient to make many definitive statements. However, the broader-spectrum look at water chemical interactions certainly provides much more information that can be applied to determine pipe conditions and the potential for human exposure than the traditional approach that only considers the calcite saturation state.

The cost of the sampling and analyses involved in this type of approach is extremely variable, and cannot be generally estimated. The computer programs used on the EPA computer system (IBM 370/168) typically cost in the range of \$5 - \$50 to compile at a low-level time priority. Calculations performed on analytical data typically cost in the range of \$5 - \$20 for several sites run at a fairly high-level time priority, once the programs have been compiled.

Sampling Considerations for Chemical Data

The most obvious, and yet often most neglected aspect of any theoretical chemical interpretation of factors influencing corrosion, is the sampling procedure itself. Because of the complex nature of the chemical equilibria involved in A/C pipe protection, the chemical analyses must include metals such as Fe, Zn, Mn and Cu plus the anions with which they can complex or form solids (ortho and polyphosphates, sulfate, fluoride, etc.) and silica, in addition to the major constituents and parameters (pH, total alkalinity, calcium, magnesium, sodium, chloride, etc.). Samples for certain constituents must be properly preserved^(25,26) on site.

To properly determine the conditions in a distribution system, a sample should be taken from the finished water tap at the plant to represent initial conditions. Additional samples must be taken from locations of frequent use, in order to prevent misleading constituent concentrations that result from contact with metal pipes. Household taps (inside or outside) that are the closest to the service connection would be the most suitable in this regard, and the water should be run at approximately half-maximum for five minutes before sample containers are filled.⁽²⁷⁾ No aerators should be in taps used for sampling, and no samples should be taken of waters treated by home or building water softeners.

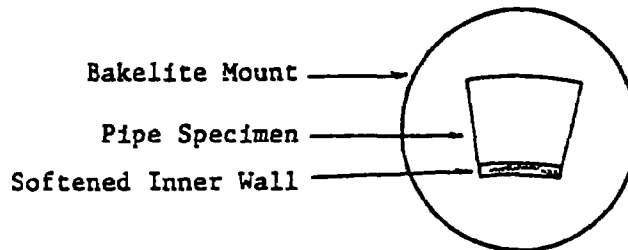
REFLECTED LIGHT MICROSCOPIC ANALYSIS

Sample Preparation

When badly corroded A/C pipes are viewed in cross section, the deteriorated portion of the pipe wall often can be distinguished by the differences in appearance between undamaged pipe and deteriorated pipe. When the pipe has been severely attacked and softened by aggressive water, the depth of attack on the inner pipe wall may be difficult to determine because cutting the pipe to examine it may disturb the condition of the softened pipe wall. So that A/C pipe condition could be evaluated in a manner less likely to damage a softened pipe wall, pipe specimens were cut and mounted in metallographic mounts by a testing laboratory.*

*Gladstone Laboratories, Inc., Cincinnati, Ohio

Pipe segments were mounted in cylindrical bakelite mounts about 3.1 cm in diameter and 2.3 cm high, with the pipe segment oriented so that the cross section of the pipe wall was visible.



This orientation permitted observation of both the interior and exterior walls of the pipe. Mounts are polished with progressively finer materials, ending with #600 grit or aluminum oxide polish.

The particular advantage of the bakelite mounting technique is that the mount holds the softened asbestos cement layer in place next to the sound portion of the pipe while the mount and pipe are being ground and polished. The soft pipe does not flake off or develop feathered edges during the grinding and polishing, so when these steps are completed, the thickness of the softened layer should be representative of the condition of the undisturbed pipe.

Evaluation of Corrosivity

In most cases the softened, deteriorated portion of the inside wall could be seen when illuminated by unpolarized light incident at a shallow angle, and viewed through an optical microscope at 50X magnification. In some cases the gradient of color and texture change was not sharp and assessing the degree of damage was difficult or impossible. Most specimens could be evaluated in this manner though, and in 14 of 20 cases results of visual inspection at 50X agreed with photomicrograph interpretations.

The optical microscopy technique of cross-sectional viewing can be particularly advantageous in showing the effects of the interaction of the pipe with the water over time. Pipes that have undergone attack in the past but are now coated with a solid deposit (such as a zinc compound) will show the alteration, whereas only the surficial coating will be visible to the scanning electron microscope. One limitation of the optical examination is that it is sometimes difficult to tell if a visible alteration of the pipe represents actual deterioration, unless the hardness of the surface is tested.

METHODS BASED ON THE ELECTRON MICROSCOPE

Fiber Counting

One obvious method to test for deterioration of A/C pipe is to determine the number of fibers input into the water during passage through the pipe. In order to determine whether or not fibers are leached from the walls of the pipe, a sample must be taken at the point of finished water inflow into the system in addition to any samples taken at other sites. Systems that contain several different water sources and that do not combine them before distribution require additional samples at each different location of water input.

In order to accurately represent distribution system conditions, samples must not be taken from dead ends or locations of infrequent flow such as fire hydrants, both of which tend to give very erroneous high results. Care must also be taken to assure that samples not be taken down flow of any system maintenance, drilling or tapping and that drilling and tapping operations flush fibers out of the system to avoid contamination. If chemical analyses and interpretation are to accompany fiber counts, the appropriate sampling considerations must be added to those just discussed.

In order to determine the number of fibers in the water, the method of Millette, et al.⁽²⁸⁾ was used. At the start of the procedure, aliquots of 100 to 250 mL from each sample were filtered by suction through a 0.1 μm pore size Nucleopore® filter backed by a 0.45 μm pore size Millipore® filter. A backing filter was used to insure uniformity of deposition of the particulate material on the filter surface. A quarter section of the filter was cut while wet, attached to a glass slide, dried, and coated with carbon in a vacuum evaporator. A small portion (approximately 2 mm²) of the carbon-coated filter was cut out with a razor blade and placed on a 200-mesh copper electron microscopy grid. A few drops of chloroform were placed on the filter with a 50 μL micro-syringe to affix the filter to the copper grid. The filter was dissolved using a modified Jaffe wick apparatus.

After the filter was dissolved, the grid containing the particulates embedded in the carbon film was placed in a carbon specimen holder in the transmission electron microscope (TEM), operated at an accelerating voltage of 80 kV and 70 μA beam current, and viewed at a magnification of 17,000 times. At least 15 grid openings from each of two grids was examined for each sample.

Identification of asbestos fibers was made on the basis of morphology (size, shape, appearance), crystal structure, and elemental composition. When examined at 170,000 times through the use of 10X binoculars attached to the TEM, chrysotile fibers usually have a distinctive central channel running the length of the fiber. The crystal structure of a fiber is revealed through the use of selected area electron diffraction (SAED). Chrysotile provides a distinctive three double-dot diffraction pattern while amphibole asbestos fibers form rows of uniformly spaced dots.

Energy dispersive x-ray analysis (EDXA) is used to obtain information about the chemistry of the fiber. An electron beam is focused on an individual fiber, producing x-rays as a result of the interaction between electrons and the atoms on the surface of the fiber. Atoms of different elements produce x-rays of different energies, which are displayed graphically as a spectra of peaks on the EDXA unit. The elements present are determined by the position of the peaks and the relative amount of an element is calculated from the peak height.

Chrysotile fibers contain silicon, magnesium and some iron. The amphiboles have a basic silicate structure but differ in the amounts of silicon, magnesium, iron, calcium, and sodium depending on mineral type.

During sample analysis, fibers are generally sized on circles inscribed on the TEM fluorescent screen. In some samples where there are high numbers of fibers or where accurate information about fiber diameter is needed, fibers are measured from electronmicrographs taken in the TEM. The concentration of millions of fibers per liter (MFL) is calculated using the following formula:

$$\text{MFL} = \frac{(F) \times (EFA)}{(A) \times (V)} \times 10^{-6}$$

in which F = average number of fibers per grid opening
 EFA = effective filter area
 A = area of grid opening, and
 V = sample volume (in liters).

More information on the development of a standardized method of asbestos analysis is given by Anderson and Long.⁽²⁹⁾

An effort has begun to store water chemical data in a computer data bank along with the corresponding fiber counts and physical descriptive information, in order to correlate the information on a larger scale when enough samples are analyzed for both chemistry and fiber counts.

Thus far, good correlations have been found between low fiber counts and high states of saturation of the solids given in Table 7. Many other systems have shown low fiber counts, and pipe inspections have revealed coatings of iron, manganese, silica and carbonate solids even though chemical analyses of the water were not performed.

At present, the cost of sample preparation and analysis by TEM and EDXA is approximately \$300 - \$600, and 8 to 10 man hours are usually spent per sample. Therefore, it is a very time consuming and expensive method. Additionally, very few laboratories across the country have the instrumentation and expertise to do the work.

Scanning Electron Microscopy and X-Ray Analysis

In order to assess the degree of reliability of using water chemistry and saturation indices to predict the interior condition of asbestos-cement pipe

and its tendency to release fibers into the drinking water, additional information about the pipe surface itself when subjected to various water qualities is necessary. It is important to know when asbestos fibers are exposed at the pipe surface, what changes in surface chemical composition occur, and what inhibitors best coat the pipe to impede the leaching of calcium with subsequent fiber release.

Because of the requirement for a more complete physical and chemical analysis, pipe sections from several of the DWRD coupon experiments and from several field samples were studied using the Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray Analysis (EDXA). The SEM micrographs showed the topographic features of the surface of the pipe interior while the EDXA spectra showed the relative changes in chemical composition of the surface of the pipe.

There are several limitations to any chemical analysis performed by EDXA. Because the detector is protected from the vacuum chamber by a beryllium window, many of the soft x-rays are completely attenuated by the window before reaching the detector. Only the elements heavier than sodium can be detected. Also, the EDXA is semi-quantitative under the sample preparation and analysis conditions normally used, so it does not give the exact concentrations of the elements present on the surface. However, the relative amounts of the elements present may be important as a means to gain information on the identity of surficial coatings and in the monitoring of Ca leaching. One must keep in mind, however, that EDAX analysis can not identify the compounds present (as would be possible with x-ray diffraction), or tell whether or not a decrease in x-ray intensity is caused by depletion of the element or if the element is being masked by a coating.

For EDXA and SEM analysis it is important to observe representative sections of the pipe, as the same pipe might vary in color and texture. Often, several sections of the same pipe have to be analyzed.

Pipe sections that were analyzed by EDXA were prepared by the method of Clark, et al.⁽³⁰⁾ Random pieces of each sample, approximately 12 mm by 6 mm, were mounted on 24 mm by 5 mm copper boats using a conductive graphite adhesive. These samples were then carbon coated in a Denton* vacuum evaporator. A sample for determining background counts was also prepared using only a copper boat and graphite adhesive. Each sample was then placed in a JEOL 100B Transmission Electron Microscope (TEM) operated at an accelerating voltage of 40 kV and a beam current of 55 - 60 μA .⁺ Using the SEM mode and a magnification of 300X, the specimen was examined both longitudinally and laterally in a regularly-spaced rectangular array with seven to ten consecutive areas the size of 0.1 mm² being analyzed by the EDXA. Count rates ranged from 52 to 444 counts per second (CPS) for a time period of 300 seconds.

* Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

⁺ Emission current near filament.

To examine the surface structure, random pieces from the same samples were coated with approximately 450 Å of gold-palladium in the vacuum evaporator. The samples were then placed in an ETEC (SEM) operated under an accelerating voltage of 20 kV, beam current of 150 µA,[†] a working distance of 20 - 22 mm and at magnifications of 100X, 300X, 700X, and 1,000X. The samples were examined for the presence of asbestos fibers and degree of deterioration.

The following examples of the use of SEM-EDXA to evaluate A/C pipe condition are taken from three DWRD experiments and one field study. Experiment 1 was a "control" experiment in which no inhibitors were added. The micrograph (Figure 11) shows fibers present and some pitting of the surface. The EDXA analysis (Figure 12) shows a large peak for silicon compared to that of calcium. The difference in peak size may be caused by leaching of the calcium, an interpretation consistent with the calcium increase that was observed in solution.⁽³⁾ Also important is the magnesium, the presence of which may indicate exposed chrysotile fibers at the pipe surface. The magnesium peak has frequently shown up in analyses of corroded pipe and it is seldom present in EDXA scans of non-corroded pipe.

Experiment 2 shows a good coating by a zinc compound with very little pitting and few fibers exposed (Figure 13). The high calcium in the EDXA (Figure 14) possibly indicates that very little leaching has occurred, an observation that would also be consistent with the small increase of calcium level in solution. The zinc present and the lack of a phosphorous peak shows that it is the zinc that is responsible for the coating, as would be predicted by chemical theory.⁽³⁾ The small magnesium peak seems to indicate that few fibers are exposed.

Experiment 6 shows some pitting and exposed fibers in the micrograph (Figure 15). Here, again, the presence of a strong magnesium peak (Figure 16) seems to demonstrate the deterioration of the pipe and the presence of fibers on the surface. An important factor here is that pipe was shown to deteriorate even when the water was kept just slightly under calcite saturation. The expense of adjusting many naturally-soft waters to maintain a state of calcium carbonate saturation, coupled with the undesirability of the harder water to many consumers may necessitate the use of other treatment methods, such as zinc addition and pH adjustment.

Two field samples were analyzed by SEM-EDXA in order to determine the degree of in-situ zinc coating on sections of A/C pipe that had been placed in a distribution system. Figure 17 shows a section of pipe from far out in the system where there was a low flow rate and the zinc concentration ranged from low to just enough to attain saturation with respect to hydrozincite during a one-year test. The SEM micrograph reveals pitting of the pipe and a few fibers exposed at the surface. Figure 18 shows a pipe section that was located closer to the treatment plant, and that had a better coating. The better coating correlates well with the exposure of this specimen to a slightly higher level of zinc, even though adequate hydrozincite supersaturation was not maintained.

Interestingly, the optical microscopic examination of the bakelite-mounted specimens from the same two sites showed a zone of alteration $1.1 - 1.2 \times 10^3$ micrometers deep at the pipe surface in the specimen from the site closest to the plant, and almost no discoloration or alteration could be seen in the specimen from farther out in the system. The optical examination correctly reveals the greater attack over time on the specimen in Figure 18, before zinc treatment was begun. As the pH and calcium concentrations increased from pipe leaching during travel through the system, the amount of original pipe degradation decreased, and the specimen shown in Figure 17 was historically under less attack. Therefore, the different kinds of information obtained by the SEM-EDXA analysis complement that obtained by optical microscopic observation, although it is a more costly analytical method. The present cost of SEM-EDXA analysis is typically \$50 - \$100 per sample, and each sample requires on the order of 5 - 6 man-hours of labor.

CONCLUSIONS

The several methods of evaluating pipe condition that have been discussed in this paper can give a very large amount of important information for assessing the corrosivity of water toward A/C pipe. The chemical methods give a theoretical understanding of the corrosion or inhibition processes involved. By collecting more pipe samples and by performing more fiber counts, it should be possible to calibrate the method to predict pipe condition even more accurately than it can now. Overall, it is one of the most convenient and least costly methods of corrosivity evaluation to anyone possessing access to a digital computer and a water analysis laboratory.

The microscopic methods are seen to complement each other, each one capable of obtaining a unique type of information. Because the electron microscope methods are costly, one must carefully decide upon the type of information that would be of most value.

All of the methods are under development to various extents, and their rigorous application to A/C pipe corrosion problems is still in its infancy. It is clear, however, that the methods discussed are very valuable tools at this early stage, and they can be expected to become even more informative as more experience is gained using them.

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TABLE 1.

Abbreviated qualities of DWRD recirculation experiments. All concentrations are in mg/L unless noted otherwise. Analyses represent concentrations at or near the end of each experiment unless a range is given.

Experiment Number	pH	<u>mg/L as CaCO₃</u>					Treatment Chemical
		Total Alkalinity	Ca	Zn	PO ₄	SiO ₂	
1	8.2	20-27	5-13	-	-	-	None
2	8.2	20-26	4-8	0.3-0.5	0.4-1	-	zinc orthophosphate ^a
3	7.0	21-25	10-22	-	-	-	none
4	7.0	20-29	9-17	0.3-0.6	0.4-1	-	zinc orthophosphate ^a
5	8.2	19-22	5-8	0.3-0.7	-	0.1-2	zinc chloride
6	7.5	116-130	133-155	0.03	-	1-4	none
7	7.9	120-131	129-160	0.04	-	1-4	CaCO ₃ saturation
8	9.0	38-42	21-30	<0.02	-	0.1-2	CaCO ₃ saturation
9	8.2	42-50	9-16	0.02	0.2	15-18	Sodium metasilicate
10 ^b	7.0	25-27	13-16	0.1	-	14-17	Sodium metasilicate
11	8.2	18-19	0.6-4	0.3-0.4	0.03	3	zinc chloride
12	7.5	18-21	9-14	0.3-0.4	0.03	2-3	zinc chloride
13	8.2	19-21	10-15	0.1-0.2	0.03	0.2	zinc chloride
14	8.2	2-4	32-43	0.3-0.4	0.06	1-8	zinc chloride
16	8.2	16-19	7-10	0.3-0.5	<0.2	<0.4	zinc sulfate
19	7.2	18-21	9-25	0.1	0.1	<0.2	zinc chloride & iron (III) chloride
22	8.2	21-25	10-16	0.2-1.0	0.2-0.9	<2.0	zinc orthophosphate ^a

Notes:

A free chlorine residual of 0.1 to 0.7 mg/L as Cl was maintained at almost all times. Iron was less than the lowest calibration standard of 0.1 mg/L except for experiment 19 in which approximately 0.1 mg/L of iron was added.

- a. Virchem 931[®], a product of Virginia Chemical Corporation.
- b. The same coupon was previously run for almost 1 month at an SiO₂ concentration of 10-30 mg/L and a zinc concentration of approximately 0.2 mg/L. The pH, total alkalinity and calcium levels were the same.

TABLE 2.

Summary of Qualitative Results of DWRD A/C Pipe Treatment Experiments

Experiment Number	pH	Treatment Process	Inner Wall of Coupon Softened?
1	8.2	none	yes
2	8.2	zinc (orthophosphate) 0.3-0.5 mg/L	no
3	7.0	none	yes
4	7.0	zinc (orthophosphate) 0.3-0.5 mg/L	slightly
5	8.2	zinc (chloride) 0.3-0.7 mg/L	no
6	7.5	none	yes
7	7.9	CaCO ₃ saturation	very slightly
8	9.0	CaCO ₃ saturation	slightly
9	8.2	Sodium metasilicate	no
10	7.0	Sodium metasilicate	no
11	8.2	zinc (chloride) 0.4 mg/L; low calcium	no
12	7.5	zinc (chloride) 0.4 mg/L	slightly
13	8.2	zinc (chloride) 0.1-0.2 mg/L	yes
14	8.2	zinc (chloride) 0.4 mg/L; low alkalinity	very slightly
16	8.2	zinc (sulfate) 0.5 mg/L	no
19	7.2	iron (III) 0.1 mg/L; zinc (chloride) 0.1 mg/L	slightly
22	8.2	zinc (orthophosphate) 1.0 mg/L for 1 week; zinc (orthophosphate) 0.2 - 0.5 mg/L for 47 weeks.	no; mottled grey coating

Table 3. Chemical compositions of four model systems.
All concentrations are totals in mg/L of the constituents shown.

System	Ca	Mg	Na	Zn	Fe(III)	CO ₃	PO ₄	Cl*
M9	4.0	1.0	20	0.15	0	24.	0	18-40
M10P	4.0	1.0	12	0.5	0	12.	0.5	15-29
M11	4.0	1.0	12	0.3	0.1	12.	0.5	15-29
M15	4.0	1.0	20	0.5	0	4.0	0	38-42

*Allowed to vary with pH to preserve electroneutrality.

Table 4. Aqueous species considered in Saturation Index and Precipitation diagram preparation.

H^+	$ZnCl^+$
OH^-	$ZnCl_2^{\circ}$
$H_2CO_3^*$	$ZnCl_3^-$
HCO_3^-	$ZnCl_4^{2-}$
CO_3^{2-}	$ZnClOH^{\circ}$
$H_3PO_4^{\circ}$	$ZnHPO_4^{\circ}$
$H_2PO_4^-$	$ZnH_2PO_4^+$
HPO_4^{2-}	$ZnOH^+$
PO_4^{3-}	$Zn(OH)_2^{\circ}$
Ca^{2+}	$Zn(OH)_3^-$
$CaHCO_3^+$	$Zn(OH)_4^{2-}$
$CaCO_3^{\circ}$	Zn_2OH^{3+}
$CaHPO_4^{\circ}$	Fe^{3+}
$CaPO_4^-$	$FeOH^{2+}$
$CaH_2PO_4^+$	$Fe(OH)_2^+$
$CaOH^+$	$Fe(OH)_3^{\circ}$
Mg^{2+}	$Fe(OH)_4^-$
$MgHCO_3^+$	$Fe_2(OH)_2^{4+}$
$MgOH^+$	$Fe_3(OH)_4^{5+}$
$MgCO_3^{\circ}$	$FeSO_4^+$
$MgHPO_4^{\circ}$	$FeCl^{2+}$
Na^+	$FeCl_2^+$
$NaCO_3^-$	$FeCl_3^{\circ}$
$^{\#} ZnCO_3^{\circ}$	$FeHPO_4^+$

$^{\#}$ A $Zn(CO_3)_2^{2-}$ complex is also suggested. See text.

Table 5. Solid species considered in Saturation Index and Precipitation diagram preparation.

<u>Solid (chemical formula)</u>	<u>Common name</u>
CaCO_3	Calcite
Ca(OH)_2	Portlandite
$\text{CaHPO}_4 \cdot 12\text{H}_2\text{O}$	Brushite
$\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$	Octocalcium phosphate
$\text{Ca}_5(\text{PO}_4)_3\text{OH}$	Hydroxyapatite
MgCO_3	Magnesite
Mg(OH)_2	Brucite
$\text{Mg}_3(\text{PO}_4)_2$	-
ZnCO_3	Smithsonite
$\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$	Hydrozincite
Zn(OH)_2	-
$\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$	α -Hopeite
Fe(OH)_3	Amorphous iron (III) hydroxide
$\text{FePO}_4 \cdot 2\text{H}_2\text{O}$	Strengite

Table 6. Very generalized operation and properties of various inorganic water constituents in A/C pipe corrosion inhibition.

constituent	at level	in conjunction with (at indicated level)			function
		OH^-	CO_3^{2-}	PO_4^{3-}	
Zn	4	4,5	1,2		H, C
Zn	4	5		3	H?,C
Fe(III)	4,5	5		3	C
Fe(II)	4,5	5	1,2		C
Mn(IV)	5	5			C
Mn(II)	5		1,2		C
Cu(II)	4	5	1,2		H?,C
Ca	1				H
Ca	2	4,5	1,2		H, C
Ca	2	4,5		3	H?,C
Si(OH)_4	2	5			H

Notes:

Levels: 1 = 100-1000 mg/L
 2 = 10 - 100 mg/L
 3 = 1 - 10 mg/L
 4 = 0.1 - 1 mg/L
 5 = < 0.1 mg/L

Functions:

H = pipe surface hardener
 C = coats surface to bind fibers, but pipe surface may soften without other inhibitive factors.

Table 7. Saturation Index calculations for several protective solids. The temperature was assumed to be 20°C. Concentrations are in mg/L, mg/L as CaCO₃ for total alkalinity (TA).

Supply	pH	TA	Ca	Mg	SiO ₂	Eh ^a	Fe	Mn	saturation indices ^b						
									AI ^c	C ^d	CPT ^e	Q ^f	MD ^g	FH ^h	Fibers ⁱ
L-raw	7.52	155	14	2.3	51	0.17	0.27	0.04	11.2	-0.6	-1.1	1.0	-14	1.8	BDL
L-system	7.54	162	14	2.5	49	0.80	0.26	0.03	11.3	-0.6	-1.1	1.0	7.2	2.7	NSS
M-raw	7.64	180	4	1.6	33	0.16	0.12	0.02	10.9	-1.0	-1.5	0.8	-15	1.7	1.0
M-system	8.11	185	6.5	0.9	36	0.80	0.12	0.02	11.6	-0.3	-0.8	0.9	5.9	2.4	2.3
N-raw	7.40	17.2	5.5	2.4	16	0.18	1.3	0.04	9.8	-2.0	-2.5	0.5	-14	2.4	BDL
N-system	8.66	26.8	9.8	2.0	11	0.80	0.05	0.02	11.5	-0.3	-0.8	0.3	3.6	1.7	NSS
O-raw	8.50	210	2.3	0.6	15	0.11	0.03	0.01	11.6	-0.3	-0.8	0.5	-13	1.6	8.4
O-system	8.71	216	2.8	0.5	10	0.80	0.02	0.01	11.9	0.0	-0.5	0.3	3.2	1.3	26.8
P-raw	6.93	130	23	8.4	60	0.21	0.24	0.42	10.8	-1.0	-1.5	1.1	-14	0.8	1.5
P-system	6.82	141	25	9.0	60	0.80	3.8	0.46	10.8	-1.0	-1.5	1.1	5.6	3.3	NSS

Notes:

- Eh in volts. Estimated at 0.80 volts for distribution system waters, all of which were chlorinated. For raw waters, Eh was estimated from the dissolved oxygen concentration measured in the field by the Sato relationship given by Plummer, L.N. et al. USGS Water-Resources Investigations 76-13 (1978).
- SI = log (IAP/K_{so}). See text.
- AI = pH + log (AH). See text.
- C = CaCO₃, calcite phase.
- CPT = Fresh CaCO₃ precipitate in soils described by Suarez, D.L. Soil Sci. Soc. Am J. 41:310(1977).
- Q = SiO₂, quartz phase
- MD = MnO₂, birnessite phase.
- FH = Fe(OH)₃, amorphous fresh precipitate
- x 10⁶ per liter. NSS = not statistically significant.
BDL = below detection limit.

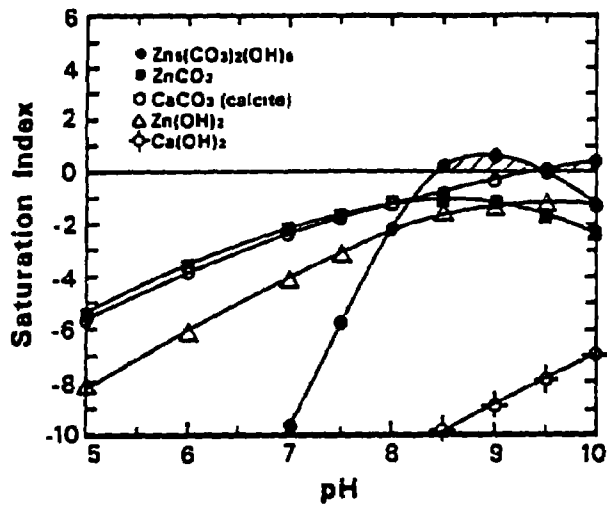


Figure 1. Saturation index diagram for model system H9 (see Table 3).

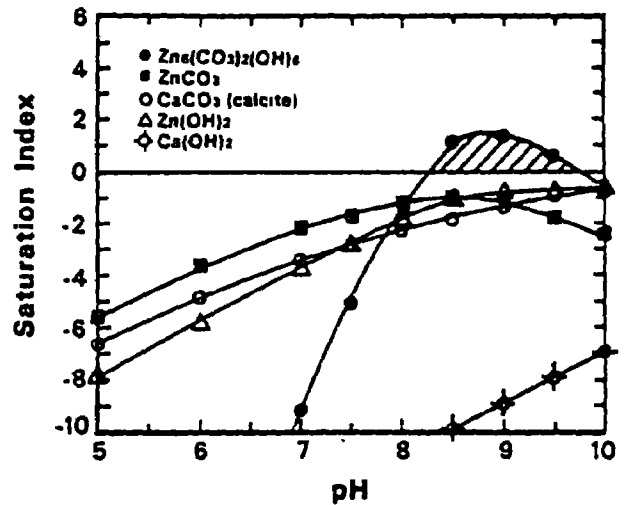


Figure 4. Saturation index diagram for model system H15 (see Table 3).

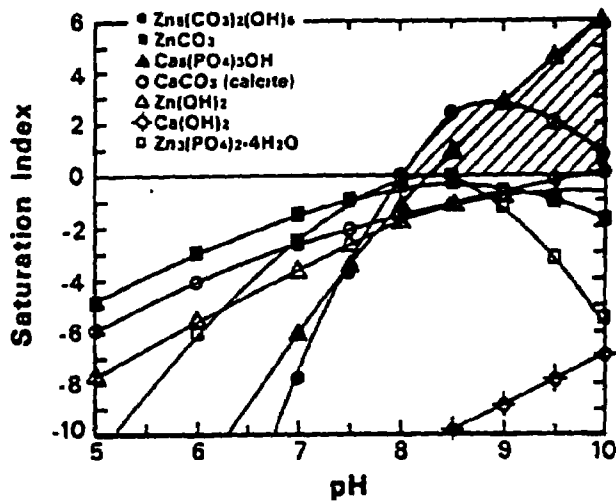


Figure 2. Saturation index diagram for model system H10P (see Table 3).

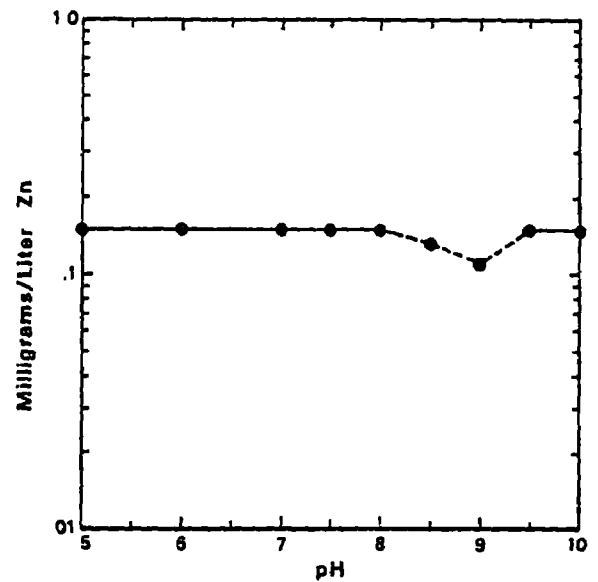


Figure 5. Precipitation diagram for zinc in model system H9 (see Table 3).

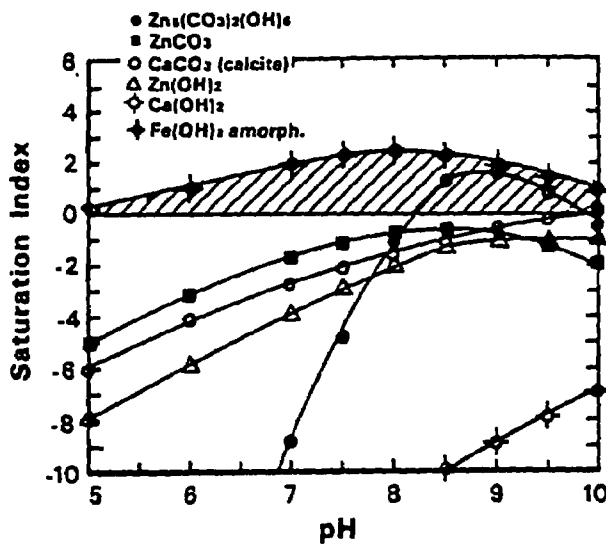


Figure 3. Saturation index diagram for model system H11 (see Table 3).

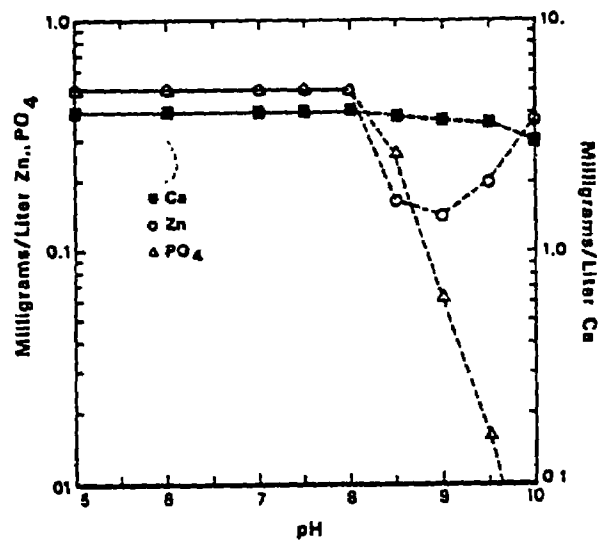


Figure 6. Precipitation diagram for zinc, calcium and orthophosphate in model system H10P (see Table 3).

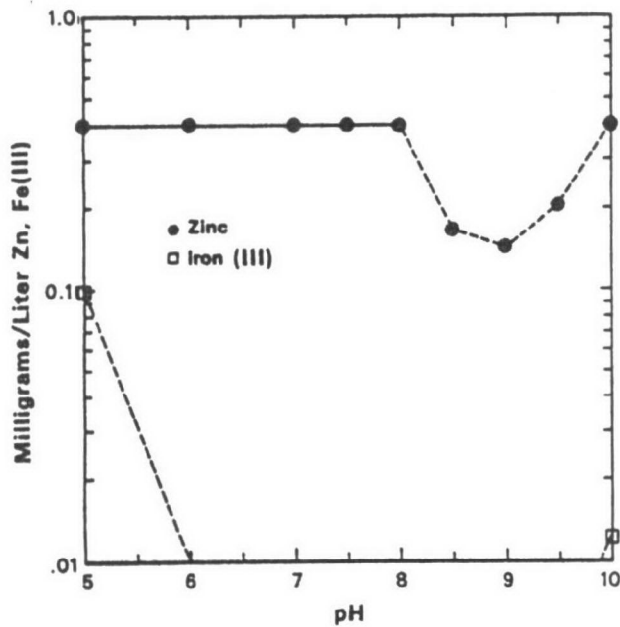


Figure 7. Precipitation diagram for zinc and iron (III) in model system M11 (see Table 3).

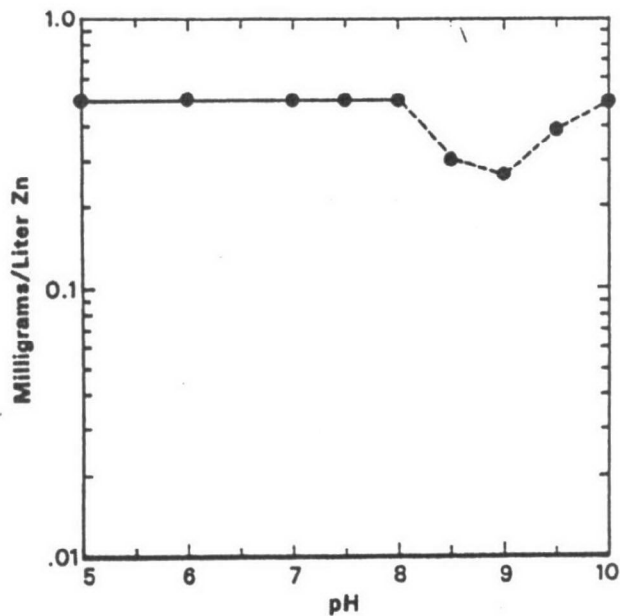


Figure 8. Precipitation diagram for zinc in model system M15 (see Table 3).

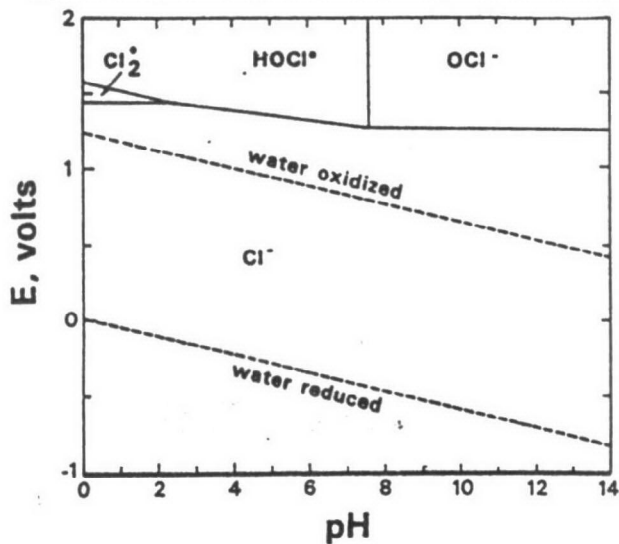


Figure 9. Potential - pH diagram for some metastable chlorination species at 25°C with dissolved activities of 1.0 mg/L as Cl-. Data is from reference 3.

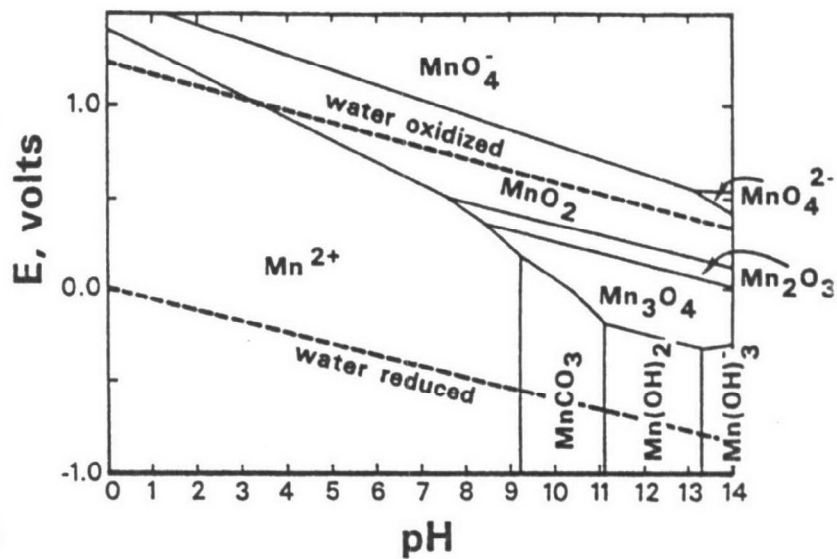


Figure 10. Potential - pH diagram of manganese in carbonate - containing water at 25°C. Stability fields are shown for dissolved manganese species activities of 0.05 mg/L and dissolved carbonate species activities of 40 mg/L as CaCO₃. Data is from reference 3.



Figure 11. Scanning electron micrograph of the pipe coupon from DWRD experiment 1 showing exposed fibers (see Tables 1 and 2). Iron and aluminum are constituents of the cement matrix.

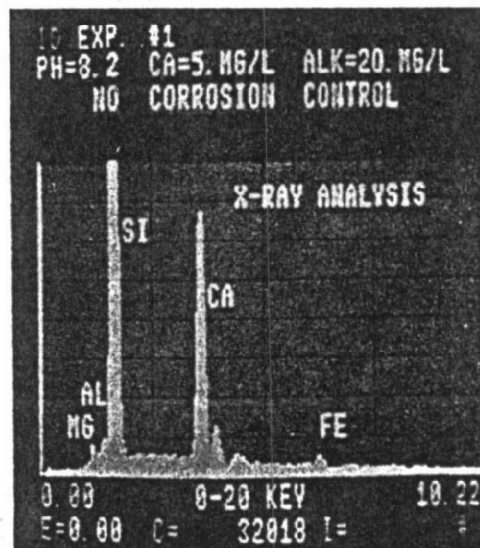


Figure 12. EDXA analysis of the pipe coupon from DWRD experiment 1 (see Tables 1 and 2).



Figure 13. Scanning electron micrograph of the pipe coupon from DWRD experiment 2 showing a uniform surficial coating (see Tables 1 and 2).

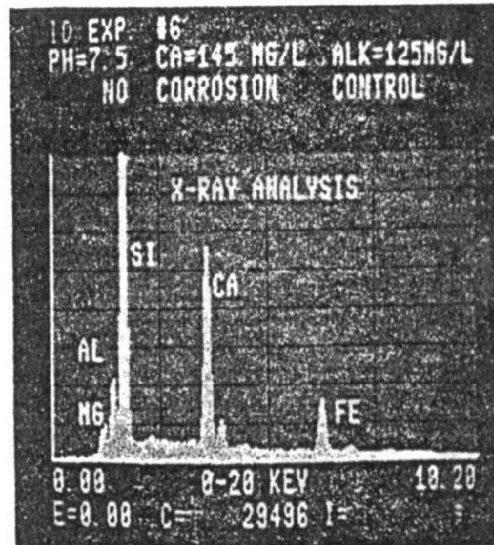


Figure 16. EDXA analysis of the pipe coupon from DWRD experiment 6 (see Tables 1 and 2). Iron and aluminum are constituents of the cement matrix.

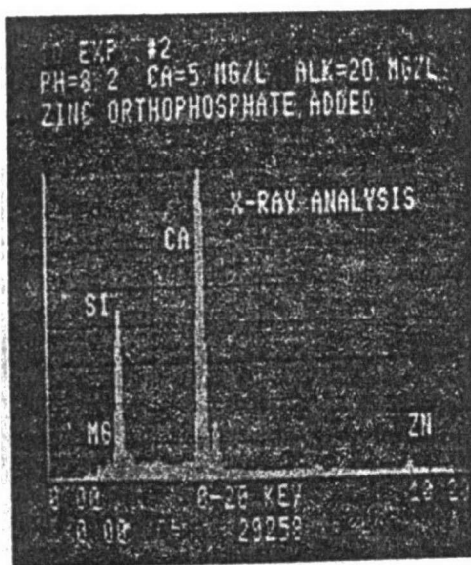


Figure 14. EDXA analysis of the pipe coupon from DWRD experiment 2 (see Tables 1 and 2). Note the presence of zinc, but not of phosphorous.



Figure 17. Scanning electron micrograph of a remote pipe section in a DWRD field experiment. Note the appearance of pitting resulting from pipe dissolution.



Figure 15. Scanning electron micrograph of the pipe coupon from DWRD experiment 6 showing some exposed fibers (see Tables 1 and 2).



Figure 18. Scanning electron micrograph of a pipe section from a DWRD field experiment, showing substantial coating by a zinc compound.