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ABSTRACT
        This document is an instructional module package
prepared in objective form for use by an instructor knowledgeable in
the chemistry of water stabilization and familiar with control of
deposition and corrosion in a water supply system. This is the second
level of a two module series. Included are objectives, instructor
guides, student handouts and transparency masters. The module
considers the stability analysis of a water, the chemistry of scale
formation, and the chemistry of corrosion and corrosion control.
(Author/RH)

ADVANCED STABILIZATION

Training Module 2.226.3.77

Prepared for the

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by

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September, 1977

2

TABLE OF CONTENTS

INSTRUCTOR GUIDE

for

Training Module II3ADWS

Advanced Stabilization

4

ABSTRACT

Advanced Stabilization is a training module for water treatment operators.
It is prepared in objective form and is intended for an instructor familiar
with stabilization and corrosion control. Upon completion of this module
the participant should have an understanding of the fundamental principles
of stabilization and corrosion chemistry and control methods. Participants
should have prior background in the subject, e.g. completion of the Basic
Stabilization or knowledge of that subject matter plus adequate background
in water chemistry. Total contact time will be 10.0 hours. The instructor
should have a black board, overhead projector and a 2 x 2 slide projector.

Module No: II3ADWS	Module Title: Advanced Stabilization
	Submodule Title:.
Approx. Time: 10.0 hours	Topic: Summary

Objectives: Upon completion of this module, the participant will be able to
1. Describe and conduct a stability analysis of a water.
2. Explain the chemistry of scale formation and the chemistry of its control or prevention.
3. Explain the fundamental chemistry of corrosion and corrosion control measures.
4. Recognize and describe special related concerns in water systems.

Instructional Aids:

Handouts
Transparencies

Instructional Approach:
Discussion
Case Studies

References:
1. New York Health Department, Manual of Instruction for Water Treatment Plant Operators, Health Education Service.
2. American Water Works Association, Basic Water Treatment Operator's Manual, AWWA No. M18, 1971.
3. Standard Methods for the Examination of Water & Wastewater, 14th Edition
4. Articles from the water supply literature.
5. Sawyer C.N. & McCarty P., Chemistry for Sanitary Engineers.

Class Assignments:
Readings
Some case studies and/or class problems.

Module No:	Module Title:
II3ADWS	Advanced Stabilization
	Submodule Title:
Approx. Time:	
1.0 hour	Topic:
	Introduction and Review

Objectives: Upon completion of this topic, the participant will be able to

1. Discuss scale formation and its concerns.
2. Discuss corrosion and corrosion concerns.
3. Describe the applicable water chemistry parameters and concepts.

Instructional Aids:

Handouts
Transparencies

Instructional Approach:

Discussion

References:

1. New York Health Department, Manual of Instruction for Water Treatment Plant Operators, Health Education Service.
2. American Water Works Association, Basic Water Treatment Operator's Manual, AWWA No. M18, 1971.

Class Assignments:

Readings

Module No: II3ADWS	Topic: Introduction and Review
Instructor Notes:-	**Instructor Outline:**
TRANS AS-1 Stability-Deposition	1. Discuss scale formation and its concerns. Stress the impact of the scale formation on the water system operation
	2. Ask participants to relate typical experiences from their system
TRANS AS-2 Corrosion Note: Attempt to obtain pipe and fittings examples of deposition and corrosion for class use.	3. Discuss corrosion and corrosion concerns. Stress the impact on the water system operation.
	4. Ask participants to relate typical corrosion problems from their experience.
TRANS AS-3 Water Quality Parameters	5. Discuss the primary water quality parameters of concern
TRANS AS-4 Water Softening	6. Discuss the water quality change with softening. Stress the quality characteristics of the treated water
TRANS AS-5 Forms of Alkalinity	7. Discuss the forms of alkalinity and the role of pH. Discuss pH + pOH equals 14 and how one can obtain the OH^- concentration. Relate the plot to softening and pH control of finished waters

Module No:	Module Title:
II3ADWS	Advanced Stabilization
	Submodule Title:
Approx. Time:	
2.0 hours	Topic:
	Deposition: Analysis and Control

Objectives: Upon completion of this topic, the participant will be able to

1. Describe solubility product concepts regarding typical water scale formation and the factors affecting it.
2. Describe the fundamentals of stability analysis of a water.
3. Discuss recarbonation chemistry.
4. Describe the chemistry of chelate action involving phosphate compounds and other chemicals.

Instructional Aids:

Handouts
Article reprints
Transparencies

Instructional Approach:
Discussion

References:

1. Sawyer C.N. & McCarty P., <u>Chemistry for Sanitary Engineers.</u>
2. Articles in the literature.

Class Assignments:

Readings
Typical stability index calculations.

9

Module No: II-3ADWS	Topic: Deposition: Analysis and Control

Instructor Notes:	Instructor Outline:

TRANS AS-6
$CaCO_3$ Equilibrium pH
 	
Note: 1. Review or present the sample problems from the Basic Module.
2. Use data from plants represented and analyze it for an example evaluation.
 	
TRANS AS-7
Saturation pH
 	
TRANS AS-8
Saturation pH - L-B Diagram
 	
TRANS AS-9
Stability Indices
 	
TRANS AS-10
Ryznar Index
 	
TRANS AS-11
Stability Index - Sample Prob.
 	
TRANS AS-12
Marble Test
 	
TRANS AS-13
Recarbonation
 	
TRANS AS-14
Chelating Compounds
 	
See reference article by Ralston
	1. Discuss equilibrium and solubility product concepts
	   a. $CaCO_3$ system
	   b. Cite other examples e.g.
	   $$Ca(OH)_2 \rightleftharpoons Ca^{++} + 2OH^-$$
	   $$CaF_2 \rightleftharpoons Ca^{++} + 2F^-$$
	   $$Fe(OH)_3 \rightleftharpoons Fe^{+++} + 3OH^-$$
	
	2. Discuss the stability analysis of water
	   a. Saturation pH
	   b. Calculation methods
	   c. Emperical nature of indices
	   d. Interpretation of indices
	   e. Laboratory analysis
	   f. Distribution system checks
	      1. Observe piping, fittings, and coupons
	      2. Monitor alkalinity change
	
	3. Discuss recarbonation
	   a. How and why it is used
	   b. Importance of pH control depending on purpose
	   c. CO_2 quantities
	
	4. Discuss chelate action
	   a. Calcium tie-up ahead of filters and distributing $CaCO_3$ in distribution systems
	   b. Ferrous iron. Prevents deposits of iron. Doesn't prevent corrosion.
	   c. Note reversion of polyphosphate to orthophosphate and temperature role.
	   d. Phosphonates - an industrial example

10

Module No:	Module Title:
II3ADWS	Advanced Stabilization
	Submodule Title:
Approx. Time:	
	Topic:
2.0 hours	Corrosion Chemistry

Objectives: Upon completion of this topic, the participant will be able to:

1. Describe the fundamental chemistry of the differential aeration cell and galvanic corrosion and factors involved.
2. Discuss and describe methods of corrosion detection including the use of coupons and probes.
3. Identify special corrosion concerns, e.g. copper.

Instructional Aids:

Handouts
Transparencies

Instructional Approach:
Discussion

References:

1. Articles from literature.

Class Assignments:

Readings

11

Module No: II3ADWS	Topic: Corrosion Chemistry

Instructor Notes:	Instructor Outline:

TRANS AS-15
Types of Corrosion Cells
 	
TRANS AS-16
Corrosion Cell
TRANS AS-17
Electrochemical Corrosion
	1. Discuss types of corrosion cells. Emphasize galvanic and differential aeration cells.
	
	2. Discuss fundamental chemistry of differential aeration cell.
	  a. Role of oxygen in removing H film
	  b. Role of iron precipitation to increase flow of Fe
	  c. Note types of iron precipitates
	  d. Comment on affect of protective film over the surface e.g. $CaCO_3$
	  e. Effect of flow velocity - remove products, DO increase
	  f. Pitting and uniform corrosion concepts

TRANS AS-18
Galvanic Series
	3. Discuss the galvanic series.
	  a. What corrodes? Current flow. Examples of problems
	  b. How would you select a metal as a sacrificial anode?

TRANS AS-19
Coupon Evaluation
See Mullen & Ritter Article.
	4. Discuss corrosion detection
	  a. Use of coupons and probes and measurements
	  b. Study of pipe sections, fittings
	  c. Note observations of staining, and red water
	  d. Monitor Fe concentration

TRANS AS-21 Material Selection-Corrosion	5. Discuss some special corrosion problems from instructor's experience and references. Note Material Selection Transparency

12

Module No: II3ADWS	Topic: Corrosion Chemistry
Instructor Notes:	Instructor Outline:
	a. Dezincification b. Graphitization c. Copper corrosion - blue-green staining

13

Module No:	Module Title:
II3ADWS	Advanced Stabilization
	Submodule Title:
Approx. Time:	
	Topic:
2.0 hours	Corrosion Control

Objectives: Upon completion of this topic, the participant will be able to

1. Describe the use of controlled $CaCO_3$ deposition.
2. Describe the chemistry of inhibitors.
3. Describe cathodic protection.
4. Discuss material selection as an alternative approach.

Instructional Aids:

Handouts
Reprints
Transparencies

Instructional Approach:
Discussion

References:

1. Articles from literature.
2. Data from chemical and equipment companies.

Class Assignments:

Readings

14

Module No:	Topic:	
II3ADWS	Corrosion Control	

Instructor Notes:	Instructor Outline:
TRANS AS-20 Approaches to Corrosion Control	1. Review approaches to corrosion control
	2. Discuss use of alkali addition and poly-phosphates to deposit a protective $CaCO_3$ film. Mention use of indices.
See Mullen-Ritter Article	3. Describe the use of corrosion inhibitors. Use Mullen-Ritter article as an example. Include discussion of
	a. Zinc - orthophosphates
	b. Phosphate only - high conc. limitations of water quality standards.
	c. Check with participants for their experiences
TRANS AS-21 Material Selection	4. Discuss material selection
	a. Role of different metals & alloys
	b. Use of PVC plastic, asbestos cement and concrete
	c. Use of liners e.g. cement
	d. Use of coatings, paints
TRANS AS-22 Cathodic Protection	5. Discuss cathodic protection
	a. Use of galvanic anodes
	b. Use of electrolytic anode
	c. Cite examples e.g. water storage, piping, plant units
	d. Ask for participant experience

15

Module No:	Module Title:
II3ADWS	Advanced Stabilization
	Submodule Title:
Approx. Time:	
	Topic:
2.0 hours	Special.Topics

Objectives: Upon completion of this topic, the participant will be able to

1. Discuss the iron bacteria problem.
2. Describe sulfate breakdown and H_2S problems.
3. Discuss external pipe corrosion.
4. Discuss well problems in scale and corrosion control.

Instructional Aids:

Handouts
Transparencies

Instructional Approach:

Discussion
Case Study

References:
1. Sawyer, C.N. & McCarty P., <u>Chemistry for Sanitary Engineers</u>.
2. Articles from the literature.

Class Assignments:

Readings
Case Studies

Module. No: II3ADWS	Topic: Special Topics
Instructor Notes:	**Instructor Outline:**

TRANS AS-23
Bacterial Action.
 	
Note: Cast Iron Pipe Research
Assoc. has handout material
and audiovisual material avail-
able. They make presentations.
 	
See Babbitt, Doland & Cleasby
	1. Discuss bacterial action
	  a. Iron bacteria - incidence, deposits,
	    control via chlorination and copper
	    sulfate
	  b. Sulfate breakdown and potential for it -
	    low flow anaerobic areas. Possible acid
	    formation .
	
	2. Discuss external corrosion
	  a. What factors are involved?
	  b. Methods of protection
	
	3. Discuss well problems with deposition,
	  corrosion and iron bacteria
	
	4. Analyze well problem case study

Module No's: II2XWS & II3ADWS	Topic: Reference Materials Utilized in Developing The Modules
Instructor Notes:	Instructor Outline:

Chlorine Feeding, p.45-58 Iron & Manganese Control, p. 59-62 Scaling & Corrosion Control, p.63-68 Fluoride feeding, p.72-73	AWWA, Basic Water Treatment Operator's Manual, AWWA No.M18, 1971
Softening, p.171-78 Corrosion & corrosion control, p.197-207 Fluoride deposition, p.214-15 Operation & Maintenance of Distribution Systems, 219-20 Plant Structures, p.234 Marble Test, p.281-83	N.Y. Dept. of Health, Manual of Instruction for Water Treatment Plant Operators, Health Educ. Service, N.Y.
Filters in Softening Plants, p.277-78 Corrosion Phenomena - Causes and Cures, p.295-312 Chemistry of the Lime-Soda Process, p.313-39 Iron and Manganese, p.378-396 Hydrofluosilicic Acid, 419-20 Nuisance organisms, p.494	AWWA, Inc. Water Quality and Treatment, 3rd Edit. McGraw-Hill, 1971
Wells, p.60-67, 73-77 Metallic Corrosion, p.274-88 Recarbonation, p.514-88 Misc. methods of treat., p. 572-77	Babbitt, H.E., Doland, J.J., Cleasby, J.L. Water Supply Engineering, 1962

Module No.'s: II2XWS & II3ADWS	Topic:	Reference Materials Utilized in Developing The Modules

Instructor Notes:	Instructor Outline:
Calcium Carbonate Saturation, p. 61-63 Iron & Sulfur Bacteria, 993-999	Amer. Public Health Assoc., Standard Methods For the Examination of Water and Wastewater, 14th Edition, 1976
Chemical equilibria, p.31-38, p.59 Alkalinity, p.327-39 Hardness, p.347-355 Water Softening, p.356-62 Iron & Manganese, p.446-52	Sawyer, C.N. & McCarty, P.L., Chemistry for Sanitary Engineers, 2nd Edit. 1967
Chemical Precipitation, Stabilization and Ion Exchange, p.29-1 to 29-34 Corrosion, 30-15 to 30-26 .	Fair, G.M., Geyer, J.C. & Okun, D.A., Water and Wastewater Engineering, Vol. 2. 1968
	Kleber, John P. "The Effect of Water Quality on the Corrosion of Pipe Lines", p264-290 Proceedings of the Second Annual Underground Corrosion Short Course, Late 1950's
	Larson, T.E. "Corrosion by Domestic Waters" Illinois State Water Survey Study, 48 pages, mid 1970's
	Ralston, P.H., "Inhibiting Water Formed Deposits with Threshold Compositions", p.39-44, V.11 No6 Materials Protection and Performance, June 1972
	Mullen E.D. & Ritter, J.A. "Potable Water Corrosion Control" p.473-79, JAWWA, Aug 1974
	Corrosion Article Series - Aug 1974, JAWWA
	Weers, Walter A. and Middlebrooks, E.J., "A Review of the Theory and Control of Corrosion", R18-R28, Water and Sewage Works, Ref. No. 1967

19

# Inhibiting. Water Formed Deposits with Threshold Compositions

P. H. RALSTON, *Calgon Corp., Pittsburgh, Pa.*

WATER used in commercial applications is not pure H_2O but contains a variety of anions, cations, dissolved gases, and particulate matter. When this aqueous raw material is concentrated, blended, pressurized, seeded or pH adjusted, combinations of scale forming anions and cations can exceed their solubility limit, and water formed deposits occur. These water formed deposits may be reduced or eliminated by the removal of undesirable anions or cations in precipitation or ion exchange reactions. Often the deposition can be controlled by pH adjustment or reduction of the number of concentration cycles. However, in many industrial applications, these alternatives are expensive or impractical. On the other hand, treatment of the problem water with small amounts of certain chemical compositions can be an effective and economical solution. This chemical process has been termed threshold treatment, and treatment rates of 0.1 to 10 mg/l have been called threshold concentrations.

Organic Threshold Inhibitors

Four general types of organic threshold inhibitors have been found particularly useful in controlling water formed deposits. Three of these compositions are phosphorus bearing and are classed as phosphonates, diphosphonates, and phosphate esters. The fourth type contains no phosphorus and is a polyacrylate.

The most representative and most widely applied phosphonates are the family of aminomethylenephosphonates (AMP) with their
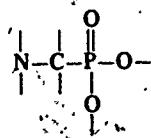
linkage. In the empirical formula (Figure 1), M represents a monovalent metal, hydrogen or ammonium group. When n = 0, the structure represents the monoaminomethylene-
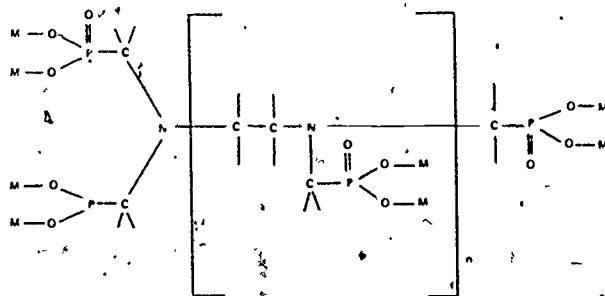
Aminomethylenephosphonate (AMP)
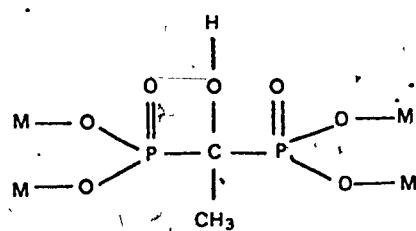
1, Hydroxyethylidene-1,1 Diphosphonate (HEOP)
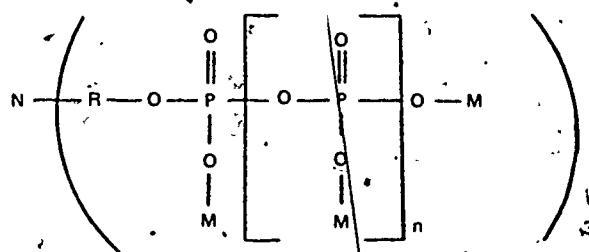
Amine Phosphate (AP)

Figure 1 — Chemical structure of AMP, HEDP, and AP.

phosphonate (AMP-0). With n = 1, the structure is the ethylenediaminomethylene phosphonic acid (AMP-1). Polymers at least as high as AMP-5 have been found to be effective threshold inhibitors.

The diphosphonates are characterized by a

$$-\overset{\overset{\displaystyle O}{\|}}{\underset{|}{P}}-\overset{|}{\underset{|}{C}}-\overset{\overset{\displaystyle O}{\|}}{\underset{|}{P}}-$$
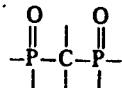
bonding arrangement. The 1-hydroxyethylidene 1, diphosphonate (HEDP), sometimes referred to as ethanol diphosphonate (EDP), is the most representative of the diphosphonates (Figure 1). In the formula, M represents hydrogen, monovalent metal, or an ammonium group.

The phosphate esters have the phosphorus in a

$$-\overset{|}{\underset{|}{C}}-O-\overset{\overset{\displaystyle O}{\|}}{\underset{|}{P}}-$$
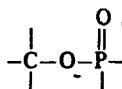
arrangement. The phosphate ester evaluated in this study was an amine phosphate (Figure 1). The M represents hydrogen, a monovalent metal, or ammonium group; R is a hydrocarbon moiety. Depending on the synthesis procedure, n may be 0 or more, and inorganic phosphates or polyphosphates may be present as by-products. Approximately 50% of the phosphorus content of the ester used in this study was present in the orthophosphate form.

The nonphosphorus bearing threshold inhibitors have been known for many years.[1,2] Long chain polymers containing repeating carboxy groups have been the most widely used. Presently, the low molecular weight polyacrylates are the most representative threshold inhibitors of the nonphosphorus type. These polyacrylates have repeating polymeric units of

$$\left[\begin{array}{c}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\\\quad\overset{\|}{\underset{}{C}}=O\end{array}\right]$$
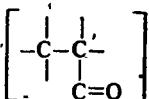
In Figure 2, M represents hydrogen, monovalent metal, or ammonium groups; n may vary from <10 to >10,000 repeating units.

Inorganic Threshold Inhibitors

The inorganic polyphosphates are prepared by molecularly dehydrating appropriate orthophosphates and have a repeating

$$-\overset{\overset{\displaystyle \|}{}}{\underset{|}{P}}-O-\overset{\overset{\displaystyle \|}{}}{\underset{|}{P}}-$$
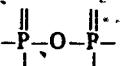
structure. The M in the polyphosphate formula (Figure 2) represents a monovalent metal, hydrogen, or ammonium group. The orthophosphate, a nonpolyphosphate form, and an ineffective threshold inhibitor, exists when n = 0. The shortest polyphosphate polymer, pyrophosphate (PP-1), exists when n = 1 and has a crystalline form. When n is greater than about 3, the products are glassy polyphosphates.

Common Threshold Properties

The organic threshold inhibitors—phosphonates, di-
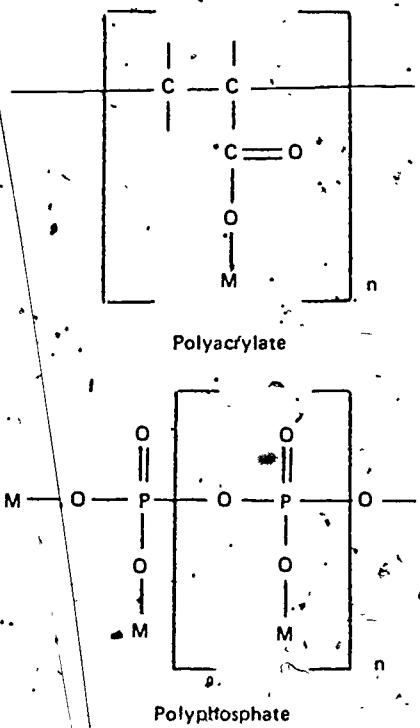
Figure 2 — Chemical structure of polyacrylate and polyphosphate.

phosphonates, phosphate esters, and polyacrylates have structural and chemical characteristics of the inorganic threshold compositions. All of the phospho-organic compositions can have multi-groups of

$$-\overset{\overset{\displaystyle O}{\|}}{\underset{\displaystyle OH}{P}}-OH$$
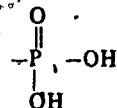
in common with the inorganic polyphosphates. On the other hand, the polyacrylates have repeating

$$-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$
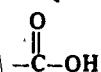
groups.

The organic threshold inhibitors, like the inorganic polyphosphates, inhibit alkaline earth metal scales at less than stoichiometric concentrations. At effective threshold treatment rates of 1 mg/l or less, molar ratios of 1 part inhibitor/300 to 10,000 parts cation ion are present. At these ratios (far below a mole to mole stoichiometric relationship), suppression of nuclei growth can only be explained by a surface phenomenon.

Organic and inorganic threshold inhibitors modify crystal growth at less than optimum threshold concentrations. When crystallization is almost completely inhibited, the crystallites are markedly reduced in number, enlarged in size, and grossly deformed.

In the laboratory, calcium carbonate crystals were allowed to develop in supersaturated solutions containing subthreshold levels of organic phosphonate (AMP-0), diphosphonate (HEDP), phosphate ester (AP), and inorganic polyphosphate (PP-12). The small, regular rhombohedrons obtained from the untreated solution contrast with the larger, rounder, distorted crystals formed in the threshold treated solutions (Figure 3).
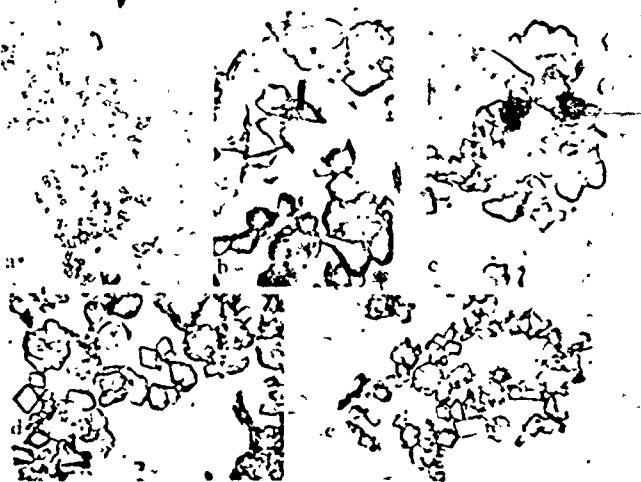
Figure 3 — Calcium carbonate (CaCO₃) crystallized in the presence of a) no inhibitor, b) polyphosphate, c) phosphonate (AMP-0), d) diphosphonate (HEDP), and e) amine phosphate (AP).

The organic threshold scale inhibitors, like the inorganic polyphosphates, are also useful corrosion inhibitors. Used alone or in combination with zinc or chromate, they effectively inhibit the oxygen corrosion of ferrous and nonferrous metals. Moreover, the organo-phosphorus threshold inhibitors, like their inorganic progenitors, have excellent sequestering properties. At concentrations in the stoichiometric range, the organic compositions chelate multivalent cations in a soluble complex in competition with scale forming anions.

Laboratory Evaluations

The polymeric nature of the inorganic and organic threshold compositions results in a multiplicity of possible products. As potential scale inhibitors, they can be evaluated in the laboratory under controlled conditions and for particular types of scale. Screening tests could involve dispersing or flocculating the solids or conditioning the particulates to make them nonadherent. However, in this evaluation, no attempt was made to alter the scale forming deposits. Rather, the inhibitors were rated for their ability to retard or inhibit the original precipitation by the threshold mechanism.

The laboratory screening test for calcium sulfate involved a stagnant, 24 hr storage period at 66 C (150 F) with the scale forming constituents at several times their normal saturation level. The supersaturation was developed by co-mixing solutions of sodium sulfate and calcium chloride. The inhibitor treatment was added to the scale forming anion solution prior to the addition of the scale forming cation solution.

The temperature and scale saturation levels were higher than encountered in most cooling water applications but were considered appropriate for a rapid screening test. Several thousand milligrams/liter of sodium and chloride ion were present as a result of the supersaturation technique, but such soluble ions are present in commercial cooling waters.

The effectiveness of the threshold scale inhibition was determined by titration of the soluble scale forming cation using the Schwarzenbach Method (EDTA). Titration volumes representing the total calcium ion present (V_T), calcium ion present in the absence of inhibitor (V_O),

and in the presence of inhibitor (V_E) yield percent inhibition data.

$$\frac{V_E - V_O}{V_T - V_O} \times 100 = \% \text{ inhibition}$$

One hundred percent inhibition represented no deposition of scale, while 0% inhibition represented precipitation when no inhibitor treatment was present.

Calcium Sulfate Stabilization

Four sodium polyacrylate polymers were evaluated as calcium sulfate inhibitors. The n-values of these acrylates were approximately 10, 25, 50, and 100; the theoretical calcium sulfate concentration in the test solutions was 6800 mg/l. This is 2.3X the control (uninhibited) concentration of 2960 mg/l CaSO₄ after 24 hrs of stagnant storage (150 F).

Experimental calcium sulfate inhibition data for the four sodium acrylate polymers show that the shortest acrylate polymer, n ~10, was an effective inhibitor for controlling CaSO₄ · 2H₂O deposits. One hundred percent inhibition was obtained at an inhibitor treatment rate of about 2.8 mg/l of active sodium polyacrylate. The polyacrylate with n ~25 was much less effective, while the higher molecular weight polymers showed very poor calcium sulfate inhibition.

Other organic threshold compositions were evaluated by the same test method. The following concentrations of 100% active inhibitor (as the acid) were required to give 100% inhibition of calcium sulfate deposition (in those cases where complete stabilization was not obtained, the experimental percent inhibition is noted in parentheses): phosphonate (AMP-1), 1.5 mg/l; amine phosphate (AP), 1.6 mg/l; polyphosphate (n = 2), 7.5 mg/l, (90%); and diphosphonate (HEDP), 30.0, mg/l, (20%).

Hydrated Iron Oxide Stabilization

Both the organic and inorganic threshold compositions inhibit the development of hydrated iron oxide (ferric hydroxide). While the molar ratios of inhibitor to iron are not as dramatic as in the case of calcium sulfate and calcium carbonate, the inhibitors do an effective job in the threshold treatment range of 1 to 2 mg/l.

The iron stabilization test was carried out at 25 C (77 F) in water containing 4 grain/gal hardness as CaCO₃ and 2 mg/l Fe. The iron was added to the water in the ferrous form; the pH was adjusted to 6.7 ±0.25 to promote oxidation to the ferric form, and the samples were stored for 18 hrs. At the end of the test period, the iron bearing waters were filtered, acidified, and analyzed for iron by atomic adsorption. The organic and inorganic threshold inhibitors were added as 100% active agents (as acid) except in the case of the polyacrylate polymer (n ~10) which was present in the neutral form.

The iron stabilization test showed that at a 1 mg/l treatment rate, the aminomethylenephosphonate (AMP-0) and the diphosphonate (HEDP) gave 90% stabilization of 2 mg/l Fe. The inorganic polyphosphate (PP-12) required about 2 mg/l for this stabilization level. The amine phosphate (AP) gave 50% inhibition at 3 mg/l treatment rates, and the polyacrylate (n ~10) was considerably less effective.

Calcium Carbonate Stabilization

Calcium carbonate deposits are the most prevalent scale

component in industrial cooling waters because of the thermal instability of bicarbonate waters during cooling tower operation. Several of the organic and inorganic threshold inhibitors are excellent calcium carbonate inhibitors. The performance of four polymeric forms of the aminomethylenephosphonate family (AMP-0 to AMP-5) were obtained in a 24-hr static test cycle (150 F) similar to the one previously described. The calcium carbonate concentration was 100 mg/l (4X the control saturation of 25 mg/l $CaCO_3$), the original pH was 10 to 10.4. Small amounts of sodium and chloride ion were present from the co-mixture of sodium carbonate and calcium chloride solutions.

The most effective AMP polymer was AMP-0 which gave complete calcium carbonate stabilization at 0.25 mg/l of 100% active acid. Polymers AMP-1 and AMP-2 required about 0.45 mg/l and 0.5 mg/l for complete calcium carbonate stabilization.

Other organic and inorganic threshold inhibitors were evaluated as calcium carbonate inhibitors by the same test method. All inhibitors were checked at 100% activity of the acid salt except in the case of the sodium polyacrylate (n ~10). The threshold treatment rates required to obtain 100% $CaCO_3$ inhibition are phosphonate (AMP-0), 0.25 mg/l, diphosphonate (HEDP), 0.25 mg/l, polyphosphate (PP-2), 0.3 mg/l, (95-100%), polyphosphate (PP-1), 0.35 mg/l, (95-100%), phosphonate (AMP-1,2), 0.45 to 0.5 mg/l; polyphosphate (PP-12), 0.5 mg/l, (95-100%), amine phosphate (AP), 0.5 to 0.7 mg/l, (90-95%), and polyacrylate, sodium (n ~10), 1.5 mg/l. In those cases where inhibition was not complete, the maximum percent inhibition is noted in parentheses.

Compatibility with Corrosion Inhibitors and Other Water Constituents

Several of the organic and inorganic compositions—the phosphonate (AMP-0, 1, 2), the diphosphonate (HEDP), the polyphosphates (PP-1, 2, 12), and the amine phosphate (AP)—effectively inhibited calcium carbonate in the short term screening tests. However, in many industrial applications, the threshold compositions must be effective over long periods of time at elevated temperatures. Likewise, since threshold scale inhibitors are regularly used in combination with corrosion inhibitor systems, compatibility with Zn^{++} and chromates is required. Organic biocides or chlorine or solid calcium carbonate "seed" are often present in threshold treated waters, and compatibility is desirable and often mandatory. The influence of these variables on the usefulness of threshold scale inhibitors was investigated.

Stability

The inorganic polyphosphates tend to degrade slowly to the orthophosphate form. This reversion product has no threshold inhibiting properties and is a source of potential calcium phosphate deposition. Elevated temperatures, acidic pH levels, bacteriologic growth, and time act to promote this reversion.

The effectiveness of four threshold inhibitors-aminomethylenephosphonate (AMP-0), diphosphonate (HEDP), amine phosphate (AP), and polyphosphate (PP-12)-in stabilizing calcium carbonate was determined over an extended test interval. The standard screening test (150 F, 4X saturation) was used, inhibitor treatment levels were the minimum concentrations which would give complete inhibition or best performance after 24 hrs. The inorganic polyphosphate (PP-12) effectiveness was reduced to 10% inhibition after 7 days. The amine phosphate (AP) stabilization efficiency leveled off at about 80% calcium carbonate inhibition for at least 10 days. Both the phosphonate (AMP-0) and the diphosphonate (HEDP) exhibited 97 to 100% inhibition after 22 days.

The loss of calcium carbonate inhibition in the presence of the polyphosphate (RP-12) can be correlated with the solution degradation of the polyphosphate. On the other hand, the organic threshold inhibitors gave little or no indication of reduced calcium carbonate inhibition with time. Any degradation of the amine phosphate (AP), the diphosphonate (HEDP), or the phosphonate (AMP-0) did not markedly affect its ability to stabilize calcium carbonate.

Compatibility with Zn^{++}

In many cooling water systems, the corrosion inhibitor contains soluble zinc as one of its components. The compatibility of the four threshold inhibitors with zinc ion was followed by the laboratory screening test for calcium carbonate stabilization. Test conditions and inhibitor concentrations were the same as those previously described with the exception that zinc ion was added at 2.5 mg/l.

The percent inhibition achieved with the zinc-phosphonate (AMP-0) and zinc-amine phosphate (AP) combinations was similar to the calcium carbonate stabilization found in the absence of zinc ion. The stabilizing power of the diphosphonate inhibitor was adversely influenced by the zinc additive. This combination exhibited only 75 to 80% calcium carbonate inhibition rather than the 95 to 100% obtained in the absence of zinc ion. The inorganic polyphosphate (PP-12) stabilized calcium carbonate more effectively in the presence of the zinc ion than in its absence (55% inhibition vs 10% inhibition @ 7 days). While the inorganic polyphosphate (PP-12)-Zn^{++} system was not as effective on calcium carbonate as the organic compositions over extended time periods, the favorable influence of zinc ion on polyphosphate performance suggested that the polyphosphate reversion rate had been reduced.

This effect of zinc ions on polyphosphate reversion rates was investigated in laboratory storage tests. Synthetic cooling water (700 mg/l solids, 95 mg/l Ca^{++}, 20 mg/l Mg^{++}, 100 mg/l HCO_3^-) was sterilized to eliminate bacteriological variables, and treatment levels of 15 mg/l polyphosphate (PP-12) and 3 mg/l Zn^{++} were added. The waters were stored in stoppered glass flasks at 93 F ±0.5 with solution pH values maintained at 7.3 ±0.2. The orthophosphate degradation product was followed regularly with colorimetric analyses.

Percent buildup of the orthophosphate reversion product with time was noted. The polyphosphate (PP-12) treated water showed 28% orthophosphate after 1 week and 45% orthophosphate after 2 weeks. The solution treated with polyphosphate (PP-12)-Zn^{++} contained 13 and 20% orthophosphate. The addition of 3 mg/l Zn^{++} to the polyphosphate solution doubled its effective life. Under the same concentration and storage conditions, waters treated with AMP-0 and Zn^{++} contained only about 1% orthophosphate.

Compatibility with Cr^{+6}

Many cooling water corrosion inhibitors contain chromates or dichromates, and threshold scale control must be effective in the presence of this environment. The four types of threshold inhibitors were evaluated as calcium

carbonate inhibitors in the presence of 2.5 mg/l chromate (as CrO_3). The laboratory screening test and the inhibitor concentrations were the same as used earlier.

The phosphonate (AMP-0)-Cr^{+6}, the diphosphonate (HEDP)-Cr^{+6}, and the amine phosphate (AP)-Cr^{+6} combinations inhibited calcium carbonate deposition completely for the 7-day test period. The amine phosphate (AP)-Cr^{+6} system gave better inhibition than was observed in the absence of chromate. Improved performance with time was also noted for the polyphosphate (PP-12)-Cr^{+6} system as compared with polyphosphate alone. These improvements suggest a slower reversion rate or the inactivation of orthophosphate in the presence of chromium ion.

Compatibility with Biocides

Threshold scale inhibitors must remain effective in combination with oxidizing and nonoxidizing biocides, normal components of industrial cooling waters. Calcium carbonate stabilization tests were carried out using the standard screening test and inhibitor concentrations necessary for complete inhibition (or maximum performance) after 24 hrs of storage. The chlorine level was 2 mg/l, and approximately 50% was present as free chlorine. After 24 hrs of storage, the four representative threshold inhibitors showed the normal 90 to 100% stabilization of calcium carbonate.

The calcium carbonate stabilization tests carried out in the presence of chlorine were supplemented with chlorine stability tests. Two mg/l of chlorine (50% free Cl_2-50% combined Cl_2) was added to solutions containing 5 mg/l (acid equivalent) of the active threshold inhibitor. The percent of free chlorine present in the test solutions after 5 minutes (pH 6 6 ±0.1) was polyphosphate (PP-12), 90%; phosphonate (AMP-0), 10%; diphosphonate (HEDP), 100%; and amine phosphate (AP), 90%.

When 5 mg/l Zn^{++} was added to the AMP-0 solution, the percent of free chlorine in solution was 80%. This suggests that in the absence of the corrosion inhibitor component-Zn^{++}, chlorination of AMP-0 treated waters should be carried out in a slug treatment cycle.

Nonoxidizing biocides were also tested for their effectiveness in the presence of the threshold scale inhibitors. The biocide was a chlorophenate (37.5 mg/l), and the test organism was the aerobic bacteria-aerobacter aerogenes. Synthetic cooling waters containing 15 mg/l of the active threshold inhibitor (as acid) or 15 mg/l inhibitor and 5 mg/l Zn^{++} were inoculated with the bacteria, held for 3 hrs at room temperature, and incubated at 35 C (95 F) for 48 hrs. The percent bacteria kill and a comparison of the bacterial counts with and without biocidal treatment are given in Table 1.

These results show that the polyphosphate (PP-12) and the phosphonate (AMP-0) have no adverse effect on the biocidal action of the chlorophenate. The presence of the diphosphonate (HEDP) appeared to reduce somewhat the bacteria kill, while the amine phosphate (AP) improved its

performance. In the presence of both Zn^{++} and threshold inhibitor, the biocidal action was markedly improved in all cases. This indicated that biocidal agents of the chlorophenate type were compatible with threshold scale inhibitor components.

Compatibility with $CaCO_3$ Solids

Calcium carbonate stabilization in industrial cooling water systems may not always be completely free of deposition. When the treatment rates are inadequate or irregular and when scaling conditions are variable or unmanageable, calcium carbonate may be deposited. To determine the effect of predeveloped crystals of calcium carbonate on threshold-treated cooling waters, 2 mg/l of calcium carbonate "seed" was added to the laboratory scaling solution. Inhibitor concentrations were just sufficient to give complete or best possible calcium carbonate stabilization under regular test conditions. The percent inhibition data were very similar to the calcium carbonate holdback observed under the same test conditions in the absence of calcium carbonate "seed". This ability of threshold scale inhibitors to stabilize water-formed calcium carbonate in the presence of preformed carbonate is another reason for their widespread and successful commercial application.

Removal of Threshold Inhibitors

The threshold scale inhibitors investigated in this study are suspect in the present emotional attack on phosphates. Even though the treatment rates of these phosphorus bearing compositions are in the low mg/l range and well known and useful methods are available for their removal, ecologists continue to class these compositions as pollutants.

Activated carbon holds some promise for the removal of the higher molecular weight organic polymers. However, present carbon efficiencies are low, and carbon renewal costs would be high. Membrane filtration may soon be a useful method based on the improved membranes and rejection rates presently being obtained.

Conventional water and sewage treatment based on bacteria, lime, conventional flocculants, or new polyelectrolytes are presently the most general and most practical approach to the removal of phosphorus compounds. Empirical data showing the relative ease of removal of these threshold compositions were obtained in simple laboratory tests. The threshold scale inhibitors were present at concentrations equivalent to 15 mg/l of active acid. Lime was added at the rate of 200 mg/l, iron (Fe^{++}) was added at a ratio of 2 Fe:1 P, and the solution was adjusted to pH 9.0. After 5 minutes of mild agitation and 2 minutes with no agitation, the solutions were filtered, and the filtrates analyzed for total phosphorus (as PO_4). The inorganic polyphosphate (PP-12) was removed most effectively (90%). The diphosphonate (HEDP), the amine phosphate (AP), and the phosphonate (AMP-0) showed less effective removal in that order.

Rapid and accurate analytical methods are desirable for following the treatment rate of threshold scale inhibitors. Waters containing polyphosphates, phosphonates, and diphosphonates can be checked at the application site by a rapid colorimetric titration using thorium nitrate and xylenol orange indicator. The thorium test is not promising for the amine phosphate evaluated in this study because it contains a substantial amount of orthophosphate, and high concentrations of orthophosphate cause interference in the

TABLE 1 – Percent Bacteria Kill

Biocide (37.5 mg/l)	Threshold Agent (15 mg/l)		Zn^{++} (5 mg/l)
56%	PP-12	58%	91%
56%	AMP-0	52%	81%
56%	HEDP	38%	75%
56%	AP	90%	100%

thorium test. Analytical tests for polyacrylates are not well adapted to field use.

In the laboratory, solutions of the polyphosphate can be analyzed colorimetrically by the reduction of the phospho-molybdenum complex following a boiling acid operation. Solutions containing the organic phosphorus-bearing compositions can be evaluated by a similar method using sulfuric acid and persulfate in the boiling step. Acrylate concentrations can be followed in the laboratory by precipitation as cupric acrylate or adsorption of the acrylate methylene blue complex, but procedures are time consuming.

Cost Effectiveness

The cost effectiveness of a threshold scale inhibitor is of prime importance. Those investigated in this study have exhibited widely different efficiencies under different scaling parameters, and their cost also varied over a broad range. Obviously, selection of a threshold scale inhibitor will be based on the most effective inhibitor at the lowest cost, but product availability, ease of application, and service will influence the overall decision.

The cost of the threshold inhibitors evaluated will be affected by the quantities purchased, the freight rates, the physical form, and the producer/nonproducer status. Assuming the polyphosphate (PP-12) can be purchased in truckload quantities, the 100% active acid compositions would cost approximately $0.15 to $0.20/lb. The amine phosphate (AP) and the phosphonate (AMP-0) costs would be about three times this range, and the diphosphonate (HEDP) and the polyacrylate (n ~10) would cost 5 to 6 times this amount.

Summary

The threshold compositions which were evaluated possess a large number of the properties desired in a good inhibitor for water formed deposits. Treatment with threshold amounts of the phosphonate (AMP-0, 1) gave excellent control of calcium carbonate, hydrated iron oxide, and calcium sulfate. Substoichiometric amounts of the diphosphonate (HEDP) also gave excellent inhibition of carbonate and iron deposits, but calcium sulfate stabilization was poor. The amine phosphate (AP) and polyacrylate (n ~10) were excellent to good as threshold inhibitors for calcium sulfate but were poor stabilizers of hydrated iron oxide. The polyphosphate (PP-12) performed well in short term tests as a threshold inhibitor for calcium carbonate and iron oxide but showed only fair inhibition of calcium sulfate.

The four phosphorus bearing threshold compositions effectively controlled calcium carbonate deposition, the most widely encountered cooling water scale. In general, the phosphonates, diphosphonate, amine phosphate, and polyphosphates were compatible with Zn^{+2}, Cr^{+6}, oxidizing and nonoxidizing biocides, and calcium carbonate "seed". In the laboratory tests, time-temperature instability was noted with the polyphosphate inhibitor (PP-12), and the diphosphonate exhibited reduced effectiveness in the presence of Zn^{++} and the chlorophenate biocide. The phosphonate (AMP-0), in the absence of Zn^{++}, reacted with chlorine, but calcium carbonate stabilization was not adversely affected. The amine phosphate (AP) appeared to be limited in its ability to completely inhibit calcium carbonate under the conditions of the test.

Analytical procedures for the determination of low concentrations of phosphorus bearing, threshold inhibitors were deemed adequate. Phosphate removal methods are well known and require only modification and upgrading to satisfy pollution standards. Laboratory screening tests related to cost effectiveness can be useful in selecting threshold scale inhibitors for commercial applications.

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TRANSPARENCIES

for

TRAINING MODULE II3ADWS

Advanced Stabilization

27

STABILITY - DEPOSITION

STABILITY - $CaCO_3$ EQUILIBRIUM. A CHARACTERISTIC OF A WATER RELATED
TO ITS TENDENCY TO DEPOSIT $CaCO_3$ OR BE-CORROSIVE TO METAL
SURFACES

DEPOSITION CONCERNS

DEPOSITION IN TREATMENT PROCESS EQUIPMENT AND PIPING - eg. $CaCO_3$,
Iron oxides, CaF. - Interference with flow and operations

DEPOSITION ON FILTER MEDIA - Media change, backwashing

DEPOSITION OF $CaCO_3$ IN DISTRIBUTION SYSTEM - Resistance to flow., Inc.
head loss

DEPOSITION IN-HEATED WATER SYSTEMS - Heat transfer, failure

IRON DEPOSITS FROM CORROSION OR NATURAL SOURCES - Iron bacteria, Tuber-
culation, Staining, Water flow

MANGANESE DEPOSITS FROM NATURAL Mn SOURCES - Staining

WELL SCREEN INCRUSTATION AND WELL EQUIPMENT DEPOSITS - Restrict flow

TRANS AS-1

CORROSION

CORROSION - THE DESTRUCTION OF A METAL BY CHEMICAL OR ELECTROCHEMICAL
REACTION WITH ITS ENVIRONMENT

CORROSION CONCERNS

LOSS OF METAL FROM PIPING DUE TO WATER-METAL SURFACE ACTION - Pitting

INCREASE IN IRON CONTENT OF WATER SUPPLY - Staining

DEVELOPMENT OF IRON DEPOSITS - Tuberculation, staining; water flow

DETERIORATION OF PROCESS EQUIPMENT IN CHEMICAL FEED AREAS - eg. Hypochlorite,
H_2SiF_6

EXTERNAL CORROSION OF METAL SURFACES IN PROCESS AREAS, PIPE GALLERIES -
Interference, Appearance

EXTERNAL CORROSION OF BURIED PIPE

COPPER CORROSION WITH SOFT WATER - Staining

WELL SCREENS, CASINGS, SHAFTS

TRANS AS-2

WATER QUALITY PARAMETERS

$$pH - \log \frac{1}{[H^+]}$$
less than 7 - Acid
greater than 7 - Alkaline

ALKALINITY - Hydroxide (OH^-)
Carbonate $(CO_3^=)$
Bicarbonate (HCO_3^-)

HARDNESS - Calcium (Ca^{++}); Magnesium (Mg^{++})
Carbonate $(\approx$ Alkalinity e.g. $HCO_3^-)$
Non-carbonate $(\sim SO_4^=)$

IRON - Ferrous (Fe^{++}); Ferric (Fe^{+++})

PHOSPHORUS - Polyphosphate e.g. $Na_3(PO_4)_6$
Orthophosphate e.g. Na_3PO_4

Polyphosphates hydrolyze in aqueous solution
to the ortho form - rate of reversion increases
with temperature increases.

TRANS AS-3

WATER SOFTENING REACTIONS

Chemical Precipitation

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2\ \underline{CaCO_3} + 2\ H_2O$$

$$Mg(HCO_3)_2 + Ca(OH)_2 = CaCO_3 + MgCO_3 + 2\ H_2O$$

$$MgCO_3 + Ca(OH)_2 = \underline{CaCO_3} + \underline{Mg(OH)_2}$$

$$MgSO_4 + Ca(OH)_2 = CaSO_4 + \underline{Mg(OH)_2}$$

$$CaSO_4 + Na_2CO_3 = \underline{CaCO_3} + Na_2SO_4$$

$$CO_2 + Ca(OH)_2 = CaCO_3 + H_2O$$

Ion Exchange

$$\left.\begin{matrix} Ca \\ Mg \end{matrix}\right\} (HCO_3) + Na_2R = \left.\begin{matrix} Ca \\ Mg \end{matrix}\right\} R + 2\ NaHCO_3$$

$$\left.\begin{matrix} Ca \\ Mg \end{matrix}\right\} SO_4 + Na_2R = \left.\begin{matrix} Ca \\ Mg \end{matrix}\right\} R + Na_2SO_4$$
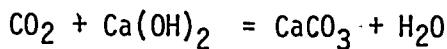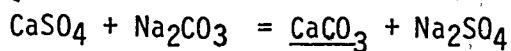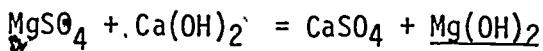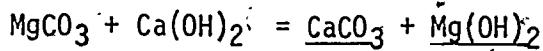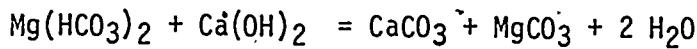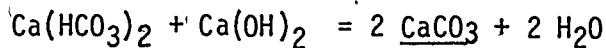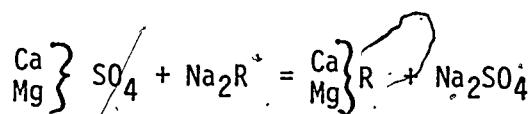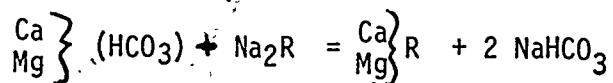
TRANS AS-4

FORMS OF ALKALINITY
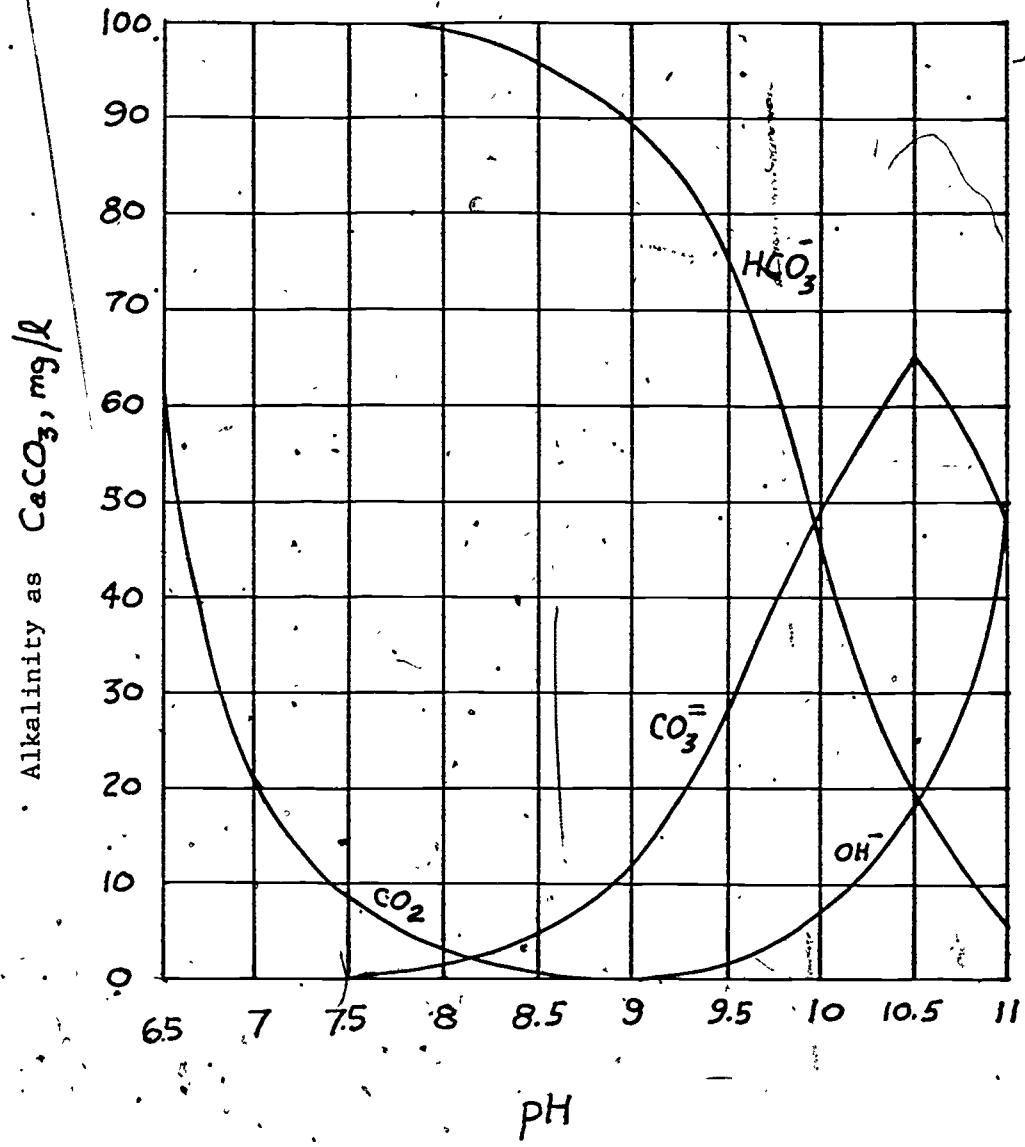
Relationship between carbon dioxide and the three forms
of alkalinity at various pH levels. (Values calculated
for a water with a total alkalinity of 100 mg/1 at 25°C)

TRANS AS-5

CaCO$_3$ EQUILIBRIUM pH

$$CaCO_3 \text{ (s)} \rightleftharpoons Ca^{++} + CO_3^{--}$$

$$Ks = \left[Ca^{++}\right]\left[CO_3^{--}\right]$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{--}$$

$$K_2 = \frac{\left[H^+\right]\left[CO_3^=\right]}{\left[HCO_3^-\right]}$$

$$\left[H^+\right]\left[OH^-\right] = Kw$$

$$\left[ALK\right] + \left[H^+\right] = 2\left[CO_3^=\right] + \left[HCO_3^-\right] + \left[OH^-\right]$$
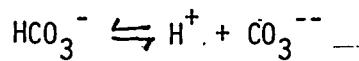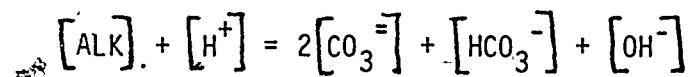
From the above Langlier derived a formula for pHs

$$pHs = pK_2 - pKs + pCa + pAlk$$

TRANS AS-6

SATURATION pH

THE pH AT WHICH WATER WOULD NEITHER DEPOSIT NOR DISSOLVE
CALCIUM CARBONATE

FACTORS AFFECTING pHs ARE: Calcium
Alkalinity
Temperature
Total Dissolved Solids

CALCULATION:

1. USE NALCO AQUAGRAPH

2. USE LARSON-BUSWELL DIAGRAM

3. USE STANDARD METHODS TABLES, (p. 62)

PAGE 35 "SATURATION PH LARSON-BUSWELL DIAGRAM"
REMOVED PRIOR TO BEING SHIPPED TO EDRS FOR
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STABILITY INDICES

LANGELIER'S SATURATION INDEX (S.I.)

S.I. = pH Actual - pHs

Where pHs is the pH of saturation

A plus value indicates:
A lack of excess CO_2
$CaCO_3$ scale-forming qualities

A minus value indicates:
An excess of CO_2
Scale dissolving properties

Note: The S.I. is not quantitative but shows
directional tendency

RYZNAR INDEX (R.I.)

R.I. = 2 pHs — pH

Values greater than 7.0 indicate a corrosive water

Values less than 7.0 indicate a scale-forming water

Note: The Nalco Aquagraph uses 6.0 as a breakpoint. Also
see figure.

RYZNAR INDEX
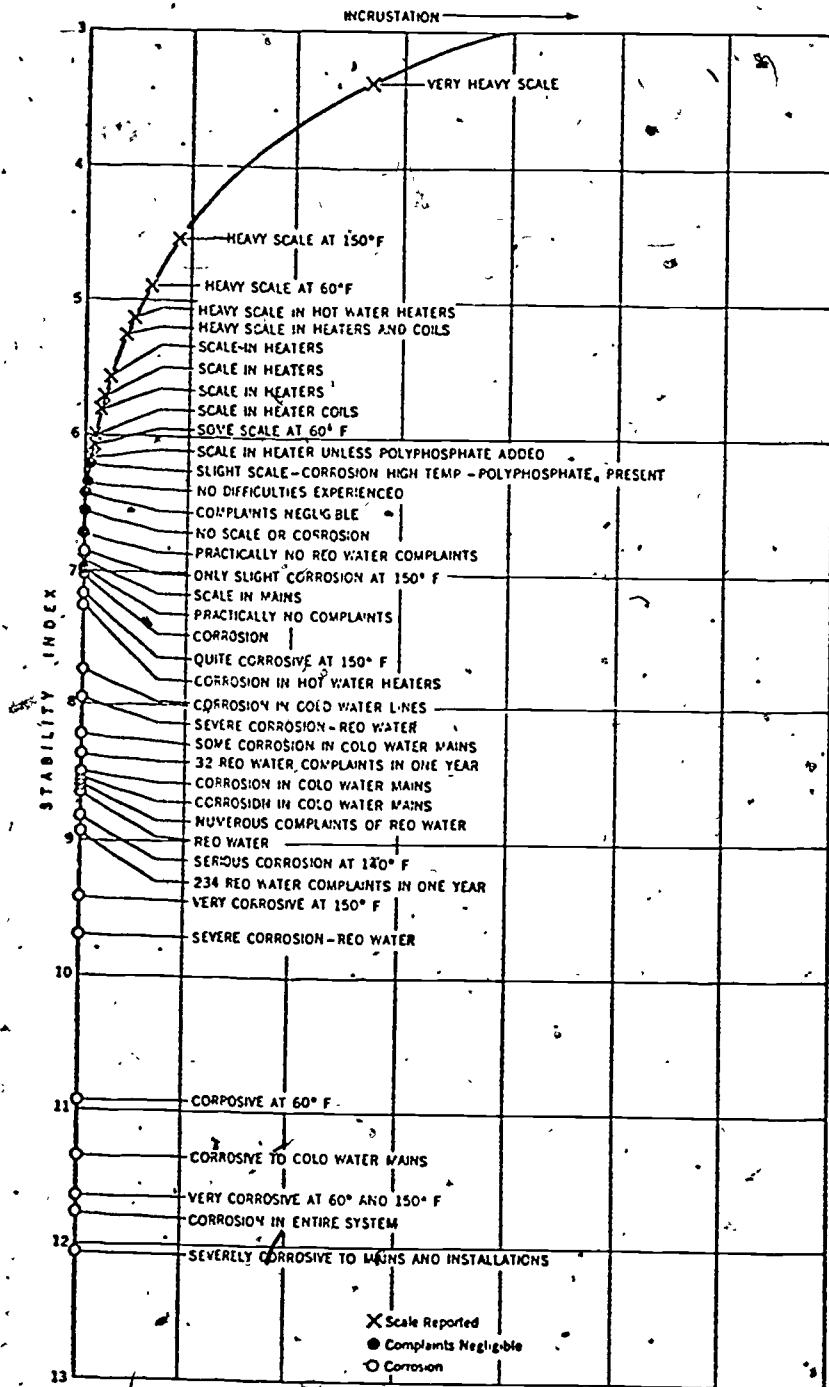
STABILITY INDEX - SAMPLE PROBLEM

WATER ANALYSIS Ca^{++} - 200 mg/l as $CaCO_3$
ALK - 60 mg/l as $CaCO_3$
TEMP - 16 ^{o}C
TDS - 650 mg/l
pH - 9.0

pHs

From Std. Methods   - 8.00
From Nalco Aquagraph - 7.87
From Larson-Buswell

pHs = 9.30 + (0.17 + 2.08) - (1.90 + 1.78) = 7.87

Langelier Saturation Index

S.I. = pH - pHs = 9.0 - 8.0 = +1.0 · Scaling Tendency

Ryznar

R.I. = 2pHs - pH = 2(8.0) - 9.0 = 7.0   Slight Corrosive Tendency

TRANS AS-11

CALCIUM CARBONATE STABILITY TEST
(The Marble Test)

Ref: AWWA Inc., "Simplified Procedures for Water Examination",
Manual M12, 1964
See p. 21-22 for detailed procedures

MAJOR FEATURES of TEST

DETERMINE ALKALINITY ON PORTION OF SAMPLE

ADD EXCESS OF $CaCO_3$ TO ANOTHER PORTION IN A 300 ml GLASS STOPPERED BOD BOTTLE.

MIX BY SHAKING FREQUENTLY FOR AT LEAST 3 HOURS, SETTLE OVERNIGHT AND FILTER THE SUPERNATANT

DETERMINE THE ALKALINITY ON FILTERED SAMPLE

IF ALKALINITY INCREASED, WATER IS NOT SATURATED WITH $CaCO_3$ AND WILL NOT BE DEPOSITING

IF ALKALINITY DECREASED, WATER IS SUPERSATURATED WITH $CaCO_3$ AND MAY BE DEPOSITING

IF ALKALINITIES ARE THE SAME, THE WATER IS STABLE

Note: From Standard Methods "...equilibrium may not be attained and the partial pressure of CO_2 in the atmosphere over the sample may influence the results adversely".

TRANS AS-12

RECARBONATION

## EXCESS LIME (Hydroxide)

$$Ca^{++} + 2\ OH^- + CO_2 \longrightarrow CaCO_3 + H_2O$$
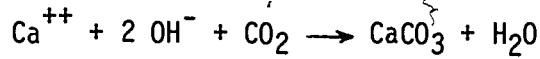
SUPERSATURATION WITH $CaCO_3$

$$CO_2 + CO_3^= + H_2O \longrightarrow 2\ HCO_3^-$$
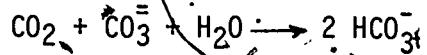
MAGNESIUM HYDROXIDE

$$Mg^{++} + 2\ OH^- + CO_2 \longrightarrow Mg^{++} + CO_3^= + H_2O$$
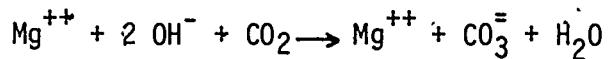
CARBON DIOXIDE QUANTITIES

Hydroxides: $\dfrac{Ca(OH)_2}{74} + \dfrac{CO_2}{44}$ $\bigg|$ $Ca(OH)_2 \times 44/74 = CO_2 (mg/1)$
(Excess)

$\dfrac{Mg(OH)_2}{58.3} + \dfrac{CO_2}{44}$ $\bigg|$ $Mg(OH)_2 \times 44/58.3 = CO_2 (mg/1)$
(Residual)
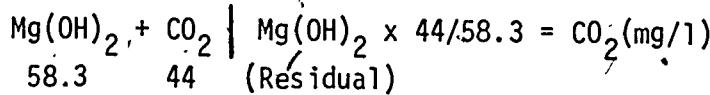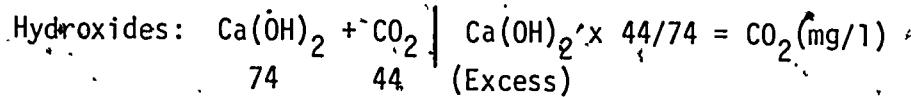
Maintain pH > 9.5 to minimize conversion of
$CO_3^=$ to HCO_3^-

Supersaturation w/ $CaCO_3$:

● Reduce pH to about 8.6. Based on the Ksp of $CaCO_3$.

CHELATING COMPOUNDS
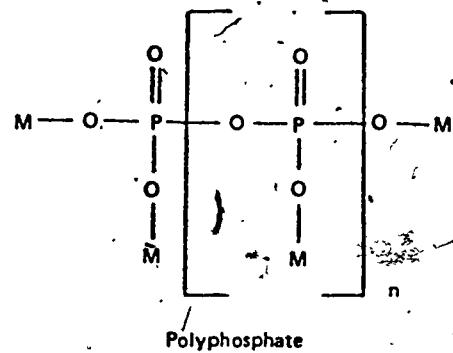
Polyphosphate

Sodium hexametaphosphate, $Na_3(PO_3)_6$

Aminomethylenephosphonate (AMP)
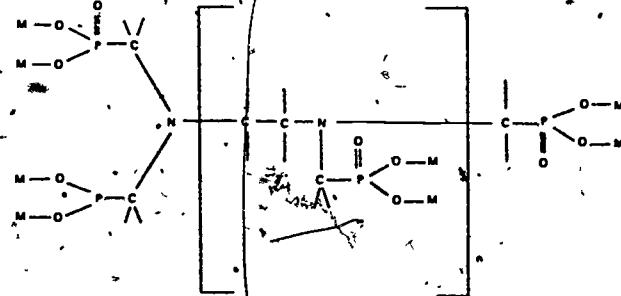
*M is a monovalent metal (e.g.Na), H or ammonium group

TYPES OF CORROSION CELLS

CORROSION CELL —   AN ELECTROLYTIC CELL IN WHICH METAL
IS REMOVED FROM THE ANODIC (Negative)
AREA DURING THE PASSAGE OF DIRECT
CURRENT BETWEEN THE CATHODIC (Positive)
AREA AND THE ANODIC AREA.

TYPES OF CELLS

GALVANIC —   DISSIMILAR METALS e.g. CAST IRON and
COPPER

DIFFERENTIAL AERATION — TWO PORTIONS OF THE METAL RECEIVE OXYGEN
AT DIFFERENT RATES

.CONCENTRATION CELLS — THE VARIATION IN CONCENTRATION OF DIFFER-
ENT SUBSTANCES IN SOILS CAN CAUSE A COR-
ROSION CELL TO BE FORMED

DIFFERENTIAL STRESS — STRESSES e.g. WELDING CHANGE THE PHYSICAL
CHARACTERISTICS OF A METAL - CAN AFFECT
ITS ELECTRO-POTENTIAL

IMPRESSED-CURRENT — WHERE "GROUNDING" IS PRACTICED. THE
LOCATION WHERE THE CURRENT LEAVES (Anodic
Area) MAY SHOW INCREASED CORROSION

TRANS AS-15

CORROSION CELL

$2H^+ + 2e \rightarrow 2H^o$
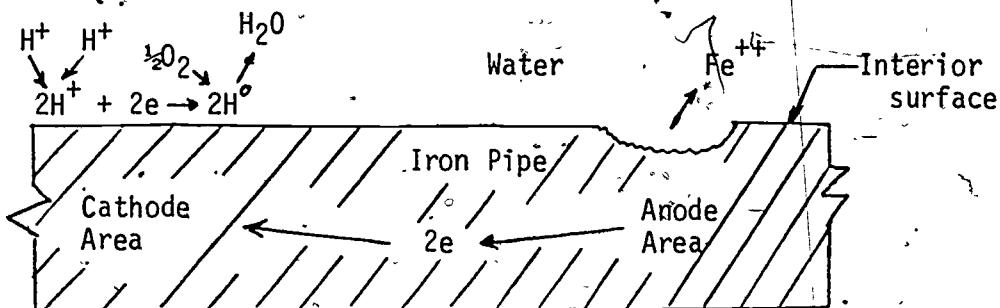
COMMENT: AREAS OF ACTIVITY

-- THE AREA TO WHICH OXYGEN HAS EASIEST ACCESS TENDS TO BECOME THE CATHODIC AREA.

-- THE AREA TO WHICH OXYGEN HAS ACCESS WITH DIFFICULTY BECOMES THE ANODIC AREA.

EXAMPLES OF ANODIC AREAS OR AREAS SHELTERED AGAINST OXYGEN ARE:

-- PITS OR DEPRESSIONS IN THE METAL

-- AREAS UNDERLYING MILL SCALE OR PRODUCTS OF CORROSION

-- AREAS BELOW BIOLOGICAL GROWTHS

TRANS AS-16

ELECTROCHEMICAL CORROSION

Four general steps

(1) ANODIC REACTION

$$Fe \text{ (metal)} \longrightarrow Fe^{++} + 2e^-$$
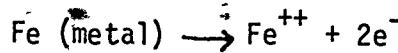
(2) CATHODIC REACTION

$$2H^+ + e^- \longrightarrow H$$

$$2H \longrightarrow H_2$$
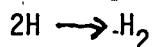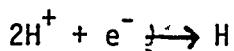
(forming of the atomic hydrogen layer is called "polarization".)

(3) DEPOLARIZATION

(removal of the hydrogen layer)

$$2H + 1/2\ O_2 \longrightarrow H_2O$$
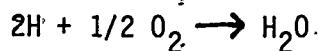
(4) REMOVAL OF THE METAL IONS

$$Fe^{++} + 2OH^- \longrightarrow Fe(OH)_2$$

$$4Fe(OH)_2 + O_2 \longrightarrow 4H_2O + 2Fe_2O_3$$

if CO_2 is present

$$CO_2 + H_2O \longrightarrow H_2CO_3 \longrightarrow H^+ + HCO_3^-$$

$$Fe(OH)_2 + 2H_2CO_3 \longrightarrow Fe(HCO_3)_2 + 2H_2O$$

$$Fe^{++} + 2HCO_3^- \longrightarrow Fe(HCO_3)_2$$

$$4Fe(HCO_3)_2 + O_2 \longrightarrow 4H_2O + 8CO_2 + 2Fe_2O_3$$
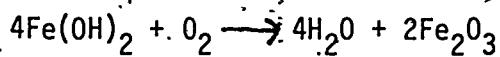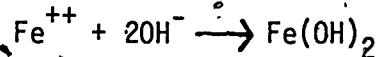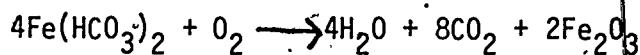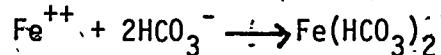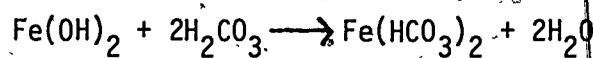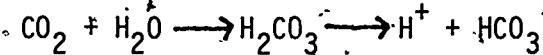
TRANS AS-17

Galvanic Series of Metals and Alloys

Corroded end
(Anodic or least noble)

Magnesium
Zinc
Aluminum (commercial pure)
Steel or iron
Cast iron
Lead
Tin
Brasses
Copper
Bronzes
Chromium -- iron (passive)
Silver
Graphite
Gold
Platinum

Protected end
(Cathodic or most noble)

TRANS AS-18

COUPON EVALUATION jn DISTRIBUTION

Rod-Stainless Steel
Nonconductor Support
Holding Screw
Coupon—D10 Mild Steel
Front View

Coupon
Rod
Nonconductor Support
Side View
Rear View
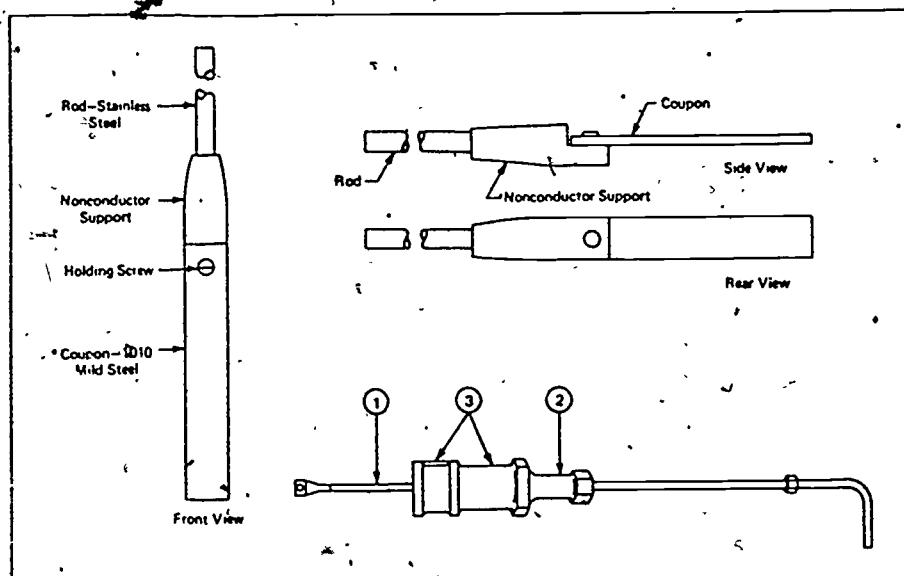
Fig. 5. Distribution-System Coupon-Holder Assembly

Flow
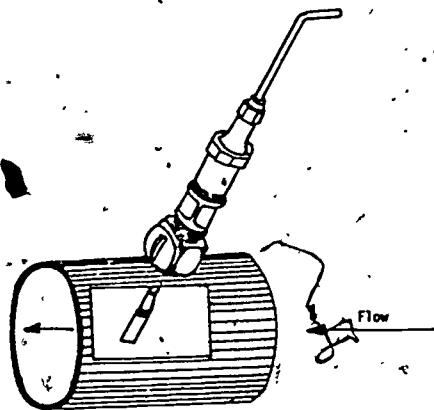
Fig. 6. Corrosion Coupon Assembly

Ref: Mullen & Ritter, "Potable Water Corrosion Control", p.473-79, J-AWWA, Aug. 1974.

AWWA WATER QUALITY GOAL: 90 day tests

Incrustation on stainless steel not to exceed 0.05 mg/sq.cm.

Loss by corrosion of galvanized iron not to exceed 5.0 mg/sq.cm.

Ref: p.62 AWWA Journal September 1973

TRANS AS-19

APPROACHES TO CORROSION CONTROL

USE CORROSION RESISTANT MATERIALS

USE COATINGS AND LININGS

DEPOSITION OF $CaCO_3$ AND pH ADJUSTMENT

PROTECTIVE CHEMICAL COATINGS

CATHODIC PROTECTION

TRANS AS-20

MATERIAL SELECTION - CORROSION

Note: From Larson, T.E. "Corrosion by Domestic Waters"

MILD STEEL - Dissolved minerals may increase corrosion e.g. chloride and sulfate. Increases in Ca and alkalinity inhibit corrosion. Elevated tanks should be painted in accordance with AWWA Std. (D102-64) and cathodic protection employed.

ZINC & GALVANIZED STEEL - With adequte Ca and alkalinity protection by zinc carbonate is often effective. Zinc protects steel in galvanizing by excluding water contact with steel and by galvanic protection.

ALUMINUM - Corrosion resistance due to inert oxide film. Do not use with copper bearing metals.

COPPER - Corrosion resistance due to an oxide film. Subject to impingement attack at high rates of flow (greater than 4 fps). Low pH carbonated water and waters containing chloride are corrosive to copper.

COPPER ALLOYS - Copper-zinc (yellow brass-67/33); (red brass - 85/15) Yellow brass is subject to dezincification in soft waters and high pH (9.0 to 9.6). Red brass is preferable. Copper-nickel alloys are superior for difficult conditions and at hot water temperatures.

STAINLESS STEEL ALLOYS - Corrosion resistance due to a thin protective oxide on the surface. Type 304 (18% Cr, 8% Ni) is frequently used. Chloride, stress and temperature are important corrosion factors.

PLASTIC PIPE & FITTINGS - Useful systems.

TRANS AS-21

CATHODIC PROTECTION
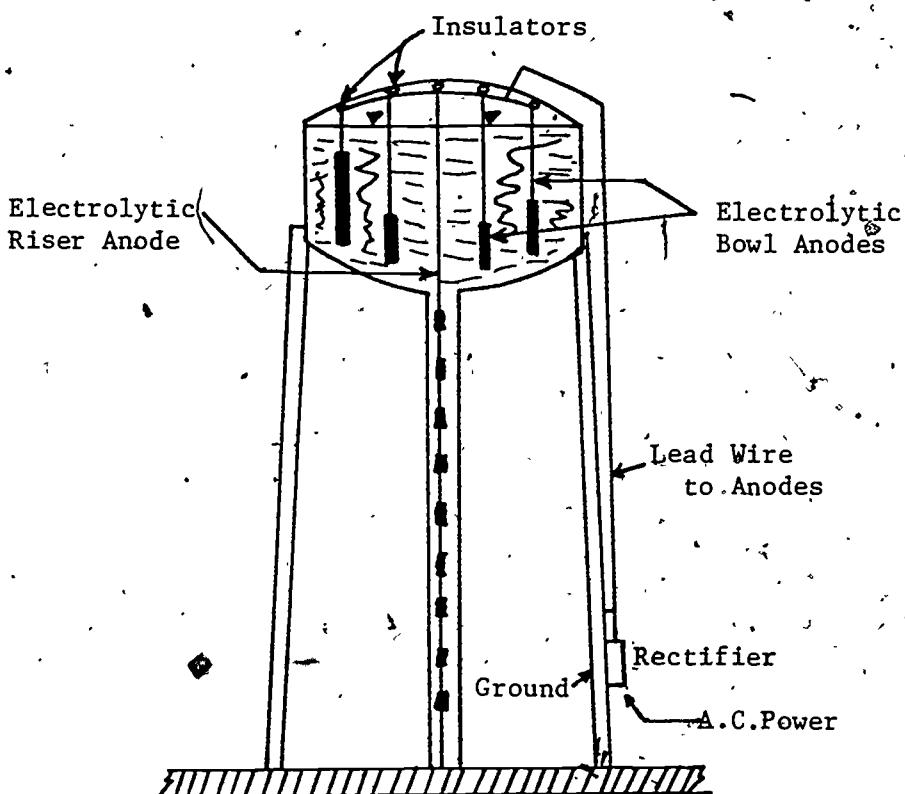
TYPICAL WATER STORAGE TANK

Galvanic Anode – Composed of a metal higher in the
                  galvanic series than the metal pro-
                  tected e.g. Mg, Zn and Al

Electrolytic Anode – Energized by an external source
                     of direct current.

Note: See Standard Specifications for Elevated Steel
        Water Tanks, Standpipes and Reservoirs by AWWA
        (7H1-1943)

TRANS AS-22

BACTERIAL ACTION

IRON BACTERIA - Capable of withdrawing iron present in
their aqueous habitat and of depositing
it in the form of hydrated ferric hydrox-
ide - Crenothrix, Gallionella

SULFUR BACTERIA - Oxidize or reduce significant amounts
of inorganic sulfur.

$$SO_4^= \longrightarrow H_2S \quad \underline{Desulfovibrio}$$
(Anaerobic)

$$H_2S \longrightarrow H_2SO_4 \quad \underline{Thiobacillus}$$
(Aerobic)

TRANS AS-23
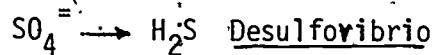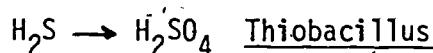
EXTERNAL PIPE CORROSION

FACTORS TO BE CONSIDERED

RESISTIVITY - Low resistivity - greater corrosive tendency

pH - 0 to 4, 6.5 to 7.5, >8.5 (Greater corrosive tendency)

OXIDATION REDUCTION POTENTIAL - Low values indicate anaerobic conditions

MOISTURE CONTENT - Wet - greater corrosive tendency

SOIL TYPES

STRAY DIRECT CURRENT

Note: Polyethylene encasement is a very satisfactory protection system.

Ref: Cast iron Pipe Research Association

TRANS AS-24

- WELL PROBLEM

Deposition - Corrosion Case Study

Background: Well stopped pumping water. Motor running.
Multi-stage pump 200' Drawdown
Discharge pressure head 400'
Shaft located between stainless steel collars
had sheared.
Upper shaft - No corrosion. Lower shaft -
Corrosion
Pump with brass impellers in good shape
Suction side - $CaCO_3$ film
Discharge side - Tubercules. Pit corrosion.
Until 10 ft. away.
Shaft similar to piping.

Water Analysis: pH 6.8   TDS - 800 mg/l
Hardness 400 mg/l Temperature 50°F
Alkalinity 300 mg/l CO_2 - 30 mg/l
D.O. - 0

Discussion Questions: Explain the corrosion and deposition
observations in the piping and on
the shaft.
Discuss the shaft failure.
What alternatives should be considered
to correct the problem?

TRANS AS-25

STUDENT-PARTICIPANT GUIDE

for

TRAINING MODULE II3ADWS

Advanced Stabilization

53

PARTICIPANT INSTRUCTIONAL MATERIALS

I. Each participant will receive an outline of the module topics with supplemental comments as appropriate. This outline is to assist the participant in preparing for class discussions and guiding the students in their study of reference materials and transparencies.

II. Students will receive a xerox copy of each transparency. If desired, NALCO aquagraphs can be obtained from the NALCO Chemical Co., Chicago, Illinois.

III. The New York Manual and the AWWA M18 Manual should probably be required for the modules. They should be owned by the participants as they are of value for other modules and as general references.

   If the participants do not own these references then permission should be obtained to provide them with xerox copies of the primary subject material.

IV. Some of the examination questions could be used as class study questions or a means for evaluation of the instruction. They could also be supplemented based on the instructor's treatment of the topics.

V. It is suggested that the participants could receive copies of some reference articles as well. The particular instructor could choose to do this and also supplement the materials with descriptions of case studies he/she is familiar with. Student participant case studies could also be duplicated for the class.

II3ADWS ADVANCED STABILIZATION MODULE

Note: Participants will receive a copy of each transparency used
in the presentations. Participants will receive appropriate
reference material from the New York Health Dept. Manual of
Instruction for Water Treatment Plant Operators and from the
AWWA M18, Basic Water Treatment Operator's Manual.

Instructors may supplement the above material with copies of
references or case studies.

Participants are encouraged to bring documented examples of
corrosion and deposition problems and solutions to the class
for group discussion and analysis. Pipe or fitting samples
and/or photographs are especially of interest.

I. Introduction and Review

A. Scale formation and its concerns (Trans AS-1)
1. Note that stability of water refers to the tendency to
deposit $CaCO_3$ or not deposit $CaCO_3$.
2. Review the types of deposition problems and observe their
effect on water system operation
3. Describe examples of deposition problems in your water
system

B. Corrosion and corrosion concerns (Trans AS-2)
1. Note the electrochemical nature of corrosion
2. Observe the types of corrosion and note the water system
effect of each type
3. Describe examples of corrosion problems in your water
system

C. Water chemistry parameters and concepts (Tran AS-3, AS-4, AS-5)
1. Review the primary water quality parameters - their meaning
and significance.
2. Note the ion groups, the pH & pOH concept and the oxidative
states e.g. ferrous and ferric
3. Review the chemical changes in water softening and note the
type of compounds present in the softened water. Note pH
requirements for excess-lime softening.
4. Note the effect of pH on the presence of CO_2 and the other
forms of alkalinity present. This relates to the softening
process and the nature of finished waters in the treatment
plant and distribution system.

II. Deposition: Analysis and Control (Trans AS-6 thru AS-13)

A. Note the equilibrium basis for deposition
1. Study the chemical equilibrium basis for the saturation pH

of $CaCO_3$.   Note the role of the various factors that affect pHs

2. The addition of alkali's and other precipitate formation also function from an equilibrium and solubility product concept e.g.

$$Ca(OH)_2 \rightleftharpoons Ca^{++} + 2OH^-$$

$$CaF_2 \rightleftharpoons Ca^{++} + 2F^-$$

$$Fe(OH)_3 \rightleftharpoons Fe^{+++} + 3OH^-$$
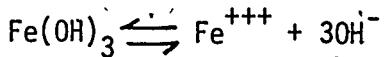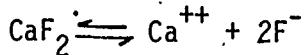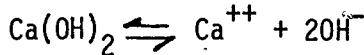
B.   Various approaches can be used in stability analysis
 1. The stability analysis of a water can be conducted by calculation from the various water quality parameters - See Nalco Aquagraph, Larson-Buswell approach and Standard Methods.

 Study the sample calculation.

 2. The stability can also be evaluated using the Marble Test. Note Std: Methods comment.
 3. The indices are indicators - note experiences with the Ryznar Index - system testing is needed to evaluate what is happening. Pipe samples can be checked, coupons used and alkalinity measurements made.

C.   Review the methods and purposes of recarbonation. Note the calculation procedure and pH control levels.

D.   Note the complex chemistry of chelates. Phosphonates have been successfully used in industrial practice. Chelates are employed ahead of rapid sand filters and to distribute $CaCO_3$ films in distribution systems.

III.   Corrosion chemistry (Trans AS-14 thru AS-18)

A.   Note the various types of corrosion cells

B.   Study the chemical interactions associated with the differential aeration cell
 1. Note how iron can leave the system as a deposit. Note the role of oxygen in removing the hydrogen film.
 2. Corrosion cells can be widely distributed over the metal surface resulting in extensive corrosion
 3. Localized pitting can occur when a corrosion cell develops within a deposit location. Chloride ions can be associated with pitting corrosion
 4. Tuberculation results from iron deposits

C.   Study the galvanic series
 1. The location of the metals in the series determine which metal will be the corroded (anode) metal
 2. This location can be used to avoid galvanic corrosion in piping. It can also be used to protect a metal surface in cathodic protection.

D. Corrosion detection includes studying pipe sections, fittings, noting staining and red water
   1. Increases in Fe concentration in the distribution system also evidence corrosion
   2. Coupons can be utilized to monitor corrosion. Note the Middlesex Water Co. study

E. Note the effect of material selection (Trans AS-21) and corrosion problems
   1. Dezincification is the result of removal of zinc from its alloy with brass. Soft waters are of special concern
   2. Graphitization is a form of corrosion of cast iron in highly mineralized water or waters with low pH. The iron-silicon alloy is removed.

IV. Corrosion control (Trans AS-20, AS-21, AS-22)

A. Note the approaches to corrosion control

B. Water chemistry may be adjusted e.g. positive Langelier Index to achieve a $CaCO_3$ depositing water
   1. Alkali feeds, $NaOH$, $Ca(OH)_2$ and Na_2CO_3 are used to accomplish pH adjustment
   2. Polyphosphates can be used to distribute the $CaCO_3$ deposition in the system

C. Inhibitors have been utilized
   1. Zinc-orthophosphates have been successful. See Middlesex study.
   2. Phosphates alone require too high a dosage to be used.

D. Cathodic protection is used for piping, storage tanks and treatment units
   1. Note selection of sacrificial anode
   2. Compare galvanic and electrolytic anodes

E. Note the various types of metals that can be utilized
   1. Linings e.g. cement and various chemical coatings and paints are successful
   2. PVC plastic, asbestos cement and concrete are examples of non-corrosive materials

F. Cite examples of successful practice from your own water system

V. Special topics. (Trans AS-23, AS-24, AS-25)

A. Iron bacteria are a nuisance filamentous organism that uses iron and forms deposits in piping and well systems

B. Sulfur bacteria can break down sulfate in low-flow zero dissolved oxygen areas of distribution systems and release

$H_2S.$ H_2S can form corrosive solutions of H_2SO_4 if it is oxidized.

C. Note the various factors that affect external pipe corrosion.

D. Well systems experience many of the deposition and corrosion problems discussed earlier. Analyze the well system case study.

EXAMINATION QUESTIONS

<u>Note</u>: The sequence of questions generally follows the pattern of topics and objectives presented in the module.

T F 1. More CO_2 can enter solution as the pressure in a water system increases.

T F 2. pOH refers to the logarithm of 1/OH concentration.

T F 3. As the pH increases the hydrogen ion concentration decreases and the hydroxyl ion concentration increases.

4. A high pH (10.5) water will tend to have which of the following combinations of alkalinity

   a. SO_4, Cl, HCO_3
   b. CO_2, HCO_3
   c. HCO_3, CO_3
   d. CO_3, OH, HCO_3

T F 5. Lime that is used to reduce magnesium carbonate hardness yields hydroxide ions which satisfy the $Mg(OH)_2$ solubility product and cause it to precipitate.

T F 6. In lime softening the alkalinity of the water supply is decreased, the pH increased and the iron content decreased.

T F 7. Increases in water temperature increase the reversion rate of polyphosphate to orthophosphate.

8. Lowering lime softened water pH below 9.5 causes an increase in hardness due to _____ but results in a decreased tendency for the water to _____.

9. Which of the following chemical test results indicate a depositing water in a distribution system

   a. Decrease in alkalinity
   b. Increase in iron concentration
   c. Increase in alkalinity
   d. Increase in sulfate concentration

10. When a water is considered to be stable

   a. It will cause iron to go into solution readily
   b. It will deposit $CaCO_3$
   c. Phosphates should be added to oxidize the iron
   d. It will not deposit $CaCO_3$

11. Deposits of $CaCO_3$ can be extended further into the distribution system by using

    a. Carbon dioxide

    b. Polyphosphates

    c. Soda ash

    d. Potassium permanganate

12. Two causes of well screen blackage or deposits are

    a. _____

    b. _____

13. A positive Langlier Index indicates that a water

    a. Contains too much manganese

    b. Tends to be a depositing water ($CaCO_3$)

    c. Tends to be corrosive to iron

    d. Has excess magnesium

14. The four water quality characteristics that are used to calculate the pHs (saturation pH) are total dissolved solids, _____ _____ and _____.

T F 15. The Ryznar Index is equal to two times the pHs minus the actual pH.

16. A laboratory test that can be utilized to analyze for calcium carbonate deposition tendencies is

    a. Oxidation-reduction

    b. Marble

    c. Crenthrix

    d. The hydroxide/carbonate ratio

T F 17. A water with high pH, high alkalinity and high calcium content would likely be a depositing water.

18. Phosphate added after recarbonation and prior to filtration in a water plant

    a. Ties up (chelates) calcium and minimizes $CaCO_3$ deposition

    b. Provides a nutrient for the bacteria to aid the filter

    c. Flocculates any bacteria or algae present

    d. Causes iron to precipitate

19. Oxygen in the water in corrosion systems

    a. Removes the hydrogen film

    b. Increases corrosion rates

    c. Reacts to form iron oxides

    d. All of the above

20. What type of corrosion cell is involved iwth grounding of water piping _____. The corrosion, if any, shows up at _____.

__ T F 21. Iron deposits can occur with iron bacteria.

22. Which of the following waters would be of most concern with copper piping _____
   a. High pH, high CO_3
   b. Low pH, CO_2 present, chlorides, low hardness
   c. High phosphonates, pH 8 to 10

T F 23. Current flows from the positive areas (anodic) to the negative areas (cathodic) and metallic ions accompany this flow.

24. If a electrochemical corrosion cell is established with copper and cast iron which metal will corrode (anodic)
   a. Copper
   b. Cast iron

25. What are two corrosion factors of concern with stainless steel
   a. _____
   b. _____

26. Cite two types of linings or coatings that can be used to protect against corrosion
   a. _____
   b. _____

27. Galvanized steel contains
   a. Platinum
   b. Lead
   c. Zinc
   d. Manganese
   as a corrosion protection mechanism.

T F 28. A metal e.g. iron or steel can be protected by galvanic cathodic protection if a metal anode lower in the galvanic series is used as a sacrifical metal

29. Which of the following metals in combination with ortho-phosphate acts as a corrosion inhibitor

a. Cadmium

b. Zinc

c. Lead

d. Manganese

30. Which of the following could be used to protect against steel or cast iron corrosion via cathodic protection

a. Chromium

b. Tin

c. Magnesium

31. Which of the following is an iron bacterium

a. Crenothrix

b. Desulforibrio

c. Coliform

d. Salmonella

32. Two soil characteristics that are significant in evaluating the corrosive tendency of soil are

a. _____

b. _____

T F 33. Hydrogen sulfide formation from bacterial breakdown of sulfates occurs in anaerobic pipe sections.

34. List one control or treatment technique for iron bacteria in a water system.