Polymeric Dispersants

A Review of the Literature

TE-114159

Polymeric Dispersants

A Review of the Literature

TE-114159

Technical Progress, December 1999

EPRI Project Manager

P. Frattini

EPRI • 3412 Hillview Avenue, Palo Alto, California 94304 • PO Box 10412, Palo Alto, California 94303 • USA
800.313.3774 • 650.855.2121 • askepri@epri.com • www.epri.com

DISCLAIMER OF WARRANTIES AND LIMITATION OF LIABILITIES

THIS DOCUMENT WAS PREPARED BY THE ORGANIZATION(S) NAMED BELOW AS AN ACCOUNT OF WORK SPONSORED OR COSPONSORED BY THE ELECTRIC POWER RESEARCH INSTITUTE, INC. (EPRI). NEITHER EPRI, ANY MEMBER OF EPRI, ANY COSPONSOR, THE ORGANIZATION(S) BELOW, NOR ANY PERSON ACTING ON BEHALF OF ANY OF THEM:

(A) MAKES ANY WARRANTY OR REPRESENTATION WHATSOEVER, EXPRESS OR IMPLIED, (I) WITH RESPECT TO THE USE OF ANY INFORMATION, APPARATUS, METHOD, PROCESS, OR SIMILAR ITEM DISCLOSED IN THIS DOCUMENT, INCLUDING MERCHANTABILITY AND FITNESS FOR A PARTICULAR PURPOSE, OR (II) THAT SUCH USE DOES NOT INFRINGE ON OR INTERFERE WITH PRIVATELY OWNED RIGHTS, INCLUDING ANY PARTY'S INTELLECTUAL PROPERTY, OR (III) THAT THIS DOCUMENT IS SUITABLE TO ANY PARTICULAR USER'S CIRCUMSTANCE; OR

(B) ASSUMES RESPONSIBILITY FOR ANY DAMAGES OR OTHER LIABILITY WHATSOEVER (INCLUDING ANY CONSEQUENTIAL DAMAGES, EVEN IF EPRI OR ANY EPRI REPRESENTATIVE HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES) RESULTING FROM YOUR SELECTION OR USE OF THIS DOCUMENT OR ANY INFORMATION, APPARATUS, METHOD, PROCESS, OR SIMILAR ITEM DISCLOSED IN THIS DOCUMENT.

ORGANIZATION(S) THAT PREPARED THIS DOCUMENT

Dominion Engineering, Inc.

ORDERING INFORMATION

Requests for copies of this report should be directed to the EPRI Distribution Center, 207 Coggins Drive, P.O. Box 23205, Pleasant Hill, CA 94523, (800) 313-3774.

Electric Power Research Institute and EPRI are registered service marks of the Electric Power Research Institute, Inc. EPRI. POWERING PROGRESS is a service mark of the Electric Power Research Institute, Inc.

Copyright © 1999 Electric Power Research Institute, Inc. All rights reserved.

CITATIONS

This document was prepared by

Dominion Engineering, Inc.
6862 Elm Street, Suite 460
McLean, VA 22101

Principal Author
Robert D. Varrin, Jr.

This document describes research sponsored by EPRI.

The publication is a corporate document that should be cited in the literature in the following manner:

Polymeric Dispersants, A Review of the Literature, EPRI, Palo Alto, CA: 1999. TE-114159.

FOREWORD

This report presents a compilation of experimental work on the use of dispersants for preventing or ameliorating the fouling of high temperature surfaces in boilers or steam generators by corrosion products. Four types of experiments are discussed in this literature survey: thermal stability investigations, precipitant characterization, settling rate experiments, and plant, pilot-plant or boiler studies. The compilation was prepared as background material for completing the 50.59 analysis for the experimental introduction of polyacrylic acid dispersants into the secondary cycle at Entergy ANO-2.

CONTENTS

LIST OF TABLES

1

INTRODUCTION

Corrosion product deposits and other impurities that reside on the secondary side of PWR steam generators (SGs) can impede heat transfer, lead to thermal hydraulic instabilities through blockage of tube supports and create regions where corrosive species can concentrate along tube free spans and tube to tube support crevices. In the future, the control of deposit formation is likely to become a crucial issue as utilities strive maintain both the performance and the integrity of their steam generators toward end of life at the plant. The performance of steam generators can be compromised either by formation of insulating scale on the tube surfaces or by the need to remove tubes from service due to corrosion.

Today, utilities rely upon two principal strategies in their attempt to minimize the effects of deposits. First, corrosion product transport may be minimized by adopting optimized chemistry control strategies or by making plant modifications (*e.g.* replacing flow assisted corrosion susceptible piping sections in the feedwater, drain and condenser systems). Second, utilities may elect to periodically remove corrosion products from the steam generator by chemical or mechanical means.

A third potential method for controlling deposits in steam generators is to use online addition of trace chemicals that can prevent corrosion products from adhering to the surfaces of the SG. For example, early Steam Generator Owners' Group (SGOG) projects investigated on-line chelate addition and off-line chemical soaks, a number of other methods for changing the way by which deposits form or behave may be applicable to PWR steam generators without resulting in unacceptable side effects. Similar strategies for "deposit control" have been used for many decades in the fossil power, chemical, petrochemical, and paper and pulp industries.

One broad class of treatments that appears promising is the use of “polymeric dispersants”. Typical polymers used as dispersants are polysulfonates, polyamides and polyacrylics. These molecules perform as both dispersants (keeping precipitated particles in suspension) and as crystal modifiers (changing the size, shape and surface properties of crystals). Either effect can improve the removal of corrosion products by blowdown.

This review will briefly cover the available literature reviewing theories of crystal modification and dispersion, the specific test data available on polymeric additives, factors effecting dispersant performance and a discussion of the possible undesirable side effects from their use. The appendix gives summaries of the literature sources used in writing this review.

2

CRYSTAL MODIFICATION

Several theories of the way in which deposits form in SGs have been proposed. These include crystallization of species such as magnetite, copper and copper oxides, and sulfate and silicate species from soluble species in the fluid stream. When a small amount of a compound known as a crystal habit modifier is added to the feedwater, the crystallization of corrosion products can be dramatically affected. Even trace amounts of crystal modifiers can effect the morphology of precipitates and consequently make large differences in deposit formation [1]. Crystal modifiers can help reduce the impact of precipitating particles in three ways: habit modification, size reduction and surface modification. Examples of crystal habit modifiers include: borates, urea, oxalic acid and citric acid.

A crystal's habit is the tendency for a given crystal face or surface to grow faster than others. Hence a crystal that forms a cube has a different habit than a crystal that forms a needle. The mechanism by which habit is changed by crystal modifiers is not well understood. For example, one sulfonated polymer has been shown to change the crystal habit of iron oxide. When iron was allowed to rust in the absence of the polymer, long needle-like crystals were formed. In the presence of 5ppm of the polymer, the crystal habit was changed so that the precipitates were roughly spherical [2]. The impact of habit on scale growth is not well understood. Under one theory, needle-like crystals would be more likely to break, and thus limited in size. Crystals growing on tube walls would frequently break off leading to a reduction in the amount of scale formed. Alternatively, needles formed on tubes might provide more surface area for nucleation of other precipitates.

Crystal modifiers alter the "natural" growth of precipitate particles, making growth less thermodynamically favorable. This may apply to the conditions on tube surfaces in steam generators. Additionally, polymeric modifiers when bound to a precipitated particle may block access to binding sites, preventing additional molecules from precipitating onto the particle and slowing its growth [3]. The nucleation of new particles thus becomes relatively more favorable, leading to a larger number of precipitated particles. Therefore, crystal modifiers act to decrease the average size of the particles. It has been shown that some modifiers can reduce the size of iron oxide precipitates to the colloidal scale [2] where surface and Brownian forces are comparable to gravitational forces and the particles remain suspended. Again, there are several ways in which altering the size of the particles could impact the formation of scale in SGs. If the crystal size is reduced far enough, colloidal forces may keep the particles from attaching to each other, or to any SG internal structures, allowing efficient removal through blowdown. Alternatively, if the crystal size were increased, particles might settle out faster and accumulate on the tube sheet instead of the tubes. It is also possible that the worst of both cases might occur, the precipitate particles are too small to drop out of suspension quickly, but the colloidal forces are not strong enough to prevent them from bonding to the tubes.

Surface modification of precipitates effects tube scaling by changing the bonding properties of the crystals. It has been shown that some sulfonated polymers can modify crystal surfaces so that twinning does not occur [2]. Twinning is the intergrowth of two crystals to form one solid mass. The absence of twinning leads to clusters of crystals which are less dense and less coherent, since each crystal is a separate particle, rather than a piece of a larger crystalline structure. Surface modification could also impact the ability of the precipitates to bond to the SG internal structure, making scale less adherent. Thus surface modifiers, while not necessarily preventing the formation of scale, should act to make cleaning much easier by reducing the density and coherence of any deposits that are formed.

Thomas and Mullins [4] hypothesize that high concentrations of charge lead to higher efficacy as a crystal modifier. They cite phosphonate groups as one example of a concentrated charge functional group and present data showing that polystyrene phosphonate has a high crystal modification efficacy. There is an extensive body of work that indicates that several crystal modifiers work by adsorption onto the surface of a growing crystal and retarding further growth. For example, Amjad [5] found that benzenepolycarboxylic acids retarded crystal growth to varying extents at different concentrations of the inhibitors. The effect of the inhibitor concentration was consistent with a model based on Langmuir adsorption of the modifier onto previously formed crystals.

3

DISPERSION

A dispersant is an organic species typically added to boiler feedwater at low concentrations in an attempt to maintain particulate species in suspension, so that they are more likely to be removed by blowdown. Dispersants act by affixing themselves to corrosion product particles and changing their surface chemistry. Examples of dispersants include: lignosulfonate, poly acrylic acid and poly maleic anhydride.

Typical boiler precipitates have a charged surface. In general the charge is negative [6] although this is neither universal nor critical to the use of dispersants. Because an ionic fluid surrounds the particle, there is a tendency for the ion concentration to adjust to provide electroneutrality. Typically, the ion concentration can be modeled as a bilayer: the layer closest to the particle is compact and strongly bound to the particle surface, the outer layer is less dense, loosely bound to the particle and extends a considerable distance into the fluid. The inner layer is known variously as the Stern, compact or Helmhotz fixed layer. The outer layer is known as the diffuse, Gouy or Gouy-Chapman layer. This division into two layers allows the surface charge of a particle to be measured by its electrophoretic mobility. Typically this surface charge is discussed in terms of the zeta potential, the potential at the boundary between the compact and diffuse layers. A high zeta potential corresponds to a highly charged particle [7].

When the zeta potential is high (highly charged particles) collisions are limited by electrostatic repulsion. When the zeta potential is low particles are more likely to collide and hence, more likely to agglomerate. Dispersants are typically large molecules with an ion density much less than that which could be formed in the compact ion layer around a charged particle. Hence, when a dispersant molecule precipitates onto a particle it occupies the space that several more neutralizing ions would occupy. It thus extends the thickness of the compact layer and increases the zeta potential [6].

Several factors are involved in determining the efficacy of a particular dispersant with a given deposit. Among these are the particle area and surface characteristics and the dispersant nature and solubility. Since the ability of dispersants to bind to precipitates is a function of the area available to precipitate, the more area available for absorption the better the dispersant will work. Dispersants bind to particles in competition with ions causing the growth of the particle. The greater the extent to which adsorption is thermodynamically favored over growth, the more effective the dispersant will be. Therefore, dispersants are more helpful with fresh precipitates that have not “ripened” into more perfect crystals. Likewise, they are also more effective with amorphous or gelatinous precipitations such as those associated with iron oxides. Similarly, high solubility, charge and polarizability of the dispersant all aid in its adsorption onto precipitate particles [8]. However, as Thomas and Mullins [4] note, the charge on a good dispersant should be relatively distributed. They cite polyacrylates as an example of a molecule with a highly distributed charge leading to excellent dispersive efficacy.

4

REVIEW OF THE EXPERIMENTAL DATA

There are four different types of experiments reported in the literature: thermal stability investigations, precipitant characterization, settling rate experiments and plant, pilot or laboratory boiler. Each contributes information to the understanding of dispersant use.

Thermal stability experiments:

Steam generators are by nature high temperature environments. Since many complex molecules begin to degrade at or near SG operating temperatures it is desirable to characterize the break down of dispersant molecules at high temperatures. Masler [9] suggests a multiple experiment plan for assessing thermal stability. Some measure of the polymer integrity should be performed. This is most easily done by a measure of the molecular weight. In determination of the molecular weight, it is important to chose measures that will reflect degradation. For example, the number molecular weight (M_n) is particularly sensitive to the breakdown of smaller molecules and may give a better indication of thermal breakdown than the weight averaged molecular weight (M_w) [9]. Second, a chemical activity test should be made both before and after the thermal testing. Since most candidate dispersants are polymeric acids, an easy way to test activity is a titration for acid concentration. Since a common degradation mechanism for dispersants is decarboxylation, titration for acid activity provides a good measure of the degree of decomposition. Finally, there is no substitute for a test of dispersant activity. It is not feasible to test efficacy under actual operating condition since these conditions lead to further degradation. However, the effectiveness of a dispersant in a controlled room temperature experiment should be a relevant indicator of its performance at higher temperatures. Therefore, a room temperature test comparing the performance of a dispersant before and after thermal stressing gives a valuable indication of thermal stability.

Table 4-1 shows Masler's results for three different polymers subjected to 250^{o}C for 18 hours. PAA is polyacrylic acid; PMAA is polymethacrylic acid; and PMA is polymaleic acid.

polymer	M_n loss	decarboxilation	effectiveness loss
PAA	23%	9.5%	-9%
PMAA	13%	16.1%	11%
PMA	27%	25.9%	59%

Table 4-1: Dispersant degradation after thermal stress (Masler, 1982) [9]

As can be seen from the behavior of PAA, the efficacy test is essential in determining whether the thermal breakdown of the dispersant will effect its performance. Masler claims that the 9% increase in the efficacy of PAA is within experimental error. Even so, compared with the considerable loss in molecular weight, even a zero change in efficacy is of note.

Precipitant characterization:

One way to examine the efficacy of various dispersants is to study their effect on the nature of the precipitants formed in their presence. Although it is not always clear how changes in particle morphology will effect the formation of scale, it is nevertheless useful to directly determine these changes. Helmstetter and Holzer [2] examined the effect of an anonymous sulfonated polymer on the morphology of various precipitates. They found that the polymer acted as a significant crystal modifier during the formation of calcium carbonate, calcium sulfate and iron oxide. The sulfonated polymer that they examined acted to modify the habit, size and surfaces of all three precipitates studied. However, Foster [10] examined the effect of PAA and HEDP (1-hydroxyethylidene-1,1-diphosphonic acid) on precipitates from synthetic boiler waters. He found that the presence of the dispersant had so significant effect either on particle size or composition.

There are thus conflicting reports on the effect of dispersants on the morphology of the precipitated particles. Since the morphology will impact the packing characteristics of agglomerated particles, it will have a large influence on the thermal transport properties and the susceptibility to lancing of any scale or deposits formed. Precipitant characterization is therefore an important part of any dispersant evaluation.

Settling experiments:

The desired function of a dispersant is the prevention or delay of the settling of precipitated particles. The mechanism through which this is accomplished must involve some kind of particle modification. However, a detailed understanding of the mechanism is not necessary for the development of a simple screening procedure. Such a procedure may be developed directly from the desired attribute: the ability to maintain particles in suspension. This direct approach involves the development of a settling experiment.

Several investigators have derived various procedures for testing the effect of dispersants on settling rates. Quantification of settling usually involves the measurement of turbidity. Turbidity is the degree to which light is scattered by the medium it is passing through, or, more simply, it is the degree of cloudiness. For a given particle type the turbidity is directly proportional to the square of the particle volume and the concentration of particles [11]:

$$\tau \propto v^2 c$$

If the precipitated solids are stable, the turbidity becomes a measure of the concentration. Foster [10] used the continuous measurement of turbidity to evaluate dispersant efficacy. By taking samples from a settling suspension at a fixed depth, Foster obtained samples that decreased in turbidity as settling progressed. From the periodic measurements a turbidity half-life was calculated which gave a quantitative measurement of the settling rate. Foster found that in the presence of iron oxides at high temperature the turbidity half-life was increased ten-fold by the presence of ~10ppm PAA and almost 300 fold by the presence of both PAA and HEDP (~6ppm). Yorke, *et al.* [12] used a single time point turbidity measurement to evaluate settling rates in their experiments. Among their other findings, they determined that the presence of HEDP decreased the dispersion of iron oxide particles. They attributed this discrepancy to the high levels of calcium in their synthetic boiler water and hypothesize that in the absence of significant concentrations of calcium this effect would not be present. In their evaluation of the settling of clay particles they found that lower molecular weight PAA is more effective. Also in experiments with clay particles, they found that a sulfonic acid acrylic acid co-polymer (SA/AA) was more effective than PAA.

Dubin and Fulks [13] used transmissivity (the opposite of turbidity) to characterize the efficacy of various polymer treatments at room temperature. They found that inorganic phosphates and surfactants were unable to disperse iron oxide particles. They also concluded that the details of the polymer used (structure, molecular weight, method of manufacture, etc.) strongly influenced its efficacy.

An alternative to the optical methods used by other investigators is the filtration method used by Lechnick, *et al.* [14]. After suspending a sample of sludge in a polymer treated beaker, a sample was taken at a fixed depth at several times. This sample was then filtered and the filter cake was weighed. Using several commercial dispersants they found that the amount of sludge remaining in suspension increased with increasing dispersant concentration.

It is worth noting that all of the settling studies cited above used pre-existing solids. For solids precipitating in the presence of the dispersant there may be additional factors effecting the performance of the polymers. When present during formation, dispersants may also effect the size and shape of the particles, as well as their surface properties and ability to agglomerate.

Boiler Experiments:

There is no systematic approach to laboratory qualification of dispersants present in the literature. The data available are thus limited to a list of anecdotal evidence. In some ways this resembles the use of dispersants in industrial steam generators. The water chemistry of each boiler is in many ways unique, thus requiring very specific analysis of the efficacy of a specific dispersant. A coherent review of the literature is also hampered by the fact that most of the research on dispersant efficacy has been sponsored by dispersant venders. Thus many of the compounds studied are proprietary and unnamed. In general, most reported studies indicate that polymer dispersants can be successfully used to prevent deposit buildup in steam generators.

5

PARAMETERS EFFECTING DISPERSANT PERFORMANCE

Molecular Weight:

Several investigators have examined the effect of the molecular weight of the dispersant on its performance. Breske [15] in a study of polyacrylate and polymethylacrylate blends found that a narrow molecular weight distribution provided better dispersing performance. However, Thomas and Mullins [4] found that for sodium polyacrylate, molecular weight distribution had no effect on dispersant performance. In a study of several different types of polymeric dispersant Cuisia and Hwa [16] concluded that lower molecular weight molecules performed better. Conversely, in a study of sodium polyacrylate and sodium polymethylacrylate, Denman and Salutsky [17] concluded that higher molecular weight polymers were better dispersants. Dubin and Fulks [13] attribute variability in their experimental data to differences in molecular weight, but do not cite a specific trend. Yorke, *et al.* [12] determined that lower molecular weight polyacrylic acid was a better dispersant than high molecular weight polyacrylic acid. For the specific case of polyacrylic acids, this conclusion is confirmed by Imai, *et al.* [18] who give further insight into the mechanism by which lower molecular weight polymers make better dispersants. According to Imai, *et al.* calcium ions cause gelation of polyacrylic acid. Gelation is a precipitation caused by mild cross linking of the polymer chains. Longer polymer chains have more flexibility and are somewhat more susceptible to cross linking. However, there is still conflicting data in the literature. Since other factors inherent in the choice of polymer lots (such as molecular weight distribution and purity) are difficult to separate and have not been addressed by all of these studies, no conclusion can be made in the absence of additional carefully controlled experiments.

Concentration:

Concentration of dispersant can refer to two aspects: the functional group concentration (i.e. how many functional groups are present in a molecule of a given size) and bulk concentration (i.e. how much dispersant is in a given weight of boiler water). Chen [19] studied the effect of the concentration of functional groups in n-(hydroxyalkyl) acrylamide copolymers and found that higher concentrations of the functional group led to greater dispersant efficacy.

In studies with sodium polyacrylate and sodium polymethylacrylate Denman and Salutsky [17] found that higher bulk concentrations led to higher dispersant performance. Ferguson [20] developed a kinetic model that assumed dispersants acted to suppress nucleation of crud particles, leading to longer suspension times. Experimental results were found to qualitatively agree with the model. Although there appears to be a general consensus in the literature that higher concentrations lead to better dispersant performance, a study by Richardson, *et al*. [21] aimed at developing better dispersant concentration control techniques found that better control of the dispersant concentration did not lead to better performance. Therefore, although higher concentrations may perform better, the performance should not depend critically on the exact level.

6

POTENTIAL SIDE EFFECTS

One reason for concern regarding the use of polymers as dispersants arises from the work of Pierson, *et al.* [22] on the effect of resin beads on the degradation of steam generator tubes. The authors of that study developed a capsule test in which a section of steam generator tube was pressurized and subjected to an external environment at high temperatures. The time at which pressure was lost (i.e. when a crack propagated all the way through the tube) was used as a measure of resistance to corrosion. One of the capsule tests performed by this group involved a comparison of a solution containing resin beads and a solution containing the equivalent sulfate content as sulfuric acid. The authors found that the solution containing the resin failed sooner than that containing the acid. This led them to conclude that the organic content of the resin bead was responsible for accelerated cracking. It has been hypothesized [23] that organic species generated from the breakdown of resin beads assist in the transport of lead species to vulnerable regions of the steam generator tubing.

In contrast with the findings of Pierson, *et al.* [22] is the fact that organics (in the form of advanced amines) have been deliberately added to feedwater in some plants with no observed ill effects [24]. In general large organic molecules that are thermally unstable, decompose into smaller organic molecules. Low molecular weight organics are considered a nuisance because their presence may mask other more harmful changes in the secondary cooling system. However, they are thought to cause damage only in high concentrations. Due to the high volatility of low molecular weight organics, high concentrations are not thought to be likely in steam generators [24]. Therefore, the presence of polymeric dispersants and their decomposition products should be benign. This conclusion is borne out by many years of use in the non-nuclear industry.

7

CONCLUSIONS

Several possibilities exist for the successful use of polymeric dispersants in steam generators. Although there is some reason for concern regarding the introduction of organic species into the steam generators, the risks associated with the use of dispersants should be small. The benefits from scale conditioning and increased blowdown efficiency should outweigh any potential side effects. Several different polymers are likely to be effective in steam generators. Because a large number of proprietary chemicals are available, the technical data needed to make a rational choice is not present in the literature. The literature indicates that most of the polymers studied have a significant efficacy. Therefore, the choice of a specific dispersant may be more dependent on non-technical factors such as cost or vendor reliability than on technical performance.

The use of polymeric dispersants has a long history of safe and useful application in the non-nuclear industry. The use of polymeric dispersants in nuclear steam generators is likely to reduce deposit buildup through sludge conditioning (improving lancing and chemical cleaning efficiency) and increasing the suspendability of the particles present (improving blowdown efficiency).

8

REFERENCES

1. R.B. Good, “Performance of HEDP in Boilers,” *Corrosion 83*, Paper 3, Anaheim, 1983.
2. G.J. Helmsetter and R.A. Holzer, “Sulfonated Polymers and Scale Formation,” *39th International Water Conference*, Pittsburgh, 1978.
3. I.J. Cotton, “Consider Polymer Treatment for High Pressure Boilers,” *Power*, May/April, 1986.
4. P.A. Thomas and M.A. Mullins, “A Current Review of Polymeric Structures and Their Potential Significance in Cooling Water Treatment,” Corrosion 85, Paper 130, Boston 1985.
5. Z. Amjad, “Kinetic Study of the Seeded Growth of Calcium Carbonate in the Presence of Benezenepolycarboxylic Acids,” *Langmuir*, **3**, 224-229, 1987.
6. G. Gibson, “Minimizing Iron and Copper Deposition,” *Proceedings of the American Power Conference*, **37**, 781-790, 1975.
7. D. F. Evans and H. Wennerström, *The Colloidal Domain Where Physics, Chemistry, Biology, and Technology Meet*, VCH Publishers, Inc. New York, 1994.
8. J.A. Kelly, “Iron Transport in Boiler Systems,” *Corrosion 80*, Paper 81, Chicago, 1980.
9. W.F. Masler, “Characterization and Thermal Stability of Polymers for Boiler Treatment,” *43rd International Water Conference*, Paper 37, Pittsburgh, 1982.
10. P.E. Foster, “Treatment and Temperature Effects on Turbidity and Morphology in Boilers,” *46th International Water Conference*, Paper 57, Pittsburgh, 1985.
11. D.H. Everett, *Basic Principles of Colloid Science*, Royal Society of Chemistry, London, 1989.
12. M.A. Yorke, B. Bendiksen and J.R. Parsons, “Clay and Iron Oxide Dispersion by Low Molecular Weight Water Soluble Polymers,” Division of Polymer Chemistry Conference, 389-391, Miami Beach, 1989.
13. L. Dubin and K.E. Fulks, “The Role of Water Chemistry on Iron Dispersant Performance,” *Corrosion 84*, Paper 118, New Orleans, 1984.

14. W. Lechnick, J.M. McDowell, P.T. Thomas and T.H. Penny, "The Use of Dispersants for Removal of Sludge from a Nuclear Steam Generator," *43rd International Water Conference*, Paper 35, Pittsburgh, 1982.

15. T.C. Breske, "Application Experience with Organic Boiler Water Treatments," *Corrosion 82*, Paper 115, Houston, 1982.

16. D.G. Cuisia and C.M. Hwa, "The Inhibition of Various Types of Boiler Scale," *Corrosion 83*, Paper 2, Anaheim, 1982.

17. W.L. Denman and M.L. Salutsky, "Boiler Scale Control with Polyacrylates and Polymethacrylates," *28th International Water Conference*, 85-93, Pittsburgh, 1967.

18. T. Imai, T. Uchida, S. Ano and T. Tsuneki, "A Newly Developed Polymer to Inhibit Scale in Cooling Water Systems," *MP*, **28:5**, 41-44, 1989.

19. F. Chen, "N-(hydroxyalkyl) acrylamide Copolymers for Corrosion Control," *Polymeric Materials for Corrosion Control*, Chicogo, 1985.

20. R.J. Ferguson, "Developing Scale Inhibitor Dosage Models," *Engineering Solutions to Industrial Corrosion Problems*, Paper 24, Sandefjorde, 1993.

21. J. Richardson, R.J.A. Tippett and P. Gabris, "Online Monitoring of Boiler Water Polymer Dispersants," *54th International Water Conference*, Paper 45, Pittsburgh, 1993.

22. E. Pierson, J. Stubbe, W.H. Cullen, S.M. Kazanjian and P.N. Paine, "How to Simulate Acid Corrosion of Alloy 600 Steam Generator Tubes," 7th Int. Symp. on Environmental Degradation of Materials in Nuclear Power Systems – Water Reactors, 303-315, Breckenridge, 1995.

23. C. Laire, G. Platbrood and J. Stubbe, "Characterization of the Secondary Side Deposits of Pulled Steam Generator Tubes," 7th Int. Symp. on Environmental Degradation of Materials in Nuclear Power Systems – Water Reactors, 387-397, Breckenridge, 1995.

24. C.J. Wood, project manager, *PWR Secondary Water Chemistry Guidelines – Revision 3*, TR-102134 Revision 3, Electric Power Research Institute, Palo Alto, 1993.

APPENDIX

Authors: Z. Amjad

Title: The Inhibition of Dicalcium Phosphate Dihydrate Crystal Growth by Polycarboxylic Acids

Source: Journal of Colloids and Interfacial Science 117:1, 98-103 (1987).

Summary: The author investigated the effect of the presence of carboxylic acids on the growth rates of dicalcium phosphate dihydrate crystals. The concentration dependency of the growth rate was consistent with a Langmuir adsorption model indicating that inhibition of crystal growth results from the adsorption of polymers onto existing crystals.

Authors: Z. Amjad

Title: Kinetic Study of the Seeded Growth of Calcium Carbonate in the Presence of Benzenepolycarboxylic Acids

Source: Langmuir 1987:3, 224-228 (1987).

Summary: The author conducted constant concentration experiments to test the inhibiting effects on calcium carbonate crystal growth rates. The relationship between the growth kinetics and the acid concentration was consistent with a Langmuir adsorption model.

Authors: Z. Amjad

Title: The Influence of Polyphosphates, Phosphonates and Polycarboxylic Acids on the Crystal Growth of Hydroxyapatite

Source: Langmuir, 1987:3, 1063-1069 (1987).

Summary: The author conducted constant concentration experiments to determine the effect of various inhibitors on the crystal growth rates of hydroxyapatite. The effects of concentration were consistent with a Langmuir adsorption model. The relative efficacies of the molecules tested were: polyacrylic acid > polyphosphonates > polyphosphonates > citric acid > tricarballylic acid.

Authors: Z. Amjad

Title: Effect of Precipitation Inhibitors on Calcium Phosphate Scale Formation

Source: Canadian Journal of Chemistry, 67, 850-856 (1989).

Summary: The author conducted constant concentration experiments on polyacrylic acid, phosphonates and polycarboxylic acids. PAA was found to have optimal efficacy at a molecular weight of 2100. The author cited other studies which had found a similar optimum for the inhibition of similar crystals. An adsorption mechanism was hypothesized, but was not well supported.

Authors: Z. Amjad

Title: Performance of Inhibitors in Calcium Fluoride Crystal Growth Inhibition

Source: Langmuir 1993:9, 597-600 (1993).

Summary: The author conducted constant concentration experiments to determine the efficacy of several acids in inhibiting the growth of calcium fluoride crystals. Two categories were found: unsaturated dicarboxylic acids and glucose were found to be ineffective, mono and di hydroxycarboxylic acids and polycarboxylic acids were found to be effective. Inhibition was found to be due to adsorption phenomena, ruling out the possibility that complexation of calcium was the sole contributing mechanism to inhibition.

Authors: Z. Amjad, J. Pugh, J. Zibrida and B. Zuhl

Title: Polymer Performance in Cooling Water: The Influence of Process Variables

Source: Corrosion 96, Paper 160 (1996).

Summary: The authors investigated the calcium carbonate inhibiting powers of several polymers under a variety of process conditions. Higher pH and higher temperature were found to decrease efficacy. Iron species adversely effected performance, but their effect was decreased if sulfonic groups were present in the polymer. Cationic polymers adversely effected the inhibition of calcium carbonate.

Authors: G. Bohnsack, K.H. Lee, D.A. Johnson and E. Buss

Title: Mechanisms of Organic Inhibitors Used in Cooling Water Corrosion Control

Source: Material Performance, May 1986, 32.

Summary: The authors discuss two types of inhibitors: interface and membrane. Interface inhibitors work by adsorption interference and generally form a thin layer on the protected metal. Membrane inhibitors create a thick protective oxide layer. Cathodic inhibition stops the formation of oxides. Anodic inhibition accelerates the formation of a protective oxide layer.

Authors: W.E. Bornak

Title: The Chemistry of Iron and Its Corrosion Products in Boiler Systems

Source: Corrosion 85, Paper 246, Boston (1985).

Summary: The author reviewed the literature relevant to the chemistry of iron deposits in boilers. The review includes a discussion of the structure of magnetite deposits.

Authors: T.C. Breske

Title: Application Experience with Organic Boiler Water Treatments

Source: Corrosion 82, Paper 115, Houston (1982).

Summary: The author reviewed experience with internal treatments as a supplement to external and phosphate treatments. The chelators EDTA and NTA were discussed. Results from several chelator case studies were presented. The historic use of dispersants was reviewed. Data on the use of PA/PMA blends were reviewed. The author concluded that wide variation in the molecular weight of the polymer used was detrimental to its function as a dispersant. The cases reviewed covered the use of dispersants for hardness control, not metal transport. Case studies of sequesterants were reviewed. A sequesterant was defined as a molecule that was midway between a dispersant and a chelator. Two sequesterants were discussed AMP and HEDP.

Authors: F. Chen

Title: N-(hydroxyalkyl) acrylamide Copolymers for Corrosion Control

Source: Polymeric Materials for Corrosion Control, Chicago (1985).

Summary: The author investigated the effect of polymer structure on dispersant efficiency. Dispersing effects on calcium, iron and clay were measured. It was concluded that a higher concentration of functional groups enhanced performance.

Authors: I.J. Cotton

Title: Consider Polymer Treatment for High Pressure Boilers

Source: Power, May/April 1986.

Summary: A general background on the use of dispersants was presented. Various mechanisms of dispersant action were discussed. Case studies involving industrial boilers were presented. General guidelines for choosing a polymer dispersant are listed. The basic types of polymer dispersants are discussed.

Authors: D.G. Cuisia

Title: Performance of a New Polysulfonated Additive for Controlling Boiler Scales

Source: Corrosion 85, Paper 359, Boston (1985).

Summary: The author presented information on a proprietary dispersant, a polysulfonated additive (PSA) as well as polyacrylate (PAA), polymethacrylate (PMA) styrene sulfonate-maleic anhydride (SSMA) and acrylate-acrylamide copolymer (AA). The chemical structures of the various additives were discussed. The work focused on the dispersing ability with respect to calcium and magnesium.

Authors: D.G. Cuisia and C.M. Hwa

Title: The Inhibition of Various Types of Boiler Scale

Source: Corrosion 83, Paper 2, Anaheim (1985).

Summary: The authors summarized the various types of scale precipitates. Several polymers were tested in a pilot scale boiler (PMA, PAA, sodium vinyl sulfonate, sulfonated styrene homopolymers, maleic anhydride homopolymers, acrylamide homopolymers and acrylamideomethylpropane sulfonic acid). Various feedwaters were fed to the boiler. Lower molecular weight polymers were better dispersants. None of the tested chemical were found to be effective for all the feedwater contaminants. Sodium vinyl sulfonate and polymer/phosphonate treatments were found to be most effective. Little actual data is presented.

Authors: R.J. Cunningham

Title: Avoiding Failures Due to Misapplication of Contemporary Industrial Boiler Treatment Programs

Source: International Water Conference, Paper 29 (1994).

Summary: The author covers possible problems with treatment implementation. Most failures are attributed to operator error. Chelator programs (focus on EDTA) are discussed. Phosphate programs to precipitate calcium out of the feedwater are discussed. Dispersant mechanisms (crystal modification and charge modification) are discussed. It is noted that polymers do not act as chelators. Several case studies are reviewed. In general, this author does not recommend dispersants. Most of the article focuses on action to reduce hardness, rather than metal transport.

Authors: W.L. Denman and M.L. Salutsky

Title: Boiler Scale Control with Polyacrylates and Polymethacrylates

Source: 28th International Water Conference, 85-93 (1967).

Summary: The authors review the history of dispersants and discuss the use of sodium polyacrylate and sodium polymethacrylate for removing hardness. Lab boiler tests were performed to test the dispersant effectiveness. A simple settling test was used to determine the dispersant effectiveness. Higher molecular weights and higher concentrations were found to be more effective. Several case studies were reviewed.

Authors: L. Dubin and K.E. Fulks

Title: The Role of Water Chemistry on Iron Dispersant Performance

Source: Corrosion 84, Paper 118, New Orleans (1984).

Summary: The authors tested various water treatments, varying pH, conductivity and the choice of polyvalent cations in the polymer dispersant. Acrylamide-acrylate copolymer was found to work well. pH had varying effects on the dispersant effectiveness. Divalent cations had a negative effect on dispersant performance. Higher conductivity had a mildly positive effect on dispersant effectiveness. The polymer specifics (structure, molecular weight, method of manufacture) were found to be important factors in determining dispersant effectiveness.

Authors: R.J. Ferguson

Title: Developing Scale Inhibitor Dosage Models

Source: Engineering Solutions to Industrial Corrosion Problems, Paper 24, Sandefjord (1993).

Summary: The author develops an "antinucleation" model to describe the action of dispersants. Data on AMP, PAA and HEDP are presented. The model assumes that the nucleation induction time varies with a power of the dispersant concentration. Rate constant data is not included in the paper. The author primarily addresses hardness rather than metal transport.

Authors: P.E. Foster

Title: Treatment and Temperature Effects on Turbidity and Morphology in Boilers

Source: 46th International Water Conference, Paper 57 (1985).

Summary: The author tested the settling behavior of synthetic boiler waters and samples of real boiler water. Solids were tested by Coulter counter, SEM and XRD. To determine the settling behavior, the half-life of the turbidity at a given height was measured. The paper covers both hardness and iron transport. PAA and HEDP were tested. The dispersants were found not to aid in the control of hardness. PAA dispersed iron ions, while HEDP did not. There was significant variation between the results with real and synthetic boiler waters, presumably due to the presence of oxygen in the synthetic waters.

Authors: G. Gibson

Title: Minimizing Iron and Copper Deposition

Source: Proceedings of the American Power Conference 37, 781-790 (1975).

Summary: The author discusses carbon dioxide control by pH adjustment, oxygen control with hydrazine and gives an overview of the use of PMA and CMC. Anecdotes on the successful use of polymer dispersants are presented. Colloidal theory is reviewed.

Authors: J.S. Gill and M.A. Yorke

Title: Calcium Carbonate Control in Highly Supersaturated Aqueous Environment

Source: Corrosion 94, Paper 195 (1994).

Summary: The authors tested polyamino polyether methylene phosphonic acid against PAA, HEDP, AMP, HMDTMP, PBTCA and HEDP-AMP-AA/AMPS polymer. Tested for calcium carbonate inhibition only. PAPMPA tested best in both boiler and cooling tower type environments.

Authors: R.B. Good

Title: Performance of HEDP in Boilers

Source: Corrosion 83, Paper 3, Anaheim (1983).

Summary: The author measured the stability and efficiency of HEDP in plants. The decay rate constant of HEDP was determined. There was a high degree of scatter in the raw data. The decay of HEDP followed an Arrhenius type behavior. HEDP was found to disperse both hardness species and iron oxides. Only plant data is presented, no theory is proposed. HEDP is claimed to be a sequesterant and a crystal modifier.

Authors: R.B. Good and J.B. Arots

Title: The Thermal Hydrolytic Stability of 1-Hydroxyethylidene-1,1-diphosphonic Acid

Source: International Water Conference, Paper 7 (1981).

Summary: The authors review various phosphonic decay theories, but not for HEDP. Laboratory autoclave experiments were conducted along with case studies on industrial boilers. The effects of pH, cation and oxygen concentration and temperature were investigated. The decomposition was catalyzed by both acidic and basic conditions (neutral solutions provided the slowest decomposition). The results on the effect of cation concentration was inconclusive, but suggested that sodium ions might accelerate decomposition. Reduced oxygen slows decomposition. An Arrhenius relationship with temperature was found with an activation energy of 60000 BTU/lb-mol and a pre-exponential constant of $8x10^{11}$/hr in the presence of sulfite and $1x10^{17}ft^3$/lb/hr in the presence of calcium. Order of magnitude agreement was found with boiler data.

Authors: D.H. Grant and N. Grassie

Title: The Thermal Decomposition of Polymethacrylic Acid

Source: Polymer, 1, 125-134 (1960).

Summary: The authors examined the decomposition of polymethylacrylic acid in vacuum at 200^{o}C. Two reactions were observed. Depolymerization produced methylacrylic acid monomer. Dehydration produced water and an insoluble anhydride. The dehydration was the more prominent reaction.

Authors: D.W. Griffiths, S.-T. Liu and S.D. Roberts

Title: Inhibition of Calcium Sulfate Dihydrate Crystal Growth by Phosphonic Acids – Influence of Inhibitor Structure and Solution pH

Source: SPE of AIME International Symposium on Oilfield and Geophysical Chemistry, Houston, 1979.

Summary: The authors studied the effect of pK_a on the inhibitory efficacy of several acids. Deprotonated molecules were found to inhibit crystal growth. Deprotonation was achieved through either high pK_a or high pH.

Authors: J.L. Haluska

Title: What to Follow If Your Goal is Effective Fouling Control

Source: Hydrocarbon Processing 55:7, 153-156 (1976).

Summary: The author measured efficiency drop in a heat exchanger due to fouling. Some case studies were cited, but no description of the particular anti-foulants used was included.

Authors: W.M. Hann, J.H. Bardsle and S.T. Robertson

Title: Comparison of Advanced Polymers for Minimizing Deposits of Iron Oxide and Insoluable Calcium Salts

Source: Corrosion 89, Paper 428, New Orleans (1989).

Summary: The authors defined six general categories of polymer SCAs: monoprotic weak acids, diprotic weak acids, monoprotic weak acid – strong acid, diprotic weak acid – strong acid, monoprotic weak acid – nonionic and monoprotic weak acid – strong acid – nonionic. The example tested from the last category, acrylic acid – sulfonate – nonionic terpolymer (AA/S/N) tested better than the examples from the other categories. In the presence of iron, the terpolymer still worked best. The authors note that testing of resuspended sludge may not be representative of boiler chemistry since dehydration of iron oxides may be irreversible. The authors also note that sludge from a boiler may behave differently from synthetic sludge because of contamination by organics which fill the reaction sites to which the polymer additive might bond.

Authors: G.J. Helmstetter and R.A. Holzer

Title: Sulfonated Polymers and Scale Formation

Source: 39th International Water Conference, 299-307 (1978).

Summary: The authors discuss the theoretical operation of polymer dispersants. Three mechanisms are described: dispersant, chelator, and crystal modifier. Sulfonated polymers have little chelating powers. Dispersants are said to lower the viscosity of suspensions. Sulfonates inhibit crystallization by preventing twinning. This paper focuses on calcium deposits and does not address issues relating to iron.

Authors: J.E. Hoots and G.A. Crucil

Title: The Mechanisms of Polymers in Alkaline Cooling Water Programs

Source: MP 26:4, 17-25 (1987).

Summary: The authors analyzed three acrylic acid based copolymers, AA/HPA, AA/ester copolymer and AA homopolymer. The focus of the study was calcium dispersion (no data on iron was presented). Higher molecular weight polymers were found to work better. In comparison with field testing, the authors found significant differences between laboratory and plant performance.

Authors: T. Imai, T. Uchida, S. Ano and T. Tsuneki

Title: A Newly Developed Polymer to Inhibit Scale in Cooling Water Sustems

Source: MP 28:5, 41-44 (1989).

Summary: The authors present data on a coplymer of acrylic acid and 2-hydroxyl-3-allyloxy-1-propane sulfonate (HAPS). From their test data they concluded that the optimal HAPS content was about 7.5~10%. Lower molecular weights were found to perform better. The tests were performed with calcium carbonate (no iron data). Calcium is known to cause gelation of polyacrylic acids. Including HAPS in the polymer prevents gelation.

Authors: N.N. Johnston

Title: Field Experience with a New High-Temperature Polymeric Dispersant

Source: Tappi Journal 76:11, 205-208 (1993).

Summary: The author presented results from plant trials of a proprietary polymer with phosphate groups. The use of the dispersant led to more efficient blow down. Polyacrylates were said to decarboxylate at high temperatures, making them less useful.

Authors: J.A. Kelly

Title: Iron Transport in Boiler Systems

Source: Corrosion 80, Paper 81, Chicago (1980).

Summary: The author covers the various sources of iron in the feedwater and the various corrosion mechanisms that contribute to transfer of iron to the boiler. The Paneth-Fajans-Hahn rule is mentioned: the most strongly adsorbing polymers make the least effective dispersants. The difference between dispersants and chelators is highlighted: dispersants dissolve particles while chelators dissolve ions. EDTA was found to chelate 54% of ferric ions, while twice the amount of EDTA was needed to dissolve magnetite. Some field studies are cited.

Authors: J.A. Kelly

Title: An Update on Controlling Iron Oxide Deposition in Boiler Systems

Source: Corrosion 82, Paper 117, Houston (1982).

Summary: The author reviews the use of dispersants in boilers. Some lab and field evaluations are discussed.

Authors: J.A. Kelly and T.R. Filipowski

Title: Controlling Iron Oxide Deposition in Boiler Systems

Source: Tappi Engineering Conference, 467-481, San Francisco (1978).

Summary: The authors briefly review corrosion control and filtration/polishing and discuss the use of EDTA as a chelator. The role of a dispersant is contrasted to that of a chelator: a dispersant maintains suspendability by preventing agglomeration, while a chelator dissolves ions. The effectiveness of a dispersant depends on its adsorption. High charge, high polarizability and low hydration energy are all good qualities in a dispersant. The use of dispersants was evaluated using scale surveys, field tests and laboratory experiments.

Authors: J.A. Kelly and M.L. Palmer

Title: Iron Oxide Deposition – Complete System Control

Source: 40th International Water Conference, 45-55 (1979).

Summary: The authors review mechanisms of iron transport and the use of chelators and dispersants. Nothing new was presented which is not found elsewhere in the first author’s other works.

Authors: C. Laire, G. Platbrood and J. Stubbe

Title: Characterization of the Secondary Side Deposits of Pulled Steam Generator Tubes

Source: 7th Int. Symp. on Environmental Degradation of Materials in Nuclear Power Systems – Water Reactors, Breckenridge, August 7-10, 1995.

Summary: The authors investigated tubes pulled from several Belgian plants. The deposits consisted mostly of iron with many other species present in minor quantities. Copper was more prevalent in the free span area. Most copper was present in metallic form, but some oxides were detected. Oils and carboxylates were present. There was a chromium oxide layer present at the metal/oxide interface. Organics were theorized to aid in Pb transport, promoting corrosion.

Authors: W.F. Langelier

Title: The Analytical Control of Anti-Corrosion Water Treatment

Source: Journal of the American Waterworks Association 28:10, 1500-1521 (1936).

Summary: The author develops a theoretical framework for analyzing the amount of calcium carbonate in a water solution. The Langelier Saturation Index is introduced. This index is the difference between the actual pH and the pH which would make the concentration supersaturated.

Authors: W. Lechnick, J.M. McDowell, P.T. Thomas and T.H. Penny

Title: The Use of Dispersants for Removal of Sludge from a Nuclear Steam Generator

Source: 43rd International Water Conference, Paper 35 (1982).

Summary: The authors tested dispersants using plant sludge with approximately 50% copper. The object of the study was to use dispersants during crevice flushing operations. The ability of the dispersant to resuspend settled sludge was also tested. The dispersants tested performed successfully. The polymers tested were commercial products: Cyanameer P-35, Wayplex 55-S, Wayplex NTP-A and Wayplex 45-K.

Authors: M. Loke and J.S. Gill

Title: The Effect of Polyamino Polyether Methylene Phosphonate on the Crystallization Kinetics of Calcium Carbonate: A Constant Composition Study

Source: Corrosion 96, Paper 157 (1985).

Summary: The authors studied PAPEMP, HEDP and propanolamine (bis) methylene phosphonate using a fed batch system to keep the calcium carbonate concentration constant. The polymer molecules were hypothesized to adsorb onto the growing calcium carbonate crystals, poisoning active growth sites and halting growth. The efficacy was found to vary with the pH and calcium ion concentration. PAPEMP was found to work best for high calcium ion concentrations.

Authors: W.F. Masler

Title: Characterization and Thermal Stability of Polymers for Boiler Treatment

Source: 43rd International Water Conference, Paper 37 (1982).

Summary: The author performed degradation studies. Polymer molecular weight, carboxyl content and calcium carbonate inhibiting threshold were measured. Polyacrylic acid, polymethacrylic acid and polymaleic acid were studied and all found to degrade. Polymaleic acid was found to lose significant dispersant capability upon degradation.

Authors: A.C. McDonal and G.J. Patek

Title: Design and Operation of a 2600 PSIG Model Steam Generator

Source: 48th International Water Conference, Paper 48 (1987).

Summary: The authors describe their model steam generator. PMAA was found to increase the efficiency of iron removal through blow down.

Authors: C.J. McDonough, D.G. Cuisia, R.J.A. Tippett and L.-D. G. Fan

Title: A Novel Polymer for Effective Boiler Water Scale Control

Source: Corrosion 95, Paper 478, Orlando (1995).

Summary: The authors developed a sequence of dispersant testing techniques including: calcium complexation, precipitating tendency, prevention of calcium phosphate deposits, iron dispersivity and thermal stability. Pilot boiler experiments were conducted to determine the effect of dispersants on the deposition of iron oxides. Several polymers were tested: SSS/MAA, PAA, PMA, AAA, SMA, ASMA and PCA. The authors concluded that several different tests were necessary to determine the overall effectiveness of a particular dispersant.

Authors: M.C. McGaugh and S. Kottle

Title: The Thermal Degradation of Poly (acrylic acid)

Source: Journal of Polymer Science B (Polymer Letters) 5, 817-820 (1967).

Summary: The authors examined the degradation of PAA when heated in air. UV spectroscopy was used to measure the degradation. Several steps were involved. The degradation began with dehydration and proceeded through decarboxilation. The conditions tested were relatively mild (150~300°C).

Authors: M.C. McGaugh and S. Kottle

Title: The Thermal Degradation of Acrylic acid – Ethylene Polymers

Source: J. Polymer Science, A1:6, 1243-1248 (1968).

Summary: The authors investigated the thermal degradation of a copolymer of acrylic acid and ethylene. The degradation was carried out in oxygen at temperatures ranging from room temperature to 500°C, as well as some experiments conducted in vacuum. The first step in the degradation is dehydration to acrylic anhydride. The second step is decarboxylation.

Authors: J.J. Mucci

Title: Consider Polymers for Control of Iron Oxide Deposition

Source: Power, 126:1, 58-61 (1982).

Summary: The author gives an overview of the use of dispersants, citing differences between dispersants and chelators and reviewing the chemistry of dispersant action. A case study of the successful use of a proprietary polymer dispersant is reviewed. The polymers tested were acrylic acids and acrylamides.

Authors: G.H. Nancollas and M.M. Reddy

Title: The Crystallization of Calcium Carbonate II. Calcite Growth Mechanism

Source: Journal of Colloids and Interfacial Sciences, 37:4, 824-830 (1971).

Summary: The authors investigated the kinetics of calcite crystallization. Crystal growth proceeded through two phases: nucleation (both from the bulk and on surfaces) and growth. The growth phase was second order. The activation energy was consistent with a surface reaction controlled mechanism.

Authors: E. Pierson, J. Stubbe, W.H. Cullen, S.M. Kazanjian and P.N. Paine

Title: How to Simulate Acid Corrosion of Alloy 600 Steam Generator Tubes

Source: 7th Int. Symp. on Environmental Degradation of Materials in Nuclear Power Systems – Water Reactors, Breckenridge, August 7-10, 1995.

Summary: The authors performed capsule tests on Alloy 600 tubes. The effects of lead, phosphate and chemical cleaning were studied. The presence of resin beads or their equivalent sulfates was tested. Organics accelerated cracking over and above that caused by the equivalent sulfates.

Authors:	E. Pierson, J. Stubbe and G. Denny
Title:	Stress Corrosion Cracking of Alloy 690, 800 and 600 in Acid Environments Containing Copper Oxides
Source:	Corrosion 96, Paper 119, (1996).
Summary:	The authors performed capsule tests on tubes of several alloys. Organics from resins were found to significantly accelerate stress corrosion cracking.

Authors:	G. Platbrood, P. Buxant, H. De Rouch and L. Goeminne
Title:	Characterization of Metal (Cr, Ni, Fe) Carboxylates by FTIR, TF Raman and Determination of Their Thermal Stability by Dynamic Differential Scanning Calorimetry
Source:	Paper 303, PittCon95, New Orleans, 1995.
Summary:	The authors present several analytical techniques that are useful in the study of polymer degradation. They note that carboxylates can have a corrosive effect.

Authors:	M.M. Reddy and G.H. Nancollas
Title:	The Crystallization of Calcium Carbonate I. Isotopic Exchange and Kinetics
Source:	Journal of Colloids and Interfacial Sciences, 36:2, 166-172 (1971).
Summary:	The authors investigated the growth kinetics of calcite through isotopic exchange studies. No crystal-solution exchange was found to occur when the solution was supersaturated. The growth kinetics were found to be second order, implying a surface reaction limited growth mechanism.

Authors:	J. Richardson, R.J.A. Tippett and P. Gabris
Title:	Online Monitoring of Boiler Water Polymer Dispersants
Source:	54th International Water Conference, Paper 45 (1993).
Summary:	The authors discuss the use of online measurements for boiler monitoring. UV-Vis spectroscopy is used to monitor the concentration of polymer dispersants. However, the authors found that improved control of dispersant concentration did not lead to improved performance of the dispersant.

Authors: J.M. Riddle

Title: Effect of Organics on Nuclear Cycles

Source: EPRI TR-100785 (1992).

Summary: The author reviewed the literature regarding the sources and effects of organics in the secondary cycle. Various possible problems are cited, however, organics were generally found to be too volatile to accumulate in damaging concentrations.

Authors: J.M. Riddle, T.O. Passell and V.J. Lineenbom

Title: Monitoring of Morpholine and Its Decomposition Products at Beaver Valley Power Station

Source: 47th International Water Conference, Paper 28 (1986).

Summary: The authors monitored morpholine and its decomposition products during trials at Beaver Valley. No discussion of the impact of the decomposition products on the water chemistry was included.

Authors: R.J. Ross, K.C. Low and J.E. Shannon

Title: Polyaspartate Scale Inhibitors – Biodegradable Alternatives to Polyacrylates

Source: Corrosion 96, Paper 162 (1985).

Summary: The authors tested the calium inhibiting powers of polyasparates. Maximum efficacy was found with molecular weights approximating 5000 (~30 mers). The authors postulate a tradeoff between better binding (from high molecular weights) and the number of molecules (higher with low molecular weights).

Authors: N.S. Sherwood

Title: Novel Calcium Carbonate Inhibitor for Maximum Acid-Free Cooling Water Use

Source: Corrosion 94, Paper 453 (1994).

Summary: The author examined the efficacy of PAPEMP in dispersing calcium carbonate when the saturation limit had been exceeded. PAPEMP was found not only to increase the solubility of calcium carbonate, but also to reduce the adherence of growing crystals.

Authors: M.L. Standish

Title: A New Polymeric Material for Scale Inhibition and Removal

Source: Corrosion 96, Paper 163 (1996).

Summary: The author tested the ability of a proprietary sulfonated polymer to stabilize calcium phosphate, inhibit calcium carbonate formation and stabilize zinc. The polymer was also tested for thermal stability. The new polymer was compared to a PA/PSA copolymer. The authors claimed that the new polymer would resuspend iron deposits. The testing was mostly limited to its ability to control calcium deposits.

Authors: J. Stubbe, C. Laire, E. Pierson, G. Platbrood and P. Van Royen

Title: Corrosion Secondaire des GV de Doel 4: Le Plom et le Cuivre Sont-ils Impliques?

Source: Fontevraud III, 356-364, (1994).

Summary: The authors present a case study on Doel 4 and the effects of chemical cleaning on stress corrosion cracking. Copper is found to accelerate corrosion, possibly due to its catalysis of organic acid formation.

Authors: P.J. Sullivan, F. O'Brien and R.J. Ferguson

Title: A Multifunctional Additive for Deposit Control

Source: Corrosion 96, Paper 158 (1985).

Summary: The authors tested a phosphonocarboxylic acid copolymer. Phosphonate groups were used for threshold inhibition (nucleation suppression) while carboxyl groups were used for dispersion. The polymer was found to be effective in controlling calcium carbonate scale formation.

Authors: D.A. Swanson

Title: The Use of Polymeric Materials with Phosphate and Chelation Type Boiler Water Treatment

Source: 28th International Water Conference, 81-84 (1967).

Summary: The author examines the use of polymers and chelators with phosphate type control schemes. Specifically an anionic polycarboxylate copolymer was examined. The combination of phosphate, chelator and polymer was found to work best. The studies focused solely on hardness (no consideration of iron oxides). Laboratory boiler results plus field anecdotes were discussed. The author claims that the polymers worked as a crystal modifier. The anions competed with the chelators to form precipitates. Some work on EDTA and polymer effects on iron was reported. The use of polymers allowed the reduction in the level of chelators that had some adverse effects on metal passivity. The use of polymer dispersants was recommended as a supplement to the use of chelators.

Authors: P.A. Thomas and M.A. Mullins

Title: A Current Review of Polymeric Structures and Their Potential Significance in Cooling Water Treatment

Source: Corrosion 85, Paper 130, Boston (1985).

Summary: The authors reviewed the then current state of the art in polymer treatments. Sodium polyacrylates have a distributed charge, which gives them dispersing powers. Phosphonates have a concentrated charge, which gives them crystal modification powers. The molecular weight distribution of sodium polyacrylates was found to have no effect on their performance. The optimal average molecular weight was found to be in the range 1000~2500 for both polyacrylates and polymaleic anhydride. PMA was found to function better than PA. High molecular weight polystyrene sulfonates did not have any efficacy at all. The authors focused on the cost/benefit ratio and found that in general, cheaper, simpler molecules, like PMA, were the most cost effective.

Authors: J. Turner

Title: Boiler Iron Deposition

Source: Anticorrosion Methods and Materials, **26**, 4-8 (1980).

Summary: The author reviews the sources of iron in the feedwater and reviews the standard treatments. It is claimed that chelators are an inefficient method for removal of iron, and polymeric dispersants are recommended.

Authors: D.L. Venezky

Title: Thermal Stability of EDTA and Its Salts

Source: 32nd International Water Conference, 37-45 (1971).

Summary: The author conducted sealed NMR tube studies to monitor the decay of EDTA. The salt form of EDTA made a large difference in the decay rate. Oxygen and lower pHs were found to accelerate the decomposition.

Authors: S.L. Wallace

Title: Chelant Enhancement of a Polymer Boiler Treatment Program

Source: Materials Performance, 24:9, 35-38 (1985).

Summary: The author tested the efficacy of polyacrylate in the presence of EDTA in conjunction with a phosphate/sulfite treatment program. The polymeric dispersant did little to aid iron transport but did help Ca and Mg transport. Test were conducted in 600 psi boilers. Transport was measured by comparing the blowdown concentrations to the feedwater concentrations.

Authors: R.L. Worthington and J.K. Jackson

Title: All-Polymer Feedwater Treatment Improves Boiler Reliability

Source: Power Engineering, 87:11, 55-57 (1983).

Summary: The authors switched boilers from an NTA/sodium sulfate program to a proprietary all polymer treatment. Iron transport was increased from 35% to 177% and hardness transport was increased from 64% to 171%.

Authors: A.G. Xyla and P.G. Koutsoukos

Title: Effect of Diphosphonates on the Precipitation of Calcium Carbonate in Aqueous Solutions

Source: JCS Faraday Transactions 1, 83, 1477-1484 (1987).

Summary: The authors investigated the influence of diphosphonate on the nucleation and growth of calcite crystals. The phosphonates inhibited growth (not nucleation) in a manner consistent with a surface adsorption model.

Authors: M.A. Yorke, B. Bendikson and J.R. Parsons

Title: Clay and Iron Oxide Dispersion by Low Molecular Weight Water Soluble Polymers

Source: Division of Polymer Chemistry Conference, 389-391, Miami Beach (1989).

Summary: The authors evaluated the dispersive powers of various polymers by measuring the turbidity of a clay suspension after allowing a set period of time for settling. Iron dispersions were also tested. Polymers tested included SA/AA and PAA. SA/AA was found to suspend clay better. Lower molecular weight PAA was a better dispersant. In the presence of calcium ions, HEDP had an adverse effect on dispersion. Without calcium present HEDP promoted dispersion.

About EPRI

EPRI creates science and technology solutions for the global energy and energy services industry. U.S. electric utilities established the Electric Power Research Institute in 1973 as a nonprofit research consortium for the benefit of utility members, their customers, and society. Now known simply as EPRI, the company provides a wide range of innovative products and services to more than 1000 energy-related organizations in 40 countries. EPRI's multidisciplinary team of scientists and engineers draws on a worldwide network of technical and business expertise to help solve today's toughest energy and environmental problems.

EPRI. Powering Progress

TE-114159

Printed on recycled paper in the United States of America

SINGLE USER LICENSE AGREEMENT

THIS IS A LEGALLY BINDING AGREEMENT BETWEEN YOU AND THE ELECTRIC POWER RESEARCH INSTITUTE, INC. (EPRI). PLEASE READ IT CAREFULLY REMOVING THE WRAPPING MATERIAL.

BY OPENING THIS SEALED PACKAGE YOU ARE AGREEING TO THE TERMS OF THIS AGREEMENT. IF YOU DO NOT AGREE TO THE TERMS OF THIS AGREEMENT, PROMPTLY RETURN THE UNOPENED PACKAGE TO EPRI AND THE PURCHASE PRICE WILL BE REFUNDED.

1. GRANT OF LICENSE

EPRI grants you the nonexclusive and nontransferable right during the term of this agreement to use this package only for your own benefit and the benefit of your organization. This means that the following may use this package: (I) your company (at any site owned or operated by your company); (II) its subsidiaries or other related entities; and (III) a consultant to your company or related entities, if the consultant has entered into a contract agreeing not to disclose the package outside of its organization or to use the package for its own benefit or the benefit of any party other than your company.

This shrink-wrap license agreement is subordinate to the terms of the Master Utility License Agreement between most U.S. EPRI member utilities and EPRI. Any EPRI member utility that does not have a Master Utility License Agreement may get one on request.

2. COPYRIGHT

This package, including the information contained in it, is either licensed to EPRI or owned by EPRI and is protected by United States and international copyright laws. You may not, without the prior written permission of EPRI, reproduce, translate or modify this package, in any form, in whole or in part, or prepare any derivative work based on this package.

3. RESTRICTIONS

You may not rent, lease, license, disclose or give this package to any person or organization, or use the information contained in this package, for the benefit of any third party or for any purpose other than as specified above unless such use is with the prior written permission of EPRI. You agree to take all reasonable steps to prevent unauthorized disclosure or use of this package. Except as specified above, this agreement does not grant you any right to patents, copyrights, trade secrets, trade names, trademarks or any other intellectual property, rights or licenses in respect of this package.

4. TERM AND TERMINATION

This license and this agreement are effective until terminated. You may terminate them at any time by destroying this package. EPRI has the right to terminate the license and this agreement immediately if you fail to comply with any term or condition of this agreement. Upon any termination you may destroy this package, but all obligations of nondisclosure will remain in effect.

5. DISCLAIMER OF WARRANTIES AND LIMITATION OF LIABILITIES

NEITHER EPRI, ANY MEMBER OF EPRI, ANY COSPONSOR, NOR ANY PERSON OR ORGANIZATION ACTING ON BEHALF OF ANY OF THEM:

(A) MAKES ANY WARRANTY OR REPRESENTATION WHATSOEVER, EXPRESS OR IMPLIED, (I) WITH RESPECT TO THE USE OF ANY INFORMATION, APPARATUS, METHOD, PROCESS OR SIMILAR ITEM DISCLOSED IN THIS PACKAGE, INCLUDING MERCHANTABILITY AND FITNESS FOR A PARTICULAR PURPOSE, OR (II) THAT SUCH USE DOES NOT INFRINGE ON OR INTERFERE WITH PRIVATELY OWNED RIGHTS, INCLUDING ANY PARTY'S INTELLECTUAL PROPERTY, OR (III) THAT THIS PACKAGE IS SUITABLE TO ANY PARTICULAR USER'S CIRCUMSTANCE; OR

B) ASSUMES RESPONSIBILITY FOR ANY DAMAGES OR OTHER LIABILITY WHATSOEVER (INCLUDING ANY CONSEQUENTIAL DAMAGES, EVEN IF EPRI OR ANY EPRI REPRESENTATIVE HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES) RESULTING FROM YOUR SELECTION OR USE OF THIS PACKAGE OR ANY INFORMATION, APPARATUS, METHOD, PROCESS OR SIMILAR ITEM DISCLOSED IN THIS PACKAGE.

6. EXPORT

The laws and regulations of the United States restrict the export and re-export of any portion of this package, and you agree not to export or re-export this package or any related technical data in any form without the appropriate United States and foreign government approvals.

7. CHOICE OF LAW

This agreement will be governed by the laws of the State of California as applied to transactions taking place entirely in California between California residents.

8. INTEGRATION

You have read and understand this agreement, and acknowledge that it is the final, complete and exclusive agreement between you and EPRI concerning its subject matter, superseding any prior related understanding or agreement. No waiver, variation or different terms of this agreement will be enforceable against EPRI unless EPRI gives its prior written consent, signed by an officer of EPRI.

EPRI • 3412 Hillview Avenue, Palo Alto, California 94304 • PO Box 10412, Palo Alto, California 94303 • USA
800.313.3774 • 650.855.2121 • askepri@epri.com • www.epri.com