

Polymer Architecture Effect on Zinc Ions Stabilization in Aqueous Systems

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ABSTRACT

The zinc ion stabilization efficacy of synthetic, biodegradable, hybrid, and natural polymers has been studied. The results show that performance of polymers tested strongly depends on the polymer architecture. Based on the data collected, the performance of synthetic polymers may be ranked as follows: ter- > co- > homopolymers. For hybrid polymers the trend is CMI-25 > CMI-15. It has also been found that among carboxyl containing homopolymers synthetic polymers perform better than bio- and natural polymers. The precipitate consisted mainly of zinc oxide which was predominant at the experimental conditions, with plate like crystallites with a wide particle size distribution. The presence of low dosage of acrylic acid homo- and terpolymers did not have any effects on the morphology of the precipitated crystals but showed reduction in zinc oxide particle size.

Keywords: zinc ions, zinc hydroxide, zinc oxide, precipitation, inhibition, polymer architecture, aqueous systems

INTRODUCTION

Fouling of equipment surface by unwanted materials is a well-documented problem in industrial water systems.¹ The foulants are generally classified into four categories: a) mineral scales i.e., calcium carbonate, calcium sulfate, calcium phosphate, magnesium hydroxide, etc., b) corrosion products i.e., iron oxide, zinc oxide, copper oxide, etc., c) microbiological mass i.e., bacteria, algae, fungi, and other organisms, and d) deposits i.e., clay, silt, calcium-inhibitor salts, corrosion products, etc. If not properly controlled, these unwanted materials may lead to severe operational and economic problems including loss of heat transfer, plugging of equipment, increased pumping costs, loss production due to downtime, inefficient use of chemicals, premature equipment

replacement, and increased operational costs. The industrial water systems plagued by these unwanted materials include boiler, cooling, desalination, geothermal, oil and gas production, semiconductor manufacturing, etc. Mitigation of mineral scales, corrosion, and suspended matter in these systems is done by incorporating different types of additives such as scale inhibitors, corrosion inhibitors, and dispersants in the formulations. Microbiological mass is controlled by biocides which are fed separately.

Corrosion is defined as the deterioration of metal by a chemical or electrochemical reaction with its environment. Numerous factors such as metallurgy, water chemistry, temperature, pH, dissolved gases, and water flow rate, influence corrosion. Since different metals corrode for different reasons, it is therefore important to keep in mind the metallurgy present while developing a treatment program with inhibitors that are effective in controlling all potential corroding surfaces. Foulants resulting from industrial water system corrosion include oxides and hydroxides of iron, copper, and zinc. Corrosion in industrial water systems is controlled by incorporating one or more of four major inhibitors and a variety of supplements in the water treatment formulation. Corrosion inhibitors are generally classified, depending on their mode of action, as anodic i.e., chromate, nitrite, molybdates, phosphates; cathodic, i.e., zinc ions, polyphosphates and phosphonates in conjunction with calcium ions; oxygen-absorbing i.e., sulfites, hydrazine; and organic i.e., benzotriazole, triazole, etc.

During the last three decades a variety of polymers containing different functional groups and molecular weight (MW) have been developed for application in industrial water systems as scale inhibitors, dispersants, and co-corrosion inhibitors.² The availability of these polymers led to the development of several new treatment programs including stabilized phosphate, all organic, and alkaline zinc.³ The zinc-based programs rely on zinc ion as a cathodic inhibitor. In these programs, inorganic phosphates or organophosphonates are incorporated in the formulations as co-corrosion inhibitors. The function of polymer in these formations is two-fold: a) to control excessive formation of corrosion inhibiting film consisting of zinc hydroxide or zinc phosphate and b) prevent precipitation of zinc hydroxide and zinc phosphate in the recirculating water.^{4,5,6}

Among the various dissolved impurities present in natural water, metal ions including aluminum, copper, iron, manganese, and zinc when present at low concentrations (e.g., few mg/L) present the most serious problems in many domestic and industrial applications. These metal ions will not only form insoluble hydroxide under acidic and/or alkaline pH conditions and deposit on equipment surfaces but will also influence the performance of scale inhibitors and dispersants commonly used in water treatment formulations. Removal of heavy metals from industrial wastewater is of primary importance because they are not only causing contamination of water bodies but are also toxic to many life form.⁷ Industrial processes such as paint manufacturing, printed circuit board manufacturing, metal polishing, and wood processing generate wastewater containing heavy metal contaminants. Since most of heavy metal ions are nondegradable into nontoxic end products, their contamination must be reduced to acceptable levels before discharging them into environment. Otherwise, these could pose threat to public health and/or affect the aesthetic quality of potable water.

The interactions of Ca^{2+} and Zn^{2+} with phosphonates have been investigated. Amjad and Zuhl,⁸ and Demadis et al.⁹ showed that these metal ions formed insoluble salts with

phosphonates. Results of these studies reveal that metal-phosphonate salt formation strongly depends on solution chemistry and phosphonate type and concentration. Coetzee et al.¹⁰ studied the effect of Zn^{2+} on CaCO_3 precipitation, and showed that trace amounts of Zn^{2+} can substantially inhibit nucleation rate of CaCO_3 .

In earlier studies from our laboratories, we have presented results on the performance of a variety of polymeric and non-polymeric additives as stabilization agents for copper, iron, and manganese ions for industrial water systems. Results of these studies reveal that additive (polymeric and non-polymeric) performance strongly depends on the water chemistry, pH, temperature, and the characteristics of the additive.^{11,12,13} This paper is concerned with the influence of polymer architecture in stabilizing zinc ions in aqueous solutions. The polymers tested fall into three types: (a) synthetic polymers with varying MW and containing different functional groups, (b) biopolymers, that is, carboxymethyl inulin, poly(epoxysuccinic acid), and (c) natural material such as lignosulfonate.

EXPERIMENTAL

Stock solutions of calcium chloride, magnesium chloride, and sodium sulfate were prepared by dissolving known amounts of the respective crystalline reagent grade chemicals in distilled water. Sodium bicarbonate solution was made fresh for each zinc stabilization experiments. Stock solution (0.1% active solids) of polymers were prepared by dissolving known amount of polymers in distilled water. The pH of polymers solutions was adjusted to 8.35 using sodium hydroxide.

A known amount of stock solution (1,000 mg/L) of $\text{Zn}(\text{NO}_3)_2$ was added to known volume of synthetic water containing varying amounts of polymer stock solution in a 125 mL glass bottle. The synthetic water was prepared by mixing stock solutions of calcium chloride, magnesium chloride, sodium sulfate, and sodium bicarbonate. The synthetic water composition was 75 mg/L Ca^{2+} , 22.5 mg/L Mg^{2+} , 109 mg/L Na^+ , 200 mg/L Cl^- , 197 mg/L SO_4^{2-} , and 40 mg/L HCO_3^- . After the addition of Zn^{2+} solution to the synthetic water, the pH of the solution was adjusted to a required value with dilute NaOH. The experimental solutions containing 5 mg/L Zn^{2+} were kept at 35°C in water bath without stirring. At known time the solutions were filtered through a 0.22 μm membrane filter paper and the filtrate analyzed by atomic spectroscopy method.

The performance of stabilizing agent for Zn ions was calculated according to the following equation:

$$\text{Percent Stabilization (\%S)} = ([\text{Zn}]_{\text{sample}} - [\text{Zn}]_{\text{blank}}) / ([\text{Zn}]_{\text{initial}} - [\text{Zn}]_{\text{blank}}) \times 100\% \quad (1)$$

Where

S is the stabilization, %

$[\text{Zn}]_{\text{sample}}$ is the Zn concentration in the presence of polymer at 20 h

$[\text{Zn}]_{\text{blank}}$ is the Zn concentration in the absence of polymer at 20 h

$[\text{Zn}]_{\text{initial}}$ is the Zn concentration in the beginning of experiment at 0 h

Zinc Oxides/Hydroxides Precipitate Characterization

At the end of precipitation experiments, samples were withdrawn and were filtered through 0.22 μm membrane filters and the solids were characterized by scanning electron microscopy (SEM) and energy dispersive x-ray diffraction spectroscopy (EDS).

RESULTS AND DISCUSSION

Experiments were run in duplicate/triplicate and results showed good reproducibility ($\pm 7\%$). In all experiments, the calculations for the driving force was done by considering all appropriate equilibria between zinc, hydroxide, and additive species in solution using PHREEQC equilibrium speciation calculation software.¹⁴ The variation of the solutions speciation as a function of pH are shown in Figure 1. As may be seen zinc is mostly present as free ion, while significant portion is bound in the form of sulfato-, carbonate, chloro- and hydroxo- complexes.

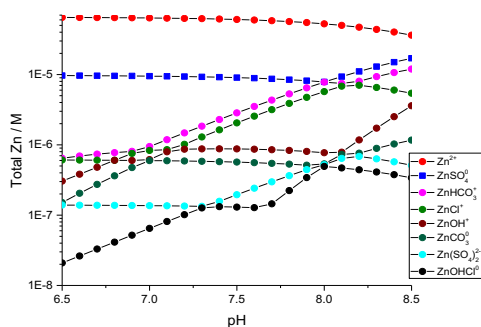


Figure 1: Zinc speciation in the supersaturated solutions over the pH range 6.50 - 8.50, 35°C.

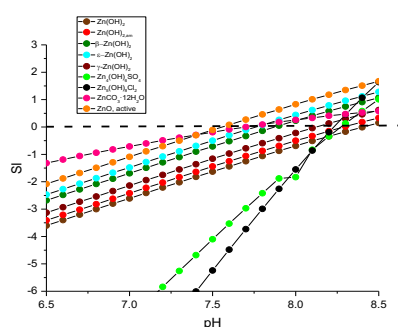


Figure 2: Variation of the SI as a function of the solutions pH, for the conditions of the present work; 35°C.

The saturation index, SI, with respect to the solids which are likely to be formed is defined as:

$$SI = \log \frac{IAP}{K_s^0} \quad (2)$$

In Equation 2, IAP is the ion activity product of the solid and K_s^0 , the corresponding thermodynamic solubility product. Positive values of SI mean that solutions at equilibrium are supersaturated with respect to the solid while negative values correspond to undersaturated solutions. The variation of the SI for a number of solids is shown in Figure 2. As may be seen, at the pH of the supersaturated solutions, 8.35, the formation of the following solids was thermodynamically possible, in the order of increasing solubility: ZnO (active), ϵ -Zn(OH)₂, β -Zn(OH)₂, ZnCO₃·12H₂O, γ -Zn(OH)₂, Zn₄(OH)₆SO₄ and Zn(OH)_{2,am}.

Polymers Performance

In the last three decades, variety of polymers have been successfully developed and are used by the water treatment industry for numerous functions including scale inhibitors,

metal ion stabilizers, crystal modification, and dispersancy. Polymers used in water treatment formulations are usually anionic and have low MW ranging from 500 to 20,000 Daltons.¹⁵ In wastewater treatment, high MW polymers are used as flocculating and coagulating agents. In detergent, use of polymers as builders is prevalent. Polymers also find applications in cosmetic and pharmaceutical industries.

Synthetic Polymers

The use of synthetic polymers e.g., poly(acrylic acid), poly(methacrylic acid), hydrolyzed poly(maleic acid), poly(acrylamide), acrylic acid/acrylamide copolymer dates back to 1950s. Researchers have shown that polymer MW, hydrolytic and thermal stability, compatibility with water treatment formulation components, water chemistry, process variables, biocides, etc., are important considerations relative to performance.^{16,17,18} Table 1 shows the ionic charge of functional groups, MW, and acronyms of the homopolymers tested.

Table 1
Homopolymers Tested

Polymer	Structure	Functional Group	Ionic Charge ^a	MW (k)	Acronym
poly(maleic acid)	$-(\text{CH}-\text{CH})_n-$ COOH COOH	-COOH	negative	0.9	PMA
poly(acrylic acid)	$-(\text{CH}_2-\text{CH})_n-$ COOH	-COOH	negative	2.3	PAA ₁
poly(acrylic acid)	$-(\text{CH}_2-\text{CH})_n-$ COOH	-COOH	negative	7.3	PAA ₂
poly(acrylic acid)	$-(\text{CH}_2-\text{CH})_n-$ COOH	-COOH	negative	120	PAA ₃
poly(methacrylic acid)	$-(\text{CH}_2-\text{CH})_n-$ COOH	-COOH	negative	6	PMAA
poly(2-acrylamido-2-methylpropane sulfonic acid)	$-(\text{CH}_2-\text{CH})_n-$ CO NH H ₃ C-C-CH ₃ CH ₂ SO ₃ H	-SO ₃ H	negative	<20	PSA
poly(vinylpyrrolidone)	$-(\text{CH}_2-\text{CH})_n-$ N O	-CN	neutral	15	PVP
poly(2-ethyloxazoline)	$-(\text{N}-\text{CH}_2-\text{CH}_2)_n-$ CO CH ₂ CH ₃	-N-CO	neutral	5	PEOX

^aat the working solution pH