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Controlling copper-based fouling by maleic acid and acrylic acid based copolymers in cooling water systems

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Abstract

The influence of polymer architecture for copper(II) ions stabilization was studied in an aqueous system. The polymers tested include: (a) homo-polymers of acrylic acid, maleic acid, itaconic acid, and vinyl pyrrolidone, and (b) co- and terpolymers of acrylic acid and maleic acid containing comonomers with different functional groups (*i.e.*, carboxylic acid, sulfonic acid, ester, alcohol, *etc.*). It was found that polymers containing stronger acidic, aromatic, and bulkier groups contribute significantly to the performance of polymers. Results on the characterization of Cu(II) hydroxide particles formed in the absence and presence of polymers by scanning electron microscopy, X-ray diffraction, and particle size analyses are presented.

Keywords: *Cu(II) ions, stabilization, industrial system, acrylic, maleic, homo-, co-, terpolymer.*

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Introduction

Metal ions such as aluminum (Al), iron (Fe), zinc (Zn), manganese (Mn), and copper (Cu) when present at low concentration (*e.g.*, few mg/L), in feed water and/or formed due to corrosion reactions are known to hydrolyze and form insoluble salts [1, 2]. Moreover, it is well recognized that these metal ions also influence the performance of scale inhibitors and dispersants [3–5]. Amjad *et al.* [6] studied the influence of recirculating water impurities on the performance of calcium phosphate inhibiting polymers. Results reveal that Mn^{2+} and Cu^{2+} ions are antagonistic to the performance of acrylate-based polymers but the adverse impact is not as great as with Fe^{3+}. Hamdona *et al.* [7] investigated the kinetics of gypsum precipitation in the presence of divalent metal ions and reported that Mg^{2+} is a better gypsum inhibitor than Fe^{2+} probably due to the formation of $MgSO_4$ ion pairs. In contrast, Weijnen *et al.* [8] found that Cu^{2+} (63 mg/L) or Zn^{2+} (65 mg/L) enhanced crystal growth rate of gypsum. The impact of low levels of Fe(III) on the performance of silica inhibitors has been reported. Results of this study show that Fe(III) exhibits antagonistic effect in inhibiting silica polymerization reaction [9].

The stabilization of Al, Cu, Fe, Zn, and Mn ions in aqueous systems by polymeric and non-polymeric additives has been the subject of numerous investigations. Smyk and Hoots [10] investigated the performance of various homo- and copolymers for their efficacy as calcium phosphate inhibitors, iron, and zinc ions stabilization for industrial water systems. Results of this study suggest that proprietary terpolymer performs better than homopolymers in inhibiting calcium phosphate scale especially in the presence of iron(III). Standish [11] in another study on the evaluation of sulfonated styrene containing polymer reported that the new polymer is not only thermally stable but also exhibits excellent calcium phosphate inhibition and metal ions stabilization properties. Amjad [12] investigated the stabilization of Al, Fe, Mn, and Zn by a variety of polymeric and non-polymeric additives. It was shown that compared to citric acid, sodium hexametaphosphate and ascorbic acid exhibit poor performance in stabilizing Fe(III) in aqueous solution. The impact of thermal treatment on the performance of polymers as Fe(III) stabilization agents was investigated. Results of this study reveal that poly(acrylic acid), PAA, made in organic solvent performs better than water polymerized PAA. Data also show that copolymers containing sulfonic acid monomers perform better than homopolymers containing carboxyl groups. In addition, results also show that copolymers containing sulfonic and non-ionic monomers experience varying degree of performance loss depending upon the degree of thermal stress and polymer composition [13].

The influence of natural polyelectrolytes (*i.e.*, fulvic acid, tannic acid), lignosulfonates, and hybrid polymers as scale inhibitors, dispersants, and metal ions stabilization agents has been reported. Carboxymethyl inulin (CMI) is a chemical derivative produced by carboxymethylation of inulin, a polysaccharide based polymer present in roots of chicory plant. The efficacy of natural and synthetic polymers as stabilization agents for Cu (II) and Mn (II) ions has been recently investigated [14–16]. Results of these studies show that CMI polymers exhibit poor performance compared to synthetic polymers. Amjad [17], in another study on the evaluation of phosphonates as Cu(II) stabilization agents showed that performance of phosphonates strongly depends on the concentration of phosphonate in solution and the phosphonate architecture.

Copper salts have long been used to kill algae in water system such as swimming pool and spas. Unfortunately, in these environments Cu(II) ions can precipitate as insoluble salts. Moreover, precipitation of copper hydroxide and/or carbonate salts not only reduces the biocidal activity of Cu(II) ions in solution but may deposit on to swimming pool surfaces. Results on the performance of various polyelectrolytes as potential Cu(II) complexing agents has been presented [18]. Industrial processes such as paint manufacturing, metal polishing or wood preservatives, generate wastewater containing heavy metal contaminants. Over the years, various methods have been developed to remove toxic metals from aqueous streams [19]. Excellent examples of corroded metal tubes are illustrated in Figure 1.

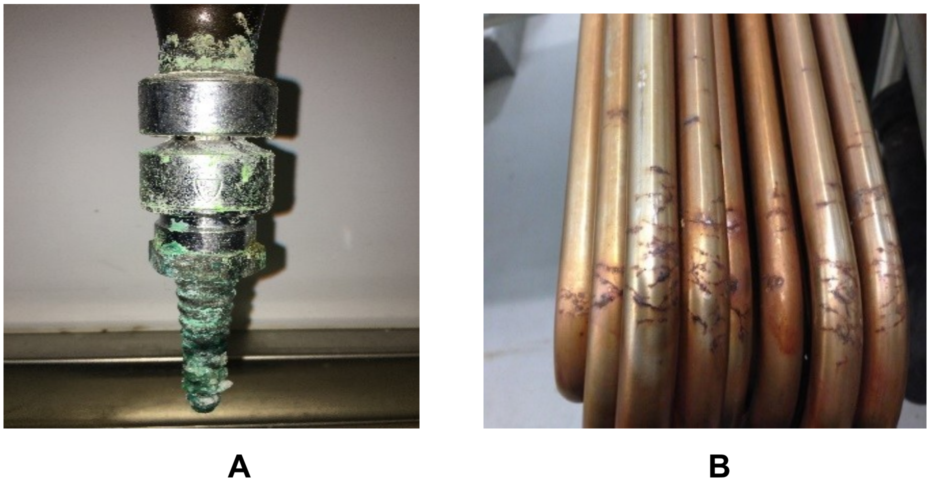


Figure 1. Photos of corroded tubes: (A) domestic water corrosion and (B) failed stain less steel heat exchangers. Photos courtesy of Guardian CSC, York, PA.

Copper oxide/hydroxide particles suspended in water, upon contact with the metallic surfaces may form deposits which grow over time causing operational problems. Since oxide particles, suspended in aqueous media bear electric charge because of the protonated/deprotonated surface –OH groups, depending on the solution pH, ionic strength and the presence of ionic species, the stability of the respective suspensions depends strongly on the interaction of the oxide particles with molecules with ionized surface groups. These interactions may lead either to surface charge neutralization which causes precipitation of the suspended particles or surface charge enhancement which makes repulsive forces predominant leading to the stabilization of the colloidal oxide particle suspensions. In the presence of macromolecules, both electrostatic and steric interactions of the macromolecules with the suspended particles should be taken into consideration [20, 21].

In industrial water systems, deterioration of metal equipment due to corrosion is controlled by using inhibitors, selected based upon the type of metallurgy. All types of metals under harsh or stressful conditions corrode and may be susceptible to microbiological attack, fouling, and scale formation. Because different metals corrode for different reasons, it is important to keep in mind the metallurgy of the matrix structures while developing a treatment program with inhibitors effective in controlling all potential corroding surfaces. Typical corrosion products include oxides and hydroxides of Al^{3+}, Cu^{2+}, Fe^{3+}, Zn^{2+}, *etc.* Commonly used corrosion inhibitors include polyphosphate, phosphonate, benzotriazole, tolyltriazole, molybdate, *etc.* Although, these inhibitors if properly applied may control corrosion, however, under certain conditions *e.g.*, system upsets, pumps failure, feed water quality variations, *etc.*, corrosion of metal equipment may lead to the formation and deposition of corrosion products on heat exchanger surfaces. In addition, the presence of corrosion products and metal ions generated during corrosion process may demand additional dosages of the treatment chemicals as documented in several investigations [22–24]. Thus, it is important to understand the potential impact of soluble and insoluble impurities on the performance of treatment programs.

In our earlier publication, we reported the performance of maleic acid-based polymers as scale inhibitors for calcium carbonate and calcium sulfate dihydrate and as dispersants for iron oxide particles [25]. Results show that maleic acid polymers containing non-ionic monomers such as vinyl pyrrolidone and vinyl acetate exhibit poor performance compared to polymers containing sulfonic acid groups. Amjad [26] recently studied the performance of maleic acid based polymers containing vinyl pyrrolidone as silica polymerization inhibitors. Data of this study suggest that these polymers exhibit good performance as silica inhibitors compared to homopolymers. Bouropoulos *et al.* [27] in their study on the evaluation of maleic acid polymers as calcium oxalate monohydrate crystal growth inhibitors showed that crystal growth rates depended on the nature of comonomer polymerized with maleic acid and the order of inhibition was found to be vinyl acetate > N-vinyl pyrrolidone > styrene. Thus, it is clear that performance of polymers as inhibitors and/or dispersants depends on the polymer architecture and the scaling system being studied. The present work was undertaken to gain understanding of the importance of ionic charge of the functional groups present in the maleic acid and acrylic acid polymers in stabilizing Cu(II) ions in aqueous system. Furthermore, various analytical techniques were employed to characterize the copper hydroxide particles formed in the absence and presence of polymers.

Experimental

Stock solutions of calcium chloride, magnesium chloride, sodium chloride, and sodium sulfate were prepared by dissolving known amounts of reagent grade chemicals in distilled water. Sodium bicarbonate solution was made fresh for copper stabilization experiments. Stock solutions (0.1% active solids) of polymers were prepared by dissolving known amount of polymers in distilled water. The pH of additive solutions was adjusted to 8.00 using sodium hydroxide.

A known amount of Cu^{2+} as $Cu(NO_3)_2$ was added to known volume of synthetic water containing varying amounts of additive stock solution in a 125 mL glass bottle. The synthetic water was prepared by mixing stock standard solutions of calcium chloride, magnesium chloride, sodium sulfate, sodium chloride, and sodium bicarbonate. The synthetic water composition was 100 mg/L Ca^{2+}, 30 mg/L Mg^{2+}, 314 mg/L Na^{+}, 192 mg/L SO_4^{2-}, 571 mg/L Cl^{-}, and 60 mg/L HCO_3^{-}. After the addition of Cu^{2+} solution to the synthetic water, the pH of the solution was adjusted to 8.00 with dilute sodium hydroxide. The experimental solutions were kept at 25°C without stirring. After 1 hr, the solutions were filtered through a 0.22 μm membrane filter, and the filtrate was analyzed for copper colorimetrically.

The performance of additive as Cu^{2+} ions stabilization agent was calculated using Equation 1:

$$S(\%) = ([Cu]_{sample} - [Cu]_{blank}) / ([Cu]_{initial} - [Cu]_{blank}) \times 100\% \qquad (1)$$

Where:

S	=	Stabilization, %
$[Cu]_{sample}$	=	Cu concentration in the presence of additive at 1 hr
$[Cu]_{blank}$	=	Cu concentration in the absence of additive at 1 hr
$[Cu]_{initial}$	=	Cu concentration in the beginning of experiment at 0 hr

Results and Discussion

In aqueous solution depending on the water chemistry, Cu^{2+} forms a variety of both soluble and insoluble complexes as illustrated in the following equilibria:

$$Cu^{2+} + H_2O \longleftrightarrow Cu(OH)^+ + H^+ \qquad (2)$$

$$Cu^{2+} + 2H_2O \longleftrightarrow Cu(OH)_2 + 2H^+ \qquad (3)$$

$$Cu^{2+} + 3H_2O \longleftrightarrow Cu(OH)_3^- + 3H^+ \qquad (4)$$

$$Cu(OH)_2(s) \longleftrightarrow Cu(OH)_2(aq) \qquad (5)$$

$$Cu^{2+} + \text{polymer} \longleftrightarrow \text{Cu-polymer complex(s)} \qquad (6)$$

Cu(II) ions present in re-circulating water whether originating from feed water and/or generated in the system due to corrosion process, undergo a variety of chemical reactions as illustrated in above equilibria (2–6) leading to the formation of both soluble and insoluble species. Some copper species may be present as large particles and/or finely dispersed colloidal particles. To differentiate between these species in an industrial water system may be difficult due to the impact of various factors including water chemistry, system operating conditions, type and amount of treatment chemicals, interactions of treatment chemicals with Cu(II) ions, biocides, *etc.* Moreover, it is worth noting that various physico-chemical processes including precipitation, complexation, dissolution, adsorption, desorption, agglomeration, dispersion, *etc.*, may be taking place concurrently. In our work, the term ‘stabilization’ refers to the ability of an additive to form soluble complexes and/or inhibit Cu(II) hydroxide precipitation. The analytical method used in the present work enabled measurements of total copper present in the filtrates of samples withdrawn from the solutions.

Using the experimental conditions outlined above, several experiments were carried out to evaluate the performance of polymers as Cu(II) stabilizing additives. The experiments were designed to test the efficacy of polymers as a function of polymer dosage and polymer architecture (*i.e.*, monomer type, molecular weight, ionic charge of the functional group). The effect of solution pH and reaction time on Cu(II) ions stabilization in the absence of polymer has been reported earlier [15]. Data presented in this study show good reproducibility (±7% or better). Table 1 lists the polymers tested in the present study. As illustrated, polymers vary significantly in terms of chemical composition, ionic charge of the functional group, and molecular weight.

Table 1. Polymers tested.

Polymer	Functional group	MW	Acronym
poly(maleic acid)	–COOH	<1k	PMA
poly(acrylic acid)	–COOH	3k	PAA
Poly(itaconic acid)	–COOH	<10k	PIA
poly(vinyl pyrrolidone)	$-\underset{\vert}{N}-\underset{\vert}{C}=O$	15k	PVP
Poly(maleic acid : sulfonated styrene)	–COOH $-SO_3H$	<20k	PMSS
Poly(maleic acid : vinyl pyrrolidone)	–COOH $-\underset{\vert}{N}-\underset{\vert}{C}=O$	15k	PMVP
Poly(maleic acid : vinyl pyrrolidone)	–COOH $-\underset{\vert}{N}-\underset{\vert}{C}=O$	60k	PMVP1
Poly(maleic acid : vinyl alcohol)	–COOH –OH	<10k	PMOH
Poly(maleic acid : itaconic acid)	–COOH	<10k	PMIA
Poly(maleic acid : vinyl pyrrolidone : vinyl acetate)	–COOH –COOR $-\underset{\vert}{N}-\underset{\vert}{C}=O$	N/A	PMVPA
Poly(acrylic acid : methacrylic acid : *t*-butyl acrylamide)	–COOH $-HNC(CH_3)_3$	<15k	PAMB
Poly(acrylic acid : carbitol acrylate)	–COOH –COOR	<15k	PACA
Poly(acrylic acid : 2-acrylamido-2-methylpropane sulfonic acid : sulfonated styrene	–COOH –SO3H	<15k	PASS

Polymer Performance

During the last two decades, a variety of natural, bio-, hybrid, and synthetic polymers, and non-polymeric materials such as phosphonates, have been developed and are currently used as components of water treatment formulations. The functions of these additives are threefold: (a) inhibit or mitigate scale formation, (b) prevent deterioration of equipment due to corrosion, and (c) stabilize metal ions and disperse suspended matter.

Homopolymers Performance

The impact of functional groups *i.e.*, anionic and non-ionic present in homopolymers on Cu(II) ions stabilization was studied. The polymers tested fall into two categories: (a) anionic carboxyl group containing polymers, *e.g.*, poly(acrylic acid), PAA; poly(maleic acid), PMA; and poly(itaconic acid), PIA, and (b) non-ionic group containing polymers, *e.g.*, poly(vinyl pyrrolidone). It is evident that polymers vary significantly in terms of functional groups and MW. Figure 2 presents stabilization data collected in the presence of 10 mg/L Cu^{2+}, pH 8.0, 25°C, and 15 mg/L of polymers. It may be seen that among the –COOH containing polymers, PMA exhibits poor performance. For example, %*S* value obtained in the presence of 15 mg/L for PMA is 22% compared to 68 and 82% obtained for PIA and PAA, respectively. As illustrated in Figure 2, PVP that is devoid of –COOH group is an ineffective Cu(II) stabilization agent. The higher effectiveness of PIA over PMA may be explained by the more favorable geometry of the carboxyl groups of the former. The data presented in Figure 4 clearly show that the ionic charge of the polymer plays an important role in stabilizing Cu(II) ions in solution. The observed difference in PAA and PMA performance may be attributed to difference in MW values, poor incompatibility with hardness ions, and/or poor adsorption of PMA on copper hydroxide precipitates.

The efficacy of additives such as lignosulfonate (LS) and 2-acrylamido-2-methyl propane sulfonic acid (PSA), as Cu(II) stabilization agents has been previously reported [15]. Results of this study show that $-SO_3H$ containing additives such as LS and PSA perform better than –COOH containing polymers such as PMA and CMI, suggesting that $-SO_3H$ group interacts and/or adsorbs strongly on Cu(II) oxide/hydroxide particles. It is worth noting that both PSA and LS have been shown to exhibit good dispersing activity for iron oxide particles [27].

Maleic Acid Based Co- and Terpolymers Performance

It is well documented that copolymers containing bulkier and hydrophobic groups such as ester, sulfonated styrene, and substituted acrylamide are not only effective inhibitors for calcium phosphate and calcium phosphonate, but they are also excellent dispersants for various particulate matter such as iron oxide and clay [29, 30]. To study the influence of copolymers in which maleic acid monomer has been partly replaced with monomer containing –SO_3H group (*e.g.*, sulfonated styrene), several experiments were conducted as a function of polymer dosage. Results on these experiments are illustrated in Figure 3. There are two points worth noting: (a) % stabilization value increases with increasing polymer dosage and (b) incorporation of sulfonated monomer exhibits marked improvement on the performance of PMSS copolymer. For example, % stabilization value obtained in the presence of 10 mg/L of PMA is 18% compared to 82% obtained for PMSS. It should be mentioned that sulfonate groups have a significantly lower pK in comparison with the respective value of the carboxyl groups.

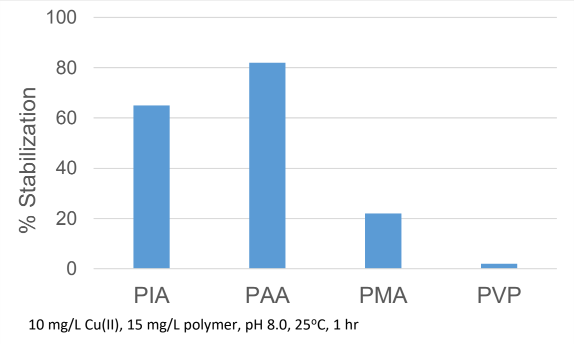


Figure 2. Cu(II) ions stabilization data on homopolymers containing different functional groups.

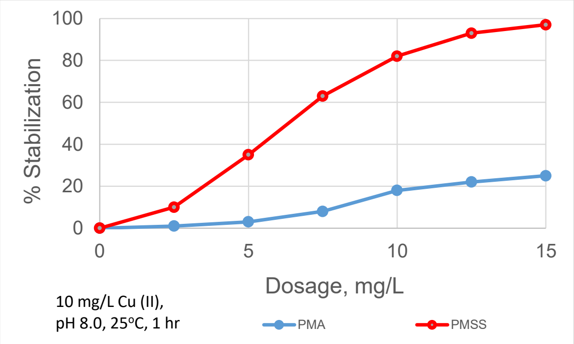


Figure 3. Plots of % stabilization vs. dosage for homo- and co-polymer of maleic acid.

Figure 4 presents data on several maleic acid containing co- and terpolymers. It may be seen that incorporation of monomers containing either acidic group or neutral group improves the performance of co- and ter-polymers to a varying degree. It is evident that incorporation of third monomer shows improvement of terpolymer over PMA. For example, % stabilization values obtained in the presence of 15 mg/L PMA is 18% compared to 38% obtained for the terpolymer of PMVPA.

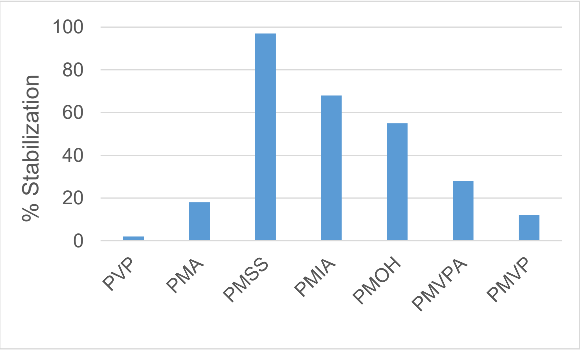


Figure 4. Performance data on maleic acid homo- and copolymers containing different functional groups.

Acrylic Acid Based Co- and Terpolymers Performance

The performance of acrylic acid based homo-, co-, and terpolymers as antiscalants, dispersants, and metal ions stabilization agents has attracted the attention of several academic researchers and industrial technologists [31–34]. Results of these studies reveal that whereas PAA are effective scale inhibitors for various scaling systems such as CaF_2, $CaCO_3$, $CaSO_4$, $BaSO_4$, *etc.*, but show poor to mediocre activity for calcium phosphate and calcium phosphonates scales, and as dispersants for particulate matter. On the other hand, acrylic acid based copolymers containing comonomers with different functional groups are not only calcium phosphate inhibitors but are also effective metal ions stabilization agents [29].

To explore the role of various functional groups with varying ionic charge present in comonomers, several Cu(II) stabilization experiments were carried out under similar experimental conditions. Results are presented in Figure 5. It can be seen that whereas PAA show poor performance as Cu(II) stabilization agent, incorporation of monomers with acidic and/or hydrophobic bulkier groups such as methacrylic acid, 2-acrylamido-2-methylpropane sulfonic acid, carbitol acrylate, and sulfonated styrene, results in significant improvement in the performance of new co- and terpolymers. For example, % stabilization value obtained in the presence of 10 mg/L of PAA is 23% compared to 66, 58, and 85% values obtained for PAMB, PACA, and PASS. It is worth noting that similar improved performance (97% stabilization value) was observed for a terpolymer of AA : SA : sulfonated styrene (SS) [15]. These observations clearly highlight the importance of both the ionic charge and the size of the comonomers in imparting power to co-and terpolymers in stabilizing Cu(II) ions in aqueous solutions. The size of comonomers is expected to affect drastically the conformation of polymers in solutions.

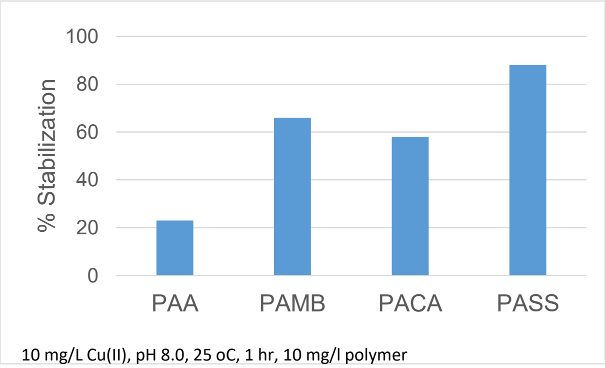


Figure 5. Plots of % stabilization for acrylic acid-based homo- and copolymers.

Characterization of $Cu(OH)_2$ Particles

In the absence and in the presence of polymers, nanocrystalline $Cu(OH)_2$ containing $Cu(OH)_2{\cdot}H_2O$ was identified in all solids. The size of the crystallites was in the nano range. The XRD profile of the precipitates is presented in Figure 6. The absence of most of the reflections of the respective crystalline material is due mainly to the fact that the precipitates were not sufficiently aged and consequently they contain amorphous phase to some extent. Moreover, the small particle size contributes to the amorphous-like appearance of the XRD profile.

The particle size distribution (PSD) of the precipitates in the absence of additives is presented in Figure 7 and was obtained from image analysis [35] (ImageJ software). More than 300 crystallites were counted for each PSD curve. As may be seen, the mean particle size was between 20–30 nm.

The morphology of the crystallites formed in the presence and absence of additive is shown in the SEM micrographs presented in Figure 8. It can be seen that in the presence of PAA (Figure 8B), although the morphology did not change compared to control (no additive, Figure 8A), strong agglomeration was observed resulting in larger size aggregates. This finding is in agreement with the poor stabilizing effect of PAA (Figure 5).

The impact of terpolymer (PASS) on the morphology of copper hydroxide crystals was also investigated. The SEM micrographs are presented in Figure 8. It can be seen that in the presence of 10 mg/L of PASS in the solution in which $Cu(OH)_2$ precipitated, seemed to cause even stronger aggregation, as shown in Figure 8A, which may be attributed to the relatively higher adsorption of this polymer on the copper hydroxide crystals.

The extent of crystal coalescence was higher for the presence of terpolymers of PASS which resulted in the formation of large (> 100 nm) flat agglomerates, as shown in the SEM pictures of Figure 9 compared to control (no polymer, Figure 8A).

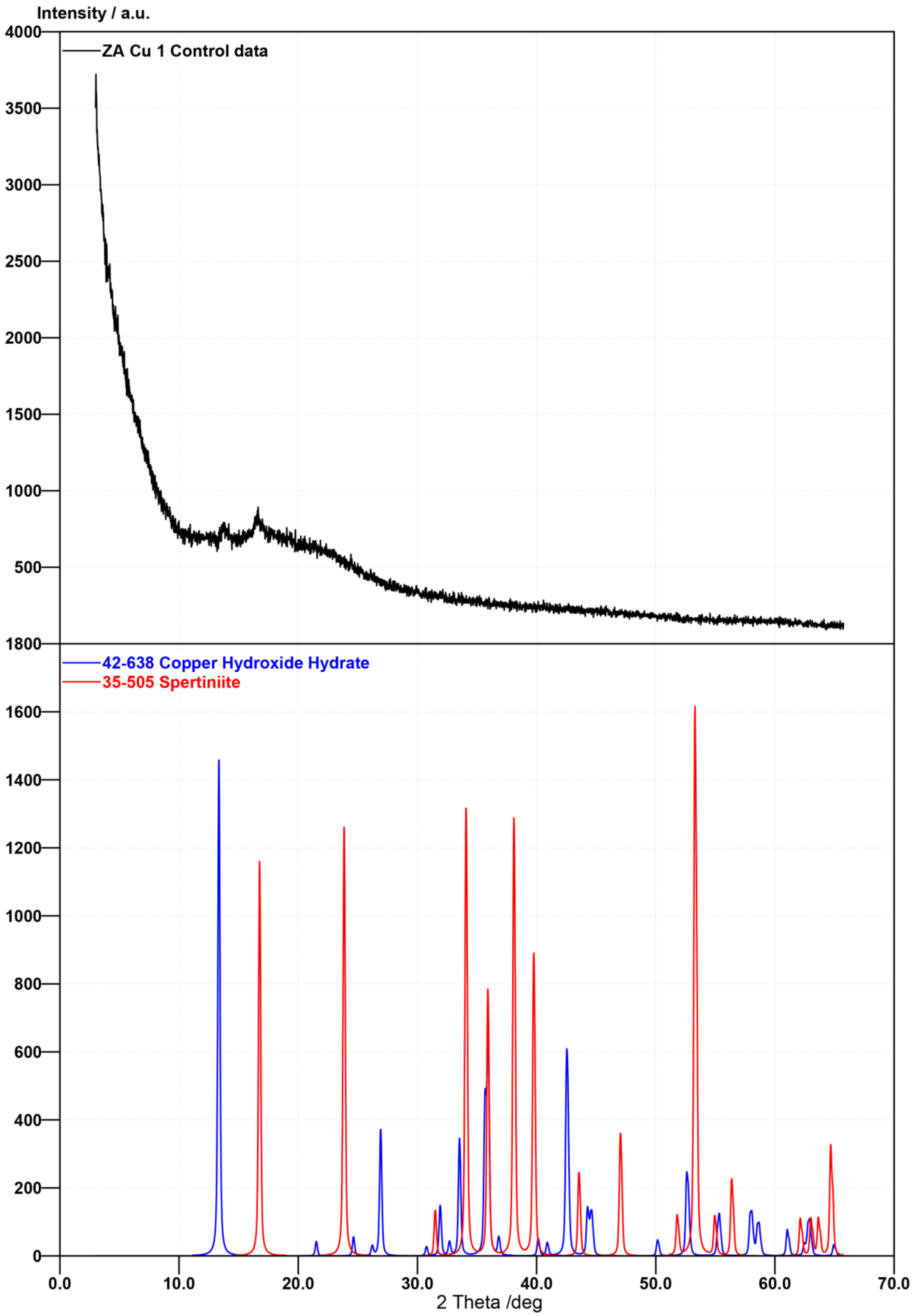


Figure 6. XRD profile of $Cu(OH)_2$–$Cu(OH)_2 \cdot H_2O$ precipitate in the absence of polymer.

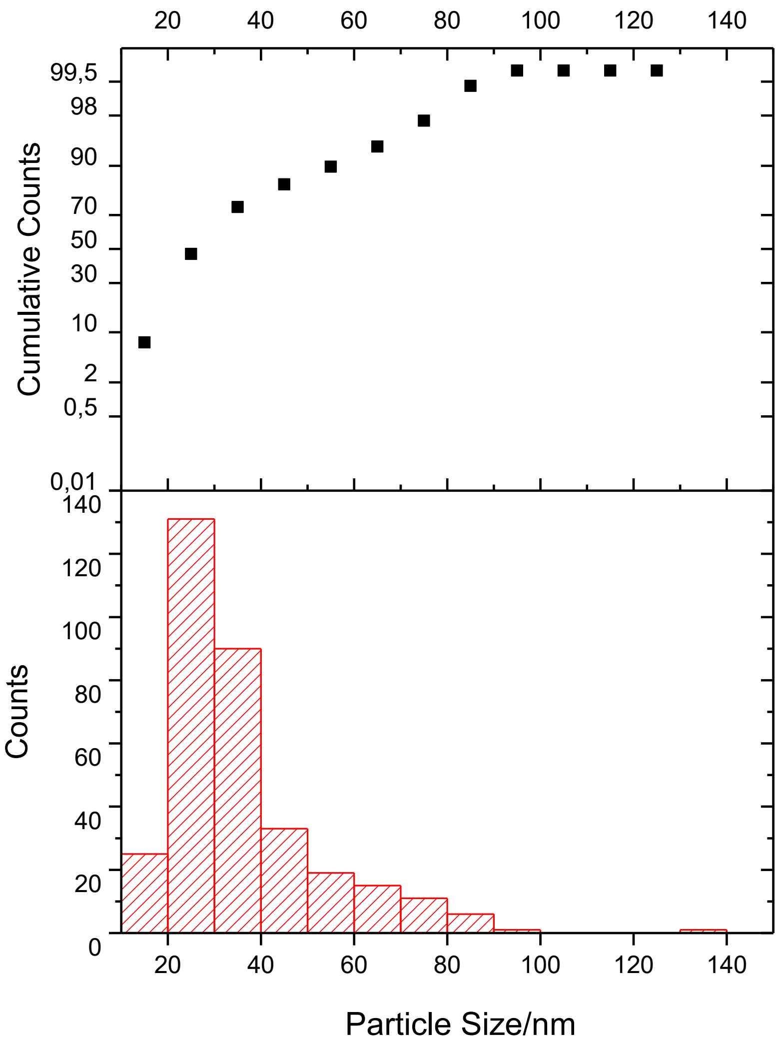
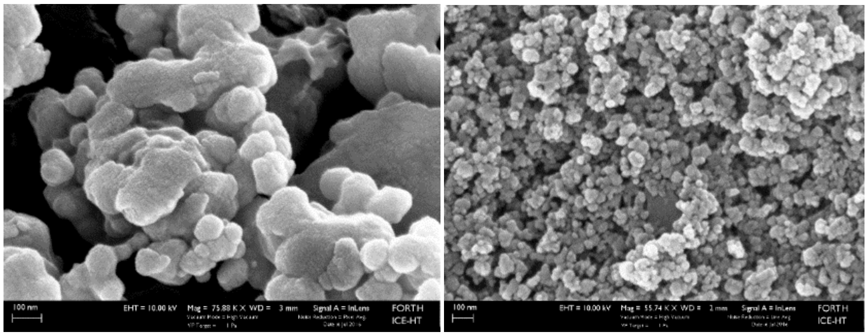


Figure 7. Particle size distribution of $Cu(OH)_2$ precipitated from aqueous solutions, in the absence of polymer at room temperature.



A B

Figure 8. SEM micrographs of $Cu(OH)_2$ precipitated spontaneously from aqueous solutions in the absence (A) and in the presence of 10 mg/L PAA (B) at room temperature.

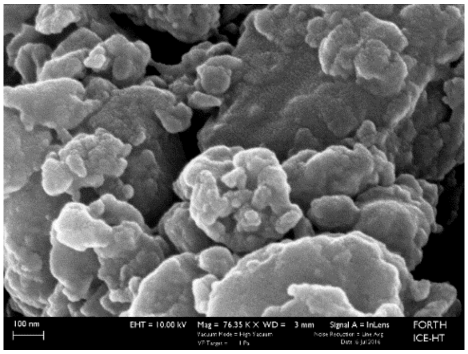


Figure 9. SEM micrographs of $Cu(OH)_2$ precipitated spontaneously in the presence of 10 mg/L PASS.

It should be noted however that the fact that most of the polymers tested, like PASS, have been shown to be dispersants of suspended particles is not necessarily contradictory with the larger mean particle size measured from SEM pictures. SEM pictures are taken under ultra-high vacuum conditions, and specimens have been previously dried under high vacuum. In solution, it is possible that loose agglomerates form, in which polymer chains act as bridges between the primary particles entrapping water molecules. Especially in the case of copper oxide particles in which copper oxide is hydrated ($CuO{\cdot}H_2O$) [36]. The loose agglomerates may have sufficiently low density so that they are dispersed. It is thus not surprising that hydrodynamic diameters of copper oxide particles suspended in water has been reported to be in the order of 300–400 nm [23]. In this case, there is a sort of steric enhancement of particle's dispersion [38]. The drying process for SEM observation however may cause particle fusion, leading to larger size estimates of particles. The larger particle size may be representative of the processes taking place in the presence of the polymers but they cannot only on the basis of size arguments explain the dispersing ability of the polymers.

Summary

Minimizing the precipitation of copper (II) hydroxides in aqueous systems is strongly dependent on polymer dosage and polymer architecture. Mono functional polymers containing –COOH group show poor to mediocre performance as Cu(II) stabilizing agents. Homopolymer containing non-ionic functional group is an ineffective Cu(II) stabilizing agent. Incorporation of monomers containing hydrophobic, bulkier, and strong acidic groups improves the performance of co- and terpolymers. Thus, to control Cu(II) ions fouling in industrial water systems the incorporation of an effective polymer (*i.e.*, PASB) in the treatment program can ensure better overall system performance.

Acknowledgement

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