

Green Polymeric Additives for Calcium Oxalate Control in Industrial Water and Process Applications

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Scale deposits, metallic corrosion, and microbiological growth are the three major issues in industrial water systems. This article covers control using environmentally benign and non-hazardous chemical inhibitors (“green” additives).

Tenacious deposits on critical equipment surfaces create major operational problems.¹ They severely impede heat transfer and can lead to catastrophic operational failures, unexpected shut-downs, and costly equipment cleanings. Industrial water technologists and operators often face the problems of preventing deposits from forming or removing deposits after their formation. Cost considerations usually drive the decision, although other factors are taken into account (e.g., potential hazards of cleaning chemicals).²

Mineral scale control is achieved either by water softening or by scale inhibitors that are introduced into the system.³ Increasing environmental concerns and discharge limitations have imposed additional challenges in treating process waters. Therefore, the discovery and successful application of chemical additives for the control of scale and corrosion that have mild environmental impact have gradually become the focus of several research efforts.⁴⁻⁶ This article focuses on a family of “green” polymeric inhibitors, carboxymethyl inulins (CMIs), for inhibition of calcium oxalate (CaOX). This research is part of our ongoing investigation into the discovery and application of green scale inhibitors.⁷⁻¹⁰

Polymeric ‘Green’ Mineral Scale Inhibitors

The technical field of green additives is constantly growing. CMI (Figure 1) is produced from a chemical reaction with a biopolymer, inulin, and selected reagents.¹¹

The biopolymer inulin¹² is extracted from the roots of the chicory plant. Inulin is a polydisperse polysaccharide consisting mainly of $\beta(2\rightarrow1)$ fructosyl fructose units with normally one glucopyranose unit at the reducing end. The fructose molecules are all present in the furanose form. Inulin is used as dietary

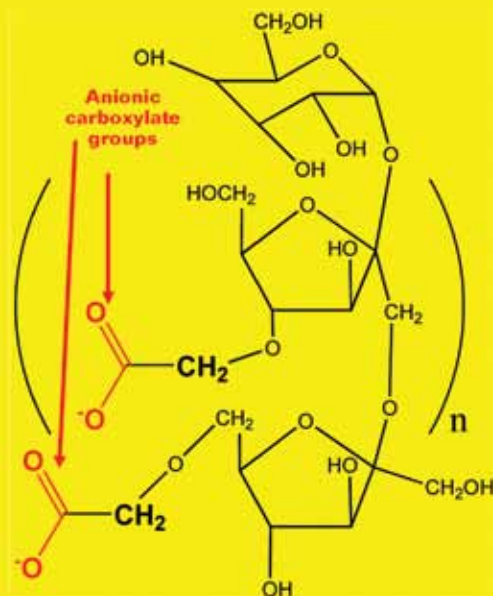
fiber, a fat substitute, and a sweetener (fructose syrups). CMI can be envisioned as a modified inulin polymer, and has been investigated in a series of acute toxicity (oral rat, >2,000 mg/kg body weight [BW]), subacute toxicity (28 days, rat 1,000 mg/kg BW), mutagenicity (Ames test, *in vitro* cytogenetics, no effect), and dermal sensitization studies (guinea pigs, no effect) to evaluate its toxicological profile.¹³ All studies followed accepted testing guidelines. No significant toxicology was evident. Tests showed that the toxicological profile of CMI is consistent with other polycarboxylates used in foods. CMI is also biodegradable. Data that support these conclusions include toxicity (ppm) $EC_{10} > 10,000$, bacteria (ppm) $EC_0 = 2,000$, *Daphnia* (ppm) $EC_{50(24\text{ h})} = 5,500$, and fish (ppm) $LC_0 > 10,000$. These results should be contrasted with those obtained for a polyacrylate polymer (MW ~ 1,500) commonly used as precipitation inhibitor:¹⁴ toxicity (ppm) $EC_{10} = 180$, bacteria (ppm) $EC_0 = 200$, *Daphnia* (ppm) $EC_{50(24\text{ h})} = 240$, and fish (ppm) $LC_0 = 200$.

Experimental Protocols

All chemicals are obtained from commercial sources. CMI-AB, available as Dequest[†] PB116AB or Dequest[†] PB136AB, came from Dequest AG¹⁵ where AB = 15 for CMI-15, AB = 20 for CMI-20, and AB = 25 for CMI-25. The AB number also indicates the degree of substitution (DS). DS is defined as the average number of carboxylate moieties per fructose unit. For CMI-15, DS = 1.5; for CMI-20, DS = 2.0; and for CMI-25, DS = 2.5. All additive dosages are reported "as actives." All other chemicals for the preparation of stock solutions were obtained from common commercial sources.

[†]Trade name.

FIGURE 1



The building blocks in the CMI polymer backbone.

Laboratory Crystal Growth Experiments

Stable supersaturated solutions for growth experiments were prepared by slow mixing of calcium chloride (CaCl₂) and sodium oxalate (Na₂C₂O₄) stock solutions. In experiments where additives were used, a similar procedure was followed with the appropriate CMI dosage, as indicated in the results. Final pH was 6.5, and temperature was kept at 37 ± 0.1 °C. In the experiments [Ca²⁺] = [C₂O₄²⁻] = 7.0 × 10⁻⁴ M. The inhibitory effect of polymers on the rate of precipitation of CaOX was determined by recording the decrease, as a function of time, in calcium concentration by atomic absorption spectroscopy. The CaOX crystals were studied by scanning electron microscopy (SEM), x-ray powder diffraction (XPD), and Fourier transform infrared (FTIR). The effect of an additive can be quantified as the ratio of the rate of crystallization of the pure solution (R₀, mg/L·min) to the rate of crystallization in the presence of additive (R_p, mg/L·min) at the same concentration and temperature. The induction period (t_{ind}) was deter-

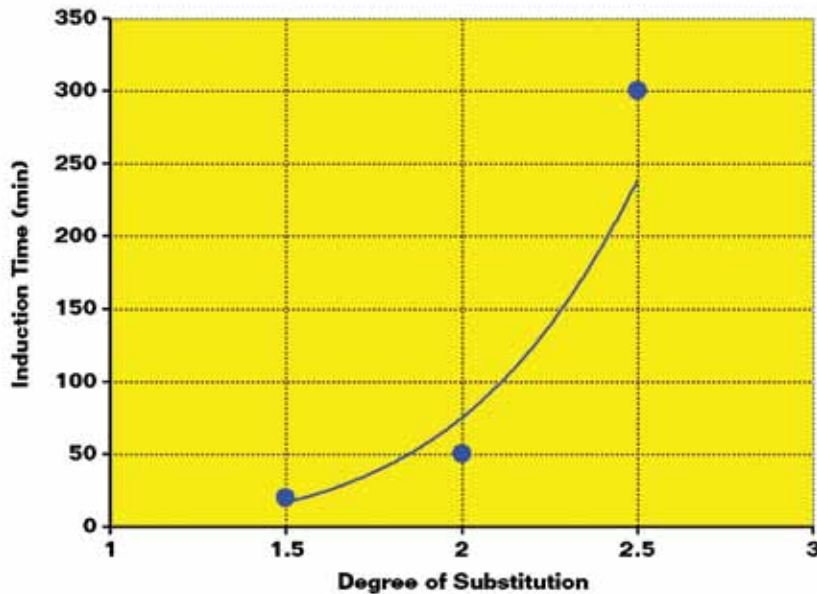
mined by monitoring the variations in the calcium concentrations accompanied by atomic absorption measurements. The time between the generation of a supersaturated state and the first observed change in calcium concentration was defined as the induction period.

Case Study on Beerstone Deposits

In the brewing process, calcium precipitates oxalate, present in malt as insoluble CaOX. During fermentation, CaOX can contribute to beerstone formation on vessel surfaces. Beerstone is composed of calcium and magnesium salts and various organic compounds from the brewing process; it promotes the growth of microorganisms that can adversely affect or ruin the flavor of the beer. CaOX forms as a component of beerstone.

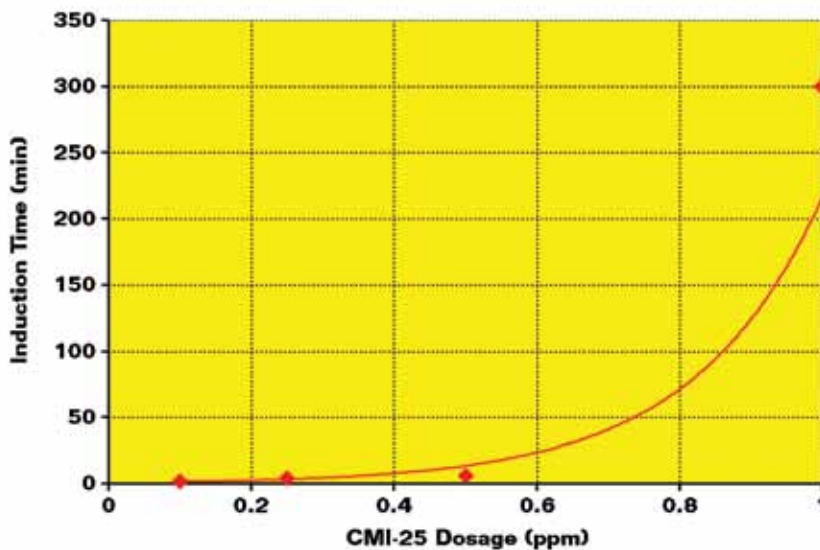
Ten fermentation cycles were carried out with and without (control) the addition of CMI. Stainless steel (SS) coupons were immersed in fermentors at 18 °C for five days to monitor CaOX scaling over repeated fermentation cycles. Testing was

FIGURE 2



The effect of carboxymethylation degree on the CMI backbone on induction time, at 1.0 ppm dosage. The line has been included to aid the reader.

FIGURE 3



Dependence of induction times on CMI-25 dosage. The line has been included to aid the reader.

done using industrial wort (14° Plato), with 100 ppm of oxalic acid ($H_2C_2O_4$) added to simulate worst-case scenarios. The ale yeast strain, *Saccharomyces cerevisiae* T58, has been pitched at 10^7 cells/mL. Two CMI inhibitors were added at 30 ppm level to evaluate their impact on

CaOX scale formation during the 10 successive fermentation cycles. A bare SS coupon was also incorporated as a reference. Surface deposits were investigated after suitable preparation using optical microscopy, FTIR, and SEM/energy dispersive x-ray (EDX).

Results and Discussion

Inhibitory Effects of CMI on CaOX in Laboratory Experiments

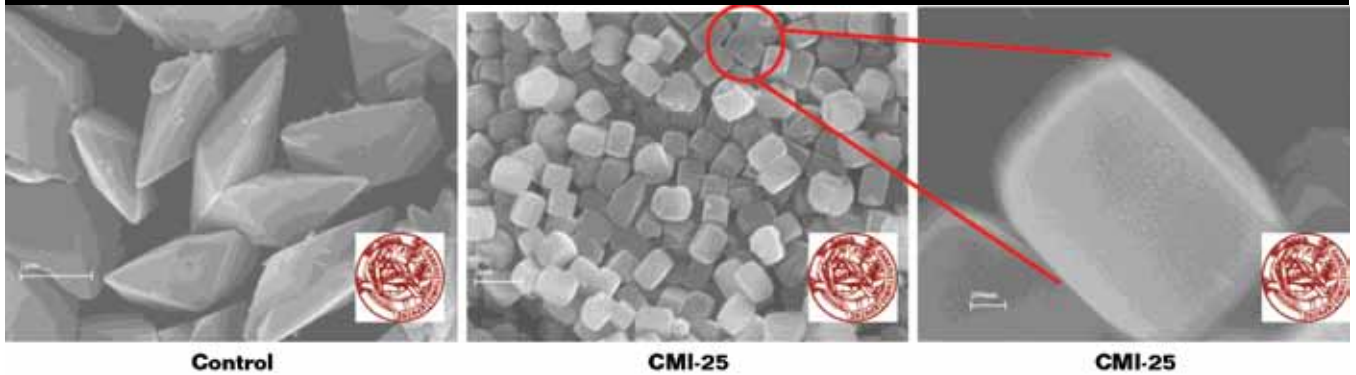
Figure 2 shows the effect of carboxymethylation degree of the polymer on CaOX inhibition in laboratory experiments. The effectiveness of biopolymers increases with increasing carboxyl content on the polymer backbone. Induction time increases from 20 to 300 min as the carboxyl content increases from 1.5 to 2.5.

It was observed that anionic polymeric additives with a higher degree of carboxyl group prolong the induction period for crystallization because of the ability of the anionic carboxylate groups to adsorb on the CaOX crystal surfaces. Several investigations have indicated that polymers that exhibit an inhibitory effect on crystallization kinetics of sparingly soluble salts are highly substituted with carboxyl groups.¹⁶ Apparently, the larger number of carboxylate functional groups increases the ionic cooperative attractive interactions between the adsorbate ($-COO^-$) and the positive sites (Ca^{2+}) at the solid/water interface.

A dosage-dependence study of CMI-25 revealed that at low dosages (0.1 to 0.5 ppm), induction times are short, but a dosage of 1 ppm prolongs precipitation beyond 300 min (Figure 3). Further dosage increase completely ceases precipitation of CaOX.

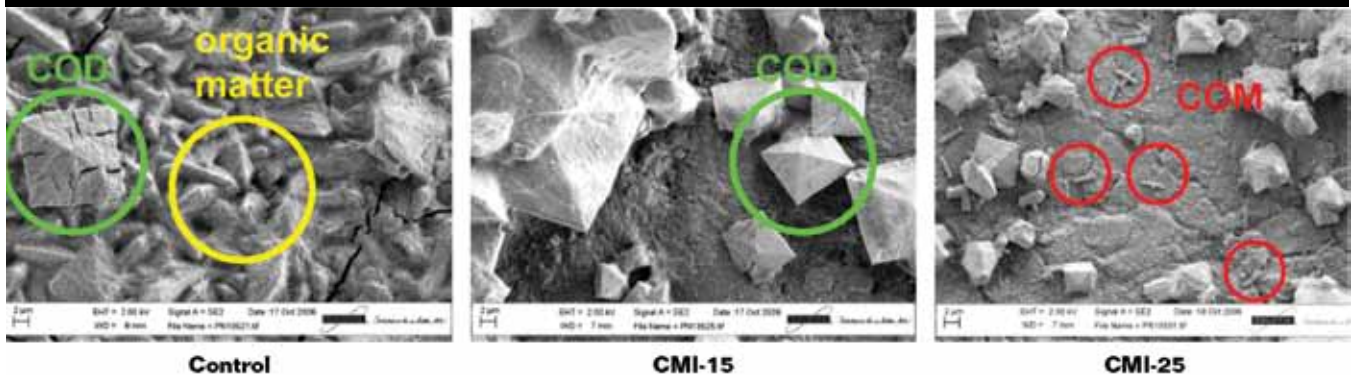
The addition of CMI polymers in CaOX supersaturated solutions affects not only crystal growth kinetics but also crystal morphology and phase transformation of CaOX crystals. In all control experiments (no additives), CaOX monohydrate (COM) was the dominant phase in all concentrations (Figure 4, left). The addition of 1.0 ppm CMI-25 causes a distinct morphological and phase change to CaOX crystals (Figure 4, center and

FIGURE 4



The effect on morphology of CMI-25 (1 ppm) on CaOX crystals.

FIGURE 5



The effect of morphology of CMI-15 (30 ppm) and CMI-25 (30 ppm) on CaOX and organic matter deposits.

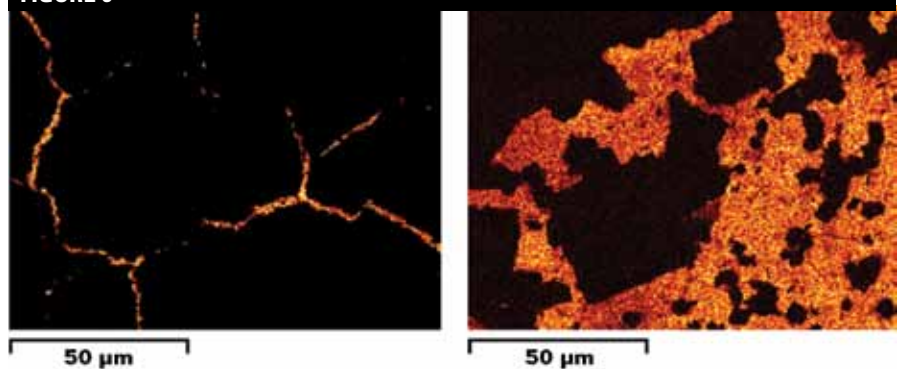
right). The prismatic COM crystals transform to tetragonal prisms of CaOX dihydrate (COD). These phase alterations were also confirmed by other methods, such as FTIR spectroscopy and XPD (data not shown).

Inhibitory Effects of CMI on CaOX in the Case Study

COD formation is evident on the control (Figure 5, left image). The crystal size appears to be $\sim 10 \mu\text{m}$. With CMI-15 (30 ppm), the organic matter layer seems to have disappeared (Figure 5, central image). With CMI-25 (30 ppm) inhibition, COD is evident, as is some COM (Figure 5, right image). Elemental mapping indicates that CMI-25 (30 ppm) treatment also inhibits organic matter deposit formation.

The fact that CMI polymers inhibit both the formation of inorganic and organic deposits is important, because often

FIGURE 6



Metal surface coverage by composite deposits: control (left) and in the presence of CMI-25 (right). The dark areas indicate surface coverage by deposits and the orange-colored areas indicate bare metal (Fe).

composite fouling presents additional challenges and problems in water systems, and it is very difficult to control. Elemental mapping (Figure 6) proves that metal surface coverage by deposits is strongly affected by the presence of CMI-25.

Additional Features of CMI Biopolymers

Some of the criteria that pose limitations for scale inhibitors are stability toward oxidizing biocides, tolerance toward hardness ions, stability (in general), and

others. The susceptibility of certain water treatment chemicals to precipitation with calcium ions yielding insoluble precipitates is a well-recognized problem. Such calcium-inhibitor precipitates can be detrimental to an otherwise well-designed water treatment program because (a) they cause depletion of soluble inhibitor, and, subsequently, poor scale control because there is little or no inhibitor available in solution to inhibit scale formation; (b) they can act as potential nucleation sites for other scales; (c) they can deposit onto heat transfer equipment and cause poor heat flux, much like calcium carbonate (CaCO_3), calcium phosphate, etc.; and (d) their precipitation as a Ca salt will eventually lead to poor corrosion control if the inhibitor in the treatment program is for corrosion inhibition. CMI-25 was studied and found to be extremely calcium-tolerant, essentially 100% tolerant to a high calcium brine. Additionally, CMI polymers effectively bind Ca^{2+} ions.

Conclusions

The following conclusions can be drawn from this study:

- CMI polymers are effective CaOX inhibitors,¹⁷⁻¹⁸ with CMI-25 being the most effective. Its inhibition performance is comparable to that of low molecular weight polyacrylate.
- The inhibition performance of CMI polymers strongly depends on and is proportional to the carboxylation degree.
- CMI polymers inhibit the growth of both CaOX (beerstone) and organic matter in fermentation environments.
- CMI polymers collectively present a number of additional attributes that make them excellent candidates as additives in high hardness fluids,

and they are capable of inhibiting a variety of scale deposits (CaCO_3 , calcium sulfate [CaSO_4], and barium sulfate [BaSO_4]).¹⁹⁻²⁰

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