

Multifunctional, Environmentally Friendly Additives for Control of Inorganic Foulants in Industrial Water and Process Applications

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Springly soluble mineral deposits formed by cation-anion association of calcium, barium, or strontium with carbonates, sulfates, or phosphates and silica/metal silicates often plague poorly treated, supersaturated process water systems. This article discusses control approaches using environmentally benign and nonhazardous chemical compounds, also known as "green additives." These findings are applicable to cooling and boiler water, pulp and paper processes, detergents, and oil and gas facilities.

Industrial operations that use water are often plagued by problems that originate from a variety of organic or inorganic deposits.¹ Inorganic deposits, often known as mineral scale deposits, can become major operational hurdles for poorly treated process waters. These deposits are troublesome because they severely impede efficient heat transfer and can lead to catastrophic operational failures and unexpected shut-downs. Industrial water users and operators are often faced with a challenging dilemma: to take measures to prevent deposits from forming or to clean up deposits after their formation. Cost considerations are often the decision criterion, although other factors such as potential hazards of cleaning chemicals are taken into account as well.²

Scale prevention is achieved either by water softening or by use of scale inhibitors that are added in threshold amounts (ppm).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 the use of "green" inhibitors for inhibition of various troublesome scales such as calcium carbonate (CaCO_3), calcium sulfate (CaSO_4), barium sulfate (BaSO_4), and colloidal silica. This research is part of an ongoing investigation on the discovery and application of "green" scale inhibitors in industrial process waters.⁷

Experimental Protocols

All chemicals were obtained from commercial sources. They include carboxymethylcellulose (CMI), polyethyleneimine (PEI), and diethylenetriaminepenta(methylenephosphonic acid) (DTPMP). Detailed procedures for instruments used, reagents, solution preparation, silica inhibition and silica dissolution protocols, and soluble silica measurements are reported elsewhere.⁸

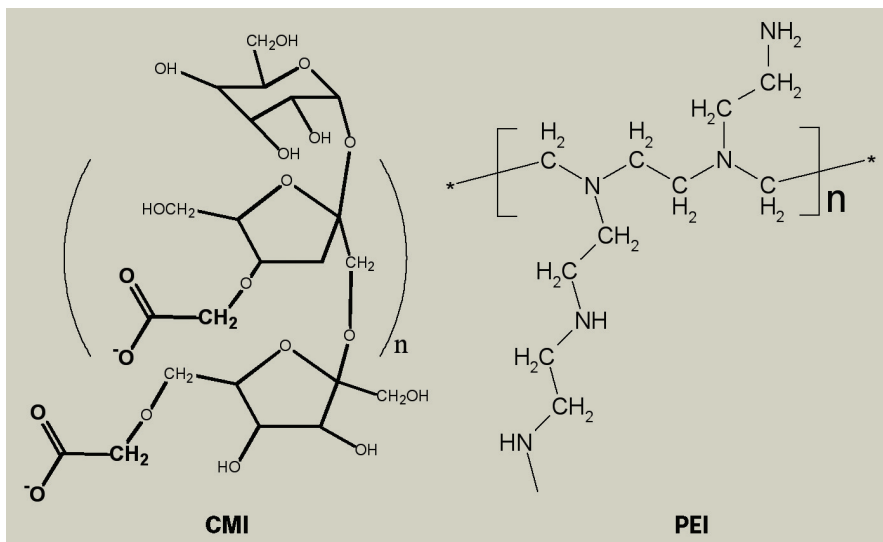
'Green' Scale Inhibitors: General Scope

Herein are results on the inhibition performance of selected environmentally friendly antiscalants. CMI (Figure 1) is produced from a chemical reaction with a biopolymer, inulin, and selected reagents. CMI has been investigated in a series of subacute toxicity, genotoxicity, and sensitization studies to evaluate its toxicological profile. All studies followed accepted testing guidelines as recommended by international regulatory agencies (the Organization for Economic Co-Operation and Development, the European Economic Community, and the U.S. Environmental Protection Agency). No significant toxicological findings were evident. Results of the toxicity studies with CMI, all conforming to internationally accepted testing standards, show that CMI has a far better toxicological profile than traditional scale inhibitors and complexing agents used in industrial applications. Its toxicological profile is consistent with additives used in food applications.⁹ PEI (Figure 1) in general is considered a nontoxic and biodegradable additive, and as such it has found several applications in the medicinal/biochemical field.¹⁰

Amorphous Silica Scale Inhibition by Polyelectrolyte Blends

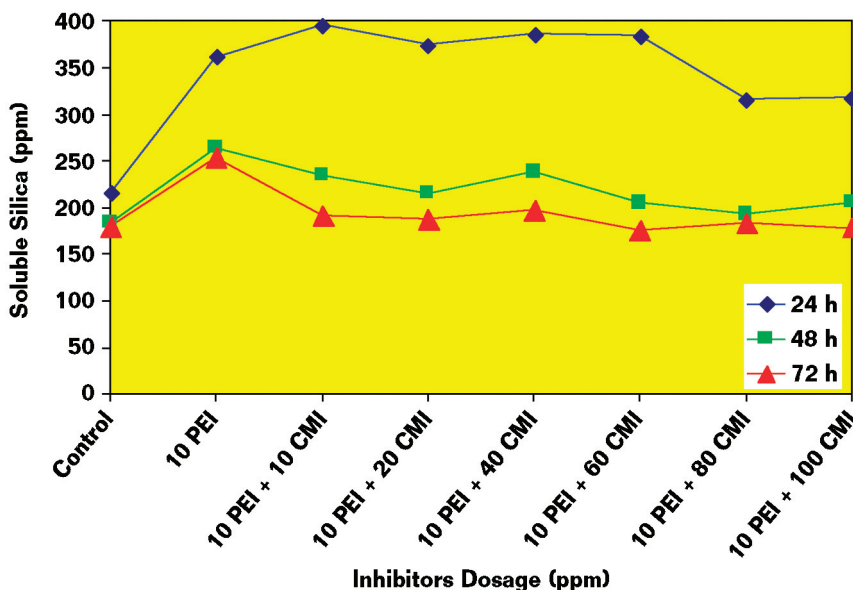
Combinations of PEI and CMI-25 mitigate silica inhibition (Figure 2). (CMI-XX is available as Dequest-PB116XX, where the numbers XX = 10, 15, 20, and 25 correspond to the degree of carboxylation per monosaccharide unit.) The PEI starting dosage was 10 ppm, as that dosage showed the most effective inhibitory activity. CMI-25 was tested at 10, 20, 40, 60, 80, and 100-ppm dosages. It appears that CMI-25 dosages of 10 to 60 ppm enhance the inhibitory activity of PEI, maintaining ~400 ppm silica soluble. Higher CMI-25 dosages cause a gradual drop in soluble silica to ~310 ppm, most likely due to excessive anionic charge.

FIGURE 1



Schematic structures of CMI and PEI.

FIGURE 2



Silica inhibition performance of PEI and CMI-25 blends.

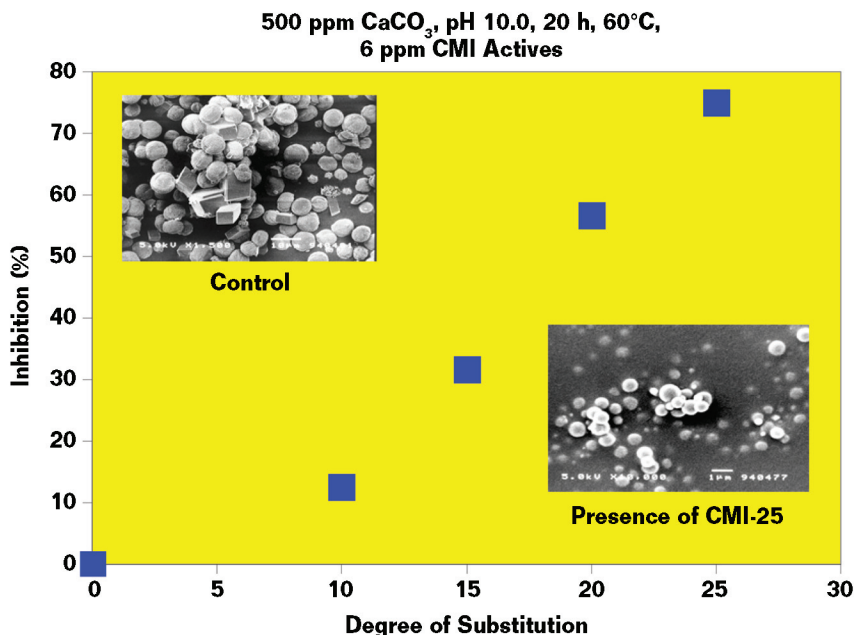
Control of Crystalline Mineral Scales: CaCO₃, CaSO₄, and BaSO₄

CALCIUM CARBONATE

CaCO₃ is one of the most abundant and frequently encountered deposits in process waters. Its formation has been noted in cooling systems, heat exchangers,

steam turbines, oilfield brines, and membrane installations. Its control can be achieved by addition of chemical additives, most commonly phosphonates in combination with dispersant polymers. CaCO₃ is strongly inhibited in the presence of CMI of varying degrees of substitution (denoting the extent of carboxymethylation). In Figure 3, the effect of

FIGURE 3



Effect of the degree of substitution of CMI-XX (XX = 10, 15, 20, and 25) on the crystallization of CaCO₃. Contrast the CaCO₃ particle size grown without additives (upper left, ~10 μm) to that grown in the presence of CMI (lower right, ~1 μm).

when the degree of substitution is maximum, indicating that the presence of the carboxylate groups is needed for effective inhibition.

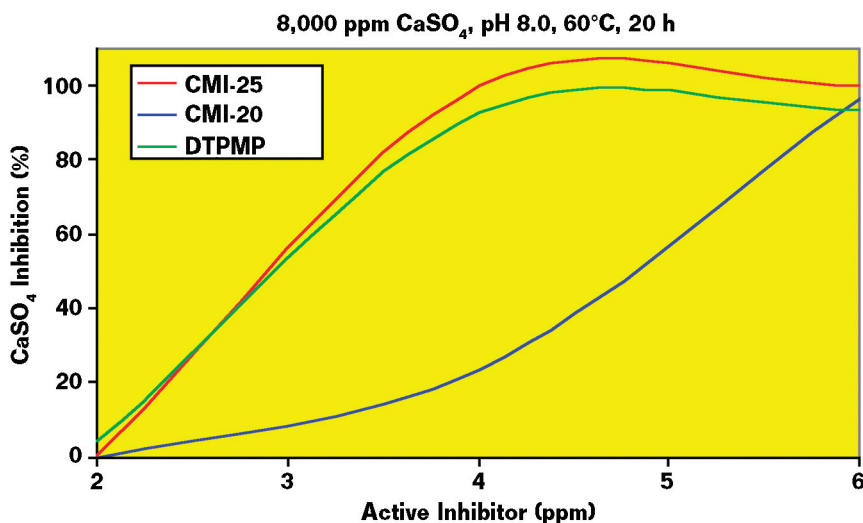
CALCIUM SULFATE

This is another troublesome deposit. It has been observed in high-sulfate oilfield brines and in cooling towers. CMI-25 shows excellent inhibitory performance (Figure 4). Its differentiation from DTPMP is evident only at higher inhibitor dosages, >3 ppm. Again, as shown previously with CaCO₃, the degree of substitution plays a significant role in inhibitory activity. CMI-20 is capable of inhibiting only ~50% of scale at a 4-ppm dosage. This can be compared with an almost 100% inhibitory activity of CMI-25 at a 4-ppm dosage. When the inhibitor dosage reaches 6 ppm, full-scale inhibition is achieved for all three inhibitors.

BARIUM AND STRONTIUM SULFATES

BaSO₄ and strontium sulfate (SrSO₄) are well recognized scale deposits that are particularly prevalent in oil production. There are several reports from the field about the necessity for operational shut-downs so the scaled well can be cleaned up. This leads to lost revenue and additional cleaning costs. BaSO₄ has a low-solubility product ($K_{sp} \sim 10^{-10}$), but its solubility increases in the presence of inhibiting additives (polyphosphonates are widely recognized for this). A substantial body of literature exists on BaSO₄ and SrSO₄ as significant industrial scale problems. Thus, they appear to be suitable choices as “model” sparingly soluble salts to investigate the effect of CMI-25 and other inhibitors on their formation. Results presented in Figure 5 show that CMI-25 is a good inhibitor in an equal dosage compared to DTPMP. Maximum inhibitory efficiency is achieved at 100-ppm dosage of CMI-25, reaching >90%. DTPMP at the same dosage reaches only 50% inhibition. This may be occurring due to loss of DTPMP as a Ba-DTPMP insoluble complex that depletes the brine of active inhibitor.

FIGURE 4



Control of CaSO₄ scale in the presence of CMI-20 and CMI-25 and, for comparison, DTPMP (Dequest 2066).

substitution on CaCO₃ scale inhibition is profound. In addition, deposit particle morphology and size is also dramatically affected. Untreated water supersaturated in CaCO₃ leads to precipitation of a mix-

ture of calcite (CaCO₃) and vaterite, whereas the same water when treated with CMI yields exclusively very small particles of vaterite. It is evident that inhibitory activity reaches optimum performance

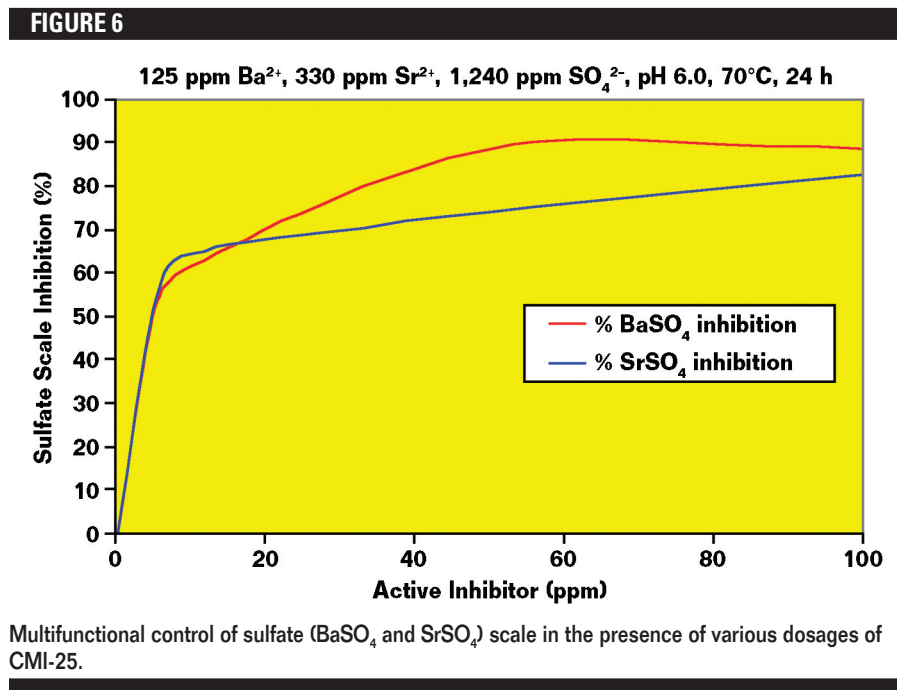
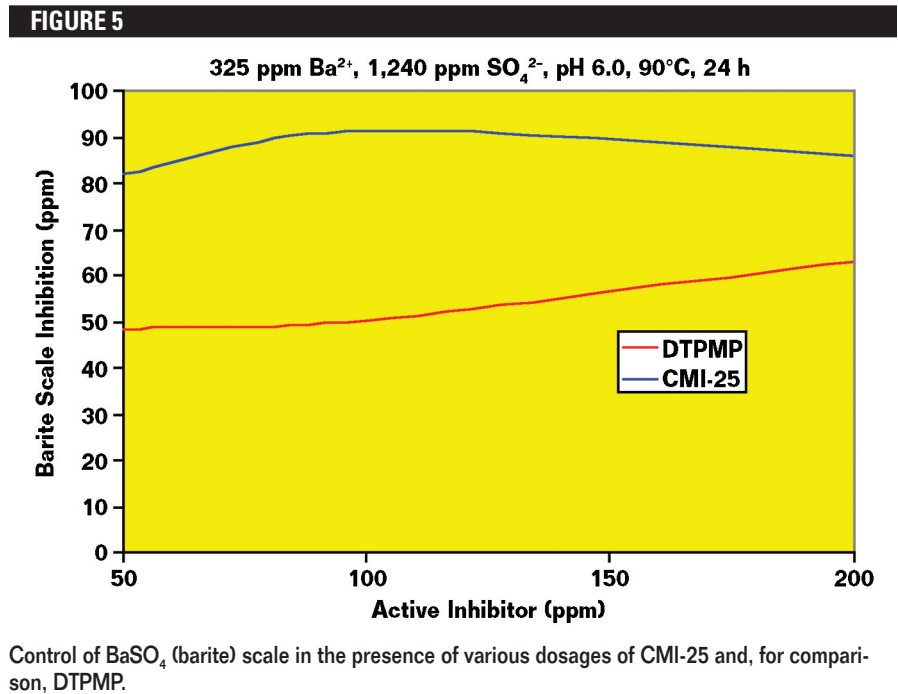
BaSO₄ and SrSO₄ can be effectively and simultaneously inhibited by CMI-25 (Figure 6). At 10-ppm dosage, inhibition efficiency reaches ~60%. Dosage increase has a gradual impact in performance. For BaSO₄, optimum dosage seems to be at 60 ppm (~90% inhibitory efficiency), whereas for SrSO₄, maximum inhibition is exhibited at 10-ppm dosage (~80%). These results support the utility of CMI-25 as a multifunctional scale inhibitor in high-sulfate brines.

ADDITIONAL ATTRIBUTES OF CARBOXYMETHYLINULIN BIOPOLYMER

Often the complexity of industrial water requires that additives possess multifunctional properties useful for the water operator/engineer. In that context, CMI-25 was successfully utilized as a dissolver of silica and CaCO₃ scale deposits. The susceptibility of certain water treatment chemicals to precipitation with calcium and other ions yielding insoluble precipitates is a well-recognized problem in the water treatment industry. Certain phosphonates are notorious for their poor calcium tolerance. Such calcium-inhibitor precipitates can be detrimental to an otherwise well-designed water treatment program because of the following:

- 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.
- They can act as potential nucleation sites for other scales.
- They can deposit onto heat transfer surfaces (they usually have inverse solubility properties) and cause poor heat flux, much like other known scales, such as CaCO₃, calcium phosphate, etc.
- If the phosphonate inhibitor in the treatment program has the purpose of corrosion inhibition, its precipitation as a calcium salt will eventually lead to poor corrosion control.

The calcium tolerance of CMI-25 was studied and found to be extremely tolerant. More specifically, CMI-25 is essentially 100% tolerant to a high-calcium



brine (Ca = 19,000 ppm, T = 95°C, at pH 5.5, for 24 h).

Conclusions

This article is part of a continuing effort to identify and exploit novel “green” water technologies to effectively inhibit mineral scale growth or remove it.^{5-6,11-13}

PEI-CMI-25 polymer blends seem to have a significant synergistic inhibitory effect on silica formation. PEI, at this point, has a prohibitive cost for large-scale, water-related applications, but full understanding of its inhibition chemistry may lead to structurally similar, more cost-effective additives. CMI-25, on the

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other hand, is already in large-scale production from a renewable source (inulin) and is cost-effective.

Crystalline mineral deposits, such as CaCO_3 , CaSO_4 , BaSO_4 , and SrSO_4 , can be effectively inhibited by CMI-25, thus demonstrating its good inhibitory power. Since such deposits often plague water systems in oilfield drilling applications, CMI-25 is an excellent inhibitor in such environments.¹⁴⁻¹⁵ Additionally, CMI-25 possesses multifunctional inhibition properties, as it is capable of inhibiting a variety of scale deposits (CaCO_3 , CaSO_4 , and BaSO_4). This may prove extremely useful in scaling environments that present a risk of composite fouling, where more than one salt is prone to precipitate and deposit.

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