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Performance of inhibitors on $CaCO_3$ scale deposition in stainless steel & copper pipe surface

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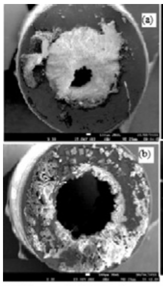
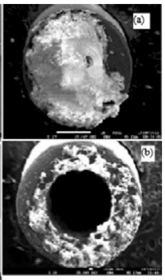
HIGHLIGHTS

- Low molecular weight maleic anhydride copolymers (YMR-polymers) as scale inhibitors
- Inhibitors were tested for $CaCO_3$ scaling at various temperatures.
- Experiment was done in pipe flow system using steel and copper pipes.
- Inhibition efficiency up to 97.79% at 60 °C and 92.74% at 70 °C was observed.
- SEM and XRD analysis show copolymer changes morphology and size of $CaCO_3$ crystals.

GRAPHICAL ABSTRACT



SEM images of $CaCO_3$ scale deposited on steel pipe walls From top:(a) Blank (without polymer (6min; 75°C).(b) YMR-74 (with polymer) (6min; 75°C).



SEM images of $CaCO_3$ scale deposited on copper pipe walls. From top: (a) Blank (without polymer) (6 min; 75°C). (b) YMR-74 (with polymer) (6 min; 75°C).

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ABSTRACT

Novel low molecular weight copolymers (termed as YMR-series polymers) prepared through reaction of maleic anhydride with n-alkylacrylamide monomers via nitroxide-mediated radical polymerization (NMRP), atom transfer radical polymerization (ATRP) and free radical polymerization have shown feasibility as a new generation scale inhibitor. The scale inhibition property of these YMR-polymers towards $CaCO_3$ in the artificial cooling water was studied in steel (316 L) and copper (90/10, CuNi alloy) pipes using a pipe flow system at various temperatures. The relationship between deposited scale mass and temperature was deduced from experimental data. The effect on formation of $CaCO_3$ scales was investigated with scanning electronic microscopy (SEM) and X-ray powder diffraction (XRD) analysis. The results showed that the low molecular weight YMR-polymers were excellent calcium carbonate scale inhibitor in copper and steel pipe flow system showing inhibition up to 98% at 60 °C.

1. Introduction

Scaling is a difficulty encountered in processing aqueous solutions containing ions of sparingly soluble salts. Scale deposits can readily form on flow surfaces when a solution is concentrated beyond the solubility limit of a dissolved sparingly soluble salt or when a solution containing an inverse solubility salt is in contact with a hot surface. Such conditions are met in both thermal and membrane desalination processes [1,2].

This paper continues our research efforts in the discovery, design and application of novel maleic anhydride based polymers (termed YMR-series polymers) as scale inhibitors. Results obtained from our previous communication [3] for YMR-series polymers have shown

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feasibility as a new generation scale inhibitor for $CaSO_4$ scales. Hence pursuance of these polymers with other mineral scales is a requisite in the final endeavor to utilize in industry. One of the most common mineral scales is $CaCO_3$ which is the subject of this paper. The formation of calcium carbonate is not only a common crystallization phenomenon that forms in natural processes (e.g. biomineralization), but represents a “fouling” problem known as scaling, which is present in various industrial processes and technologies [4–6]. Scale deposition cannot be tolerated because of its highly deleterious effects on production capacity and specific energy consumption.

To mitigate the problem of mineral scaling, chemicals and antiscalants are commonly used. The antiscalant technique is cost effective: in many cases scaling can be suppressed with less than 10 mg/L of the antiscalant due to physical mechanisms rather than chemical mechanisms [7]. Some functionalities of antiscalants are: (1) At the submicroscopic level of crystallization, negatively charged groups located on the antiscalant molecule target the positive charges on scale nuclei and distort the ionic balance that propagates crystal growth. (2) Antiscalants will adsorb to the crystal forming constituents and repel other ions, keeping them in solution, preventing particles from fixing to anionic charges present on the membrane surface. (3) Sub-stoichiometric amounts of antiscalants prevent the precipitation of salts once the salt has exceeded its solubility product, called threshold inhibition. (4) At equimolar amounts of antiscalants and scale forming ions, antiscalants may act as a chelating agent. Antiscalants form soluble complex molecules with particular metal ions, inactivating the ions so that they cannot react with other elements or ions to produce precipitates or scale [8]. Commonly used antiscalants include condensed polyphosphates, organophosphonates, and polyelectrolytes. Effective polyelectrolyte inhibitors are mostly polycarboxylic acids, e.g., polyacrylic acid, polymethacrylic acid and polymaleic acid.

Polyphosphonate inhibitors easily lead to the formation of orthophosphate because of their own hydrolysis or decomposition and orthophosphate itself can react with calcium ions to form relatively insoluble calcium phosphate scale [9]. High levels of phosphonates are becoming increasingly restricted in terms of release to the environment. As a result phosphorous free and less toxic scale inhibitors such as polyacrylates and derivatives of polycarboxylic acid and various maleic and sulfonic acid homo- and co-polymers are gaining importance [10–13]. Anti-scalants based on polycarboxylic acid also have the additional advantage of having dispersion properties with regard to calcium carbonate. Polymers with negatively charged groups can adsorb onto the surfaces of crystals and particles in suspension and impart a like charge, hence repelling neighboring particles, thereby preventing agglomeration and keeping the particles suspended in solution [14,15].

However the antiscalant performance of polycarboxylate is dependent on the number of carboxyl groups, spatial arrangement of the functional group and molecular weight. Polyacrylates with molecular weight in the range of 500–6000 are the most widely used due to their high scale inhibition power and environmental compatibility [16–18]. Polymers are generally of low molecular weight to prevent bridging of suspended solids, but of sufficient structure to adhere to developed scale formation i.e. they can be adsorbed onto the active growth sites of the crystal surface, and disturb the regular outgrowth of $CaCO_3$ crystal [19].

This work forms part of ongoing research projects aiming to synthesize and characterize novel low molecular weight maleic-anhydride–n-alkylacrylamide copolymers (YMR-series polymers) and to provide an objective assessment of the effectiveness of these YMR-series antiscalants, on the suppression of calcium carbonate scales. These low molecular weight maleic anhydride based polymers were synthesized by us via free radical polymerization [20,21], atom transfer radical polymerization (ATRP) [22] and nitroxide mediated radical polymerization (NMRP) mechanism [23]. The performance of these polymers as an antiscalants for the inhibition of $CaCO_3$ precipitation was studied through static scale inhibition test [24].

1.1. Objective of this study

In order to develop effective antiscalant on industrial level it is necessary to clarify whether maleic anhydride based copolymers (termed YMR-series polymers) are good scale inhibitors for calcium scale growth. In this study we first examined the effectiveness of the polymers on $CaCO_3$ scales at different dosage level of the antiscalant (as per the standard NACE TM 0374-95 and ASTM D 1126-02). Based on the scale inhibition efficiency, polymers showing highest scale inhibition efficiency were selected and investigated in suppressing $CaCO_3$ scale deposition in steel (316 L) and copper (90/10, Cu–Ni alloy) pipes using a pipe flow system. As the next step five best performing antiscalants were chosen and tried at various temperatures. Finally a comparative study of scaling rate at different temperatures with time for best performing antiscalant in steel and copper pipe flow system is carried out. The morphologies and crystal structures of precipitates were investigated using scanning electron microscope and X-ray powder diffraction analysis.

2. Experimental

2.1. Synthesis and experiments

All these YMR-series polymers which were evaluated for scale inhibition property towards $CaCO_3$ scales are depicted in Table 1. The brief synthesis of these polymers is given below:

2.1.1. General monomer synthesis

Substituted amine (n-alkyl amines/benzamide) and barium hydroxide (w/w; 1%) were placed in the 200 ml round bottom flask placed in an ice bath. Acrolyl chloride was added with continuous stirring till the reaction mixture thickened. The reaction mixture was then heated gradually up to 85 °C, until hydrogen chloride was eliminated. The resulting solution was whitish-yellow and turbid. Doubly deionized water or water $CHCl_3$ mixture (1:3) was added to the vessel with vigorous stirring to separate the monomer. Similarly five different monomers i.e. N-Octylacrylamide (AAO), N-Propylacrylamide (AAP), N-Butylacrylamide (AAB), N-Hexylacrylamide (AAH) and N-Acryloylbenzamide (ABA) were synthesized [20–24].

2.1.2. Free radical polymerization

All homo-polymerization studies were conducted with 0.0617 mol monomer maleic anhydride in 250 ml of solvent O-Xylene or Toluene under N_2 atm at temperatures 110 °C and 143 °C [20,21]. Two different initiators Azo-isobutyronitrile (AIBN) and Benzoyl peroxide (BPO) at concentration of (5, 7.5, 10, 12 and 15 mol% of monomer) were used for homopolymerization.

Copolymerization of MA with AAO was conducted at four different concentrations [20,21]. The samples were labeled as: MA/30 AAO, MA/50 AAO, MA/60 AAO and MA/40 AAO indicating 70:30, 50:50, 40:60 and 60:40 mol% of MA:AAO, respectively. Two different initiators azo-isobutyronitrile (AIBN) and benzoyl peroxide (BPO) at varying concentrations (5, 7.5, 10 and 12 mol% of monomers) were used in the copolymerization study.

2.1.3. Copolymerization by ATRP

Copolymerization of MA with n-alkylacrylamide monomers was conducted at 5:5 monomer ratios in o-xylene using a $FeCl_2$/SA catalyst system initiated by 2-chloropropionitrile (CPN) or methyl-2-chloropropionate (MCPN) [22]. The contents were purged with N_2 to eliminate O_2 for approximately 15 min. The reaction was conducted at three different molar ratios of [monomers]/[initiator]/[$FeCl_2$]/[SA], i.e. (100:1:1:1), (100:1:1:2) and (100:1:1:4) respectively. The temperature of the reaction was maintained at 140 °C.