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Phosphino-polycarboxylic acid modified inhibitor nanomaterial for oilfield scale control: Synthesis, characterization and migration

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ABSTRACT

A facile synthesis approach is reported to prepare scale inhibitor nanomaterial for oilfield scale control. The presence of a polymeric scale inhibitor can considerably change the morphology of the nanomaterial with a reduced particle size and an enhanced particle stability. In addition, the presence of electrolyte and sonication methods can impact the morphology and stability of the nanomaterial as well. Laboratory transport experiments suggest that the inhibitor nanomaterial has the future potential for oilfield mineral scale control. This is the first report of the synthesis and characterization of a template-free scale inhibitor nanomaterial combining both phosphonate and polymeric scale inhibitors.

Introduction

Since early 2011, the global oil production rate has been steadily increasing from 88 million barrels per day (mmbpd) to over 95 mmbpd in middle 2016 [1]. For a typical oil-producing well, formation water is normally produced together with the hydrocarbons. The produced water is typically corrosive and tends to form mineral scale deposition [2]. Next to corrosion and gas hydrate, mineral scale deposition is one of the top three production problems related to water [3]. Mineral scale (scale) deposition is basically the precipitation of sparingly soluble inorganic deposits out of aqueous solution [3–5]. Scale damage includes wellbore formation blockage leading to flow rate reduction, and also production system blockage resulting in narrowed tubing inner diameter and reduced flow [3–5]. In order to manage the scale threat, a number of scale control strategies have been evaluated and field tested, including production system surface modification, isolation of scaling production regimes, scale inhibition using scale inhibitor chemical, etc. [4–8]. Among them, chemical scale inhibition is the most common and widely used scale control technique for global oil production facilities [6–10]. Scale inhibitor (inhibitor) is a class of specialty chemicals delivered to the production systems to control scale deposition. Inhibitors, regardless of water based or non-water based, need to be dissolved into produced water to control scale deposition [3–5]. For most oilfields, the objective of scale management is to reliably provide efficient inhibition against scale deposition by means of inhibitor injection. This effort involves selecting the appropriate inhibitor chemical(s) and effectively mixing inhibitor(s) with produced water.

The most widely used inhibitors in the oilfields include aminophosphonate (phosphonate) and polymeric inhibitors. Both types of inhibitors are threshold inhibitors since these chemicals can effectively inhibit scale formation at a low concentration, minimally a few milligram per liter or less [4]. As a broad generalization, phosphonates are effective at preventing crystal growth while polymers are good nucleation inhibitors and dispersants [3]. The readers are also referred to the books written by Fink [2], Kelland [3] and Frenier and Ziauddin [4] for detailed discussions on common oilfield scale inhibitors. Other than these conventional scale inhibitors, in the past few decades an appreciable amount of effort has been made to develop alternative scale inhibitor products. For example, Vazquez et al. [11]

Abbreviations: ESI, electronic supplementary information; mmbpd, million barrels per day; SINM, scale inhibitor nanomaterial; DTPMP, diethylenetriamine pentakis (methylene phosphonic acid); PPCA, phosphino-polycarboxylic acid; DI water, deionized water; XRD, X-ray diffraction; DLS, dynamic light scattering; ID, inner diameter; PV, pore volume; cryo-TEM, cryogenic transmission electron microscopy; ICP-OES, inductively coupled plasma-optical emission spectrometer; 1-D ADE, 1-D advection dispersive equation; TE, transport experiment.

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summarized the availability of a few types of non-aqueous inhibitor products for scale squeeze treatment. In another study, a two-phase simulator was developed to model the treatment of non-aqueous scale inhibitor [12]. Among these non-conventional scale inhibitor products, a number of publications detail the synthesis and laboratory testing of scale inhibitor nanomaterials and their suspension (nanofluid) [13–18]. Normally, the objective of these investigations is to utilize the nanomaterials as a delivery vehicle to expand their use in the delivery of phosphonate inhibitors into downhole formation for scale control. These authors typically followed the scheme of testing the viability of placing the fabricated inhibitor nanomaterials in reservoir conditions to allow them to gradually release inhibitors into the production streams for scale control. Transportability of these nanomaterials was tested via laboratory column transport studies, similar to those on the colloidal particles [19]. According to these authors, the prepared inhibitor nanomaterials could be stabilized in aqueous solution by different methods variously as sonication treatment, surface modification, particle templating, etc. Furthermore, the inhibitor nanomaterials were transportable in formation materials at representative formation conditions. However, typically these synthesized inhibitor nanomaterials contained either a phosphonate or a polymeric scale inhibitor, instead of both of these two types of inhibitors. In other words, these existing inhibitor nanomaterials focus on either scale particle crystal growth inhibition or scale particle crystal nucleation distortion. In addition, the synthesis of these nanomaterials was complicated by involving foreign particles, such as SiO_2 nanoparticles, as a template.

In this study, a simple two-step synthesis route has been reported to prepare a template-free phosphonate nanomaterial by use of a polymeric inhibitor as dispersant. The first synthesis step involves mixing of a divalent metal solution with a phosphonate solution to yield a metal-phosphonate precipitate. The second step is the dispersion of the resultant precipitate into a phosphino-polycarboxylic acid (PPCA) inhibitor solution with the assistance of ultrasonication. The prepared inhibitor nanomaterial and its nanofluid were systematically characterized to understand their physiochemical properties. The presence of the polymeric inhibitor can considerably modify the surface morphology and reduce the particle size of the inhibitor nanomaterial. In addition, the transport behavior of this nanomaterial was studied by laboratory column transport experiments. Attention has been focused on examining the impacts of polymer, electrolyte and sonication methods on nanomaterial properties and transport behavior. To the best of our knowledge, this is the first report of the synthesis and characterization of a template-free scale inhibitor nanomaterial combining both phosphonate and polymeric scale inhibitors. In other words, the prepared inhibitor nanomaterial in this study is expected to be able to effectively inhibit scale deposition by controlling both scale particle crystal growth and crystal nucleation. The experimental investigation outlined in this study provides a simple and economical method in preparing inhibitor-containing nanomaterial, which has the potential for oilfield scale control application.

Materials and methods

Chemicals

Commercial grade diethylenetriamine pentakis (methylene phosphonic acid) (DTPMP) with 50% activity was used as the scale inhibitor (Solutia Inc.). Commercial grade PPCA solution with 50% activity (wt./wt.) was acquired from BWA Water Addictives. The average molecular weight of PPCA is approximately 3800 g mol^{-1}, and it is composed of about 52 monomer repeat units. Chemicals such as calcium chloride, sodium chloride, potassium chloride, sodium hydroxide, acetic acid and hydrochloric acid were reagent grade and purchased from Fisher Scientific. Tritiated water was purchased from Sigma-Aldrich. Deionized water (DI water) was prepared by reverse osmosis and ion exchange water purification process.

PPCA modified Ca-DTPMP nanofluid synthesis

A DTPMP solution (0.1 mol per kg water) was prepared by diluting the acidic DTPMP stock solution with DI water and the solution pH was adjusted to 11.3 with 10 M NaOH. $CaCl_2$ solution (0.4 mol per kg water) was prepared in DI water. PPCA solution (0.2% wt./wt.) was prepared by diluting the stock PPCA solution with DI water and adjusted to 7.0 pH with 2 M NaOH. In a typical synthesis experiment, 100 mL DI water was added into a 250 mL two-neck flask and heated to 90 °C in a water bath. While the DI water inside the flask was stirred at 90 °C, $CaCl_2$ solution (25 mL) and DTPMP solution (25 mL) were simultaneously added dropwise into the flask using a syringe pump (Harvard Apparatus Inc.). Immediately upon injection of $CaCl_2$ and DTPMP, white Ca-DTPMP precipitates formed from the aqueous solution. The addition of $CaCl_2$ and DTPMP solutions was generally completed within 2 min and the mixture was stirred for an additional 1.5 min before the mixture was air cooled to room temperature (22 °C). Upon completion of solution addition and subsequent cooling, a white suspension was obtained with a final pH of ca. 7.2. Subsequently, the white suspension was centrifuged at 6500 rpm for 10 min. After discarding the supernatant solution, the solid sample was washed by DI water to remove the salt and saved as a wet paste. Ca-DTPMP nanomaterial suspension (nanofluid) was prepared by re-dispersing the obtained Ca-DTPMP paste into a PPCA solution (0.2% wt./wt.) via an ultrasonication method. Typically, 1 g of the prepared Ca-DTPMP solid was dispersed into a 100 mL solution of PPCA or PPCA/KCl solution. In this study, the ultrasonication treatment involves a probe sonicator (Sonics & Materials Inc.) and a bath sonicator (Model FS-14, Fisher Scientific). As a comparison, the formed Ca-DTPMP wet paste was also sonication treated in DI water free of PPCA. The inhibitor DTPMP loading in the tested nanofluid was about 0.8% (wt./wt.). The detailed conditions of each ultrasonication dispersion treatment were tabulated in Table 1.

Characterization of the nanomaterial and the nanofluid

A fraction of the obtained Ca-DTPMP wet paste was air dried to prepare for X-ray diffraction (XRD) characterization to investigate the crystallinity of the precipitate. The XRD characterization was conducted on a Ragaku D/max Ultra II Powder Diffractometer equipped with a Cu Kα radiation source at 40 kV and 40 mA. The dry Ca-DTPMP nanomaterial was obtained by centrifuging the freshly sonicated nanofluid at 6500 rpm for 20 min and subsequently drying the solid in an oven overnight to remove the interstitial water. The stoichiometric ratio of calcium to DTPMP for the dried Ca-DTPMP nanomaterial was determined by dissolving the dried solid in 1 M HCl. As for inhibitor nanofluid characterization, Ca-DTPMP suspensions prepared from Exp. #1 and #2 in Table 1 were compared to evaluate the impact of PPCA on Ca-DTPMP properties. Nanofluids #2 to #5 in Table 1 were prepared to assess the impact of KCl and sonication methods. The nanofluid characterization methods included particle size measurement, electrophoretic mobility measurement and cryogenic transmission electron microscopy (cryo-TEM) analysis. Each nanofluid characterization was performed immediately after the ultrasonication treatment. The size of the Ca-DTPMP nanomaterials in the nanofluid was measured by dynamic light scattering (DLS) (Zetasizer Nano, Malvern Instruments). Electrophoretic mobility of

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