Iron Oxide Colloidal Suspension Stabilization by Polymeric Dispersants

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ABSTRACT

Stabilizing colloidal suspensions helps prevent scale deposition and inorganic particulate matter fouling in aqueous systems. Colloidal suspension stabilization was modeled using iron oxide ($\text{Fe}_3\text{O}_3$) suspensions in synthetic tap water containing a mixed electrolyte system that included a variety of ions interacting with suspended particles. Zeta potential measurements of suspended particles were conducted over a wide pH range (3.5 to 10) both in the absence and in the presence of deposit control polymers (DCPs). Results suggest that both polymer functional group type(s) and molecular weight (MW) impact dispersion efficiency.

Key Words: iron oxide, suspension, colloidal, zeta potential, deposit control polymers

INTRODUCTION

Waters used in industrial applications (boilers, cooling, etc.) often contain dissolved or particulate iron (from the feed stream and/or equipment corrosion) which contributes to scale formation and deposition.\(^1\) There are 16 known iron oxides (oxides, hydroxides or oxide hydroxides); predominantly iron is present in the +3 oxidation state.\(^2\) Several iron oxides including hematite, magnetite and goethite may be present in industrial waters causing water coloration. The fully dispersed iron oxides do not scatter light and are therefore transparent.\(^3\) Controlling suspended matter is a major challenge which is met through the use of corrosion inhibitors, iron ion stabilizers, chelating agents, and/or dispersants.\(^4\) Dispersing oxide particles in water is important in the paint industry, ink formulations, and many other applications.\(^5-7\) Dissolved oxygen oxidizes soluble iron present in subsurface waters leading to the formation of colloidal $\text{Fe}_3\text{O}_3$ suspensions which causes water coloration (red water) and clogs fluid handling equipment. Similar deposits occur in potable water systems especially following repair works in the distribution systems.\(^8\)

Iron oxide nanoparticles have been used in medical diagnostics, magnetic resonance imaging, and cancer therapies assisted by magnetic fields.\(^9\) Ten to 100 nm mean diameter iron oxide particles have been found to be optimal for intravenous injection. Iron oxide agglomerates with mean diameter exceeding 200 nm may decrease blood circulation in certain capillaries.\(^10\) Medical applications have used organic polymers to encapsulate particles to enhance chemical stability, dispersability, and functionality of the magnetic particle suspensions.\(^11\) Iron particle dispersion has also been attempted through nanoparticle surface modification. Several fatty acids (e.g., phosphonic acids) have been successfully used as surface modification agents.\(^12\) Polymers have been used for the stabilization of superparamagnetic iron oxide particles.\(^13\)
Industrial water processes and equipment (e.g., cooling systems, boilers, pumps, heat exchangers) frequently encounter low iron concentrations primarily due to metal corrosion which can cause iron-based deposits that promote more scale formation and deposits that include sparingly soluble salts and metal oxides.\textsuperscript{14} The most commonly encountered iron oxides in industrial water applications include hematite ($\alpha$-Fe$_2$O$_3$) and magnetite (Fe$_3$O$_4$).

The present work investigated the role of DCPs (i.e., polyacrylates with varying MWs and made in different polymerization solvents, copolymers with different MWs and functional groups) as hematite suspension stabilizers in aqueous electrolyte solutions. Both DCP MW and functional groups are expected to differentiate interactions between hematite particles and DCPs present in the aqueous medium at relatively low concentrations. The interactions (mainly adsorption governed by electrostatic interactions) directly impact the surface potential of the suspended particles. Therefore, particle zeta potential (ZP) measurements (without and with DCPs present) were selected as the most appropriate evaluation tool.

**EXPERIMENTAL PROCEDURES**

Reagent grade chemicals and grade A glassware were used. Stock solutions of calcium chloride, magnesium chloride, sodium chloride, and sodium sulfate were prepared using distilled water and analyzed as described previously.\textsuperscript{15} Table 1 lists the DCPs evaluated. DCP stock solutions were prepared in distilled water on a dry weight basis.

Iron oxide suspension were prepared by adding 0.12 g iron oxide as Fe$_2$O$_3$ (Fisher Scientific) to 600 mL of synthetic water containing a known amount of DCP solution in an 800 mL beaker. Synthetic tap water (hereafter “STW”) was prepared by mixing standard solutions of calcium chloride, magnesium chloride, sodium sulfate, sodium chloride, and sodium bicarbonate. The STW composition was 100 mg/L Ca, 30 mg/L Mg, 314 mg/L Na, 200 mg/L SO$_4$, 571 mg/L Cl, and 60 mg/L HCO$_3$. ZP values were measured after suspension pH adjustments by adding standard hydrochloric acid and/or sodium hydroxide as needed and sonication for 20 seconds using a Nanosize S Instrument (Malvern). The distributions were symmetrical and in all cases the mean values are given. The measurements were done in triplicate and the mean value variation were less than 5%.

DCP dispersant performance was evaluated using the procedure described previously.\textsuperscript{14}

<table>
<thead>
<tr>
<th>Table 1: Deposit Control Polymers Evaluated</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Type</strong></td>
</tr>
<tr>
<td>Solvent polymerized poly(acrylic acid) or “SPPAA”</td>
</tr>
<tr>
<td>SPPAA</td>
</tr>
<tr>
<td>Water polymerized PAA or “WPPAA”</td>
</tr>
<tr>
<td>WPPAA</td>
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<tr>
<td>WPPAA</td>
</tr>
<tr>
<td>WPPAA</td>
</tr>
<tr>
<td>Poly(acrylic acid: [2-acrylamido-2-methylpropane sulfonic acid]) or “AA/SA” with 74/26 monomer weight ratio</td>
</tr>
<tr>
<td>Poly(AA : SA: sulfonated styrene) or “AA/SA/SS”</td>
</tr>
<tr>
<td>AA/SA/SS</td>
</tr>
<tr>
<td>AA/SA/SS</td>
</tr>
</tbody>
</table>

* Determined by gel permeation chromatography.

**RESULTS AND DISCUSSION**

Zeta potential (ZP) is an important characteristic used often for evaluating the behavior of suspended particles in aqueous media either from the point of view of prediction of their colloidal stability or investigating particle deposition in water cooling process equipment.\textsuperscript{15,16} Using the experimental procedure described above, a series of experiments were carried out to determine the ZP of iron.
oxide particles in the presence of DCPs. The studies were designed to evaluate DCPs as iron oxide particle suspension stabilization agents as impacted by (a) solution pH, ionic strength, and water hardness as well as (b) DCP dosage, MW, and composition.

**Solution pH and Polyacrylate Dosage Effects**

Figure 1 presents ZP measurements for hematite (α-Fe₂O₃) particles suspended in STW as a function of solution pH and CK732 (6k MW SPPAA) dosage.

![Figure 1: Hematite Particle ZP vs. pH & CK732 Dosage](image)

Figure 1 shows that hematite particles have an isoelectric point (IEP) at pH 4.1 and the surface potential over the pH range (3.5 to 10.5) studied was low (-12 ± 6 mV), suggesting that the suspensions are unstable in STW. The ZP data indicate that as CK732 dosages increase, the hematite particles become more negatively charged and the suspensions are more stable. This observation agrees with findings from studies on the interaction of PAA with alumina surfaces. Even in the presence of very low CK732 concentrations, there were no IEPs for the composite hematite-DCP particles. CK732 adsorption on the suspended particles resulted at the predominance of the ionized DCP functional groups on particle surfaces yielding negative ZP values over the pH range investigated. For >5 pH, the ZP does not change significantly because all the adsorbed CK732 functional groups are ionized.

Figure 2 presents ZP measurements for hematite (α-Fe₂O₃) particles suspended in STW at pH 8 as a function of CK732 dosage (0 to 2.0 mg/L). As indicated, very low (<0.5 mg/L) CK732 dosages markedly affect the ZP values.

![Figure 2: Hematite Particle ZP vs. CK732 Dosage @ pH 8.0](image)
DCP Polymerization Solvent Effect

Previous investigations have shown that polymerization solvent plays an important role in the PAA performance as both precipitation inhibitors for sparingly soluble salts and suspended matter dispersants.\textsuperscript{20,21} It was also reported that SPPAAs are more tolerant to calcium ions than WPAAAs of similar MW.\textsuperscript{23} Several experiments were carried out to understand the impact of manufacturing process polymerization solvent (i.e., organic and water) as a function of solution pH. Figure 3 presents ZP values in the absence and presence of 2.0 mg/L PAA [CK752 (SPPAA) and CK7028 (WPAAA) of similar MW (2k and 2.3k, respectively)] at pH 8.0. The data indicate that the SPPAA (CK752) has a more pronounced impact on ZP than WPPAA (CK7028).

**Figure 3: PAA Polymerization Solvent Effect on ZP**

<table>
<thead>
<tr>
<th>ZP (mV)</th>
<th>Control</th>
<th>CK752</th>
<th>CK7028</th>
</tr>
</thead>
<tbody>
<tr>
<td>-30</td>
<td></td>
<td>2 mg/L PAA dosages</td>
<td></td>
</tr>
<tr>
<td>-20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
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</table>

Polyacrylate Molecular Weight Effect

Numerous studies have shown that DCP MW markedly impacts scale inhibition effectiveness. Studies show that optimum inhibitory performance for scale forming salts (e.g., calcium carbonate, calcium sulfate, barium sulfate) is obtained by 2k MW PAAs.\textsuperscript{23,24} To study DCP MW effect on ZP, a series of experiments were conducted in the presence of 2.0 mg/L WPPAAs at pH 8.0. The data presented in Figure 4 clearly show the impact of PAA MW on ZP values. The data suggest that adsorption on iron oxide particles occurs more slowly and less efficiently as PAA MW increases. The adsorption of higher MW DCPs is impacted more by the DCP loops and tails thereby resulting in lower negative surface charge vs. lower MW DCP that adsorb flat on the oxide substrate surfaces becoming more negatively charged.\textsuperscript{20} This MW effect on ZP values is consistent with a previous study evaluating PAA adsorption on barium sulfate crystals.\textsuperscript{25}

**Figure 4: PAA MW Effect on ZP (pH 8.0, 2.0 mg/L PAA)**

<table>
<thead>
<tr>
<th>ZP (mV)</th>
<th>2.3k</th>
<th>123k</th>
<th>345k</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CK7028</td>
<td>CK7600N</td>
<td>CK702</td>
</tr>
</tbody>
</table>

DCP Architecture Effect

DCP composition was expected to impact oxide suspension stabilization. Three DCP types were evaluated: Homopolymer (CK7028), copolymer (CK775), and terpolymer (CK798). ZP measurements for hematite particles suspended in STW at pH 8.0 in the presence of 2.0 mg/L DCP were evaluated and the results are shown in Figure 5.

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Figure 5 shows that the AA/SA/SS terpolymer caused in the greatest negative ZP suggesting the highest hematite particle dispersion efficiency. Clearly the presence of sulfonic groups (SA) in the AA/SA copolymer and AA/SA/SA terpolymer impacts ZP. Furthermore, the sulfonated styrene (SS) in the terpolymer maximizes the hematite particles' negative charge causing stronger repulsion and hence higher suspension stability. These ZP (surface potential values) induced by the DCP adsorption and particle suspension stabilization is consistent with previously reported on iron oxide dispersion by polymers.14,21

Terpolymer Composition and Molecular Weight Effects

Figure 6 presents ZP values in the presence of 2 mg/L AA/SA/SA terpolymers at pH 8.0. The data indicate that terpolymer impact on ZP depends on the DCP monomer ratios (CK797 vs. CK798) and MW (CK781 vs. CK798). The data presented suggest AA/SA/SA ZP impact (greatest to least) is CK781 > CK798 > CK797.

Solution Ionic Strength Effect

The ionic strength of the aqueous medium suspending hematite particles is also an important factor impacting surface potential and thus DCP adsorption capability. A colloidal particle suspension’s stability depends on the overall system energy (V), which depends on the interplay of repulsive and attraction forces according to the DLVO theory in Equation 1 below:

\[
V = V_R + V_{OW}
\]  (1)
Where “V_r” is the repulsive energy due to electrostatic repulsive forces developed between the similarly charged suspension particles and “V_{vDW}” are the attractive Van der Waals Forces.\(^{21}\) Equation 2 below determines the repulsive energy contribution to the overall system energy:

\[
V_r = 2\pi R e \epsilon_0 \phi_d^3 \ln\left(1 + e^{-\kappa^{-1}}\right)
\]

(2)

Where “D” is the separation distance between the particles (concentration of the suspension), “\(\epsilon\)” is the dielectric constant of water, “\(\epsilon_0\)” the vacuum permittivity, “\(\phi_d\)” the potential at the shear plane of the electrical double layer around the particles (zeta potential), and “\(\kappa^{-1}\)” the Debye length (i.e., the thickness of the electrical double layer which depends on the ionic strength). Equation 2 shows, other things kept constant, that the higher the ionic strength, the smaller the \(\kappa^{-1}\) value and the less significant are the repulsive forces. The attractive, Van der Waals contribution to the overall energy is:

\[
V_{vDW} = -\frac{A_{HHW}\alpha}{12D}
\]

(3)

Where “A_{HHW}” is the Hamaker constant for the system Hematite-Water-Hematite and “\(\alpha\)” is the hematite particle radius. Equations (1) to (3) indicate that the more significant the electrostatic repulsion term (depending upon the ZP value) the more stable the suspension. Figure 7 shows the ZPs measured for hematite particles suspended in an inert electrolyte KNO\(_3\) and in STW.

![Figure 7: Solution Ionic Strength Effect on ZP @ pH 8.0](image)

Figure 7 indicates the IEP in the presence of the 1:1 inert electrolyte KNO\(_3\) was pH 6.0. In the presence of STW (containing divalent ions: Ca\(^{2+}\), Mg\(^{2+}\), SO\(_4^{2-}\)) the IEP was shifted to pH 4.1, suggesting specific anion adsorption. Normally, the presence of the divalent ions reduces the thickness of the electrical double layer which is inversely proportional to the ion charge and the specific anion adsorption reduces the negative ZP values. This trend has also been observed for other oxides.\(^{22,23}\)

From a water conservation viewpoint, there has been an increasing trend towards operating cooling water systems at higher cycles of concentration resulting in greater driving forces for scale forming salt precipitation and suspended matter accumulation. Collectively, these factors necessitate higher DCP dosages to prevent deposition of unwanted materials on equipment surfaces.

Figure 8 presents ZP values vs. pH for 2 mg/L CK798 dosage in the presence of varying concentrations of dissolved ions or total dissolved solids (TDS; i.e., STW, 2x STW, 3x STW). The data indicate that the presence of increasing TDS shifts the iron oxide particle surface charge to more positive ZP values. The trend shift to more positive ZP values with increasing hardness is anticipated because of the increasingly higher TDS concentrations which reduce the electrical double layer thickness. Increasing water hardness is anticipated to reduce hematite particles suspension stability.
Iron Oxide Dispersion Impacted by DCP Dosage and Composition

Iron oxide dispersion in STW was studied using the standard test method as described in the experimental section. Figure 9 presents 3 hr % D (iron oxide dispersed) values for three (3) DCP listed in Table 1: CK732, CK775, and CK798. The data clearly indicate that both DCP dosage and their molecular structure strongly affect a DCP’s ability to disperse iron oxide.

The Figure 9 iron oxide dispersion (or performance) vs. DCP dosage profiles show performance initially increases rapidly with dosage and then plateaus. For example iron oxide dispersion at 1 mg/L CK732 is poor (≈25%) and increases sharply with dosages up to 1 mg/L and then plateaus (≈40%). The data suggest that the sulfonate group(s) in CK775 and CK798 have a strong influence altering iron oxide particle size distributions in aqueous solutions. Figure 9 indicates that the DCP ranking (highest to lowest) as iron dispersant is CK798 > CK775 > CK732.
CONCLUSIONS

The presence of water soluble DCPs in hematite particle suspensions in STW shifted the ZP (surface potential) to significantly more negative values over a broad pH range (3.5 to 10). Increasing water hardness shifts ZPs to more positive values due to combination of ionic strength and specific adsorption of ion on the charged hematite particles. Adsorption and subsequent hematite particle suspension stabilization depends on DCP architecture. Lower MW weight PAAs shifted hematite particle ZPs to more negative values most likely because more effective adsorption on the particles. Higher MW PAAs adsorb on particles by forming loops and tails thus yielding less negative ZP values.

The lowest MW PAAs provided the best iron oxide dispersion performance. Moreover, polymerization solvent affects PAA dispersion efficacy; PAAs made in organic solvent polymerization process were more efficient dispersants than PAAs made in water. Based on ZP values as well as performance testing herein, terpolymers were found to be more efficient than copolymers and homopolymers as iron oxide suspension stabilization agents and dispersants; the performance rank order (highest to lowest) was terpolymers > copolymers > homopolymers.

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