The Impact of Thermal Stability on the Performance of Polymeric Dispersants for Boiler Water Systems

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Introduction

The quality of feed water available for the efficient operation of a large number of boiler and steam plants is extremely poor. This, coupled with the lack of adequate treatment, often leads to boiler tube failures and system breakdowns. Thus, from the perspective of efficient operation of steam generation plants, feed water has to be properly treated in order to minimize damage to boiler equipment and to eliminate unforeseen production losses. The major challenges facing the water technologists that seek to provide high levels of steam purity from boilers include prevention of scale and deposit on heating surfaces; corrosion control in the boiler, steam lines, and condensate system; and minimizing carryover. Table 1 below presents an overview of boiler water system pressure categories, corresponding temperatures, feed water types, and water treatment challenges.

Over the years, a variety of treatment programs have been developed to treat boiler systems. These treatment programs include: (a) precipitation (i.e., carbonate cycle, phosphate, coordinated phosphate), (b) chelant (incorporating EDTA or NTA to chelate Ca/Mg), and (c) All-polymer. Successful application of boiler treatment programs requires multi-multifunctional deposit control agents to condition sludge, stabilize hardness ions, and disperse particulate matter.

Natural and Synthetic Polymeric Dispersants

The earliest dispersants used in boiler water systems were naturally occurring polymers such as starches, alginates, lignins, tannins, and cellulose derivatives. Subsequently, modifications of these materials such as lignosulfonates were used to treat boiler systems. Occasionally one may still find these natural materials used to treat some boiler systems, particularly those operating at less than 100 psig. However, while natural materials are effective for dispersing calcium carbonate scale they perform poorly as calcium phosphate dispersants. Thus, as phosphate-based treatment programs have gained more popularity, so has the need for new synthetic polymers and most of the natural polymers have now been replaced with more effective synthetic polymers especially in higher (>100 psig) pressure boiler applications.

The use of synthetic polymers [i.e., polyacrylates (PAAs), polymethacrylates (PMAAs), hydrolyzed polyacrylamides, acrylic acid/acrylamide copolymers] dates back to the 1950s. The early synthetic polymers used were high molecular weight (MW) homopolymers of acrylic acid (>100,000). With the passage of time, lower MW polyacrylates (<100,000), as well as polymethacrylates and polymaleic acids, were found to be more efficacious. Researchers have shown that polyacrylate MW is an important consideration relative to performance.

Eventually, copolymers of acrylic acid, methacrylic acid, and/or maleic acids with a variety of other co-monomers [e.g., sulfonated styrene (SS), 2-acrylamido-2-methyl propane sulfonic acid (SA), substituted acrylamides] were found to provide improved performance characteristics in various applications including, boiler, cooling, geothermal, oil field, and desalination (thermal and membrane based) processes.

Thermal degradation of polymers is a well studied area. However, there is little information available of practical value to a water technologist concerned with using low MW polymers. In 1982, Masler presented Lubrizol’s initial research efforts on the thermal stability of several homopolymers [i.e., PAAs, PMAAs, polymaleic acids (PMAs)] commonly used in boiler applications. These

<table>
<thead>
<tr>
<th>Type</th>
<th>Temp.</th>
<th>Feed water Types*</th>
<th>Water Treatment Challenges</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low Press. (&lt;150)</td>
<td>&lt;177°C (&lt;351°F)</td>
<td>SN and/or RO or SN/RO and/or DM</td>
<td>• Hardness- (leakage) and iron-(condensate &amp; corrosion) based deposit control</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Corrosion control</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Shutdown &amp; lay-up procedures</td>
</tr>
<tr>
<td>Medium Press. (&gt;150 and &lt;600)</td>
<td>&gt;177°C (&gt;351°F) &amp; &lt;251°C (&lt;483°F)</td>
<td>SN and/or RO or SN/RO and/or DM</td>
<td>• Hardness- (leakage) and iron-(condensate &amp; corrosion) based deposit control</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Process contamination</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Corrosion control</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Shutdown &amp; lay-up procedures</td>
</tr>
<tr>
<td>High Press. (&gt;600)</td>
<td>&gt;251°C (&gt;483°F)</td>
<td>DM</td>
<td>• Process contamination</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Corrosion control</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Shutdown &amp; lay-up procedures</td>
</tr>
</tbody>
</table>

* Key to feed water types above: SN = Softened, RO = Reverse Osmosis, DM = Demineralized

Table 1: Boiler Water Systems Overview
homopolymers were (before and after thermal stress) (a) characterized by various analytical techniques and (b) evaluated for their performance. It was demonstrated under the conditions employed [pH 10.5, 250 °C (592 psig), 18 hr] that PAA, PMAA, and PMA all underwent some degradation. In terms of MW loss, PMAA lost slightly less than PAA, which lost considerably less than PMA. Additionally, PAA and PMAA had minimal performance changes whereas PMA displayed a substantial performance loss.

The goal of the work and data presented herein is to provide guidance to industrial water technologists seeking to design boiler water treatment programs where thermal stability and/or deposit control polymer performance retention during thermal stress is a critical performance criterion.

Experimental
Lubrizol interviewed several individuals in an effort to define the types of deposit control polymers and boiler water system operating conditions of interest to most AWT member companies. This resulted in the characterization of a typical low to medium pressure boiler water systems operating up to 200°C (equivalent to 241 psig) as the basis for Lubrizol's laboratory testing simulating typical boiler water conditions discussed herein.

Sample Preparation
A solution of polymer was prepared containing 10% polymer (as active solids) at pH 10.5 using sodium hydroxide to neutralize the polymer. Sodium sulfite was added as an oxygen scavenger. The polymer solution was subjected to heat treatment according to the procedure described previously.4

Polymer Characterization
The MW of polymers were determined by GPC method according to procedure described previously.2 Attenuated total reflectance infrared (FT-IR) of all samples were acquired on a Nicolet Magna 560 Fourier Transform Infrared (FT-IR) spectrometer, equipped with the Pike MIRacle.tm

Performance Tests
The iron oxide dispersion, calcium phosphate inhibition, and calcium ion compatibility tests were performed
according to the procedures described in previous studies.2,3,5 The water chemistry for the calcium hydroxyapatite (HAP) dispersion tests included 105 mg/L Ca, 31 mg/L Mg, 353 mg/L Na, 209 mg/L SO₄, 116 mg/L HCO₃, 599 mg/L Cl, 23°C, and pH 7.8. To the 100 mL solutions, 2,500 mg/L of HAP was added along with 5 mg/L active polymer dosages. Ca–HAP dispersion was monitored by measuring the solution transmittance at 3 hrs. The polymers used in this study were commercial polymers and their analytical characteristics are shown in Table 2.

## Results and Discussion

### Polymer Performance Evaluation

#### Iron Oxide Dispersion

Among many dissolved impurities present in natural waters, iron-based compounds are among the most problematic to the efficient operation of industrial water systems. Figure 1 presents performance data for several polymers under standard test conditions (200 mg/L iron oxide, 1 mg/L active polymer, 3 hr, 7.8 pH, 100 mg/L Ca, 30 mg/L Mg, 314 mg/L Na, 200 mg/L sulfate, 571 mg/L Cl, 60 mg/L bicarbonate, 23°C).2 As shown in Figure 1, the acrylate-based homopolymers (K732, K7058, PAA-P, K766) before thermal treatment provide relatively poor (<50 %) iron oxide dispersion. Furthermore, the iron oxide dispersion values for both heat-treated and non-heat treated homopolymers including PMA are very similar. This indicates that thermal stress has a negligible detrimental effect on the dispersing ability of the polymers.

Comparative dispersion data presented in Figure 1 show that both the co- and terpolymers in the absence of thermal stress exhibit excellent (>80%) iron oxide dispersion. However, when these co- and terpolymers are exposed to thermal stress (200 °C for 20 hr), the iron oxide dispersion decreases drastically (by a factor 4). For example, “% iron oxide dispersion” values obtained for CASN and K781 before heat treatment were both >85 % compared to 18 % and 26 %, respectively, after thermal stress. It is interesting to note that the performance of heat-treated terpolymers is similar to that obtained for homopolymers.

### Table 2: Polymers Evaluated

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Polymer Typea</th>
<th>Acronym</th>
<th>Mol. Weightb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignosulfonate</td>
<td>Sodium-lignosulfonate</td>
<td>SLS</td>
<td>&lt;20,000</td>
</tr>
<tr>
<td>CBSK732  c</td>
<td>Solvent polymerized poly-AA</td>
<td>K732</td>
<td>=6,000</td>
</tr>
<tr>
<td>CBSK7058 c</td>
<td>Water polymerized poly-AA</td>
<td>K7058</td>
<td>=7,000</td>
</tr>
<tr>
<td>BS161</td>
<td>Poly(AA) with phosphate groups</td>
<td>PAA-P</td>
<td>&lt;2,000</td>
</tr>
<tr>
<td>BC200</td>
<td>Poly-MA</td>
<td>PMA</td>
<td>&lt;2,000</td>
</tr>
<tr>
<td>CBSK766 c</td>
<td>Poly-MAA</td>
<td>K766</td>
<td>5,000</td>
</tr>
<tr>
<td>TRC233HS</td>
<td>Poly(AA:SA) copolymer</td>
<td>CASA</td>
<td>&gt;10k &amp; &lt;40k</td>
</tr>
<tr>
<td>CBSK776 c</td>
<td>Poly(AA:SA) copolymer</td>
<td>K776</td>
<td>&gt;10k &amp; &lt;40k</td>
</tr>
<tr>
<td>AC3100</td>
<td>Poly(AA:SA:NI) terpolymer</td>
<td>CASN</td>
<td>&lt;10,000</td>
</tr>
<tr>
<td>CBSK781 c</td>
<td>Poly(AA:SA:SS) terpolymer</td>
<td>K781</td>
<td>&lt;10,000</td>
</tr>
</tbody>
</table>

a* Key to polymer type abbreviations (in table above):
b Expressed as polyacrylia acid as determined by an aqueous GPC method.
c Carbosperse™ (formerly Good-Rite®) K-700 polymer supplied by Lubrizol Advanced Materials, Inc. (formerly Noveon, Inc.)

AA = acrylic acid  
MAA = methacrylic acid  
MA = maleic acid  
SS = sulfonated styrene  
SA = sulfonic acid or 2-acrylamido 2-methylpropane sulfonic acid  
NI = non ionic monomer
As shown, SLS exhibits good performance before (70%) and after (55%) thermal stress only losing approximately 20% of its dispersing power due to heat treatment. Although SLS exhibits good iron oxide dispersion, it is used infrequently today for several reasons: inconsistent quality, breakdown products may deposit on boiler surfaces, poor calcium phosphate inhibition and dispersion.

The influence of temperature level on the thermal stability of polymers was also investigated at both 150 °C and 200 °C. Performance data presented in Figure 2 indicate excellent thermal stability for the sodium PMAA (K766) and two PAAs (K7058 and PAA-P) evaluated at both 150 °C and 200 °C. The baseline performance (without thermal treatment) for the two acrylate terpolymers is better than for the homopolymers tested.

Figure 2 also shows a comparison of the two acrylate terpolymers that have the same baseline performance before thermal stress, but the thermal stability of K781 is better than for CASN. Although two (i.e., AA and SA) of the three monomers used to manufacture these acrylate terpolymers are the same, the functionality of third monomer (as will be shown later) plays a key role in explaining the performance difference between two terpolymers.

Figure 2. Iron Oxide Dispersion by Polymers before and after Varying Thermal Stress

Hydroxyapatite Dispersion
The Ca–HAP dispersing ability of several commercial polymers was investigated using the test method described earlier. Figure 3 presents the Ca–HAP dispersion data on homo, co-, and terpolymers before and after thermal treatment at 200 °C for 20 hours. As shown, there is a significant performance difference between the homopolymers and the co- and terpolymers tested. Among the homopolymers, K732 exhibits the best Ca–HAP dispersion. By comparison, the non-thermally stressed co- and terpolymers exhibit good Ca–HAP dispersion activity with varying degrees of performance loss for the thermally treated polymer samples. It is also interesting to note the following pertaining to Ca–HAP dispersion:

- SLS (shown in Figure 1 to be a good iron oxide dispersant) performs poorly
- Thermally treated AA:SA copolymers and the CASN terpolymer perform similar to that obtained for homopolymers
- K781 provides the best performance before thermal stress and is superior to the other polymers tested after thermal stress

Figure 3. Calcium HAP Dispersion by Polymers before and after Thermal Stress

Calcium Phosphate Inhibition and Calcium Compatibility
The influence of heat treatment on the performance of terpolymers as calcium phosphate inhibitor indicates that K781 is a better inhibitor than CASN. Similar observation in terms of Ca ion tolerance was also observed for K781 and CASN (see details in Lubrizol's AWT-05 paper).

Polymer Characterization
A. Molecular Weight
All polymers degrade to varying degrees as a result of exposure to elevated temperature and pressure. The extent of degradation depends upon several factors including temperature, duration of heat treatment, and polymer architecture. Figure 4 depicts the “% MW loss” for homo, co- and terpolymers. The data indicate a relatively small loss of MW for homopolymers after heating at 200 °C. Figure 4 also shows that SA-based terpolymers are degraded to a lesser extent than AA:SA copolymers. For example, the MW loss obtained for terpolymers was
approximately 11% compared to approximately 22% loss in the case of copolymers. It is interesting to note that the natural dispersant (SLS) lost approximately 75% of its MW compared to a 22% molecular weight loss for K781.

Figure 4. Polymer Molecular Weight Loss Due to Thermal Treatment (200°C)

B. FT-IR Spectroscopy

Before and after thermal treatment FT-IR spectra of K732, K776, and CASN are shown in Figures 5, 6, and 7, respectively. Figure 8 shows the FT-IR spectra for K781 before as well as after both 4 and 20 hr of thermal treatment at 200 °C.

In all cases, polyacrylic carboxylate salt carbonyl, which is near 1,565 cm⁻¹ shifted to a 7-8 cm⁻¹ lower frequency after thermal stress. The reason(s) for this is not fully understood, but may reflect a change in pH caused by the heat treatment.

For those samples containing sulfonic acid (i.e., Figures 6, 7, and 8), the amide carbonyl band near 1,655 cm⁻¹ diminishes and eventually diminishes during heat treatment, as the amide functionality is oxidized. As the amide carbonyl diminishes, a complementary carboxylate salt band near 1,565 cm⁻¹ grows; this band is indistinguishable from the carboxylate salt band observed in polyacrylate salt type products (i.e., K732). As the SA component is degraded, the primary sulfonate salt asymmetric SO₃ stretch band near 1,195 cm⁻¹ shifts to an approximately 15 cm⁻¹ higher frequency. The position of asymmetric SO₃ stretch band near 1,047 cm⁻¹ is essentially unchanged. However, the relative intensity of this band is somewhat less in heat-treated samples than in the untreated samples.

The spectra in Figure 8 indicate that the majority of the thermal degradation occurred after only 4 hr. Furthermore, the greater thermal stability of K781 vs. CASN is evident by comparing the spectra in Figures 8 and 7, respectively.
Figure 8: FT-IR Spectra of K781 before and after Thermal Stress (200 ºC for 4 & 20 hr)

Summary

The results of the investigation discussed herein lead to the following observations:

- All polymers undergo some degradation under the conditions employed in this study.
- Before heat stress, the co- and terpolymers provide significantly better iron oxide dispersion than the homopolymers. However, after heat stress, K781 is clearly a better overall iron oxide dispersant than the co- and terpolymers tested. Iron oxide dispersion data also suggest that heat treatment of all the homopolymers tested does not significantly degrade their performance.
- As calcium HAP dispersant, K781 provides the best performance before thermal stress and is superior to the other polymers tested after thermal stress.
- Heat stress testing data indicate that homopolymers lost slightly less MW than terpolymers which lost less MW than copolymers.
- The FT-IR and NMR analysis of the polymers exposed to heat treatment reveal that the SA containing copolymers and SA and CASN containing terpolymers underwent more severe degradation than terpolymer containing SS (K781).

When selecting deposit control polymers as components of boiler water treatment programs it is important to understand the operating conditions of the system and the thermal stability of the polymers. Operating conditions such as boiler pressure (or temperature), residence time, pH, and polymer dosage should be part of the deposit control polymer selection criteria.

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References


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