The Impact of pH and Protonation State on Scale Inhibitor Activity

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ABSTRACT

Water treatment chemists have long observed that some scale inhibitors work better at high pH rather than low pH, and that some inhibitors have little, if any activity at very low pH. Examples would be the effectiveness of polyacrylic acid at high pH as a calcium carbonate inhibitor, as in ash sluice and some mining applications, mediocre performance near a neutral pH, as in cooling water applications, and very low activity in an acid pH range, as in gypsum control in the pH range from 2 to 4. This paper provides a framework for evaluating relative inhibitor activity using dissociation profiles for common inhibitors and calculating the distribution of inhibitor species versus pH. Minimum effective dosages and inhibitor species concentrations are used to calculate the relative efficacy of different dissociation states for common technical grade scale inhibitors.

BACKGROUND

The impact of pH and protonation state on treatment efficacy is observed in many areas of water treatment. Chlorination provides an example with the protonated form of hypochlorous acid being observed to have much more biocidal activity than the dissociated hypochlorite form. Adsorption studies of inhibitors used as squeeze treatments in oil field applications provide another example of the efficacy of dissociated versus protonated inhibitor forms (Breen 1990). In some cases, such as bromination, the impact of dissociation state on efficacy is arguably negligible.

Similar observations have been made concerning the impact of pH and protonation state on efficacy in the case of scale inhibition by phosphonates and polymers, (Griffiths, 1979, Ramsey, 1985, Tomson, 2002, Hunter, 1993).

Understanding the impact of pH upon the relative efficacy of an inhibitor can be key to providing the optimum inhibitor dosage and in assuring that the minimum effective active inhibitor is present.

In the simplest case, a simple inhibitor may have almost 100% in a pH range where it is almost completely dissociated, and close to 0% efficacy in a pH range where the inhibitor is almost completely protonated. This scenario has been reported for simple phosphonates such as HEDP (1-hydroxyl ethylidene-1,1-diphosphonic acid). Profiles comparing the protonation state and inhibitor efficacy for the simple phosphonates indicate that the final dissociation constant (pKa) is controlling with minor, if any, contribution from lower dissociation states.

In a more complex case, such as HDTMPA (hexamethylene diamine-tetra(methylene phosphonic) acid), the various protonation states appear to have significant efficacy, so their combined efficacy is greater than might be expected based upon experience with a simpler inhibitor.

Griffiths et al developed dissociation profiles for common phosphonates and compared them to inhibition studies over the same pH range. They summarized their laboratory results for simple phosphonates as follows:

"The general trend … is an improvement in performance with increasing pH. The improvement runs parallel to the titration curve with full activity occurring only at a pH value that approaches the final phosphonic acid pKa value." (Griffiths, 1979)

Figures 1, 2 and 3 profile the protonation state (fraction) for the phosphonates HEDP, ATMP (amino tris(methylene phosphonic) acid), and HDTMPA versus pH.

Figure 1: HEDP Distribution of Species

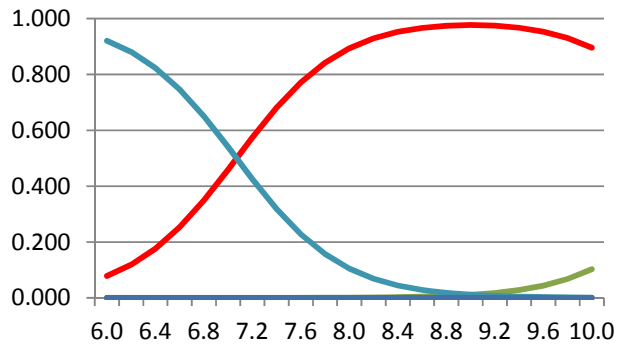


Figure 2: ATMP Distribution of Species

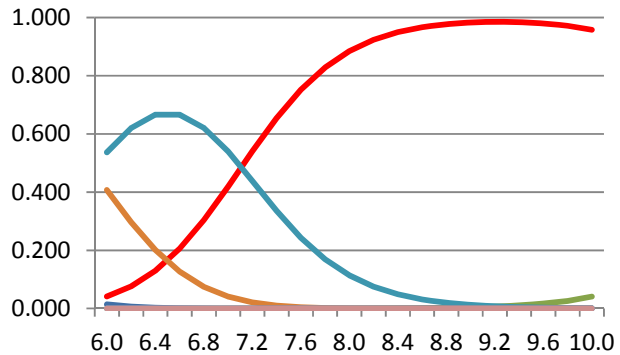
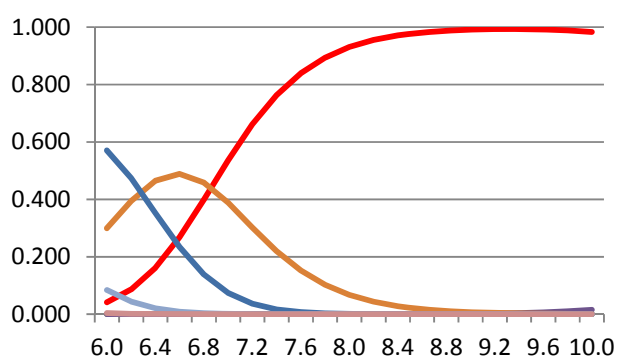
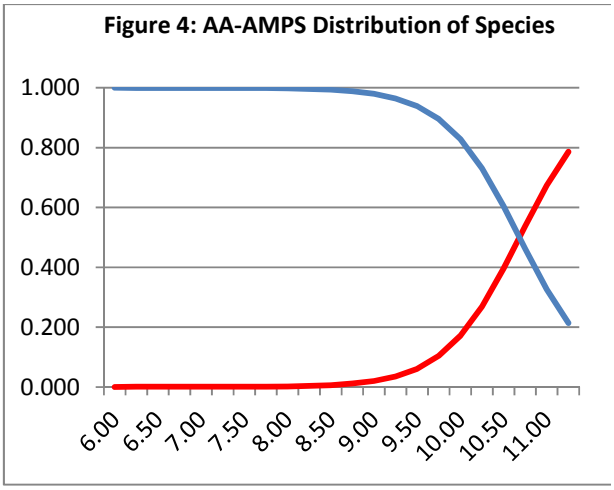


Figure 3: HDTMPA Distribution of Species





pH has a similar impact on polymer dosages for scale inhibition. The first time the author encountered the need to correct the dosages and models for speciation was in the development of a model for calcium phosphate scale inhibition by AA-AMPS (copolymer of acrylic acid and 2-acrylanmido-2-methylpropanesulfonic acid).

The data of minimum effective dosage versus saturation ratio and temperature was developed at four (4) distinct pH in the cooling water range of 7.5 to 9.0 . Four distinct scatter plots resulted from the first model attempted:

Equation 1 **Dosage = f(SR,time,temperature)**

Where

- SR is the ion association model saturation ratio for tricalcium phosphate;
- dosage is the active AA-AMPS concentration in the test solution;
- temperature is the absolute temperature; and
- time is the last time before failure.

Adding pH to the parameters modeled reduced the scatter plot to one zone. pH had a negative coefficient, indicating that dosage, when treated independently of saturation ratio, decreased with increasing pH (Ferguson, 1993). The pH factor in this case followed the dissociation fraction and corrected for the speciation at the various pHs studied.

Figure 4 profiles the distribution of species for an AA-AMPS copolymer.

APPLICATION

A knowledge of inhibitor speciation and activity versus pH is useful in selecting and matching inhibitors to a specific application, for developing performance test experimental design to develop inhibitor performance models against specific scales, and for optimizing dosages.

Selecting Inhibitors: A knowledge of dissociation profiles is useful in selecting inhibitors for an application. For a low pH application, select an inhibitor with a low pKa, preferably below, or within the pH range for the application. This assures that the maximum amount of inhibitor will be in the active form in the application pH range.

Optimizing Dosages: Tomson et al (Tomson, 2002) recommend the use of a factor to correct dosage models for the active specie concentration expected. They incorporated the correction into models for minimum effective dosage. For example, if the minimum effective dosage calculated from a model is $\mathbf{D_{min}}$, and the alpha (fraction) for

the final dissociation species is **α**, the use dosage is D_{use}, the use dosage would be:

Equation 2 $$D_{use} = D_{min} / \alpha$$

For a optimized dosage D_{min} of 1.0 mg/L and a dissociation fraction **α** of 0.8:

$$D_{use} = 1.0 / 0.8 \text{ or } 1.25 \text{ mg/L}$$

This method provides a simple, reasonably conservative, approach to correcting for active species versus total inhibitor concentration. It assumes that the final dissociation species is the only active material.

Developing New Models: Ideally, the experimental design for developing inhibitor models (Ferguson, 1992) would allow the researcher to calculate the relative efficacy of each inhibitor form in relation to the final dissociated form. An experimental design with a broad range of pH and saturation ratio would allow the researcher to calculate the relative efficacy for each significant specie from the inhibitor dissociation profile.

Once the relative efficacies were calculated, the dosage model would expand to:

Equation 3

$$D_{use} = D_{min} / (\alpha_1 * eff_1 + \alpha_2 * eff_2 + \ldots \alpha_n * eff_n)$$

This equation reduces to equation 2 when only the final dissociated form is significant.

SUMMARY

pH can affect the efficacy of scale inhibitors. Some species of inhibitors are more active than others. The dissociated form, at the highest pH, tends to be the active specie.

FURTHER WORK

Laboratory studies are planned to develop dissociation profiles for commercial phosphonate and polymeric scale inhibitors, followed by inhibitor optimization studies over a broad pH range. The objective of the application research is to quantify the impact of pH on the efficacy of commercial inhibitors, with initial tests studying $BaSO_4$, $CaSO_4$, and $CaCO_3$ inhibition. This paper provides background information and the rationale for the work.

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