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## Degradation of Phosphonate-Based Scale Inhibitor Additives in the Presence of Oxidizing Biocides: “Collateral Damages” in Industrial Water Systems

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**Abstract:** Organic, phosphorus-based additives are commonly used in water treatment technologies such as mineral scale and corrosion inhibitors, and dispersing agents. Phosphonates find extensive use as anti-precipitation inhibitors for sparingly soluble salts such as calcium carbonates and phosphates, calcium/barium/strontium sulfates and others, commonly formed in supersaturated process waters in a wide spectrum of industrial applications. In open recirculating cooling water systems strong oxidizing biocides (eg.  $\text{ClO}^-$ ,  $\text{BrO}^-$ , etc.) are also added to control microbiological growth but have detrimental effects on other water treatment chemicals that are sensitive to oxidative degradation. In this paper we report the effect of a hypobromite-based biocide towards the scale inhibitor AMP (amino-*tris*-(methylene phosphonate)). AMP reacts rapidly with the biocide at room temperature. AMP degradation continues, but it slowly reaches a plateau after 1000 minutes. Even after 50 h the reaction time, only 20% of AMP has decomposed. AMP reacts with the biocide to give the orthophosphate much more rapidly at 43°C than at 25°C due to faster kinetics of decomposition. Results on various other oxidizing biocides on PBTC (2-Phosphonobutane-1,2,4-Tricarboxylic acid) are also presented. PBTC is a very “robust” scale inhibitor. This is confirmed by our degradation studies using biocides such as chlorine ( $\text{ClO}^-$ ), bromine ( $\text{BrO}^-$ ), their stabilized analogs, BCDMH, and

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$\text{ClO}_2$ . Degradation (reversion to orthophosphate) of only up to 5% is observed in our experiments. These results are compared to others reported in the literature showing that PBTC degradation can be up to 25% under “harsher” conditions of higher biocide dosage and temperature. PBTC is virtually stable to the effects of a variety of oxidizing microbiocides, including chlorine, bromine and others.

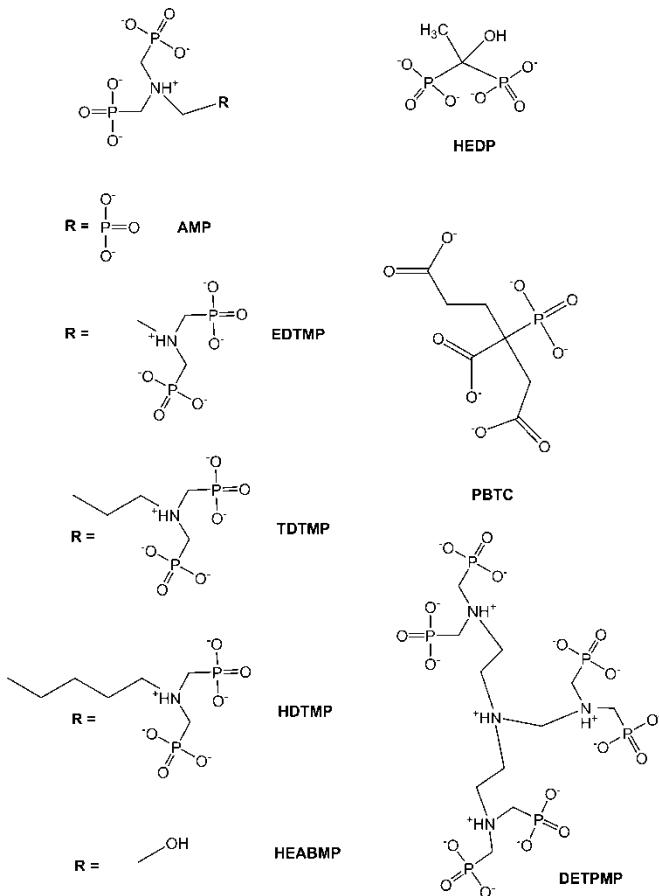
**Keywords:** Oxidizing biocides, water treatment, phosphonates, scale inhibitors, degradation, disinfection

## INTRODUCTION

Water is the universal cooling medium used for industrial cooling because of its cost-effectiveness and its high heat capacity (1). Industrial cooling water systems are the major users of water to support other functions. Cost considerations impose water recycling and reuse. Among the numerous operational challenges they face, is the precipitation and deposition of sparingly soluble salts from supersaturated streams (2). Such undesirable deposition issues can be avoided with the careful application of chemical water treatment approaches (3).

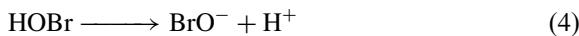
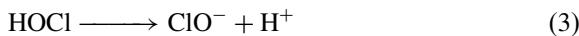
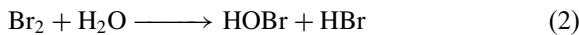
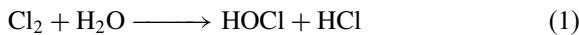
Phosphonates act as scale inhibitors by adsorbing onto specific crystal nuclei surfaces of insoluble salts, thus poisoning further crystal growth (4). They usually contain multiple phosphonate groups ( $\text{R}-\text{PO}_3\text{H}_2$ ,  $\text{R}$  = organic chain) most commonly found in their deprotonated form, due to the particular pH range of operation. Aminomethylene phosphonates (containing the  $\text{N}-\text{CH}_2-\text{PO}_3\text{H}_2$  moiety) in particular are used extensively in cooling water treatment programs (5), oilfield applications (6), and corrosion control (7). AMP (amino-*tris*-(methylene phosphonate)) is one of the most common aminomethylene phosphonates and a very effective scale inhibitor (8). Schematic structures of some aminomethylene phosphonate scale inhibitors are shown in Fig. 1.

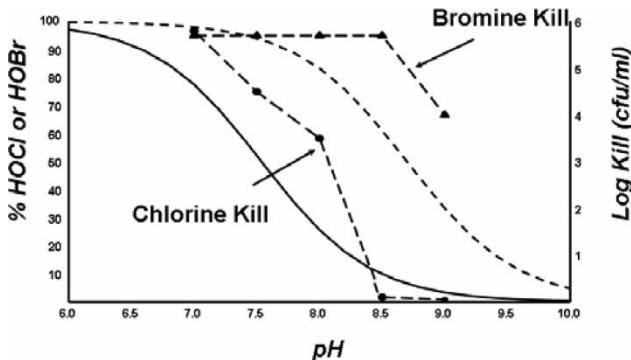
A drawback of certain scale inhibitors, such as HEDP (Hydroxyethyllydene-1,1-diphosphonate), AMP, as well as other aminomethylene phosphonates (see Fig. 1) is their sensitivity to oxidizing microbiocides, such as chlorine or bromine-based biocides, necessary to control microbiological growth (9). Orthophosphate ( $\text{PO}_4^{3-}$ ), one of the degradation products, can cause calcium phosphate scale deposition in high hardness process waters (10). Phosphonate degradation also results in inhibitor depletion from solution. Knowledge of this susceptibility to oxidizers may help water system operators on decisions regarding which phosphonate additive to apply, at what dosage level, and for how long. The most common biocidal species in water are hypochlorous acid ( $\text{HOCl}$ , if gaseous chlorine is used as the biocide) and hypobromous acid ( $\text{HOBr}$ , for brominated water). These



**Figure 1.** Chemical structures of some organophosphonate scale inhibitors. Abbreviations are as follows: AMP amino-tris-(methylenephosphonate), HEABMP 2-hydroxyethyl-amino-bis(methylenephosphonate), EDTMP ethylene-diamine-tetrakis(methylene-phosphonate), TDTMP tetramethylenediamine-tetrakis(methylene-phosphonate), HDTMP, hexamethylenediamine-tetrakis(methylene-phosphonate), PBTC 2-phosphonobutane-1,2,4-tricarboxylate, HEDP hydroxyethylidene-1,1-diphosphonate, DETPMP, diethylenetriamine-pentakis(methylenephosphonate).

are the species that provide the real biocidal performance. The simple chemistry that takes place is described by the following equations:





**Figure 2.** Availability of HOCl and HOBr and their effectiveness vs. pH (left y-axis). The right y-axis indicates the reduction in cell viability as measured by the colony-forming units (CFU) per volume unit (mL). This figure is courtesy of the Nalco Co.

While hypochlorite and hypobromite are effective biocides, they can be up to two orders of magnitude less effective than their acid forms (11). Therefore, as indicated by Fig. 2, biocidal activity drops as pH increases, supporting the fact that HOBr is much more effective at high pH than HOCl. Therefore, effective biocontrol by HOCl can only be achieved if system pH is below 7. However, most small-size cooling systems operate at pH  $>8.5$ , which makes HOCl an unsuitable choice of biocide. For such systems HOBr is the obvious choice, as cell kill is still at a 100% at pH 8.5. The dissociation constants at 25°C for HOCl and HOBr are  $3.98 \times 10^{-8}$  and  $1.58 \times 10^{-9}$ , respectively (12, 13).

Phosphonate degradation by oxidizers, therefore, can be viewed as a “collateral damage” of the disinfection process. Knowledge of phosphonate stability is necessary for complete control of scale, corrosion, and microbiological growth. There are several cases reported from the field on mineral salt deposition, even though it was thought that inhibitor levels were thought to be adequate. The reason for this is that the true inhibitor levels were much lower than initially thought because of inhibitor degradation by the oxidizing biocide. This degradation can create an additional problem. Inorganic phosphate, the ultimate degradation product of phosphonates, can initiate calcium phosphate precipitation in high hardness waters.

## EXPERIMENTAL METHODS

### Materials

Deionized water was used for all experiments. Materials were obtained from commercial sources. AMP (Dequest 2000, in acid form, 50% in water) was

obtained from Solutia UK, Newport, United Kingdom and was used as received with no further purification in order to better simulate conditions in real cooling water systems. The hypobromite-based biocide is a proprietary product from the Nalco Company, Naperville IL, U.S.A. and was used as received (14).

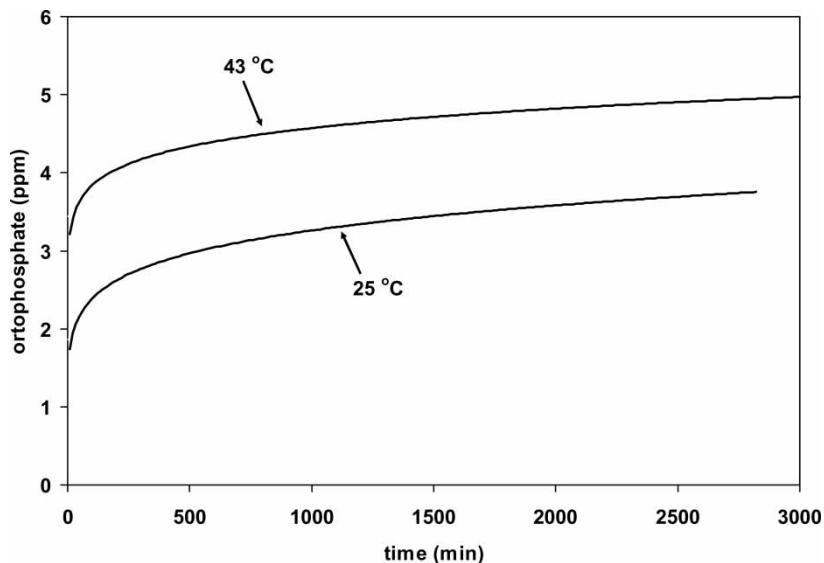
### Phosphonate Degradation Study

The following procedure is employed to study the decomposition chemistry of AMP by the biocide. A solution (500 mL) is prepared that contains  $\text{Ca}^{2+}$  (400 ppm as  $\text{CaCO}_3$ ),  $\text{Mg}^{2+}$  (200 ppm as  $\text{CaCO}_3$ ),  $\text{HCO}_3^-$  (300 ppm as  $\text{CaCO}_3$ ) and AMP (20 ppm as actives). This solution is placed in a glass beaker and pH is adjusted to 8.0. Then, an amount of biocide (7.5 mL of a 1000 ppm solution) is added with concomitant pH increase to  $\sim 8.6$ . This corresponds to 15 ppm biocide expressed as "ppm  $\text{Cl}_2$ ". The pH is finally adjusted to 9.0 by addition of dilute NaOH solution. The final solution is maintained under continuous stirring at ambient temperature. Samples (30 mL) are withdrawn at time intervals as follows:  $t = 0$ , 10 min, 30 min, 45 min, 75 min, 2 h, 3.5 h, 5 h, 22.5 h, 29 h, and 46 h. A sufficient quantity of the sample is withdrawn and used to test for residual free and total halogen by an established procedure (15). The remainder is quenched with ascorbic acid (to deactivate the remaining halogen by chemical reduction) and is analyzed for orthophosphate by the phosphomolybdate spectrophotometric method (16). The above procedure is repeated, except that the reaction container is maintained at a constant temperature of  $43^\circ\text{C}$  in a thermostated water bath. Similar sampling procedures are employed.

### Results and Discussion

Two different temperatures are tested,  $25^\circ\text{C}$  and  $43^\circ\text{C}$ , and results are shown in Fig. 3 and 4. The choice for these temperatures was based on the premise that the lower temperature ( $25^\circ\text{C}$ ) is representative of "cold" water, whereas the higher temperature ( $43^\circ\text{C}$ ) represents the cooling water that has gone through a cooling cycle. It is a common temperature for cooling waters in contact with a heat exchanger. The biocide is added in relatively large excess in order to "stress" the system in the oxidant. It should be noted that in industrial cooling systems a residual of 0.5 to 1.0 ppm biocide is maintained at all times. However, overdose upsets are a common phenomena and this is the reason why an exaggerated biocide dosage is selected in our studies.

AMP reacts with the biocide at room temperature immediately, producing  $\sim 1.5$  ppm orthophosphate (Fig. 3). AMP degradation continues



**Figure 3.** Decomposition of AMP to orthophosphate as a function of time at 25°C and 43°C.

rapidly, but it slowly reaches a plateau after 1000 minutes. Even after 50 h of reaction time, only 20% of AMP has decomposed. AMP reacts with the biocide to give orthophosphate much more rapidly at 43°C than at 25°C due to the faster kinetics of decomposition. Examination of Fig. 4 reveals that organic phosphonate consumption is consistent with biocide consumption (Figs. 5 and 6) and orthophosphate production. Figures 5 and 6 support the conclusion that essentially all biocide is in its “free” form.

The degradation of AMP in the presence of O<sub>2</sub> and Mn<sup>2+</sup> has been recently reported (17, 18). A radical mechanism was suggested that leads to the generation of orthophosphate and iminobis(methylenephosphonate), that is similar to AMP but without the third methylenephosphonate arm.

There are literature reports that support the premise that the C-P bond is stable towards hydrolytic cleavage and oxidative and thermal decomposition.(19, 20) In addition, rapid radical-based dephosphorylation of phosphonates has been reported upon biodegradation by *Escherichia coli* (21). Our results are consistent with literature that the C-P bond of aminopolyphosphonates is susceptible to rapid oxidative cleavage in the presence of oxidizers. Orthophosphate in our experiments is produced only by the C-P bond cleavage. Direct conclusions about potential cleavage of the C-N bond cannot be drawn at this point because other possible by-products of this reaction were not measured. However, organic phosphorus measurements presented in Fig. 4 give interesting clues. If only one C-N bond was cleaved

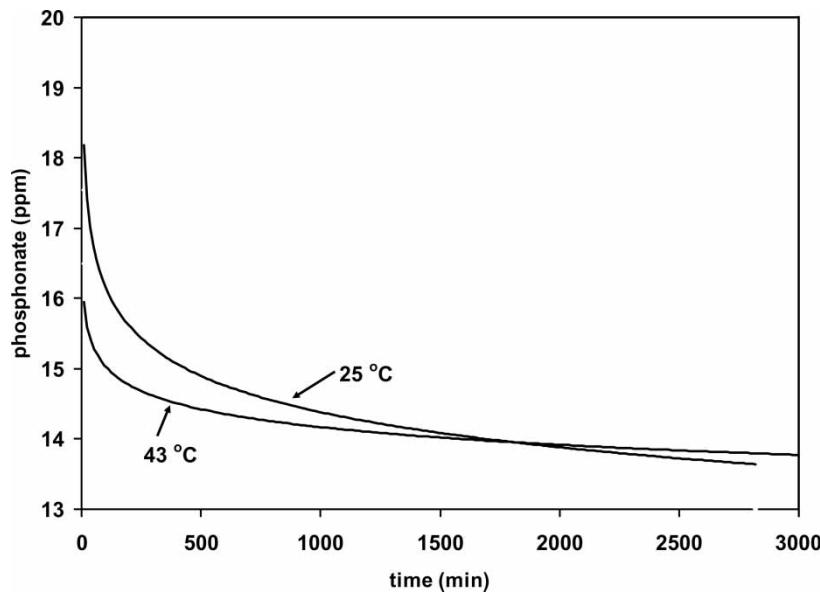


Figure 4. Degradation of AMP as a function of time at 25°C and 43°C.

(but not a C-P bond), the possible product would have been one methyl phosphonate molecule and one amino-*bis*-(methylenephosphonate) molecule. In the case of the cleavage of two C-N bonds (but not of any C-P bonds) the possible products would have been two methyl phosphonate molecules and one amino-

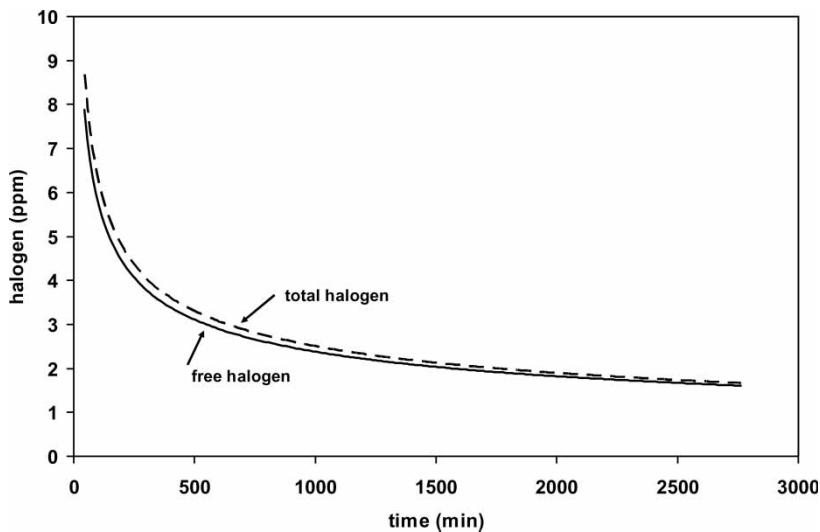


Figure 5. Halogen consumption as a function of time at 25°C.

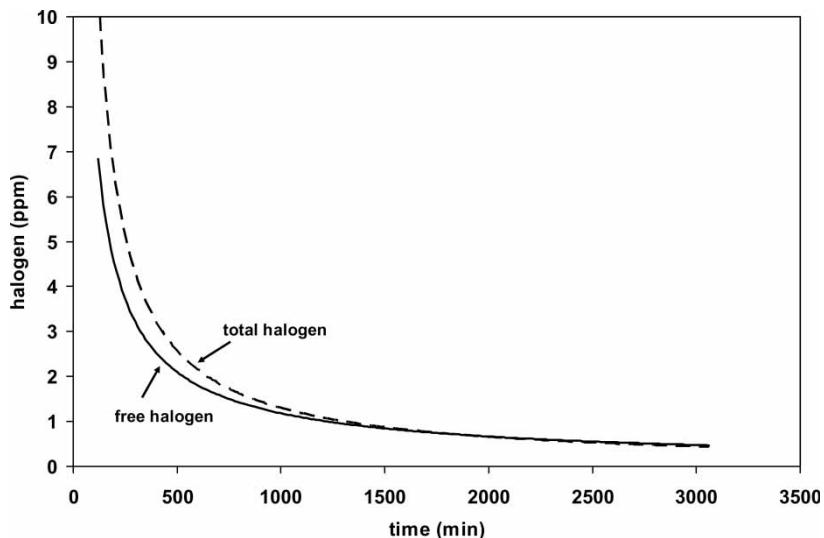
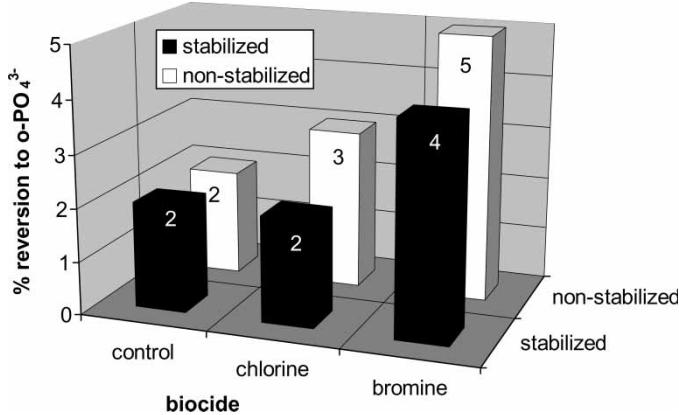


Figure 6. Halogen consumption as a function of time at 43°C.

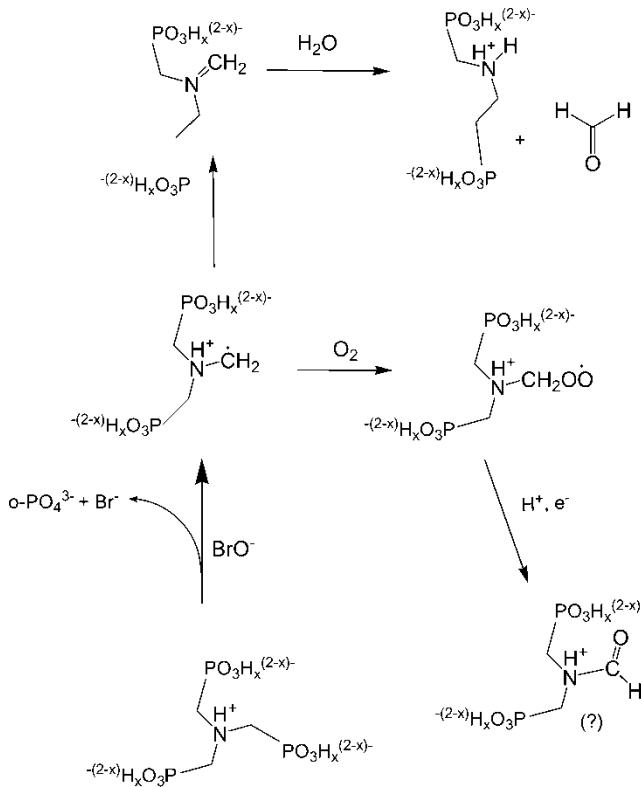
methylenephosphonate molecule. Finally, if all three C-N bonds are broken (with no C-P bond rupture) the possible products would have been three methyl phosphonate molecules and one ammonia (most likely  $\text{NH}_4^+$ ) molecule. In all three possible cases mentioned above, the products are organic phosphonates that possess a P-C bond. Therefore, analytical measurements of organic phosphate would have shown an unchanged level of organic phosphate since  $t = 0$ , i.e. 20 ppm. However, the fact that organic phosphate levels are reduced with time, together with the observation that orthophosphate is being generated as well, is convincing evidence that the C-P bond is ruptured.

At this point scission of the C-P bond without rupture of the C-N bond cannot be ruled out. If that were the case, orthophosphate and trimethylamine would have been the possible products. Trimethylamine detection experiments were not carried out at this time.

In contrast to the sensitivity of aminomethylene phosphonates, there are other additives—mixed carboxyphosphonates that show remarkable resistance to oxidizers. Recently, we reported the insensitivity of 2-Phosphonobutane-1,2,4-tricarboxylate (PBTC) towards a variety of oxidizing biocides such as chlorine, bromine, hypochlorite, and others, and does not decompose to any appreciable extent, at least at “normal” biocide dosage (Fig. 7) (22). PBTC is virtually immune to biocides. The biocide level used in these experiments (5 ppm) is considered to be rather high. Even under these “high stress” oxidizing conditions, PBTC does not undergo any appreciable decomposition.



**Figure 7.** PBTC degradation by chlorine (HOCl) and bromine (HOBr) and their stabilized analogs (adapted from data reported in reference 22).



**Figure 8.** Proposed decomposition pathways for AMP based on oxidative degradation by  $\text{BrO}^-$ .

Vaska and Go have studied the effects of various biocides on PBTC (23). Their results indicate a more pronounced decomposition of PBTC. This occurs because of the following reasons: (a) The reaction time is longer (2 h vs. 1 h) than our experiments (b) The reaction temperature is much higher (70°C vs. 25°C) (c) Biocide levels are significantly higher (d) The reaction pH is somewhat lower (8.0 vs. 8.3). This affects effectiveness of hypochlorite, which functions more effectively in lower pH regions.

Decomposition of HEDP (Fig. 1) by  $\text{ClO}^-$  is sensitive to cations present in solution (24). HEDP is more sensitive to oxidation than AMP, but this observation cannot be explained on the basis of the structures of the two phosphonates because they present profound structural differences (see Figure 1). Figure 8 presents possible degradation pathways of AMP. These are consistent with literature reports and the results presented herein.

## CONCLUSIONS

AMP is susceptible to partial oxidative decomposition by the bromine-based biocide tested. AMP is not degraded completely, but only to a ~20% level (at 25°C) and up to a ~25% level (at 43°C). Therefore, use of AMP in combination with the specific biocide can be recommended on the basis of the present results.

There is intense research on the design, synthesis, and applications of an “ideal” scale inhibitor. Prevention of the inhibitor oxidative degradation may lead to a better and more economical control of a chemical water treatment program. Knowledge of the actual inhibitor level in the bulk water is very important. This is achieved by close and careful monitoring of the phosphonate level frequently. Lastly, industrial water operators need to know the sensitivity of a given inhibitor to various oxidative biocides, as this will dictate the choice of the scale inhibitor or biocide.

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