

Mechanistic Modeling of Anaerobic THPS Biocide Degradation Under Alkaline Conditions

KAILI ZHAO, JIE WEN, AND TINGYUE GU, *Ohio University, Athens, Ohio*
 ARDJAN KOPLIKU, *BP America, Inc., Houston, Texas*
 IVAN CRUZ, *Saudi Aramco, Dhahran, Saudi Arabia*

This article presents a mechanistic model based on experimental data to predict THPS (tetrakis hydroxymethyl phosphonium sulfate) degradation in seawater as a function of time, temperature, and pH.

Microbiologically influenced corrosion (MIC) is increasingly becoming a significant problem in the oil and gas industry because of enhanced recovery and aging equipment. Apart from pigging of pipelines, mitigation of MIC relies mostly on biocides. Seawater, used regularly for seawater injection in production, is also routinely used for hydrotesting. The water used for hydrotesting is usually treated, typically with biocides. Even treated seawater, however, can be a source of sulfate-reducing bacteria (SRB) inoculum, according to Sanders.¹ THPS (tetrakis hydroxymethyl phosphonium sulfate) is a popular biocide used in oil-field operations because it is environmentally green and relatively easy to handle. THPS vendors recommend acidic pH for its use.² Corrosion engineers, however, prefer not to accept pH < 7, especially for hydrotesting.

THPS can easily degrade to THPO (trihydroxymethyl phosphine oxide), a process facilitated by hydrolysis, oxidation, photo-degradation, and biodegradation. Equation (1) shows the THPS chemical structure and its two major degradation products.³⁻⁴

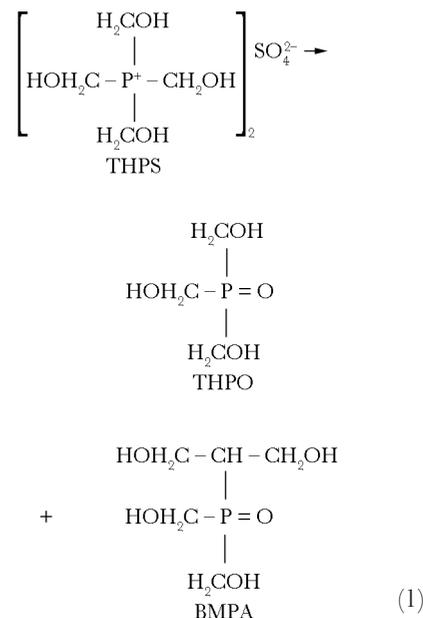


TABLE 1

Test matrix for THPS degradation investigation in the presence of mild steel

Test Conditions	
Test Media (All Sterilized)	Initial pH after THPS was Added
1. Persian Gulf seawater	8.12
2. pH-adjusted Persian Gulf seawater at low pH	6.06
3. pH-adjusted Persian Gulf seawater at high pH	9.33

Notes: Initial THPS concentration was 160 ppm. Media were tested at 4, 23, 31, and 37 °C.

THPS degradation has been studied by several researchers.^{3,5-8} Unfortunately, almost all the THPS degradation data in the literature are for acidic or neutral pH. Usually, a minimum of 50 or 100 ppm THPS is needed to prevent planktonic bacterial growth and biofilm establishment. A much higher concentration is needed to treat established biofilms.

Because of THPS degradability, it is important to predict residual THPS concentration to ensure a desired minimum after a certain period of time without an excessively high initial concentration. This article presents a mechanistic model based on experimental data to predict THPS degradation as a function of time, temperature, and pH. The model is aimed at alkaline pH under which THPS degrades much faster than under acidic pH.

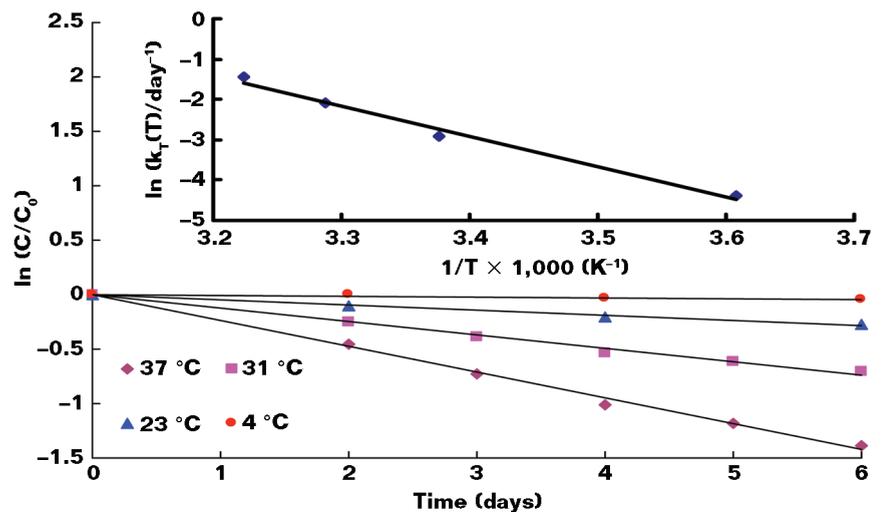
Experimental Methods

All tests were carried out using 100-mL serum bottles. Test media were deoxygenated by N₂ sparging before use and sterilized in an autoclave. Each bottle contained an X65 pipeline steel coupon with dimensions of 1.87 by 0.43 by 0.06 in (47.5 by 10.92 by 1.52 mm). The coupon surface area to liquid volume ratio was set close to that in 12-in (0.3-m) inside diameter (ID) pipes. Natural seawater was used together with artificial seawater. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) solutions were used for pH adjustment. An assay kit (CODE 8776†) from the LaMotte Co. was used to measure THPS concentration.

Results and Discussion

Table 1 shows a test matrix using Persian Gulf seawater with different initial pH values at different test temperatures. When pH was fixed as shown in Figure 1 using pH 8.1 as an example,

FIGURE 1



THPS degradation at pH 8.1 and the change of specific reaction rate $k_r(T)$ with temperature in Persian Gulf seawater.

THPS degradation was found to follow the first-order kinetics and the relationship between the specific reaction rate $k_r(T)$ and temperature follows the Arrhenius equation.

The effect of pH on THPS degradation initially appeared to be quite complicated. During the first two or three days after the introduction of THPS into seawater, pH shifted but it then became quite stable.⁹ This could be due to the slow-acting buffering power of the seawater. When the stable pH values were used to explore the pH impact on THPS degradation, a definitive trend was revealed. Figure 2 shows the pH effect on k at different temperatures. All the lines

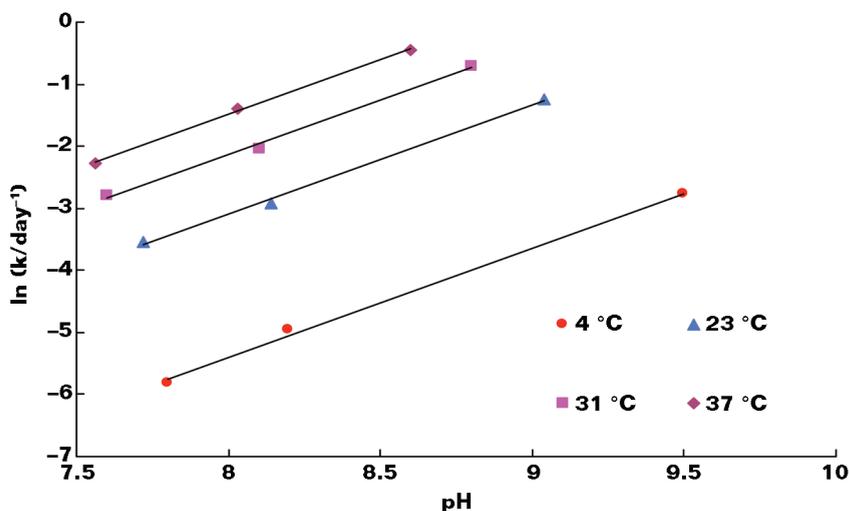
are surprisingly straight and parallel to each other. This suggests a linear relationship of $\ln k \propto \text{pH}$ with a slope that is independent of temperature. Based on the definition $\text{pH} = -\log_{10} [\text{H}^+]$, the $\ln k$ vs. pH relationship now translates to a proportional relationship of $k \propto [\text{H}^+]^{-n}$, in which the parameter n (that is equal to slope 2.303 in Figure 2) is positive. Because n is independent of temperature, we may use $k(T, \text{pH}) = k_r(T) \cdot [\text{H}^+]^{-n}$, where $k_r(T)$ is the rate constant with a fixed pH.

The first-order kinetics equation for THPS concentration can be modified to include $[\text{H}^+]$ as shown in Equation (2).

$$-\frac{dC}{dt} = k(T, \text{pH}) \times C = k_r(T) \times [\text{H}^+]^{-n} \times C \quad (2)$$

†Trade name.

FIGURE 2



The relation of $k(T, \text{pH})$ with pH at four different temperatures in Persian Gulf seawater.

This shows that the effect of pH can be viewed as proton inhibition of THPS degradation. In terms of reaction kinetics, $[\text{H}^+]$ appears in the rate expression as a negative order ($-n$) of reaction. Equation (2) can be reformulated using a linearized Arrhenius equation to obtain Equation (3).

$$\ln k(T, \text{pH}) = \ln k_r(T) - n \times \ln [\text{H}^+] = \ln A - \frac{E}{R \times (T + 273.15)} + 2.303n \times \text{pH} \quad (3)$$

where E and A are activation energy and frequency factor, respectively. The universal gas constant $R=8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. Equation (2) shows a linear relationship of $\ln k$ vs. $1/T$ and pH with A , E , and n as correlation parameters.

Table 2 lists $k(T, \text{pH})$ data obtained from Table 1 at different pH values and different temperatures in Persian Gulf seawater. The pH values in Table 2 were stabilized pH values. Multi-linear regression of the data in Table 2 using

MATLAB[†] Version 7 software quickly yielded $A = 3.10 \times 10^7$, $E = 8.448 \times 10^4 \text{ J}\cdot\text{mol}^{-1}$, and $n = 0.76$. The R^2 value of the multi-linear regression is 0.998. With the $\ln k(T, \text{pH})$ function known, Equation (2) can be solved with the initial THPS condition $C = C_0$ at $t = 0$ to give THPS concentration as a function of temperature (in °C) and pH and time (in days) as shown in Equation (4).

$$\ln\left(\frac{C}{C_0}\right) = -k(T, \text{pH}) \times t = -3.10 \times 10^7 \times \exp\left[\frac{-10,161}{T + 273.15}\right] \times \exp(1.75 \times \text{pH}) \times t \quad (4)$$

Table 3 compares the model prediction with experimental data at 31 °C with three different pH values. Table 3 also shows experimental data of THPS degradation in another two test media, Gulf of Mexico seawater and artificial seawater, which were also used to test the model. The results show that the model fit the experimental data with coupon

presence very well. This demonstrates the robustness of the mechanistic model. The presence of mild steel accelerated THPS degradation as demonstrated by the slower THPS degradation at pH 8.1 without coupon presence (Table 3). The acceleration was most likely the result of THPS reactivity with mild steel as indicated by the pitting pattern in Figure 3 that was not observed in a control without THPS.

In our lab tests using the borosilica glass serum bottles, no appreciable ultraviolet degradation was observed under normal fluorescent lighting conditions. Persian Gulf seawater (that has salinity 1.6 times than that of the Gulf of Mexico seawater) and fresh water were used as test media to study the effect of salts on THPS degradation at 31 and 37 °C with a fixed stable pH of 6.3. After 10 days, it was found that the THPS degradation rate remained almost the same in seawater and fresh water at the same temperature and pH. The results showed that salts may have very little intrinsic effect on THPS degradation after pH is fixed. Salts may only affect THPS degradation by pH buffering, but such an effect is not intrinsic.

Conclusions

- THPS degradation follows the first-order kinetics. Our mechanistic model shows that it is strongly dependent on temperature and pH. THPS degradation increases with the increase of temperature and pH as well as the presence of mild steel, while salts have almost no intrinsic effect on THPS degradation.

TABLE 2

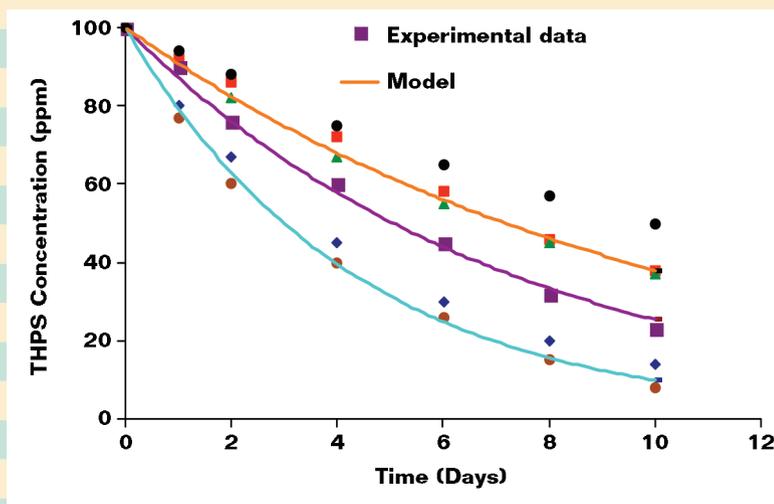
Data for multi-linear regression

Temperature (°C)	4	4	4	23	23	23	31	31	31	37	37	37
pH	7.8	8.2	9.5	7.72	8.14	9.04	7.6	8.1	8.8	7.56	8.03	8.6
$-\ln k(T, \text{pH})$	5.81	4.96	2.78	3.54	2.92	1.25	2.78	2.04	0.71	2.27	1.39	0.45

TABLE 3

Comparison of THPS degradation model predictions with experimental data (all model and experimental data involved coupon unless specifically indicated)

Input Parameters				
T (°C)	Time (Days)	C ₀ (ppm)	pH	Symbol
31	10	100	8.1	(In Persian Gulf seawater without coupon presence)
			7.9	(In artificial seawater)
			7.9	(In pH-adjusted Persian Gulf seawater)
			8.1	(In Persian Gulf seawater)
			8.4	(In pH-adjusted Gulf of Mexico seawater)
			8.4	(In pH-adjusted Persian Gulf seawater)



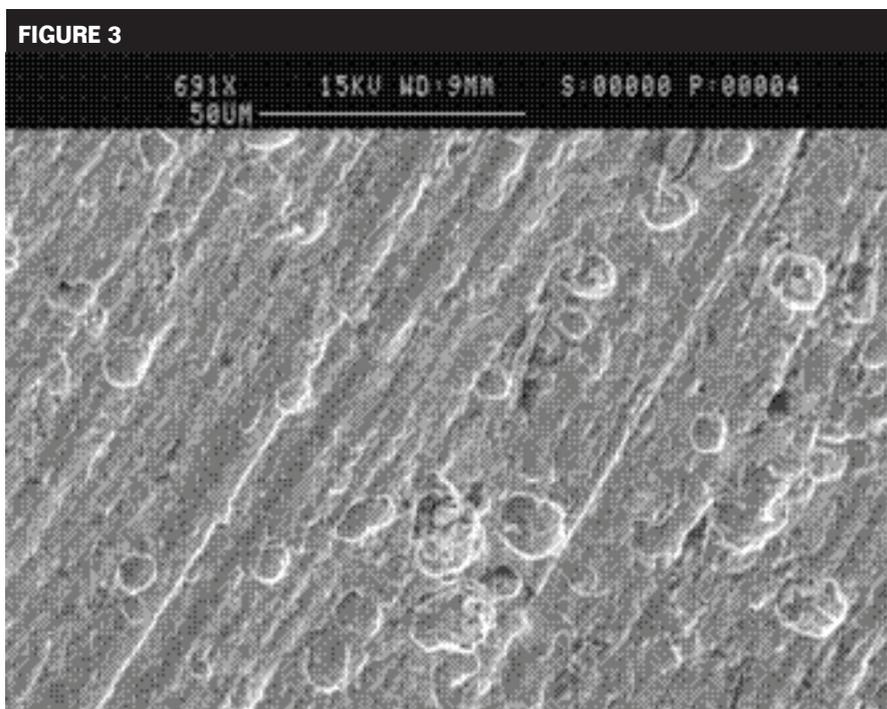
- pH effect can be decoupled from temperature. Experimental data indicated that proton acted as an inhibitor of THPS degradation in the form of a negative order reaction.

The proposed THPS degradation model is applicable to alkaline pH in the presence of mild steel with the fixed coupon size ratio to medium volume. It is recommended that future work should include the quantitative effects of mild steel, and other factors, like microbes and the presence of other treatment chemicals such as oxygen scavenger and corrosion inhibitor also need to be studied.

Acknowledgments

The authors would like to thank BP America and Saudi Aramco for their financial support of this work as part of a project and for their permission to present the results.

FIGURE 3



Scanning electron microscopy image of X65 coupon surface after acid cleaning (five-month test in Gulf of Mexico seawater with initial THPS 50 ppm at 4 °C).

References

- P.F. Sanders, "Overview of Souring, Corrosion and Plugging Due to Reservoir Organisms," U.K. Corrosion 98, paper no. 15 (Sheffield, U.K., Oct. 20-21, 1998).
- Rhodia, *Product Technical Data on TOLCIDE®PS75*, Issue No. 6, October 2004.
- WHO, "Flame Retardants: Tris(2-Butoxyethyl) Phosphate, Tris(2-Ethylhexyl) Phosphate and Tetrakis(Hydroxymethyl) Phosphonium Salts," *Environmental Health Criteria* 218, 2000, World Health Organization, Geneva, <http://www.inchem.org/documents/ehc/ehc/ehc218.htm>.
- "ACG Phase I—Supplementary Lenders Information Package, Executive Summary," April 2003, http://www.bp.com/liveassets/bp_internet/bp_caspian_en/STAGING/local_assets/downloads_pdfs/t/ACG_English_SLIP_Content_ACG_Phase_1_SLIP.pdf.
- G.R. Lloyd, "UV Degradation of THPS," Albright & Wilson U.K. Ltd., 1994, Specialties Technical Laboratory, Oldbury, U.K.
- J. O'Connor, "THPS: Determination of Hydrolysis as a Function of pH," Eye, 1992, Life Science Research Ltd., U.K.
- M. Gorman, "Anaerobic Aquatic Metabolism of 14C-tetrakis(hydroxymethyl) Phosphonium Sulfate (THPS): Final report," 1997.
- P. McWilliam, "Tolcide PS355A: Biodegradability in Seawater-Closed Bottle Test," 1994.
- K. Zhao, J. Wen, T. Gu, A. Kopliku, I. Cruz, "Mechanistic Modeling of Anaerobic THPS Degradation in Seawater Under Various Conditions," CORROSION 2008, paper no. 512 (Houston, TX: NACE, 2008).

This article is based on CORROSION 2008 paper no. 08512, presented in New Orleans, Louisiana.

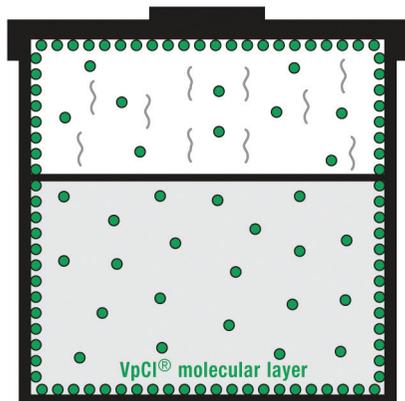
KAILI ZHAO obtained a Ph.D. in chemical engineering at Ohio University, Stocker Center, Athens, OH 45701. He also holds an M.S. degree in chemical engineering from Tianjin University, China. His corrosion research experience includes MIC in hydrotests using seawater, biocides and biocide enhancers for MIC mitigation, and MIC modeling. He has been a NACE International member for four years.

JIE WEN is a Ph.D. candidate in the Department of Chemical and Biomolecular Engineering at Ohio University, e-mail: jw205304@ohio.edu. He earned an M.S. degree in chemical engineering from Louisiana Tech University. He is a four-year member of NACE.

TINGYUE GU is an associate professor of chemical and biomolecular engineering and assistant director of the Institute for Corrosion and Multiphase Technology at Ohio University, e-mail: gu@ohio.edu. He has a Ph.D. in chemical engineering from Purdue University. He has published approximately 40 articles in 20 different peer-reviewed journals as well as one book, two encyclopedia articles, two handbook articles, and three book chapters. He is a member of the *Bioprocess & Biosystems Engineering* journal editorial board and is the primary creator of a MIC pitting progression prediction software based on a new mechanistic model. He is a five-year member of NACE.

ARDJAN KOPLIKU is a senior materials and corrosion engineer at BP America, Inc., 501 Westlake Park Blvd., Westlake 1, Houston, TX 77079, e-mail: ardjan.kopliku@bp.com. His primary areas of expertise are corrosion management, material selection and testing, failure analysis, risk assessment, and corrosion control. He is a company trainer in the area of material selection for well completions, subsea equipment, and surface (topside) facilities. Before joining BP in 2004, he served as a materials and corrosion engineer at ENI-E&P Division (formerly Agip) in Italy. He has a degree in physics from the University of Tirana, Albania, and a Ph.D. in materials engineering from the Polytechnic of Milan, Italy. He has published 26 papers, mainly on materials and corrosion in the oil and gas industry. A nine-year member of NACE, he is a member of ASM International and ASME.

IVAN CRUZ is a senior engineering consultant at Saudi Aramco, PO Box 6891, Dhahran, 31311, Saudi Arabia. Prior to joining the company in 1992, he was senior engineering advisor at the Mobil Exploration & Producing Technical Center in Dallas, Texas. He has extensive corrosion engineering experience in the oil and gas industry. He has a B.S. degree in chemical engineering and is a NACE-certified Corrosion Specialist, Materials Selection and Design Specialist, and NACE instructor. He received a 2007 NACE Distinguished Service Award. He has been a member of NACE for 32 years. *MP*



Cortec® Vapor phase Corrosion Inhibitors (VpCI®) 3-phase protection for liquid, interphase, and vapor contact.



VpCI® protected mild steel panel



Unprotected mild steel panel

Easily add VpCI® 3-phase, environmentally friendly Protection

Cortec® Patented VpCI® Technology gives you the building blocks to stop corrosion during system operation and shut-down/lay-up. You can easily add Cortec's VpCI® as liquid or powder to your current treatment program. They are ideal for both closed and open loop systems, providing a complete multi-metal corrosion inhibitor protection. An easy way to move to the new generation of water treatment, Cortec's VpCI® Technology replaces nitrites, amines, phosphonates, azoles, and other corrosion inhibitors. VpCIs are completely water-soluble, easy to formulate and stable in wide ranges of pH and hard water. For details, please call or visit:



www.CortecVCI.com
1-800-4-CORTEC
info@CortecVCI.com

White Bear Parkway, St. Paul, MN 55110 USA