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MECHANISTIC MODELING OF ANAEROBIC THPS DEGRADATION IN SEAWATER UNDER VARIOUS CONDITIONS

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ABSTRACT

Microbially influenced corrosion (MIC) is increasingly becoming a major problem in the oil and gas industry as well as in the water treatment industry. Currently, MIC mitigation mostly depends on biocides. THPS (Tetrakis Hydroxymethyl Phosphonium Sulfate) is one of the commonly used biocides because it is degradable and non-bioaccumulative in the environment. 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 remove established biofilms. THPS degradability, however, shortens its effectiveness in time. Prediction of THPS degradation is essential in proper dosing for operations such as hydrotesting. THPS degradation may be affected by many factors such as temperature, pH, O_2, light, presence of microbes and presence of mild steel. This work presents a mechanistic model，based on experimental data, to predict THPS degradation as a function of time, temperature and pH.

Keywords: MIC, Tetrakis Hydroxymethyl Phosphonium Sulfate, THPS, degradation, modeling

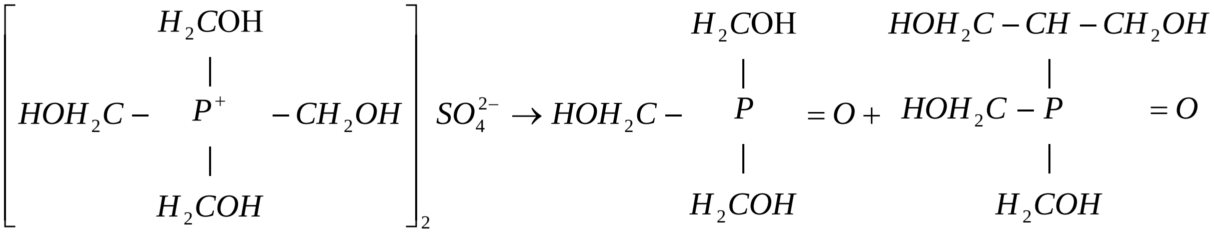
INTRODUCTION

MIC can cause damages such as corrosion of steel pipes and equipment, plugging of injection or disposal wells and souring of fluids and reservoirs[1]. Sulfate-reducing bacteria (SRB) are known as the culprits most frequently implicated in MIC of iron, copper and ferrous alloys[2, 3]. Currently, biocides are often used to mitigate the MIC during hydrotesting. Hydrotesting is a common practice to test pipeline for damage and to ensure the pipeline's integrity before it is commissioned. During hydrotesting, a pipeline is filled with water and pressurized to a pressure greater (usually 10% higher) than the anticipated future operating pressure. In general, hydrotesting itself lasts only eight to ten hours. However, quite often in the oil and gas industry, test water may remain in the system afterwards for a long period of time before it is discharged or transferred from one section to the next. During this holding time biofilm may establishment and corrosion can occur[4]. Poor or inappropriate hydrotesting practices can result in MIC that causes pitting attacks and also produces the so-called black powder leading to clogging problems[5]. Harmful biofilms established during hydrotest may contribute to MIC pitting attacks in future long term operations. Seawater is routinely used in the hydrotesting of subsea pipelines, and the other water sources such as aquifer water and produced water are also used sometimes. Any untreated water source for hydrotesting contains microorganisms. Natural seawater contains viruses, prokaryotes, protists (mainly flagellates) and algae[6]. The water for hydrotesting can be treated with biocide to avoid internal MIC of the pipeline. THPS (Tetrakis Hydroxymethyl Phosphonium Sulfate) and glutaraldehyde are the popular choices because they are environmentally green and non-bioaccumulative, and they have the advantage of rapid reaction. THPS is highly effective in controlling SRB because it causes rapid and severe damage to the cell membrane integrity of target microorganisms[7].

THPS is synthesized in a high-yield reaction below:

$$2PH_3+H_2SO_4+8CH_2O \rightarrow [(HOCH_2)_4P]_2\,SO_4 \qquad (1)$$

THPS degrades relatively fast under both aerobic and anaerobic conditions. Trihydroxymethyl phosphine oxide (THPO) and bishydroxymethyl phosphonic acid (BMPA) have been identified as two major breakdown products[8]. Another breakdown product is possibly a formaldehyde adduct of trihydroxy compound. Reaction (2) below shows the THPS chemical structure and its major degradation products. (Equation (2) is not stoichiometrically balanced due to the uncertainty of the third breakdown product.)



$$\left[HOH_2C- \overset{\overset{H_2COH}{|}}{\underset{\underset{H_2COH}{|}}{P^+}} -CH_2OH \right]_2 SO_4^{2-} \rightarrow HOH_2C- \overset{\overset{H_2COH}{|}}{\underset{\underset{H_2COH}{|}}{P}} =O+ \overset{HOH_2C-CH-CH_2OH}{HOH_2C-\overset{|}{\underset{\underset{H_2COH}{|}}{P}}} =O \qquad (2)$$

(THPS) (THPO) (BMPA)

THPO and BMPA were found to have low toxicities and are not considered hazards to the environment[9]. Both of them will further degrade to CO_2 and inorganic matters[10].

THPS degradation can result from biodegradation, hydrolysis, oxidation and photo degradation. It was reported that THPS exposure to UV within 2 hrs would completely degrade it to THPO when the initial concentration is low like 20 ppm[8]. Lloyd[11] and O'Connor[12] concluded that pH also affects THPS photo-degradation and hydrolysis. A few other studies on THPS degradation rate can be found in the open literatures[13, 14]. No THPS degradation prediction model can be found in the open literature. Apart from the THPS degradation itself, in field operations, it is well known that THPS could easily react with oxygen scavengers[15]. All the factors above can affect the dosing of THPS in the mitigation of MIC. Anecdotal words from field operators were that the protection against MIC is lost when THPS concentration is below around 50 ppm (100 ppm to be safer). A much higher biocide concentration is needed once the biofilms are established[3]. Thus, it is important to predict residual THPS concentration to make sure that it does not fall below the desired minimum required to prevent biofilm formation. This paper presents a mechanistic model to predict THPS degradation in seawater, from two locations, as a function of time, temperature and pH.

METHODS

Experiments were carried out in 100 ml anaerobic serum bottles with 20 mm rubber septa and aluminum crimp seals (Figure 1). Anaerobic manipulations were performed in a glove box deoxygenated with N_2 gas. All liquids in the tests were deoxygenated using N_2 sparging before use and sterilized to circumvent the involvement of microorganisms. For tests involving coupons to study the presence of mild steel, X65 carbon steel was used with dimensions of 1.87″×0.43″×0.06″ (Figure 1). The coupon surface area to liquid volume ratio was set close to that in 12″ID pipes. Prior to use, coupon surfaces were polished successively with 200 and 400 grit SiC abrasive papers, rinsed with alcohol, and then sonicated in a beaker with ethanol in an ultrasonic bath. THPS (75% w/w) was a gift from Nalco. Artificial seawater was made from Instant Ocean®[*] salt mix, and the two kinds of natural seawater were obtained from Gulf of Mexico (site #1) and the Arabian Gulf (site #2).

Standard iodine titration was applied to test THPS concentration. The assay kit (CODE 8776) from the LaMotte Company (www.lamotte.com) was used. The kit can test the effective THPS concentration in both fresh water and seawater. A kit from CHEMetrics (www.chemetrics.com, product code: K-7540) was used to test the oxygen concentration in the experimental vials. All pH values were measured under room temperature with a Corning 320 pH meter.

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[*] Instant Ocean® is a registered trademark of Aquarium Systems, Inc.

RESULTS AND DISCUSSION

A WHO report[8] mentioned that UV could accelerate THPS degradation when its concentration is low. Under exposure to normal fluorescent lighting in our lab, tests lasting for 5 days using the common clear borosilica glass vials that are not UV-transparent did not show appreciable THPS degradation compared to samples kept in the dark. Therefore, all the test samples in this paper were not kept in the dark. The dissolved oxygen concentration in all the sample fluids was found to be below 40 ppb after the vials were opened at the end of tests.

Effect of temperature

Table 1 shows a test matrix in which 6 test conditions at fixed pH were investigated. The chemical composition of the artificial water is similar to that of typical natural seawater (Table 2). Experimental data on THPS degradation in natural seawater (site #1) are shown in Figure 2. The experimental data shows that THPS degradation follows the first-order kinetics expressed in Equation (3) below. Based on Equation (4), the values of the specific reaction rate k at 4 individual temperatures were obtained (Figure 3). Equation (6) was applied to correlate k with temperature T (Figure 4), and the activation energy E and frequency factor A can be calculated according to the slope and y-axis intercept in Figure 4. Equation (7) shows the mechanistic mathematic model for THPS degradation in the natural seawater (site #1) with time and temperature with a fixed pH.

The following equations that depict the model of THPS degradation with fixed pH is based on first-order kinetics.

$$-r_A = -\frac{dC_A}{dt} = k \bullet C_A \tag{3}$$

$$\ln\left(\frac{C}{C_0}\right) = -k \bullet t \tag{4}$$

Arrhenius equation $k = A \bullet \exp\left[\frac{-E}{R \bullet (T + 273.15)}\right]$ (5)

where A is the frequency factor, E activation energy in J/mol, R gas constant (8.314 J/mol•K), T reaction temperature in ºC and t time in day. Equation (5) leads to Equation (6).

$$\ln k = \ln A - \frac{E}{R \bullet \left(T + 273.15\right)} \tag{6}$$

Thus,

$$\ln\left(\frac{C}{C_0}\right) = -k \bullet t = -A \bullet \exp\left[\frac{-E}{R \bullet (T + 273.15)}\right] \bullet t \tag{7}$$

where A and E can be obtained from Figure 4 through linear regression.

Table 3 shows a spreadsheet version of the temperature effect model shown in Equation (7) with input parameters time and temperature and initial THPS concentration. The results showed that THPS degradation rates under 6 different test conditions increased with temperature increases, and that THPS degrades faster at higher pH. The artificial seawater data in Table 3 indicate that the presence of a coupon accelerated THPS degradation. The MSDS sheet from www.accepta.com states that THPS should avoid contact with mild steel[16]. Concentrated THPS has a very low pH that is harmful to mild steel. Even dilute THPS solutions with pH above 7 showed corrosivity in our experimental data (Figures 5-7) while control samples without THPS (images not shown) did not show this particular kind of pitting pattern and the associated weight losses. Compared to the 5-month image, the 11-month image showed coalescence of smaller pits. This observation was supported by weight loss data.

Effect of pH

Table 4 shows a test matrix used to study the pH effect on THPS degradation in natural water from site #2 without coupons. The pH of low and high pH tests was adjusted by using HCl or NaOH after THPS addition. Figure 8 shows THPS degrades faster under higher pH conditions.

Table 5 shows a test matrix using natural seawater from site #2 with different initial pH values at different test temperatures. It was found that THPS reduced pH right after it was added into the seawater. For example, adding THPS to seawater to achieve 160 ppm THPS immediately reduced initial solution pH from 8.6 to 7.6. And also, it was found that the first experimental data obtained at t=2 days showed a pH shift from its initial value for all the tests with three different initial pH settings. The solution pH values stabilized after around 2 days. This was probably due to the seawater's buffering ability. Therefore, only the stabilized pH data were used in modeling. This is permissible since THPS degradation evaluation is typically over many days.

Figure 9 shows that when temperature is fixed, a lower pH slows down THPS degradation and the degradation still follows the first-order kinetics with respect to THPS concentration. To study the effect of pH on k at different temperatures, more experiments were carried out. Figure 10 shows a surprisingly revealing trend for pH effect on k. All the lines are straight and parallel to each other. This suggests a linear relationship lnk $\propto$ pH with a slope that is independent of temperature. Based on the definition pH= $-\log_{10}[H^+]$, the lnk vs. pH relationship now translates to a proportional relationship of k $\propto [H^+]^{-n}$, in which the parameter n is positive and independent of temperature. Because n is independent of temperature, we may use k(T, pH)=k(T)•$[H^+]^{-n}$. Equation (3) can be modified to include $[H^+]$. We can now modify the temperature effect THPS degradation model in Equation (7).

$$-r_A = -\frac{dC_A}{dt} = \mathrm{k(T,pH)} \bullet C_A = \mathrm{k(T)} \bullet [\mathrm{H}^+]^{\text{-n}} \bullet C_A \tag{8}$$

This suggests that the effect of pH can be viewed as proton inhibition of THPS degradation. In terms of reaction kinetics, $[H^+]$ appears in the rate expression as a negative order (-n) of reaction.

Equation (6) can be reformulated to give

$$\ln k(T, pH) = \ln\left\{k(T) \bullet \left[\mathrm{H}^+\right]^{\text{-n}}\right\} = \ln(k) - n \bullet \ln\left(\left[H^+\right]\right) = \ln A - \frac{E}{R \bullet (T + 273.15)} + 2.303n \bullet pH \tag{9}$$

Or,

$$\ln \mathrm{k}(\mathrm{T,pH}) = \mathrm{b} + \frac{-\mathrm{E}}{\mathrm{R} \bullet (\mathrm{T} + 273.15)} + 2.303\mathrm{n} \bullet \mathrm{pH} \tag{10}$$

Multi-linear regression of lnk vs. 1/(T+273.15) and pH experimental data would give parameters b, E and n values.

Table 6 shows k(T,pH) data at different pH values and four different temperatures. The pH values in Table 6 were stabilized pH values instead of the initial pH values. Multi-linear regression of the data in Table 6 using MATLAB (www.mathworks.com) Version 7 quickly yields b=17.25, activation energy E=8.445x10^4 J/mol and a=1.750, i.e. n=0.76. The R^2 of the multi-linear regression is 0.998. Equation (10) can now be written as:

$$\mathrm{k}(\mathrm{T,pH}) = \exp(17.25) \times \exp\left(\frac{-10161}{\mathrm{T} + 273.15}\right) \times \exp(1.75 \bullet \mathrm{pH}) \tag{11}$$

And the THPS model with temperature and pH effects can be expressed as,

$$\ln\left(\frac{\mathrm{C}}{\mathrm{C}_0}\right) = -\mathrm{k}(\mathrm{T,pH}) \bullet \mathrm{t} = -3.1 \times 10^7 \times \exp\left[\frac{-10161}{\mathrm{T} + 273.15}\right] \times \exp(1.75 \bullet \mathrm{pH}) \times \mathrm{t} \tag{12}$$

where the pH is the stabilized pH of the seawater after THPS introduction. Table 7 compares the experimental data with the model. The dots at 31ºC with pH 7.9 and 8.4 are experimental data from the tests listed in Table 1, and the dots at pH 8.1 are the experimental data from the test in Table 5. These data in Table 1 were not used in the regression to get b, E and n values above. The results show that the model fit the data very well, which indicates that the mechanism proposed for the pH effect is quite reasonable. It is interesting to note that at pH

8.4 and also at 7.9 THPS degradations in two different seawater samples were similar even though the salinity of the seawater from site #2 is about twice of that from site #1 and the artificial seawater. More experimental data with a wide salt concentration range are need to determine whether salt content has an intrinsic effect on THPS degradation after pH is fixed.

CONCLUSIONS

1. THPS degradation is a complex process and is affected by many factors. Our mechanistic model shows that it is strongly dependent on temperature and pH. THPS degradation increases with the increase of temperature and pH and the pH effect can be decoupled with temperature. Experimental data indicated that proton acted as an inhibitor of THPS degradation in the form of a negative order reaction.

2. THPS degradation follows the first-order kinetics. The proposed mechanistic model for THPS concentration prediction as a function of time, temperature and pH fits the experimental data very well. The model shows that THPS degradation is highly sensitive toward temperature and pH changes.

FUTURE WORK

We plan to further our investigation on biocide degradation modeling. Below is a list of proposed tasks.

1. Rhodia (www.rhodia.com) indicated that THPS is "effective in both acid and neutral/alkaline pH[17]." They recommend acidic pH because THPS acts faster against microorganisms. Field operators tend to be reluctant to lower pH below 7 because of concerns over non-MIC corrosion rates. So far, we tested THPS degradation mostly in the basic pH range because we anticipate a basic pH used in hydrotest fluids. Because the model is mechanistic, its robustness should be much better than empirical correlations. THPS degrades much slower at lower pH values. We will expand the model based on experimental data in the acidic pH range in the future.

2. For field applications, THPS is often blended with other chemicals. It is desirable to upgrade the existing THPS degradation model by incorporating more parameters, such as surfactant, salt content, O_2 scavenger, corrosion inhibitor, scale inhibitor and mild steel reactivity.

3. To increase the accuracy of THPS assay and to eliminate interference from other chemical species, ion chromatography with an in-line post-column reactor will be used.

4. The model is based on anaerobic data. Aerobic degradation will be investigated.

5. Because glutaraldehyde is another widely used green biocide, mechanistic modeling for its aerobic degradation and anaerobic degradation will prove valuable to the oil and gas industry.

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REFERENCES

1. J. Luo, I. Vance, "MIC of Mild Steel in Oilfield-Produced Water," CORROSION/94, paper no. 265, (Houston, TX: NACE, 1994).
2. I. T. E. Fonseca, M. J. Feio, A. R. Lino, M. A. Reis, V. L. Rainha, "The influence of the media on the corrosion of mild steel by *Desulfovibrio desulfuricans* bacteria: an electrochemical study," *Eletrochemica Acta*, Vol. 43, p.213, 1998.
3. H. A. Videla, *Manual of Biocorrosion*, Lewis Publishers, Boca Raton, Florida, 1996.
4. W. S. Borenstein, P. B. Lindsay, "MIC failure of 304L stainless steel piping left stagnant after hydrotesting," *Materials Performance*, Vol. 41, No. 6, pp.70-73, 2002.
5. R. M. Baldwin, "Black Powder In The Gas Industry - Sources, Characteristics And Treatment," Technical Assessment for the Gas Machinery Research Council, Mechanical and Fluids Engineering Division, Southwest Research Institute, May 1998.
6. M. G. Weinbauer, D. F. Wenderoth, "Microbial Diversity and Ecosystem Functions - the Unmined Riches," *Electronic Journal of Biotechnology*, April 15, 2002.
7. "Performance biocides in industry applications"-brochure, Rhodia Water, Phosphorus and Performance Derivatives, http://www.rhodia-ppd.com/index.asp.
8. WHO, "Flame Retardants: Tris(2-Butoxyethyl) Phosphate, Tris(2-Ethylhexyl) Phosphate And Tetrakis(Hydroxymethyl) Phosphonium Salts," http://www.inchem.org/documents/ehc/ehc/ehc218.htm, Environmental Health Criteria 218, World Health Organization, Geneva, 2000.
9. B.L. Downward, R.E. Talbot, T.K. Haack, "TetrakisHydroxymethylPhosphonium Sulfate (THPS): A new industry biocide with low environmental toxicity," CORROSION/97, Paper No.401, (Houston, TX; NACE, 1997).
10. "ACG Phase I - supplementary lenders information package, executive summary." http://www.bp.com/liveassets/bp_internet/bp_caspian/bp_caspian_en/STAGING/local_assets/downloads_pdfs/t/ACG_English_SLIP_Content_ACG_Phase_1_SLIP.pdf, April 2003.

11. G. R. Lloyd, “UV degradation of THPS,” Oldbury, United Kingdom, Albright & Wilson UK Ltd, Specialties Technical Laboratory, 1994.
12. J. O’Connor, “THPS: Determination of hydrolysis as a function of pH,” Eye, United Kingdom, Life Science Research Limited, 1992.
13. P. McWilliam, “Tolcide PS355A: Biodegradability in seawater-closed bottle test,” 1994.
14. M. Gorman, “Anaerobic aquatic metabolism of $_{14}$C-tetrakishhydroxylmethyl phosphonium sulfate (THPS): Final report,” (1997).
15. P. Wilfried, *Directory of microbicides for the protection of materials, a handbook,* Kluwer Academic Publishers, 2004.
16. Accepta, MSDS sheet for Accepta 2102 (a THPS formulation). http://www.accepta.com/prod_docs/2102.pdf, 2004.
17. Rhodia, Product Technical Data on TOLCIDE® PS75, Issue No. 6, October 2004.

TABLE 1
Test matrix for THPS degradation investigation

Test media (all sterilized)	**Stable pH after THPS added with/without X65 coupon**
1. Natural seawater (site #1)	pH: 7.3; No coupon present
2. Artificial seawater	pH: 8.0; No coupon present
3. Artificial seawater	pH: 7.9; Coupon present
4. Natural seawater (site #2)	pH: 7.9; Coupon present
5. pH-adjusted natural seawater (site #1)	pH: 8.4, Coupon present
6. pH-adjusted natural seawater (site #2)	pH: 8.4, Coupon present
Initial THPS concentration (ppm)	180 for the #1 medium and 100 for the rest
Test temperature (ºC)	4, 17, 25, 37
Light condition	Normal fluorescent lighting (off in after hours)

TABLE 2[*]
Major element comparison between natural seawater and artificial seawater

	Salinity (1000 pm)	Na^+	Mg^{2+}	Ca^{2+}	K^+	Sr^{2+}	Cl^-	SO_4^{2-}	BO_3^{3-}	CO_3^{2-} HCO_3^-
Seawater	35	470	53	10.3	10.2	0.09	550	28	0.42	1.90
Salt mix	29.65	462	52	9	9.4	0.19	521	23	0.43	1.90

[*] All in millimoles per kilogram, except salinity.

TABLE 3
Preliminary THPS degradation prediction model

Input parameters

T (°C)	Time (days)	C_o (ppm)
31	10	100

Output

Residual THPS Concentration (ppm)

90.83	(In natural seawater (site #1) without coupon presence), pH 7.3
49.3	(In artificial seawater without coupon presence), pH 8
38.46	(In artificial seawater with coupon presence), pH 7.9
37.43	(In natural seawater (site #2) with coupon presence), pH 7.9
17.98	(In pH-adjusted natural seawater (site #1) with coupon presence), pH 8.4
15.83	(In pH-adjusted natural seawater (site #2) with coupon presence), pH 8.4

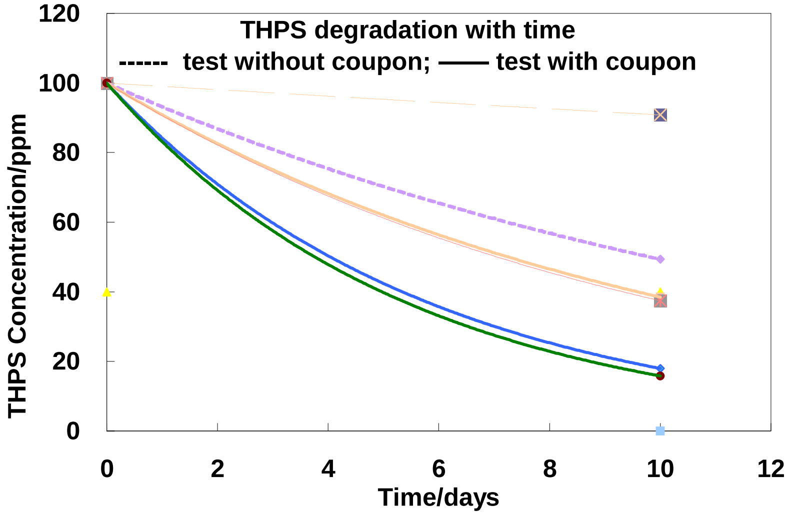

TABLE 4
Test matrix for pH effect on THPS degradation

Test media (all sterilized)	**Initial pH after THPS was added without coupon presence**
1. Natural seawater (site #2)	8.52
2. pH-adjusted natural seawater (site #2) at low pH	6.76
3. pH-adjusted natural seawater (site #2) at high pH	10.00
Initial THPS concentration (ppm)	55
Test temperature (ºC)	37
Light condition	Normal fluorescent lighting

TABLE 5
Test matrix for THPS degradation investigation

Test media (all sterilized)	**Initial pH after THPS was added**
1. Natural seawater (site #2)	8.12 with coupon presence
2. pH-adjusted natural seawater (site #2) at low pH	6.06 with coupon presence
3. pH-adjusted natural seawater (site #2) at high pH	9.33 with coupon presence
Initial THPS concentration (ppm)	160
Test temperature (ºC)	4, 23, 31, 37
Light condition	Normal fluorescent lighting

TABLE 6
Data for multi-linear regression

Temperature (ºC) **pH**	4 7.8	4 8.2	4 9.5	23 7.72	23 8.14	23 9.04	31 7.6	31 8.1	31 8.8	37 7.56	37 8.03	37 8.6
-lnk(T, 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 7
Modified THPS degradation prediction model

Input parameters

T (°C)	Time (days)	C_o (ppm	pH
31	10	100	8.4 **(In pH-adjusted natural seawater (site #1) with coupon presence)**
			8.4 **(In pH-adjusted natural seawater (site #2) with coupon presence)**
			8.1 **(In pH-adjusted natural seawater (site #2) with coupon presence)**
			7.9 **(In natural seawater (site #2) with coupon presence)**
			7.9 **(In artificial seawater with coupon presence)**

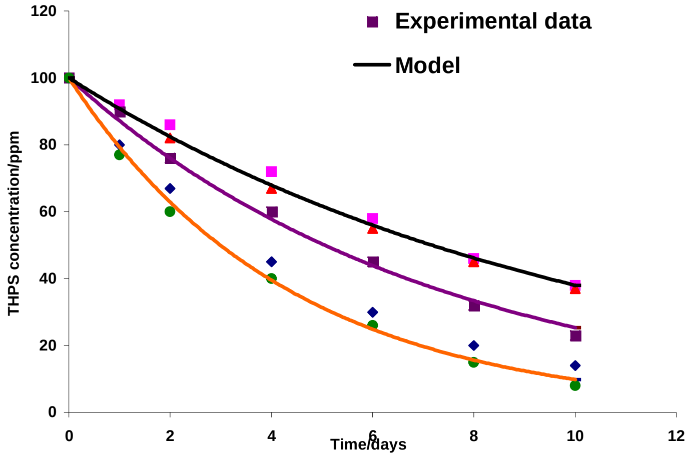

FIGURE – 1. X65 coupon in an anaerobic serum bottle

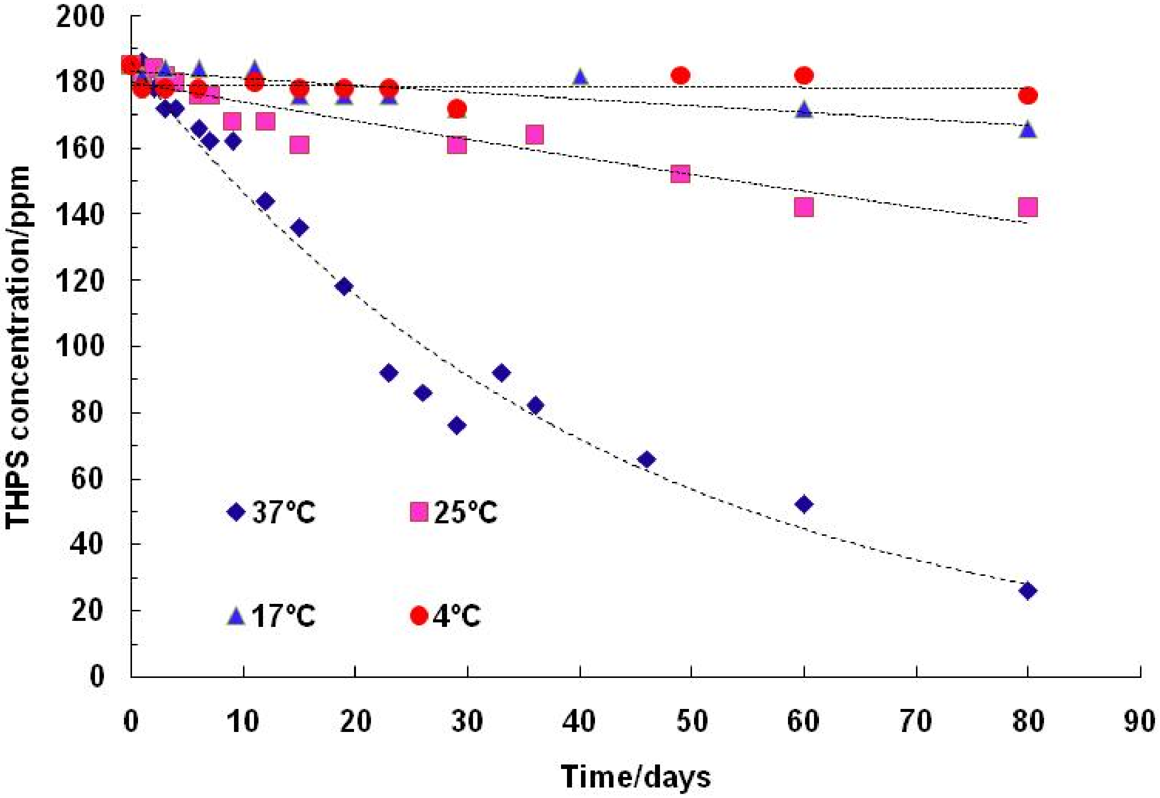

FIGURE – 2. THPS degradation in natural seawater (site #1) without coupon presence at different temperatures

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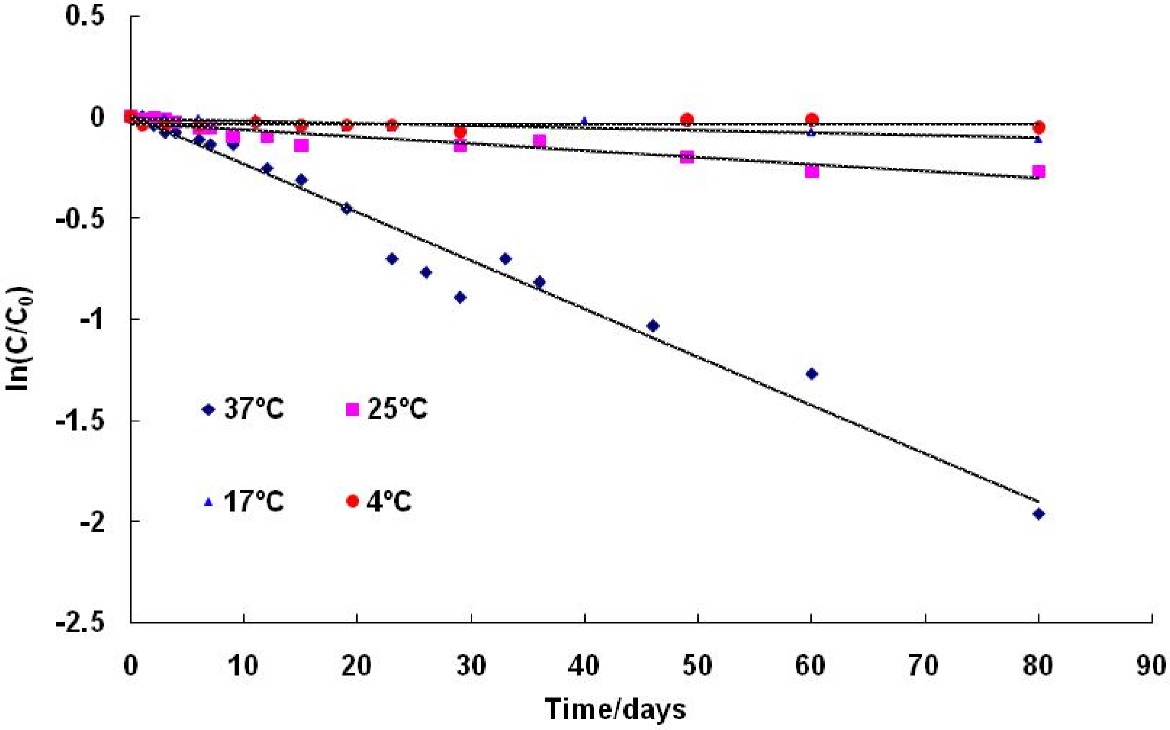

FIGURE – 3. The values of specific reaction rate k at different temperatures (Test in natural seawater #1 without coupon)

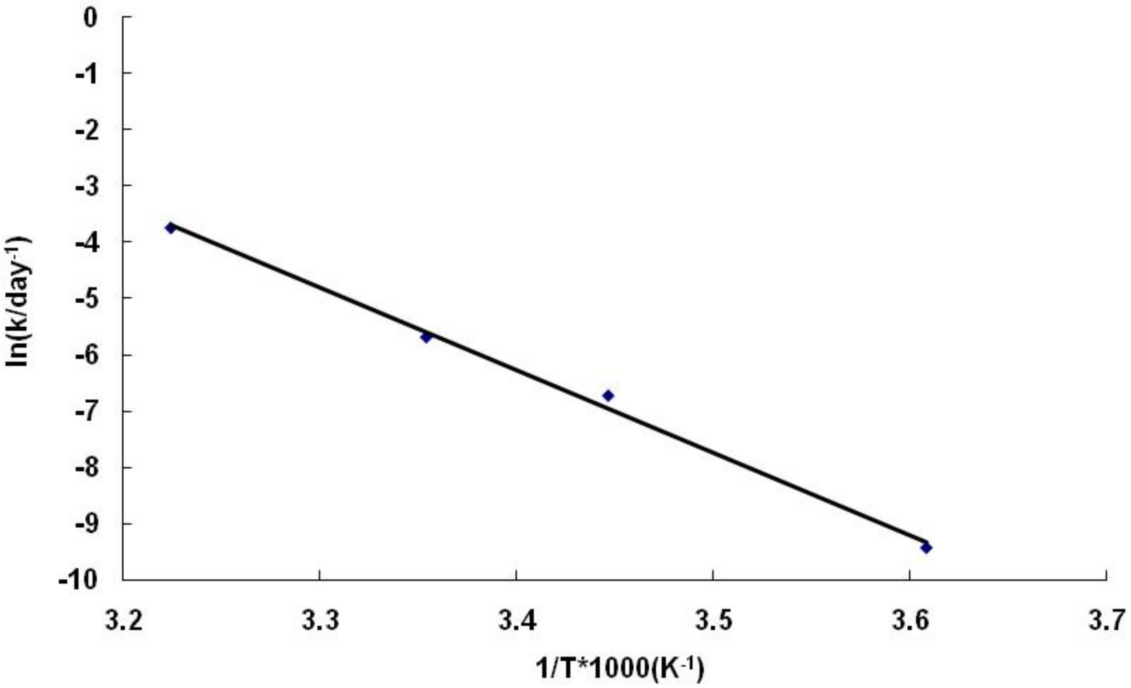

FIGURE – 4. The change of specific reaction rate k with temperature (Test in natural seawater #1 without coupon)

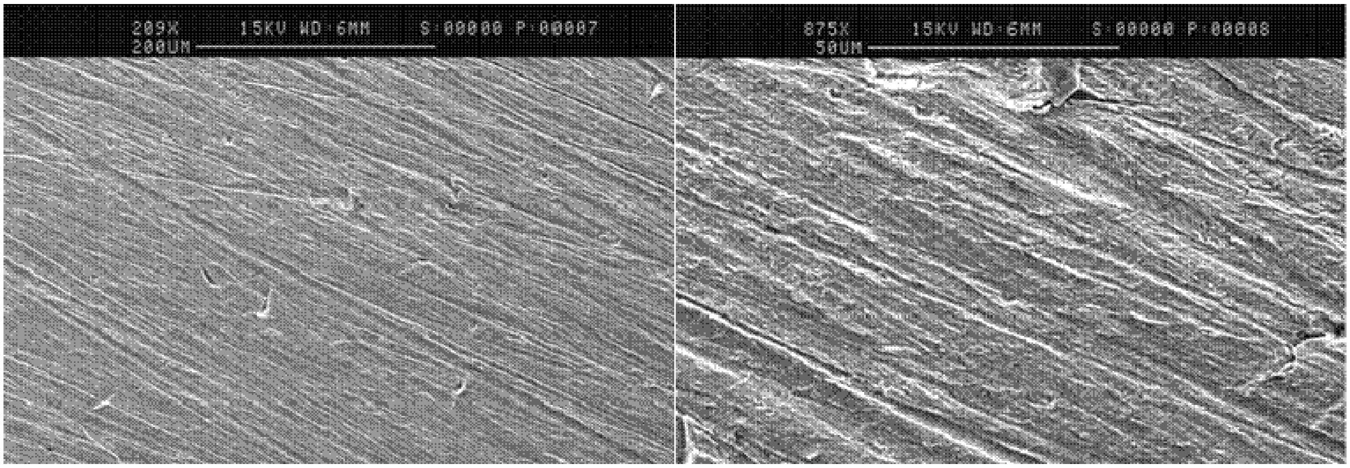

FIGURE – 5. SEM images of coupon surface after acid cleaning (3-month test in natural seawater (site #1) with initial THPS 50 ppm at 4 ºC, weight loss: 6 mg, initial pH 8.0 and final pH 8.3)

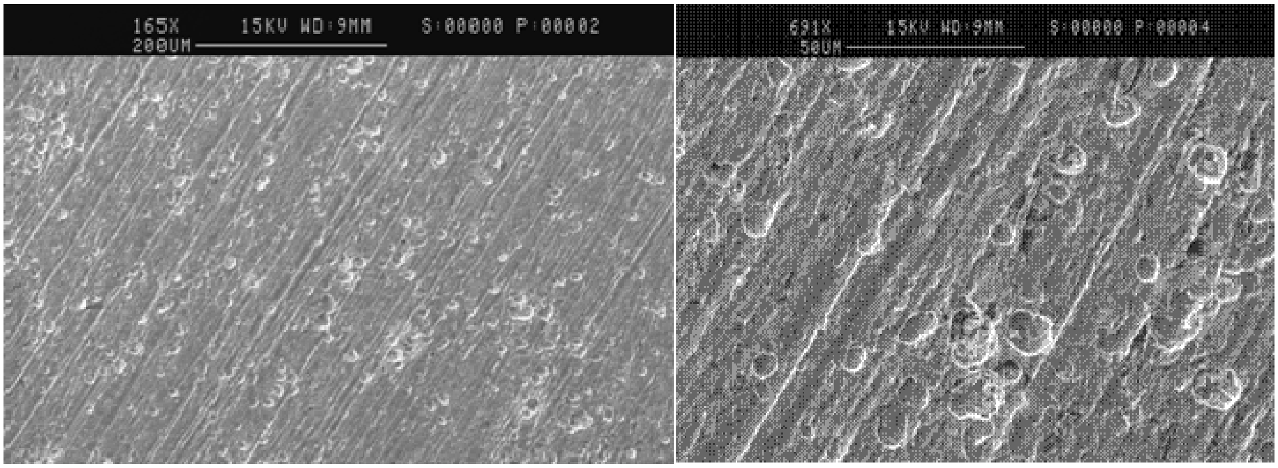

FIGURE – 6. SEM images of coupon surface after acid cleaning (5-month test in natural seawater (site #1) with initial THPS 50 ppm at 4 ºC, weight loss: 11 mg, initial pH 8.0 and final pH 8.4)

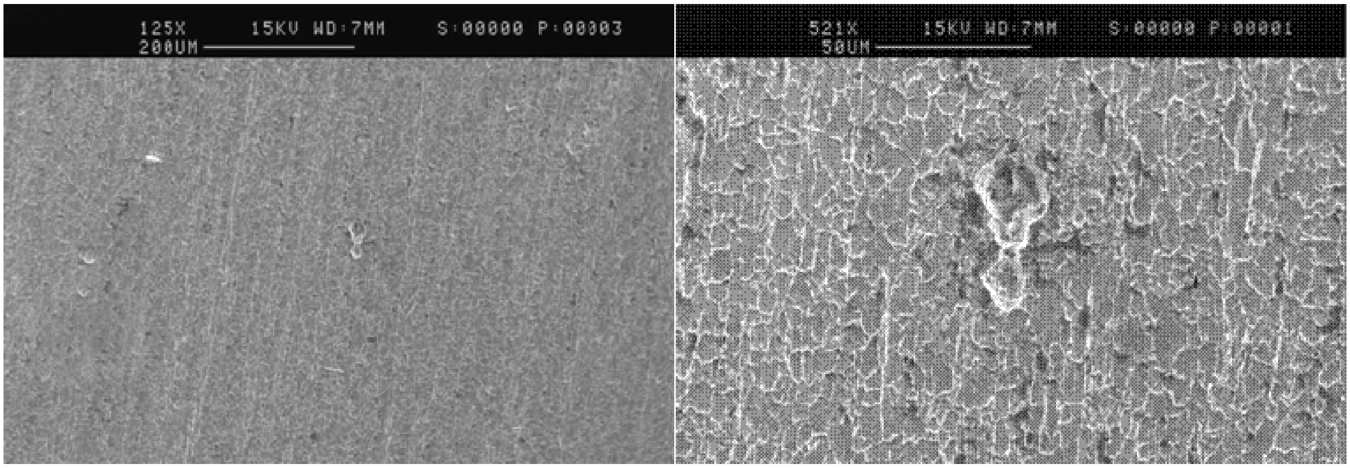

FIGURE – 7. SEM images of coupon surface after acid cleaning (11-month test in natural seawater (site #1) with initial THPS 50 ppm at 4 ºC, weight loss: 17 mg, initial pH 8.0 and final pH 8.3)

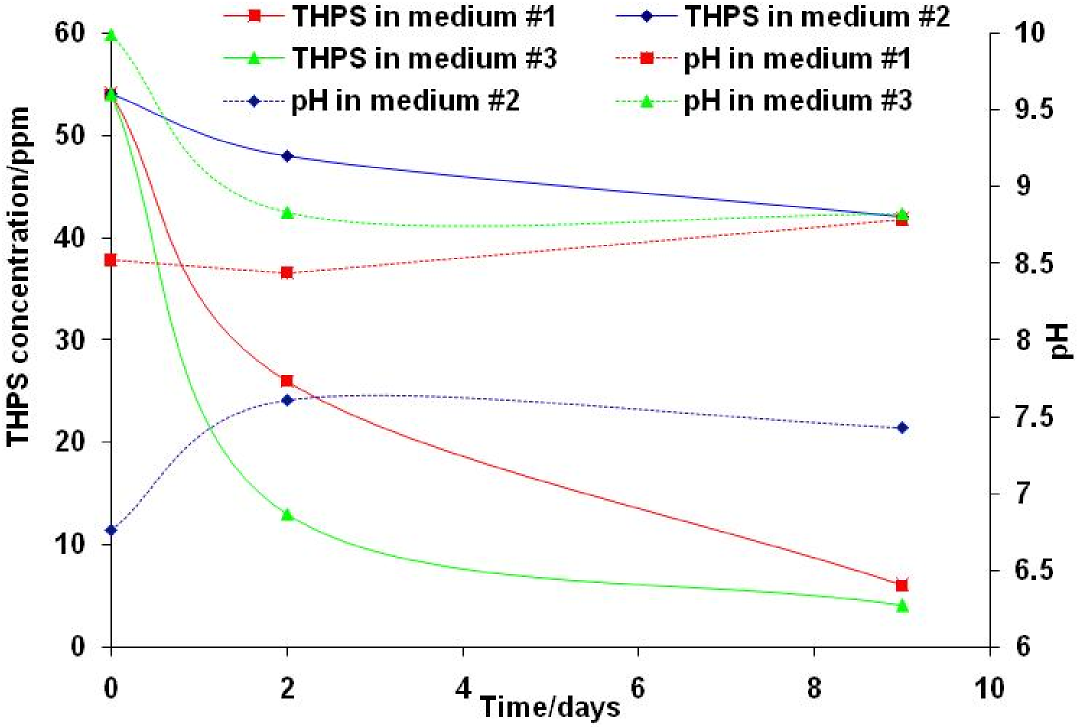

FIGURE – 8. pH effect on THPS degradation in natural seawater (site #2) (medium #1: natural seawater (site #2); medium #2: pH-adjusted natural seawater (site #2) with lower initial pH; medium #3: pH-adjusted natural seawater (site #2) with higher initial pH)

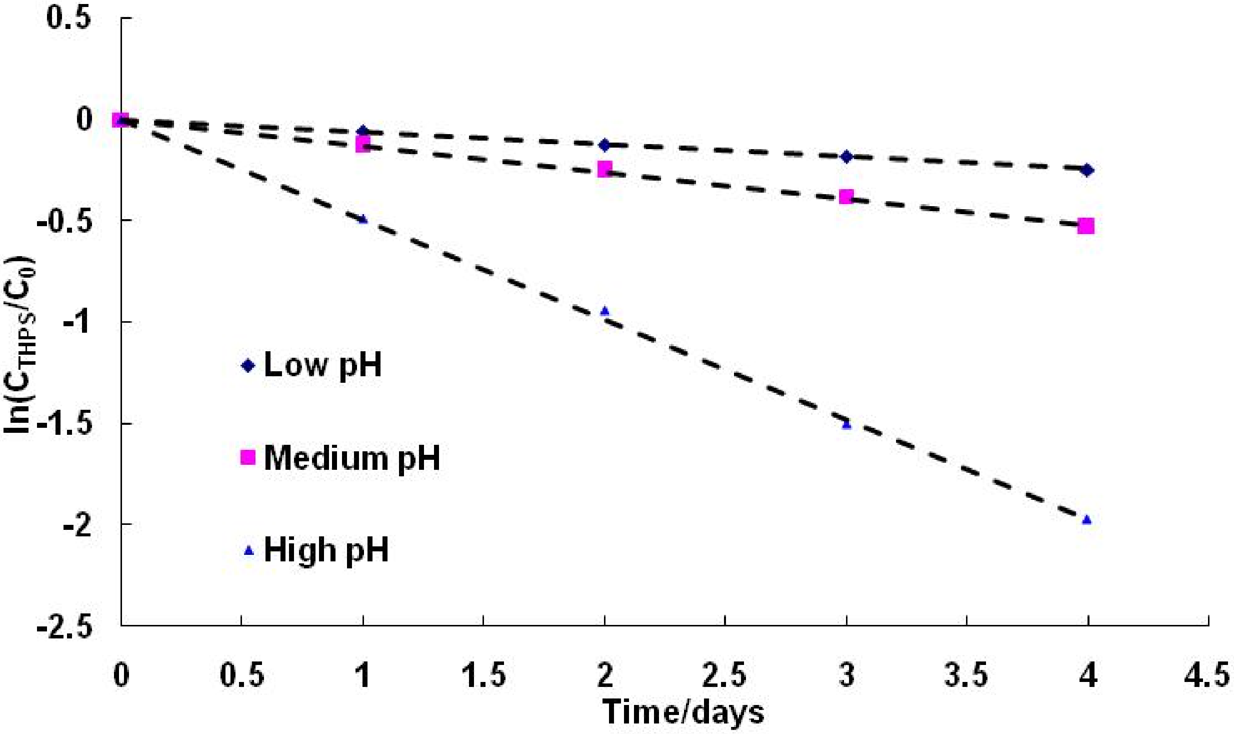

FIGURE – 9. The specific reaction k(T, pH) at different pH at temperature 31 ºC (Test in natural seawater #2 with coupon)

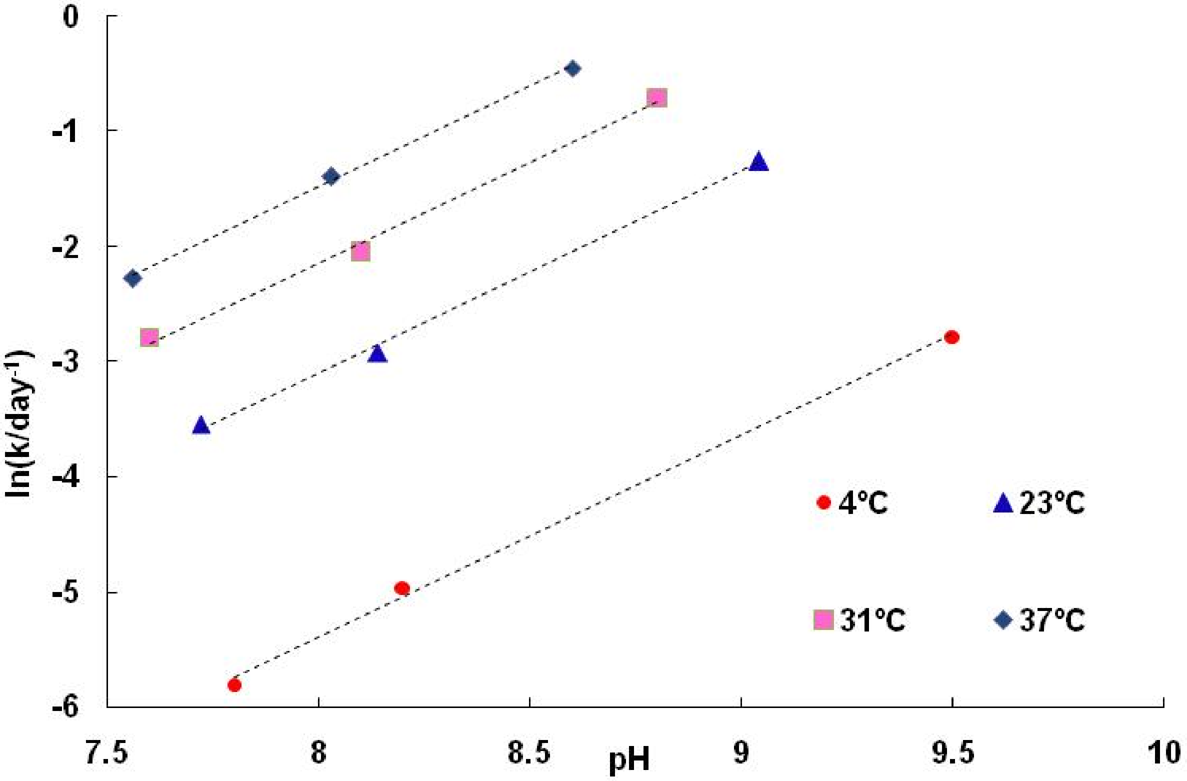

FIGURE – 10. The relation of k(T, pH) with pH at 4 different temperatures (Test in natural seawater #2 with coupon)