BREAKDOWN OF HYDROGEN SULFIDE IN SEAWATER UNDER DIFFERENT RATIO OF DISSOLVED OXYGEN / HYDROGEN SULFIDE

(Penguraian Hidrogen Sulfida dalam Air Laut dengan Nisbah Oksigen Terlarut / Hidrogen Sulfida yang Berbeza)

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Abstract
Breakdown of hydrogen sulfide (H2S) in seawater is highly dependent on both the concentration of dissolved H2S and dissolved oxygen (DO). A simple correlation was found in the H2S dissociation and ratio of [DO/H2S]. When the [DO/H2S] ratio is more than one, H2S breakdown rapidly, resulting in a short half-life of H2S in the seawater (in a time scale of minute). When the dissolved oxygen is not a limiting factor, H2S breakdown in a first order reaction. Nevertheless, when [DO/H2S] ratio is less than 1, H2S breakdown in the seawater becomes slower, resulting in a longer H2S half-life (in a time scale up to hours). In this case, the H2S breakdown in a pseudo-second order reaction. This pseudo-second order reaction is commonly reported by other investigators. This study also investigated the relation between the concentration of dissolved H2S and pH changes during H2S dissociation in the seawater. The pH is lowered with increasing concentration of initial H2S in the seawater but appears to reach an asymptotic low value of about 4 as the dissolved H2S approaches its saturation limit in the seawater at about 2,500 mg L−1.

Keywords: hydrogen sulfide, dissolved oxygen, oxidation, seawater, H2S dissociation

Abstrak
Penguraian hidrogen sulfida (H2S) dalam air laut sangat bergantung kepada kepekatan kedua-dua H2S terlarut dan oksigen terlarut (DO). Satu kolerasi mudah telah ditemui antara penguraian H2S dan nisbah [DO/H2S]. Apabila nisbah [DO/H2S] melebihi satu, penguraian H2S adalah cepat, menyebabkan separuh hayat H2S yang pendek dalam air laut (dalam skala masa minit). Dalam keadaan yang mana oksigen terlarut bukan faktor penghad, penguraian H2S merupakan tindak balas tertib pertama. Namun, apabila nisbah [DO/H2S] kurang daripada satu, penguraian H2S dalam air laut menjadi lambat, menyebabkan separuh hayat H2S yang lebih lama (dalam skala masa jam). Dalam kes ini, penguraian H2S adalah tindak balas pseudo tertib kedua. Tindak balas pseudo tertib kedua ini biasa dilaporkan oleh ramai penyelidik. Kajian ini turut menyiaskan hubung kait antara kepekatan H2S terlarut dan perubahan pH semasa penguraian H2S dalam air laut. Nilai pH jadi rendah dengan peningkatan kepekatan awal H2S dalam air laut tapi ia mencapai nilai asimptot yang rendah dalam lingkungan 4 apabila kepekatan H2S terlarut menghampiri had ketepuaninya dalam air laut pada kepekatan 2,500 mg L−1.

Kata kunci: hidrogen sulfida, oksigen terlarut, pengoksidaan, air laut, penguraian H2S
Introduction

Hydrogen Sulfide (H$_2$S) gas is one of the potential contaminants found in oil and gas production. H$_2$S is normally formed in oil and/or gas reservoirs through the decomposition of organic matter under anaerobic condition by microbes. Typically, such H$_2$S will be removed from the main hydrocarbon stream and disposed off to increase the sales value of the sweetened hydrocarbon. In the ocean, H$_2$S is mainly formed through geochemical processes during deep sea volcanic activities including hydrothermal vents [1]. When H$_2$S is present in the seawater in dissolved form, it dissociates into hydrosulfide (HS$^-$), which is the product of the first dissociation equilibrium (K$_{a1}$). The second dissociation equilibrium (K$_{a2}$) produces the sulfide ion (S$^{2-}$). H$_2$S is a weak acid, with pK$_{a1}$ being reported by various investigators in the order of 7.0 [2-5] and pK$_{a2}$ in the order of 12.5 [6]. Due to the first dissociation of H$_2$S to HS$^-$, the concentration of aqueous H$_2$S will decrease with increasing pH in water. At pH 7.0, the concentration ratio of the aqueous H$_2$S to HS$^-$ is approximately 1:1. As the pH increases beyond 7.0, the ratio of the concentration of HS$^-$ to aqueous H$_2$S increases. Sulfide ion (S$^{2-}$), which is the product of the second dissociation becomes significant, only when pH is above 12.

The hydrosulfide ion is susceptible to oxygenation reactions under aerobic condition in seawater. The oxygenation of HS$^-$ is rather complex, involving a multitude of chemical reactions, producing various intermediate and final products, amongst others, the following possible reactions 1 – 3 [7, 8]:

\[
\begin{align*}
2\text{HS}^- + 3\text{O}_2 & \rightarrow 2\text{SO}_3^{2-} + 2\text{H}^+ \\
\text{HS}^- + 2\text{O}_2 & \rightarrow \text{SO}_4^{2-} + \text{H}^+ \\
2\text{HS}^- + 2\text{O}_2 & \rightarrow \text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O}
\end{align*}
\]

In the presence of relatively high concentration of dissolved oxygen (DO), the ion species of sulfite (SO$_3^{2-}$) is stable. Even so, some of the SO$_3^{2-}$ species would also be oxidized to sulfates (SO$_4^{2-}$) [7, 9]. Hence, it is apparent that the actual overall oxidation rate of H$_2$S in seawater varies depending on the conditions studied. A simplified gross measure of the overall breakdown of H$_2$S in seawater due to various reactions shown above can be depicted by the H$_2$S half-life; which is a measure of the time taken to lower the H$_2$S concentration from its initial value to half the initial value. Various publications have provided different H$_2$S half-life values, depending on the reaction conditions investigated. Göte and Alexander [10] reported that the H$_2$S half-life of about 17 minutes at constant dissolved oxygen concentration of 5.4 mg L$^{-1}$ and 25 °C in seawater. Sharma and Yuan [11] reported H$_2$S half-life of 25 minutes for treated domestic wastewater initially containing about 6 mg L$^{-1}$ of H$_2$S and 8 mg L$^{-1}$ DO, while Asaoka et al. [12] reported an in-situ half-life of approximately 50 minutes in the Etajima Bay, which contains about 28 mg L$^{-1}$ of sulfide.

Decomposition of the H$_2$S becomes more complicated when microbial degradation is also taking place [13] or when catalytic metals are present [14]. Oxidized metals such as Fe(III), Mn(III) and Mn(IV), for example, are efficient catalysts to overcome the kinetic barrier for the chemical oxidation of sulfides [15]. The interaction of all these factors in the seawater leads to unpredictable outputs in the tropical marine environment. It is apparent that the half-life of H$_2$S dissociation in such waters is quite complex and dependent on the physical chemical properties as well as biological assemblage of the seawater. Thus, whenever the rate of H$_2$S decomposition is the intended subject, invariably there is a need to conduct in-situ verification using the actual seawater source. Understanding the rate of H$_2$S breakdown in seawater is important in environmental management as it plays an important role in toxicity and ecological footprint of the toxic gas in the marine environment. Hence, this paper describes the experiments undertaken to determine the rate of H$_2$S breakdown in seawater obtained from the Terengganu offshore, as representative of the offshore water of Peninsular Malaysia. The study includes analysis to derive appropriate rate equations and rate constant(s) for the H$_2$S breakdown in seawater as well as estimations of the dissociation half-life. In addition, the effect of H$_2$S dissociation on the pH of the resultant solution is of particular interest. In freshwater, the dissolution of H$_2$S into HS$^-$ ions generate protons, which effectively lowers the pH of the solution. However, in seawater, the natural alkalinity of the seawater tends to counteract the lowering of the pH through various carbonaceous compounds in the seawater carbonate equilibrium. This can result in a complex, non-linear pH correlation with concentration of H$_2$S dissolution. In this study, it is desired to establish an empirical relationship between the effect of H$_2$S dissolution and resultant pH of the seawater solution.
Materials and Methods

Materials

Seawater used in this experiment was collected from the South China Sea off Terengganu. The seawater was then filtered and acclimatized for one week before use. 1 L Kipps apparatus was used to produce the hydrogen sulfide (H₂S) gas used in this study. In the Kipps apparatus, excess pyrite (Fe₂S) was allowed to react with hydrochloric acid (20%) to generate H₂S gas. The gas was bubbled into 1 L oxygen-free deionized water for 24 hours to produce an approximately 2000 mg L⁻¹ H₂S aliquot for the subsequent experiments. Oxygen free water was prepared by purging deionized water with pure nitrogen at 30 mL s⁻¹ for 40 minutes. High Purity oxygen and nitrogen (> 99 %) gases were used in this study. All the chemicals used in the study were of analytical grade and supplied by Merck Co.

Determination of hydrogen sulfide in seawater

Hydrogen sulfide (H₂S) probe (MS-AQUA) was used to monitor H₂S concentration in the experiments. Analysentechnik GmbH develops the amperometric MS-AQUA H₂S micro sensor for in-situ determination of dissolved H₂S or Total sulfide in aqueous solution within a pH range of 0 to 8. Other than the ion sensitive electrode (ISE), the MS-AQUA is the only method for in-situ [H₂S/ Total Sulfide] measurement. MS-AQUA is more relevant as compared to the other ISEs because the workable pH range of MS-AQUA is more relevant to the study undertaken. The accuracy and the concentration of the MS-AQUA below 3 mg L⁻¹ is essentially better than the other ISEs. Table 1 shows the technical data extracted from the technical manual of the sensor. The H₂S probe was pre-calibrated by the manufacturer and was validated with standard solutions by comparing the concentration obtained from the probe and the standard methods (APHA 4500-S²-F., Iodometric method and APHA 4500-S²-H, calculation of unionized H₂S) [16]. Dissolved oxygen and pH were determined by using YSI 550a and the pH probe of the MS-AQUA respectively.

Table 1. Technical specification of MS-AQUA H₂S probes used in the study

| Technical Specification | Range |
|-------------------------|-------|
| Measurement range       |       |
| - Type I*               | 10 µg L⁻¹ – 3 mg L⁻¹ H₂S |
| - Type II               | 50 µg L⁻¹ – 10 mg L⁻¹ H₂S |
| - Type III*             | 500 µg L⁻¹ – 50 mg L⁻¹ H₂S |
| Accuracy of the sensor  | 2 %   |
| Temperature range       | 0°C – 30°C |
| pH range                | 0 – 8 |
| Salinity range          | < 40 ppt (g L⁻¹) |
| Signal interference     |       |
| - Carbon dioxide        | Up to 25.38% |
| - Methane               | Up to 5.78% |
| - Hydrogen              | Up to 0.544% |
| - Ammonia               | Up to 1000 ppm |
| - Carbon monoxide       | Up to 92 ppm |
| - Carbon disulfide      | Up to 5% |
| - Acetic acid           | Up to 1 mol L⁻¹ |
| - Dimethyl sulfide      | Up to 10% |
| - Ethanol               | Up to 10% |

* Sensors used in this study

APHA Method 4500–S²-F [16] was also used to validate the reading from the probe as well as to determine those concentration that fell beyond the measurement range of the MS-AQUA. In the case where the H₂S level exceeded the measurement range, water sample was collected from the experimental chamber by using syringe acted as a
piston to drive water sample out of the vessel. Samples drawn out from the experiment was analyzed for its pH and H$_2$S level right after sampling. Briefly, 20 mL of iodine solution (0.025 N) followed by 2 mL 6N HCl was poured into a 500 mL flask. An amount 200 mL sample was discharged under the solution surface into the flask. More iodine solution was added if the color of the iodine disappeared. The sample was then back-titrated with standard sodium thiosulfate solution (0.025 N). A few drops of starch solution were added as indicator for the end point (disappearance of blue color). The concentration of total sulfide was then calculated, taking into account the dilution factor during titration. The concentration of unionized H$_2$S is then calculated by multiplying the dissociation factor at the measured pH with the total sulfides as stipulated in APHA Method 4500–S$^2$-H [16].

**Breakdown of hydrogen sulfide in seawater**

Experimental chamber as shown in Figure 1 was used in this study. The chamber consists four major components: 1. H$_2$S, temperature and pH probes, 2. Aliquot injection port, 3. Dissolved oxygen probes, and 4. Magnetic bar and stirrer. The experimental chamber was incubated in a 20 L water bath. The reactor vessel was first filled with 2 L of seawater. Pure oxygen and nitrogen from gas cylinders were used to adjust the level of dissolved oxygen in the seawater. 50 mL syringe was used to inject concentrated H$_2$S aliquot through the injection port into the reactor. The volume of concentrated H$_2$S solution injected into the reactor was obtained based on dilution equation ($M_1V_1 = M_2V_2$) to make up the desired H$_2$S concentration. The volume of injection was limited to less than 2% of the total reactor volume. No head space was permitted in the chamber throughout the experiment. In order to avoid leakages, all ports were sealed with silicon glue. Magnetic bar and stirrer (300 rpm) were used to homogenize the aliquot and seawater in the experimental vessel. The experiments were conducted in the laboratory at 28°C, pH 8.0 and 30 ppt. Experiment started one minute after injection of the H$_2$S aliquot. This is to ensure sample homogeneity in the vessel. Readings were recorded continuously by using a camcorder and then manually transferred into excel spreadsheet. The data were then used to determine the reaction order, rate and constant. All the experiments were conducted in triplicate.

**H$_2$S solubility and pH changes in seawater**

Prior to the main H$_2$S breakdown rate experiments, solubility of the H$_2$S in seawater was tested using the experimental setup as shown in Figure 2. In the experiment, H$_2$S gas generated from Kipps apparatus was bubbled through the seawater at 28°C, 30 ppt and pH 8.0 in a 2 L vessel through port 2. Port 4 is the vent for excess gas. During sample withdrawal, port 4 was clipped and the syringe (5) was used as a piston to drive water sample out of the vessel through port 3. The concentration of the H$_2$S, temperature, pH and dissolved oxygen were determined.
immediately. The experiments were conducted in a 20 L water bath for consistent temperature at 28 °C (±0.5 °C). All the experiments were conducted in three replicates.

Figure 2. Experimental setup for investigating hydrogen sulfide solubility. 1. Piston inlet for sampling, 2. Gas inlet from Kipps apparatus, 3. Sample outlet, 4. Excess gas exhaust, 5. Syringe, 6. Magnetic bar

**Determination of reaction order, rate constant and half-life**

Data obtained from H$_2$S breakdown experiments were used to determine the reaction order, rate constant and half-life of the H$_2$S removal. Reaction kinetics were studied based on computation procedure of Han et al. [17]. The reaction orders, rate constants and half-life were obtained by using graphical method. In the case where the dissolved oxygen is in excess, the reaction constant and the breakdown rate of the H$_2$S would resemble the pseudo-first order (K$_1$) reaction as (4):

$$\frac{d[H_2S]}{dt} = -K_1[H_2S]_t$$  \hspace{1cm} (4)

Where, [H$_2$S]$_t$ is defined as concentration of hydrogen sulfide at time t and K$_1$ is defined as rate constant.

While, the reaction constant and the breakdown rate of the H$_2$S resemble a second order reaction, it is represented as (5):

$$\frac{d[H_2S]}{dt} = -K_2[H_2S]_t[O_2]_t$$  \hspace{1cm} (5)

where, [H$_2$S]$_t$ is defined as concentration of hydrogen sulfide at time t, [O$_2$]$_t$ is defined as concentration of dissolved oxygen at time t and K$_2$ is rate constant.

The reaction constant for second order reaction, K$_2$, can be assessed by dividing K$_1$ with [O$_2$]$_t$. K$_1$ can also be derived from the concentration graphs by computing the gradient of the H$_2$S concentration over the linear portion of the decline and dividing by the average concentration of H$_2$S over the considered range. Comparing equations (4) and (5), K$_2$ can be estimated from K$_1$/[O$_2$]$_t$. Since the DO concentration in the seawater for the case of lower DO/H$_2$S concentration ratio is expected to decline in tandem with the breakdown of H$_2$S, estimation of K$_2$ in this case, is applicable only over a narrow time range where the DO concentration within that time range does not resulted in a significant differences in K$_2$ and K$_1$. In this study, such approximations are restricted to the first few minutes of the experiments, where the H$_2$S concentration decline is still linear and the DO has not declined more than 50% of its
initial concentration. Integrating equation (5) provides a mathematical estimate of the \( \text{H}_2\text{S} \) dissociation half-life for the experiments (equation 6 - 8):

\[
\int \frac{d[\text{H}_2\text{S}]}{[\text{H}_2\text{S}]} = -1 \int K_2 [\text{O}_2] \ln \frac{[\text{O}_2]_t [\text{H}_2\text{S}]_t}{[\text{O}_2]_0 [\text{H}_2\text{S}]_0} = K_2 t
\]

(6)

When \([\text{O}_2]_0\) is much higher than \([\text{H}_2\text{S}]_0\), \([\text{O}_2]_0 \approx [\text{O}_2]_t\), equation (6) become (7)

\[
\frac{1}{[\text{O}_2]_t} \ln \frac{[\text{H}_2\text{S}]_t}{[\text{H}_2\text{S}]_0} = K_2 t
\]

\[ [\text{H}_2\text{S}]_t = [\text{H}_2\text{S}]_0 e^{-[\text{O}_2]_t K_2 t} \]

(7)

Half-life can be determined based on equation (7), as \([\text{H}_2\text{S}]_t = 0.5[\text{H}_2\text{S}]_0\), thus

\[
t_{1/2} = \frac{\ln 0.5}{-K_2 [\text{O}_2]_0}
\]

(8)

**Statistical analysis**

Paired t-test was performed to compare if there is significant different in the reading obtained from \( \text{H}_2\text{S} \) probe (MS-AQUA) and the standard methods [16]. The statistical analysis was performed by using open source software, R statistics version 3.3.2.

**Results and Discussion**

**Validation of \( \text{H}_2\text{S} \) probe**

Data obtained by using the \( \text{H}_2\text{S} \) probe (MS-AQUA) was cross checked with APHA 4500-\( \text{S}^2\text{F} \) standard method. Experiments and analysis on different concentration of \( \text{H}_2\text{S} \) standard solution was conducted to validate the corresponding measurement on the sensor. Results obtained from the probe were not significantly different (paired t-test, \( p>0.05 \)) from those obtained by using APHA standard method and there is a correlation between the data values. (Pearson, \( P < 0.05, R^2 = 0.9974 \)). Figure 3 shows the correlation of \( \text{H}_2\text{S} \) concentration obtained by using probe and the standard method. Validation of the \( \text{H}_2\text{S} \) probe is important because the probe is considered new in the market and there are only few reports on its efficiency in measurement. The probe is responsive towards \( \text{H}_2\text{S} \) even it exceeded the measurement range recommended by the manufacturer although the last two points in the validation curve (Figure 3) starts showing deviation from the proportionality.

![Figure 3. \( \text{H}_2\text{S} \) Probe (MS-AQUA) measurement correlated with concentration determined by using APHA standard methods (4500-\( \text{S}^2\text{F} \) and APHA 4500-\( \text{S}^2\text{H} \))](image_url)
**H₂S solubility and pH changes in seawater**

When H₂S was continuously bubbled into the seawater, the seawater pH dropped from an initial value of pH 8.01 down to pH 4.27 as the H₂S concentration was approaching 2312 mg L⁻¹ (Figure 4). At 28 °C, the concentration of H₂S was saturated at about 2500 mg L⁻¹ in 30 ppt seawater in the experiments. It is anticipated that H₂S would equilibrate and evolve into the vapor space at the saturation state. Hence, the H₂S concentration used in this study was limited to 1500 mg L⁻¹ to reduce experimental errors and in terms of safety consideration.

![Figure 4. Effect of hydrogen sulfide concentration on seawater pH](image)

**Hydrogen sulfide breakdown in seawater at different [DO]/[H₂S] ratio**

In the presence of excess dissolved oxygen in seawater, dissolved hydrogen sulfide (H₂S) is oxidized rapidly in the seawater. Figure 5 shows the H₂S breakdown against time in seawater under aerobic condition. At an initial dissolved oxygen of 10.2 mg O₂ L⁻¹ (Figure 5a), the H₂S decomposed from initial 3.2 mg L⁻¹ into half of its initial concentration at 1.6 mg L⁻¹ in about 10 minutes when the ratio of [DO/H₂S] is 3.4 (Figure 5a). The H₂S concentration was further decomposed in the seawater. The subsequent half-life of the H₂S concentration 1.6 to 0.79 mg L⁻¹ was about 9 minute. We repeated the experiment by introduced an initial concentration of 5.2 mgL⁻¹ H₂S under a [DO/H₂S] ratio of 3.2 (Figure 5b) at an initial dissolved oxygen of 17.4 mg O₂ L⁻¹, after 10.6 minutes, the H₂S concentration dropped to half of its initial concentration. The H₂S concentration in this experiment further decomposed to 1.3 mgL⁻¹ after 10.4 minutes. In both experiments, the dissolved oxygen remained above 4 mgL⁻¹ at the end of the experiments. On average, H₂S breakdown at 9.9 ± 0.8 minute in the seawater when dissolved oxygen is in excess. The H₂S breakdown reaction appears to be a first order reaction, when the dissolved oxygen is not a limiting factor.
Hydrogen sulfide breakdown in seawater at low [DO/H$_2$S] molarity ratio

Under low [DO/H$_2$S] molarity ratio, as the hydrogen sulfide (H$_2$S) is oxidized, the concentration of DO in the seawater decreased in tandem with the decrease in H$_2$S concentration. In this case, H$_2$S breakdown no longer resemble a first order reaction due to the dissolved oxygen depletion in the seawater. The H$_2$S breakdown is rather regulated by the availability of the dissolved oxygen. Figure 6 shows a typical H$_2$S concentration decline as it is reacted with DO under a low [DO/H$_2$S] concentration ratio. The H$_2$S half-life at initial conditions of the experiment was estimated based on equation (4) provided earlier. Further experiments were conducted at low [DO/H$_2$S] ratios to derive the correlations of H$_2$S breakdown in seawater and determine the approximate H$_2$S half-life under those conditions. The experiments were conducted such that the [DO/H$_2$S] molarity ratio range spanned from less than 0.1 to above 10. This would provide adequate evidence of any correlation between the concentration ratio and the dissociation half-life. Table 3 below provides the measured H$_2$S half-life for various [DO/H$_2$S] ratio.

Figure 6. Typical hydrogen sulfide breakdown in seawater at low [DO/H$_2$S] concentration ratio [H$_2$S initial concentration = 114 mg L$^{-1}$; DO initial concentration = 5 mg L$^{-1}$]. Open blank circle indicates dissolved oxygen while filled circle indicates concentration of hydrogen sulfide in seawater.
Table 3. H$_2$S Half-life at various [DO/H$_2$S] ratio

| [DO/H$_2$S] Ratio | H$_2$S Initial Conc. (mg L$^{-1}$) | DO Initial Conc. (mg L$^{-1}$) | H$_2$S Half-life (min) |
|-------------------|-----------------------------------|--------------------------------|-----------------------|
| 0.05              | 114.0                             | 5.0                            | 82.1                  |
| 0.16              | 92.7                              | 14.0                           | 35.7                  |
| 0.49              | 43.2                              | 20.0                           | 17.3                  |
| 3.41              | 3.2                               | 10.2                           | 10.3                  |
| 12.02             | 1.5                               | 16.4                           | 3.3                   |

As can be seen from Table 3 and Figure 7, the H$_2$S half-life versus [DO/H$_2$S] concentration ratio reveal a non-linear regression. The log transformed half-life and [DO/H$_2$S] ratio showed a significant regression (P < 0.05, y = -0.54x + 1.16, R$^2$ = 0.9687). Figure 7 shows the H$_2$S half-life plotted against the molarity ratio of [DO/H$_2$S] in a log-log plot. The relationship between the [DO/H$_2$S] versus H$_2$S half-life resembles an inverse relationship, where decomposition of H$_2$S is very much dependent on the presence of dissolved oxygen in the seawater. Based on Figure 7, when [DO/H$_2$S] concentration ratio is lower than 0.07, the H$_2$S half-life will extend beyond hour. When the [DO/H$_2$S] ratio is higher than 1.1, the H$_2$S half-life will fall within 10 minutes.

Figure 7. Hydrogen sulfide half-life versus the molarity ratio of [DO/H$_2$S] in a log-log plot

Table 4 shows a compilation of H$_2$S half-life reported in various reports. The H$_2$S half-life reported ranged from 17 minutes up to 55 days. Our current finding is consistent with the previous reports which reported that oxidation of H$_2$S resembles a first order reaction in seawater when the dissolved oxygen is high and unlimited and becomes a second order reaction when dissolved oxygen is depleting [7, 8]. Nevertheless, both group of researchers reported that oxidation of H$_2$S in seawater involved a series of complicated processes that are dependent on the composition and conditions of seawater. Different seawater conditions; which include physical, chemical and biological parameters is interacting and will influent H$_2$S breakdown in the seawater.

Pos et al. [18] reported H$_2$S in seawater subjects to photo-oxidation that had a half-life of 45 ± 15 minutes in Biscayne Bay water and 147 ± 15 minutes in the Gulf stream while Heitmann and Blodau [19] reported oxidation and incorporation of H$_2$S by dissolved organic matter in seawater. Luther et al. [20] reported a complicated inorganic and biological mediated processes in the fate of H$_2$S in the seawater environment. To the best of our survey, we have not encounter any comprehensive report that reveals the total interaction of physical, chemical and
biological factors into the H$_2$S breakdown in seawater and the complicated interaction is probably the reasons that lead to various H$_2$S half-life reported in the seawater.

Table 4. H$_2$S breakdown half-life reported in seawater

| Medium         | Experimental Conditions                                                                 | Half-Life | References |
|----------------|----------------------------------------------------------------------------------------|-----------|------------|
| Seawater       | Temperature = 28 °C<br>Salinity = 30 ppt<br>Hydrogen sulfide = 1.5 – 114 mg L$^{-1}$<br>DO = 5 – 16.4 mg L$^{-1}$   | 3.3 – 82.1 min | Present study |
| Seawater       | Temperature = 9.8 °C<br>Salinity = 30.27 ppt<br>Total sulfide = 2.0 mg L$^{-1}$<br>DO = DO: Total sulfide ratio from 8 - 2<br>pH = 9.6 | 6-28 h | [7] |
| Seawater       | Temperature = 25 °C<br>Salinity = 35 ppt<br>H$_2$S = 0.85 mg L$^{-1}$<br>pH = 8.0 | 26 h | [8] |
| Seawater       | Temperature = 25 °C<br>Salinity = Not reported<br>H$_2$S = Not reported<br>DO = 3.8 ml/l<br>pH = Not reported | 17 min | [10] |
| Seawater       | Temperature = Not reported<br>Salinity = 30 ppt<br>H$_2$S = 20 mg L$^{-1}$<br>DO = Not reported<br>pH = Not reported | 45 min | [11] |
| NaCl solution  | Temperature = 25 °C<br>Salinity = Not reported<br>H$_2$S = Not specified<br>DO = Saturation<br>pH = 12 | 55 day | [20] |
| Artificial seawater | Temperature = Not reported<br>Salinity = 16.5 ppt<br>H$_2$S = 25 mg L$^{-1}$<br>DO = Not reported<br>pH = Not reported | 57 min | [21] |
| Seawater       | Not reported<br>H$_2$S = 513 µg L$^{-1}$<br>DO = Not reported<br>pH = 9.6 | 2 – 5 h | [22] |
| Seawater       | Not reported<br>H$_2$S = 513 µg L$^{-1}$<br>DO = Not reported<br>pH = 9.6 | 30 min | [23] |
Conclusion
Hydrogen sulfide (H$_2$S) breakdown in seawater is highly dependent on the concentration of dissolved H$_2$S and the concentration of dissolved oxygen (DO). The rate of H$_2$S breakdown can be generally estimated based on the molarity ratio of [DO/H$_2$S]. At high [DO/H$_2$S] ratio (> 1), the H$_2$S breakdown rate can be rapid, resulting in short half-life of H$_2$S dissociation (within 10 minutes). Under this circumstance where the dissolved oxygen is not a limiting factor in the H$_2$S oxidation, the breakdown rate appears as a first order reaction. However, when the ratio of [DO/H$_2$S] ratio is lower than 0.07, the breakdown rate became slower, resulting in longer half-life of H$_2$S breakdown (more than an hour’s). In this case, the breakdown rate displays a second order reaction form, which concurred with reports from other investigators. This study also investigated relation between the dissolved H$_2$S content and pH changes in the seawater. The pH of seawater became lowered with increasing initial H$_2$S concentration in the seawater. It reached an asymptotic low value of about 4 as the dissolved H$_2$S content approaches its saturation limit in the seawater at about 2,500 mg L$^{-1}$.

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References
1. Karl, D. M. (1995). The microbiology of deep sea thermal vents. CRC Press, New York, pp. 299.
2. Ellis, A. J. and Golding, R. M. (1959). Spectrophotometric determination of the acid dissociation constants of hydrogen sulphide. Journal of the Chemical Society, 1959: 127 – 130.
3. Savenko, V. S. (1977). The dissociation of hydrogen sulfide in seawater. Oceanology, 16: 347 – 350.
4. Barbero, J. A., McCurdy, K. G. and Tremaine, P. R. (1982). Apparent molal heat capacities and volumes of aqueous hydrogen sulfide and sodium hydrogen sulfide near 25°C: The temperature dependence of H$_2$S ionization. Canadian Journal of Chemistry, 60(14): 1872 – 1880.
5. Millero, F. J., Plese, T. and Fernandez, M. (1988). The dissociation of hydrogen sulfide in seawater. Limnology and Oceanography, 33(2): 269 – 274.
6. Zavodnov, S. S., and Kryukov, P. A. (1960). The value of the second dissociation constant of hydrogen sulfide. Bulletin of the Academy of Sciences of the USSR, Division of Chemical Science, 9(9): 1583 – 1585.
7. Cline, I. D. and Richards, F. A. (1969). Oxygenation of hydrogen sulfide in seawater at constant salinity, temperature and pH. Environmental Science and Technology, 3(9): 838 – 843.
8. Millero, F. J., Hubinger, S., Fernandez, M. and Garnett, S. (1987). Oxidation of H$_2$S in seawater as a function of temperature, pH, and ionic strength. Environmental Science and Technology, 21(5): 439 – 443.
9. Chen, K. Y. and J. C. Morris. (1972). Kinetics of oxidation of aqueous sulphide by O$_2$. Environmental Science and Technology, 6(6): 529 – 537.
10. Göté, H. Ö. and Alexander, J. (1963). Oxidation rate of sulfide in seawater, a preliminary study. Journal of Geophysical Research, 68(13): 3995 – 3997.
11. Sharma, K. R. and Yuan, Z. (2010). Kinetics of chemical sulfide oxidation under high dissolved oxygen levels. Proceedings of 6th International Conference of Sewer Processes and Networks: 1 – 3.
12. Asaoka S., Yamamoto, T., Takahashi, Y., Yamamoto, H., Kim, K. H. and Orimoto, K. (2012). Development of an on-site simplified determination method for hydrogen sulfide in marine sediment pore water using a shipboard ion electrode with consideration of hydrogen sulfide oxidation rate. Interdisciplinary Studies on Environmental Chemistry - Environmental Pollution and Ecotoxicology, 6: 345 – 352.
13. Baumgartner, L. K., Reid, R. P., Dupraz, C., Decho, A. W., Buckley, D. H., Spear, J. R., Przekop, K. M. and Visscher, P. T. (2006). Sulfate reducing bacteria in microbial mats: changing paradigms, new discoveries. Sedimentary Geology, 185: 131 – 145.
14. Poulton, S. W., Krom, M. D., Raiswell, R. and Raiswell, R. (2004). A revised scheme for the reactivity of iron (oxyhydr)oxide minerals towards dissolved sulfide. Geochimica et Cosmochimica Acta, 68: 3703 – 3715.
15. Yao, W., and Millero, F. J. (1996). Oxidation of hydrogen sulfide by hydrous Fe(III) oxides in seawater. Marine Chemistry, 52: 1 – 16.
16. American Public Health Association (2005). Standard methods for examination of water and wastewater, American Public Health Association, W.W.A, Washington, D.C.
17. Han, K., Chu, T., Hirst, J., Smith, I. W. M., Canneaux, S., Kim, Y., Calvo, F., de la Lande, A. Skodje, R. T., Kawai, S., Petters, B., Kapral, R., Kim, H. J., Zhao, Y., Yan, Y., Zhang J., Swiatla-Wojcik, D., Bertrand, P., Varandas, A. J. S., Borgis, D., Senthilkumar, K., Hase, W. L. and Gao, J. (2013). Reaction rate constant computations: Theories and applications. *Royal Society of Chemistry*, London pp. 572.

18. Pos, W. H., Milne, P. J., Riemer, D. D. and Zika, R. G. (1997), Photoinduced oxidation of H$_2$S species: A sink for sulfide in seawater, *Journal of Geophysical Research*, 102(11): 12831 – 12837.

19. Heitmann, T., and Blodau, C. (2006). Oxidation and incorporation of hydrogen sulfide by dissolved organic matter. *Chemical Geology*, 235(1): 12 – 20.

20. Luther, G. W., Findlay, A. J., MacDonald, D. J., Owings, S. M., Hanson, T. E., Beinart, R. A., and Girguis, P. R. (2011). Thermodynamics and kinetics of sulfide oxidation by oxygen: A look at inorganically controlled reactions and biologically mediated processes in the environment. *Frontiers in Microbiology*, 2(62): 1 – 9.

21. Dermendzhieva N., Razkazova-Velkova E., Martinov M., Ljutzkanov L. and Beschko V. (2013). Oxidation of sulfide ions in model solutions of seawater using of metal catalysts built in carbon matrix. *Journal of Chemical Technology and Metallurgy*, 48(5): 465 – 468.

22. Almgren T., Dyrrsen D., Elgquist B. and Johansson H. (1976). Dissociation of hydrogen sulfide in seawater and comparison of pH scale. *Marine chemistry*, 4: 289 – 297.

23. Aumond V., Waeles M., Salaün P., Gibbon-Walsh K., van den Berg C. M. G., Sarradin P. and Riso R. D. (2012). Sulfide determination in hydrothermal seawater samples using a vibrating gold micro-wire electrode in conjunction with stripping chronopotentiometry. *Analytica Chimica Acta*, 753: 42 – 47.