Degradation Kinetics of Fe-EDTA in Hydrogen Sulfide Removal Process

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1. Introduction

The polyamino polycarboxylate-chelated iron process is extremely effective and allows total conversions of hydrogen sulfide to be obtained. It is also a very flexible process and has in fact been widely diffused throughout the world. This process, however, has various drawbacks. Above all, when operating in an alkaline solution, there is the radical oxidation of the iron ligand with the degradation of the ligand itself and the precipitation of iron as sulfide. This has two strong consequences on the process: the ligand, which is expensive, must be continuously reintegrated; furthermore, the sulfur produced is impure of iron sulfide, and this makes it absolutely unsuitable for commercialization. In practice, the lost of the chelating agents turns out to be the most significant factor affecting the economic feasibility of large scale operation.

A few of the prior art workers have acknowledged that chelated iron solutions are unstable and that undesirable precipitation of iron compounds may occur. Nichol and Sapiro [1, 2] recommended careful control of the regeneration of the catalyst solution to avoid overoxidation of the iron chelate. Thompson [3] indicates that restricting the molar ratio of chelating agent to iron is an important consideration in avoiding breakdown of the chelate molecule. Lynn and Dubs [4] suggest the addition of selected amine salt stabilizers to achieve chelate stability at low pH levels. Diaz [5–7] and Blytas [8] propose the addition of various sulfur-containing and nitrogen-containing compounds as stabilizers to reduce the rate of chelate degradation. Bedell [9] disclosed that soluble chemical compounds having a high affinity for hydroxyl radicals are effective stabilizers for chelating agents used in the hydrogen sulfide removal process. The researcher exposed the aromatic compounds that can further retard the degradation of the original metal chelate solution by reducing the amount of free hydroxyl radicals in the solution and by later complexing with metal ions released by degraded chelating agents before the
aromatic compounds are degraded by additional hydroxyl radicals. Preferred compounds can be selected based upon solubilities, costs, and relative effectiveness. These prior arts have not provided an effective, environmentally acceptable, and inexpensive solution to the problem of chelate degradation. Moreover, there has been no adequate explanation of the mechanism of chelate instability in a hydrogen sulfide removal process. Until Chen et al. [10, 11] observed that polyaminocarboxylic acid trends to rupture at the weak locations, for example, ethylene moiety of EDTA which leads to dechelation and then degradation of Fe-EDTA. Cleavage is presumably ascribed to the presence of hydroxyl-free radicals produced from the reoxidation of ferrous chelate product into active ferric chelate via a Fenton mechanism.

Mcmanus and Kin [12] studied the effectiveness of sodium thiosulfate as a stabilizing additive in an aqueous NTA-iron chelate solution when used in a cyclic hydrogen sulfide removal catalyst regeneration process. The result showed the NTA concentration changed from 10.09 g/L to 8.73 g/L (a decrease of 13.5%) in 92.5 hours, whereas in the control run the NTA was totally degraded shortly after 47 hours. The soluble Fe changed from 990 to 900 g/L (10%) in the presence of sodium thiosulfate whereas in the control run the soluble Fe concentration decreased about 30% within 92.5 hours.

Sunda and Huntsman [13] investigated that temperature, pH, and light had also effect on equilibrium dissociation constant for Fe-EDTA chelates, which indicates the strength of binding between Fe and EDTA. They found that increases in pH (7.7–9) increased equilibrium dissociation constants for Fe-EDTA chelates, apparently due to the formation of mixed EDTA-hydroxy chelates. Light also increased the dissociation constant due to photoreductive dissociation of ferric-EDTA chelates. A decrease in temperature from 20 and 10°C had little effect on dissociation constants in the dark, indicating that rate constants for Fe-EDTA association and dissociation were about equally affected by temperature.

More recently, de Algelis et al. [14] studied the oxidation of hydrogen sulfide to sulfur by mean of treatment with an aqueous acid solution containing trivalent iron and a heteropolyacid. The oxidation cycle of hydrogen sulfide to sulfur (10 hours), filtration of the sulfur, and re-oxidation of the solution with air (4 hours) was repeated four times, on the same solution. They found that no decrease in the catalyst performance. However, the preparation of this oxidation solution is very complex.

To our knowledge, no kinetics study has been done on the degradation of Fe-EDTA in H₂S removal system, and no Fe-EDTA degradation rate equation has been presented. The prediction of the extent and rate of Fe-EDTA degradation is vital in the estimation of the exact Fe(III)EDTA make-up rate needed to maintain the H₂S absorption capacity of the removal process. The goal of this research was to determine the potential for Fe-EDTA degradation as a function of degradation parameters such as the H₂S molar flow rate, the initial Fe(III)EDTA concentration, and the concentration of the new stabilizer which were investigated in this study based on the initial Fe-EDTA degradation rate.

2. Materials and Method

2.1. Chemical. 40% w/w Ferric chloride solution (FeCl₃) and EDTA(Na₄·4H₂O) powder with commercial grade were purchased from L.B. Science LTD, Thailand. Sodium thiosulfate 5·H₂O (99.5%, Ajax Finechem) and sodium citrate (99.0%, Ajax Finechem) were used. Biogas (1, 300–1, 600 ppm H₂S content) produced from Mongkol pig farming located at Phattalung province was used in this study.

A Fe(III)EDTA solution was prepared using the following recipe. A 187 g of EDTA-4Na powder was dissolved into 900 mL of water wherein 100 mL of 40% FeCl₃ solution was added. The Fe(III)EDTA solution was obtained with the concentration of 0.35 mol Fe/L. And the mole ratio of iron and EDTA in the solution was 1:1.2. Working solution for experiments was freshly prepared with deionized water. The calculated stabilizers amount was mixed with the 0.35 mol Fe/L Fe-EDTA solution to obtain the expected concentration. The solution was adjusted to pH 7.0 by adding 3 N HCl.

2.2. Experimental Procedure. The oxidation reaction of H₂S by Fe(III)EDTA in the presence and absence of the stabilizers was performed in the 1000 mL semibatch reactor where the biogas was continuously fed into liquid Fe-EDTA solution as illustrated in Figure 1. From Figure 1 the gas phase, biogas, and air were introduced separately as bubble into the 750 mL of predetermined concentration Fe(III)EDTA solution. Air flow rate used in all experiments was 1 L/min throughout the reaction in order to reoxidize ferrous into the active ferric form. The ferrous regeneration efficiency was more than 90% in all experiments. The biogas volumetric flow rate was varied between 0.5 and 2.0 L/min. As Fe-EDTA degradation is a very slow process, each experiment requires a long experimentation time of 30 h. During the experiment, the gas and liquid samples were collected at every 3 h. To ensure actual representation of samples collected at each time interval, the gas introduction and sample removal dip tube was first rinsed to get rid of the old sample left in the tube from the last sample collection. The H₂S concentrations in biogas were determined at the inlet and the outlet of reactor by iodometric method. Because of the ferric in the form of ion in solution, it can oxidize H₂S to the element sulfur. Thus, the degradation of Fe-EDTA is the abatement of iron concentration in the solution. The concentration of soluble Fe in the solution was determined using atomic absorption spectroscopy. All experiments were performed at ambient temperature of 30 ± 2°C.

After 30 h of reaction time the solid product was filtered, washed, dried, and analyzed with CHNS-analyzer to determine % weight of carbon, hydrogen, nitrogen, and sulfur element.

3. Results and Discussion

3.1. Degradation of Fe-EDTA Kinetics Studies. The rate equation was formulated based on the assumption that Fe(III)EDTA reacted only in the liquid phase with dissolved H₂S, which allowed the degradation kinetics to be formulated as a homogeneous liquid phase system. Although
mass transfer could possibly control the degradation rate of H₂S, the mass transfer limitation is insignificant during the degradation time (e.g., 0–30 h of degradation time) since an appropriate stirring speed is applied [15]. The interference from degradation products could also be neglected. These assumptions were used to formulate the kinetic model in this study.

Figures 2 and 3 represent soluble Fe concentration versus time relationship which indicates a first approach. Thus, the degradation of Fe-EDTA can be described by pseudo first-order kinetics with respect to Fe concentration as expressed in the following equation:

\[ R_d = -\frac{dC_{Fe}}{dt} = k_d C_{Fe}. \]  

(1)

Separating and integrating (1), we obtain the following:

\[ -\ln \left( \frac{C_{Fe,t}}{C_{Fe,0}} \right) = k_d t, \]  

(2)

where \( R_d \) represents the Fe-EDTA degradation rate, \( k_d \) represents the pseudo first-order degradation rate constant, \( C_{Fe,0} \) and \( C_{Fe,t} \) represent the concentration of soluble Fe at an initial and at any reaction time, respectively. In this case, a plot of \(-\ln(C_{Fe,t}/C_{Fe,0})\) versus time in every experiment must lead to a straight line with slope of \( k_d \). \( k_d \) may be a function of several variables as follows:

\[ k_d = f_n(Q_{H_2S}, C_{Fe,0}, C_{Cl}, \ldots), \]  

(3)

where \( Q_{H_2S} \) represents H₂S molar flow rate, and \( C_{Cl} \) represents the concentration of sodium citrate.

The effect of H₂S molar flow rate was evaluated by using 5.78 mol/m³ initial Fe(III)EDTA concentration, while the average H₂S molar flow rate of 2.0 × 10⁻³ mol/h was used to study the effect of the initial Fe(III)EDTA concentration. The Fe-EDTA degradation rates \( (R_d) \) of each experimental run are listed in Table 1. It can be observed that \( R_d \) increases rapidly with increasing \( Q_{H_2S} \), but it only slightly decreases with increasing \( C_{Fe,0} \). This can conclude that the effect of \( Q_{H_2S} \) on \( R_d \) is greater than the effect of \( C_{Fe,0} \).

This result is consistent with Chen et al. [10] who observed that the iron chelate degradation occurs during...
Table 1: Fe-EDTA degradation rate ($R_d$) at various H$_2$S molar flow rate ($Q_{H2S}$) and initial Fe(III) EDTA concentration ($C_{Fe,0}$).

<table>
<thead>
<tr>
<th>Run no.</th>
<th>$Q_{H2S} \times 10^3$ (mol/h)</th>
<th>$C_{Fe,0}$ (mol/m$^3$)</th>
<th>$R_d$ (mol m$^{-3}$ h$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.08</td>
<td>5.78</td>
<td>0.00356</td>
</tr>
<tr>
<td>2</td>
<td>1.05</td>
<td>5.78</td>
<td>0.00323</td>
</tr>
<tr>
<td>3</td>
<td>2.06</td>
<td>5.78</td>
<td>0.00528</td>
</tr>
<tr>
<td>4</td>
<td>2.01</td>
<td>5.78</td>
<td>0.00535</td>
</tr>
<tr>
<td>5</td>
<td>2.73</td>
<td>5.78</td>
<td>0.00746</td>
</tr>
<tr>
<td>6</td>
<td>2.79</td>
<td>5.78</td>
<td>0.00707</td>
</tr>
<tr>
<td>7</td>
<td>3.40</td>
<td>5.78</td>
<td>0.00939</td>
</tr>
<tr>
<td>8</td>
<td>3.20</td>
<td>5.78</td>
<td>0.00950</td>
</tr>
<tr>
<td>9</td>
<td>1.79</td>
<td>2.17</td>
<td>0.00493</td>
</tr>
<tr>
<td>10</td>
<td>1.81</td>
<td>2.17</td>
<td>0.00508</td>
</tr>
<tr>
<td>11</td>
<td>1.94</td>
<td>3.94</td>
<td>0.00511</td>
</tr>
<tr>
<td>12</td>
<td>1.90</td>
<td>3.94</td>
<td>0.00515</td>
</tr>
<tr>
<td>13</td>
<td>2.16</td>
<td>5.73</td>
<td>0.00556</td>
</tr>
<tr>
<td>14</td>
<td>2.13</td>
<td>5.73</td>
<td>0.00539</td>
</tr>
<tr>
<td>15</td>
<td>2.37</td>
<td>8.16</td>
<td>0.00556</td>
</tr>
<tr>
<td>16</td>
<td>2.40</td>
<td>8.16</td>
<td>0.00514</td>
</tr>
</tbody>
</table>

The re-oxidation of the ferrous to ferric system with air (molecular oxygen). They suggested that only free radicals have enough energy to degrade these chelating ligands which lead to dechelation (degradation) of iron chelate and also indicates that the hydroxyl radical may be formed under the reaction conditions.

The main degradation products identified by Chen et al. [11] are iminodiacetic acid (IDA) and ethylenediaminediacetic acid (EDDA). All of the oxidation intermediates being formed by hydroxylation of one of the CH$_2$ groups, either on the ethylene bridge or side chain acetate groups. Following hydroxylation, the aldehyde formed by hydrolytic cleavage is rapidly converted to the corresponding carboxylate. It is worth noting that the pH in all the experiments decreased during the reaction going from 7.0 to 4.5. Under this acidic condition the Fe-chelated degradation rate can also be slightly promoted [10].

All results can be described by the pseudo first-order kinetics as evident by the plot of $-\ln(C_{Fe,t}/C_{Fe,0})$ versus time as illustrated in Figures 4 and 5. It can be observed in these figures that the linear relationship between $-\ln(C_{Fe,t}/C_{Fe,0})$ and time was highly with the coefficients of determination greater than 0.91. In experiments carried out in duplicate as can be seen in Figures 6 and 7, the pseudo first-order rate constant, $k_d$, with respect to H$_2$S molar flow rate ($Q_{H2S}$) and initial Fe(III)EDTA concentration ($C_{Fe,0}$), respectively, varied by less than 10%. The observed degradation rate constant, $k_d$, increase with increasing H$_2$S molar flow rate while the increasing of the initial Fe(III)EDTA concentration decrease $k_d$.

The relationship between $k_d$ and $Q_{H2S}$ and $C_{Fe,0}$ was formulated using linear regression method. Result is given in the following equation:

$$k_d(Q_{H2S}, C_{Fe,0}) = 3.446 - 0.784C_{Fe,0} + 0.0452C_{Fe,0}^2 + 0.111 \times 10^{-3}Q_{H2S}^2.$$  (4)

The empirical equation was evaluated based on the coefficient of determination value $R^2$ and adjusted $R^2$ of 0.982 and 0.978, respectively. This indicated that there was
3.2 Analysis of Sulfur Cake. The species presented in the precipitate or sulfur cake from H$_2$S oxidation were identified in this studied. The main species that assume to be in the sulfur cake are C, H, N, and O from EDTA degradation, S from H$_2$S oxidation, and Fe from Fe-EDTA dechelation. The CHNS analyzer and UV-VIS spectrophotometer (samples were treat treated by phenanthroline method) was used to analyze the quantity of C, H, N, and S element, and Fe, respectively. The analyzed sulfur cake result is shown in Table 2. The sum of amount of elements in sulfur cake showed a mass balance of about 100%. As expected, S (more than 98% by weight) was the main element in the sulfur cake with small amount Fe and very small amount of C, H, and N. The amount of Fe found in sulfur cake was almost consistent with Fe degraded from the solution. It can be noted that no
significant EDTA degrades into the solid form. The remained EDTA and its ruptured products were still in the solution. However, the products cleavage from EDTA does not have high affinity enough to maintain Fe in the solution from.

3.3. The Effect of Chemicals Additive into Fe-EDTA Solution. Fe(III)EDTA is capable use for the oxidation of H2S to element sulfur. The main difficulty with the process is the degradation of Fe-EDTA catalyst. The loss of Fe-EDTA is caused by the degradation of EDTA. Chen et al. [10] suggested that degradation is promoted by hydroxyl radicals. Many additives that function as radical scavengers have been used to slow down radical induced oxidative degradation. There are many such additives that may be used. A very effective and inexpensive free radical scavenger is thiosulfate ion (300 mol/m3), usually supplied as sodium thiosulfate. In this study, the common hydroxyl scavenger, sodium citrate was used. Citric acid and its salts have many applications in everyday life. Among others, it is used as an additive in food and in the production of cold drinks [16]. Many literatures reported that citrate has ability to reduce free radical formation [17, 18] and also is a ligand with high affinity complex with iron. The comparison of the capability to reduce Fe-EDTA degradation rate between using sodium citrate and sodium thiosulfate in this study is shown in Table 3. The result demonstrated that the effectiveness of sodium citrate as a stabilizer was slightly higher than sodium thiosulfate. A suitable stabilizer is required to reduce the degradation rate and keep the iron in solution. Sodium citrate was chosen as a stabilizer in this degradation kinetics study based on the following reasons. Using thiosulfate, the sulfur compounds in the system is raised that it can be converted to H2S or other toxic compounds such as sulfite. This is not a problem of sodium citrate. The cost of citrate is lower than thiosulfate because sodium citrate can be produced from citric acid and sodium hydroxide which are cheap and commercial. Thus, sodium citrate is a suitable stabilizer for reducing the Fe-EDTA degradation rate.

3.4. The Effect of Sodium Citrate Concentration in Fe-EDTA Degradation. According to the previous section, sodium citrate is the suitable additive which can be used as stabilizer based upon the solubility, cost, and relative effectiveness. The experiments were set to determine the relationship of sodium citrate concentration (C_CI) and the Fe-EDTA degradation rate (R_d). The experimental runs were conducted using the sodium citrate concentration of 0–300 mol/m3 with the H2S molar flow rate and the initial Fe(III)EDTA concentration of 1.84 x 10^{-3} mol/h and 5.80 mol/m3, respectively.

Again, the degradation of Fe-EDTA followed by the first-order degradation rate as supported by the relationship between −ln(C_{Fe,0}/C_{Fe,t}) and time which is shown in Figure 10 with the coefficients of determination value higher than 0.93.

kd decreases with an increase in C_CI as illustrated in Figure 11. It is also observed that the reduction of R_d may be constant as C_CI greater than that 300 mol/m3. The relationship between kd and C_CI up to 300 mol/m3 was fitted.

The empirical model with R^2 and adjusted R^2 of 0.983 and 0.976, respectively, was obtained as given by the following equation:

\[
kd(C_{CI}) = 0.921 - 0.00526C_{CI} + 1.176 \times 10^{-5}C_{CI}^2. \tag{5}
\]

It can be noted from (5) that the kd at the absence of sodium citrate was equal to 0.921 h^{-1}. This value represents the effect of Q_{H2S} and C_{Fe,0} on the degradation of Fe-EDTA. Thus, the truly effect of C_{CI} is just the last two terms of (5).

Moreover, the kd evaluated from slope of Figures 4, 5, and 10 at corresponding Q_{H2S}, C_{Fe,0}, and C_{CI} were together...
Table 2: The composition of sulfur cake for each sample.

<table>
<thead>
<tr>
<th>(Q_{H_2S}) \times 10^3 (mol/h)</th>
<th>C_{Fe,0} (mol/m^3)</th>
<th>Sulfur cake (g)</th>
<th>N</th>
<th>C</th>
<th>H</th>
<th>S</th>
<th>Fe</th>
<th>Sum</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.08</td>
<td>5.78</td>
<td>0.805</td>
<td>0.19</td>
<td>0.96</td>
<td>0.12</td>
<td>98.36</td>
<td>0.40</td>
<td>100.03</td>
</tr>
<tr>
<td>2.73</td>
<td>5.78</td>
<td>2.251</td>
<td>0.11</td>
<td>0.83</td>
<td>0.10</td>
<td>99.10</td>
<td>0.35</td>
<td>100.49</td>
</tr>
<tr>
<td>3.20</td>
<td>5.78</td>
<td>2.675</td>
<td>0.12</td>
<td>0.68</td>
<td>0.08</td>
<td>99.01</td>
<td>0.56</td>
<td>100.45</td>
</tr>
<tr>
<td>1.81</td>
<td>2.17</td>
<td>1.535 (&lt;0.01)</td>
<td>0.74</td>
<td>0.09</td>
<td>98.62</td>
<td>0.28</td>
<td>99.73</td>
<td></td>
</tr>
<tr>
<td>1.94</td>
<td>3.94</td>
<td>1.693 (&lt;0.01)</td>
<td>0.72</td>
<td>0.08</td>
<td>98.97</td>
<td>0.24</td>
<td>100.01</td>
<td></td>
</tr>
<tr>
<td>2.13</td>
<td>5.73</td>
<td>1.922 (&lt;0.01)</td>
<td>0.56</td>
<td>0.07</td>
<td>99.93</td>
<td>0.23</td>
<td>100.79</td>
<td></td>
</tr>
<tr>
<td>2.40</td>
<td>8.16</td>
<td>2.106 (&lt;0.01)</td>
<td>0.59</td>
<td>0.07</td>
<td>99.23</td>
<td>0.32</td>
<td>100.21</td>
<td></td>
</tr>
</tbody>
</table>

Table 3: Fe-EDTA degradation rate ($R_d$) with and without additive.

<table>
<thead>
<tr>
<th>(Q_{H_2S}) \times 10^3 (mol/h)</th>
<th>C_{Fe,0} (mol/m^3)</th>
<th>Additive</th>
<th>Additive concentration (mol/m^3)</th>
<th>$R_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.07</td>
<td>5.84</td>
<td>No additive</td>
<td>0</td>
<td>0.00536 ± 0.00001</td>
</tr>
<tr>
<td>2.04</td>
<td>5.85</td>
<td>Sodium citrate</td>
<td>300</td>
<td>0.00278 ± 0.00012</td>
</tr>
<tr>
<td>2.41</td>
<td>5.70</td>
<td>Sodium thiosulfate</td>
<td>300</td>
<td>0.00322 ± 0.00004</td>
</tr>
</tbody>
</table>

analyzed by linear regression method. The best fitted model with $R^2$ and adjusted $R^2$ of 0.986 and 0.982 is shown as follows:

$$kd(Q_{H_2S}, C_{Fe,0}, C_{CI}) = 3.429 - 0.773C_{Fe,0}$$

$$+ 0.0443C_{Fe,0}^2 + 0.110 \times 10^{-3}Q_{H_2S}$$

$$- 0.00698C_{CI} + 1.546 \times 10^{-5}C_{CI}^2$$

(6)

It can be noticed that all terms in (4) and (5) are presented in (6) with quite same magnitude of coefficient except the intercept in (5). This supported the assumption above that the intercept in (4) is the effect from $Q_{H_2S}$ and $C_{Fe,0}$ only. Thus, it can say that the equation of $kd$ related to all parameters can be obtained by the summation of each (real) $kd$ equation.

The $R_d$ calculated using the $kd(Q_{H_2S}, C_{Fe,0}, C_{CI})$, in (6) have a good agreement with the measured $R_d$ as demonstrated in Figure 12.

The concentration of Fe-EDTA at anytime in the reaction can be predicted by (7) which is rewriting from (2)

$$C_{(Fe,t)} = C_{(Fe,0)} e^{-kd t}$$

(7)

where $kd$ can be calculated using (6).

Equation (7) is very useful in the $H_2S$ removal by oxidation with Fe(III)-EDTA. When all parameters, $Q_{H_2S}$, $C_{Fe,0}$, and $C_{CI}$, are known, it can used to predict the concentration of Fe-EDTA at any interested time, so we can predict that how long the system still gave high efficiency and when the system needs to be made up with new Fe(III)-EDTA solution.

4. Conclusion

The degradation rate of Fe-EDTA followed pseudo first order. The effect of $H_2S$ molar flow rate, the initial Fe(III)EDTA, and sodium citrate concentration were investigated, and the empirical correlations expressed the degradation rate constant as a function of significant $H_2S$ molar flow rate, and initial Fe(III)EDTA and sodium citrate concentration were successfully developed. The result demonstrated that the degradation rate of Fe-EDTA in $H_2S$ removal system could be predicted with sufficient precision via the developed correlation model. Sulfur cake was also recovered. It was found that the sulfur cake contained more than 98% sulfur element and almost balances with iron, and no significant EDTA was degraded into the solid form.

The kinetics knowledge obtained from this work can be used to develop the $H_2S$ removal process from biogas or other gas stream, particularly the chemical quantity used in
A kinetic evaluation also helps in the formulation of a degradation prevention strategy which is considered to be the overall goal of degradation studies.

References

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