Investigation of Corrosivity of Sulphide Solutions By S-H₂O And Fe-S-H₂O E-Ph Diagrams

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Abstract: The S-H₂O and Fe-S-H₂O diagram are drawn for sulphur water systems. These diagrams show that within the range of pH 7 to 14, the sulfur species present in the solution could be HS⁻, to some extent S²⁻, S₃O₇²⁻ and SO₃²⁻. The E-pH diagram of Fe-S-H₂O shows that corrosion products forming on SS304L will be pyrite or iron oxide and on duplex steel SS2205 it could be pyrrhotite/troilite/mackinawite depending upon the potential. Except mackinawite and troilite, other sulfides/oxides provide protection. This could be the reason for observing lesser corrosion rates in stainless steels.

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I. Introduction

The beginning of potential-pH (E-pH) diagrams, prevalently entitled as Pourbaix diagrams, into electrochemistry produced a novel period into the study of electrochemical reactions taking place into an aqueous medium in the vicinity of an electrode. The Pourbaix diagrams are based on reliance of equilibrium potential on pH and composition of aqueous solution at a specified temperature. By means of these diagrams, it is probable to envisage all the possible reactions between the elements, its ions and its solid and gaseous phases in the presence of water and other aqueous solutions at different temperatures. The application of data enclosed in these diagrams is restricted by reactions which have been considered in ascertaining them as well as by the values assumed for standard chemical potentials of the substances taking part into these reactions ¹. These diagrams are merely based on activities of ions and not on their genuine concentrations. In present case, the potential-pH diagrams apprehension only pure metals and non-metals. Therefore, these diagrams cannot give information regarding performance of the alloys, which frequently fluctuate from the pure metals. However, with these limitations, it is apparent that in numerous cases these diagrams make available important information which lead to vital conclusions concerning all the feasible reactions. A number of these conclusions are predominantly imperative in study of corrosion in aqueous media e.g. whether in specified aqueous media, a given material will be corroding or protected to corrosion or will be under the passivation. These diagrams also help in finding the possibility of experiencing localized type corrosion.

These diagrams further also helps in predicting the protective nature of diverse corrosion products and which is further useful in estimating the conditions thermodynamically for electrochemical protection ¹, ². The Potential–pH diagrams for the S-H₂O and Fe-S-H₂O systems are very useful for the study and the understanding of corrosion of iron and carbon steels in the subsistence of sulfides and of other sulphur compounds in aqueous solutions.

II. Materials and Methods

Thermodynamic Data and Activities of Various Sulphur Species

To construct the E-pH diagrams for the S-H₂O and Fe-S-H₂O systems, compositions and pH, as experiential for pulping liquors, were considered for forming the equations. These equations show E-pH dependence of various thermo-dynamical equilibrium reactions. Further, these diagrams may be used for analyzing the results of the corrosion tests at room temperature. The different equations were formed at 25°C using activity of various sulphur species corresponding to the chemical concentrations found in the Indian pulp mill liquors (Table-1). The total activity of sulfur species was found mainly on the basis of concentration of Na₂S and Na₂S2O₃ in different sulphide solutions as these species are major cause of corrosion in pulping liquors ³, ⁶. The value of the activity corresponding to Na₂S and Na₂S2O₃ amount is given in (Table-2). The activity was considered for drawing E-pH diagrams, irrespective of the form of sulphur species. In the current study to draw E-pH diagrams, the different iron and sulfur species along with their chemical potential considered, are given in (Table-3) at temperature 25°C ¹, ².
Table 1: Composition of cooking liquor (gram per liter)

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Indian Mills</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH</td>
<td>65.00 - 80.00</td>
</tr>
<tr>
<td>Na₂S</td>
<td>15.00 - 28.00</td>
</tr>
<tr>
<td>S₂</td>
<td>00.20 - 19.40</td>
</tr>
<tr>
<td>Na₂S₂O₃</td>
<td>02.30 - 35.00</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>05.00 - 25.33</td>
</tr>
<tr>
<td>Na₂SO₃</td>
<td>02.00 - 13.50</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>00.20 - 01.79</td>
</tr>
</tbody>
</table>

Table 2: Activity (gram mol per liter) of different chemicals

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Concentration (gpl)</th>
<th>Total activity gram mole per liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂S</td>
<td>20.00</td>
<td></td>
</tr>
<tr>
<td>NaOH</td>
<td>80.00</td>
<td>00.22</td>
</tr>
<tr>
<td>Na₂S₂O₃</td>
<td>05.00</td>
<td></td>
</tr>
</tbody>
</table>

Table 3: Standard chemical potentials (µ°) (Calorie/mol) at 25°C

<table>
<thead>
<tr>
<th>Chemical Species</th>
<th>µ° (Calorie/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>-56687</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>-21880</td>
</tr>
<tr>
<td>FeOH⁻</td>
<td>-65847</td>
</tr>
<tr>
<td>Fe(OH)₂ atol.</td>
<td>-107154</td>
</tr>
<tr>
<td>H₂FeO₃</td>
<td>-95089</td>
</tr>
<tr>
<td>Fe⁴⁺</td>
<td>-4130</td>
</tr>
<tr>
<td>Fe₂O₄</td>
<td>-243191</td>
</tr>
<tr>
<td>γFe₂O₃</td>
<td>-175500</td>
</tr>
<tr>
<td>H₂S₄</td>
<td>-6674</td>
</tr>
<tr>
<td>HS</td>
<td>2860</td>
</tr>
<tr>
<td>SO₂⁻</td>
<td>-248.701</td>
</tr>
<tr>
<td>S₂O₃⁻</td>
<td>-124899</td>
</tr>
<tr>
<td>S</td>
<td>21958</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>-128668</td>
</tr>
<tr>
<td>HSO₃⁻</td>
<td>-126130</td>
</tr>
<tr>
<td>SO₃²⁻</td>
<td>-116299</td>
</tr>
<tr>
<td>FeS</td>
<td>-38256</td>
</tr>
<tr>
<td>FeS₂</td>
<td>-24368</td>
</tr>
<tr>
<td>FeS₃</td>
<td>-29123</td>
</tr>
<tr>
<td>FeS₄</td>
<td>-22300</td>
</tr>
<tr>
<td>Amorphous FeS</td>
<td>-571258</td>
</tr>
</tbody>
</table>

Redox Reactions and Equations for S-H₂O System

To construct the E-pH diagrams for S-H₂O system (Figure 1 and Figure 2), the following sulfur species were considered e.g. H₂S, HS⁻, S²⁻, S₂O₃²⁻, S, S₂O₄²⁻, SO₃²⁻, H₂SO₃ and HSO₃⁻. Further the different thermodynamic reactions and their corresponding equations along with the thermodynamic data e.g. chemical potential for different species were taken from Pourbaix et al.¹ and Singh et al.². These equations were modified for concentration of total sulfur corresponding to total amount of various sulfur species considered in the different pulping liquors. Thus activity of total sulfur was considered to be aₙ = 0.22 gram mole/liter on the basis of total amount of sulphur species found in the pulping liquors.³⁴

Following are given special equations used in constructing the E-pH diagrams.

1. H₂S ↔ H⁺ + HS⁻ (reaction and equation 1)
   \[ \text{log (HS/H}_2\text{S)} = \text{pH} - 06.992 \]

2. HS⁻ ↔ H⁺ + S⁻ (reaction and equation 2)
   \[ \text{log (S'/HS)} = \text{pH} - 14.01 \]

3. H₂SO₃ ↔ H⁺ + HSO₃⁻ (reaction and equation 9)
   \[ \text{log (HSO}_3^-/\text{H}_2\text{SO}_3) = \text{pH} - 01.861 \]

4. HSO₄⁻ ↔ H⁺ + SO₄²⁻ (reaction and equation 10)
   \[ \text{log (SO}_4^{2-}/\text{HSO}_4^-) = \text{pH} - 07.210 \]

Above equations are irrespective of value of the activity of sulphur species.

5. 6H⁺ + S₂O₃⁻ + 8e⁻ ↔ 3H₂O + 2S²⁻ (reaction and equation 20)
   \[ \text{E} = 0.007 - 0.0074 \text{log (a) - 0.0443pH} \]

   \[ \text{E} = 0.012 - 0.04pH \quad (a_s = 0.22gram mol/lit) \]

6. 8H⁺ + S₂O₅⁻ + 8e⁻ ↔ 3H₂O + 2HS⁻ (reaction and equation 21)
   \[ \text{E} = 0.214 - 0.0074 \text{log (a) - 0.0591pH} \]

   \[ \text{E} = 0.219 - 0.0591pH \quad (a_s = 0.22gram mol/lit) \]
Irrespective of activity of sulphur species, activities can predict the corrosivity of the cooking liquor depending upon its composition and temperature exposed to liquors having various sulfur species. Since some of these corrosion products contain iron, the redox reactions equations for iron are given below:

**Redox Reactions Equations for Fe**

Using above equations, E-pH diagram constructed for S-H2O system having pH ~ 14 and aFe = 0.22 gram mol per liter. Corresponding to Na2S = 20 gpl and Na2S2O3 = 05 gpl, is shown in Figure-1.

**Redox Reactions Equations for Fe-S-H2O Systems**

E-pH diagrams for Fe-S-H2O system shows which corrosion products are likely to form when steel is exposed to liquors having various sulfur species. Since some of these corrosion products will be protective type, therefore, under the circumstances when such corrosion products form, the steel will show corrosion resistance. Accordingly, one can predict from these diagrams as to for which conditions of cooking liquor, steel will resist the corrosion attack or it will be attacked through general corrosion or localized corrosion. In other words, one can predict the corrosivity of the cooking liquor depending upon its composition and temperature. Activity of sulphur species is considered as in S-H2O system and for Fe**, Fe** is considered 10^{-6} gram ion per liter.

Activity of iron compounds is considered 1. Following equations formed on above considered activities.

1. Fe^{2+} + 2e^- \rightarrow Fe \quad (reaction and equation 1)
   
   E = 0.029 log (Fe^{2+}) - 0.474
   
   E = -0.65

Irrespective of activity of sulphur specie

2. 4H^{+} + FeS_{2} + 2e^- \rightarrow 2H_{2}S + Fe^{2+} \quad (reaction and equation 2)
   
   E = -0.066 - 0.029 log (Fe^{2+}) - 0.059 log (H_{2}S) - 0.118pH
   
   E = 0.146 - 0.118pH \quad (a_{Fe} = 0.22 gram mol/lit)

3. 2.280H^{+} + FeS_{14} + 0.280e^- \rightarrow 1.14H_{2}S + Fe^{2+} \quad (reaction and equation 3)
   
   E = -0.056 - 0.241log (H_{2}S) - 0.481pH - 0.221 log (Fe^{2+})
   
   E = 1.43 - 0.481pH \quad (a_{Fe} = 0.22 gram mol/lit)

4. 2.280H^{+} + FeS_{14} + 2.280e^- \rightarrow 1.14H_{2}S + Fe \quad (reaction and equation 4)
Investigation of Corrosivity of Sulphide Solutions By S-H₂O And Fe-S-H₂O E-Ph Diagrams

$$E = -0.409 - 0.029 \log (H_2S) - 0.059pH$$

$$E = -0.389 - 0.059pH$$  
\[a_e = 0.22 \text{gram mol/lt}\]

5. 1.140H⁺ + FeS₁₄ + 2.280e⁻ ⇌ 1.14HS⁺ + Fe (reaction and equation 5)
$$E = -0.616 - 0.029 \log (HS⁻) - 0.029pH$$

$$E = -0.596 - 0.029 pH$$  
\[a_e = 0.22 \text{gram mol/lt}\]

6. 1.720H⁺ + FeS₂ + 1.720e⁻ ⇌ 0.860H₂S + FeS₁₄ (reaction and equation 6)
$$E = -0.085 - 0.029 \log (H_2S) - 0.059pH$$

$$E = -0.0658 - 0.059pH$$  
\[a_e = 0.22 \text{gram mol/lt}\]

7. 0.860H⁺ + FeS₂ + 1.720e⁻ ⇌ 0.860HS⁻ + FeS₁₄ (reaction and equation 7)
$$E = -0.292 - 0.029 \log (HS⁻) - 0.029pH$$

$$E = -0.272 - 0.029pH$$  
\[a_e = 0.22 \text{gram mol/lt}\]

8. 2S⁺ + Fe⁺⁺ + 2e⁻ ⇌ FeS₂ (reaction and equation 8)
$$E = 0.355 + 0.029 \log (Fe⁺⁺)$$

$$E = 0.335$$  
\[a_e = 0.22 \text{gram mol/lt}\]

9. S₄O₆⁻⁻ + 2Fe⁺⁺ + 12H⁺ + 14e⁻ ⇌ 6H₂O + 2FeS₂ (reaction and equation 9)
$$E = 0.384 + 0.008 \log (Fe⁺⁺) + 0.004 \log (S_4O_6^{-2}) - 0.051pH$$

$$E = 0.333 - 0.051pH$$  
\[a_e = 0.22 \text{gram mol/lt}\]

10. S₄O₆⁻⁻ + yFe₂O₃ + 18H⁺ + 16e⁻ ⇌ 9H₂O + 2FeS₂ (reaction and equation 10)
$$E = 0.44 + 0.0037 \log (S_4O_6^{-2}) - 0.066pH$$

$$E = 0.437 - 0.066pH$$  
\[a_e = 0.22 \text{gram mol/lt}\]

11. 3S₂O₃⁻⁻ + Fe₂O₃ + 26H⁺ + 20e⁻ ⇌ 13H₂O + 3FeS₂ (reaction and equation 11)
$$E = 0.506 + 0.0088 \log (S_2O_3^{-2}) - 0.077pH$$

$$E = 0.500 - 0.077pH$$  
\[a_e = 0.22 \text{gram mol/lt}\]

12. 2S₂O₃⁻⁻ + yFe₂O₃ + 18H⁺ + 14e⁻ ⇌ 9H₂O + 2FeS₂ (reaction and equation 12)
$$E = 0.5 + 0.008 \log (S_2O_3^{-2}) - 0.076pH$$

$$E = 0.494 - 0.076pH$$  
\[a_e = 0.22 \text{gram mol/lt}\]

13. 6H⁺ + yFe₂O₃ + 2e⁻ ⇌ 3H₂O + 2Fe⁺⁺ (reaction and equation 13)
$$E = 0.83 - 0.059 \log (Fe⁺⁺) - 0.177pH$$

$$E = 1.184 - 0.177pH$$  
\[a_e = 0.22 \text{gram mol/lt}\]

14. 1.886H⁺ + FeS₀₄₉₃ + 1.886e⁻ ⇌ 0.943H₂S + Fe (reaction and equation 14)
$$E = -0.368 - 0.029 \log (H_2S) - 0.059pH$$

$$E = -0.348 - 0.059pH$$  
\[a_e = 0.22 \text{gram mol/lt}\]

15. 0.943H⁺ + FeS₀₄₉₃ + 1.886e⁻ ⇌ 0.943H₂S + Fe (reaction and equation 15)
$$E = -0.575 - 0.029 \log (HS⁻) - 0.029pH$$

$$E = -0.555 - 0.029pH$$  
\[a_e = 0.22 \text{gram mol/lt}\]

16. 0.943H₂S + Fe⁺⁺ + 0.114e⁻ ⇌ 1.886H⁺ + FeS₀₄₉₃ (reaction and equation 16)
$$E = -2.234 + 0.489 \log (H_2S) + 0.978pH + 0.518 \log (Fe⁺⁺)$$

$$E = -5.65 + 0.978pH$$  
\[a_e = 0.22 \text{gram mol/lt}\]

17. 2.114H⁺ + FeS₂ + 2.114e⁻ ⇌ 1.06H₂S + FeS₀₄₉₃ (reaction and equation 17)
$$E = -0.183 - 0.029 \log (H_2S) - 0.059pH$$

$$E = -0.163 - 0.059pH$$  
\[a_e = 0.22 \text{gram mol/lt}\]

18. 1.057H⁺ + FeS₂ + 2.114e⁻ ⇌ 1.057H₂S + FeS₀₄₉₃ (reaction and equation 18)
$$E = -0.389 - 0.029 \log (HS⁻) - 0.029pH$$

$$E = -0.369 - 0.029pH$$  
\[a_e = 0.22 \text{gram mol/lt}\]

19. 2H⁺ + 3yFe₂O₃ + 4e⁻ ⇌ 2H₂O + 2FeO₃ (reaction and equation 19)
$$E = 0.359 - 0.059pH$$  
\[a_e = 0.22 \text{gram mol/lt}\]

20. 2FeO₃ + 3S₂O₃⁻⁻ + 52H⁺ + 46e⁻ ⇌ 26H₂O + 6Fe₂S₂ (reaction and equation 20)
$$E = 0.444 + 0.0038 \log (S_2O_3^{-2}) - 0.067pH$$

$$E = 0.441 - 0.067pH$$  
\[a_e = 0.22 \text{gram mol/lt}\]

21. S₂O₃⁻⁻ + Fe⁺⁺ + 6H⁺ + 6e⁻ ⇌ 3H₂O + FeS₂ (reaction and equation 21)
$$E = 0.445 + 0.0098 \log (Fe⁺⁺) + 0.0098 \log (S_2O_3^{-2}) - 0.059pH$$

$$E = 0.379 - 0.059pH$$  
\[a_e = 0.22 \text{gram mol/lt}\]

22. 2H⁺ + FeS⁺⁺ + 2e⁻ ⇌ H₂S⁺ + Fe (reaction and equation 22)
$$E = -0.364 - 0.059pH$$  
\[a_e = 0.22 \text{gram mol/lt}\]

23. H⁺ + FeS⁺⁺ + 2e⁻ ⇌ HS⁻ + Fe (reaction and equation 23)
$$E = -0.59 - 0.029 \log (HS⁻) - 0.029pH$$

$$E = -0.570 - 0.029pH$$  
\[a_e = 0.22 \text{gram mol/lt}\]

24. 2H⁺ + FeS⁺⁺ ⇌ H₂S + Fe⁺⁺ (reaction and equation 24)
$$\log (Fe⁺⁺) = 3.071 - \log (H_2S) - 2pH$$
\[ pH = 4.86 \quad (a_0 = 0.22 \text{ gram mol/lit}) \]

25. \( 2H^+ + FeS_2 + 2e^- \leftrightarrow H_2S + FeS \) (reaction and equation 25)
\[ E = -0.156 - 0.029 \log (H_2S) - 0.059pH \]
\[ E = -0.137 - 0.059pH \quad (a_0 = 0.22 \text{ gram mol/lit}) \]

26. \( H^+ + FeS_2 + 2e^- \leftrightarrow HS + FeS \) (reaction and equation 26)
\[ E = -0.363 - 0.029 \log (HS) - 0.029pH \]
\[ E = -0.344 - 0.029pH \quad (a_0 = 0.22 \text{ gram mol/lit}) \]

27. \( 8H^+ + FeS_4^{2-} + 2e^- \leftrightarrow 4H_2O + 3Fe^{2+} \) (reaction and equation 27)
\[ E = 1.066 - 0.089 \log (Fe^{2+}) - 0.236pH \]
\[ E = 1.6 - 0.236pH \quad (a_0 = 0.22 \text{ gram mol/lit}) \]

28. \( Fe^{3+} + e^- \leftrightarrow Fe^{2+} \) (reaction and equation 28)
\[ E = 0.769 - 0.059 \log (Fe^{2+}) + 0.059 \log (Fe^{3+}) \]
\[ E = 0.769 \quad (a_0 = 0.22 \text{ gram mol/lit}) \]

29. \( 6H^+ + Fe_2O_3 \leftrightarrow 3H_2O + 2Fe^{3+} \) (reaction and equation 29)
\[ pH = 2.3 (a_0 = 0.22 \text{ gram mol/lit}) \]

30. \( 3H^+ + HFeO_4^- + 2e^- \leftrightarrow 2H_2O + Fe \) (reaction and equation 30)
\[ E = 0.396 + 0.029 \log (HFeO_4^-) - 0.088pH \]
\[ E = 0.222 - 0.088pH \quad (a_0 = 0.22 \text{ gram mol/lit}) \]

31. \( HS + HFeO_4^- + 2H^+ \leftrightarrow H_2O + FeS \) (reaction and equation 31)
\[ \log (HFeO_4^-) = -33.367 - \log (HS) + 2pH \]
\[ pH = 13.35 \quad (a_0 = 0.22 \text{ gram mol/lit}) \]

32. \( 3HS + FeO_2 + 5H^+ + 2e^- \leftrightarrow 4H_2O + 3FeS \) (reaction and equation 32)
\[ E = 1.114 + 0.088 \log (HS) - 0.147pH \]
\[ E = 1.056 - 0.147pH \quad (a_0 = 0.22 \text{ gram mol/lit}) \]

33. \( 2H_2O + FeS_4^{4-} + 0.28e^- \leftrightarrow 1.14HS^+ + HFeO_4^- \) (reaction and equation 33)
\[ E = -0.575 - 0.029 \log (HS) + 1.86H^+ - 0.029pH \]
\[ E = -6.41 + 0.391pH \quad (a_0 = 0.22 \text{ gram mol/lit}) \]

34. \( 3.42HS + FeO_4^- + 4.58H^+ + 1.16e^- \leftrightarrow 4H_2O + 3FeS_1.14 \) (reaction and equation 34)
\[ E = 2.498 + 0.174 \log (HS) - 0.232pH \]
\[ E = 2.383 - 0.232pH \quad (a_0 = 0.22 \text{ gram mol/lit}) \]

35. \( 2H_2O + FeO_4^- + 2e^- \leftrightarrow H^+ + 3HFeO_2^- \) (reaction and equation 35)
\[ E = -1.846 - 0.088 \log (HFeO_2^-) + 0.029pH \]
\[ E = -1.32 + 0.029pH \quad (a_0 = 0.22 \text{ gram mol/lit}) \]

36. \( H_2O + yFeO_3 + e^- \leftrightarrow 2HFeO_3 \) (reaction and equation 36)
\[ E = -0.556 - 0.059 \log (HFeO_3^-) \]
\[ E = -0.502 \quad (a_0 = 0.22 \text{ gram mol/lit}) \]

37. \( 4H_2O + FeS_2 + 4e^- \leftrightarrow 6HS^+ + 2H^+ + FeO_2^- \) (reaction and equation 37)
\[ E = -1.101 - 0.088 \log (HS) + 0.029pH \]
\[ E = -1.042 + 0.029pH \quad (a_0 = 0.22 \text{ gram mol/lit}) \]

38. \( 2H_2O + FeS_2 + 2e^- \leftrightarrow 2HS^+ + HFeO_2^- \) (reaction and equation 38)
\[ E = -1.349 - 0.029 \log (HFeO_2^-) - 0.059 \log (HS) + 0.029pH \]
\[ E = -1.136 + 0.029pH \quad (a_0 = 0.22 \text{ gram mol/lit}) \]

39. \( 2HSO_4^- + Fe^{3+} + 10H^+ + 10e^- \leftrightarrow 6H_2O + FeS_2 \) (reaction and equation 39)
\[ E = 0.452 + 0.0059 \log (Fe^{3+}) + 0.012 \log (HSO_4^-) - 0.059pH \]
\[ E = 0.408 - 0.059pH \quad (a_0 = 0.22 \text{ gram mol/lit}) \]

Using the above equations, the E-pH diagrams constructed for Fe-S-H_2O system having pH up to ~14 and a_0 = 0.22 gram mol per lit corresponding to Na_2S = 20 gpl, Na_2S_2O_3 = 0.5 gpl, is shown in Figure -2.

### III. Results and Discussion

**S-H_2O System**

For S-H_2O System (Figure-1), the diagrams show that within the pH range (7 to 14) likely to be observed for the cooking liquor, indicates that sulfur species present in the solution could be HS^-, to some extent S^2-, S_2O_5^2- and SO_4^2- depending upon the potential, which will in turn be governed by the nature of material exposed, mild steels, stainless steels and non conventional materials. The redox potential of SS304L, SS2205 and non conventional materials Ni-P-TiO_2-ZrO_2 in pH ~ 14 solution having sulfidity, as considered in drawing E-pH diagram, shows that sulphur species near SS304L electrode will be mainly HS^- while those near the SS2205 and non conventional material Ni-P-TiO_2-ZrO_2 electrode will be mainly HS^- (potentiodynamic polarization curves).
Fe-S-H$_2$O System

Fe-S-H$_2$O diagram (Figure-2) was constructed considering above sulfur species and activities. Thus if the liquor consists of S$_2$O$_3^{2-}$, different corrosion products likely to form in the pH range of interest (pH ~ 12-14) are mackinawite, troilite, pyrrhotite and pyrite. Of these, the first two products are non-protective type while the other two are protective type. However, the region of protection also indicates the possibility of localized corrosion if the protective layer breaks. This usually happens at higher potentials which one can observe, if the amount of S$_2$O$_3^{2-}$ increases. It indicates that if the amount of S$_2$O$_3^{2-}$ is higher, the steel is likely to experience localized corrosion.

Figure -1 : E-pH diagram of S-H$_2$O system at room temperature, $a_s = 0.22$ g mol/lit

Figure -2: E-pH diagram for Fe-S-H$_2$O system at room temperature, $a_s = 0.22$ g mol/lit
IV. Conclusions

The S-H₂O diagram shows that within the range of pH 7 to 14, the sulfur species present in the solution could be HS⁻, to some extent S²⁻, S₂O₃²⁻ and SO₃²⁻ depending upon the potential. The E-pH diagram of Fe-S-H₂O shows that corrosion products forming on SS304L will be pyrite or iron oxide and on duplex steel SS2205 it could be pyrrhotite/troilite/mackinawite depending upon the potential. Except mackinawite and troilite, other sulfides /oxides provide protection. This could be the reason for observing lesser corrosion rates in these stainless steels. Since these aspects are dependent on the amount of sulfur species, alloying elements in steels and the temperature, therefore it is necessary to draw these diagrams at higher sulfidity values, for alloying elements and higher temperature also.

References


[7]. Scan-N4: 63, Scandinavian Pulp & Paper Testing Board.


