Investigation of Corrosivity of Sulphide Solutions By S-H$_2$O And Fe-S-H$_2$O E-Ph Diagrams

Manoj Kumar [1], Sulaxna Sharma[2*] And Awanish Sharma[1]*

[1]*(Department of Physics, Graphic Era Deemed To Be University, Dehradun, India)*
[2]*(Department of AS&H, THDC, Institute of Hydropower Engineering and Technology, Tehri, India).*
Corresponding Authors: Manoj Kumar

Abstract: *The S-H$_2$O and Fe-S-H$_2$O diagram are drawn for sulpher 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 S^{2-}, S$_2$O$_3^{2-}$ and SO$_3^{2-}$. The E-pH diagram of Fe-S-H$_2$O 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.*

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, still 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-H$_2$O and Fe-S-H$_2$O 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 Sulpher Species

To construct the E-pH diagrams for the S-H$_2$O and Fe-S-H$_2$O 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 Na$_2$S and Na$_2$S$_2$O$_3$ in different sulphide solutions as these species are major cause of corrosion in pulping liquors [3-6]. The value of the activity corresponding to Na$_2$S and Na$_2$S$_2$O$_3$ 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 25ºC [1,2].

Table 1: Composition of cooking liquor (gram per liter)

Chemicals	Indian Mills
NaOH	65.00 - 80.00
Na_2S	15.00 - 28.00
S_x^{2-}	00.20 - 19.40
$Na_2S_2O_3$	02.30 - 35.00
Na_2CO_3	05.00 - 25.33
Na_2SO_4	02.00 - 13.50
Na_2SO_3	00.20 - 01.79

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

Chemicals	Concentration (gpl)	Total activity gram mole per liter
Na_2S	20.00	
NaOH	80.00	00.22
$Na_2S_2O_3$	05.00	

Table-3: Standard chemical potentials (μ^o) (Calorie/mol) at 25^0C

Chemical Species	(μ^o) Calorie/mol
H_2O	-56687
Fe^{++}	-21880
$FeOH^+$	-65847
$Fe(OH)_{2aq}$	-107154
$HFeO_2^-$	-95089
Fe^{+++}	-4130
Fe_3O_4	-243191
yFe_2O_3	-175500
H_2S_{aq}	-6674
HS^-	2860
$S_4O_6^{--}$	-248701
$S_2O_3^{--}$	-124899
S^{--}	21958
H_2SO_3	-128668
HSO_3^-	-126130
SO_3^{--}	-116299
FeS_2	-38256
FeS	-24368
$FeS_{1.14}$	-29123
$FeS_{0.943}$	-22300
Amorphous FeS	-571258

Redox Reactions and Equations for S-H_2O System

To construct the E-pH diagrams for S-H_2O system (Figure-1 and Figure-2), the following sulfur species were considered e.g. H_2S, HS^-, S^{2-}, $S_2O_3^{2-}$, S, $S_4O_6^{2-}$, SO_3^{2-} H_2SO_3 and HSO_3^-. 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 a_S = 0.22 gram mole/liter on the basis of total amount of sulpher species found in the pulping liquors [7-8].

Following are given special equations used in constructing the E-pH diagrams [1,2]

1. $H_2S \leftrightarrow H^+ + HS^-$ (reaction and equation 1)

log (HS^-/H_2S) = pH - 06.992

2. $HS^- \leftrightarrow H^+ + S^{--}$ (reaction and equation 2)

log (S^{--}/HS^-) = pH - 14.01

3. $H_2SO_3 \leftrightarrow H^+ + HSO_3^-$ (reaction and equation 9)

log (HSO_3^-/H_2SO_3) = pH -01.861

4. $HSO_3^- \leftrightarrow H^+ + SO_3^{--}$ (reaction and equation 10)

log (SO_3^{--}/HSO_3^-) = pH - 07.210

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

5. $6H^+ + S_2O_3^{--} + 8e^- \leftrightarrow 3H_2O + 2S^{--}$ (reaction and equation 20)

E = 0.007– 0.0074 log (a_s) - 0.0443pH

E = 0.012 - 0.04pH   (a_s=0.22gram mol/lit)

6. $8H^+ + S_2O_3^{--} + 8e^- \leftrightarrow 3H_2 + 2HS^-$ (reaction and equation 21)

E =0.214– 0.0074 log (a_s) - 0.0591pH

E =0.219 - 0.0591pH   (a_s=0.22gram mol/lit)

7. $10H^+ + S_2O_3^{--} + 8e^- \leftrightarrow 3H_2O + 2H_2S$ (reaction and equation 22)

$\qquad$ E = 0.317 – 0.0074 log (a$_s$) - 0.0739pH

$\qquad$ E = 0.322 - 0.0739pH $\qquad$ (a$_s$ = 0.22gram mol/lit)

8. $20H^+ + S_4O_6^{--} + 18e^- \leftrightarrow 6H_2O + 4H_2S$ (reaction and equation 25)

$\qquad$ E = 0.285 – 0.0098 Log (a$_s$) - 0.0657pH

$\qquad$ E = 0.291 - 0.066pH $\qquad$ (a$_s$ = 0.22gram mol/lit)

8a. $7H^+ + SO_3^{--} + 6e^- \leftrightarrow 3H_2O + HS^-$ (reaction and equation 29a)

$\qquad$ E = 0.368 - 0.069pH $\qquad$ (a$_s$ = 0.22gram mol/lit)

9. $S_4O_6^{--} + 2e^- \leftrightarrow 2S_2O_3^{--}$ (reaction and equation 40)

$\qquad$ E = 0.033 - 0.0295 log (a$_s$

$\qquad$ E = 0.053 $\qquad$ (a$_s$ = 0.22gram mol/lit

10. $6H^+ + 2SO_3^{--} + 4e^- \leftrightarrow 3H_2O + S_2O_3^{--}$ (reaction and equation 41)

$\qquad$ E = 0.676 + 0.0148 log (a$_s$) - 0.0887pH

$\qquad$ E = 0.67 - 0.0887pH (a$_s$ = 0.22gram mol/lit)

11. $4H^+ + 2HSO_3^- + 4e^- \leftrightarrow 3H_2O + S_2O_3^{--}$ (reaction and equation 42)

$\qquad$ E = 0.463 + 0.0148 log (a$_s$) - 0.0591pH

$\qquad$ E = 0.453 - 0.0591pH $\qquad$ (a$_s$ = 0.22gram mol/lit)

12. $8H^+ + 4HSO_3^- + 6e^- \leftrightarrow 6H_2O + S_4O_6^{--}$ (reaction and equation 43)

$\qquad$ E = 0.606 + 0.0295 log (a$_s$) - 0.0788pH

$\qquad$ E = 0.586 - 0.0788pH $\qquad$ (a$_s$ = 0.22gram mol/lit)

13. $4H^+ + 4H_2SO_3 + 6e^- \leftrightarrow 6H_2O + S_4O_6^{--}$ (reaction and equation 44)

$\qquad$ E = 0.533 + 0.0295 log (a$_s$) - 0.039pH

$\qquad$ E = 0.513 - 0.039pH $\qquad$ (a$_s$ = 0.22gram mol/lit)

14. $H^+ + S + 2e^- \leftrightarrow HS^-$ (reaction and equation 60)

$\qquad$ E = -0.062 -0.0295 log (a$_s$) - 0.0295 pH

$\qquad$ E = -0.043-0.0295 pH $\qquad$ (a$_s$ = 0.22gram mol/lit)

15. $2H^+ + S + 2e^- \leftrightarrow H_2S$ (reaction and equation 61)

$\qquad$ E = 0.144 -0.0295 log (a$_s$) -0.0591 pH

$\qquad$ E = 0.163 -0.0591 pH $\qquad$ (a$_s$ = 0.22gram mol/lit)

16. $6H^+ + S_2O_3^{--} + 4e^- \leftrightarrow 3H_2O + 2S$ (reaction and equation 63)

$\qquad$ E = 0.494 + 0.0148 log (a$_s$) - 0.0887pH

$\qquad$ E = 0.484 - 0.089pH $\qquad$ (a$_s$ = 0.22gram mol/lit)

17. $12H^+ + S_4O_6^{--} + 10e^- \leftrightarrow 6H_2O + 4S$ (reaction and equation 64)

$\qquad$ E = 0.401 + 0.0059 log (a$_s$) - 0.0709pH

$\qquad$ E = 0.397 - 0.071pH $\qquad$ (a$_s$ = 0.22gram mol/lit)

Using above equations, E-pH diagram constructed for S-H$_2$O system having pH ~ 14 and a$_s$=0.22 gram mol per lit. Corresponding to Na$_2$S =20 gpl and Na$_2$S$_2$O$_3$ = 05gpl, is shown in Figure-1.

Redox Reactions Equations for Fe-S-H$_2$O Systems

$\qquad$ E-pH diagrams for Fe-S-H$_2$O 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 [3-9]. Activity of sulpher species is considered as in S-H$_2$O system and for Fe^{++}, Fe^{+++} is considered 10^{-6} gram ion per liter.

$\qquad$ Activity of iron compounds is considered 1. Following equations[1,2] formed on above considered activities.

1. $Fe^{++} + 2e^- \leftrightarrow Fe$ $\qquad$ (reaction and equation 1)

$\qquad$ E = 0.029 log (Fe^{++}) - 0.474

$\qquad$ E = -0.65

Irrespective of activity of sulpher specie

2. $4H^+ + FeS_2 + 2e^- \leftrightarrow 2H_2S + Fe^{++}$ (reaction and equation 2)

$\qquad$ E = -0.066 - 0.029 log (Fe^{++}) – 0.059 log (H$_2$S) - 0.118pH

$\qquad$ E = 0.146 - 0.118pH $\qquad$ (a$_s$ = 0.22gram mol/lit)

3. $2.280H^+ + FeS_{1.14} + 0.280e^- \leftrightarrow 1.14H_2S + Fe^{++}$ (reaction and equation 3)

$\qquad$ E = -0.056 – 0.241log (H$_2$S) - 0.481pH - 0.221 log (Fe^{++})

$\qquad$ E = 1.43 - 0.481pH $\qquad$ (a$_s$ = 0.22gram mol/lit)

4. $2.280H^+ + FeS_{1.14} + 2.280e^- \leftrightarrow 1.14H_2S + Fe$ (reaction and equation 4)

$$E = -0.409 - 0.029 \log (H_2S) - 0.059pH$$
$$E = -0.389 - 0.059pH \qquad (a_s = 0.22 \text{gram mol/lit})$$

5. $1.140H^+ + FeS_{1.14} + 2.280e^- \leftrightarrow 1.14HS^- + Fe$ (reaction and equation 5)
$$E = -0.616 - 0.029 \log (HS^-) - 0.029pH$$
$$E = -0.596 - 0.029 \, pH \qquad (a_s = 0.22 \text{gram mol/lit})$$

6. $1.720H^+ + FeS_2 + 1.720e^- \leftrightarrow 0.860H_2S + FeS_{1.14}$ (reaction and equation 6)
$$E = -0.085 - 0.029 \log (H_2S) - 0.059pH$$
$$E = -0.0658 - 0.059pH \qquad (a_s = 0.22 \text{gram mol/lit})$$

7. $0.860H^+ + FeS_2 + 1.720e^- \leftrightarrow 0.860HS^- + FeS_{1.14}$ (reaction and equation 7)
$$E = -0.292 - 0.029 \log (HS^-) - 0.029pH$$
$$E = -0.272 - 0.029pH \qquad (a_s = 0.22 \text{gram mol/lit})$$

8. $2S + Fe^{++} + 2e^- \leftrightarrow FeS_2$ (reaction and equation 8)
$$E = 0.355 + 0.029 \log (Fe^{++})$$
$$E = 0.335 \qquad (a_s = 0.22 \text{gram mol/lit})$$

9. $S_4O_6^{--} + 2Fe^{++} + 12H^+ + 14e^- \leftrightarrow 6H_2O + 2FeS_2$ (reaction and equation 9)
$$E = 0.384 + 0.008 \log (Fe^{++}) + 0.004 \log (S_4O_6^{--}) - 0.051pH$$
$$E = 0.333 - 0.051pH \qquad (a_s = 0.22 \text{gram mol/lit})$$

10. $S_4O_6^{--} + yFe_2O_3 + 18H^+ + 16e^- \leftrightarrow 9H_2O + 2FeS_2$ (reaction and equation10)
$$E = 0.44 + 0.0037 \log (S_4O_6^{--}) - 0.066pH$$
$$E = 0.437 - 0.066pH \qquad (a_s = 0.22 \text{gram mol/lit})$$

11. $3S_2O_3^{--} + Fe_3O_4 + 26H^+ + 20e^- \leftrightarrow 13H_2O + 3FeS_2$ (reaction and equation 11)
$$E = 0.506 + 0.0088 \log (S_2O_3^{--}) - 0.077pH$$
$$E = 0.500 - 0.077pH \qquad (a_s = 0.22 \text{gram mol/lit})$$

12. $2S_2O_3^{--} + yFe_2O_3 + 18H^+ + 14e^- \leftrightarrow 9H_2O + 2FeS_2$ (reaction and equation 12)
$$E = 0.5 + 0.008 \log (S_2O_3^{--}) - 0.076 \, pH$$
$$E = 0.494 - 0.076pH \qquad (a_s = 0.22 \text{gram mol/lit})$$

13. $6H^+ + y \, Fe_2O_3 + 2e^- \leftrightarrow 3H_2O + 2Fe^{++}$ (reaction andequation 13)
$$E = 0.83 - 0.059 \log (Fe^{++}) - 0.177pH$$
$$E = 1.184 - 0.177pH \qquad (a_s = 0.22 \text{gram mol/lit})$$

14. $1.886H^+ + FeS_{0.943} + 1.886e^- \leftrightarrow 0.943H_2S + Fe$ (reaction and equation 14)
$$E = -0.368 - 0.029 \log (H_2S) - 0.059pH$$
$$E = -0.348 - 0.059pH \qquad (a_s = 0.22 \text{gram mol/lit})$$

15. $0.943H^+ + FeS_{0.943} + 1.886e^- \leftrightarrow 0.943HS^- + Fe$ (reaction and equation 15)
$$E = -0.575 - 0.029 \log (HS^-) - 0.029pH$$
$$E = -0.555 - 0.029pH \qquad (a_s = 0.22 \text{gram mol/lit})$$

16. $0.943H_2S + Fe^{++} + 0.114e^- \leftrightarrow 1.886H^+ + FeS_{0.943}$ (reaction and equation 16)
$$E = -2.234 + 0.489 \log (H_2S) + 0.978pH + 0.518\log (Fe^{++})$$
$$E = -5.65 + 0.978pH \qquad (a_s = 0.22 \text{gram mol/lit})$$

17. $2.114H^+ + FeS_2 + 2.114e \leftrightarrow 1.06H_2S + FeS_{0.943}$ (reaction and equation 17)
$$E = -0.183 - 0.029 \log (H_2S) - 0.059pH$$
$$E = -0.163 - 0.059pH \qquad (a_s = 0.22 \text{gram mol/lit})$$

18. $1.057H^+ + FeS_2 + 2.114e^- \leftrightarrow 1.057HS + FeS_{0.943}$ (reaction and equation 18)
$$E = -0.389 - 0.029 \log (HS^-) - 0.029pH$$
$$E = -0.369 - 0.029pH \qquad (a_s = 0.22 \text{gram mol/lit})$$

19. $2H^+ + 3y \, Fe_2O_3 + 2e^- \leftrightarrow H_2O + 2Fe_3O_4$ (reaction and equation 19)
$$E = 0.359 - 0.059pH \qquad (a_s = 0.22 \text{ gram mol/lit})$$

20. $2Fe_3O_4 + 3S_4O_6^{--} + 52H^+ + 46e^- \leftrightarrow 26H_2O + 6FeS_2$ (reaction and equation 20)
$$E = 0.444 + 0.0038 \log (S_4O_6^{--}) - 0.067pH$$
$$E = 0.441 - 0.067pH \qquad (a_s = 0.22 \text{gram mol/lit})$$

21. $S_2O_3^{--} + Fe^{++} + 6H^+ + 6e^- \leftrightarrow 3H_2O + FeS_2$ (reaction and equation 21)
$$E = 0.445 + 0.0098 \log (Fe^{++}) + 0.0098 \log (S_2O_3^{--}) - 0.059pH$$
$$E = 0.379 - 0.059pH \qquad (a_s = 0.22 \text{gram mol/lit})$$

22. $2H^+ + FeS + 2e^- \leftrightarrow H_2S + Fe$ (reaction and equation 22)
$$E = -0.364 - 0.059pH \qquad (a_s = 0.22 \text{gram mol/lit})$$

23. $H^+ + FeS + 2e^- \leftrightarrow HS^- + Fe$ (reaction and equation 23)
$$E = -0.59 - 0.029 \log (HS^-) - 0.029pH$$
$$E = -0.570 - 0.029pH \qquad (a_s = 0.22 \text{gram mol/lit})$$

24. $2H^+ + FeS \leftrightarrow H_2S + Fe^{++}$ (reaction and equation 24)
$$\log (Fe^{++}) = 3.071 - \log (H_2S) - 2pH$$

pH = 4.86   (a$_s$ =0.22gram mol/lit)

25. $2H^+ +FeS_2 + 2e^- \leftrightarrow H_2S +FeS$ (reaction and equation 25)
    E = -0.156 - 0.029 log (H$_2$S) - 0.059pH
    E = -0.137 - 0.059pH   (a$_s$ =0.22 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   (a$_s$ =0.22 gram mol/lit)

27. $8H^+ +Fe_3O_4 +2e^- \leftrightarrow 4H_2O +3Fe^{++}$ (reaction and equation 27)
    E = 1.066 -0.089 log (Fe^{++})- 0.236pH
    E = 1.6 - 0.236pH   (a$_s$ =0.22 gram mol/lit)

28. $Fe^{+++} + e^- \leftrightarrow Fe^{++}$ (reaction and equation 28)
    E = 0.769 - 0.059 log (Fe^{++}) +0.059 log (Fe^{+++})
    E = 0.769   (a$_s$ =0.22 gram mol/lit)

29. $6H^+ +yFe_2O_3 \leftrightarrow 3H_2O + 2Fe^{+++}$ (reaction and equation 29)
    pH = 2.3(a$_s$ =0.22 gram mol/lit)

30. $3H^+ +HFeO_2^- + 2e^- \leftrightarrow 2H_2O +Fe$ (reaction and equation 30)
    E =0.396 +0.029 log (HFeO$_2^-$) - 0.088 pH
    E =0.222 -0.088 pH   (a$_s$ =0.22 gram mol/lit)

31. $HS^- + HFeO_2^- + 2H^+ \leftrightarrow H_2O +FeS$ (reaction and equation 31)
    log (HFeO$_2^-$) = -33.367 - log (HS$^-$) + 2pH
    pH = 13.35   (a$_s$ =0.22 gram mol/lit)

32. $3HS^- +Fe_3O_4 +5H^+ +2e^- \leftrightarrow 4H_2O +3FeS$ (reaction and equation 32)
    E = 1.114 + 0.088 log (HS$^-$)- 0.147pH
    E = 1.056 - 0.147pH   (a$_s$ =0.22 gram mol/lit)

33. $2H_2O +FeS_{1.14}+0.28e^- \leftrightarrow 1.14HS^- + HFeO_2^-$ (reaction and equation 33)
    E = -0.575 - 0.029 log (HS$^-$) + 1.86H$^+$- 0.029pH
    E = -6.41 +0.391pH   (a$_s$=0.22 gram mol/lit)

34. $3.42HS^- + Fe_3O_4+4.58H^+ +1.16e^- \leftrightarrow 4H_2O +3FeS_{1.14}$ (reaction and equation 34)
    E = 2.498 + 0.174log (HS$^-$)- 0.232pH
    E = 2.383 - 0.232pH   (a$_s$=0.22 gram mol/lit)

35. $2H_2O +Fe_3O_4 + 2e^- \leftrightarrow H^+ +3 HFeO_2^-$ (reaction and equation 35)
    E = -1.846 - 0.088 log (HFeO$_2^-$) + 0.029pH
    E = -1.32 +0.029pH   (a$_s$=0.22 gram mol/lit)

36. $H_2O +yFe_2O_3 +e^- \leftrightarrow 2HFeO_2^-$ (reaction and equation 36)
    E = -0.556- 0.059 log (HFeO$_2^-$)
    E = -0.202   (a$_s$=0.22 gram mol/lit)

37. $4H_2O +FeS_2 + 4e^- \leftrightarrow 6HS^- +2H^+ + Fe_3O_4$ (reaction and equation 37)
    E = -1.101 - 0.088 log (HS$^-$)+ 0.029 pH
    E = -1.042 + 0.029 pH   (a$_s$=0.22 gram mol/lit)

38. $2H_2O +FeS_2 + 2e^- \leftrightarrow 2HS^- +H^+ +HFeO_2^-$ (reaction and equation 38)
    E = -1.349 - 0.029 log (HFeO$_2^-$) -0.059 log (HS$^-$)+ 0.029 pH
    E = -1.136 + 0.029 pH   (a$_s$=0.22 gram mol/lit)

39. $2HSO_3^- + Fe^{++} +10H^+ +10e^- = 6H_2O +FeS_2$ (reaction and equation 39)
    E = 0.452+ 0.0059 log (Fe^{++}) +0.012 log HSO$_3^-$) - 0.059pH
    E = 0.408 - 0.059pH   (a$_s$=0.22 gram mol/lit)

Using the above equations, the E-pH diagrams constructed for Fe-S-H$_2$O system having pH up to ~14 and a$_s$= 0.22 gram mol per lit corresponding to Na$_2$S= 20 gpl, Na$_2$S$_2$O$_3$= 05 gpl, is shown in Figure -2.

III. Results and Discussion

S-H$_2$O System

For S-H$_2$O 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$_2$O$_3^{2-}$ and SO$_3^{2-}$ depending upon the potential, which will in turn be governed by the nature of material exposed, mild steels, stainless steels and non conventional materials [1-7,9,10]. 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 SO$_3^{2-}$ and S$_2$O$_3^{2-}$ while those near the SS2205 and non conventional material Ni-P-TiO$_2$-ZrO$_2$ electrode will be mainly HS$^-$ (potrntiodynamic polarization curves).

Fe-S-H₂O 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 [1-3]. 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 [2,11].
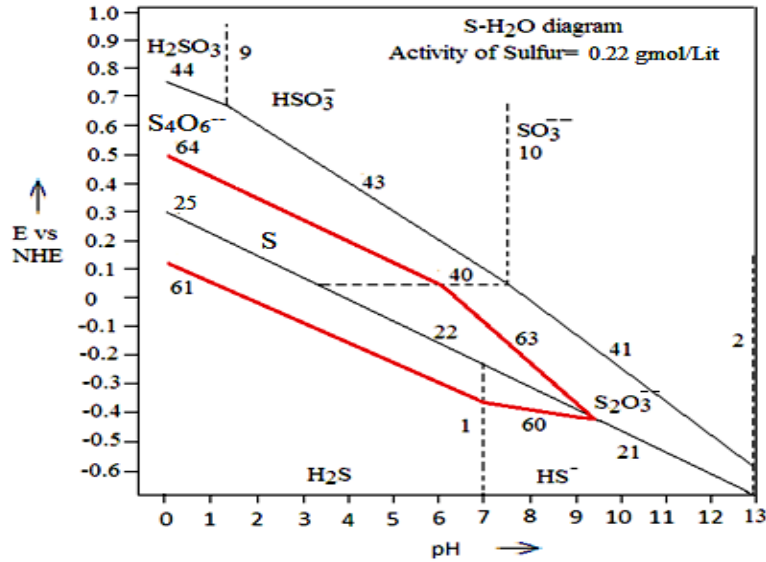

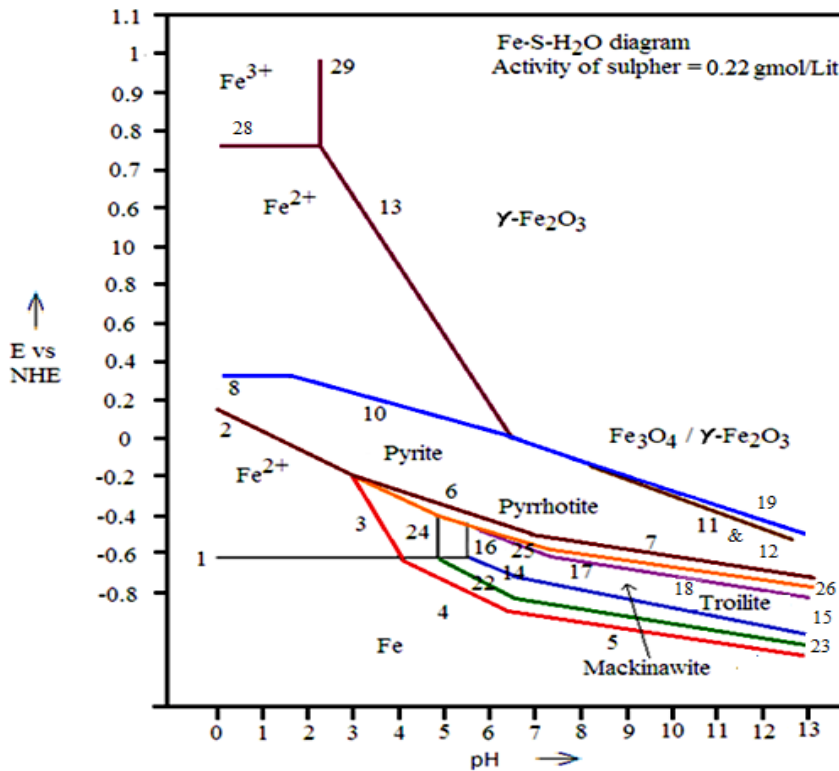**Figure -1 :** E-pH diagram of S-H$_2$O system at room temperature , a$_s$ = 0.22 g mol/lit

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-H$_2$O diagram show that within the range of pH 7 to 14, the sulfur species present in the solution could be HS$^-$, to some extent S^{2-}, S$_2$O$_3^{2-}$ and SO$_3^{2-}$ depending upon the potential. The E-pH diagram of Fe-S-H$_2$O 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

[1]. Pourbaix, M., Pourbaix, A.;"Potential-pH diagrams for the system S-H$_2$O From 25ºC to 150ºC.Influence of access of oxygen in sulphide solutions", Rapports Techniques, Vol159, RT299, October1990.

[2]. A. K. Singh, Pourbaix, A.;"E-pH diagrams for the system Fe-S-H$_2$O From 25ºC to 150ºC "Rapports Techniques, Vol. 166, RT318, June1997.

[3]. Smook, G.A., Handbook for pulp and paper technologist", Tappi, Atlanta.

[4]. Aroma, J., Klarin, A.; "Materials, Corrosion Prevention and Maintenance", Book 15 of series on "Papermaking Science and Technology" Gummerous Printing, Jyvaskyla, finland , p.12, 1999.

[5]. McDonald, R.G. (Ed);"Pulp and Paper Manufacture" McGraw Hill, N. Y; 1989, Mueller, W.A; Proc, Pulp and Paper Industry Corrosion Problems, TAPPI, NACE, Vol. 1, 1974.

[6]. G. Singh, "Corrosion Investigation on Materials in Bleach Media of Paper Industry", Ph.D. Thesis IIT-Roorkee, 2003.

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

[8]. SCAN-N2: 63 and SCAN N3:63 Scandinavian Pulp & Paper Testing Board.

[9]. Metals Handbook 9th Edition, Volume 13 Corrosion (ASM International, USA)

[10]. 1987.

[11]. Singh, D.D.N., "Awareness of Corrosion Problems can save millions; Economical impact of corrosion inhibitors'' Trans. Ind. Inst. Mat. Vol.51, No.-5, p. 291, 1988.

[12]. M.G. Fontana and N.D. Green, "Corrosion Engineering", McGraw-Hill London, 1978.