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Corrosion Investigations Due to Increased Sulfidity in Digester House of Paper Mill

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Abstract

Increased demand of paper, pollution control and better energy management are the driving forces for the development of the paper industry aspiring to enter 21st century in a big way. High sulfidity pulping of wood is one of the approaches in this direction, which attacks lignin in a more selective way thereby increasing pulp yield and makes it possible to bleach pulp to higher degree of brightness with less pollution load. Higher sulfidity has been found to affect corrosion of the digester house and related machinery and through this a question mark on the credibility of materials of construction. Citing example of a typical paper mill, which increased sulfidity in their pulping procedure, attempts have been made to analyze the increase in corrosivity due to changed concentrations of sodium sulfide, polysulfide and thiosulfates in the cooking liquor of the mill in question. E-pH diagram, popularly known as the Pourbaix diagram, have been constructed for S-H_2O and Fe-S-H_2O system with relevant concentrations of the different type of sulfur species and have been used in this endeavor.

Key Words : Sulfidity, Corrosivity, Pourbaix diagrams, Pulp and Paper

1. Introduction

Pulp and paper making technology has undergone rapid changes during the last decade. The factors behind these changes have been pollution control strategy, better energy management and increased production alongside improvement of quality of paper. The purpose is to meet the ever growing need of paper and paper products in the lowest possible cost and more importantly, without affecting the eco-balance of nature. Perhaps the strongest driving force in the modification of paper making process is to develop and adopt new technology which are environment friendly and do not pollute water as well as air. In this endeavor, changes being adopted are with regard to pulping and bleaching practices in pulp and paper industry. To a large extent, bleaching is solely responsible for enhancing colour and increasing BOD,COD, dioxin etc. level of water stream to which discharge of paper mill are thrown while recovery boilers are responsible for bad odour and air pollution of the surrounding environment. To minimize and ultimately bring down pollution to 'ZERO' level from both of these sources, the normal practice has been (i) to change over to elemental chlorine free (ECF) or total chlorine free (TCF) bleaching and (ii) modification in the pulping procedure such that requirement of bleach chemicals (indicated by 'kappa' no.) drops to lower levels, which also helps in bringing down pollution level.

One most likely modification in pulping process is applicable process is application of rapid displacement heating (RDH) or super batch cooking [1, 2]. In this process, cooking of chips (delignification) is done with cooking liquor of higher sulfidity, which accelerates delignification because it more selectively attacks lignin. The result is that (i) pulp strength is improved (ii) pulp yield is = 1.5-2% higher (iii) pulp has low kappa no. (less demand of bleach chemicals and hence less pollution). This process also shows better heat economy and better brown stock washing thereby improving recovery of chemicals also. Since most sulfide is removed in the pulping stage itself, decreased sulfide in black liquor has advantage in reduced corrosion of recovery systems and also less TRS (total reduced sulfur) emissions from recovery boilers (TRS)emission is responsible for bad odour. However, increased sulfidity in cooking liquor affects corrosion of digesters and related plant machinery thereby cutting short their useful life drastically [3]. The present paper deals with this aspect of operation in digester house.

2. Chemicals and Cooking Liquor :

Paper industry uses 'kraft' process most widely for pulping of wood (Table-1).

Table 1: Pulping Process (Global Data)

Category	Amount (metric tone)
Mechanical Pulp	$31x10^6$
Chemical Pulp Kraft	88×10^6
Sulfite	9×10^6
Neutral Sulfite Semi Chemical NSSC, etc	8×10^6

According to above, share of 'kraft' process is about 84% of all the chemical pulping and 64% of the total pulping processes. The cooking liquor in kraft pulping consists mainly of NaOH and Na_2S. The pH of this solution is 13.2-14 at room temperature. In addition, the liquor also contains (i) Na_2SO_4 (added as a make up chemical in recovery boiler as 'salt cake') due to its incomplete reduction in furnace (ii) Na_2CO_3 (formed in furnace), due to incomplete causticizing (iii) $Na_2S_2O_3$, due to air oxidation of sulfate (iv) Na_2S_{x+1}, formed due to following equilibrium:

$$Na_2S + Na_2S_2O_3 = Na_2S_{x+1} + X.\ Na_2SO_3$$

and (v), as contaminant from wood, fresh water or recycled filtrates in the process. Average composition of typical cooking liquor from mills in Western countries and from Indian mills is given Table 2.

The amount of sulfidity in cooking liquor of US mill is ~ 40% while that of Indian mill is ~20%. This corresponds to 0. 7gm mole/liter and 0.2 gm mole/liter of total dissolved sulfur (considering all forms of sulfur) in former and latter respectively.

Table 2: Composition of cooking liquor (amount in gpl)

Chemicals	Indian Mills	U. S. Mills
NaOH	65	44.7
Na_2S	15	28
Na_2CO_3	25.33	25
Na_2SO_4	13.5	9.8
Na_2SO_3	1.79	1
$Na_2S_2O_3$	2.3	6
Na_2S_{x+1}	2.4	1.8

2.1. Cases of enhanced corrosion:

Case 1: In one mill [4] a stationary digester fabricated of C-steel was observed experiencing corrosion at a rate of about 100 mpy to 120 mpy. Cooking liquor corrosion related failures were also observed within 2 years of operation of white liquor lines of mild steel. This was in spite of the fact that the mill was practicing operating conditions as per the norms of the industry.

The analysis of liquor showed the presence of 3 gpl of thiosulfate ($S_2O_3^{2-}$) which was responsible for increased corrosion. Addition of elemental sulfur (S) to white liquor at concentration greater than 7 gpl was found to decrease corrosion significantly. Addition of sulfur increases polysulfide concentration in liquor which decreases corrosion rate.

Case 2: In another mill [5] their batch digesters were found to have been affected by severe corrosion within ten years of operation. Analysis of cooking and white/green liquor from pulp mill and causticizing plant respectively showed increase in sodium thiosulfate from 1.9 to 3 gpl while average polysulfide was 2.44 gpl. Corrosion experiments conducted on white liquor with varying polysulfide concentration to 19 -20 gpl lowers the corrosion rate to ~ 1.83 mm/year. Obviously the amount of polysulfide in the digester liquor was at a dangerous level from corrosion point of view. Remedial measures for reducing corrosion included increasing polysulfide content to a level of 19-20 gpl by either adding Sulfur to white liquor or by oxidizing the white liquor. This change of Na_2S to polysulfides is as per following reactions:

$2H_2O + 2Na_2S + O_2 = 2S + 4\ NaOH$
$XS + Na_2S = Na_2S_{x+1}$

However, the authors feel that (i) corrosion rate of 1.84 mm/year (~73 mpy) at 19 gpl polysulfide level is very high. Even with this rate, thinning of digester wall will be rapid (ii) localized corrosion may be observed at higher concentration (> 19 gpl) of polysulfide (iii) long term experiments should also be conducted to know real corrosion rate and about localized corrosion. Experiments in present work were of 3-4 hours.

Case 3: Another mill increased sulfidity from 21-22% to 26-27%, which has resulted into increased corrosion of digester house machinery [6]. Following corrosion effects were noticed in a time spam of three years:

- original thickness of inner casing of mild steel circulating pump in digester decreased from 6 mm to < 1 mm (corrosion rate ~ 67 mpy). Roof and walls of top dome of liquor preheated was affected by pitting. Bottom plate of dome, where heat exchanger tubes of liquor preheated are welded, is affected by grooving and uniform corrosion. Other affected portions are joints of liquor heater line with digester, blow lines and liquor lines.

These are the cases where one notices that not only general corrosion, but even localized corrosion can get initiated with increased sulfidity as one suspects on the basis of effect of polysulfide on corrosivity.

3. Analysis and Discussion :

Considering concentration of OH^- ions cooking liquor is from 0.5 to 2.5 gm mole/liter and the ionization constant of water at temperature from 25^0C to 150^0C [1] the pH of cooking liquor at temperatures will be as given in Table 3 below.

Table 3: pH of cooking liquor at different temperatures

Temperature	pH
25^0C	13.20-14.40
100^0C	11.96-12.66
130^0C	11.60-12.30
150^0C	11.34-12.04

Thus as the liquor is heated during pulping from room temperature to 150^0C, its pH varies from 14.4 to 11.34. These pH ranges will therefore be interest from viewpoint of investigating corrosion in cooking liquor.
E-pH diagrams for S-H_2O system were drawn to understand (i) the nature of sulfide species likely to be present in cooking liquor depending upon the temperature, pH and concentration and (ii) to draw, in turn, Fe-S-H_2O Pourbaix diagram so as to understand the type of iron sulfides likely to form. The diagrams were drawn for liquors of 20% and 40% sulfidity at room temperature. These diagrams shows that in cooking liquor (with pH varying 11.6-14.4), sulfide species at reducing conditions will be mostly HS^- and only small amount of S^{2-}. Only at room temperature, where pH of cooking liquor is ~ 14, both HS^- and S^{2-} will be in similar amount. In the presence of oxidants, these species would be in the form of $S_2O_3^{2-}$ and/or polysulfide ions S_n^{2-} with n varying from 2-5 at temperatures $\leq 120^0$C as at higher temperatures polysulfides are unstable. Polysulfide has been found in highly alkaline and hot solutions (case of cooking liquor) [7].
Carbon steel corrodes in alkaline solution (without sulfide) through following reactions:

$Fe \rightarrow Fe^{2+} + 2e^-$ (anodic)
$2H^+ + 2e^- \rightarrow H_2$ (Cathode)
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (Cathode)

At the concentration of OH^-, 0.5 – 2.5mole/liter, prevailing in cooking liquor Fe_3O_4 is the stable oxide providing protection [8]. Fe_3O_4 forms as a result of following reactions:

$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$
$Fe(OH)_2 + OH^- \rightarrow Fe(OH)_3^-$
$3Fe(OH)_3^- + H^+ \rightarrow Fe_3O_4 + 5H_2O + 2e^-$

On increasing temperature, formation chances of Fe_3O_4 recedes (On the basis of E-pH diagram) [9, 10] and $HFeO_2$- or $\gamma - Fe_2O_3$ may form depending upon presence of oxidants (e.g. dissolved oxygen etc.). Both of these are not as protective as Fe_3O_4. Hence even in the absence of any sulfide, steel will corrode though at moderate rate [8]. Presence of Na_2S in the cooking liquor increases corrosion rate, because a less protective film of corrosion products form which consists of oxides and sulfides. The latter may be forming as a result of following reaction:

$Fe^{2+} + 2HS^- \rightarrow$ iron sulfide

Corrosion products formed on carbon steel exposed to sulfide solutions have appearance of black top and yellow-red bottom close to the metal surface [9]. The former ones appear to be sulfides while yellow-red coloured products are iron oxides. Also a higher redox potential is required in the solution for the formation of a protective oxide layer on carbon-steel in the presence of sulfide ions. From Fe-H_2O Pourbaix diagram at room temperature [10], redox potential required for forming Fe_3O_4 is volt (SHE) while in sulfide containing solutions, this potential is -0.52 Volt (SHE) (See fig.2 Fe-S-H_2O diagram at 25^0C). When Na_2S of white liquor oxidizes in recovery boiler, it changes to $Na_2S_2O_3$ according to following reaction:

$$2Na_2S + 2O_2 + H_2O \rightarrow Na_2S_2O_3 + 2\ NaOH$$

Presence of thiosulfate in liquor further enhances corrosivity as it helps in accelerating reduction reaction, given below, which in turn increases corrosion of iron:

$$S_2O_3^{2-} + 8H^+ + 8e^- \rightarrow 2HS^- + 3\ H_2O$$

Thus reduction of thiosulfate ion will also be accompanied by increase in pH of liquor. In the presence of thiosulfate, corrosion of iron will be governed mainly by above reaction. Corrosion products formed here will be iron sulfides.

Thiosulfate also converts into polysulfide as per following equilibrium:

$$HS^- + XS_2O_3^{\ 2-} \leftrightarrow S_{1+x}^{2-} + XSO_3^{2-} + H^+ \text{ (X varying from 2 to 5)}$$
$$HS^- + S_2O_3^{2-} \leftrightarrow S$$

A higher concentration of $S_2O_3^{2-}$ ions along with higher sulfidity will result into formation of S_2^{2-}, S_3^{2-} etc. depending upon concentration.

These polysulfides enhance corrosion, since they undergo following cathodic reactions:

$$S_2^{2-} + 2H^+ + 2e^- \rightarrow 2HS^-$$
$$S_3^{2-} + 3H^+ + 4e^- \rightarrow 3HS^-$$

Following can be seen from above discussion:

a. Formation of higher polysulfide (S_3^{2-}, S_4^{2-} etc.) will enhance corrosion more than S_2^{2-} i.e. higher sulfidity which results in formation of higher sulfides will end up in forming more corrosive media.
b. Reduction of polysulfides also increases alkalinity of liquor. It is also interesting to note that corrosivity due to polysulfides is highly dependent upon its concentration. Corrosion rate increases in concentration of polysulfides up to 2-5 gpl. However, corrosion rate decreases on further increases the amount of polysulfide beyond 5 gpl (up to 19-20 gpl), by passivating the steel surface. It seems at low concentration, steel corrodes in active region. On initially increasing concentration, corrosion increases due to shifting of cathodic polarization curve, representing $S_2^{2-} + 2H^+ + 2e^- \rightarrow 2HS^-$, towards anodic values. Beyond 5 gpl, this curve cuts the anodic polarization curve of iron in passivation region thereby passivating steel.

Two questions arise here:

a. On further increasing concentration, steel must transit into transpassivation region thereby increasing the possibilities of pitting and crevice corrosion. It is worth investigating such limits of polysulfide concentration where steel is likely to experience localized corrosion.
b. What is the nature of sulfides under active and passive corrosion?
   In order to know the possibility of forming various sulfides and hence passivation of carbon steels in cooking liquor, E-pH diagrams for Fe-S-H_2O systems were constructed for total dissolved sulfur content of 0.2gm mole/liter (corresponding to 20% sulfidity) and 0.7 gm mole/liter (corresponding to

40% sulfidity) at room and high temperature (Figs. 1 to 4). Details about the various equilibrium and the chemical potentials of various issues are given in ref. [11]. The conditions considered are those which generally prevail for cooking liquor in digester.

A comparison of these diagrams with those of Fe-H_2O system indicates about following aspects:

a. Thermodynamic stability regions of various iron sulfides namely mackinawite, troilite, pyrrhotite and pyrite exist up to ~0.52 Volts (at pH ~14 and 25^0C). At more anodic potentials only one expects to observe protective oxide Fe_3O_4 in sulfide solutions. In case of carbon-steel in H_2O, Fe_3O_4 is observed at a lesser anodic potential. Thus corrosion products forming on carbon-steel should be mainly sulfides with a small amount of oxides. As some of these sulfides namely mackinawite and troilite are of non-protective type [12, 13] their formation in place of oxides increases the corrosion attack on carbon-steel in sulfide solution. It will be interesting to observe the potential of carbon-steel in sulfide solution and identity the nature of sulfides formed in such cases.

b. At more active potentials, among the sulfides, one expects to observe mackinawite/troilite. Both of these are non-protective type and dissolve very easily in solution. As such, as carbon-steel comes in contact with sulfide solution, this solution becomes dark in colour due to dissolution of mackinawite in solution.

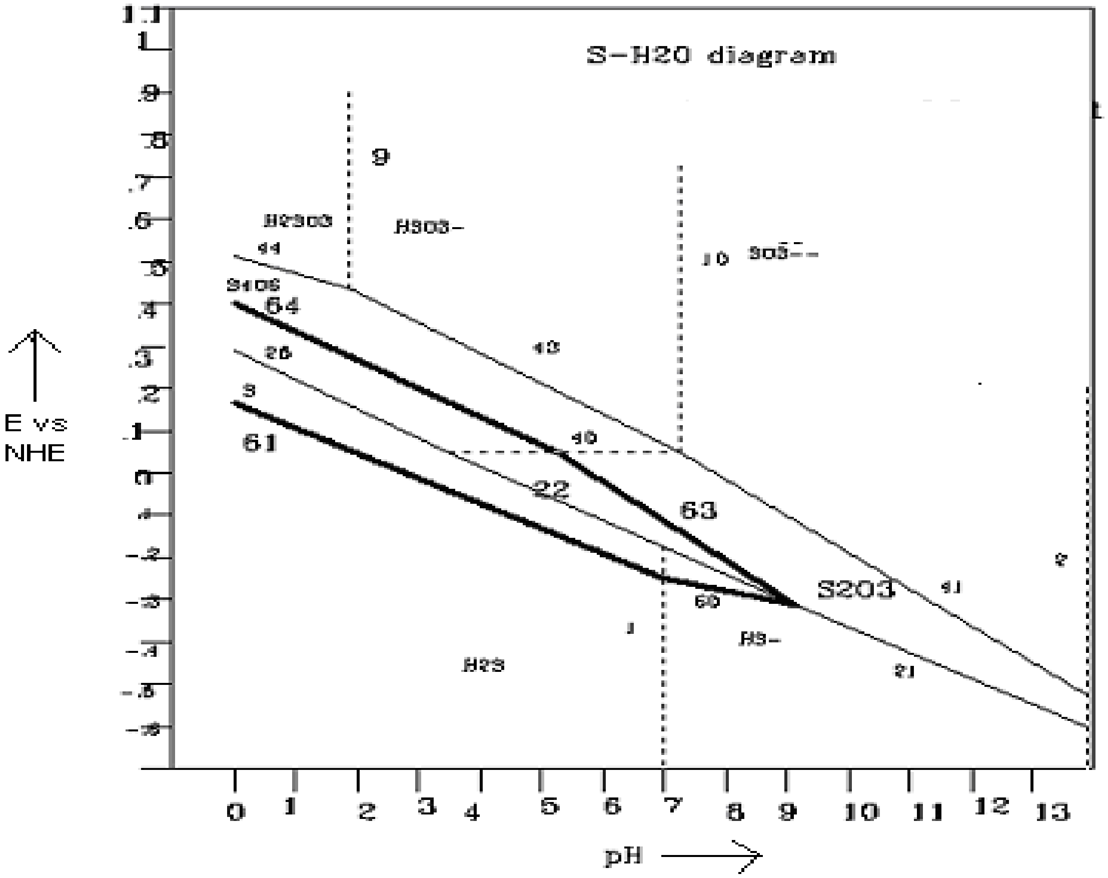

Figure 1: E-pH diagram E(NHE) Vs pH for S-H_2O system a_s=0.2 gmole/lit

In the presence of oxidants e.g. oxygen or addition of sulfur, the nature of iron sulfides may change to pyrrhotite and then to pyrite. Both of these sulfides have been observed to form under oxidizing conditions and/or at high temperatures [13]. Also pyrrhotite and pyrite are protective type of sulfides [12, 13]. Perhaps that is the reason why on adding polysulfide (which form at oxidizing potentials in alkaline solutions) or sulfur, corrosion rate of digester steel is found to decrease as it is protected by pyrrhotite and pyrite. Since at potentials (~-0.5 V_{SHE}), at which polysulfide are stable, γ- Fe_2O_3 is also stable (Figs. 1-4), it is also expected to observe γ- Fe_2O_3 along with pyrrhotite and pyrite [9-11] in sulfide solutions up to ~ 120^0C.

c. The above aspects also forms the basis of protective digester by polarizing it anodically (anodic protection) when steel gets passivated. While anodic protection systems for digesters have been reported in literature [14-18] one report [4] that anodic protection for plant handling cooking liquor is not feasible seems not correct.

   It will be of interest to see nature of sulfides formed on steel (under anodic protection) and compare them with their nature when formed on steel passivating by adding sulfur or polysulfide.
d. Once passivation is achieved, there is also a possibility of observing breakdown potential and hence onset of localized corrosion. It should be tried to find upper limit of polysulfide in cooking liquor so that steel does not experience localized corrosion.
e. Corrosion of increased sulfidity can be checked by comparing E-pH diagrams at 20% and 40% sulfidity (Fig. 1 to 4). One finds an increased area of stability of sulfides at the cost of oxides. A higher amount of sulfides in the corrosion [19-24] products is obviously going to retard the protective characteristics of the rust layer provided that corrosion potential of steel does not shift much in anodic direction.

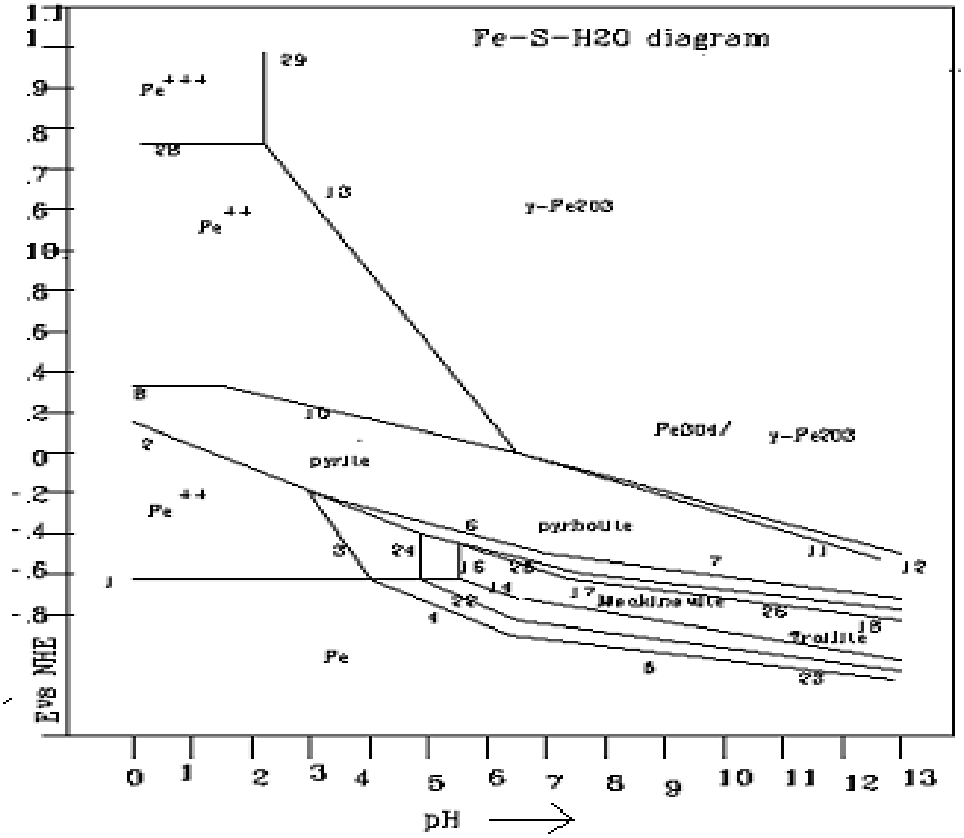

Figure 2: E-pH diagram E(NHE) Vs pH for Fe- S-H_2O system a_s=0.2 gmole/lit

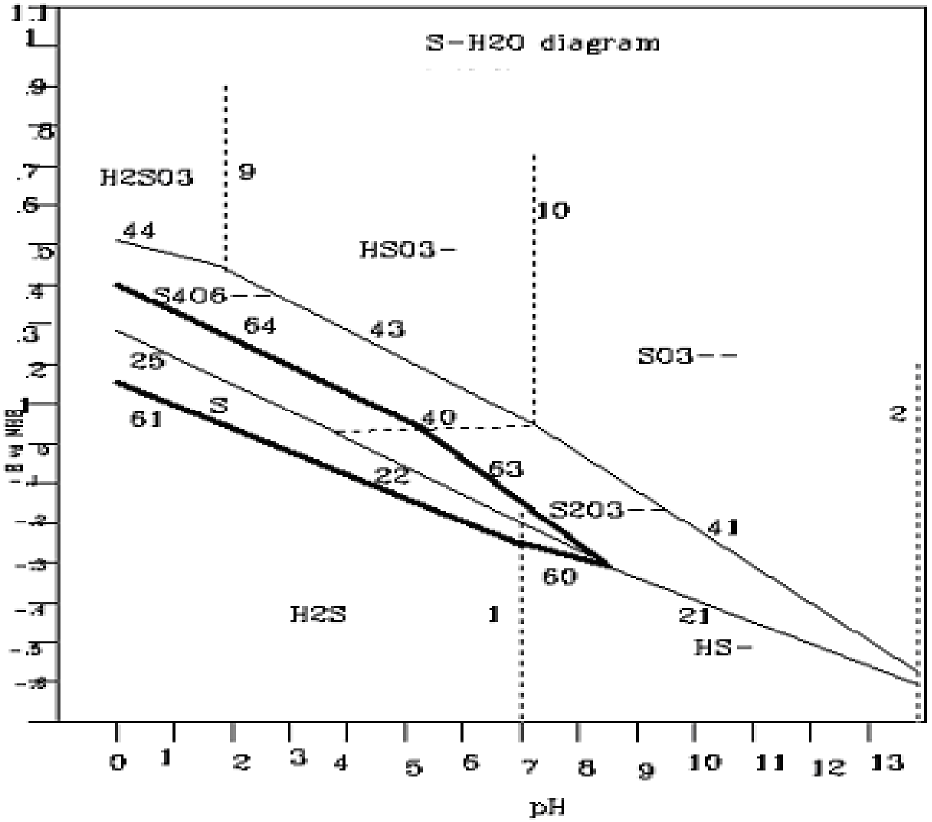

Figure 3: E-pH diagram E(NHE) Vs pH for S-H_2O system a_s=0.7 gmole/lit

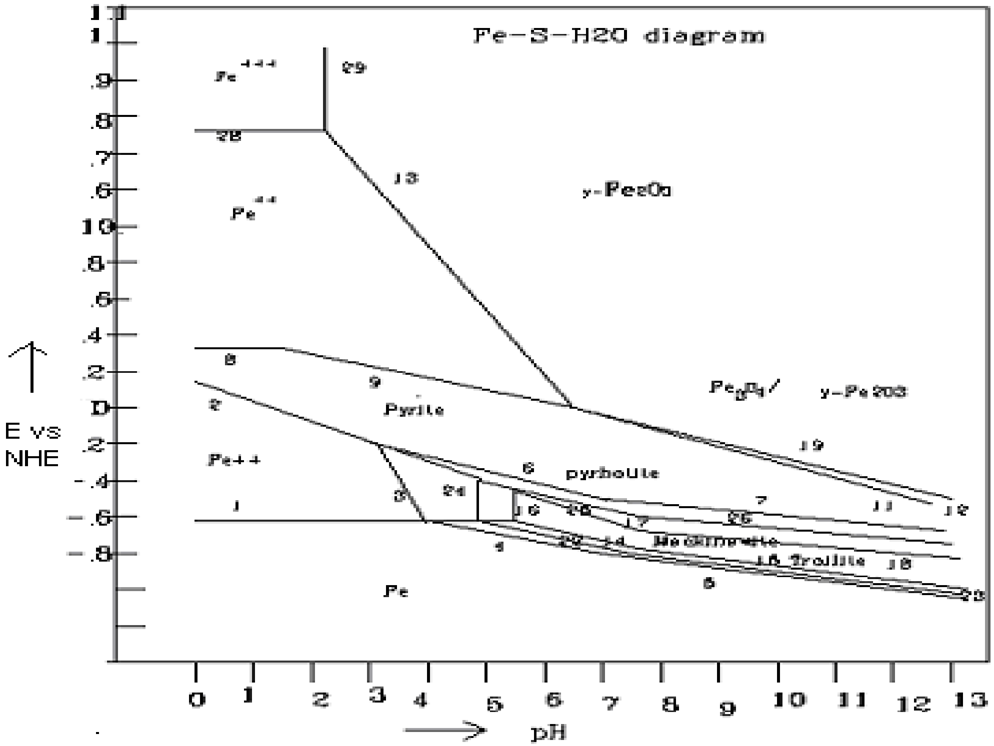

Figure 4: E-pH diagram E(NHE) Vs pH for Fe- S-H_2O system a_s=0.7 gmole/lit

4. Conclusion

The present study reports the effect of presence of sulfur species in cooking liquor on corrosion of digester and other related machinery and that how the corrosivity of liquor is affected due to increased practice of pulping wood chips at higher sulfidity. On the basis of E-pH diagrams drawn for S-H_2O and Fe-S-H_2O system considering 20% and 40% sulfidity in the solutions, following conclusions can be drawn. In drawing conclusions, help of E-pH diagrams for Fe-H_2O [7] and Fe-S-H_2O systems at 25^0C has also been taken

a. The alkalinity and sulfidity of cooking liquor and operating conditions in digester are such that pH of liquor varies from ~ 14.05 to 11.69 as its temperature is raised from 25^0C to 150^0C. Under these conditions, sulfur containing species are HS- with small amount of S^{2-} in reducing conditions and polysulfide (S_n^{2-}) and ($S_2O_3^{2-}$) under oxidizing conditions.
b. Presence of thionates and polysulfides increases corrosion with increased sulfidity and more oxidizing conditions, the cooking liquor is expected to have more of polysulfide (higher values of n in S_n^{2-}) which increases corrosion further.
c. In cooking liquor, the corrosion products are expected products are expected to be mixture of sulfides and oxide. With increased sulfidity, a larger parts of corrosion products are expected to be consisting of sulfides. In reducing conditions, the sulfides could be mackinawite/troilite which are non-protective type and hence may be responsible for increased corrosion attack on steel. While in oxidizing conditions pyrrhotite and pyrite could be the iron sulfides which are protective type. As such when polysulfide is increased in amount by more than 5 gpl, the corrosivity of cooking liquor starts decreasing. However, beyond certain amount of polysulfide, the steel is likely to experience localized corrosion.
d. The above aspects need to be verified by experiments which are expected to start soon.
e. The likelihood of formation of protective sulfides under oxidizing conditions gives a possibility of protecting digester and related machinery of steel by polarizing it anodically (anodic protection).

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