

Effect of Sulfidity on Corrosion of 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 however, 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 analyse 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 Fe-S-H₂O system with relevant concentrations of the different type of sulfur species and have been used in this endeavour.

INTRODUCTION

Paper and Pulp making technology has undergone rapid changes during the last decade. Main forces 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 evergrowing 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 technology which are environment friendly and do not pollute water as well as air. In this endeavour, changes being adopted are with regard to pulping and bleaching practices in paper industry. To minimise and ultimately bring down pollution to 'ZERO' level from both of these sources, the normal practice has been (i) modification in the pulping procedure such

that requirement of bleach chemicals (indicated by 'kappa' no.) drops to lower levels, which helps in bringing down pollution level and (ii) change over to elemental chlorine free (ECF) or total chlorine free (TCF) bleaching.

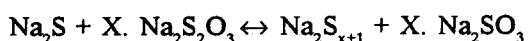
One most likely modification in pulping process is application of Rapid Displacement Heating (RDH) or superbatch cooking (1,2). In this process, cooking of chips (delignification) is done with liquor of higher sulphidity, which accelerates delignification because it more selectively attacks lignin. The result is that (i) pulp strength is improved (ii) pulp yield is $\approx 1.5-2\%$

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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 sulphide is removed in the pulping stage itself, decreased sulphide in black liquor has advantage in reduced corrosion of recovery systems and also less TRS (total reduced sulphur) emissions from recovery boilers (TRS emission is responsible for bad odour). However, increased sulphidity 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.

CHEMICALS IN COOKING LIQUOR

'kraft' process is the most widely used pulping process in paper industry. According to an estimate, roughly $\approx 84\%$ of all the chemical pulping and $\approx 64\%$ of the total pulping is done by 'kraft' process. The cooking liquor in kraft pulping consists mainly of NaOH and Na_2S . pH of this solution is 13.5 -14 at room temperature. In addition, the liquor also consists of (i) Na_2SO_4 (added as a make up chemical in recovery boiler as 'salt cake'), because of its incomplete reduction in furnace (ii) Na_2CO_3 (formed in furnace), due to incomplete causticizing (iii) $\text{Na}_2\text{S}_2\text{O}_3$, due to air oxidation of sulphide (iv) $\text{Na}_2\text{S}_{x+1}$, formed due to the following equilibrium



and (v) NaCl, as contaminant from wood, fresh water or recycled filtrates in the process. Average composition of a typical cooking liquor from mills in

Table-1 : Composition of cooking liquor (amount in gpl)

	U.S. mill	Indian mill
NaOH	44.7	65
Na_2S	28	15
Na_2CO_3	25	25.33
Na_2SO_4	9.798	13.5
Na_2SO_3	1	1.79
$\text{Na}_2\text{S}_2\text{O}_3$	6	2.3
$\text{Na}_2\text{S}_{x+1}$	1.8	2.4

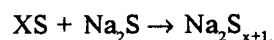
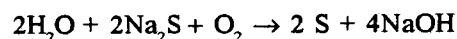
western countries and from Indian mills are given Table-1.

The amount of sulphidity in cooking liquor of US mill is 38% while that of Indian mill is $\sim 20\%$. This corresponds to 0.5 gmol/litre and 0.21 gmol/litre of total dissolved sulphur (considering all forms of sulphur) in former and latter respectively.

CASES OF ENHANCED CORROSION AND PROBLEM STATEMENT

Case I: 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 norm of the industry. The analysis of liquor showed the presence of 3 gpl of thiosulphate ($\text{S}_2\text{O}_3^{2-}$) which was responsible for increased corrosion. Addition of elemental sulphur (S) to white liquor at concentration greater than 7 gpl was found to decrease corrosion significantly. Addition of sulphur increases polysulphide concentration in liquor which decreases corrosion rate.

Case II: 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 causticising plant respectively showed increase in sodium thiosulphate from 1.9 to 3 gpl while average polysulphide was 2.44 gpl. Earlier reported results on corrosion experiments (6), conducted on white liquor with varying polysulphide concentration, show maximum corrosion rate (~ 33 mm/year) at 2-2.5 gpl polysulphide. Increasing concentration to 19-20 gpl lowers the corrosion rate to ~ 1.83 mm/year. The amount of polysulphide in the digester liquor, therefore, was at a dangerous level from corrosion point of view. Remedial measures suggested for reducing corrosion included increasing polysulphide content to a level of 19-20 gpl by either adding S to white liquor or by oxidising the white liquor. This change of Na_2S to polysulphides is as per following reactions:



However, the authors feel that (i) corrosion rate of 1.84 mm/year at 19 gpl polysulphide level is very high. Even with this rate, thinning of digester wall

will be rapid and life of digester cannot be expected beyond 7-8 years. (ii) localised corrosion may be observed at higher concentration (>19 gpl) of polysulphides which may result into premature failure of digester (iii) effect of thiosulfate has been ignored. It may be worth mentioning here that the steps as suggested in the report (5), have not shown the desired results and hence require further investigations.

Case III. In another mill where sulphidity was increased from 21-22% to 26-27% (7), following corrosion effects were noticed in a time span of three years:

- original thickness of inner casing of mild steel circulating pulp in digester decreased from 6 mm to < 1 mm (corrosion rate ~ 1.7 mm/year).
- roof and walls of top dome of liquor preheater was affected by pitting. Bottom plate of dome, where heat exchanger tubes of liquor preheater 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 localised corrosion can get initiated with increased sulphidity, as the authors suspect in Case II above on the basis of effect of polysulphide on corrosivity. Similarly localised corrosion in the presence of thiosulfate has also been observed (8). The suggestions that corrosivity increases with sodium sulfide, thiosulfate and polysulfides, with the possibility of corrosion reduction at higher polysulfide level needs to be corroborated with the laboratory experiments. Further, it is also required to investigate the effect of thiosulfate ions, hitherto not studied, on corrosivity of white liquor. Attempts should also be made to understand these effects on the basis of electrochemical theory, so that effective steps for protecting digesters may be taken. The present paper reports the work done on this basis.

ANALYSIS AND DISCUSSION

Considering concentration of OH⁻ ions in cooking liquor from 0.5 to 2.5 gmol/litre and the ionisation constant of water at temperatures from 25°C to 150°C (1), the pH of cooking liquor varies with temperatures as given in Table -2. Thus as the liquor is heated during pulping from room temperature to 150°C, its pH varies from 14.4 to 11.34. These pH ranges will therefore be of interest from viewpoint of investigating

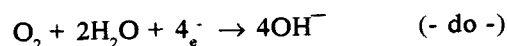
Table-2 : pH of Cooking Liquor at Different Temperatures

Temperature°C	pH
25	13.70 - 14.40
100	11.96 - 12.66
130	11.60 - 12.30
150	11.34 - 12.04

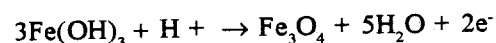
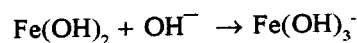
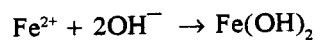
corrosion in cooking liquor.

E-pH diagrams for S-H₂O system were drawn to understand (i) the nature of sulphide species likely to be present in cooking liquor depending upon the temperature, pH and concentration and (ii) to draw, in turn, Fe-S-H₂O Pourbaix diagram so as to understand the type of iron sulphides likely to form. These diagrams were drawn for liquors of 20% and 38% sulphidity at 150°C. A comparison of these diagrams with that at room temperature shows that in cooking liquor (with pH varying between 11.6-14.4), sulphide specie at reducing conditions will be mostly HS and only small amount of S²⁻ Only at room temperature, where pH of cooking liquor ~ is 14, both HS⁻ and S²⁻ will be in similar amount. In the presence of oxidants, these species would be in the form of S₂O₃²⁻ and/or polysulphide ions S_n²⁻ with n varying from 2-5 at temperatures ≤ 120°C as at higher temperatures polysulphides are unstable. Polysulphides have been found in highly alkaline and hot solutions (case of cooking liquor) (9).

C-steel corrodes in alkaline solution (without sulphide) by following reactions:



At the concentration of OH⁻, 0.5-2.5 mole/litre, in cooking liquor Fe₃O₄ is the stable oxide providing protection (10). Fe₃O₄ forms due to following reactions:



On increasing temperature, formation of Fe₃O₄

recedes (E-pH diagram) and HFeO_2^- or $\gamma\text{-Fe}_2\text{O}_3$ may form depending upon presence of oxidants (e.g. dissolved oxygen etc.). Both of these are not so protective as Fe_3O_4 . Hence steel will corrode though at moderate rate (10).

EFFECT OF SULFIDE

Corrosion tests performed in alkaline sulfide solutions show a corrosion rate of ~ 10 mpy and it increases from 9 mpy to 11 mpy as sulfidity increases from 20% to 26%. Presence of Na_2S in the liquor increases corrosion rate, because a less protective film of corrosion products form which consists of oxides and sulphides. The latter may be forming as a result of reaction: $\text{Fe}^{2+} + 2\text{HS}^- \rightarrow$ iron sulphide.

Corrosion products formed on carbon steel exposed to sulphide solutions have appearance of black top and yellow red bottom close to the metal surface (II). The former ones appear to be sulphides 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 sulphide ions. From Fe- H_2O Pourbaix diagram at room temperature (12), redox potential required for forming Fe_3O_4 is -0.66 volt (SHE) while in sulphide containing solutions, this potential is 0.52 volt (SHE) (see Fig. 1- Fe-S- H_2O diagram at 25°C).

EFFECT OF THIOSULFATE

When Na_2S of white liquor oxidises in recovery

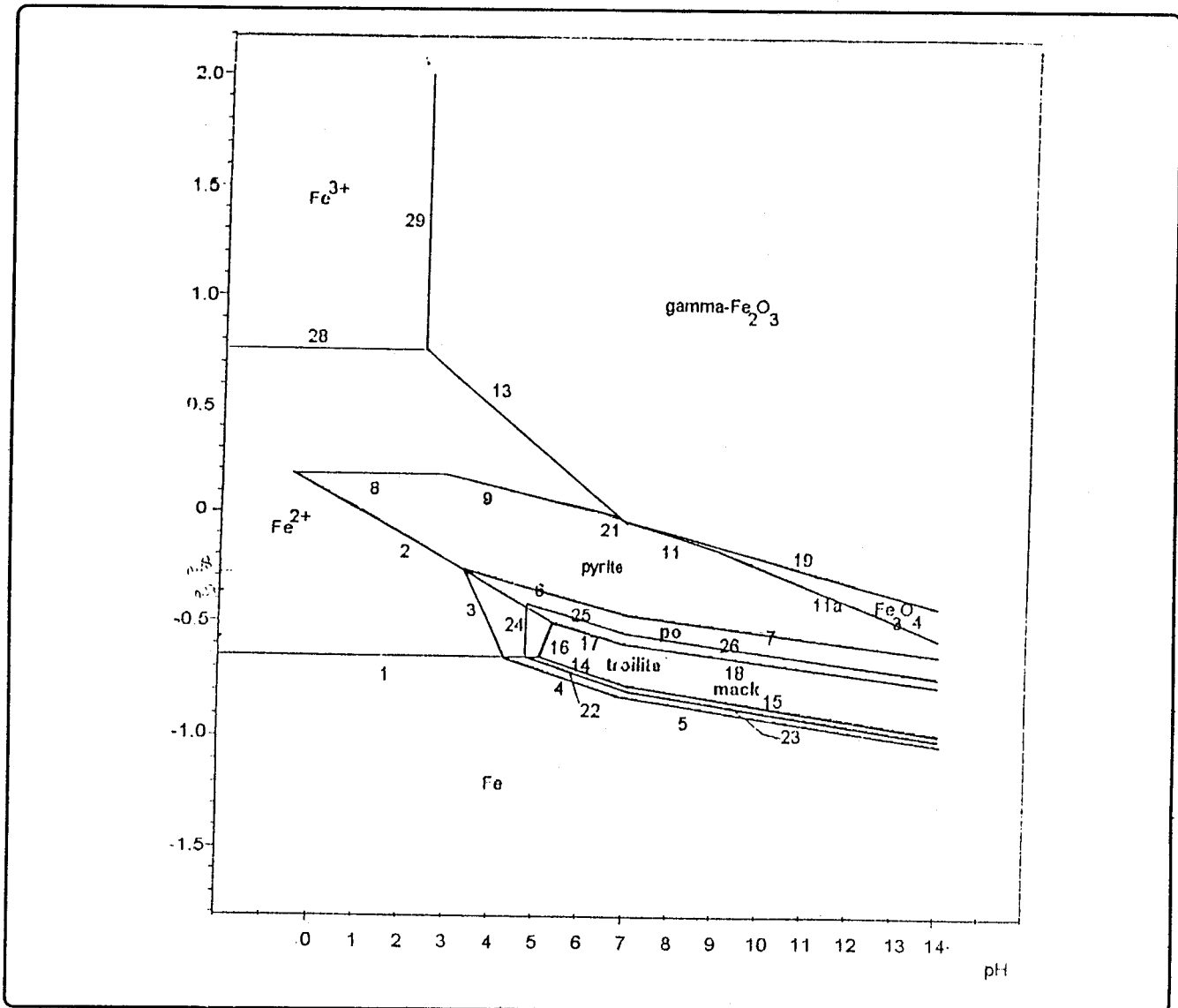
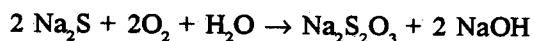
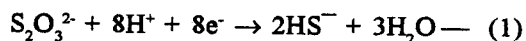


Figure 1 : Fe-S- H_2O diagram for $a_{\text{H}_2\text{S}} = 0.4046$ gmol/lit ($\text{H}_2\text{S} \rightarrow 5000$ ppm) at temp. = 298 K

boiler, it changes to $\text{Na}_2\text{S}_2\text{O}_3$ (sodium thiosulphate) according to following reaction:



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

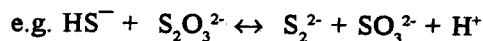
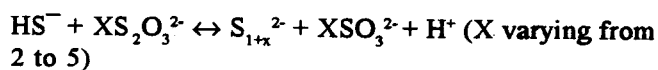


In the presence of thiosulphate, corrosion of iron will be governed mainly by above reaction. Increase in $\text{S}_2\text{O}_3^{2-}$ has been observed to show increase in corrosion rate (13). Corrosion products formed here will be iron sulphides.

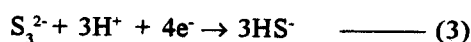
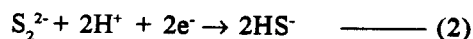
EFFECT OF POLYSULFIDES

Polysulphide forms from thiosulphate as per

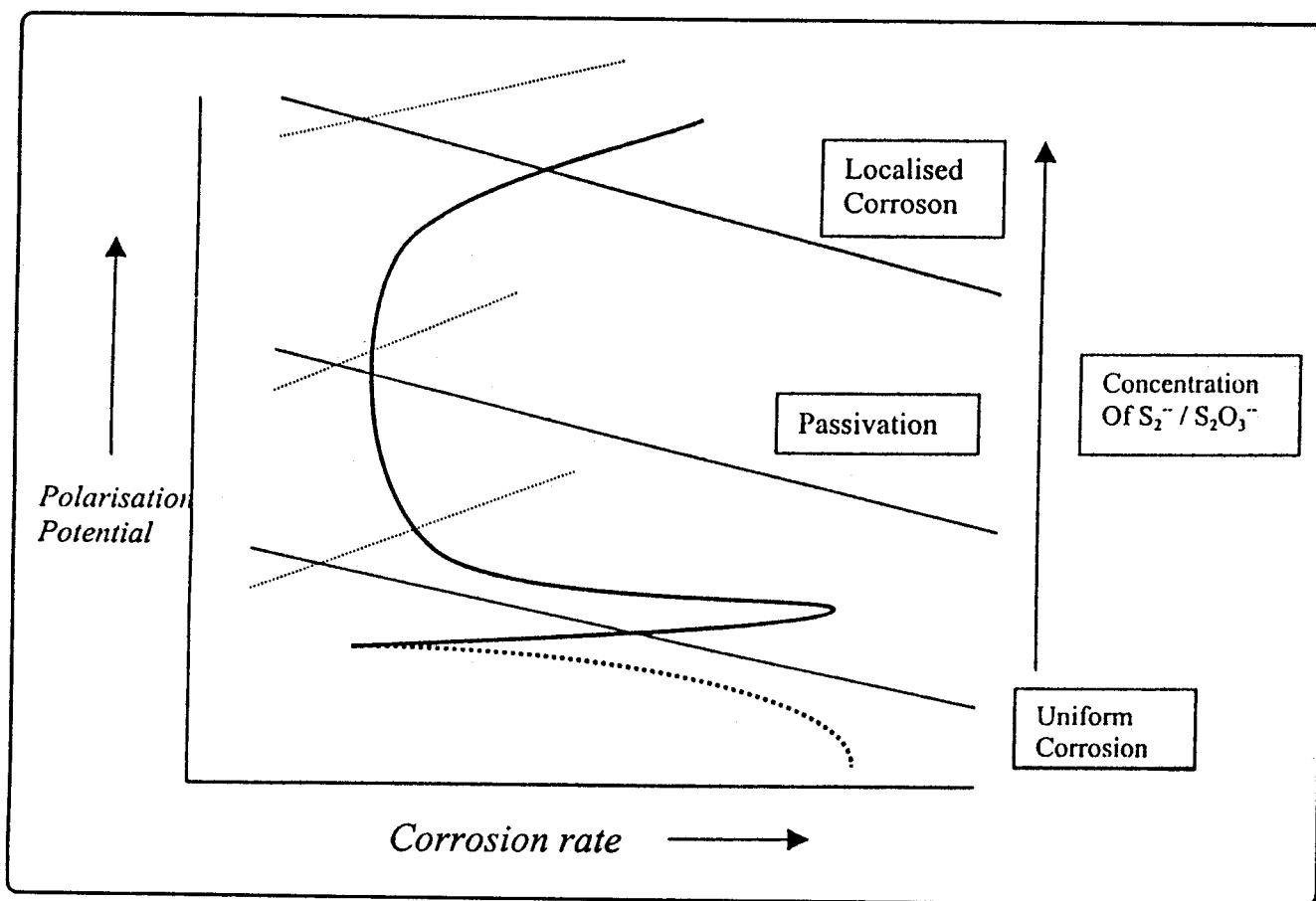
following equilibrium:



A higher concentration of $\text{S}_2\text{O}_3^{2-}$ ions along with higher sulfidity will result in formation of S_2^{2-} , S_3^{2-} ,..... depending upon concentration. These polysulphides enhance corrosion, since they undergo following cathodic reactions and increase reduction reaction rate:



Also, as per equations (2) and (3), higher polysulphides (S_3^{2-} , S_4^{2-} ,) will enhance corrosion



Oxidation reaction of steel ———
 Reduction reaction of S_2^- or S_2O_3^- ———

Figure 2 Anodic (oxidation) and cathodic (reduction) polarisation curves showing the possibility of steel experiencing uniform corrosion, passivation (sudden decrease in corrosion rate) and localised corrosion (e.g. pin hole attack, corrosion under joints/deposits) as amount of S_2^- or S_2O_3^- increases.

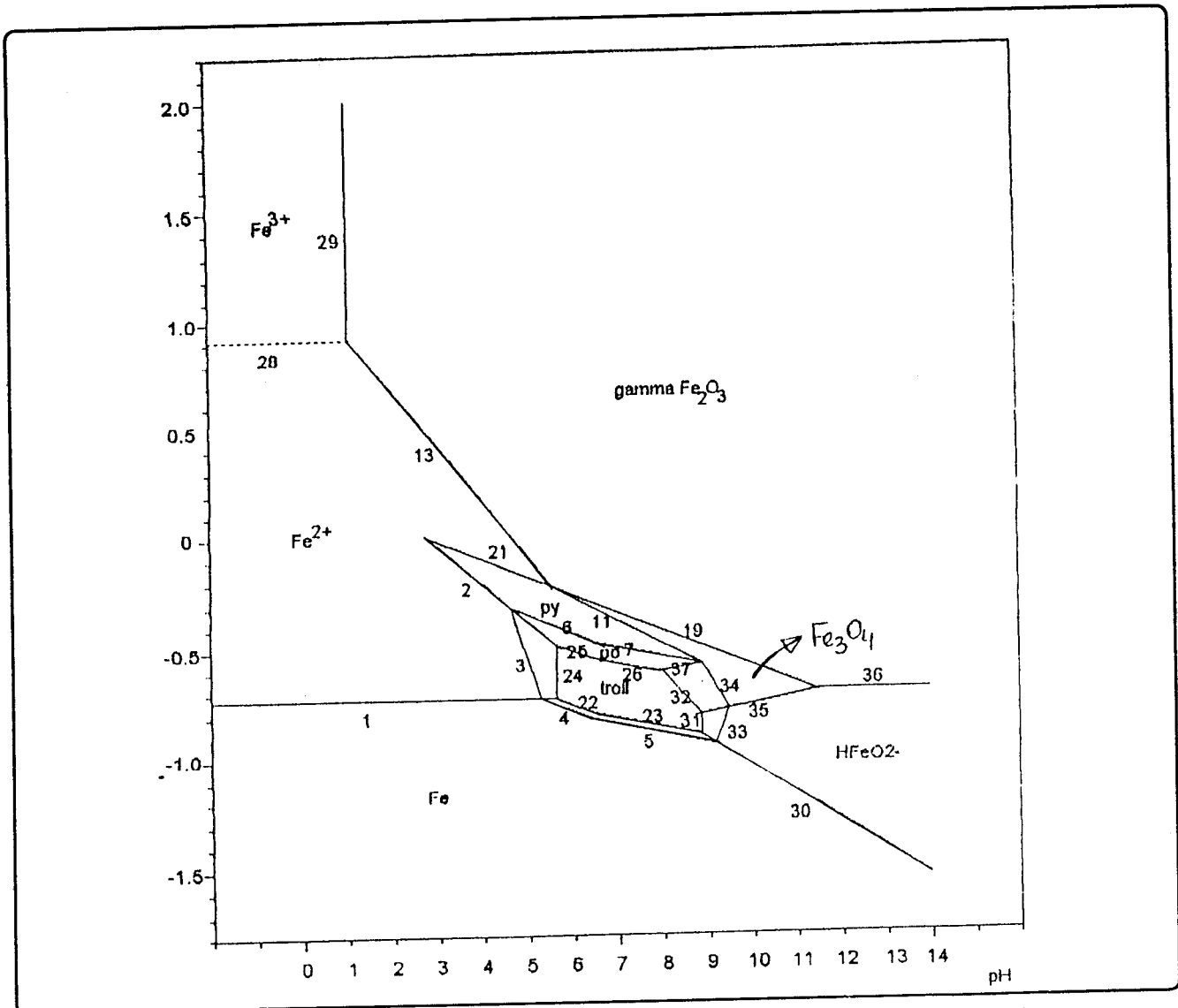


Figure 3: Fe-S-H₂O diagram at 150°C for total dissolved sulphur = 0.21 gmol/lit
(Corresponding to 20% sulfidity in cooking liquor)

more than S_2^{2-} . In other words, higher sulphidity which results in formation of S_3^{2-} , S_4^{2-} , etc. along side S_2^{2-} will end up in forming more corrosive media. Thus corrosion rate of mild steel at room temperature increase from 0.1 mpy to 2.53 mpy on adding 2 gpl polysulfide. It is also interesting to note that corrosivity due to polysulphides is dependent upon its concentration (6). Corrosion rate increases with increase in concentration of polysulphides upto 2-5 gpl. However, corrosion rate decreases on further increasing the amount of polysulphide beyond 5 gpl (upto 19-20 gpl), by passivating the steel surface. The redox potential of reduction reaction (eqn.2) which is cathodic reaction is given as

$$(E)_2 = (Eo)_2 - 0.059pH + 0.0295 \log (S_2^{2-}) - 0.059$$

$\log (HS^-) - (4)$

E_2 will increase as concentration of polysulfide (i.e. S_2^{2-}) increases. If steel is corroding in active region, corrosion rate will increase as E_2 increases. When S_2^{2-} level increases above 5 gpl, the value of E increase to such level that the cathodic polarisation curve (corresponding to eqn.2) cuts the anodic polarisation curve of iron in passivation region thereby passivating steel (Fig.2.)

Above discussion on the effect of thiosulfate and polysulfide on corrosion of mild steel and their analysis in terms of the involved cathodic reactions e.g. eqns. (1) and (2), compels one to investigate several aspects as given below:

(a) On increasing concentration of S_2^{2-} further (may be beyond 20 gpl or so), steel must transit into transpassivation region due to still higher value of potential of eqn.4. This increases the possibility of pitting and crevice corrosion. It is worth investigating such limits of polysulphide concentration where steel is likely to experience localised corrosion.

(b) Redox potential for cathodic reaction of thiosulfate showing its reduction is

$$(E)_1 = (E_0)_1 - 0.059\text{pH} + 0.007 \log (S_2O_3^{2-}) - 0.014 \log (HS^-) \quad (5)$$

E_1 will also increase with concentration of $S_2O_3^{2-}$. Hence, like the case of S_2^{2-} first corrosion rate of steel

should increase (as it is active corrosion region), then it should transit in passive region showing decreased corrosion rate and by transiting into transpassive region as concentration of $S_2O_3^{2-}$ increases. It should therefore be possible to restrict corrosion rates by increasing concentration of $S_2O_3^{2-}$. It will then also be interesting to see the limits upto which concentration of $S_2O_3^{2-}$ may be increased so as to avoid possibility of localised corrosion. Incidentally, such an option has not been tried for decreasing corrosion in digesters.

(c) What is the nature of sulphides under active and passive corrosion?

In order to know the possibility of forming various sulphides and hence passivation of carbon steels in

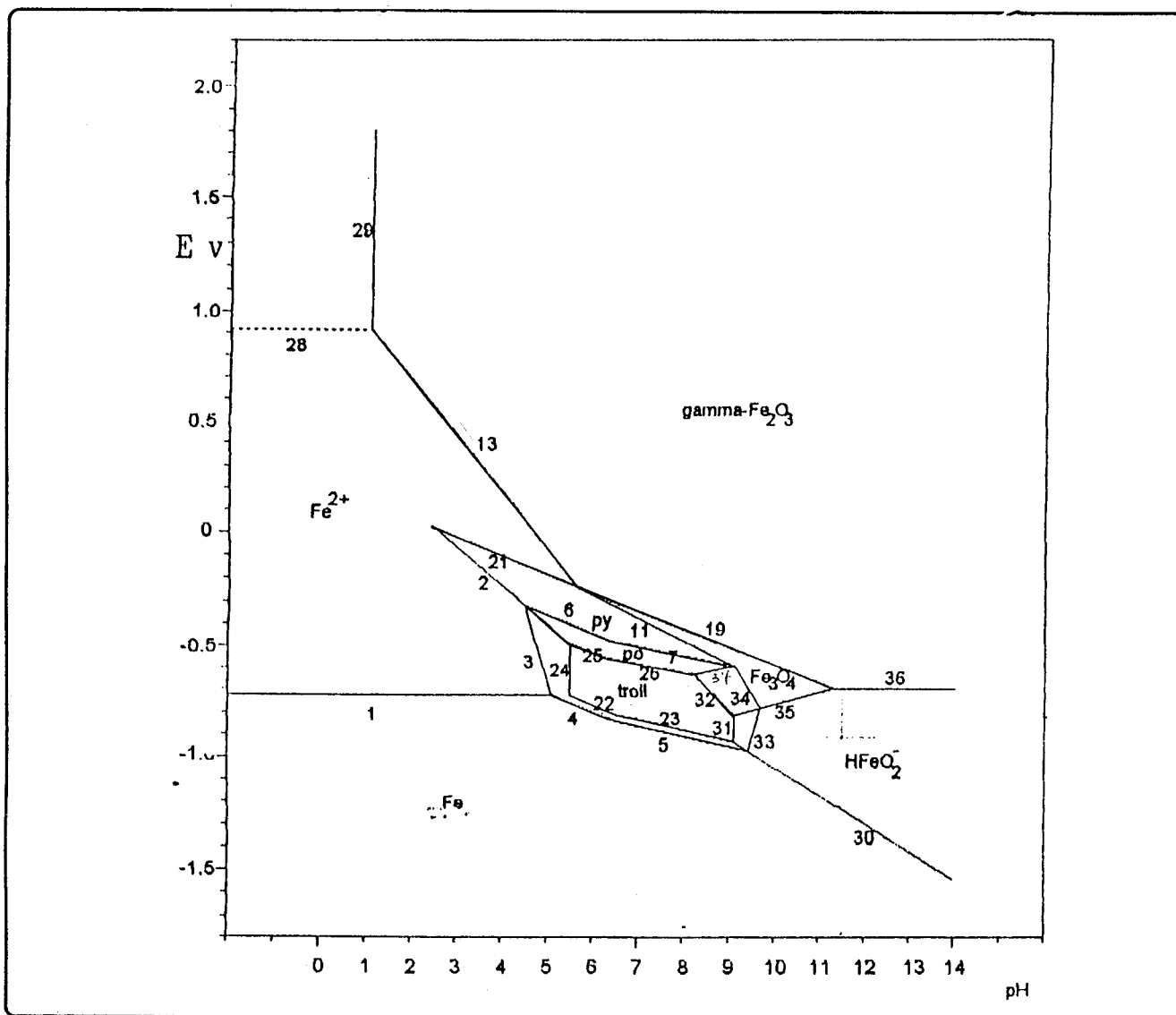


Figure 4: Fe-S-H₂O diagram at 150°C for total dissolved sulphur = 0.5 gmol/lit (Corresponding to Sulfidity 38%)

cooking liquor, E-pH diagrams for Fe-S-H₂O system were constructed for total dissolved sulphur content of 0.21 gmol/litre (corresponding to 20% sulphidity) and 0.50 gmol/litre (corresponding to 38% sulphidity) at 150°C (Fig 3 and 4). Details about the various equilibria and the chemical potentials of various species are given in ref. 14. The conditions considered are those which generally prevail for cooking liquor in digester. A comparison of these diagrams with those of Fe-H₂O system indicates about following aspects:

- (a) Thermodynamic stability regions of various iron sulphides namely mackinawite, troilite, pyrrhotite and pyrite exists upto -0.52 volts (at pH ~ 14 and 25°C). At more anodic potentials only, one expects to observe protective oxide Fe₃O₄ in sulphide solutions. In case of carbon - steel in H₂O, Fe₃O₄ is observed at a lesser anodic potential. Thus corrosion products forming on carbon-steel should be mainly sulphides with a small amount of oxides. As some of these sulphides namely mackinawite and troilite are of non-protective type (15,16), their formation in place of oxides increases the corrosion attack on carbon-steel in sulphide solution. It will be interesting to observe the potential of carbon-steel in sulphide solutions and identify the nature of sulphides formed.
- (b) At more active potentials, among the sulphides, one expects to observe mackinawite-troilite. Both of these are non-protective type and dissolve very easily in solution. As such, as soon as, carbon - steel comes in contact with sulphide solution, this solution becomes dark in colour due to dissolution of mackinawite in solution.

In the presence of oxidants e.g. oxygen or addition of sulphur, the nature of iron sulphides may change to pyrrhotite and then to pyrite. Both of these sulphides have observed to form under oxidising conditions and/or at high temperatures (16). Also pyrrhotite and pyrite are protective type of sulphides (15,16). Perhaps that is the reason why on adding polysulphides (which form at oxidising potentials in alkaline solutions) or sulphur, 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 polysulphides are stable, γ -Fe₂O₃ is also stable (Fig. 1, 3, 4) it is also expected to observe γ -Fe₂O along with pyrrhotite and pyrite in sulphide solutions upto ~ 120°C. Similar effect should also be observed with S₂O₃⁻² because they also are expected to be present in the solutions in the prevailing conditions of cooking liquor, on the basis of E-pH diagram of S-H₂O.

- (c) The above aspects also form the basis of protecting digester by polarising it anodically when steel gets passivated. While anodic protection systems for digesters have been reported in literature (17), one report (4) claims that anodic protection for plant handling cooking liquor is not feasible. It will be of interest to see nature of sulphides formed on steel (under anodic protection) and compare them with their nature when formed on steel passivating by adding sulphur/polysulphides or thiosulfate.
- (d) Once passivation is achieved, there is also a possibility of observing breakdown potential and hence onset of localised corrosion. It should be tried to find upper limit of polysulphides/thiosulfate in cooking liquor to avoid localised corrosion.
- (e) Effect of increased sulphidity can be checked by comparing E-pH diagrams at 20% and 38% sulphidity (Fig. 3 and 4). One finds an increased area of stability of sulphides at the cost of oxides. A higher amount of sulphides in the corrosion 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.

CONCLUSION

The present study reports the effect of presence of sulphur 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 sulphidity. On the basis of E-pH diagrams drawn for S-H₂O and Fe-S-H₂O system considering 20% and 38% sulphidity in the solution at 150°C, following conclusions can be drawn. (In drawing conclusions, help of E-pH diagrams for Fe-H₂O and Fe-S-H₂O systems at 25°C has also been taken.):

- (a) The alkalinity and sulphidity 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°C to 150°C. Under these conditions, sulphur containing species are HS⁻ with small amount of S²⁻ in reducing conditions and polysulphides (S_N²⁻) and thiosulfate (S₂S₃²⁻) under oxidising conditions.
- (b) Presence of thiosulfate and polysulphides increases corrosion. With increased sulphidity and more

oxidising conditions, the cooking liquor is expected to have more of higher polysulphides (e.g. S_3^{2-} , S_4^{2-} etc.) which increases corrosion further.

- (c) In cooking liquor, the corrosion products are expected to be a mixture of sulphides and oxide. With increased sulphidity, larger fraction of corrosion products is expected to consist of sulphides. In reducing conditions, the sulphides could be mackinawite/troilite which are non-protective type and hence may be responsible for increasing corrosion attack on steel. In oxidising conditions, pyrrhotite and pyrite could be the iron sulphides which are protective type. As such when polysulphides are increased in amount by more than 5 gpl, the corrosivity of cooking liquor starts decreasing. However, beyond certain amount of polysulfides, the steel is likely to experience localised corrosion. The above aspects need to be verified by experiments.
- (d) Electrochemical thermodynamic suggests that, in the same manner as polysulfide, thiosulfate should also reduce the corrosion attack on digester if its amount is increased beyond a certain limit. Similarly if the amount is increased further, there should also exist a possibility of steel experiencing localised corrosion. These aspects of corrosion control have not been tried earlier and required to be checked.
- (e) The likelihood of formation of protective sulphides under oxidising conditions gives a possibility of protecting digester and related machinery of steel by electrochemically polarising it anodically thereby developing anodic protection system for corrosion control. Such a system, though commonly used in developed countries is non-existent in India and needs to be developed for the local pulping conditions.

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