CORROSION INVESTIGATIONS IN PULPING AND BLEACHING MEDIA

A THESIS

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **Corrosion Investigations in Pulping and Bleaching Media** in fulfilment of the requirements for the award of the Degree of Doctor of Philosophy and submitted in the Department of Paper Technology of the **Indian Institute of Technology Roorkee, Roorkee** is an authentic record of my own work carried out during a period from July 2000 to July 2006 under the supervision of Dr. A. K. Singh.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other University/Institute.

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ABSTRACT

The thesis starts with introducing the process and conditions of paper making with a view to have an idea about the corrosivity of the liquors and possible candidate materials of construction. Since pulping and bleaching sections are among the more corrosion prone sections, the investigations were performed related to these sections. Accordingly, emphasis has been given on the description of pulping and bleaching section. A review of the literature has been presented in the first chapter dealing with corrosion aspects and materials performance in pulping and bleach plant and related liquors. The second chapter deals with the experimental aspects of the various laboratory and in-plant tests conducted. The next three chapters discuss and analyze the results of various tests done as a part of the present dissertation. Attempt has also been made to suggest possible materials of construction. The last chapter deals with the conclusion on the work and recommendations about the work that needs to be done in future. A brief idea of the above has been given in following paragraphs.

Chapter - 1 : Introduction

This chapter introduces about paper making process and gives an account of corrosion prevailing in pulping and bleaching sections, being the more corrosive sections of a paper mill. A survey of the literature has been done to show various attempts made in past for controlling corrosion in pulping and bleaching sections by appropriate material selection or otherwise. The prevailing process conditions in pulping section indicate to be corrosive due

to various sulphur compounds. In bleaching section it is mainly due to the application of oxidizing bleaching chemicals. Consequently following was proposed for investigation:

1. Construction of E-pH diagram for S-H_2O and Fe-S-H_2O system for the electrolyte having sulfide and thiosulfate in the amount as observed in pulping liquor. Long term immersion test in laboratory prepared pulping liquor at room temperature on mild steel, austenitic stainless steel 304L, 316L and duplex stainless steel 2205. This had to be followed by quantitative estimation of uniform and localized corrosion attack and the analyses of the result on the basis of liquor composition and E-pH diagram, wherever possible.(Chapter 3)

2. In-plant corrosion test in Kraft digester on newly developed grade of duplex stainless steels LDX, SAF 2304, 2205 including conventional materials as mild steel, 304L, 316L, to investigate the extent of corrosion attack, its correlation with the process parameters and to compare the suitability of the test materials.(Chapter 4)

3. Electrochemical polarization tests and long term immersion tests on mild steel and stainless steel 304L, 316L, 254SMO and 2205 in peracid solutions simulating to those likely to be observed in peracid bleaching of pulp with the aim of understanding the corrosivity of peracid solutions, suitability of the test materials and mechanism of corrosion in these solutions (Chapter 5).

Chapter - 2 : Experimental Procedure

Various experimental techniques, brief technical discussion of experimental equipments and formulae used have been described in this chapter. For long term immersion tests and in-plant test, the coupons from plates of different steels namely mild steel, 304L, 316L, 2205, SAF2304, LDX were selected. The surface preparation was done as per ASTM specification. For immersion test, the coupons fitted with serrated washer were immersed in the test solution. For in-plant test, the coupons were mounted on the rack and fitted in digester near strainer. After exposure the corroded coupons were analyzed for uniform corrosion and localized type attack.

In the electrochemical polarization tests, E vs time curve, potentiodynamic polarization, potentiostatic and cyclic polarization curve were performed on cylindrical samples obtained from rods of SS304L, 316L, 2205 and 254SMO. Electrochemical polarization techniques were used to investigate the corrosion mechanism and effect of process variables on corrosion behavior of steels. Chemical compositions of plate and rod samples used in corrosion study are given in this chapter.

Chapter - 3 : Corrosion in Solutions having Sulfur Compounds

In this chapter E-pH diagrams for S-H_2O, Fe-S-H_2O systems have been drawn for concentration of various sulphur species as observed in pulping liquor. For S-H_2O systems following sulfur species were considered H_2S, HS^-, S^{2-}, $S_2O_3^{2-}$, S, $S_4O_6^{2-}$, SO_3^{2-} H_2SO_3 and HSO_3^-. The diagrams show that within the pH range likely to be observed for the cooking liquor, sulfur species present in the solution could be HS^- and to some extent S^{2-}, $S_2O_3^{2-}$ and SO_3^{2-} depending upon the potential, which will in turn be governed by the nature of material exposed e.g. mild steels or stainless steels. Fe-S-H_2O diagrams were constructed considering above sulfur species and concentrations. Thus if the liquor consists of $S_2O_3^{2-}$, 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 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 $S_2O_3^{2-}$ increases. It indicates that if the amount of $S_2O_3^{2-}$ is higher, the steel is likely to experience localized corrosion.

Long term immersion test in sulfide solutions having varying $S_2O_3^{2-}$ in the presence/absence of Cl^- (pH ~13.6) and ~20% sulfidity was performed on test materials mild steel, stainless steel 304L, 316L and 2205. The test solutions covered with a layer of paraffin oil to avoid contact of atmospheric oxygen with the solution. The later was found to change the solutions' composition by oxidizing Na_2S to $Na_2S_2O_3$. The exposure duration of test was 6 months. After exposure the corroded test materials analyzed for uniform and localized type attack. The results of this test showed no significant corrosion on the tested stainless steels. Mild steel experiences uniform corrosion and crevice corrosion. Corrosion rates increased with the increased amount of $S_2O_3^{2-}$ content in the solution. This behavior becomes more pronounced in the presence of Cl^- ions.

Measurement of redox potential of 304L and 2205 in pH = 14 solution having sulfidity, as considered in drawing E-pH diagram, shows that sulphur species near 304L electrode will be mainly SO_3^{2-} and $S_2O_3^{2-}$ while those near the 2205 electrode will be mainly HS^-. Accordingly, E-pH diagram 0f Fe-S-H_2O shows that corrosion products forming on 304L will be pyrite or iron oxide and on 2205 it could be pyrrhotite/troilite/mackinawite depending upon the potential. Except mackinawite and troilite, other sulfides /oxide provide protection. This could be the reason for observing lesser corrosion rates in these stainless steels.

Chapter - 4 : In-Plant Corrosion test of Steels in Digester of Paper Mill

This chapter discusses the results of in-plant test done in digester of an Indian paper mill. This mill used 80% poplar and 20% eucalyptus as raw material for making printing/writing and packaging grade paper. The capacity of digester was 85 m^3 and it was constructed of mild steel. Liquor to wood ratio was kept as 1:2.8. Volume of cooking liquor inside the digester was kept between 37- 42 m^3. The cooking liquor consists of mainly NaOH (92 gpl as NaOH) and Na_2S (22.4 gpl as NaOH) having pH ~13.2. Maximum temperature attained during the pulping process was 162 ^{0}C and it operates at a pressure of 6.2 Kg/Cm^2.

The selection of materials for the in-plant test was done on the basis of their utilization presently and their possible applications in future for constructing the digester and related allied machinery in pulp and paper industry. Consequently, autogenously welded coupons of austenitic stainless steels 304L and 316L, duplex stainless steels 2205, SAF2304 and LDX and mild steel were considered for the in-plant test. After exposure of six month duration the corroded coupons were analyzed for uniform and localized type attack. The results of in-plant test show varying degree of uniform corrosion and pitting was observed on different steels. Crevice corrosion was observed but was non measurable while no weld related attack has been observed on these coupons. Mild steel experienced maximum uniform corrosion. Pitting was maximum in case of 304L whereas duplex stainless steel did not show any pitting attack. The attack can be correlated with the amount of Cr and N present in steels. At these pH (~14), Mo content of stainless steel does not provide protection as it gets dissolved as MoO_4^{2-}. The extent of attack shows that, for lower sulfidity levels, mild steel may be suitable for cylindrical section of the batch digester. However, for cooking liquors with increased sulfidity and /or for parts of the digester which are affected by the erosive action of the liquors (e.g bottom cone, liquor heater tubes etc.), one may have to opt for duplex stainless steels with Cr and N as preferable alloying elements. The performance of materials was compared with other in-plant tests, conducted elsewhere.

Chapter - 5 : Corrosion Study of Steels in Peracid Bleach Solutions

In this chapter, the results of the electrochemical and weight loss test conducted on steels in peracid solutions have been discussed. The electrochemical polarization tests E vs time curve, potentiodynamic polarization, potentiostatic and cyclic polarization curve were performed on stainless steels 304L, 316l, 2205 and 254SMO in solutions of peracetic acid (P_a), caro's acid (P_x) and mixture of P_a and P_x (P_{xa}) simulating to those observed for peracid bleaching. The pHs of these solutions for electrochemical test were kept 6 and 9 with chloride and without chloride. Chloride content varied from 0 to 1000ppm. Weight loss test was also conducted on mild steel, stainless steels 304L, 316L and 2205 in above peracid solutions with chloride content of 1000 ppm. After the exposure of six months, corroded coupons were analyzed for uniform and localized type attack.

Electrochemical results of tested steels in per acid solutions with Cl^-, show high degree of localized corrosion whereas it is less severe in case of solutions without Cl^-. In general, corrosivity of the solutions is observed to increases in following order : $P_x < P_{xa} < P_a$. Higher degree of corrosivity of peracetic acid as compared to that of Caro's acid can be attributed to the former's higher electrophilic character. Mild steel is found to observe very high degree of uniform corrosion hence can not be suggested for handling these media. Stainless steels therefore have to be used. For this reason their resistance against localized corrosion has to be checked as they are observed to experience very less uniform corrosion. In Cl^- containing solutions, very high degree of localized corrosion is observed on the tested stainless steels except on 254 SMO. Both electrochemical and weight loss tests on stainless steel showed increased resistance against corrosion in order of : 304L<316L<2205<254SMO.

Chapter - 6 : Conclusion and Recommendations

In this chapter, conclusions drawn on the basis of work done are discussed. The E-pH diagrams for S-H_2O system show that HS^- and S^{2-} are the species depending on the pH of the sulfide solution and $S_2O_3^{2-}$ and SO_3^{2-} are the species depending upon the nature of material exposed in it. Fe-S-H_2O diagrams show that around pH ~ 12-14, products mackinawite, troilite, pyrrhotite and pyrite are formed. Of these, the first two are non-protective type while other two are protective type .The laboratory test in sulphide solutions showed that none of the tested stainless steels experienced significant corrosion attack. Mild steel experiences uniform corrosion and crevice corrosion. Corrosion rates increased with the increased amount of $S_2O_3^{2-}$ content in the solution. This behavior becomes more pronounced in the presence of Cl^- ions. The nature of variation has been hypothesized on the basis of mixed potential theory. This needs to be verified by electrochemical polarization experiments in sulfides solutions.

The in-plant test conducted in batch digester showed varying degree of uniform corrosion and pitting on different steels. Crevice corrosion is observed but is non measurable while no weld related attack has been observed on these coupons. Mild steel experienced maximum uniform corrosion and pitting was maximum in case of 304L. Duplex stainless steel did not show any pitting attack. For the lower sulfidity levels, mild steel may be suitable for cylindrical section of the batch digester. However, for cooking liquors with increased sulfidity and /or for parts of the digester which are affected by stress corrosion cracking (top part of digester) and the erosive action of the liquors (e.g. bottom cone, liquor heater tubes etc.), mild steel may not be suitable. For such cases, in-plant test needs to be done in which coupons should be fixed either at top or in the bottom cone of the digester.

Corrosion investigation in peracids, reported in present thesis concludes that peracetic acid is most corrosive whereas caro's acid is least corrosive. The comparison of

performance of different test materials showed Avesta254SMO to be most resistant while 304L least resistant against corrosion attack. It is concluded that Avesta254SMO is appropriate for handling Cl^- containing peracid solutions and duplex stainless steel 2205 for handling these solutions without Cl^- on the basis of degree of attack alongside comparison of cost vis-à-vis strength of different stainless steels. It is recommended that, to suggest guidelines for fabricating machinery for handling peracid bleach solutions, in-plant corrosion tests should be conducted in peracid bleach media. Weight loss and electrochemical tests for varying % of active oxygen, with and without fibrous raw materials, in the presence and absence of chloride at room and at high temperature should also be conducted in these solutions.

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Awanish

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RESEARCH PAPERS

1. Investigation on digester corrosion

   International Conference On Corrosion, CORCON 2003, Mumbai.

2. In-Plant test in Kraft digester for evaluating performance of steels against corrosion.

   12th National Congress On Corrosion Control, Vishakhapatnam
   Sept. 20-22, 2004.

3. Corrosion due to extractives from paper making raw material -An aspect of digester corrosion in paper industry.

   International Conference On Corrosion, Chennai, 28-30 Nov., 2005.

4. In-Plant test of steels in Kraft batch digester for evaluating corrosion Performance.

   Tappi Journal, USA, (Communicated).

5. Corrosion study of steels in peracid bleach solutions.

   Appita Journal, Australia, (Communicated).

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'Corrosion' is probably the commonest electrochemical phenomenon whose effects on metal bodies are observable in our day to day life. Common examples of corrosion include rusting/staining of iron and steel utensils/railings/other structural items, the blistering of chromium plating and paint work on cars, discharge of colored water from domestic taps, tarnishing of silver and copper wares, seizure of nuts and bolts etc. From industrial application point, the term 'Corrosion' is used to describe an unintentional electrochemical reaction between a metal and its environment e.g. air, marine, steam, high temperatures and chemicals etc., which results in degradation of the former. This happens due to the conversion of metal into metal oxide or some other compound which are weak and brittle. This causes overall reduction in the load bearing capability of the metal. Thus, corrosion adversely affects those very properties of metal e.g. strength, ductility, stability etc., that are to be preserved in order for the metals to be used as material for constructing process equipment/machinery, Bolton (24).

In industry, corrosion is responsible not only for weakening of metal structures and consequent premature failure of plant but also for pollution of process liquors and contamination/discoloration of products. The losses due to purely mechanical forces are known as wear, fretting etc. However, in some cases, chemical or electrochemical attack may be accompanied by the mechanical forces leading to stress corrosion cracking, corrosion-erosion, corrosion fatigue or fretting corrosion. Such shortcoming of metal affects the production through unwanted shutdowns due to sudden failures, excessive leakage of chemicals/steam etc., Ravindranath et al (104), which escalate maintenance and operating costs. In some industries e.g. food, pulp and paper etc, contamination of product due to corrosion is another disadvantage. All this enhances the production cost hence affects the economy. Also it makes the working environment less safe. These negative aspects of a natural phenomenon 'corrosion' forced the scientists and technologists to develop necessary preventive measures against corrosion and thereby reduce the revenue loss.

Corrosion in chemical industries requires more attention which otherwise will reduce the production efficiency, quality of products and at the same time making it costlier. Paper industry, being chemical industry, is no exception to corrosion problems. Corrosion problems in this industry are quite serious, as it is using wide variety of corrosive chemicals like chlorine, chlorine dioxide, sodium sulfide, caustic soda, etc. and generating other similar corrosive substances as reaction products at various stages. The liquid media in this industry range from highly alkaline type (pH~14) to highly acidic (pH~1-2). Additionally, the process involves high pressure as well as high temperatures in some stages, Garner (45), Yaske (149), In fact the paper industry was first to utilize molybdenum bearing stainless steels more than seventy years ago and also it has shown enthusiastic acceptance of FRP construction. An idea about severity of corrosion in pulp and paper industry can be had from the estimate of huge losses in terms of repair and replacement. Unexpected failures, due to corrosion, of pressure vessels have resulted in to loss of life thus making the working environment less safe. Consequently, industry looses considerable amount of money on account of corrosion. Several studies/ surveys (Table -1.1) have been reported which try to estimate the losses due to corrosion and the amount of wealth that can be saved by adopting suitable corrosion protection measure, Aroma et al (7), Bhaskaran et al (22), Chandler et al (26), Chakrapani et al (28), Raman (102), Singh, A. K. (111), Singh, D. D. N. (112), As per the report of Battelle and the Specialty Steel Industry of North America, Aroma et al (7), about one-third of the cost of corrosion is avoidable and could be saved by broader application of corrosion resistant materials and application of proper anti-corrosive methods. Moreover, human costs associated with the catastrophic failure of corrosion damaged equipments are beyond measure.

In recent years, the Paper industry is undergoing rapid changes in the process to meet the demands of market keeping in view the depleting resources of fiber raw material and government regulations with regard to specially the pollution control and abatement. Developments in the industry are aimed at improvement in paper quality, reduction in manufacturing costs, adoption of environment friendly and energy efficient paper technology and introduction of new and modified paper products. Accordingly, the changes coming up in the paper making process include reduction and elimination of chlorine and its compounds etc., decrease in overall water use, recycle of as much of the bleaching effluents as possible, higher degree of delignification during pulping stage etc. These changes have brought drastic effect on process conditions of the working environment. Since the corrosion phenomenon is closely related with the process parameters, the above mentioned changes in the process are likely to alter corrosion in industry. It is, therefore, important to investigate the effects of these changes on corrosion performance of materials of construction. As such, the thesis deals with studies carried on corrosion and its control by suitable measures in changed scenario of pulping and bleaching process. To introduce the reader with subject of thesis, a brief is given about paper making process and then a review of corrosion in pulp and paper industry has been given. Finally, justification of the problem dealt in the present work and being presented in the thesis with objectives has been outlined.

1.1. The Paper Making process :

Paper is used by the world community to satisfy various needs. It is an essential component in the process of business and communication through newspapers, periodicals, magazines, books etc. It contributes to industrial development with improved packaging for protection and conservation in transport and storage of goods. In fact, it is important material in the economic development of a country and the extent of paper usage is a pararneter of the standard of living in a country. Paper is a fiber network formed on the fine screen from water suspension. These fibers are extracted from various wood/non-wood species. Paper making process essentially involves the pulping of wood species to draw fibers from wood. In pulping process, individual or small agglomerate fibers are withdrawn from wood by mechanical, thermal, chemical or by a combination of these treatments. The Kraft process (chemical pulping) is most popular among the pulping process. In this process, pulping is carried out in a pressure vessel called 'digester', by chemical reaction between constituents of wood chips namely lignin and cooking liquor at a pressure around 6.5-7 Kg/cm^2 and temperature 165 -170°C. The cooking liquor is composed of sodium hydroxide and sodium sulfide in the approximate proportion of 5 parts of NaOH and 2 parts of Na_2S. Alongside, $Na_2S_2O_3$, Na_2SO_3, polysulfides etc. are also present as by products. The liquor has a pH of 13.5 to14.0.The resulting pulp is send in brown stock washer for removal of all the traces of liquor and unwanted foreign particle e.g. sand, metal etc. The filtrate from brown stock washer, known as black liquor, is processed in the recovery system to recover unused NaOH and Na_2S, which is used as cooking liquor for pulping after making up for the lost chemicals. Organic constituents from black liquor are burnt in recovery boiler to recover energy. Washed pulp from brown stock washers is sent to bleaching section for brightening the fibers. Bleaching is generally carried out in a multistage process with bleaching stages e.g. chlorination (C), alkali extraction (E), hypochlorite (H), chlorine dioxide (D), peroxide oxygen (O), ozone (Z), per acetic acid (P_a) or caro acid (P_x) or mixture of per acetic acid and caro's acid named (P_{xa}) etc. The pulp after bleaching is then subjected to beating and refining by mechanical action to develop good bonding between fibers. Afterwards various chemicals like alum, talcum, rosin etc. are added for getting special properties in the pulp. This mixture called stock is passed over paper machine comprising of head box, fourdrinier, couch roll, suction rolls, press rolls and lastly dryers and Calendars for making the final product paper, McDonald (82), Smook (118).

1.2. Corrosion in Paper Industry :

The corrosion problem in pulp and paper industry is more serious as compared to any other industry because paper industry uses wide variety of very corrosive chemicals and environment, Garner (45), Yaske (149). Further, paper making technology is experiencing continuous changes due to shortage of fibrous raw material, ecological restriction, demand of quality paper, efforts for increasing output to meet growing demand of paper. These continuous changes along with the rising cost of equipment's replacement make problem due to corrosion as a matter of growing concern. As such, various forms of corrosion are experienced in different sections of a paper mill. Various factors affecting corrosion are type of raw material, cooking liquor concentration, digester operation, bleaching chemicals and sequence of bleaching, dissolved gases differential aeration, bacteria, existence of stresses etc. From the standpoint of corrosion, a typical paper mill can be divided in the following four sections: Pulping section, Bleaching plant, recovery section and paper machine. Out of these, pulping and bleaching are the sections where corrosion is a major problem in the industry. Since the thesis deals with corrosion aspects related to pulping and bleaching section, a brief idea about corrosion and related investigations in these sections is given in the following paragraphs.

1.2.1. Pulping Section :

In this section, corrosion problems are more serious in digester house which consists of digester, preheaters, circulation pump, white liquor storage tanks, cooking liquor feed lines, digester blow line and blow tanks as various units. Generally two types of digesters are in use in paper industry (a) continuous digester and (b) batch digester. In Indian mills, mostly batch digesters are used. A typical batch digester consists of a vertical cylindrical vessel with a hemispherical or ellipsoidal top head and conical bottom. Batch digesters are typically 8 to 13 ft (2.4 to 4.0m) in diameter and about 60-ft (18.3m) high. In most cases, these are used to cook the wood chips with Kraft cooking liquor. The Kraft cooking liquor contains inorganic chemicals like sodium hydroxide, sodium sulfide, sodium sulfite, sodium carbonate, sodium chloride, sodium thiosulfate, polysulfides, sodium sulfate etc. Cooking is usually performed at pH ~ 13.5 -14 and temperature of 170°C. Until the 1950s, only batch digesters were used to produce kraft pulp, Gullicbsen et al (56), in conventional batch cooking. In the early 1960s, continuous cooking systems, due to better energy economy, began to compete seriously with batch plants. In the early 1980s, energy efficient Kraft batch processes using various displacement technologies became available (RDH method). In addition, increased pressure to minimize environmental impact and effluent volumes during the 1970s contributed to the development of batch cooking using modified cooking chemistry and extended cooking. In the early 1980s, trials of combined modified cooking chemistry with energy efficient liquor displacement were undertaken (cold blow cooking). In the late 80s, the development of liquor displacement batch cooking systems continued with the aim of providing greater optimization of pulp quality, resulting in super batch concept. The RDH, Superbatch, Enerbatch cooking techniques find use today. Later as development in the technology of continuous digesters, the implementation of extended modified cooking (EMCC),isothermal cooking (ITC),black liquor impregnation (BLI), diamondback pre –steaming, the Lo-level feed system, and solids cooking system have resulted in improved performance, decreased capital costs, and lower maintenance costs.

The efforts have been, Maspers (81), to search for optimal cooking conditions that allow cooking to very low kappa numbers so that after oxygen delignification, final bleaching to full brightness can now take place in ECF/TCF sequence. Further, additional steps towards closing up the bleaching systems will in the near future result in totally closed pulp mill TEF, totally effluent free. All recent research and development, though important from the economical and environmental point of view, have introduced accelerating influence on the corrosion conditions in the digester. Some digesters already show clear signs of shell corrosion, and as the intensive inspection goes on the list of corroded digesters will most probably increase.

Many reports related to digester corrosion have been published/ presented in conferences in past years. Most serious corrosion problem with carbon steel continuous digesters has been caustic stress corrosion cracking (SCC) of un-stress-relieved seam welds in the impregnation zone or in the impregnation vessel for two vessel systems, Crowe (35). In one study, Olsson et al (88), reported the corrosion rate of digester approximately 5 mils after three years of service, where selective phase corrosion occurred. Various factors responsible for wide spread of corrosion, are type of raw materials, cooking liquor composition, concentration, sulfidity, hot plate boiling on digester surface during liquor charging, circulation and impingement and direct steaming, temperature galvanic effect, violent agitation of pulp and blowing causing erosion of passivation film, Presence of thiosulfate in white liquor, presence of lignin compounds, chlorides etc., Banks et al (13), Mall et al (80).The acids for cleaning such as sulfamic acid and formic acid are less corrosive to digesters, Crowe (33). Cooking liquor and numerous organic species arising from dissolution of cellulosic raw material, many of them are responsible for corrosion in digester. Sulfur is used in pulp mill for improving the sulfidity which is converted to polysulfide and causes severe corrosion. Sodium sulfide and sodium thiosulfate activate corrosion and act to impair passivation. The corrosion is dependent on the equilibrium of reaction, Kiessling (68),

$$S^{2-}+S_2O_3^{2-}\text{--->}\ SO_3^{2-}+S_2^{2-}$$

The $S_2O_3^{2-}$ / SO_3^{2-} molar ratio can be used as a corrosion factor of the liquor, Kiessling (68). Mueller (84) indicated that the corrosion rate of mild steel could vary from 1-100 mpy. The increased amount of silicon in the batch digester steel result in the increasing rate of corrosion. Many mills have therefore insisted that the rimmed steel rather than killed steel should be used for digester. The corrosion in digester is basically uniform in nature but chip loading, liquor circulation, and scale can cause localized attack e.g. pitting, crevice or cracking. Stress corrosion cracking of continuous digester became a serious problem in 1980's following a catastrophic failure of a pressure vessel weakened by extensive stress corrosion of a girth weld. Corrosion rates are generally, higher in batch digester than continuous one. The application of stainless steel cladding or weld overlay to in-service digesters has been effective in reducing the internal corrosion of the batch digester and prolonging their service lives, Tuthill (128). Digesters blow bends and blow tank at the top also get corroded very rapidly and their rates have increased substantially with the use of more and more hard wood and higher percentage of oversized chips and knots. The zone of most severe corrosion varies from mill to mill, and perhaps from digester to digester. In most digesters the corrosion is most pronounced in the cylindrical section. In other digesters it is worst in the bottom cone, in yet others, it is the top dome. Corrosion of stainless steels (both in wrought form and overlays) is primarily a function of the chromium content of the overlay. Austenitic stainless steel grades such as type 316L (16-18% Cr, Mo ~ 2%) and Type 304L (18-20% Cr) can experience rapid corrosion up to 40 mpy. Digesters usually, are constructed of mild steel plate with stainless steel linings; however carbon steels are susceptible to stress corrosion cracking in the caustic environment and temperature prevailing in the alkaline digester, Bennet (20). Study by Wensley (138), corrosion has been observed to increase with the concentration of thiosulfate in the digester. Lignin has no passivating effect in shell and increases corrosion. Work by Audouard (8-12), to investigate corrosion during "hot plat boiling" has revealed that duplex stainless steel with even higher chromium content (22-27% Cr) resists corrosion better than conventional austenitic grades. In another study, Delblanc et al (37), the use of SS to reduce the corrosion risk due to the Kraft process, a new cooking process for continuous digesters, in the paper industry is discussed. The corrosion rates for 304L and 316L have been measured at ~0.02 mm/year. The corrosion damages are prevented by regulating the processes and by selecting the appropriate material.

1.2.2. Bleach Plant Section :

Bleach plant in a paper mill is meant for brightening the pulp which otherwise is brown in colour. The brightening of pulp is achieved by bleaching through a multistage process. Thus bleaching sequences e.g. CEH, CH1H2, CEDED etc. (C-chlorination, E-alkali extraction, H-hypochlorite, D-chlorine dioxide) are among the more commonly used sequences. In addition some sequences use or may start using peroxide (P), oxygen (O), ozone (z), peracids (PA) etc. Due to severe objections on usage of chlorine and chlorine compounds because of their tendency of forming compounds with lignin having carcinogenic character, the trend now-a-days is to use more and more non-chlorine bleach chemicals. Each bleach stage consists of mainly three parts – reaction tower, washer, pumps and pipe line. Due to process conditions existing in bleach plant, corrosion is the most serious problem in bleach plant and accounts for nearly 50% of total mill corrosion. The corrosivity of this section has been found to increase on adoption of filtrate recycling to reduce water consumption as well as water pollution. Such aggressive corrosivity is due to strong oxidants along with several corrosion promoting factors like pH, chloride etc. in bleach plant. Average process conditions prevailing in bleach plant are shown in Singh (113). Corrosion damage in bleach plant usually appears in the form of pitting, crevice corrosion, stress corrosion cracking (SCC), and inter granular corrosion (IGC) or weld decay. Reaction tower, where the pulp is combined with various bleaching chemicals are generally constructed of brick and tiles or other non-metallic materials and hence face comparatively much lesser corrosion problem. It is mainly the pulp washing and conveying machinery that is affected badly. This has led to increasing application of higher grade of stainless steel, titanium and non-metals as construction material of bleach plant machinery and structure. 'Electrochemical protection' has also been applied effectively by Femina (42), Quraishi (101), Roy et al (105) and Wallinder et al (137), to minimize the localized corrosion in this area. Now a brief idea about corrosion in different stages of bleach plant is given.

1.2.2.1 Chlorination (C) Stage :

Highly acidic and oxidizing (residual chlorine) environment prevails in chlorination section. Washer in this stage experiences maximum corrosion. Presence of Cl^- in the process liquor, due to reduction of chlorine and also because of their presence in water, facilitate the propagation of localized attack .Corrosion in the gaseous phase has generally more serious than that of liquid or wet/dry phase existing in the washer, Garner (48,49,50,51), Gaur et al (53), Henrikson et al (60,62) and report (120).The

SS under wet deposits in atmosphere containing ClO_2 can be investigated quantitatively. Feng et al (41), indicated the diffusion coefficient of ClO_2 in resin 199 and life of resin coating when the consistency was 10g/l. One study, Laliberte (75), showed that the austenitic SS with more than 6% Mo like 254SMO, 654SMO cronifer 1925HMO, AL-6X and ferrite with 4% Mo appears to provide resistance in all of C, D and H stage liquid phase even in welded condition. One In- plant study, Singh et al (115), showed the duplex SS 2205 as the appropriate material for C, D, and H liquid media. Laliberte et al (76), reveals that the installation and running cost of electrochemical protection system are small as compared to the resulting cost savings.

1.2.2.3. Hypochlorite (H) Stage :

The corrosion problem in this washer is less serious, than observed in C and D washers, primarily due to presence of alkaline environment, Ahlers (1). Pitting and crevice are the dominant forms of corrosion, usually, found in this washer. Degree of corrosivity mainly depends upon pH and available residual chlorine. Maximum corrosion rate is observed near neutral pH, it is probably because of conversion of hypochlorite ion to hypochlorous acid (1) which is more corrosive than Cl_2. With fall in pH (i.e. below 7) HOCl increasingly converts into less corrosive chlorine while at higher pH (above 7), hydroxyl ions act as an inhibitor and hence reduces the corrosion rate. The liquid phase, Garner (49), corrosion is more severe than in gaseous phase generally higher rate is observed when residual chlorine concentration is higher at pH. A significant reduction of corrosion rate may be obtained by maintaining pH in the range of 10.0 - 11.0., Henrickson (60). SS 316L and 317L are the principal construction material of washer drum, piping and mixing equipments. In-plant study by Gaur et al (53), for different phases in washers, the degree of corrosivity is in the order of gas> liquid> wet/dry. Exceptions are the hypochlorite washers of mill A, where the degree of crevice /general corrosion is more in the wet/dry phase, in the H1 stage and in the liquid phase in the H2 stage. In yet another laboratory study by Gaur et al (54), study corrosion on mild steel in hypochlorite solutions indicate that corrosion rates increase with free available chlorine concentration and are independent of chloride ions. Polarization curves indicate that reactions can be understood in terms of three redox systems.

1.2.2.4. Peroxide (P) Stage :

Peroxide is a strong oxidizer and can create an aggressive condition to candidate material in presence of equivalent chloride concentration. H_2O_2 is degradable by some metal ions ferric, cupric, manganese etc., which might enter in the solution through corrosion reaction with washer materials, Yau (150), and thereby reducing bleaching efficiency. Though the corrosion reactions due to peroxide appear less severe as compared to those due to Cl_2 and ClO_2 yet zirconium and titanium have been suggested for the construction materials of peroxide washer. Application of these metals may also reduce degradation of peroxide. Yang (151), studied the corrosivity of m-benzol unsaturated polyester resin containing filler in H_2O_2. Results show that (i) anticorrosion of m-benzol unsaturated polyester resin in H_2O_2 is relatively good; (ii) the environmental temperature should be controlled below 180 degrees. Been et al (18), studied the corrosion of grade 2 titanium in alkaline hydrogen peroxide environments and found calcium and pulp was as corrosion inhibitors. Been et al (19), showed that in hydrogen peroxide stage, calcium and pulp acts as corrosion inhibitors. Presently stainless steel 316L is generally used for construct of washer equipments. In another study by Singh et al (116), it was found that in peroxide media of TCF bleaching, one may use SS 304 or 316 without localized corrosion while SS316 is suitable for peroxide media of ECF bleaching. Chelant addition increases the upper limit of Cl^- content in liquors.

1.2.2.5. Oxygen (O) Stage :

High pH (~11), significant amount of chloride along with high temperature (130°C), in this washer, increase the possibilities of stress corrosion cracking. One study by Laliberte (73), has shown that at pH = 13 and 10 gpl NaCl, cracking occurs in both liquid as well as in gaseous phase. It also has concluded that the invariable presence of monoxide in oxygen bleaching process reduces the risk of SCC of austenitic stainless steel containing molybdenum at sodium chloride concentration of 10 gpl. Most of the equipments are made of Mo containing stainless steel for this washer, but oxygen reactors are often made of high nickel containing steel such as 20cb3 to guard against chloride cracking. Wensley (144), studied about external stress cracking of stainless steel vessels (oxygen reactor, concentrators, evaporators steaming vessels and tanks).

1.2.3. Recovery Section :

Various corrosive environments which are responsible for corrosion in various sections of recovery plants are chloride, thiosulfate, sulfide, polysulfide, CO_2, high temperature, dissolved oxygen etc. Corrosion in evaporator occurs when hot black liquor inadvertently comes in contact with carbon steel surfaces because of foaming excessive liquor through-put and other operative misadventures. SS304 or 316 are frequently as evaporator tube. To avoid SCC SAF2205 are suitable alternatives.

Carbon steel tubes in recovery boiler experiences extensive corrosion in certain areas as a result of reaction by the furnace gases. Type SS-304 clad carbon steel tubes appears to provide a solution to these problems, Klarin (71). In recausticizing plant, plain carbon steel storage tanks, clarifiers, piping, lime and slurry pumps suffer severe corrosion. The corrosion rate as high as 20-30 mpy are experienced on the walls and trays of storage tanks and clarifiers where liquors relatively stagnant, Yaske (149).

1.2.4. Paper Machine Section :

The paper machine section of paper industry also is very corrosive. Different parts of paper machine section suffering serious corrosion include machines head boxes, suction and cough rolls etc. paper machine environment is acidic pH (~4-6), temperature 40 - 55°C, very high humidity and contain 300 to 2000ppm dissolved solids. Sulfate and chloride anions have also been identified for promoting pitting and crevice corrosion of stainless steel component, Yoshitake et al (153). In yet another study by Perdomo et al (94), investigated corrosion fatigue of heat treated duplex stainless steel in paper machine white water. Cracking of suction rolls is favored by corrosion fatigue included by fluctuating stresses that are imposed during routine operations. Corrosion of paper machine becomes, further, a matter of great concern with introduction of system closure, either directly or after treatment.

1.3. Recent Developments in Pulping and Bleaching :

In recent past, paper making practice has observed several changes, because of reasons outlined above. Important among these changes are : higher degree of delignification in pulping, oxygen delignification, partial replacement of chlorine by chlorine dioxide thereby decreasing use of chlorine or use of non-chlorine bleach chemicals and water reuse or closure of mills

1.3.1. Higher degree of delignification in pulping :

Global demand for paper is rising every year and current market conditions require papermakers to increase quantity of paper with improved product quality at lower cost without increasing pollution load. An effective way to meet these conflicting requirements is to use high yield pulp, with its superior bulk and other desirable characteristics. High yield of pulp could be obtained by higher degree of delignification of fibrous raw material in pulping section and this also reduces the bleach plant discharge. In higher degree of delignification wood chips are cooked more selectively to increase the pulp yield without degradation of pulp. The higher degree of delignification is achieved by cooking wood chips in higher sulfidity liquor which is being practiced in the normal kraft process compared to an aspect of RDH or super batch cooking. One survey, Clarke (32), shows that mills with higher sulfidity experiences more corrosion with than mills with lower sullfidity.

1.3.2. Oxygen delignification :

Use of Oxygen in alkaline delignification process and to assist the delignification in extraction bleaching stages has the primary effect of making these hot, alkaline environments more strongly oxidizing in nature. In some cases, this may result in increased localized corrosion. Although limited data exist so far on corrosion performance of stainless steels in oxygen delignification service. Such environment causes pitting of stainless 304 and 316 where chloride level is high. Although the oxygen delignification before chlorination reduces the chlorine consumption in chlorination stage and hence tends to be less corrosive, Garner (50).

1.3.3. Decreasing use of chlorine or use of non-chlorine bleach chemicals :

It has now become a common practice in pulp bleaching to substitute some Cl_2 with ClO_2 to keep control on pulp quality and pollution due to effluent discharge from chlorination washer. The use of ClO_2 in chlorination stage reduces the amount of chloride produced. Consequently the aggressiveness of environment should also reduce. Whereas experimental report, Ahlers (2), has shown the opposite, concluding that the addition of ClO_2 or chlorite, even in small amount to chlorine containing solution activate the chlorine almost equally corrosive as chlorine dioxide for stainless steels. While, under some conditions it was more corrosive than D–stage environment. In recent years, Hatch (58), developments are being directed towards the use of ozone, per acids, enzymes and biological treatments for delignification and bleaching of pulps. Per acids such as per acetic acid (P_a), caro's acid (P_x) and mixed per acids (P_{xa})

containing both P_a and P_x have been evaluated as delignification agents or bleaching agents for chemical pulp and textile since the early 1950's. In other studies, Bennett (21), Kirk-Othmer (69), Panda et al (91), Thierry et al (123), Zhu et al (154), it is found that per acids act both as delignification and brightening of chemical pulp. According to Pehkonen et al (92), on corrosion in ozone and per acetic acid bleaching solution, the results indicate that higher alloy content steels, 254SMO, 654SMO and duplex 27, are resistant to pitting corrosion in 1g/L PAA solution having 1gpl Cl^- at 80°C. In another laboratory study by Sing et al (114), corrosive effect of per acids with acidic pH studied at room and also at high temperature. The results of this study show that P_a is most corrosive while P_x is least corrosive. Tested materials show order of increasing corrosion resistance 304l<316l<317l<2205. Alloy 2205 could be handled in all the solutions. Bio-bleaching is another good option from environmental point of view, requires longer reaction time and yet to be recognized. Baily et al (17), published a research paper describing the use of per acetic acid for both delignification and brightening of chemical pulp. This initial work found that minimum pulp degradation occurred in the pH range of 5.0 to 9.0, temperature and consistency did not have an effect in this pH range.

Ozone and enzymes are also attractive candidates for replacement of chlorine-based bleaching agents due to their good brightening ability at around pH = 3.5-6.0.

1.3.4. Water reuse or closure of mills :

Of late, paper industry is increasingly adopting bleach plant closure with a view of pollution abatement as well as energy saving measure. However, this strategy changes the parameters of washer vat which are of great concern from the standpoint of corrosion mechanism. Laliberte (74), shows the significant increase in the residual Cl_2/ClO_2 concentration, dissolved solids (e.g. Cl^-) and temperature followed by lowering of pH to more acidic range. All these parameters enhance the corrosivity of liquors to the bleach plant washer materials. This indicates that the more resistant alloys are needed to withstand the bleach plant environment according to degree of closure made.

1.3.5. Closure in case of non-chlorine bleach plants :

The liquors of the new bleaching stages, having non-chlorine bleach chemicals, may not have Cl^- and therefore expected to be less corrosive than chlorine and chlorine containing bleaching stages, Nutt et al (87), Turner et al (127). Also the closure of bleach plant to the zero discharge level may be exercised with much lesser corrosion hazards. However, extensive corrosion study in the solutions of these bleaching chemicals is required. Higher consistency bleaching practice may result into the more corrosive bleaching environment because of increased concentration of residual oxidants, dissolved salts (especially chloride) and high temperature associated with lower pulp dilution levels.

The displacement bleaching practiced to meet the demand of energy conservation and environmental control reduces effluents from pulp mill. The corrosion conditions here are more severe than its conventional counterpart. High temperature bleaching is practiced for pulp at high consistency. The latter is desired for reducing fresh water demand while need of shortening the reaction time requires the temperature to be raised. Thus the material's susceptibility to localized corrosion, in case of high consistency bleaching, is expected to increase.

1.4. Statement of the Problem :

The process modifications have been necessary due to the clear market demand and the mills that have converted to modern process systems have achieved positive effects both economically and environmentally. Pulping now is being done at higher sulfidity, so as to achieve better delignification, which increases the concentration of other sulfur compounds present in cooking liquor. A negative side effect of this, however, is the influence on the corrosion condition in the digester area and shell thinning has been registered in some digesters all over the world. This aspect therefore needs to be investigated further. Starting in mid 1960's, pollution control measures and reduced supply of fresh waters led to recycling of filtrate in the bleach plant and thereby concomitant increase in the corrosivity in bleach washers. The bleaching section of the paper industry provides one of the most corrosive environments for machinery materials as obvious from previous section. A number of modifications introduced in the bleaching practices in the last few years have contributed to the changed corrosivity of chemical environment thereby affecting the performance of materials of construction. Today is the era of closed bleach plant, D and C/D bleaching, total chlorine free bleaching, high temperature bleaching and displacement bleaching. Some countries, averse to the idea of using Cl_2 or chlorine based bleach chemicals, started adopting new technology for its bleaching stage. Consequently, the elemental chlorine free (ECF) or total chlorine free bleaching (TCF) came into existence, Kinstrey et al (70), Yang et al (152). As such, ClO_2 in ECF and much lesser toxic bleach chemicals e.g. per acids, hydrogen peroxide, ozone, enzyme etc. in TCF process are likely to play an important role in bleaching. Alongside the above scenario on the changes in bleaching, it is also worthwhile to take a stock of the situation as regards the material performance in present day bleach plants and that expected in plants of the future. Per acids have not been adopted by Indian paper industry up to now but these are the futuristic bleach chemicals. Further, there are very few studies related to corrosivity in per acids solutions, Pehkonen et al (92) and Sing et al (114). It is with this background that, the author planned to do the following investigations and address the related problems:

1. Construction of E-pH diagram for S-H_2O and Fe-S-H_2O system for the electrolyte having sulfide and thiosulfate in the amount as observed in pulping liquor and long term immersion test in laboratory prepared pulping liquor at room temperature on mild steel, austenitic stainless steel 304L, 316L and duplex stainless steel 2205. This had to be followed by quantitative estimation of uniform and localized corrosion attack and the analyses of the result on the basis of liquor composition and E-pH diagram, wherever possible. (Chapter 3)

2. In-plant corrosion test in Kraft digester on newly developed grade of duplex stainless steels LDX, SAF 2304, 2205 including conventional materials as mild steel, 304L, 316L, to investigate the extent of corrosion attack, its correlation with the process parameters and to compare the suitability of the test materials (Chapter 4).

3. Electrochemical polarization tests and long term immersion tests on mild steel and stainless steel 304L, 316L, 254SMO and 2205 in peracid solutions simulating to those likely to be observed in peracid bleaching of pulp with the aim of understanding the corrosivity of peracid solutions, suitability of the test materials and mechanism of corrosion in these solutions (Chapter 5).

Table - 1.1

Estimated Annual Corrosion Cost

S.No.	Country	Industry	Year of Survey	Annual Loss
1.	U.K.	General	1971	3.5% of GNP[7]
2.	USA	General	1996	$ 300 billion[7]
		Paper & Pulp	1984	$ 525 -1170 million[111]
3.	Canada	Paper & Pulp	1989	$ 300 million[111]
4.	India	Paper & Pulp	1985	Rs. 160 millions[102]
			2005	$ 130,000[22]

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Experimental Procedure

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Corrosion testing provides the basis for the practical control of corrosion by selecting appropriate material of construction or lining material, monitoring the corrosiveness of process streams and thereby controlling the excess amount of chemicals or by opting an electrochemical protection system, Rai et al (103), Shrier et al (110). Thus in order to select a corrosion resistant material or opt for suitable protective measures for pulping and bleaching sections, the present study was carried out through (i) In-plant test in digester and (ii) long term immersion test in laboratory in liquors simulating to digester white liquor at room temperature.(iii) long term immersion and electrochemical tests, in laboratory, in futuristic bleach plant solutions e.g. per acids . The in-plant tests are the best and often only way to monitor the effect of process variables on the material performance in "real life" conditions, since it may not be possible to replicate plant conditions in the laboratory or it may be very difficult because of intricacies involved in sustaining the temperature, pressure, flows, contaminant etc. as prevailed in the actual mill conditions. It is, therefore, possible to predict on the basis of mill tests about the life of material for any given environment. However, there are pitfalls in the field-testing. The test may not faithfully reproduce such factors as crevices, stresses or weld-related phenomenon. Sometimes, this testing takes a long time and for this reason it is impractical in many circumstances. On the other hand, laboratory corrosion testing are useful when service history is lacking time and budget constraints prohibit simulated field testing. They can also be used as screening tests prior to simulated service testing. Laboratory tests are particularly useful for quality control, material selection, material and environmental comparison and the study of corrosion mechanism. These tests cover a spectrum ranging from simple immersion test to sophisticated electrochemical tests. Standardized tests methods, especially electrochemical tests are very useful for specifications and for routine use to compare experimental alloys and such products as inhibitors, coating and insulation materials. These are accelerated tests and can give material's life only in relative sense. In the following paragraphs are given the details of the procedures adopted in the proposed work.

2.1. Material Selection :

Recent Survey shows that Carbon steel has been the principal material of construction for kraft batch/continuous digesters since last many decades. Change in processing conditions during last several years has seen increase in corrosion rates of digesters up to 100 mpy in new steel digesters. Accordingly digesters are provided with corrosion allowance. Alternatively they have been formed of corrosion resistant materials e.g. low alloy steel (Cr 0.8%,Mo 0.5%,Si 0.25%), SS304L, 316L, 317L, 321, 347, duplex 2205, superduplex (higher Cr than duplex SS), Inconel 625, ferritic SS. Carbon steel digesters have been provided with protective layer of the above mentioned resistant materials by cladding /weld overlaying/thermal spraying. In very few cases, low alloy steel, ferritic SS and Inconel have been used. Duplex SS is a recent addition due to its better resistance against cracking in digester liquor and chloride stress cracking, Davison (36), in addition to better strength/weight ratio. It has been documented that the austenite stainless steels possess a wide spectrum of corrosion resistance making them suitabile for the bleach plant service, Krisher (72). Newer generation ferritic stainless steel (low interstitial) grades e.g. 29-4-2, 29-4C, Crucible SC-1 etc. provide satisfactory performance in many bleach plant environment but have limited availability in the product forms needed for wide spread applications, Bennett et al (21). Also these steels are not easy to weld and are prone to embrittlment when thick sections are welded. The austenitic stainless steels generally have good and high ductility alongside corrosion resistance. An elevated nickel amount in them increases their resistance to stress cracking and higher molybdenum content imparts better resistance against crevice and stress corrosion cracking, Avesta Bulletin (65, 66). Accordingly, for In-plant test in digester, mild steel, austenitic grade steels 304L, 316L and three duplex grades 2205, LDX, SAF2304 stainless steels were selected as the test materials. For weight loss tests in sulfide solutions mild steel, austenitic stainless steel 304L, 316L, and a duplex stainless steel 2205 were selected. For weight loss and electrochemical tests in per acid solutions mild steel, austenitic stainless steel 304L, 316L, and 254SMO and duplex stainless steel 2205 were selected.

2.2. Specimen Preparations :

2.2.1. Shape and Size of Specimen :

To get a meaningful data on corrosion performance, test specimens are selected in specific size and shape. These are influenced by several factors. Sufficient thickness of specimens is required to minimize the possibility of perforation of coupon during the test exposure. Their size should be so large that they can be conveniently handled, the limitation being imposed by the problem of effective entry into the operating equipment. The most common shape of coupons, for the test purpose, is rectangular. Circular and disk type shapes are also used but rectangular is common because most alloys are available in plate or sheet form. Also materials are exposed such that their major exposed area to corrosive media is their surface. As such their thickness is much smaller as compared to surface area hence they are tested in plate or sheet form. For the mill test and weight loss test in sulfide and per acid solutions, coupons of the size 6 cm × 6cm with thickness varying between 2 – 4 mm with a hole of diameter 0.375" at its center were used in case of all steels except mild steel whose coupons were of 4cm×4cm and thickness 5 mm. The chemical composition of samples is given in Table - 2.1.

For electrochemical tests, the corrosion cell used employs cylindrical shaped samples. Accordingly the test materials were obtained from rods of the test materials. Size of the test specimen was 1.0cm in diameter and 1.31cm in length. The chemical composition of samples is given in Table -2.2.

2.2.2. Surface Preparation :

The condition of the surface of test sample can markedly affect the corrosion test results. An unprepared surface may facilitate the corrosion because of scratches and unevenness. Accordingly, the general and localized corrosion e.g. pitting and crevice closely depend upon the surface of test specimen and, therefore, a clean surface is required. Standard surface conditions are therefore desirable and necessary in order to compare the corrosion resistance of different materials and also the effect of process variables on the corrosion of metal specimen. It is necessary to remove any extra soil or greases from finished surface so as to allow free access of corrodants, Carter et al (25), other (67). For the present work, polishing machine with two different speeds of rotation i.e. 300 and 600 rev. /min. was used for grinding and polishing the surface. The surface finishing was done by abrading the specimens on emery or silicon carbide paper with grit sequence starting from coarser towards fine i.e. 120, 240, 320, 600 and 800 fitted of motor driven polishing wheels. The coupons were held by hand and water stream was made to fall continuously during the grinding process. This was done to avoid any heat generated metallurgical damages. Moderate to heavy pressure was applied evenly. It was ensured that the surface was completely scratch free and also sharp corners were machined to avoid preferential attack. The specimens were then subjected to polishing by using self adhesive cloth sprinkled with fine polishing alumina (prepared by adding 1 part of alumina slurry to ten parts of water) at a speed varying up to 600 rev/min. Finally the coupons were degreased ultrasonically in 50% acetone solution in distilled water and then dried. The dried coupons were weighed on semi micro balance and dimensions were measured by vernier calipers. These coupons were exposed for in-plant study and weight loss study. Similarly surface preparations were done on cylindrical samples for electrochemical tests.

2.3. Exposure Details :

2.3.1. In-plant test :

The In-plant test was conducted on mild steel and stainless steel coupons in the digester of nearby paper mill. The duplicate coupons of each test material were fitted in a rack formed of five SS-316 rods and nuts so as to support the coupons rigidly (photograph 2.1) the coupons were separated from each other by serrated washers of teflon with the aim to (i) avoid bimetallic corrosion (ii) form crevices to investigate corrosion. The test rack was fitted somewhere near strainer in digester and it was removed after six months exposure for analyzing the corroded coupons.

2.3.2. Laboratory Tests :

(i)Weight Loss tests :

In this test, various steel and stainless steel coupons were exposed in sulfide and per acid solutions simulating those in digester and bleach plant. Duplicate coupons of each test samples, with serrated washer, were hanged in the test solution using nylon thread. The test duration of these tests was six months. After the exposure the above coupons were analyzed for degree of uniform and localized corrosion.

(ii) Electrochemical tests :

These tests were performed at room temperature on cylindrical specimens of steel and stainless steel in per acid bleach solutions namely paeracetic acid, caro's acid and mixture of paeracetic and caro's acid. Cylindrical shape of the specimen is desired as per the geometry of polarization cell (Green's cell) (Fig. 2.1), used in the electrochemical testing. More details about this test are discussed later.

2.4. Solution preparation for Laboratory Tests :

2.4.1. Sulfide Solutions :

For sulfide solutions, first stock solutions of known amount of sodium hydroxide, sodium sulfide and sodium thiosulfate separately were prepared in deoxygenenated distilled water and analyzed. After analysis these stock solutions were mixed so that a required level of concentration of solution could be obtained. Desired chloride level was obtained by adding A.R. grade sodium chloride. All chemicals were analyzed after the preparation of the solution so as to ensure required composition. The solutions were covered rapidly by half inch paraffin oil layer so that oxidation of the liquor could be prevented.

2.4.2. Peracids solutions :

The per acids (P_a - Peracitic acid, P_x - Caro's acid, P_{xa} - mixture of P_a and P_x) were prepared by H_2O_2, CH_3COOH and H_2SO_4, Bijan (23). Peracitic acid was prepared by adding glacial acetic acid to hydrogen peroxide containing about 1 ml of sulfuric acid as catalyst. The mixture was then warmed to 45°C, held at this temperature for two hours, stored overnight in a refrigerator to allow the mixture to come to equilibrium. Caro's acid was prepared by adding sulfuric acid to hydrogen peroxide, while maintaining the reaction temperature at 30-35°C. P_{xa} solutions were prepared by adding the required amount of glacial acetic acid to the cold solution of P_x. Then these solutions were analyzed to determine their active oxygen content prior to use and diluted to a required level. The pH was increased by adding diluted NaOH. Desired chloride level was maintained by A.R. grade sodium chloride (NaCl) crystals.

2.5. Analysis of Kraft white Liquors of Lab and mill Tests and peracid solutions :

2.5.1. Chloride Ion Determination :

Two procedures were used for the estimatetion of Cl^- in these solutions.

(i) In white liquors, sodium chloride was estimated by Scan (108) methods (Chloride determination in white liquor). The reagents used were hydrogen peroxide, H_2O_2 =30%,0.1 N silver nitrate solution, 10% acetic acid and 0.1% in ethanol Phenolphthalein indicator and 10% Potassium chromate solution in distilled water. Pipette 10 ml liquor into a 250 ml conical flask and dilute with about 25 ml of distilled water. add several ml portions of H_2O_2 while heating until the oxidation is complete and the solution becomes colorless and then boil for 5 min. after cooling add three drops of Phenolphthalein indicator and neutralize with acetic acid until the red color disappears. Add 10 drops of Potassium chromate solution and titrate with silver nitrate solution until the precipitate remains faintly red .denote the consumption as A ml. to obtain a blank, titrate the same volume of distilled water with 10 drops of Potassium chromate solution added until the solution is of the same color as when titrating the sample. Denote the consumption as B ml. Content of sodium chloride, gram of NaCl/l as X.

$X=5.85(A-B)\,n$ where n= normality of silver nitrate solution

(ii) This procedure was used for peracid solutions. The chloride containing per acid solution is treated with an excess of standard silver nitrate solution. Thus precipitated silver chloride is separated by filtration and silver nitrate is determined by titrating the filtrate. against thiosulfate solution using ferric ion indicator observe end point, Chlorination Washer (30), Henrikson (62), Laliberte (73).

2.5.2. pH Determination :

This was determined by a pH meter. The pH meter was calibrated by 0.05M potassium hydrogen phthalate and 0.01M sodium tetra borate (borax) for pH= 4.0 and 9.0 respectively at room temperature.

2.5.3. Analysis of white liquor :

For Analysis of white liquor Scandivian methods (109) were used.

Reagents : Hydrochloric acid 1.0N, standardized., Barium chloride solution, 200g of $BaCl_2.2H_2O$ per lit., Formaldehyde HCHO,40% neutralize with I.0N sodium hydroxide solution to a faint red colour with phenolphthalein as the indicator. Thymolphthalein indicator, 0.1%.dissolve 0.1g in 100ml of ethanol (equivalent point pH 9.5)., Phenolphthalein indicator, 0.1%. Dissolve 0.1 g in 100 ml of ethanol (equivalent point pH 8.0). Bromophenol-blue indicator 0.1%. Dissolve 0.1 g in 100 ml of distilled water (equivalent point pH 4.0).

2.5.3.1. Determination of total alkali and active alkali :

Pipette 5.0 ml of liquor into a 200 ml conical flask, dilute with about 30.0 ml of distilled water and add 20 ml of barium chloride solution. Titrate in a hood immediately with the hydrochloric acid using 0.5 ml of the thymolphthalein solution as the indicator the consumption, a ml is equivalent to $NaOH+0.5Na_2S$ in a 5.0 ml sample. Add immediately 5.0 ml of neutralized formaldehyde solution wait 0.5 min. and titrate to a very faint blue colour .add 0.5 ml of phenolphthalein solution and titrate to a faint blue colour. The acid consumption, b ml, is equivalent to $NaOH+Na_2S$ in 5.0 ml sample. Add 0.5 ml of bromophenol- blue solution and continue the titration to the end point .the total consumption of acid, c ml is equivalent to the $NaOH+Na_2S+Na_2CO_3$ in a 5.0 ml sample.

Total alkali, calculated as g of NaOH per lit= 8.0 c.n

Active alkali, calculated as g of NaOH per lit. = 8.0 b.n

Sodium carbonate calculated as g NaOH per lit. =TA - AA,

Where TA= Total Alkali, AA= Active Alkali

a= consumption of acid to the thymolphthalein end point, ml

b=consumption of acid to the phenolphthalein end point, ml

c=consumption of acid to the bromophenol-blue end point, ml

n= normality of the hydrochloric acid.

and then converted all chemicals as gpl as chemicals.

2.5.3.2. Determination of Na_2S, $Na_2S_2O_3$ and NaOH :

Pipette 25.0 ml of liquor into a 500.0 ml of volumetric flask, dilute with distilled water to the mark and mix thoroughly.

A: Determination of a and b :

Preliminary test1: pipette 10.0 ml of diluted liquor into a conical flask, add 3 drops of phenolphthalein solution and titrate slowly with the acetic acid. Note the consumption.

Preliminary test 2: acidify 10.0 ml of the diluted liquor with about 2.0 ml of acetic acid and titrate with 0.1N iodine solution using starch solution as the indicator. Note the amount of solution consumed in the titration.

Measure from a buret into a conical flask 5 times the amount of 0.1N iodine solution consumed in preliminary test 2, measured to the nearest milliliter plus an excess of 7.0 ml add 5 times the amount of acetic acid consumed in preliminary test1 plus an excess of about 4.0 ml pipette 50.0ml of the diluted liquor into the acidified iodine solution and titrate with 0.1N sodium thiosulphate solution using starch solution as the indicator. Note the consumption of sodium thiosulphate solution, a ml, and the volume of iodine solution added, b ml.

B: Determination of c :

Prepare a zinc carbonate suspension by mixing equal volumes (200.0ml) of the zinc sulphate and sodium carbonate solution .pipette 100.0 ml of liquor in to a 1000.0ml volumetric flask and add 50.0ml glycerol. Precipitate the sulphide with about 300.0 ml of the freshly prepared zinc carbonate suspension, added in portions .shake the flask after each addition .when the precipitate has settled, transfer one drop of the clear solution to a lead acetate paper. If the paper blackens, indicating the presence of residual sulfide, add more of the zinc carbonates suspension to the liquor. When all the sulphide is precipitated, dilute with distilled water to the mark and shake the flask. Filter the solution through a dry, pleated filter paper or a sintered glass filter.

Preliminary test 3: determine the consumption of acetic acid by 10.0ml of filtrate as described under preliminary test1. Pipette 100.0 ml of the filtrate into a conical flask and acidify with 10 times of the amount of acetic acid consumed in preliminary test 3 plus an excess of 4.0 ml. titrate immediately with 0.1N iodine solution with starch solution as the indicator. Determine the consumption as c ml.

$X=3.9(4b.n_1 - 4a.n_2 - c.n_1)$ where

X=content of sodium sulfide, g of Na_2S/l.

a= 0.1N sodium thiosulphate consumed in titration A, ml.

b= 0.1N iodine solution added in titration A. ml

c= 0.1N iodine solution consumed in titration C, ml.

n_1=normality of the iodine solution.

n_2 =normality of the sodium thiosulphate solution.

C: Determination of d :

Now pipette100.0 ml from the filtrate obtained under B into a conical flask and adds 5.0 ml of formaldehyde. Mix and acidifies with 10 times the amount of acetic acid consumed in preliminary test 3 plus an excess of 4.0 ml .titrate after 1 min. with 0.1N iodine solution using starch solution as the indicator. Denote the consumption as d ml.

$Z=15.8\ d.n_1$ where

Z=content of sodium thiosulphate, g of $Na_2S_2O_3$/l.

n_1=normality of the iodine solution.

d= consumption of iodine used in above titration.

Sodium hydroxide is calculated by Subtracting sodium sulfide as sodium hydroxide from AA (active alkali) as sodium hydroxide.

2.5.3.3. Determination of Polysulfide as free sulfur :

A gravimetric method for measuring polysulfide sulphur concentration in unoxidized and oxidized samples of white liquor is described, Dorris et al (38). A 25.0 ml volume of clear liquor was transferred by pipette into 100.0 ml of distilled water in a 250.0 ml beaker equipped with a magnetic stirrer. The beaker was then placed in a fume hood and a combination glass pH electrode inserted in the beaker. Using a Pasteur pipet, the liquor was rapidly acidified to a pH of 8 with HCl (3 mol/l) and constant agitation .the pH was then adjusted to 5.0-5.5 with HCl (1 mol/l).the solution then had a milky white appearance as a result of the finely divided elemental sulpher. A 4.7 cm diameter Millipore –type GS filter with a pore size of 0.22μm, weighed on an analytical balance without drying, was fitted on a 4.7 cm Millipore filter holder to filter the fine precipitate .the filter assembly was mounted on a 250 ml filtering flask which contained a solution of NaOH (0.1 mol/l, 100.0ml) to reduce H_2S emission. The whole slurry was filtered under vacuum .small aliquot of distilled water (a total 50.0 ml) were used to transfer the precipitate quantitively to the filter. After dewatering, the precipitate was washed with an additional 25.0 ml of distilled water and dewatered again under vaccum. At this stage the wet precipitate have a yellow color .using a pair of tweezers, the membrane filter was transferred to watch glass for drying results were obtained by placing the samples in a desiccator for 2.0 hours. During the filtration, washing and drying steps, the filter membrane lost between 0.4 and 0.6 mg an average negative correction of 0.5 mg was therefore applied to the original weight of the filter .The concentration of polysulfide sulpher in gpl. was then calculated from the difference between the dry weight of the membrane filter with the precipitated sulpher and the weight of the filter, divided by the volume of liquor acidified.

2.5.4. Analysis of Per acid Solutions (23) :

These solutions were analyzed for active oxygen content. For this purpose about 0.3-0.4 g of the Caro's acid was added to a 500.0 ml Erlenmeyer flask containing 100.0 ml of distilled water and 10.0 ml of 20% sulfuric acid. One to three drops of ferroin indicator was then added to the flask (solution turns reddish-orange in color) and it was titrated immediately with 0.1 ceric ammonium sulfate to a pale blue end point. Approximately 10.0 ml of 25% potassium iodide was then added to the Erlenmeyer flask and the mixture was titrated with 0.1 N sodium thiosulfate until the dark reddish color of iodine began to fade. A starch indicator, 2.0-3.0 ml, was added at this point and the titration was continued until the dark blue color disappeared to a pale reddish-orange color end point. The concentration of per acids in terms of active oxygen was determined by using the following formula:

$$\% \text{ A.O.} = \frac{(\text{V thiosulphate} \times 0.1 \times 0.8)}{\text{Sample weight}}$$

Where A.O. = Active oxygen.

2.6. Weight-Loss Determination :

In this test, the weight of the metal is lost uniformly with time from exposed to corrosive media. Change in the weight or thickness of the material should therefore give a good estimation of the severity of corrosion. This is denoted by a parameter called 'corrosion rate,' defined in two ways. Firstly, it is weight loss per unit exposed surface area of metal per unit exposure time in corrosive environment. Secondly, it has been defined from engineering point of view. In this case rate of metal penetration (due to corrosion) or rate of thinning of material per unit time is considered. Corrosion rate is represented as mils per year 'mpy' (1000 mil=1.0 inch). In the estimation of weight loss and corrosion rate determination, a cleaned metal coupon, of measured size and weight, is allowed to corrode for a specific duration. The corroded coupons then are cleaned off the rust mechanically by light brushing of the specimen to remove lose bulky corrosion products. Later they are cleaned by chemical cleaning procedures, Ailor et al (3), in which coupons were treated with cold solution of concentrated HCl acid + 50.0gpl $SnCl_2$ +

20.0gpl $SbCl_3$ which has been specifically suggested for cleaning corroded steel surfaces Ailor et al (3). Cleaned coupons thus obtained are weighed to know weight loss. Following formula was used for corrosion rate calculations, Fontana et al (44).

$$\text{Corrosion Rate (mpy)} = \frac{3.45 \times 10^6 \times w}{D\,A\,T}$$

W = weight loss in grams, D = density of metal in gm/cm^3, A = area in cm^2 and
T = exposure time in hours

2.7. Nature and Degree of Localized Corrosion :

Weight loss is not a realistic indicator of material performance if the material experiences pitting/crevice corrosion in a given environment. As such, separate determination of degree of pitting and crevice corrosion was made in present case. Crevice on the coupons is formed around the holes due to its covering by serrated washers. Preferential attack on the covered surface is a good representation of crevice corrosion. For this purpose, the pit and crevice depth measurements were done to know the extent of localized corrosion. Thus on the basis of maximum depth under pit /crevice corrosion resistance against pitting/ crevice corrosion of various alloys can be categorized by Singh (113), Tuthill et al (131).

In present study pit depth measurement was done by examining the cleaned coupons under optical metallurgical microscope (Reichert Jung, USA make). A single pit was located on the surface under the microscope at low magnification. This was followed by increasing magnification until the pit area covered most of the field under view. Microscope was then focused at the top of pit by fine focusing knob and initial reading was recorded. Microscope was refocused at bottom of the same pit and final reading was noted down. The difference of initial and final reading was obtained as a pit depth, ASTM (40).

2.8. Electrochemical Measurements :

2.8.1. Basics :

Metals undergo corrosion when it comes in contact with liquid (mostly aqueous solutions). In this state, the metal and liquid both undergo several redox reactions which are chemical and electrochemical in nature, because of which metal is corroded. Consequently, the phenomenon of metal corrosion is termed as electrochemical corrosion. Test methods depending upon study of these redox reactions are known as electrochemical methods. These methods provide useful tool for studying the corrosion phenomenon. Thus the electrochemical kinetics (corrosion rate) in specific environments can be investigated and also these methods help to measure and control the oxidizing power i.e. the potential of the environment. Moreover, these techniques may also be used to predict about resistance of metal to localized corrosion e.g. pitting, crevice, etc. The earliest applications of these techniques were attractive because they offered direct method of accelerating a corrosion process without changing the environment namely by adding strong oxidizer or increasing temperature as in other non-electrochemical laboratory testing. In this technique, the corrosion rate can be measured without removing the specimen from the environment or altering the sample itself. This capability offers distinct advantages over weight-loss and visual observation testing procedures in the sense that kinetics of corrosion process can be studied quantitatively. In Electrochemical tests, the material to be studied is put in (Corrosion Cell Fig. 2.1) the test solution as one of the three electrodes of an electrical cell. The other two electrodes are a counter electrode and a reference electrode. Connections from these electrodes are sent to equipment named potentiostat which does several jobs. Using potentiostat, one measures for the test material (i) electrode potential (ii) current-potential relationship where potential is changed in predetermined manner (potentiostatic, potentiodynamic/cyclic polarization tests) (iii) potentiostatic (current vs. time behavior) etc. In present investigations, corrosion potential measurement, potentiodynamic/cyclic polarization and Potentiostatic (current vs. time plot) measurements were recorded in order to understand the electrochemical kinetic of stainless steels in different media. These are now discussed briefly.

2.8.2. Corrosion Potential Measurement :

On dipping a metal in solution, the metal oxidizes thereby relieving metal ions in solution with the electronic charge remaining on the metal sample itself. On attaining equilibrium, the metal is surrounded by metal ions and therefore develops electrical potential known as corrosion potential (E_{corr}) or open circuit potential (OCP). Time taken to achieve this potential depends upon material- solution system and could vary from a few hours to even days. For corrosion potential measurements, the test sample is immersed in the test solution and potentiostat records a potential versus time curve until a reasonable steady state value is achieved. This potential indicates about the tendency of metal to corrode and also whether the material is in passive state or is in transpassive region.

(i) Potentiodynamic / Cyclic Polarization :

These are the polarization characteristics measured as a function of applied potential by gradually polarizing the specimen anodically, at a preselected scan rate, by several 100 mv with respect to corrosion potential (Fig.2.2). It can yield the important information such as (i) the ability of material to spontaneously passivate in the particular medium (ii) the potential region over which the specimen remains passive (iii) materials tendency to experience localized corrosion i.e. pitting, crevice corrosion and (iv) the corrosion rate. This plot can be described in following way. Region A in (Fig.2.2) is the active region in which the metal specimen corrodes as applied potential is made more positive. At B, further increase in the current ceases due to passivation which is typical of iron, stainless steels, Ni and Cr alloys. This point is characterized by the primary passive potential (E_{pp}) and critical current density (I_c). In the region C, termed as passivation region termed as passivation region, the current, hence corrosion rate, decreases rapidly to minimum value as the passivating film is formed over the surface of specimen. As one proceeds to potential beyond passivation region, the current again increases (region D). This high current behavior is referred to as transpassive region, and results from breakdown of passive film. The metal in this region experiences pitting. The potential at which protective passive film breaks is know as critical pitting or breakdown potential. A slight modification of the potentiodynamic polarization plot, called as 'cyclic polarization', is if external applied potential of metal is made to decrease after reaching some value in the transpassive region, a part of polarization curve termed as 'reverse scan'. The polarization curve then crosses the passive region somewhere or it does not cut at all (Fig. 2.2), the former is a case where pits get passivated. The corresponding potential is termed as repassivation potential and is an indication that at potential higher than repassivation potential only, metal experiences crevice corrosion. If during reverse scan, polarization curve does not cut the passivation curve then either pits do not passivate indicating that metal is not resistant to crevice corrosion or probably reverse scan was initiated even before the onset of pitting. The more noble the repassivation potential, obtained at fixed scan rate, the less susceptible is the alloy to initiate crevice corrosion. To record polarization curves, clean polished specimen was immersed in test solution for an hour so as to reach the steady state before initiating polarization. Potential was scanned at the rate of 0.166 mV / sec. The change of current with the potential was recorded in computer loaded with corrosion software supplied with the potentiostat. The scanning direction was reversed when current reaches corresponding to vertex potential (100 mv above the pitting potential) or current reaches 1 mA/cm^2 ,Wilde et al (146).The scanning is continued until reverse scan curve crosses the forward scan curve or until the corrosion potential is reached (Fig. 2.2).

(ii) Potentiostatic :

Although the tendency of pitting/ crevice corrosion can be measured by potentio-dynamic test, the technique can not measure the critical pitting potential (E_p) and repassivation potential (E_c), accurately, since these vary with scan rate. In case of higher scan rates, these values are observed to have higher magnitude, Bennett et al (21) and Wilde et al (147).

Therefore, for determining tendency of pitting and crevice corrosion, potentiostatic test method is used. In this method, ASTM (96), active pits are initiated at the potential more noble than pitting potential (E_p) (obtained from potentiodynamic polarization curves). This is confirmed by recording current vs. time plot indicating continuous increase in current density with time or current density exceeds 50uA/cm^2. After stimulation of localized corrosion, the potential is returned as rapidly as possible to preselected value e.g. E_1 ($E_1 \geq$ Ecorr.) to determine if the specimen will repassivate or localized corrosion will continue to propagate at the preselected potential. If the pitted or creviced local regions repassivate at the preselected potential, the polarizing current drops quickly to zero or to low values consistent with a passive conditions and monitor the current for 15 minutes (Fig. 2.3a), After ensuring repassivation at E_1, by observing decreasing trend of current for 15 minutes, stimulation step is repeated and changed the potential to the second preselected value which is 0.05 V more noble than E_1. The current vs. time plot is again recorded this potential (E_1+50) mv. If current immediately starts rising and continue to rise (Fig.2.3b), test is stopped after 20 sec. If current first drops, the test is continued until 15 minutes. It is quite possible that at later stage, the current rises as shown in curve III of (Fig.2.3b), at this stage the test is stopped. The pitting potential is considered to be between E_1 and (E_1 + 50 mv). To ascertain that this is really pitting potential, the sample is checked under microscope for pitting attack. For determining repassivation potential (E_c), the specimen is fixed in a collar of PTFE which forms crevices. Rest of the procedure is same as for determining E_p.

2.9. Experimental Equipments :

The equipments used in present study, to perform different type of electrochemical measurements is computer controlled Electrochemical Measurement System Voltalab 40 model PGZ301 of Radiometer France supplied with compatible corrosion measurement software and a corrosion cell, (Photograph 2.2). Different parts of this system are summarized below:

2.9.1. Corrosion Cell :

The corrosion cell selected for the present study is versatile, contaminant free e.g. rubber, etc, temperature resistant and can provide reproducible conditions from one to another experiment. The most important components of the cell are the working electrode, reference electrode and auxiliary electrode (counter electrode). Working electrode is internally threaded cylinder of the alloy being tested. It is fixed against the tubular glass holder using a threaded metal rod and a Teflon gasket to avoid crevices. The reference electrode, saturated calomel electrode (SC) rests in a luggin capillary which is adjusted so that the tip is close to the test electrode. This reduces error in the measurement of electrode potential which is attributed to I-R drop. During polarization and potentiostatic tests, current flows between the test and auxiliary electrodes. These electrodes are graphite rods. Auxiliary electrodes are arranged symmetrically around the test electrode to provide an even distribution of current. The cell atmosphere is controlled by the gas inlet and outlet continuously through the inlet tubes. The desired gas is admitted continuously through the inlet tubes and dispersed throughout the solution by means of fritted glass tube

2.9.2. Saturated Calomel Electrode (SCE) :

The saturated calomel electrode was used as a reference electrode in present study. It does not poison easily or contaminate because of its design. Another advantage of SCE over the others is that its potential is fairly constant with temperature ($dE/dT = 7.6 \times 10^{4}$ V/ °C). The electrode consist of pool covered with a layer of mercurous chloride, Hg_2Cl_2 (calomel) and immersed in a solution of saturated KCl, electrolyte. Electric contact on to mercury is made with a platinum wire which is often fused through the glass wall of the container. The half cell reactions are :

$$Hg_2Cl_2 \longrightarrow Hg^{++} + 2Cl^{-}$$

$$Hg^{++} + 2e^{-} \longrightarrow Hg$$

$$Hg_2Cl_2 + 2e^{-} \longrightarrow 2Hg + 2Cl^{-}$$

Its corresponding Nernst equation at 25°C is

$$E_{calomal} = E^{\circ}Hg_2Cl_2/Hg - 0.0592 \log (a\ Cl^{-})$$

$E_{calomal}$ (for saturated KCl solutions) = +0.242 V. The value of E° at 25°C for the calomel half cell has been found to be 0.2677V. Consequently, above equation becomes

$$E_{calomal} = 0.2677 - 0.0592 \log (a\ Cl^{-})$$

The values of potentials given in this thesis are with respect to SCE.

2.9.3. Potentiostat / Galvanostat :

The electrochemical measurement system measures polarization curves through potentiostat/galvanostat. It is a device which controls and measures the potential of the test electrode vs. a reference electrode. When it works as a current controlling device, it is called as a galvanostat. Potentiostat supplies a current of a needed magnitude and polarity to the test electrode using an auxiliary electrode in the cell. Therefore, the potential measurement is done between test and reference electrode while potential adjustment is achieved by passing the current between the test and auxiliary electrodes. The potentiostat is, generally, used for conducting potentiostatic (constant potential) and potentiodynamic (variable potential) polarization experiments. The potentiostat used in present work implements analog and microcomputer design advances to provide high performance and unlimited versatility in electrochemical measurements. This extends the range from -10 to +10 V with constraints that the difference.

2.9.4. Electrometer :

It is an electronic voltmeter with extremely high input impedance (10^8 ohms).it can be used to measure the electrode potential directly or in conjunction with a potentiometer as a null point indicator. For present study, it was in association of potentiostat. The electrometer should have very high input impedance i.e. order of 10^8 ohms or greater for electrochemical measurements. This ensures that only negligible current will be drawn from the system during the potential measurements.

2.9.5. Metallurgical Microscope :

The metallurgical microscope Reichert Jung, USA make Epi Star model, has been used to examine the pit / crevice depth and area has also been measured by metallurgical microscope. The light microscope has been designed by combining various lenses to resolve and reveal the fine details of microstructure of the sample being examined. It illuminates the specimen with incident (reflected) light. There are two basic types of microscope: upright and inverted type, the term upright and inverted refers to orientation of the face of the polished sample that is examined. The microscope used in present study is upright type (Photograph 2.3) having single illuminator (incident light only). In this microscope, the specimen is placed on a slide on the stage so that the polished surface may be perpendicular to the light beam. Various components of microscope are described below:

(i)Illuminating System :

Tungsten-halogen filament lamps are used in the microscope (Epi Star model) procured for present study. The incident light illuminator using a long life high intensity 6V (20W) quartz lamp. The 4.5 V setting is recommended for the most bright field work, the red 5V and 6V settings are usually required for microphotography, phase contrast and dark field application. These are widely used for their high intensity and high color temperature. Light intensity can be control by varying the current or by use of neutral density filter.

(ii) Condenser :

An adjustable lens, free of spherical aberration and coma, is placed in front of the light source to focus the light at the desired point in optical path. A field diaphragm is adjusted for best image contrast. A second adjustable diaphragm, the aperture diaphragm, is placed in the light path before the vertical illuminator. Opening or closing of this diaphragm alters the amount of light and the angle of cone of the light entering the object. The optimum setting for this aperture varies with each objective lens and compromise among the image contrast, sharpness and depth of the field. Opening this aperture increases the image sharpness but reduces contrast while closing the aperture increases contrast but impairs image sharpness. The aperture diaphragm should not be used for reducing light intensity. It should be adjusted for contrast and sharpness.

(iii) Light Filters :

These are used to modify the light for ease of observation, for improved photomicroscopy, or to alter contrast. Neutral density filters are used to reduce the light intensity uniformly across the visible spectrum. Thus they are useful for safe comfortable viewing and reducing the light intensity without reducing the numerical aperture the system.

(iv)Objective Lens :

The objective lens forms the image of the specimen and is the most important component of the optical microscope. The numerical aperture (NA) is a measure of light collection capability of the objectives and is define as NA = n Sin α
where n is minimum refraction index of various materials between the specimen and the objective lens and α is half angle of the most oblique rays the front lens of the objective. Objective lenses have been mounted on a nosepiece turret that can accept four to six objectives. The vertical illuminator contains a reflector or prism that deflects tile light down the objectives on to the specimen surface. it usually holds the aperture, field diaphragms and filters as well. This illuminator provides only one or two type of illumination, such as bright field and dark field and polarized light illumination. The tube length is the length of the body tube from the eye line of the eye piece to the objective thread. This length is not standardized and can vary. The objectives are designed for use with tube length of 170 mm and can not be interchanged.

The microscope used for present study have Plano chromatic objective which are corrected for chromatic aberration and flatness of the field. This provides relatively long working distance, that is the working distance from front lens o f the specimen surface. Working distance decreases as magnification of the objective increases. All the objectives in this microscope are per focal, indicating that the specimen is essentially in focus when nosepiece is rotated to change from one magnification to another. Perfocality does not adversely affected by any random selection or arrangement of objectives on the nosepieces. This series of objectives is also par centered i.e. when a is selected in the centre of the field for a given magnification, it remains well within field of view for the next highest magnification.

(v) Eyepieces (Ocular) :

The major function of eyepiece is to magnify the primary image produced by the objective so that the eye can use the full resolution of the objectives. Microscope produces a virtual image of the specimen at the point of most distinct generally, 250 mm (10 inch) from the eye. The eyepiece magnifies this image permitting achievement of useful magnification. Epi Star Industrial Microscope is equipped four 10x wide field eyepieces of different field of view. In the compound microscope image produced by the objective lens system is further magnified by the eyepiece. Total magnification is therefore, the product of the magnification of the objective lens and the eyepiece Me

$$\text{Magnification total} = Mo \times Me$$

2.10. Microstructure Examination :

The stainless steel samples were mounted on plastic base for polishing and etched for microscopically examination. Before etching, the samples were cleaned off scale by grinding them from 120 to 1200 grit on polishing machine without excessive heating. Then they were polished by emery papers no. 0 to 4/0 grade followed by final finish on adhesive cloth paper sprinkled with alumina slurry. All the microstructures were taken by Axiovert 200 Mat. The materials, their respective time of etching and etchant chemicals are given in Table 2.3.

Table - 2.1

Composition of Stainless Steels Plate Samples

Alloy	C	Si	Mn	P	S	Cr	Ni	Mo	N	Cu	Ti
MS	0.18	0.04	1.66	-	-	-	-	-	-	-	-
304L	0.036	0.44	1.84	0.024	0.001	18.11	8.01	0.26	0.058	0.46	0.002
316L	0.019	0.5	1.11	0.027	0.002	17.43	11.26	2.03	0.048	0.40	0.001
2205	0.022	0.35	1.47	0.02	0.001	22.13	5.55	3.16	0.188	0.21	0.004
2304	0.019	0.42	1.45	0.026	0.0005	22.94	4.73	0.33	0.104	0.25	0.004
LDX	0.024	0.69	5.07	0.017	0.0	21.36	1.49	0.30	0.232	0.32	0.0

Table - 2.2

Composition of Stainless Steels Cylindrical Samples

Alloy	C	Fe	Ni	Co	Mn	P	Cr	Mo	S	Cu	N	Si
304L	0.02	-	11.52	-	1.92	-	18.1	-	-	-	-	0.59
316L	0.02	BAL*	10.87	0.18	1.69	0.03	17.44	2.16	0.03	0.31	0.04	0.69
2205	0.02	BAL*	5.48	-	1.45	0.026	22.25	3.08	0.002	-	0.15	0.52
254SMO	0.009	BAL*	18.00	-	0.44	0.028	20.10	6.15	0.001	0.74	0.20	0.31

* BALANCE

Table - 2.3

Materials, Their Respective Time of Etching and Etchant Chemicals

Materials	**Time of Etching**	**Etchants**
Mild Steel	10 seconds	HNO_3 (1-5 ml) mixing in 100 ml methanol
Austenitic Stainless Steels 304L,316L	10-15 seconds	Solution of 100 gm of oxalic acid(A.R grade) crystals in 900 ml of distilled water
Duplex Stainless Steels 2205, LDX, SAF2304	45 seconds	Solution of 20 ml glycerin,20 ml HCl, 10 ml HNO_3 and 10 ml H_2O_2

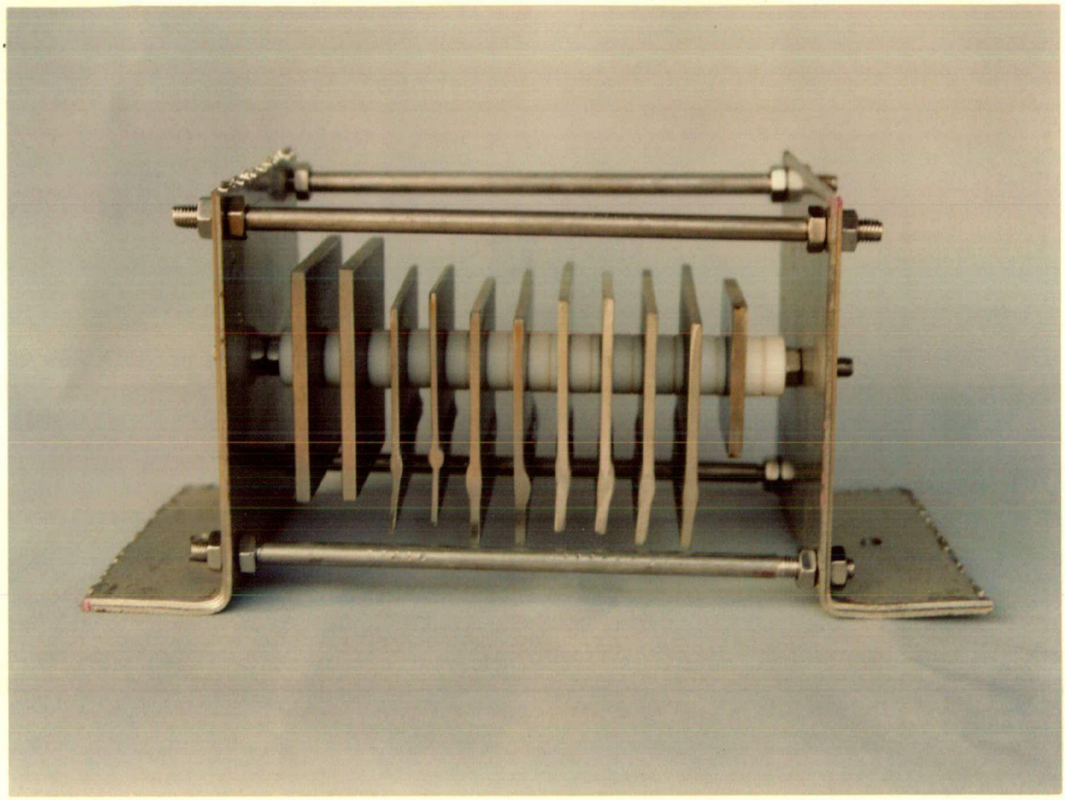

Photo. 2.1. : TEST RACK USED IN DIGESTER

Photo. 2.2. : ELECTROCHEMICAL EXPERIMENTAL SET- UP FOR CORROSION MEASUREMENTS

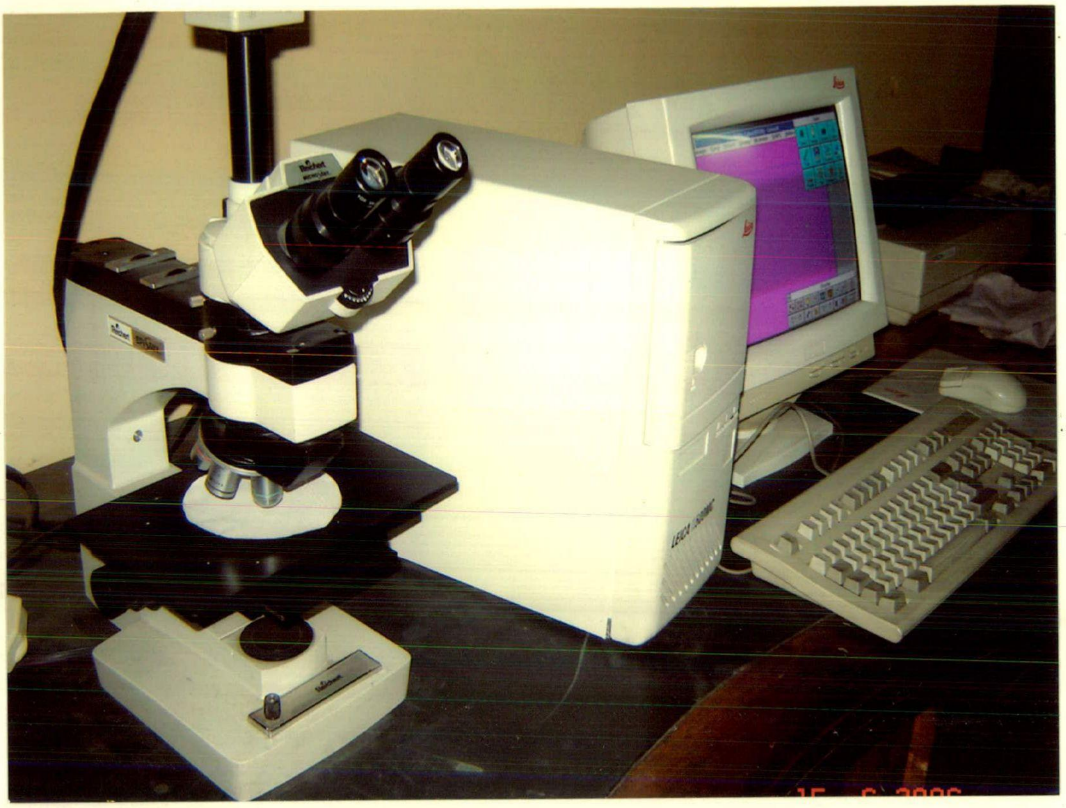

Photo. 2.3. : METALLURGICAL MICROSCOPE USED FOR MICROSCOPICAL OBSERVATIONS

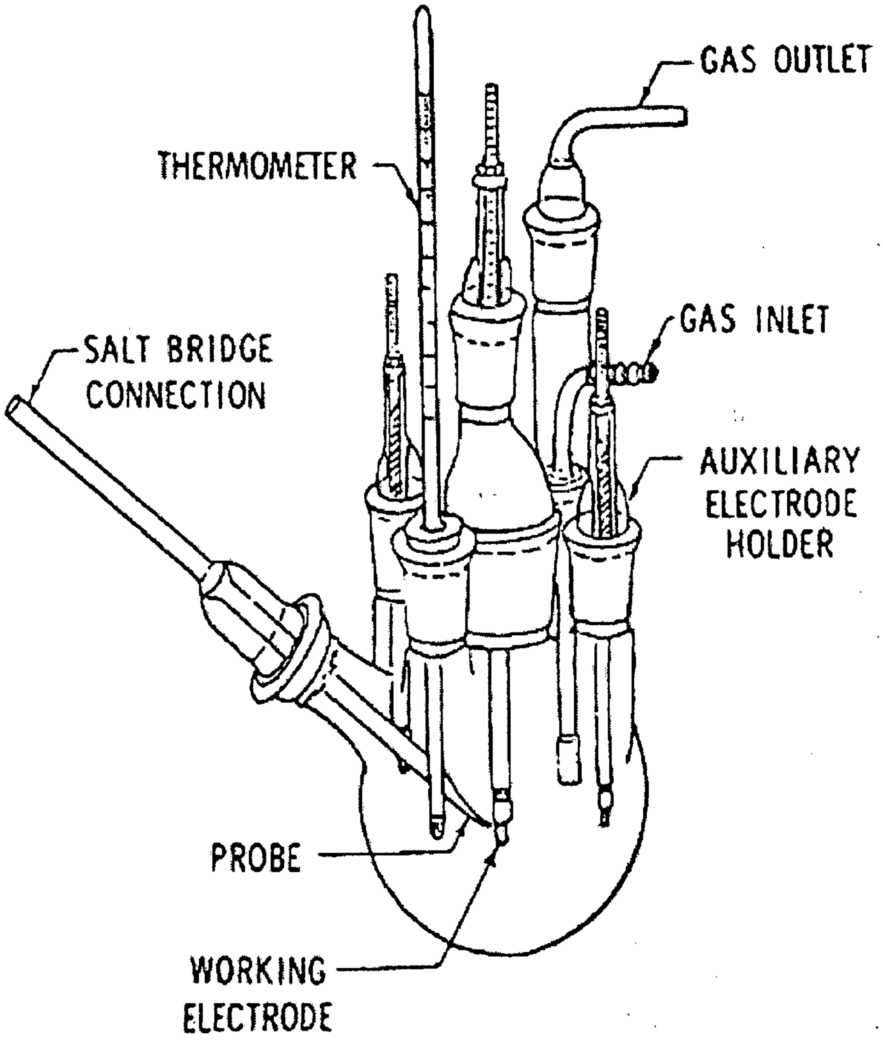

Fig. 2.1. : SCHEMATIC DIAGRAM OF POLARIZATION CELL

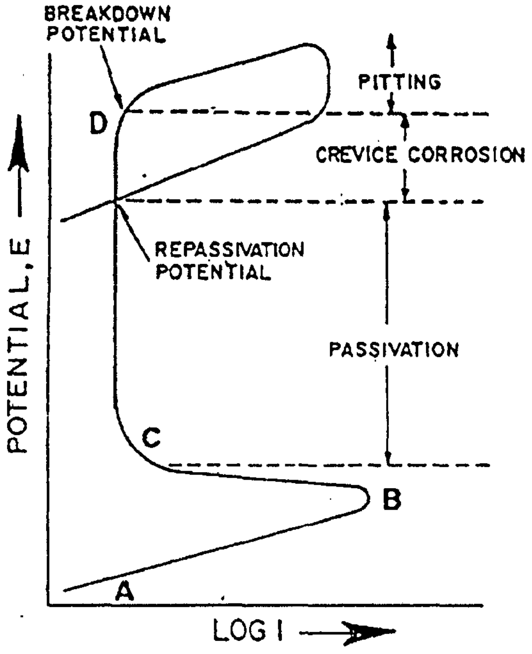

Fig. 2.2. : ACTIVE PASSIVE TRANSITION CURVE

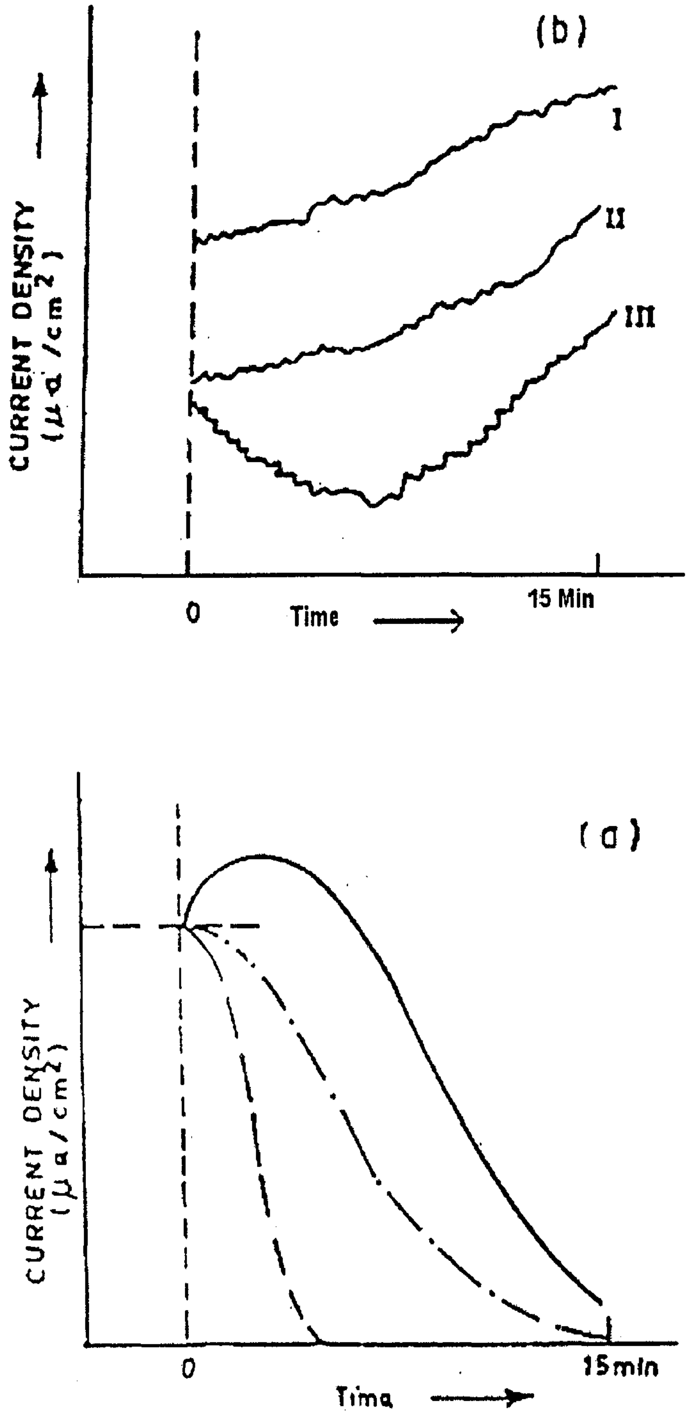

Fig. 2.3. : POTENTIOSTATIC CURVES (I Vs TIME)

Chapter : 3

Corrosion in Solutions having Sulfur Compounds

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3.1. Introduction :

Due to the prevailing practice of making paper by kraft pulping process, ~ 84% of chemical pulping and ~ 64% of all pulping processes, it is obvious that most work related to corrosion in pulping section has considered the composition of test liquor and test conditions as those observed in case of kraft pulping. Kraft process uses alkaline sulfide solution for the purpose of delignification of wood/nonwood species in order to draw cellulose fibers from them, which in turn are made into paper. This alkaline sulfide liquor (pH ~14) consists of NaOH and Na_2S mainly, but due to recycling of unused chemicals of pulping process after the liquor containing unused chemicals has been treated in recovery and recausticizing sections, the cooking liquor also contains various other sulfur compounds and chemicals. In addition the liquor may also have Cl^- ions as contaminants from wood, fresh water or filtrates in the case of mill closure etc. A typical composition of cooking liquor in Indian mills is given in Table - 3.1.

Since last few years, paper making is experiencing significant changes because of several reasons. These are pressures to reduce effluent discharge and air pollution, dwindling papermaking fiber resources, goals to reduce energy/water/chemical consumption with a view to make the product more competitive etc. Important one among them being the pollution control measures and efforts to increase fiber yield. One option is to cook the wood chips more selectively so as to increase pulp yield. This in turn also reduces chemical demand in the succeeding bleaching stages which help in reducing the concentration of effluents in the bleach plant discharge. The selective delignification of wood chips is achieved by cooking them in liquor of higher sulfidity which is being practiced in the normal kraft process and is also an aspect of Rapid Displacement Heating (RDH) or superbatch cooking, Christofer et al (31) and Superbatch (122). Adoption of this change is observed in the difference of sulfidity levels in Indian (~ 20%) and American mills (~ 38%) (Table - 3.1).

Out of these ions, S^{2-}, $S_2O_3^{2-}$, S_x^{2-} and Cl^- affect, Metals Handbook (83) and Wensley (145), corrosivity of liquor significantly. Cooking liquor with higher sulfidity will obviously have higher concentration of these sulfur ions which is expected to result in increased corrosivity of liquor. This is evident from several cases reported of increased corrosion in digesters, after the mills opted for liquor of higher sulfidity. It seems the corrosion in digesters depends very strongly on the relative amount of the different sulfur species in cooking liquor, which is likely to be different in different mills, rather than simply on temperature, pH and sulfide content only. In the past, several cases have been reported by Maspers (81), Pvt. Discussion (100), Report (121), Udayshankar (135), Wensley (138) of increased corrosion, in digesters where not only increased general corrosion associated with erosion corrosion but also localized corrosion e.g. pitting, grooving, cracks etc. have been observed. To address these issues of enhanced corrosion, corrosion experiments were planned in solutions having sulfur containing compounds with their composition matching with those observed in paper mills. In order to analyze the corrosion attack and corrosivity of the solutions, it was planned to use E-pH (Pourbaix) diagram for $S-H_2O$ and $Fe-S-H_2O$ system. Since these diagrams were not available for the conditions corresponding to the pulping process, they were constructed accordingly. This chapter therefore describes first the construction of E-pH diagram for $S-H_2O$ and $Fe-S-H_2O$ system for the solutions simulating to the composition of pulping liquor. This is followed by the description of the corrosion test done in the solutions having sulfur compounds (similar to those observed in pulping liquor) and the analysis of the test result on the basis of the constructed E-pH diagram.

3.2. Pourbaix (E-pH) diagrams for S-H_2O and Fe-S-H_2O system :

The introduction of potential– pH (E-pH) diagrams, popularly called as Pourbaix diagrams, into electrochemistry created a new era in the study of electrochemical reactions occurring in an aqueous medium near an electrode. These diagrams are based on the dependence of equilibrium potential on pH and composition of the aqueous solution at a given temperature. With the help of these diagrams, it is possible to predict, on a thermodynamic basis, for a given element, the equilibrium states of all the possible reactions between this element, its ions and its solid and gaseous phases in the presence of water and other aqueous solutions at different temperatures. Application of the data contained in these diagrams is limited by the reactions which have been considered in establishing them as well as by the values assumed for the standard chemical potentials of the substances taking part in these reactions. The diagrams are based on the activities of ions and not on their real concentrations. Presently, the potential - pH diagrams concern only pure metals and non-metals, these diagrams therefore cannot give us information about the behavior of alloys, which often differs from that of pure metals. However, even with these restrictions, it is evident that in many cases the diagrams provide information which lead to important conclusions concerning the possible reactions. Some of these conclusions are particularly important in the study of corrosion in aqueous media e.g. whether in given aqueous media, a given material will be corroding or immune to corrosion or will be under passivation. The later also indicates the possibility of experiencing localized corrosion. Also it helps in predicting the protective nature of various corrosion products and hence is useful in estimating the conditions for electrochemical protection thermodynamically. Potential – pH diagrams for the systems S-H_2O and Fe-S-H_2O are useful for the study and the understanding of corrosion of iron and carbon steel in the presence of sulfides and of sulphur compounds as aqueous solution.

3.2.1. Thermodynamic data and activities of various sulfur species :

To construct these diagrams for the systems S-H_2O and Fe-S-H_2O, composition and pH, as observed for pulping liquors, were considered for forming the equations showing E–pH dependence for various thermo dynamical equilibrium reactions. Since these diagrams were used for analyzing the results of the corrosion tests at room temperature, different equations were formed at 25°C using activity of various sulphur species corresponding to the chemical concentrations found in the pulping liquors. (Table - 3.2).

Thus except one case, total activity of sulfur species was found on the basis of concentration of Na_2S and $Na_2S_2O_3$ in different solutions meant for immersion test. Values of the activity are given in Table -3.2. This activity was considered for drawing E-pH diagram, irrespective of the form of sulphur species. Different iron and sulfur species considered, in the present study, to draw E-pH diagrams, are given in Table -3.3 along with their chemical potential at 25°C, Pourbaix et al (97) and Singh et al (117).

3.2.2. Redox Reactions and Equations for S-H_2O System :

To construct the E-pH diagrams for S-H_2O system (Fig- 3.1, 3.2), following sulfur species were considered : H_2S, HS^-, S^{2-}, $S_2O_3^{2-}$, S, $S_4O_6^{2-}$, SO_3^{2-} H_2SO_3 and HSO_3^-.

Various thermodynamic reactions and their corresponding equations along with the thermodynamic data e.g. chemical potential for different species were taken from Pourbaix et al (97) and Singh et al (117).These equations were modified for concentration of total sulfur corresponding to total amount of various sulfur species considered in the pulping liquors. Thus activity of total sulfur was considered to be a_S = 0.2, 0.3, 0.44 and 0.7 gram mole/liter on the basis of total amount of S^{2-} and $S_2O_3^{2-}$ found in the pulping liquors.

Following are given different equations used in constructing the E-pH diagram:

1. $H_2S \leftrightarrow HS^- + H^+$ (Reaction and Equation 1 ref 97)

   $\log (HS^-/H_2S) = -6.992 + pH$

2. $HS^- \leftrightarrow S^{--} + H^+$ (Reaction and Equation 2 ref 97)

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

9. $H_2SO_3 \leftrightarrow HSO_3^- + H^+$ (Reaction and Equation 9 ref 97)

   $\log (HSO_3^-/H_2SO_3) = -1.861 + pH$

10. $HSO_3^- \leftrightarrow SO_3^{--} + H^+$ (Reaction and Equation 10 ref 97)

    $\log (SO_3^{--}/HSO_3^-) = -7.210 + pH$

Above equations are Irrespective of the value of activity of sulpher species, a_s,

20. $S_2O_3^{--} + 6H^+ + 8e^- \leftrightarrow 2S^{--} + 3H_2O$ (Reaction and Equation 20 ref 97)

$E = 0.007 - 0.0443pH - 0.0074 \log (a_s)$

$E = 0.011 - 0.04pH$ (a_s=0.2gram mol/lit)

$E = 0.0109 - 0.044pH$ (a_s=0.3grammol/lit)

$E = 0.009 - 0.044pH$ (a_s=0.44gram mol/lit)

$E = 0.0078 - 0.044pH$ (a_s=0.7gram mol/lit)

21. $S_2O_3^{--} + 8H^+ + 8e^- \leftrightarrow 2HS^- + 3H_2O$(Reaction and Equation 21 ref 97)

$E = 0.214 - 0.0591pH - 0.0074 \log (a_s)$

$E = 0.22 - 0.0591pH$ (a_s=0.2gram mol/lit)

$E = 0.219 - 0.059pH$ (a_s =0.3gram mol/lit)

$E = 0.217 - 0.059pH$ (a_s =0.44gram mol/lit)

$E = 0.215 - 0.059pH$ (a_s =0.7gram mol/lit)

22. $S_2O_3^{--} + 10H^+ + 8e^- \leftrightarrow 2H_2S + 3H_2O$ Reaction and Equation 22 ref 97)

$E = 0.317 - 0.0739pH - 0.0074 \log (a_s)$

$E = 0.318 - 0.0739pH$ (a_s =0.2gram mol/lit)

$E = 0.318 - 0.0739pH$ (a_s =0.3gram mol/lit)

$E=0.317 - 0.0739pH$ (a_s =0.44gram mol/lit)

$E=0.317 - 0.074pH$ (a_s =0.7gram mol/lit)

25. $S_4O_6^{--} + 20H^+ + 18e^- \leftrightarrow 4H_2S + 6H_2O$ (Reaction and Equation 25 ref 97)

$E = 0.285 - 0.0657pH - 0.0098 \log (a_s)$

$E = 0.285 - 0.066pH$ (a_s =0.2gram mol/lit)

$E = 0.287 - 0.066pH$ (a_s =0.3gram mol/lit)

$E = 0.288 - 0.066pH$ (a_s =0.44gram mol/lit)

$E = 0.29 - 0.066pH$ (a_s=0.7grammol/lit)

29a. $SO_3^{--} + 7H^+ + 6e^- \leftrightarrow HS^- + 3H_2O$ (Reaction and Equation 29a ref 97)

$E = 0.368 - 0.069pH$ (a_s =0.2gram mol/lit)

$E = 0.368 - 0.069pH$ (a_s =0.3gram mol/lit)

$E = 0.368 - 0.069pH$ (a_s =0.44gram mol/li)

$E = 0.368 - 0.069pH$ (a_s =0.7gram mol/lit)

40. $S_4O_6^{--} + 2e^- \leftrightarrow 2S_2O_3^{--}$ (Reaction and Equation 40 ref 97)

$E = 0.033 - 0.0295 \log (a_s)$

$E = 0.053$ (a_s =0.2gram mol/lit)

$E = 0.050$ (a_s =0.3gram mol/lit)

$E = 0.0436$ (a_s =0.44gram mol/lit)

$E = 0.0375$ (a_s =0.7gram mol/lit)

41. $2SO_3^{--} + 6H^+ + 4e^- \leftrightarrow S_2O_3^{--} + 3H_2O$ (Reaction and Equation 41 ref 97)

$E =0.676 - 0.0887pH + 0.0148 \log (a_s)$

$E =0.665 - 0.0887pH$ (a_s =0.2gram mol/lit)

$E =0.666 - 0.0887pH$ (a_s =0.3gram mol/lit)

$E =0.668 - 0.0887pH$ (a_s =0.44gram mol/lit)

$E =0.670- 0.0887pH$ (a_s =0.7gram mol/lit)

42. $2HSO_3^- + 4H^+ + 4e^- \leftrightarrow S_2O_3^{--} + 3H_2O$(Reaction and Equation 42 ref 97)

$E =0.463 - 0.0591pH + 0.0148 \log (a_s)$

$E =0.453 - 0.0591pH$ (a_s =0.3gram mol/lit)

$E =0.455 - 0.0591pH$ (a_s =0.3gram mol/lit)

$E =0.46 - 0.0591pH$ (a_s =0.3gram mol/lit)

$E =0.461 - 0.0591pH$ (a_s =0.3gram mol/lit)

43. $4HSO_3^- + 8H^+ + 6e^- \leftrightarrow S_4O_6^{--} + 6H_2O$ (Reaction and Equation 43 ref 97)

$E = 0.606 - 0.0788pH + 0.0295 \log (a_s)$

$E = 0.58 - 0.0788pH$ (a_s =0.2gram mol/lit)

$E = 0.59 - 0.0788pH$ (a_s =0.3gram mol/lit)

$E = 0.595 - 0.0788pH$ (a_s =0.44gram mol/lit)

$E = 0.601 - 0.0788pH$ (a_s =0.7gram mol/lit)

44. $4H_2SO_3 + 4H^+ + 6e^- \leftrightarrow S_4O_6^{--} + 6H_2O$(Reaction and Equation 44 ref 97)

$E = 0.533 - 0.039pH + 0.0295 \log (a_s)$

$E = 0.51 - 0.039pH$ (a_s =0.2gram mol/lit)

$E = 0.52 - 0.039pH$ (a_s =0.3gram mol/lit)

$E = 0.523 - 0.039pH$ (a_s =0.44gram mol/lit)

$E = 0.528 - 0.039pH$ (a_s =0.7gram mol/lit)

60. $S + H^+ + 2e^- \leftrightarrow HS^-$ (Reaction and Equation 60 ref 97)

$E = -0.062 - 0.0295 pH - 0.0295 \log (a_s)$

$E = -0.041 - 0.0295 pH$ (a_s =0.2gram mol/lit)

$E = -0.05 - 0.029 pH$ (a_s=0.3gram mol/lit)

$E = -0.051 - 0.0295 pH$ (a_s=0.44gram mol/lit)

$E = -0.057 - 0.0295 pH$ (a_s=0.7gram mol/lit)

61. $S + 2H^+ + 2e^- \leftrightarrow H_2S$ (Reaction and Equation 61 ref 97)

$E = 0.144 - 0.0591 pH - 0.0295 \log (a_s)$

$E = 0.16 - 0.0591 pH$ (a_s =0.2gram mol/lit)

$E = 0.16 - 0.0591 pH$ (a_s =0.3gram mol/lit)

$E = 0.154 - 0.0591 pH$ (a_s=0.44gram mol/lit)

$E = 0.154 - 0.0591 pH$ (a_s =0.7gram mol/lit)

63. $S_2O_3^{--} + 6H^+ + 4e^- \leftrightarrow 2S + 3H_2O$ (Reaction and Equation 63 ref 97)

$E = 0.494 - 0.0887pH + 0.0148 \log (a_s)$

$E = 0.48 - 0.089pH$ (a_s =0.2gram mol/lit)

$E = 0.483 - 0.089pH$ (a_s =0.3gram mol/lit)

$E = 0.488 - 0.089pH$ (a_s =0.44gram mol/lit)

$E = 0.492 - 0.089pH$ (a_s =0.7gram mol/lit)

64. $S_4O_6^{--} + 12H^+ + 10e^- \leftrightarrow 4S + 6H_2O$ (Reaction and Equation 64 ref 97)

$E = 0.401 - 0.0709pH + 0.0059 \log (a_s)$

$E = 0.395 - 0.071pH$ (a_s =0.2gram mol/lit)

$E = 0.397 - 0.071pH$ (a_s =0.3gram mol/lit)

$E = 0.398 - 0.071pH$ (a_s =0.44gram mol/lit)

$E = 0.40 - 0.071pH$ (a_s =0.7gram mol/lit)

Using above equations, the E-pH diagram constructed for $S-H_2O$ system having pH ~ 14 and a_s= 0.2 and 0.7 gram mol per lit. Corresponding to Na_2S =20 gpl and $Na_2S_2O_3$ = 0 and 35 gpl, is shown in (Fig -3.1, 3.2).

3.2.3. Redox Reactions Equations for Fe-S-H_2O system *:*

E-pH diagrams for this 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 sulpher species is considered as in S-H_2O system and for Fe^{++}, Fe^{+++} is considered 10^{-6} gram ion per lit. Activity of iron compounds is considered 1. Following equations formed on above considered activities.

1. $Fe^{++} + 2e^{-} \leftrightarrow Fe$ (Reaction and Equation 1 ref 117)

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

$E = -0.65$

Irrespective of activity of sulpher specie

2. $FeS_2 + 4H^{+} + 2e^{-} \leftrightarrow Fe^{++} + 2H_2S$ (Reaction and Equation 2 ref 117)

$E = -0.066 - 0.118pH - 0.029 \log (Fe^{++}) - 0.059 \log (H_2S)$

$E = 0.149 - 0.118pH$ (a_s =0.2gram mol/lit)

$E = 0.14 - 0.118pH$ (a_s =0.3gram mol/lit)

$E = 0.13 - 0.118pH$ (a_s =0.44gram mol/lit)

$E = 0.117 - 0.118pH$ (a_s =0.7gram mol/lit)

3. $FeS_{1.14} + 2.280H^{+} + 0.280e^{-} \leftrightarrow Fe^{++} + 1.14H_2S$ (Reaction and Equation 3 ref 117)

$E = -0.056 - 0.481pH - 0.221 \log (Fe^{++}) - 0.241 \log (H_2S)$

$E = 1.38 - 0.481pH$ (a_s =0.2gram mol/lit)

$E = 1.34 - 0.481pH$ (a_s =0.3gram mol/lit)

$E = 1.3 - 0.481pH$ (a_s=0.44gram mol/lit)

$E = 1.25 - 0.481pH$ (a_s =0.7gram mol/lit)

4. $FeS_{1.14} + 2.280H^+ + 2.280e^- \leftrightarrow Fe + 1.14H_2S$ (Reaction and Equation 4ref 117)

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

$E = -0.389 - 0.059pH$ (a_s =0.2gram mol/lit)

$E = -0.39 - 0.059pH$ (a_s =0.3gram mol/lit)

$E = -0.398 - 0.059pH$ (a_s=0.44gram mol/lit)

$E = -0.404 - 0.059pH$ (a_s =0.7gram mol/lit)

5. $FeS_{1.14} + 1.140H^+ + 2.280e^- \leftrightarrow Fe + 1.14HS^-$ (Reaction and Equation5ref 117)

$E = -0.616 - 0.029pH - 0.029 \log (HS^-)$

$E = -0.595 - 0.029pH$ (a_s =0.2gram mol/lit)

$E = -0.6 - 0.029pH$ (a_s =0.3gram mol/lit)

$E = -0.605 - 0.029pH$ (a_s=0.44gram mol/lit)

$E = -0.611 - 0.029pH$ (a_s=0.7gram mol/lit)

6. $FeS_2 + 1.720H^+ + 1.720e^- \leftrightarrow FeS_{1.14} + 0.860H_2S$ (ReactionandEquation6 ref117)

$E = -0.085 - 0.059pH - 0.029 \log (H_2S)$

$E = -0.065 - 0.059pH$ (a_s=0.2gram mol/lit)

$E = -0.07 - 0.059pH$ (a_s=0.3gram mol/lit)

$E = -0.0745 - 0.059pH$ (a_s=0.44gram mol/lit)

$E = -0.08 - 0.059pH$ (a_s=0.7gram mol/lit)

7. FeS2 + $0.860H^+ + 1.720e^- \leftrightarrow FeS_{1.14} + 0.860HS^-$(ReactionandEquation7 ref117)

$E = -0.292 - 0.029pH - 0.029 \log (HS^-)$

$E = -0.271 - 0.029pH$ (a_s=0.2gram mol/lit)

$E = -0.28 - 0.029pH$ (a_s=0.3gram mol/lit)

$E = -0.28 - 0.029pH$ (a_s=0.44gram mol/lit)

$E = -0.287 - 0.029pH$ (a_s=0.7gram mol/lit)

8. $Fe^{++} + 2S + 2e^{-} \leftrightarrow FeS_2$ (Reaction and Equation 8 ref117)

$E = 0.355 + 0.029 \log (Fe^{++})$

$E = 0.335$ (a_s=0.2gram mol/lit)

$E = 0.33$ (a_s=0.3gram mol/lit)

$E = 0.181$ (a_s=0.44gram mol/lit)

$E = 0.180$ (a_s=0.7gram mol/lit)

9.$2Fe^{++} + S_4O_6^{--} + 12H^{+} + 14e^{-} \leftrightarrow 2FeS_2 + 6H_2O$ (Reaction and Equation 9 ref117)

$E = 0.384 - 0.051pH + 0.008 \log (Fe^{++}) + 0.004 \log (S_4O_6^{--})$

$E = 0.333 - 0.051pH$ (a_s=0.2gram mol/lit)

$E = 0.333 - 0.051pH$ (a_s=0.3gram mol/lit)

$E = 0.335 - 0.051pH$ (a_s=0.44gram mol/lit)

$E = 0.335 - 0.051pH$ (a_s =0.7gram mol/lit)

10. $yFe_2O_3 + S_4O_6^{--} + 18H^{+} + 16e^{-} \leftrightarrow 2FeS_2 + 9H_2O$(Reaction andEquation10 ref117)

$E = 0.44 - 0.066pH + 0.0037 \log (S_4O_6^{--})$

$E = 0.437 - 0.066pH$ (a_s =0.2gram mol/lit)

$E = 0.438 - 0.066pH$ (a_s =0.3gram mol/lit)

$E = 0.44 - 0.066pH$ (a_s=0.44gram mol/lit)

$E = 0.44 - 0.066pH$ (a_s =0.7gram mol/lit)

11.$Fe_3O_4+3S_2O_3^{--}+26H^{+}+20e^{-}\leftrightarrow 3FeS_2+13H_2O$(ReactionandEquation11ref117)

$E = 0.506 - 0.077pH + 0.0088 \log (S_2O_3^{--})$

$E = 0.499 - 0.077pH$ (a_s=0.2gram mol/lit)

$E = 0.499 - 0.077pH$ (a_s=0.3gram mol/lit)

$E = 0.503 - 0.077pH$ (a_s=0.44gram mol/lit)

$E = 0.504 - 0.077pH$ (a_s=0.7gram mol/lit)

12. $yFe_2O_3 + 2S_2O_3^{--} + 18H^+ + 14e^- \leftrightarrow 2FeS_2 + 9H_2O$(Reaction and Equation12ref117)

$E = 0.5 - 0.076pH + 0.008 \log (S_2O_3^{--})$

$E = 0.494 - 0.076pH$ (a_s=0.2gram mol/lit)

$E = 0.49 - 0.076pH$ (a_s=0.3gram mol/lit)

$E = 0.497 - 0.076pH$ (a_s=0.44gram mol/lit)

$E = 0.498 - 0.076pH$ (a_s=0.7gram mol/lit)

13. $y\ Fe_2O_3 + 6H^+ + 2e^- \leftrightarrow 2Fe^{++} + 3H_2O$ (Reaction andEquation13ref117)

$E = 0.83 - 0.177pH - 0.059 \log (Fe^{++})$

$E = 1.184 - 0.177pH$ (a_s=0.2gram mol/lit)

$E = 1.18 - 0.177pH$ (a_s=0.3gram mol/lit)

$E = 1.18 - 0.177pH$ (a_s=0.44gram mol/lit)

$E = 1.18 - 0.177pH$ (a_s=0.7gram mol/lit)

14.$FeS_{0.943} + 1.886H^+ + 1.886e^- \leftrightarrow Fe + 0.943H_2S$ (ReactionandEquation14ref117)

$E = -0.368 - 0.059pH - 0.029 \log (H_2S)$

$E = -0.347 - 0.059pH$ (a_s=0.2gram mol/lit)

$E = -0.353 - 0.059pH$ (a_s=0.3gram mol/lit)

$E = -0.36 - 0.059pH$ (a_s=0.44gram mol/lit)

$E = -0.363 - 0.059pH$ (a_s=0.7gram mol/lit)

15. $FeS_{0.943} + 0.943H^+ + 1.886e^- \leftrightarrow Fe + 0.943HS^-$ (Reaction andEquation15ref117)

$E = -0.575 - 0.029pH - 0.029 \log (HS^-)$

$E = -0.554 - 0.029pH$ (a_s =0.2gram mol/lit)

$E = -0.556 - 0.029pH$ (a_s =0.3gram mol/lit)

$E = -0.56 - 0.029pH$ (a_s=0.44gram mol/lit)

$E = -0.57 - 0.029pH$ (a_s =0.7gram mol/lit)

16.Fe^{++}+0.943H_2S + 0.114e^- ↔ $FeS_{0.943}$+1.886H^+(ReactionandEquation16ref117)

E = -2.234 + 0.978pH +0.518log (Fe^{++}) + 0.489 log (H_2S)

E = -5.68 + 0.978pH (${a_s}$ =0.2gram mol/lit)

E = -5.6 + 0.978pH (${a_s}$ =0.3gram mol/lit)

E = -5.52 + 0.978pH (${a_s}$=0.44gram mol/lit)

E = -5.42 + 0.978pH (${a_s}$ =0.7gram mol/lit)

17. FeS_2+ 2.114H^+ +2.114e↔$FeS_{0.943}$ +1.06H_2S (ReactionandEquation17ref117)

E = -0.183 - 0.059pH - 0.029 log (H_2S)

E = -0.163 - 0.059pH (${a_s}$ =0.2gram mol/lit)

E = -0.17 - 0.059pH (${a_s}$ =0.3gram mol/lit)

E = -0.172 - 0.059pH (${a_s}$ =0.44gram mol/lit)

E = -0.178 - 0.059pH (${a_s}$ =0.7gram mol/lit)

18. FeS_2+1.057H^++2.114e^-↔$FeS_{0.943}$+1.057HS (ReactionandEquation18ref117)

E = -0.389 - 0.029pH - 0.029 log (HS^-)

E = -0.368 - 0.029pH (${a_s}$=0.2gram mol/lit)

E = -0.374 - 0.029pH (${a_s}$=0.3gram mol/lit)

E = -0.38 - 0.029pH (${a_s}$=0.44gram mol/lit)

E = -0.384 - 0.029pH (${a_s}$=0.7gram mol/lit)

19. 3y Fe_2O_3 +2H^+ +2e^- ↔ 2Fe_3O_4 + H_2O (Reaction and Equation19 ref117)

E = 0.359 - 0.059pH (${a_s}$ =0.2gram mol/lit)

E = 0.359 - 0.059pH (${a_s}$ =0.3gram mol/lit)

E = 0.359 - 0.059pH (${a_s}$ =0.44gram mol/lit)

E = 0.359 - 0.059pH (${a_s}$ =0.7gram mol/lit)

20.$2Fe_3O_4+3S_4O_6^{--}+52H^++46e^-\leftrightarrow 6FeS_2+26H_2O$ (Reaction and Equation20 ref117)

$E = 0.444 - 0.067pH + 0.0038 \log (S_4O_6^{--})$

$E = 0.441 - 0.067pH$ (a_s =0.2gram mol/lit)

$E = 0.442 - 0.067pH$ (a_s =0.3gram mol/lit)

$E = 0.442 - 0.067pH$ (a_s =0.44gram mol/lit)

$E = 0.443 - 0.067pH$ (a_s =0.7gram mol/lit)

21. $Fe^{++} +S_2O_3^{--} +6H^+ + 6e^- \leftrightarrow FeS_2 +3H_2O$ (Reaction and Equation21 ref117).

$E = 0.445 - 0.059pH + 0.0098 \log (Fe^{++}) +0.0098 \log (S_2O_3^{--})$

$E = 0.379 - 0.059pH$ (a_s =0.7gram mol/lit)

$E = 0.38 - 0.059pH$ (a_s =0.7gram mol/lit)

$E = 0.381 - 0.059pH$ (a_s =0.7gram mol/lit)

$E = 0.384 - 0.059pH$ (a_s =0.7gram mol/lit)

22. $FeS + 2H^+ + 2e^- \leftrightarrow Fe + H_2S$ (Reaction and Equation 22 ref117)

$E = -0.364 - 0.059pH$ (a_s =0.2gram mol/lit)

$E = -0.37 - 0.059pH$ (a_s =0.3gram mol/lit)

$E = -0.373 - 0.059pH$ (a_s =0.44gram mol/lit)

$E = -0.379 - 0.059pH$ (a_s =0.7gram mol/lit)

23. $FeS + H^+ + 2e^- \leftrightarrow Fe +HS^-$ (Reaction and Equation23 ref117)

$E = -0.59 - 0.029pH - 0.029 \log (HS^-)$

$E = -0.569 - 0.029pH$ (a_s =0.2gram mol/lit)

$E = -0.574 - 0.029pH$ (a_s =0.3gram mol/lit)

$E = -0.58 - 0.029pH$ (a_s =0.44gram mol/lit)

$E = -0.585 - 0.029pH$ (a_s =0.7gram mol/lit)

24. $FeS + 2H^+ \leftrightarrow Fe^{++} + H_2S$ (Reaction and Equation 24 ref117)

$\log(Fe^{++}) = 3.071 - 2pH - \log(H_2S)$

$pH = 4.88$ (a_s =0.2gram mol/lit)

$pH = 4.86$ (a_s =0.3gram mol/lit)

$pH = 4.71$ (a_s =0.44gram mol/lit)

$pH = 4.61$ (a_s =0.7gram mol/lit)

25. $FeS_2 + 2H^+ + 2e^- \leftrightarrow FeS + H_2S$ (Reaction and Equation 25 ref117)

$E = -0.156 - 0.059pH - 0.029 \log(H_2S)$

$E = -0.135 - 0.059pH$ (a_s =0.2gram mol/lit)

$E = -0.141 - 0.059pH$ (a_s =0.3gram mol/lit)

$E = -0.145 - 0.059pH$ (a_s =0.44gram mol/lit)

$E = -0.151 - 0.059pH$ (a_s =0.7gram mol/lit)

26. $FeS_2 + H^+ + 2e^- \leftrightarrow FeS + HS^-$ (Reaction and Equation 26 ref117)

$E = -0.363 - 0.029pH - 0.029 \log(HS^-)$

$E = -0.343 - 0.029pH$ (a_s =0.2gram mol/lit)

$E = -0.35 - 0.029pH$ (a_s =0.3gram mol/lit)

$E = -0.352 - 0.029pH$ (a_s =0.44gram mol/lit)

$E = -0.358 - 0.029pH$ (a_s =0.7gram mol/lit)

27. $Fe_3O_4 + 8H^+ + 2e^- \leftrightarrow 3Fe^{++} + 4H_2O$ (Reaction and Equation 27 ref117)

$E = 1.066 - 0.236pH - 0.089 \log(Fe^{++})$

$E = 1.6 - 0.236pH$ (a_s =0.2gram mol/lit)

$E = 1.6 - 0.236pH$ (a_s =0.3gram mol/lit)

$E = 1.6 - 0.236pH$ (a_s =0.44gram mol/lit)

$E = 1.6 - 0.236pH$ (a_s =0.7gram mol/lit)

28. $Fe^{+++} + e^{-} \leftrightarrow Fe^{++}$ (Reaction and Equation 28 ref117)

$E = 0.769 + 0.059 \log (Fe^{+++}) - 0.059 \log (Fe^{++})$

$E = 0.769$ (a_s =0.2gram mol/lit)

$E = 0.769$ (a_s =0.3gram mol/lit)

$E = 0.769$ (a_s =0.44gram mol/lit)

$E = 0.769$ (a_s =0.7gram mol/lit)

29. $yFe_2O_3 + 6H^{+} \leftrightarrow 2Fe^{+++} + 3H_2O$ (Reaction and Equation 29 ref117)

pH = 2.3 (a_s =0.2gram mol/lit)

pH = 2.3 (a_s =0.3gram mol/lit)

pH = 2.3 (a_s =0.44gram mol/lit)

pH = 2.3 (a_s =0.7gram mol/lit)

30. $HFeO_2^{-} + 3H^{+} + 2e^{-} \leftrightarrow Fe + 2H_2O$ (Reaction and Equation 30 ref117)

$E = 0.396 - 0.088\ pH + 0.029 \log (HFeO_2^{-})$

$E = 0.22 - 0.088\ pH$ (a_s =0.2gram mol/lit)

$E = 0.22 - 0.088\ pH$ (a_s =0.3gram mol/lit)

$E = 0.22 - 0.088\ pH$ (a_s =0.44gram mol/lit)

$E = 0.22 - 0.088\ pH$ (a_s =0.7gram mol/lit)

31. $HFeO_2^{-} + HS^{-} + 2H^{+} \leftrightarrow FeS + H_2O$ (Reaction and Equation 31 ref117)

$\log (HFeO_2^{-}) = -33.367 + 2pH - \log (HS^{-})$

pH = 13.3 (a_s =0.2gram mol/lit)

pH = 13.42 (a_s =0.3gram mol/lit)

pH = 13.5 (a_s =0.44gram mol/lit)

pH = 13.6 (a_s =0.7gram mol/lit)

32. $Fe_3O_4 + 3HS^- + 5H^+ + 2e^- \leftrightarrow 3FeS + 4H_2O$ (Reaction and Equation 32 ref117)

$E = 1.114 - 0.147pH + 0.088 \log (HS^-)$

$E = 1.052 - 0.147pH$ (a_s =0.2gram mol/lit)

$E = 1.07 - 0.147pH$ (a_s =0.3gram mol/lit)

$E = 1.08 - 0.147pH$ (a_s =0.44gram mol/lit)

$E = 1.1 - 0.147pH$ (a_s =0.7gram mol/lit)

33.$FeS_{1.14} + 2H_2O + 0.28e^- \leftrightarrow HFeO_2^- + 1.14HS^-$ (Reaction and Equation 33ref117)

$E = -0.575 - 0.029pH - 0.029 \log (HS^-) + 1.86H^+$

$E = -6.41 + 0.391pH$ (a_s=0.2gram mol/lit)

$E = -6.46 + 0.391pH$ (a_s=0.3gram mol/lit)

$E = -6.5 + 0.391pH$ (a_s=0.44grammol/lit)

$E = -6.54 + 0.391pH$ (a_s=0.2gram mol/lit)

34$Fe_3O_4 + 3.42HS^- + 4.58H^+ + 1.16e^- \leftrightarrow 3FeS_{1.14} + 4H_2O$ (ReactionandEquation34ref117)

$E = 2.498 - 0.232pH + 0.174 \log (HS^-)$

$E = 2.376 - 0.232pH$ (a_s=0.2grammol/lit)

$E = 2.4 - 0.232pH$ (a_s=0.3gram mol/lit)

$E = 2.43 - 0.232pH$ (a_s=0.44gram mol/lit)

$E = 2.47 - 0.232pH$ (a_s=0.7gram mol/lit)

35. $Fe_3O_4 + 2H_2O + 2e^- \leftrightarrow 3 HFeO_2^- + H^+$ (Reaction and Equation 35 ref117)

$E = -1.846 + 0.029pH - 0.088 \log (HFeO_2^-)$

$E = -1.32 + 0.029pH$ (a_s=0.2grammol/lit)

$E = -1.32 + 0.029pH$ (a_s=0.3grammol/lit)

$E = -1.32 + 0.029pH$ (a_s=0.44grammol/lit)

$E = -1.32 + 0.029pH$ (a_s=0.7grammol/lit

36. $yFe_2O_3 + H_2O + e^- \leftrightarrow 2HFeO_2^-$ (Reaction and Equation 36 ref117)

$E = -0.556 - 0.059 \log (HFeO_2^-)$

$E = -0.556$ (a_s=0.2grammol/lit)

$E = -0.556$ (a_s=0.3grammol/lit)

$E = -0.556$ (a_s=0.44grammol/lit)

$E = -0.556$ (a_s=0.7grammol/lit)

37. $FeS_2 + 4H_2O + 4e^- \leftrightarrow Fe_3O_4 + 6HS^- + 2H^+$ (Reaction and Equation 37 ref117)

$E = -1.101 + 0.029\ pH - 0.088 \log (HS^-)$

$E = -1.039 + 0.029\ pH$ (a_s=0.2grammol/lit)

$E = -1.05 + 0.029\ pH$ (a_s=0.3grammol/lit)

$E = -1.07 + 0.029\ pH$ (a_s=0.44grammol/lit)

$E = -1.08 + 0.029\ pH$ (a_s=0.7grammol/lit)

38. $FeS_2 + 2H_2O + 2e^- \leftrightarrow HFeO_2^- + 2HS^- + H^+$ (Reaction and Equation 38 ref117)

$E = -1.349 + 0.029\ pH - 0.029 \log (HFeO_2^-) - 0.059 \log (HS^-)$

$E = -1.349 + 0.029\ pH$ (a_s=0.2grammol/lit)

$E = -1.145 + 0.029\ pH$ (a_s=0.3grammol/lit)

$E = -1.15 + 0.029\ pH$ (a_s=0.44grammol/lit)

$E = -1.166 + 0.029\ pH$ (a_s=0.7grammol/lit)

39. $Fe^{++} + 2HSO_3^- + 10H^+ + 10e^- = FeS_2 + 6H_2O$ (Reaction and Equation 39 ref117)

$E = 0.452 - 0.059pH + 0.0059 \log (Fe^{++}) + 0.012 \log HSO_3^-)$

$E = 0.408 - 0.059pH$ (a_s=0.2grammol/lit)

$E = 0.408 - 0.059pH$ (a_s=0.3grammol/lit)

$E = 0.410 - 0.059pH$ (a_s=0.44grammol/lit)

$E = 0.414 - 0.059pH$ (a_s=0.7grammol/lit)

Using above equations, the E-pH diagram constructed for Fe-S-H_2O system having pH up to ~14 and a_s= 0.2 and 0.7 gram mol per lit corresponding to Na_2S= 20 gpl, $Na_2S_2O_3$= 0 and 35gpl, is shown in (Fig - 3.3, 3.4)

3.3. Corrosion test in alkaline sulfide solution :

Long term immersion corrosion test was conducted for duration of six months in alkaline sulphide solutions under anaerobic conditions having 20% sulfidity. The materials considered for this test were: ms (mild steel), austenitic stainless steels 304L, 316L and duplex stainless steel 2205.

3.3.1. Material Selection :

Carbon steel has been the principal material of construction for kraft batch/ continuous digesters since last many decades. Change in processing conditions during last several years has seen increase in corrosion rates of digesters up to ~ 100 mpy in new steel digesters. Accordingly digesters are provided with corrosion allowance. Alternatively they have been formed of corrosion resistant solid materials/steel e.g. low alloy steel (Cr~0.8%, Mo~0.5%, Si~0.25%), SS-304L, 316L, 317L, 321, 347, duplex 2205, superduplex (higher Cr than duplex SS), Inconel 625, ferritic stainless etc. or C-steel digesters have been provided with protective layer of the above mentioned resistant materials by cladding/ weld overlaying/ thermal spraying. In very few cases, low alloy steel, ferritic SS and Inconel have been used while duplex SS is a recent addition. Accordingly mild steel, austenitic grade 304L, 316L and duplex grade 2205 stainless steels have been selected as the test materials. Composition of these tested steels has been given in, Table -2.1.

3.3.2. Test Liquor :

Since cooking liquors in different mills are likely to differ in terms of the relative amount of S^{2-}, $S_2O_3^{2-}$, S_x^{2-} and Cl^-, even though having same pH and sulfidity, it was decided to prepare test liquors having varying amount of these species. Accordingly, following composition of liquors were planned on the basis of amount of different species observed in different mills

NaOH	80 gpl
Na_2S	20 – 34 gpl (considering 20% - 30% sulfidity level)
$Na_2S_2O_3$	5 - 35 gpl
S_x^{2-}	2 – 20 gpl
Cl^-	1.21 gpl (corresponding to 2 gpl NaCl)

The preparation of liquor with varying S_x^{2-} content has posed biggest problem. Several methods, referred from literature, Barker(16), Dorris et al (38) , Greene et al (55), Hassler (59), Sanyer et al (107), have been attempted but it has not been possible to obtain amount of S_x^{2-} by more than 2.5 gpl (as free sulfur) although amount of sulfur added was ~ 10 gpl. It seems that requirement for efficient conversion of free sulfur into polysulfide are not being met, and most of sulfur is getting converted mainly into $S_2O_3^{2-}$. Efforts are being made to improve the equipment for generating polysulfide. Meanwhile, the solutions having 80 gpl NaOH, 20 gpl Na_2S and varying amount of $S_2O_3^{2-}$ (5 to 35 gpl) and Cl^- (up to 1.2 gpl) were prepared for the long term immersion test. Composition and variation of various test solutions is given in Table -3.4

3.3.3. Long term immersion test :

Long term immersion test in sulfide solutions was undertaken to understand the effect of varying $S_2O_3^{2-}$ in the presence/absence of Cl^- in sulfide solutions (pH ~ 14), having ~20% sulfidity, on corrosion attack on test materials. The test materials, including autogenously welded part, of stainless steels 304L, 316L and 2205 of size 6cmx6cm and thickness varying between 2-4 mm along with mild steel of 4cmx4cm and thickness 5mm were used. The test materials were cleaned using emery paper from coarse to fine up to 800 grit on a polishing machine. The coupons were fitted with cerrated washers (photo. 3.1a) to know the affect of crevice corrosion. This assembly was immersed in the test solution for the weight loss test (photo3.1 b). The test solutions had to be covered with a layer of paraffin oil to avoid contact of atmospheric oxygen with the solution. The later was found to change the solutions' composition by oxidizing Na_2S to $Na_2S_2O_3$. Hence these solutions are prepared in nitrogenous atmosphere and the tests are being carried under anaerobic conditions. This test was carried for duration of 6 months. Since the beginning of the test, parameters e.g. pH, sulfidity, $S_2O_3^{2-}$ and Cl^- were monitored weekly by Scan methods (108,109).

3.3.4. Evaluation of Corrosion Attack :

The corroded coupons, after taking out from the test solutions were cleaned initially mechanically and later chemically using solution of 50 gpl $SnCl_2$ +20 gpl $SbCl_3$ in concentrated HCl, as per ASTM guidelines (98). The corroded cleaned test samples were also analyzed for any localized attack namely pitting, crevice corrosion and weld related attacks using metallurgical microscope (Reichert Jung, USA). The results of the analysis are given in Table -3.5

3.4. Results and Discussion :

On the basis of E-pH diagrams and long term immersion corrosion test following results and discussion are given.

3.4.1. S-H_2O System :

For S-H_2O System (Fig-3.1,3.2), the diagrams show that within the pH range likely to be observed for the cooking liquor, indicates that sulfur species present in the solution could be HS^-, to some extent S^{2-}, $S_2O_3^{2-}$ and SO_3^{2-} depending upon the potential, which will in turn be governed by the nature of material exposed, mild steels or stainless steels. Measurement of redox potential of 304L and 2205 in pH ~ 14 solution having sulfidity, as considered in drawing E-pH diagram, shows that sulphur species near 304L electrode will be mainly SO_3^{2-} and $S_2O_3^{2-}$ while those near the 2205 electrode will be mainly HS^-.

3.4.2. Fe-S-H_2O system :

Fe-S-H_2O diagrams (Fig-3.3, 3.4) were constructed considering above sulfur species and activities. Thus if the liquor consists of $S_2O_3^{2-}$, 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 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 $S_2O_3^{2-}$ increases. It indicates that if the amount of $S_2O_3^{2-}$ is higher, the steel is likely to experience localized corrosion. Accordingly, E-pH diagram Of Fe-S-H_2O shows that corrosion products forming on 304L will be pyrite or iron oxide and on 2205 it could be pyrrhotite/troilite/mackinawite depending upon the potential. Except mackinawite and troilite, other sulfides /oxide 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 and the temperature, it is necessary to draw these diagrams at higher sulfidity values and higher temperature. Further, one also has to consider polysulfides S_x^{2-} as one of the sulfur species while drawing these E-pH diagrams. This will be useful for digester operation because the digester material experiences temperature varying from room temperature to about 180°C. Further, above 120°C, polysulfides are not stable; one has to consider this aspect also while drawing these diagrams for temperatures > 120°C.

3.4.3. Long Term Immersion test :

A visual examination of the corroded specimens, after cleaning, shows no observable pitting attack but crevice attack is visible in case of mild steel samples only but not measurable. The extent of uniform attack, assessed from corrosion rate, was obtained on the basis of weight loss observed by the samples during the six months test. Corrosion rates experienced by different steels are given in Table- 3.5 One observes that mild steel experiences maximum corrosion. Corrosion rates on stainless steels are negligible. Only mild steel shows crevice attack. A visual examination show the crevice attack to be higher in case of steel samples immersed in solutions having chloride in comparison to those without chloride.

Comparison of corrosion rate on ms shows (a) increase in $S_2O_3^{2-}$ concentration increases corrosion rate (Table -3.5). (b) There appears a sudden increase in corrosion rate when concentration of $S_2O_3^{2-}$ increases from 25 to 35 gpl. (c) Inclusion of Cl^- in the solution also increases corrosion rate in the solution having corresponding amount of $S_2O_3^{2-}$. Corrosion rates on stainless steels are negligibly small and the variation between their values basically reflects the experimental error, hence there does not appear any definite correlation between corrosion rate experienced by stainless steels and the composition of the solutions.

Corrosion of steel in these solutions is the consequence of following oxidation and reduction reactions:

$Fe \leftrightarrow Fe^{2+} + 2e^-$ (oxidation reaction) - (eq.1 of Fe-S-H_2O)

$S_2O_3^{2-} + 8\ H^+ + 8\ e^- \leftrightarrow 2\ HS^- + 3\ H_2O$ (reduction reaction)- (eq.21of S-H_2O)

$Fe^{2+} + 0.943\ HS^- + 0.114\ e^- \rightarrow FeS_{0.943} + 0.943\ H^+$ (reduction reaction) - (iii)

Since the conditions are anaerobic, reduction of O_2 can not be considered here. Thus as the steel is brought in contact with test solutions, the pH of the solution should change to less acidic values because of the reduction reaction (eq.21of S-H_2O) while pH will change to more acidic values due to reduction reaction (iii), as the corrosion of steel proceeds. The monitoring of pH, during the test, although does not show much change but it is definitely decreased of pH in all the cases. This indicates the rate of reaction (iii) to be more than that of reaction (eq.21 of S-H_2O) which thereby results into net decrease in pH of the solution. At this stage, one should look at the possibility of other reduction reactions also, so as to get a better qualitative idea on the rates of the different reactions. Reaction (iii) results into formation of iron sulfide (mackinawite) which is highly soluble type, is non-protective type and is dark in colour. This is corroborated by the findings of the test that (a) the solutions turns dark in colour after steel samples have been put in them for some time (b) on cleaning the corroded samples by acidic solution, one feels the smell of H_2S (c) corrosion rates are high in case of mild steel samples.

The dependence of corrosion rate on the amount of $S_2O_3^{2-}$ can be understood by considering the variation of redox potential for reduction reaction (eq.21 of S-H_2O) given below

$E = E_0 - 0.059\ pH + 0.007 \log (S_2O_3^{2-}) - 0.014 \log (HS^-)$ (eq.21 S-H_2O)

E becomes more anodic on increasing the amount of $S_2O_3^{2-}$. On the basis of mixed potential theory, as the value of E increases, the cathodic polarization line showing $S_2O_3^{2-}$ / HS^- cuts the anodic polarization curve of steel through activation polarization part, then the passivation region and lastly the transpassive region. This results into observation of first increase of corrosion current, followed by its decrease and lastly a sudden increase in its value. On introducing the Cl^- in the solution, the anodic polarization curve seems to shift towards higher currents and decreased value of transpassive potential (Fig.-3.5), thereby showing the increase in corrosion rates in the case of solutions having Cl^-. These suggestions need to be checked by recording electrochemical polarization curves for this system, which forms part of the future work.

Table – 3.1

Composition of Cooking Liquor (gpl)

Chemicals	U. S. Mills	Indian Mills
NaOH	44.7	65
Na_2S	28	15
S_x^{2-}	1.8	2.4
$Na_2S_2O_3$	6	2.3
Na_2CO_3	25	25.33
Na_2SO_4	9.79	13.5
Na_2SO_3	1	1.79

Table - 3.2

Activity (in gram mol per liter) of Different Chemicals

Chemicals	Concentration (gram per liter)			
Na_2S	20	20	20	20
$Na_2S_2O_3$	0	5	15	35
	Total activity (gram mol per liter)			
	0.2	0.3	0.44	0.7

Table - 3.3

Standard Chemical Potentials (μ^0) (Cal/mole) at 25^0C

Chemical Species	(μ^0) Cal/mole
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

Table - 3.4

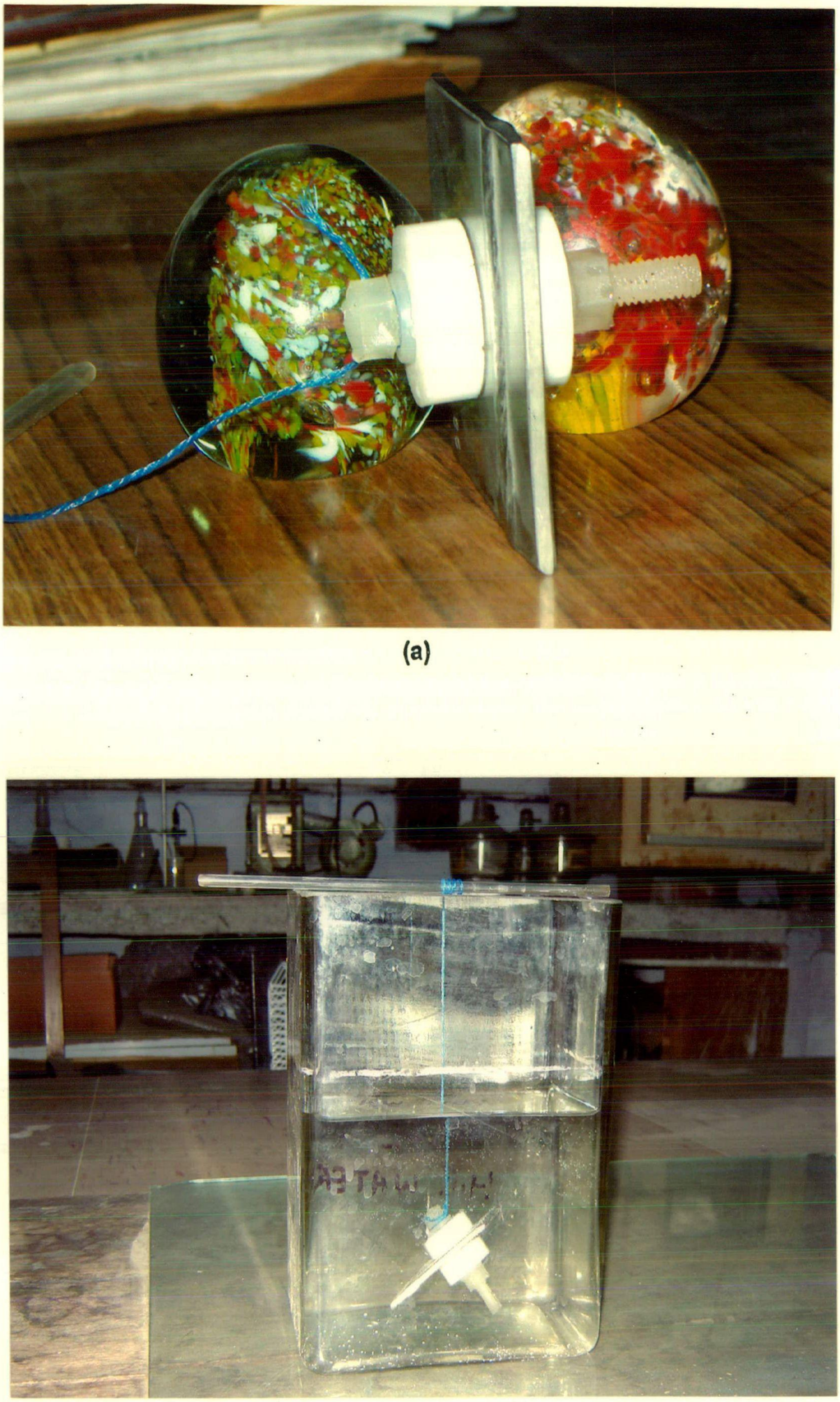
Variation of Chemicals (gpl) during Long Term Immersion Test

Solutions	NaOH	Na_2S	$Na_2S_2O_3$	NaCl	pH
1	80±0.3	19.8±0.25	5±0.3	0	13.6±0.21
2	80±0.21	19.8±0.2	15±0.21	0	
3	80±0.42	19.8±0.22	25±0.21	0	
4	80±0.46	19.8±0.2	35±0.3	0	
5	80±0.27	19.7±0.23	5±0.23	2±0.01	
6	80±0.51	19.7±0.3	15±0.22	2±0.01	
7	80±0.44	19.8±0.2	25±0.3	2±0.01	
8	80±0.34	19.8±0.3	35±0.3	2±0.01	

Table- 3.5

Corrosion Rates (mils per year) of Steels in Alkaline Sulfide Liquor

Materials	Soln.1	Soln.2	Soln.3	Soln.4	Soln.5	Soln.6	Soln.7	Soln.8
ms	0.601	0.981	0.771	3.26	1.112	1.213	1.012	3.256
SS304L	0.003	0.003	0.004	N	0.001	0.001	0.008	N
SS316L	N	0.002	0.002	N	N	0.002	N	N
2205	N	0.001	0.001	0.001	0.001	N	0.001	0.009



(a)

(b)

Photo. 3.1. : LONG TERM IMMERSION TEST SPECIMEN

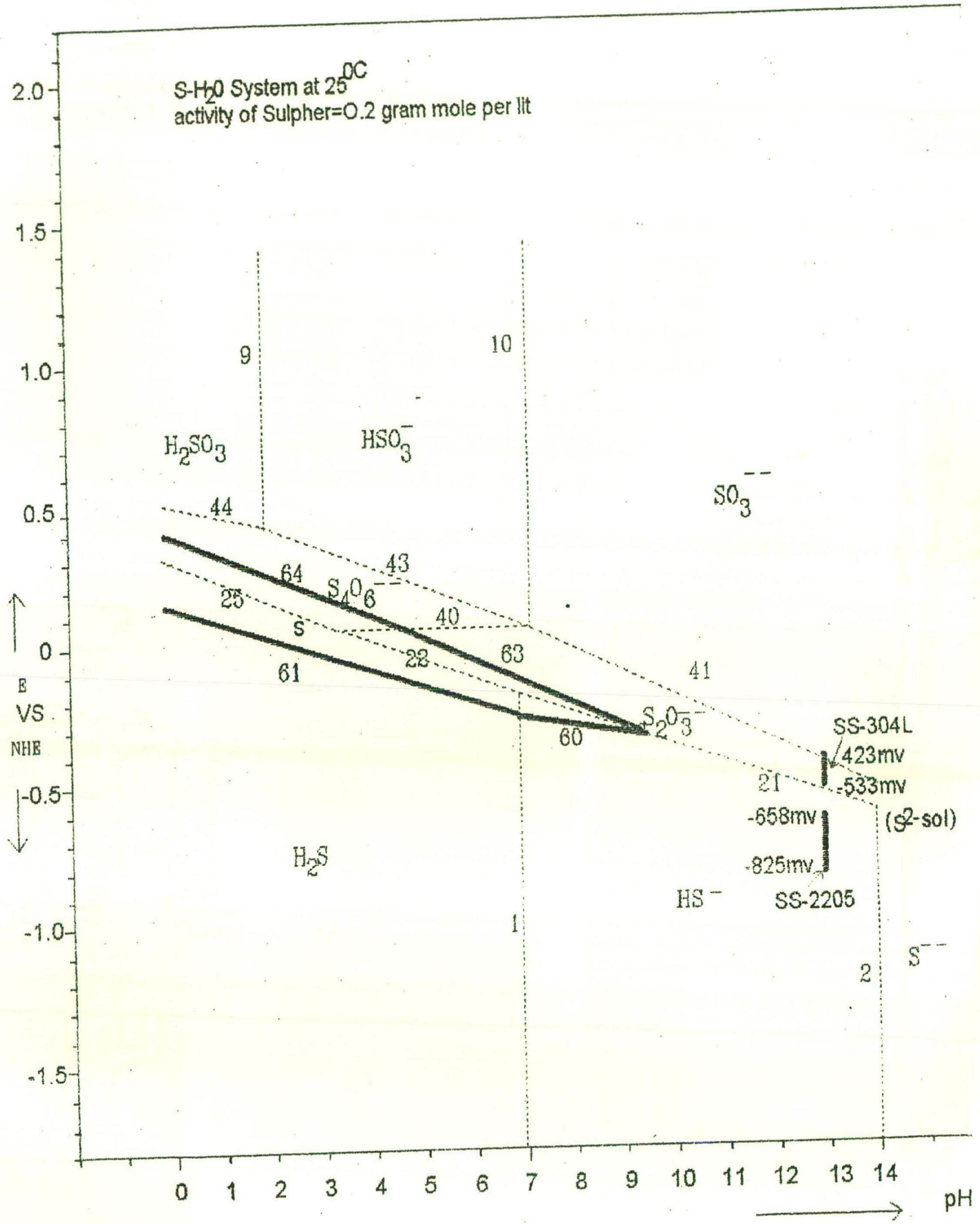


Fig. 3.1. E-pH diagram for S-H_2O system, a_s=0.2 gram mol per lit.

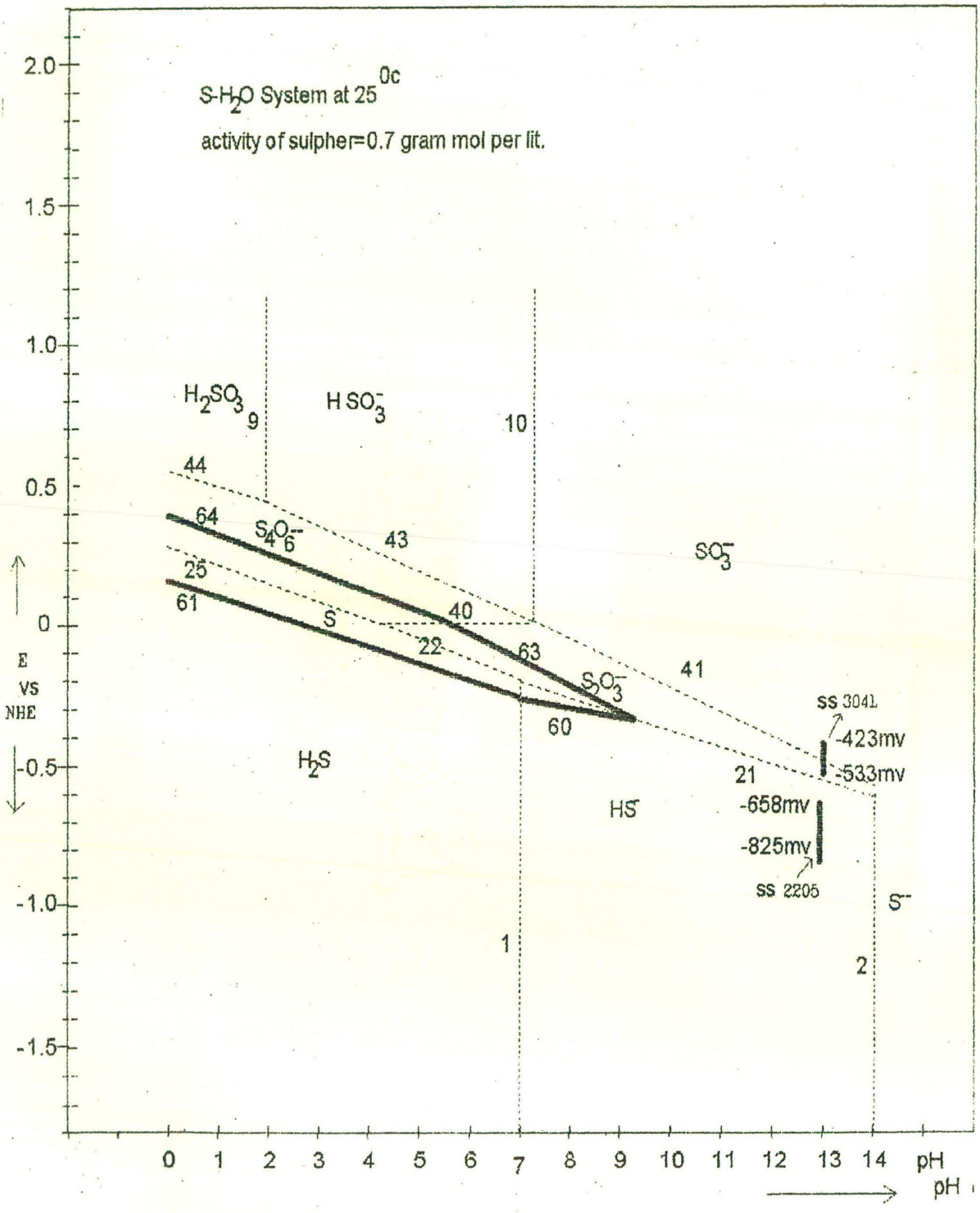


Fig. 3.2. E-pH diagram for S-H$_2$O system, a$_s$=0.7gram mol per lit.

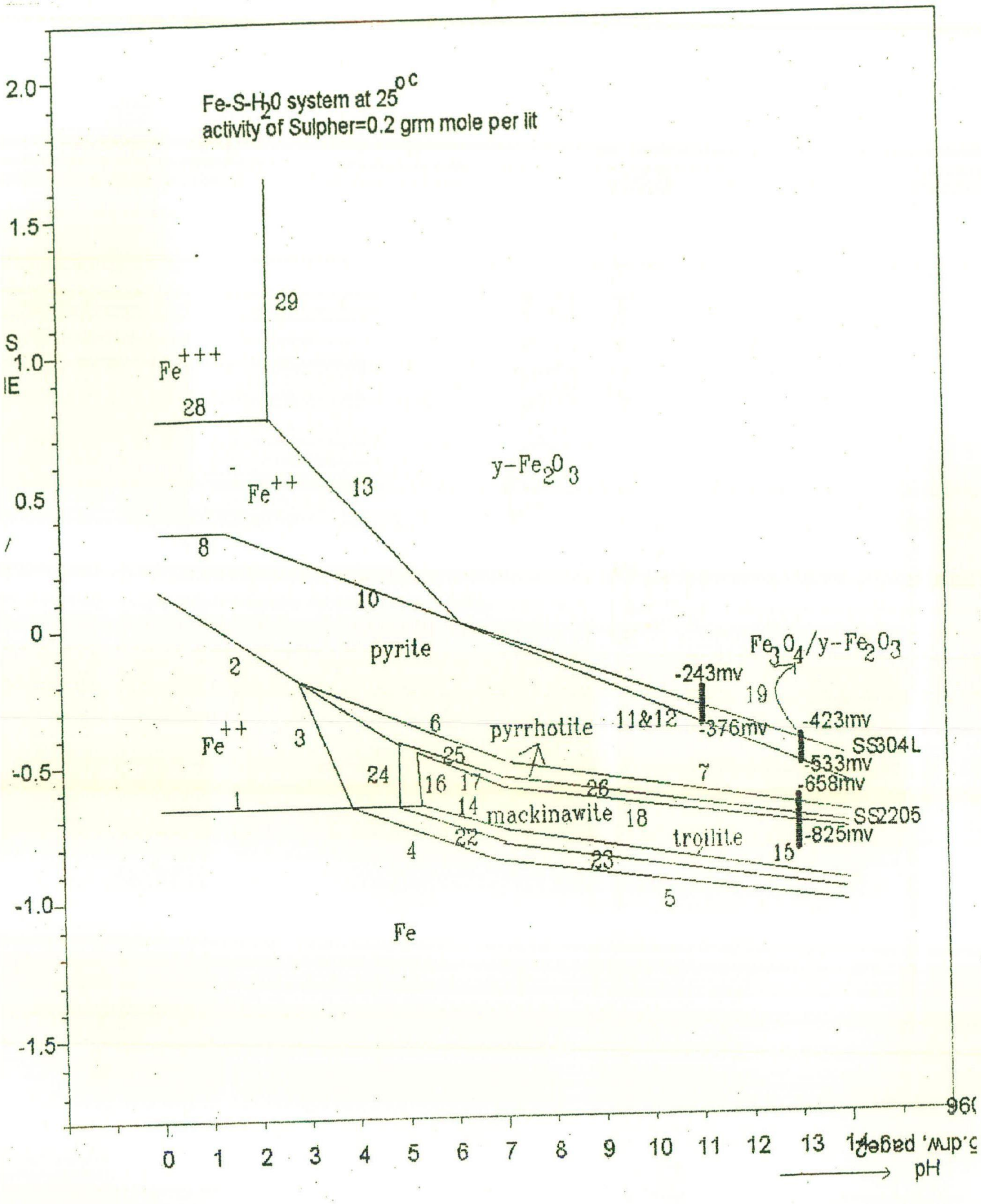


Fig. 3.3. E-pH diagram for Fe- S-H$_2$O system, a$_s$=0.2 gram mol per lit.

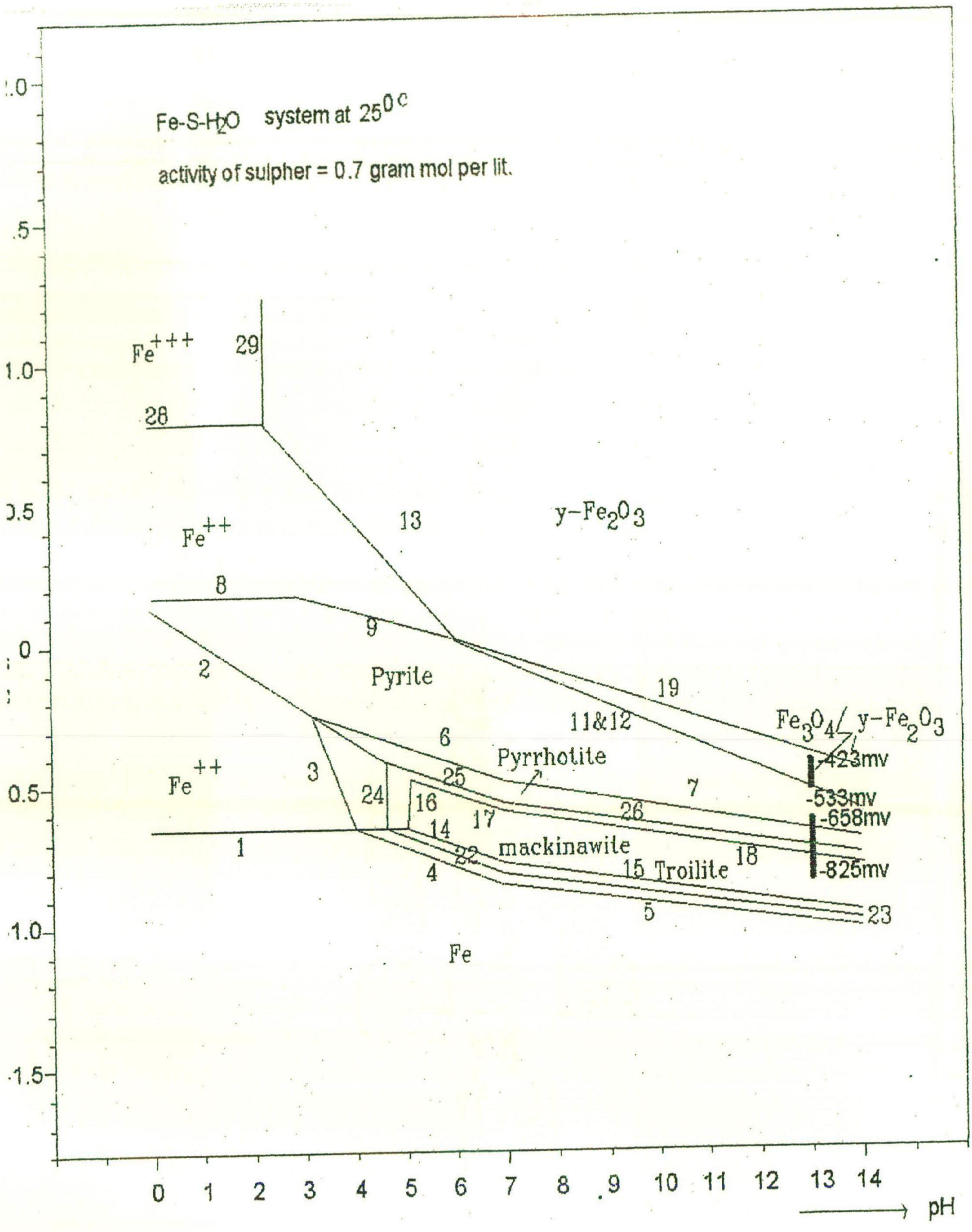


Fig. 3.4. E-pH diagram for Fe-S-H$_2$O system, a$_s$=0.7 gram mol per lit.

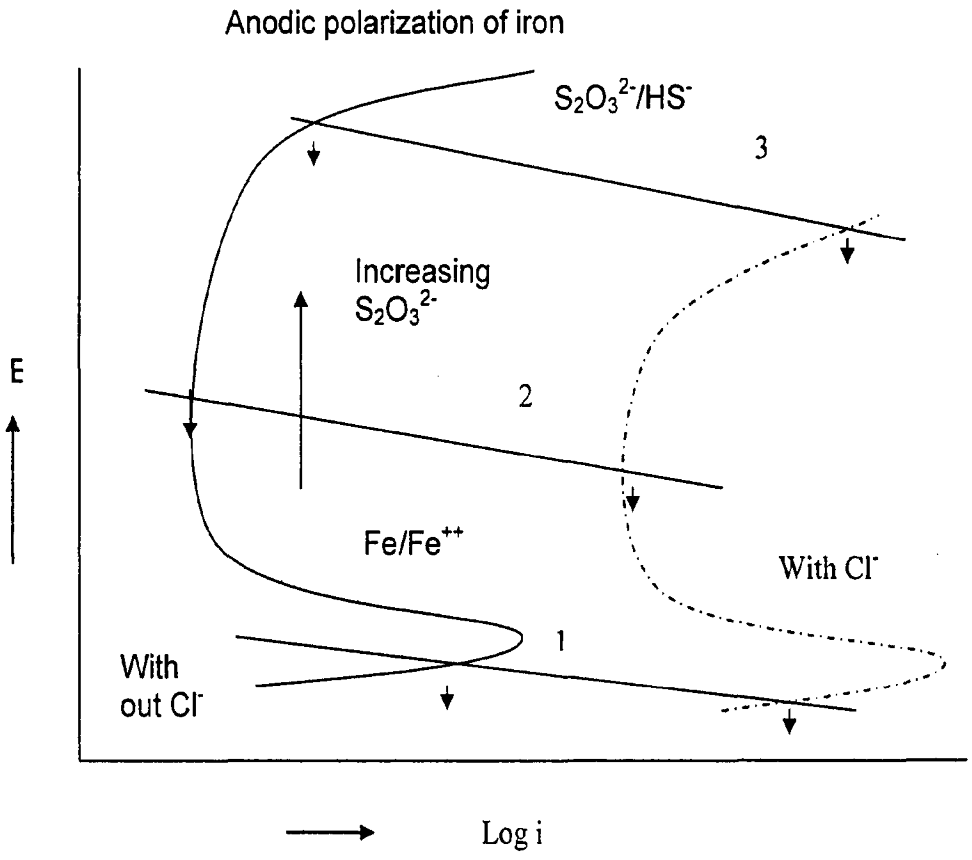


Fig.3.5. ANODIC/CATHODIC POLARIZATION CURVE

Chapter : 4

In-Plant Corrosion test of Steels in Digester of Paper Mill

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4.1. Introduction :

Extensive corrosion is experienced by the process equipment and machinery items in different sections of paper mill. Digester house is one such section which is severely affected by corrosion. Carbon steel kraft digesters generally gave good service life up to 1935. Since then some undetermined changes have been found to cut the life to as little as 1-2 years. An extensive review by Wensley (141), about different aspects related to corrosion in digesters and its control has appeared in 1996. Two cases of sudden failure of digesters due to corrosion have been reported in past, Bennet et al (20), Pulp and paper week (99). Interest about corrosion of digester can be gauged from reporting of large number of articles dealing with mill survey, in - plant tests, in-situ corrosion monitoring, inspection for digester etc. In the first ever reported mill survey, Essen (39), on corrosion problems in sulfate pulp mills, increased corrosion was observed due to presence of (i) sulfide in liquor and (ii) Si in digester steel. A mill questionnaire by Peoples et al (95), found the corrosivity in kraft operations to have increased considerably between 40's and 50's. Another survey by Clarke (32), observed that ~75% of the digesters were 28-48 years old. Approximately 73% of the digesters had SS weld overlay at at-least some part of the digester. Mills with higher sulfidity were found to have higher corrosion. An inspection on corrosion in digester house, Flynn et al (43), revealed uneven corrosion in digesters formed of 405 stainless alloys as lining material in approximate 5 years. The cause of this type of attack was related to hot plate boiling action. In yet another inspection, Hopper (63), corrosion in kraft digester was observed to due to (i) high C and Si in killed steel (ii) circulation of gases and liquor impinging on the walls of digester (iii) change in chemical concentration. Similarly, in –

plant tests have been conducted to investigate corrosion performance of the candidate materials. Thus in first ever reported in-plant test by Huseby et al (64), done on mild steel (ms) and ms-welds in sulfate mills showed (i) corrosion rate of ms varying from 28 to 138 mpy linearly with Si content, (ii) surface preparation and heat treatment affecting the degree of attack (iii) galvanic coupling, for the purpose of protective lining, of SS 347 or inconel with ms does increase corrosion of ms significantly. In another in-plant test by Troselious (126), C-steel and SS coupons were exposed to 6 kraft digesters. Corrosion rate of C-steel was very high while that of SS was very low in all cases with no sign of localized corrosion. Duplex SS showed least corrosion. Cause of increased corrosion was found to be higher concentration of oxidizing chemicals e.g. thiosulfate and polysulfide etc. Similar conclusion has been drawn in test reports (78,121), with regard to the dependence of the corrosivity of liquor on its composition. It has been argued that a higher concentration of polysulfides may show passivating effect. Addition of sulfur was suggested as means of reducing corrosion. In yet another in-plant test, Delblanc et al (37), corrosion rate for 304L and 316L have been measured at ~0.02 mm/year.

With a view to enhance production of paper with better pulp quality and reduce pollutants in their stream, the process of cooking of wood chips has undergone marked changes. Thus digesters now operate at increasingly higher temperature and use cooking liquors having higher sulfidity. These liquors also have higher concentration of other sulfur compounds namely thiosulfate, polysulfide which along with increased amount of Cl^- enhance corrosion attack on digester material. Accordingly, instance of severe corrosion attack in the form of caustic cracking and higher metal loss assisted with water, pitting and crevice corrosion have been reported inrecent years by Clarke

(32), Heikki (61), Pvt. Discussion (100), Rooks (106), Report (121), Tuthill (132), Udayshankar (135), Wensely (142,143). In this changed scenario, it was thought appropriate, to conduct an in-plant corrosion test for investigating the performance of materials normally used in kraft digesters. Based on a report, Thorpe (124), on the experiences of digesters fabricated of duplex Stainless steel, coupons of several newly developed duplex steels were also considered for the present test. Incidentally, the present reported test appears to be the first ever in-plant test performed in the digester of mills in South/South East Asia.

4.2. Details of In-Plant test :

4.2.1. Paper Mill and conditions in Digester :

The in-plant test was done in the batch digester of a paper mill which uses 80% poplar and 20% eucalyptus as raw material for making printing/writing and packaging grade paper. The digester used in the in–plant study has a capacity of 85 m^3 and it is constructed of mild steel. The wood chips are filled in the digester and cooking liquor is then charged keeping liquor to wood ratio as 1:2.8. Volume of cooking liquor inside the digester is kept between 37 to 42 m^3. The cooking liquor consists of mainly NaOH (92 gpl as NaOH) and Na_2S (22.4 gpl as NaOH) having pH ~13.1. Maximum temperature attained during the pulping process is 162^0C and it operates at a pressure of 6.2 Kg/Cm^2.

4.2.2. Materials :

The selection of materials for the in-plant test was done on the basis of their current utilization and their possible applications in future for constructing the digester and related allied machinery in pulp and paper industry. While mild steel have been used as the basic material of construction, SS304L and 316L have been suggested for cladding or weld overlaying the digester requiring refurbishment as a result of enhanced corrosion attack. Of late, newly developed duplex Stainless steels have been suggested to be the prospective material of construction for digesters by Thorpe (124), Tuthill (132), Wensley (142) because of their better corrosion resistance not only against localized attack but also against caustic stress corrosion cracking (an important factor in digester corrosion). Consequently, following materials were considered for the in-plant test : mild steel, austenitic SS 304L and 316L, duplex Stainless Steels 2205, SAF2304 and LDX. The stainless steel samples were supplied courtesy M/S Avesta AB, Sweden along with their chemical analysis (Table -2.1) and mechanical properties (Table - 4.1). Coupons of these materials were selected for the present test.

4.2.3. Exposure of Coupons :

For exposure in digester, duplicate coupons, including autogenously welded part, of stainless steel of size 6cmx6cm and thickness varying between 2-4mm along with mild steel coupon of 4cmx4cm and thickness 5mm were fixed in a rack formed of SS-316 rods and plates .The coupons were cleaned using emery paper from coarse to fine up to 800 grit on a polishing machine .These cleaned and acetone degreased coupons were weighed and their surface area was measured prior to putting for the test. The coupons were mounted in the rack having spacers between them which also acted as sites for initiating crevice corrosion (photograph 2.1) after this the test rack was welded in digester near strainer (Fig.4.1). The rack was kept in this position for duration of six months after which coupons were removed for the analysis of corrosion attack. During this period, the pulping liquor was analyzed weekly for its chemical constituents following SCAN procedure (108,109) and Dorris et al (38). The chemical analysis of various chemicals found in pulping white liquor, on the basis of average values, is given in Table - 4.2.

4.2.4. Evaluation of Corrosion Attack :

The corroded coupons (photograph 4.1), after removing them from the rack, were cleaned initially mechanically and later chemically using solution of 50 gpl $SnCl_2$ +20 gpl $SbCl_3$ in concentrated HCl, as per ASTM guidelines (98). The cleaned coupons were also analyzed for any localized attack namely pitting, crevice corrosion and weld related attacks using metallurgical microscope (Reichert Jung, USA) (photo graph 2.3).The results of the analysis are given in Table - 4.3.

4.3. Results and Analysis :

Microstructures of the tested steels of base metal as well as welded part are shown in (Fig. 4.2, 4.3). Microstructure of base metal of LDX, duplex stainless steel, shows that it is a rolled structure. Rolling direction is in the horizontal direction. It shows two phases' ferrite and austenite. Lighter part is probably ferrite whereas darker part is austenite. Microstructure of SAF2304, base metal structure shows two phases' ferrite and austenite. The welded part of this steel shows absence of any rolling direction. It shows two phases and a typical weld metal. Most of the area has acicular structure. Some areas are free from acicular ties. Acicular plates are in the direction of heat flow. This is a cast metal structure. The microstructure of 2205, base metal structure shows that it is a rolled structure and have elongated grains. It consist ferrite and austenite phase. Welded part structure of 2205 shows that directionality is gone due to rolling. Long needle like ferrite is visible in austenite phase. This is typical cast structure. In middle portion equiaxed ferrite is also visible. The base metal structure of 316L, austenite stainless steel shows that it consist of single phase. At grain boundaries carbide is precipitated, thick boundary grains are elongated in the rolling direction. Rolling direction is horizontal. Welded structure of 316L shows that it has acicular, coarse structure. The microstructure of 304L, base metal structure shows that it is a single phase structure. It shows austenite grains. Twins are also visible. Welded part of this steel shows that it is a cast structure. Structure is refined. Absence of twins across the grains and some carbide are visible in the grains. Cast structure is aligned in one heat flow direction. The microstructure of mild steel shows that it is a two phase structure black portion is pearlite whereas white part is ferrite. Grains are not visible clearly.

Chemically analyzed pulping liquor of the mill has a sulfidity of ~19%. This is the sulfidity usually observed in Indian mills. However, it is much lesser than that observed in mills of USA, Canada and Scandinavia etc. (~40% or so). Polysulfide and thiosulfate content is also lesser in the mill under report. Higher sulfidity, polysulfides and thiosulfates have been indicated to be the factors responsible for higher corrosivity of the cooking liquor. The corroded coupons show uniform corrosion. Pitting is observed significantly in some cases while in others no visible attack is observed .Crevice corrosion is also observed on the coupons. A comparison of corrosion attack on different materials indicates uniform corrosion of lesser degree even in case of mild steel Table - 4.3. The degree of pitting attack in case of 304L and 316L is within the limit of acceptability, Singh (113), for a material of construction.

Maximum corrosion rate is experienced by mild steel followed by 304L, 316L and duplex stainless steels. Thus mild steel show least resistance from the standpoint of uniform corrosion. Duplex stainless steels show lesser corrosion rate in comparison to the austenitic stainless steels, in accordance with earlier observation by Troselious et al (126). Their better resistance, in digester liquor, can be attributed to the higher amount of Cr and N in all the three of them 2205, SAF2304, LDX as compared to 304L and 316L. Whereas Cr provides protection against corrosion by forming stable $Cr(OH)_3$ layer at higher pH, Mo has not been considered for imparting corrosion resistance since it dissolves as MoO_4^{2-} at these pH, Andreasson (4), Normally resistance against corrosion attack (including pitting), in acidic chloride environments is estimated on the basis of pitting resistance equivalent number (PRE), Garner (46). It is, however, not applicable and may give misleading result if applied to alkaline environments of the digesters, Tuthill (133).

No non uniform corrosion is observable on mild steel samples. Pitting is observed in case of 304L and 316L whereas the duplex stainless steels do not show any visible attack. 304L is observed to be lesser resistant against pitting in comparison to 316L. As indicated in above paragraph, for alkaline pH as in digester, Cr and N in SS appear to be more important than Mo in providing the corrosion resistance. Probably this may result into development of duplex stainless steels, without Mo, having equivalent mechanical properties and resistance against localized corrosion. Such steels are also likely to be cost effective. It may be noted here that higher proof strength, comparable ductility and better resistance against localized corrosion and cracking (due to lesser Ni content) of duplex Stainless steels in comparison to 316L is slowly but surely turning duplex stainless steels as the preferable material in comparison to the conventional 316L in case of digesters, Thorpe (124).

4.4. Comparison with Other In-Plant Test :

Findings of the present in-plant test could be compared with those of Swedish test, Troselious et al (126), only because the other test relate to different aspects of material performance, Huseby et al (64), and third test by Delblanc et al (37), is related to continuous digester. Comparisons of the results reveal the following. In general, the Swedish mills (having a sulfidity of ~40%) show a higher corrosion rate of mild steels (1.7-5.9 gm/m^2 .cook with an average of 3.3 gm/m^2 cook). The amount of silicon in the tested mild steel varies between 0.06 - 0.1 %. In the present test, mild steel shows lesser corrosion rate (~0.74 gm/m^2.cook, considering ~ 500 cooks in the test duration of 6 months). This could be due to lesser Si content (~0.4%) in the mild steel and less (~19%) sulfidity in the digester liquor. Both these factors have been suggested to affect corrosion rate in the manner as observed here, Troselious et al (126). Lesser sulfidity probably is also responsible for lower corrosion rates in case of stainless steels as compared to those in Swedish mill. Unlike the case of Swedish mill, mild steel does not show non uniform attack. Pitting is observed on SS-304L (max. pit depth ~ 95 µm and average pit depth ~ 55 µm) and 316L (max. ~ 60 µm and average 52 µm) coupons while other coupons showed no visible pitting. The steel coupons do not show any crevice attack. Non- observance of crevice attack could be due to highly alkaline nature of the digester liquor.

4.5. Material Performance :

An overall view of the corrosion attack indicates that all the materials, including mild steel, tested have sufficient corrosion resistance in the tested media. However, since the liquor composition is likely to change in future so as to have higher sulfidity, thiosulfate and polysulfide content because of advantages associated with high sulfide pulping, it is likely that mild steel will no more be considered suitable and one may have to opt for duplex stainless steels. This aspect needs to be checked in laboratory prepared solutions using long term immersion and electrochemical tests on various steels. Secondly, the part of digester that is affected most by corrosion reactions is due to erosion assisted corrosion and this part is the bottom cone of digester. The present in-plant test seems to support this hypothesis as near strainer (where the rack of coupons was fixed) the materials experience only corrosion and practically no erosion. This test, therefore, also seems to indicate that with the present liquor and the process conditions, the middle cylindrical part of the digester (near strainer) can be constructed of mild steel without severe risk of corrosion. However, to look for the alternate material for the bottom part of the cone, another in-plant test needs to be conducted where the metal coupons are fixed in the bottom cone of the digester so that they experience corrosion as well as erosion in successive batches of pulping cycle.

Table- 4.1

Mechanical Properties of Stainless Steels

Grade	Proof Strength (N/mm^2)	Tensile Strength (N/mm^2)	Elongation (%)
304L	276	616	62
316L	276	575	61
2205	636	712	40
SAF2304	538	749	33
LDX	-	-	-

Table- 4.2

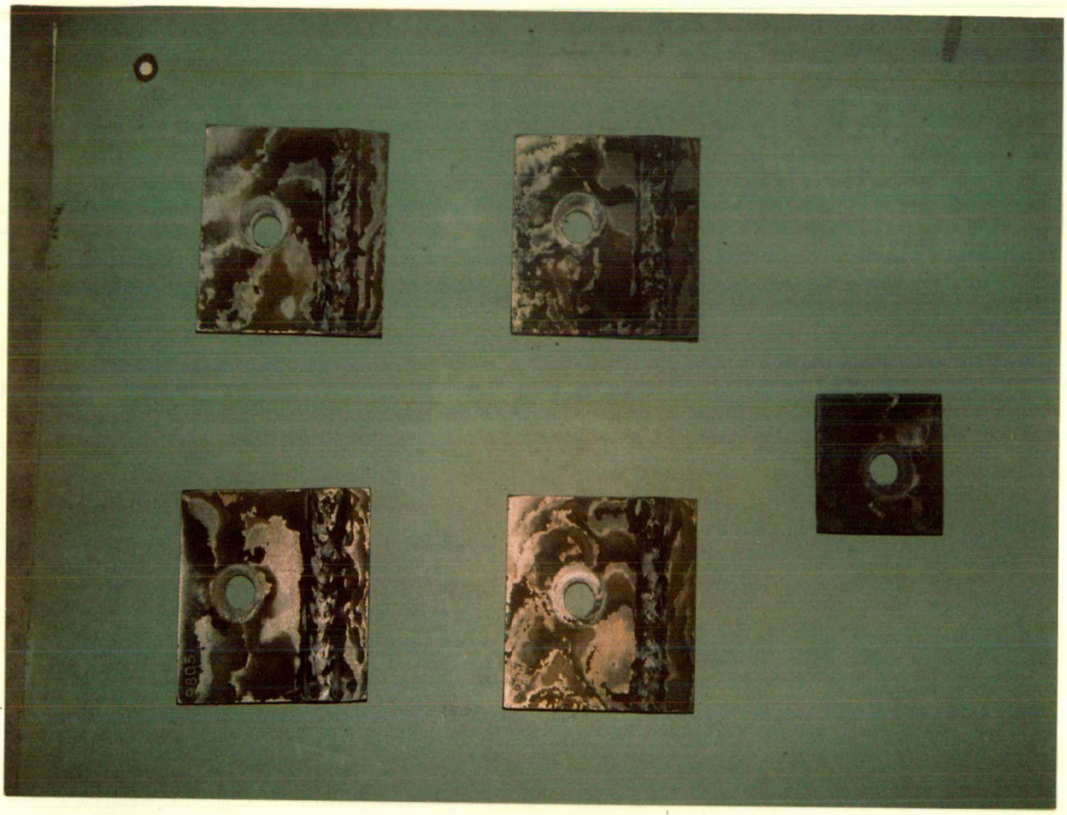
Chemical Composition of White Pulping Liquor

pH	13.1
Sulfidity	19.1%
NaOH (Sodium hydroxide)	91.5±0.3 gpl
Na_2S (sodium Sulfide)	21.1±0.4 gpl
S_x^{2-} (Poly Sulfides)	0.056±0.016 gpl
$Na_2S_2O_3$ (Sodium thiosufate)	2.3±0.9 gpl
Na_2CO_3 (Sodium Carbonate)	16.7±3.0 gpl
Cl^- (Chloride)	1.29±0.24 gpl

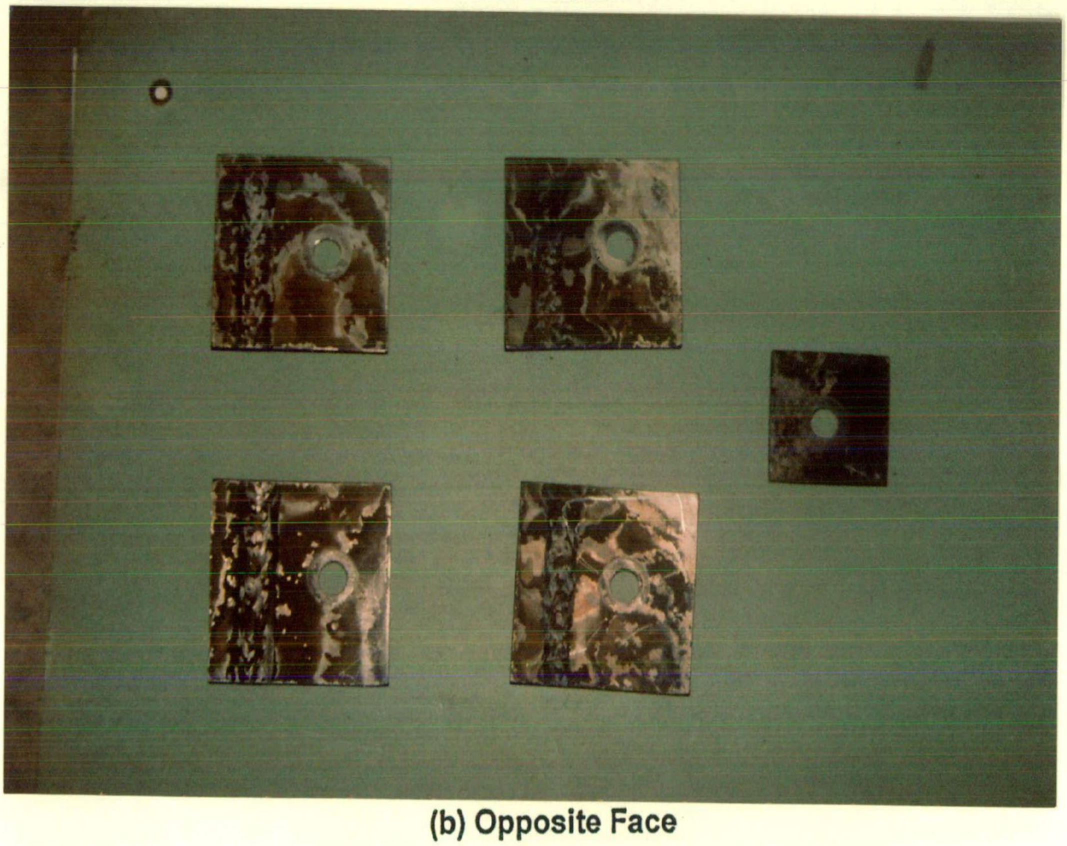
Table- 4.3

Corrosion Attack on the Tested Coupons

Grade	Corrosion Rate (mils per year)	Max. Pit Depth (mm)	Crevice Corrosion
MS	3.74	NVA	No Measurable Attack
304L	0.01	0.095	
316L	0.006	0.060	
2205	0.003	NVA	
SAF 2304	0.001	NVA	
LDX	0.005	NVA	



(a) Front Face



(b) Opposite Face

Photo. 4.1. : CORRODED COUPONS AFTER SIX MONTH EXPOSURE IN DIGESTER

(c) Front Face

(d) Opposite Face

Photo. 4.1. : CORRODED COUPONS AFTER SIX MONTH EXPOSURE IN DIGESTER

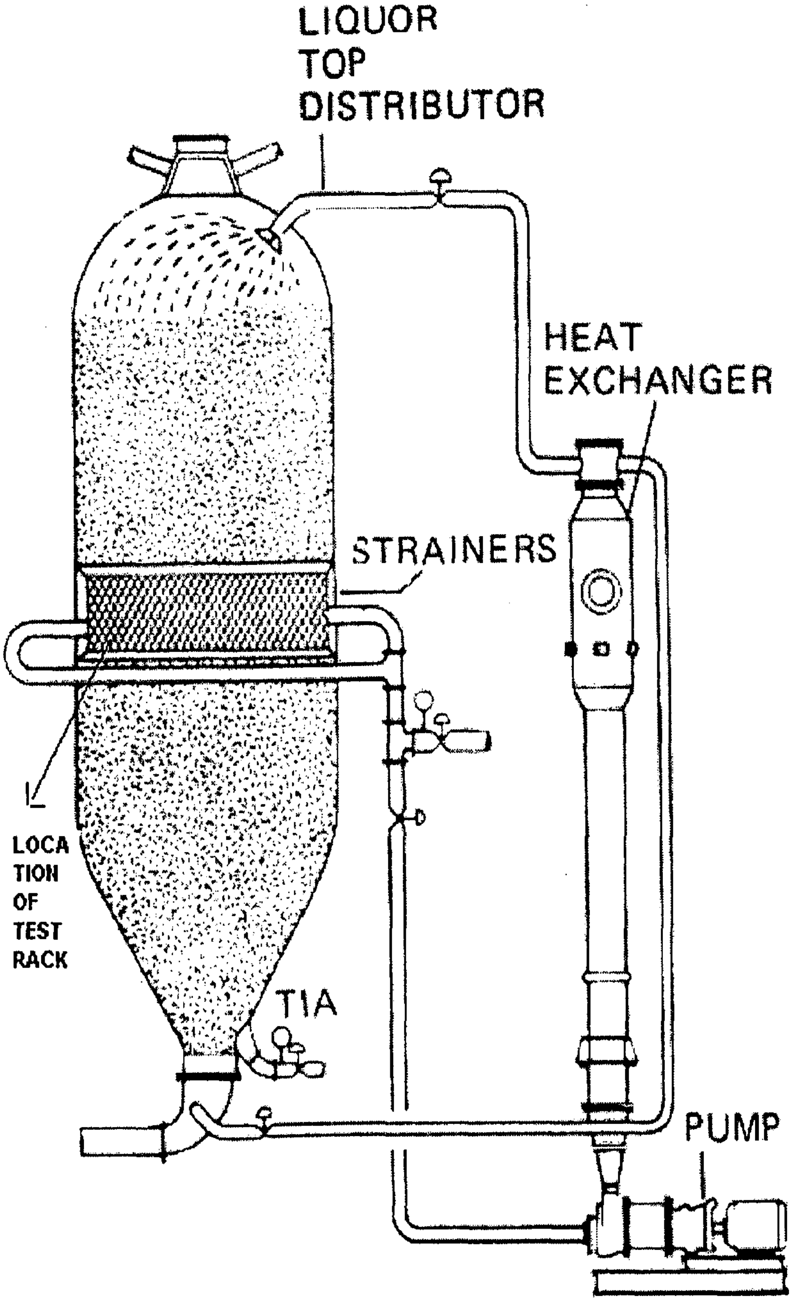
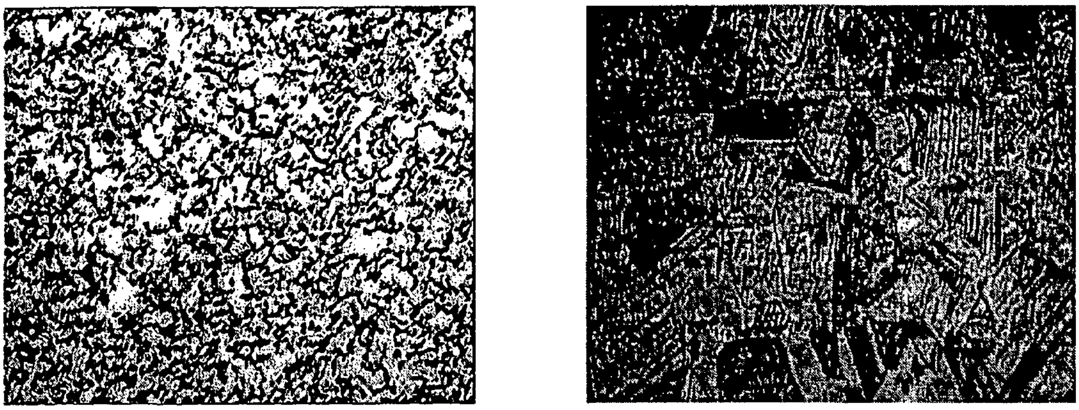
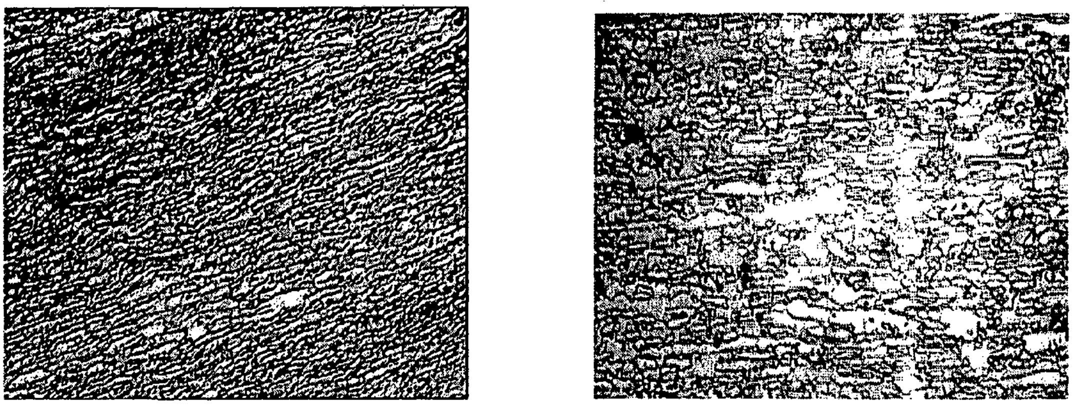


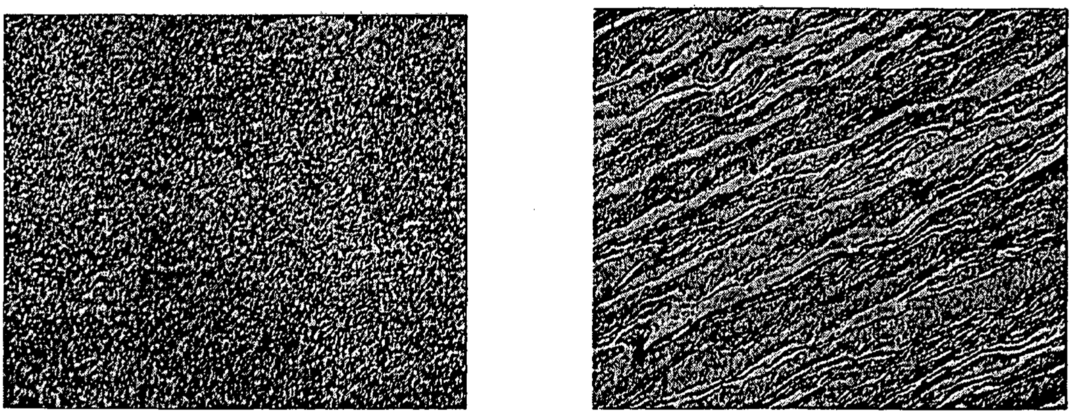
Fig. 4.1. : KRAFT BATCH DIGESTER WITH LOCATION OF TEST RACK



(a) MS (X200) (b) 304L (X500)

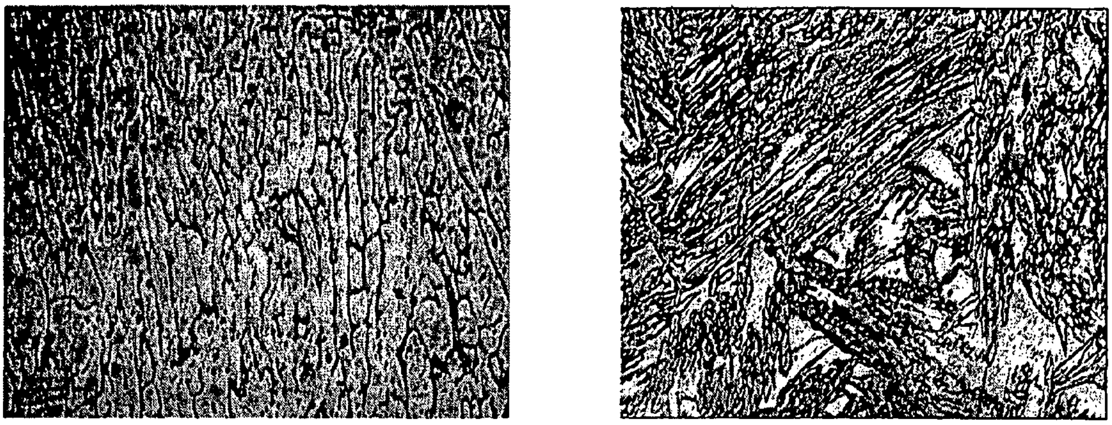


(c) 316L (X200) (d) 2205 (X500)

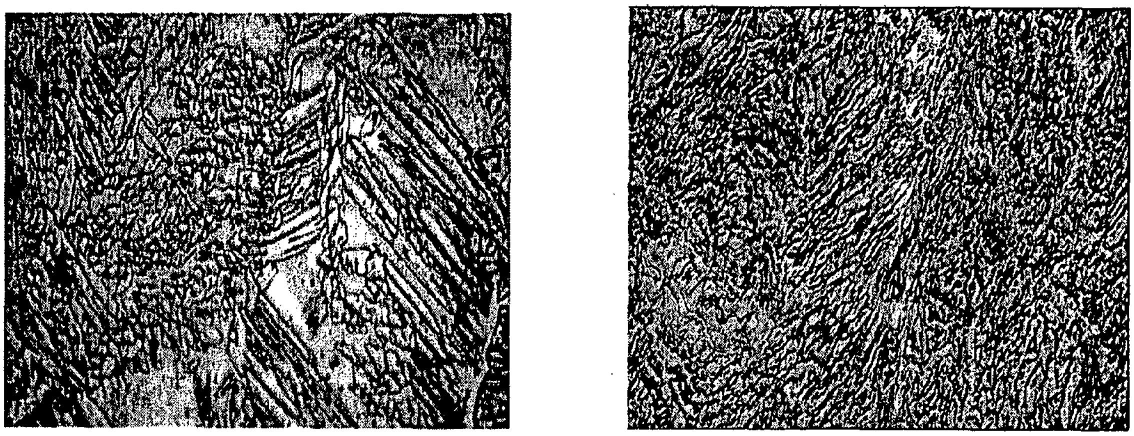


(e) SAF 2304 (X200) (f) LDX (X200)

Fig. 4.2. : MICROSTRUCTURE OF MILD STEEL AND STAINLESS STEELS (BASE METAL)



(a) 304L (X500) (b) 316L (X200)



(c) 2205 (X500) (d) SAF 2304 (X200)

Fig. 4.3. : MICROSTRUCTURE OF STAINLESS STEELS
(WELD METAL)

Chapter : 5

Corrosion Study of Steels in Peracid Bleach Solutions

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5.1. Introduction :

Paper industry is adopting non-chlorine chemicals e.g. hydrogen peroxide, peracids, oxygen, ozone etc. for bleaching with the aim of reducing pollution. The peracids namely per acetic acid (P_a), Caro's acid (P_x) and (P_{xa}) mixture of P_a and P_x, have been used as brightening agent and as activating agents for lignin. Chemically, P_a is CH_3COOOH with molecular weight of 76.05 and active oxygen as 21% whereas, P_x is peroxymonosulfuric acid (H_2SO_5) having molecular weight of 114.08 gram and 14% active oxygen content. Peracids are considered as effective for bleaching as peroxide and ozone but they are preferred over the latter two alternatives on account of their superiority with regard to associated safety hazards, ingredient costs and effluent loads, Bijan et al (23) and Liebergott (77). With the use of newer chemicals, their corrosive effect has also been studied. Thus Varjonen et al (136) while studying corrosion of Ti in peroxide found that $MgSO_4$ was not an effective inhibitor, in contradiction to Macdiarmid et al (79). In a similar study, Wyllie (148), sodium silicate and calcium nitrate were found to be effective inhibitor for pH ~12 but not EDTA. Been et al (19), doubts the effectiveness of calcium as inhibitor for Ti in peroxide media. Singh et al (116) studied the effect of chelants on the corrosivity of peroxide solutions. Pehkonen et al (92) studied corrosion of stainless steel in ozone and per acetic acid without Cl^-. Sodium sulfate was found to inhibit the corrosive effect of Cl^- in ozonated solutions. Singh et al (114) recently studied corrosive effect of per acids with acidic pH. Present work reports about the investigations performed on corrosion of mild steel and stainless steels in per acids of acidic as well as alkaline pH. The corroded samples were evaluated for localized and uniform corrosion for their possible use in per acid bleach plant.

5.2. Experimental :

5.2.1. Material :

Corrosion test coupons from plate samples of mild steel, austenitic stainless steel 304L, 316L and duplex stainless steel 2205 were selected for the weight loss test. Cylindrical samples from the rods of the above steels including 254SMO (except mild steel) were used for electrochemical tests. The compositions of the stainless steels are given in Table -2.1 and Table -2.2. All the test samples were solution annealed as per ASTM specification A240. Before exposure, they were polished up to 600 grit, then degreased using acetone solution and weighed in case of weight loss test.

5.2.2. Solutions :

Samples were exposed to peracid solutions namely P_a, P_x and P_{xa}, prepared as described earlier, Bijan (23). Accordingly, Pa was prepared by adding glacial acetic acid to hydrogen peroxide (1 molar ratio) containing 1 ml. of concentrated sulfuric acid as catalyst. The mixture was then warmed to 45^0C, held at this temperature for two hours, and stored overnight in a refrigerator to allow the mixture to come to equilibrium. P_x was prepared by adding sulfuric acid to hydrogen peroxide (one molar ratio) while maintaining the reaction temperature at $30\text{-}35^0C$. P_{xa} solutions were prepared by adding equal amount of P_a and P_x. NaCl was added in the solutions to get desired level of Cl^-. The pH of these solutions was kept 6.0, 7.5 and 9.0 by adding required amount of NaOH. Table -5.1 gives the test conditions and composition of the solutions.

5.2.3. Tests :

Immersion test and electrochemical polarization tests were conducted in the present study. In the immersion test, the steel coupons were exposed for duration of six months at room temperature. Each coupon was immersed in the solutions (Table-5.1) with the serrated washers for initiating crevice corrosion. During the test, % active oxygen (A.O.) and pH of the solutions were monitored and maintained each day. While pH did not change much (±0.1), decrease in %A.O. was compensated, to keep it within limit as per table-5.1, by adding requisite amount of peracetic acid, Caro's acid and mixture of both (P_{xa}). After the exposure, the corroded coupons were cleaned mechanically and by treating with cold solution of concentrated HCl with 50 gpl $SnCl_2$ and 20gpl $SbCl_3$(98).The coupons were then weighed for determining weight loss and corrosion rate and viewed under the microscope for estimating the extent of localized attack. The electrochemical tests E versus time, potentiodynamic, cyclic polarization and potentiostatic tests were conducted in P_a , P_x and P_{xa} solutions having pH=6.0 and 9.0, using potentiostat and polarization cell having five necks meant for a working electrode, two counter electrodes, a reference electrode (saturated calomel electrode in present case) and for gas purging. Open circuit potential (OCP), Corrosion (E_{corr}), pitting (E_p) and repassivation potential (E_c) were evaluated from these tests.

5.3. Results :

Corrosion rate was calculated from weight loss, determined by subtracting the weight of the corroded and cleaned coupons from its original weight. The extent of pitting was evaluated by measuring the maximum depth of pits formed on freely exposed surface and crevice corrosion was estimated by measuring the maximum depth of attack on occluded surface formed by serrated washers. Values of these parameters are given in Table -5.2. The OCP values for different cases was determined from E vs. time curves (Fig. 5.1 shows some E vs. time curves for SS 304L in pH = 9 solutions). The potentiostatic test (current versus time behavior at a pre-selected potential applied to metal electrode) (Fig. 5.2 shows some representative curves) was conducted to evaluate E_p which decides the vortex potential/current required for recording the cyclic polarization curves. The closed loop (Fig. 5.3) indicates that the localized corrosion has begun and that the downward curve therefore shows a weighted average of the alloys behavior in the base solution and the localized corrosion environment. Various parameters e.g. E_{corr}, E_p and E_c obtained from the electrochemical polarization tests are given in Table -5.3.

5.4. Discussion :

5.4.1. Corrosivity of solutions :

Table -5.3 shows that the OCP's of different steels are higher than their respective E_{corr}. E_{corr}/OCP of steels is higher for pH=6.0 solutions than pH=9.0. Also increase in Cl^- and decrease in pH decrease passivation range.

In all solutions without Cl^-, no pitting was observed, under microscope (6.5X), in samples after having undergone the potentiostatic test up to ~1300-1400 mv, indicating

E_p for such cases to be higher than this range. Exceptions were 304L and 316L in P_a solutions. However, in case of all steel samples, the anodic polarization curves in these solutions show a kink indicating onset of pitting around 1000-1050 mv in most cases. Cyclic polarization curves, in these cases, also show hysteresis behavior (Fig. 5.4) when polarization scan reverses to cathodic direction on reaching vortex potential. This is an indication that pits were formed and now have started passvating. Probably the pits formed were not observable under the microscope, due to their small size, but their effect is clear in polarization curves. P_x although overall seems less corrosive, yet the tested steels show lesser in this solution as compared to that in p_a and P_{xa} solutions, as appears from low expected values of $E_{c,}$ in former solutions. This observation needs further investigation.

In all the three solutions with Cl^- =1000ppm, all test samples except 254SMO showed significant amount of metal dissolution after the potential reaches near E_p or crosses E_p, while performing polarization test. In them, one observes non –passivating pits (Fig. 5.5), except for 2205 in P_x , pH=9.0 solution which is a case of material, more resistant than 304l and 316L, exposed to least corrosive solution. Even in this case, (E_c – E_{corr}) does not appear to be very high (< 190 mv), representing 2205 not very dependable material for handling these media. One observes higher degree of pitting attack on all samples, except 254SMO, exposed to these solutions in potentiostatic test at pre-selected potential ≥ E_p. In one such case, maximum pit depth of 40 μm was observed on 2205 in P_a solution of pH=9.0. Maximum resistance against localized corrosion of 254SMO is exhibited by the observance of passivating pits in all the tested solutions (Fig. 5.3 and 5.6). However, (E_c – E_{corr}) for this material, was measured to be < 172 mv when exposed to Pa solution (pH=6.0) with Cl^- , exhibiting its limited performance in handling most corrosive of the test solutions.

Thus in general, P_a solutions are most corrosive followed by P_{xa} and P_x solutions. This can be understood on the basis of (i) the prevailing reduction reactions which in turn affect the corrosion of materials and (ii) the nature of peracetic acid and peroxomonosulfuric acid. Following reduction reactions can be considered to be responsible for corrosion in these solutions :

$$CH_3COOO^- + 3H^+ + 3e^- \leftrightarrow CH_3COOH + H_2O \quad -(i)$$

$$2HSO_5^- + 2H^+ + 2e^- \leftrightarrow S_2O_8^{2-} + 2H_2O \quad -(ii)$$

From the reduction reactions (i) and (ii), 2 ions of CH_3COOO^- are responsible for consumption of 6 e^- whereas 3 ions of HSO_5^- are required for the same purpose. Thus corrosion of steel should be higher when exposed to peracetic acid as compared to the steel exposed to same amount of caro's acid.

Peracids (peracetic acid, CH_3COOOH, and peroxomonosulfuric acid, H_2SO_5) are considered to be more oxidizing than hydrogen peroxide due to the capability of former showing electrophilic/ nucleophilic character which is not shown by the peroxide, Thierry et al (123). Further a comparision of kinetics of several peroxyacids, Chang et al (29), shows that electrophilicity of CH_3COOOH is greater than that of H_2SO_5. Accordingly, peracetic acid, at a given pH, is likely to show higher corrosivity than Caro's acid.

5.4.2. Material Performance :

In P_x solutions with/without chloride, degree of corrosion resistance varies as 2205> 316L> 304L. This is due to (i) higher E_p in P_x solutions (except in case of pH=9.0 solution without Cl^-) (ii) passivation range for 2205 is maximum while that of 304L is lowest. (Except in case of pH= 6.0 solution without Cl^-).

In P_a and P_{xa} solutions without Cl^-, passivation range and E_p is highest for 304L and lowest for 316L/ 2205 (In contrast to observed higher resistance of 2205/316L than 304L against pitting). This has been predicted in an earlier report by Pehkonen et al (92). However, resistance against crevice corrosion is observed to be higher in case of 2205/316L than 304L. This aspect of corrosion behavior needs to be further investigated.

For P_a solution of pH=9.0 having Cl^-, 304L and 316L show a very low value E_p (potentiostatic test) and their E_c is likely to be around E_{corr}. For 2205, E_p and passivation range is slightly higher. Cyclic polarization curves show non passivating pits ($E_c< E_{corr}$) in all cases, thereby showing practically no resistance against crevice corrosion, except in case of 2205 exposed to P_x solution of pH=9.0. Only in case of 254SMO, exposed to peracid solution, one observes passivating pits hence $E_c> E_{corr}$. This, stainless steel also shows maximum passivation range among the tested metals. The above observations lead to conclude that stainless steels 304L and 316L show practically no resistance against either pitting or crevice corrosion, 2205 shows to some extent resistance against pitting only. Only 254SMO shows resistance against both pitting and crevice corrosion. In case of pH=6.0 solution, the performance is still poorer with none of the steels, except 254SMO, showing resistance against localized corrosion.

For P_{xa} solutions, resistance of 304L and 316L against pitting was checked only through potentiostatic tests. No cyclic polarization tests were performed on them since they were expected to show non passivating pits, like in the case of lesser corrosive P_x solutions. Since the performance of 2205 against localized corrosion in P_x solutions is observed to be unsatisfactory, this steel was not tested in case of more corrosive P_{xa} solutions. However, more resistant stainless steel 254SMO was tested in these solutions through potentiostatic and cyclic polarization test. Thus in P_{xa} solutions also, 304L and 316L are expected to experience localized corrosion while only 254SMO is expected to show satisfactory performance against both pitting and crevice corrosion. Performance of different tested materials, as compared to that in respective P_a solutions, indicates P_{xa} solutions to be, in general lesser corrosive than P_a.

Thus, in solutions with Cl^- = 1000ppm, in general resistance against localized corrosion is maximum for 254SMO followed by 2205, 316L and 304L. In solutions without Cl^- however 304L appears more resistant than 316L and 2205 on the basis of E_p but lesser resistant on the basis of E_c.

Corrosion rates of mild steel and stainless steels, determined on the basis of long term immersion tests, in general, show P_a to be most corrosive followed by P_{xa} and P_x. Extent of localized corrosion, as observed in these tests, also in most cases show similar grading on the comparative corrosivity of liquors.

The results of these tests show high degree of uniform corrosion on mild steel as is evident from corrosion rates (Table -5.2).So mild steel has to be ruled out as a material of construction for handling these media even at alkaline pH. In case of stainless steels, uniform corrosion is very low hence suitability of these materials has to be checked on the basis of localized corrosion .On the basis of degree of pitting and crevice corrosion, 304L and 316L show similar resistance while 2205 exhibit maximum resistance against corrosion attack. Site of welded joint does not show significant attack basically indicating the absence of stress related corrosion effects especially in view of the fact that the coupons were autogenously welded.

5.4.3. Material Selection :

A proposition is now given about the appropriate material for handling peracid solutions with Cl^- considering the results and analysis of immersion and electrochemical polarization tests. Thus on the basis of immersion test and criterion by Tuthill (134), 304L and 316L are not appropriate for P_a and P_{xa} solutions with pH=6.0 and 7.5. In case of pH=9.0 solution also, their use is doubtful in view of the electrochemical measurements. Immersion test show better performance of 2205, however, electrochemical tests indicate its vulnerability to localized corrosion in these solutions. Exhibition of resistance of Avesta 254SMO against localized corrosion in these solutions indicate this steel to be more appropriate. Further, 254SMO for P_x solutions with pH=6.0 and 2205 for solutions with pH=9.0 appear suitable on the basis of two tests. In case of peracids without chloride, considering the result of electrochemical tests alone, even where 316L could be an appropriate material, application of 2205 is more cost effective on the basis of its improved cost/strength ratio in addition to better corrosion resistance. Accordingly, a list of proposed suitable materials for handling peracids is given in Table -5.4.

Table - 5.1

Chemical Composition of the Peracid Solutions

Solutions	Chemical Charge (as % A. O.)*	pH	Chloride (ppm)	
			0	1000ppm
Caro's Acid	0.47 ± 0.05	6.0±0.1	P_x 1	$P_{x\,Cl}$ 1
		7.5±0.1	P_x 2	$P_{x\,Cl}$ 2
		9.0±0.1	P_x 3	$P_{x\,Cl}$ 3
Mixture of Caro's Acid + Peracetic acid		6.0±0.1	P_{xa} 1	$P_{xa\,Cl}$ 1
		7.5±0.1	P_{xa} 2	$P_{xa\,Cl}$ 2
		9.0±0.1	P_{xa} 3	$P_{xa\,Cl}$ 3
Peracetic Acid		6.0±0.1	P_a 1	$P_{a\,Cl}$ 1
		7.5±0.1	P_a 2	$P_{a\,Cl}$ 2
		9.0±0.1	P_a 3	$P_{a\,Cl}$ 3

* A . O. – Active Oxygen

Table - 5.2

Corrosion Parameters in Peracid Solutions (IMMERSION TEST)

Metal		Mild Steel				SS – 304L				SS – 316L				2205			
Solution	pH	Corrosion rate(mpy)	Pit depth(µm)	Crevice attack((µm)	Welded attack((µm)	Corrosion rate(mpy)	Pit depth(µm)	Crevice attack((µm)	Welded attack((µm)	Corrosion rate(mpy)	Pit depth(µm)	Crevice attack((µm)	Welded attack((µm)	Corrosion rate(mpy)	Pit depth(µm)	Crevice attack((µm)	Welded attack((µm)
Pa	6.0	34.7	145	80	-	0.43	80	70	nva	0.49	110	60	nva	0.09	nva	nva	nva
	7.5	27.1	60	60	-	0.53	120	60	nva	0.41	80	70	nva	0.04	nva	nva	nva
	9.0	22.8	nm	85	-	0.21	60	50	nva	0.21	70	55	nva	.002	nva	nva	nva
Pxa	6.0	32.5	205	180	-	0.32	60	55	nva	0.43	100	80	nva	0.08	nva	nva	nva
	7.5	26.9	110	110	-	0.16	100	60	nva	0.23	55	45	nva	0.02	nva	nva	nva
	9.0	22.1	60	60	-	0.37	55	50	nva	0.41	70	65	nva	0.03	nva	nva	nva
Px	6.0	21.9	nm	60	-	0.22	105	70	nva	0.26	100	65	nva	0.08	nva	nva	nva
	7.5	18.9	80	85	-	0.21	60	nva	nva	0.19	50	50	nva	0.03	nva	nva	nva
	9.0	18.0	nm	nm	-	0.16	60	50	nva	0.17	50	50	nva	0.02	nva	nva	nva

All solutions having chloride 1000ppm,
nm - Not measurable attack, nva -No visible attac

Table - 5.3

Electrochemical Polarization Test Results

pH		6.0											
Solution		Caro's Acid				P_{xa}				Peracetic Acid			
Cl^-	Metal	304L	316L	2205	254 SMO	304L	316L	2205	254 SMO	304L	316L	2205	254 SMO
nil	OCP	-	292.5	266	Not Tested	197.4	263.7	-	-	222.4	224.8	250.6	-
	E_{corr}	195	179.5	228.5		151	145	-	-	130.8	161.5	154	-
	Pass.	820	851.5	807.5		985	778	-	-	879.2	747.5	712.4	-
	E_p*	1015	1031	1036		1136	923	-	-	1010	909	866.4	-
	E_p**	>1300	>1400	>1400		~1300	~1325	-	-	1350	1350	>1300	-
	E_c	<665	-	-		<254	849	-	-	<491	814.6	865.3	-
1000 ppm	OCP	280.6	241.1	-		208.9	213.1	-	296.6	213.3	232.7	231.5	301.3
	E_{corr}	199.3	130	-		-	-		165.5	-	-	-	175
	Pass.	737.5	801.5	-		-	-	-	633.8	-	-	-	597
	E_p*	936.8	931.5	-		-	-	-	799.3	-	-	-	771.5
	E_p**	875	875	-		-	-	-	1050	<250	<250	375	1025
	E_c	npp	npp	-		-	-	-	556.8	-	-	-	<347
pH		9.0											
Solution		Caro's Acid				P_{xa}				Peracetic Acid			
nil	OCP	129.4	154.2	-	Not Tested	82.2	80.2	-	-	102.7	114	139.1	-
	E_{corr}	74.8	56.9	-		32.7	59.9	-	-	75.9	53.1	92.4	-
	Pass.	953.2	960.1	-		982.3	818.9	-	-	942.1	932.9	731.6	-
	E_p*	1028	1017	-		1015	878.8	-	-	1018	986	824	-
	E_p**	>1400	>1300	>1400		1325	1325	-	-	1400	1400	>1350	-
	E_c	309	263.7	-		864.6	914.2	-	-	931.4	870.2	?	-
1000 ppm	OCP	88.7	102.7	96.8		77.1	80.6	-	113.6	130.1	122	167.8	112.3
	E_{corr}	48.1	60.8	61.9		33.5	-	-	90.3	68.1	-	61.9	90.8
	Pass.	>869	951.2	963.1		146.2	-	-	930.7	323.8	-	338	739
	E_p*	>917	1012	1025		179.7	-	-	1021	391.9	-	400	829.7
	E_p**	875	875	1325		<100	175	-	1075	175	175	375	1075
	E_c	-	npp	<253		-	-	-	761.8	-	-	npp	782.6

Table- 5.4

Materials for Handling Peracid Solutions

Solution	Chloride=0ppm		Chloride=1000ppm	
	pH		pH	
	6.0	9.0	6.0	9.0
P_a	2205	2205	254SMO	254SMO
P_{xa}	2205	2205	254SMO	254SMO
P_x	2205	2205	254SMO	2205

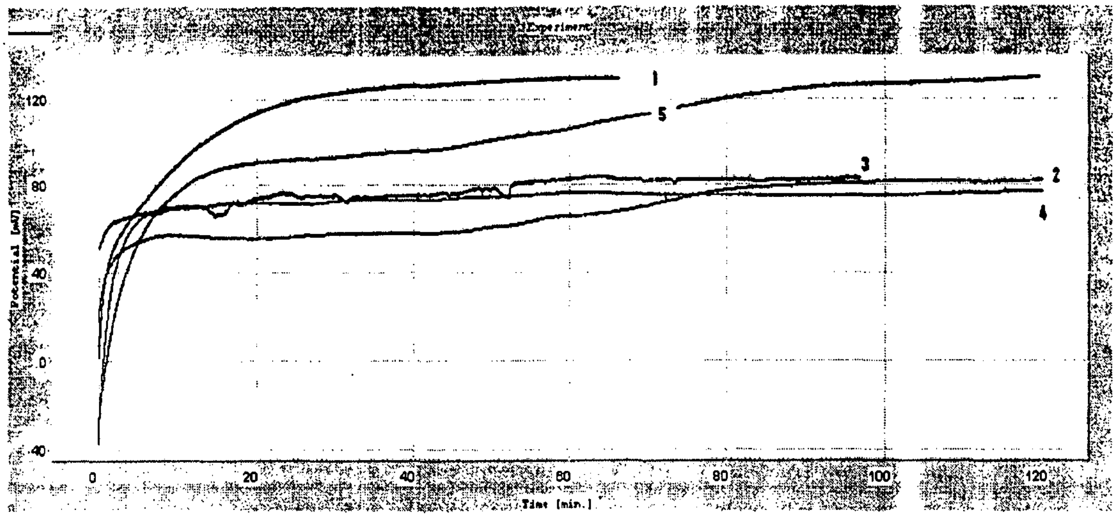

Fig. 5.1 : E vs. time curve for calculating OCP for stainless steel 304L in pH=9 Peracid solutions (1) P_x (w/o Cl^-), (2) P_{xa} (w/o Cl^-) (3) P_x (Cl^- ~1000 ppm), (4) P_{xa} (Cl^- ~ 1000 ppm) (5) P_a (Cl^- ~ 1000 ppm) solutions.

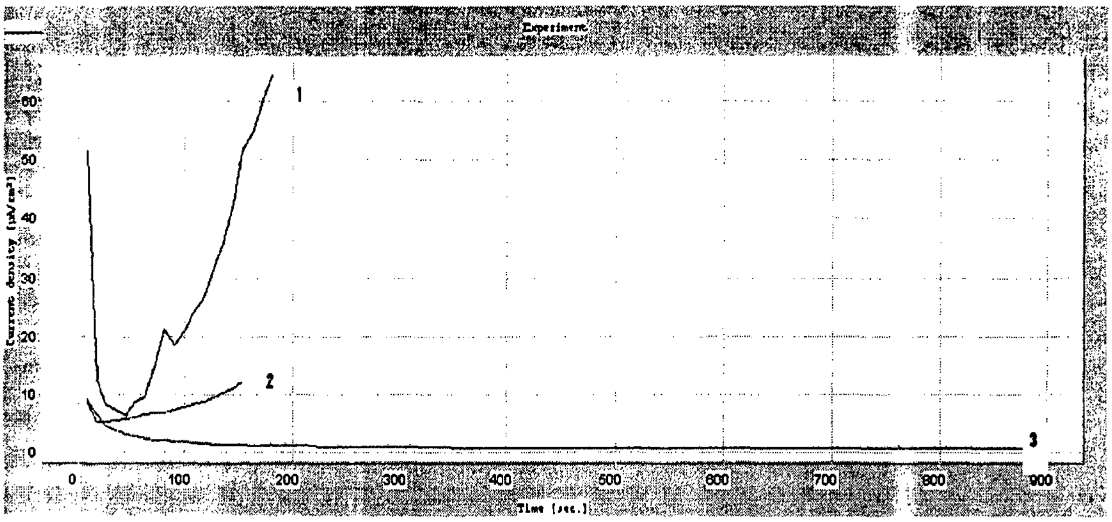

Fig. 5.2 : Potentiostatic Test (Current density vs. time curves) for SS-304L in P_a solution with pH=9 and Cl^- = 1000 ppm. Applied potential for Curve 1 = 300 mV, Curve 2 = 200 mV and Curve 3 = 150 mV (w.r.to SCE)

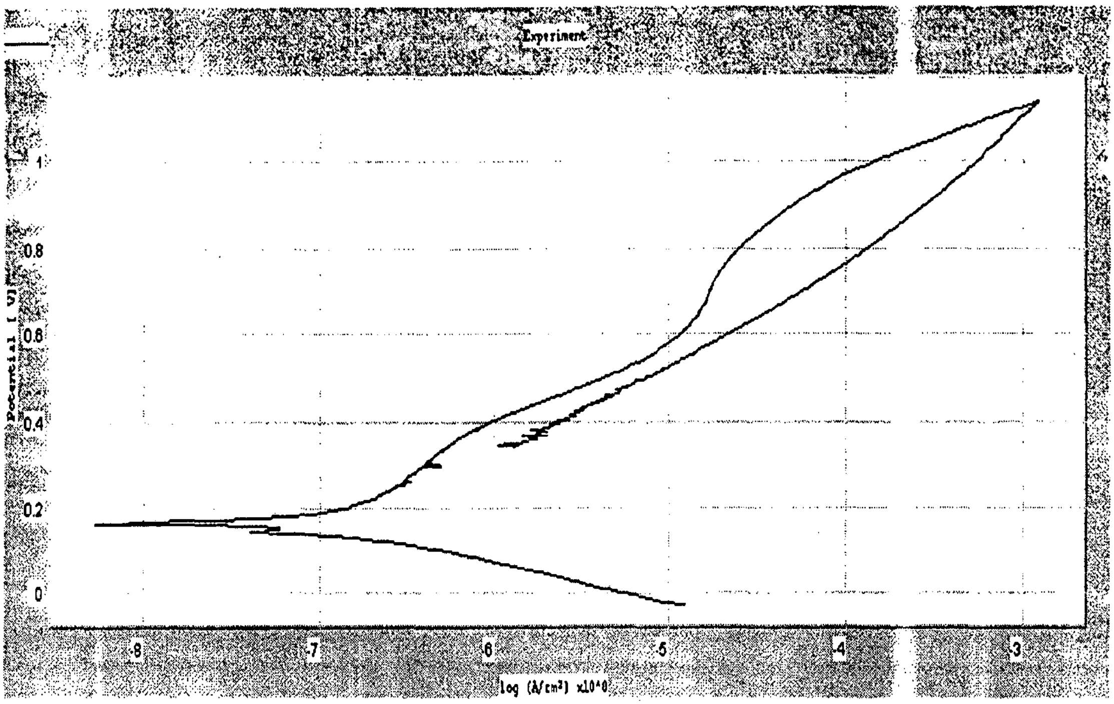

Fig. 5.3 : Cyclic polarization curve of Avesta 254SMO in P_a solution having pH = 6 and Cl^- = 1000 ppm.

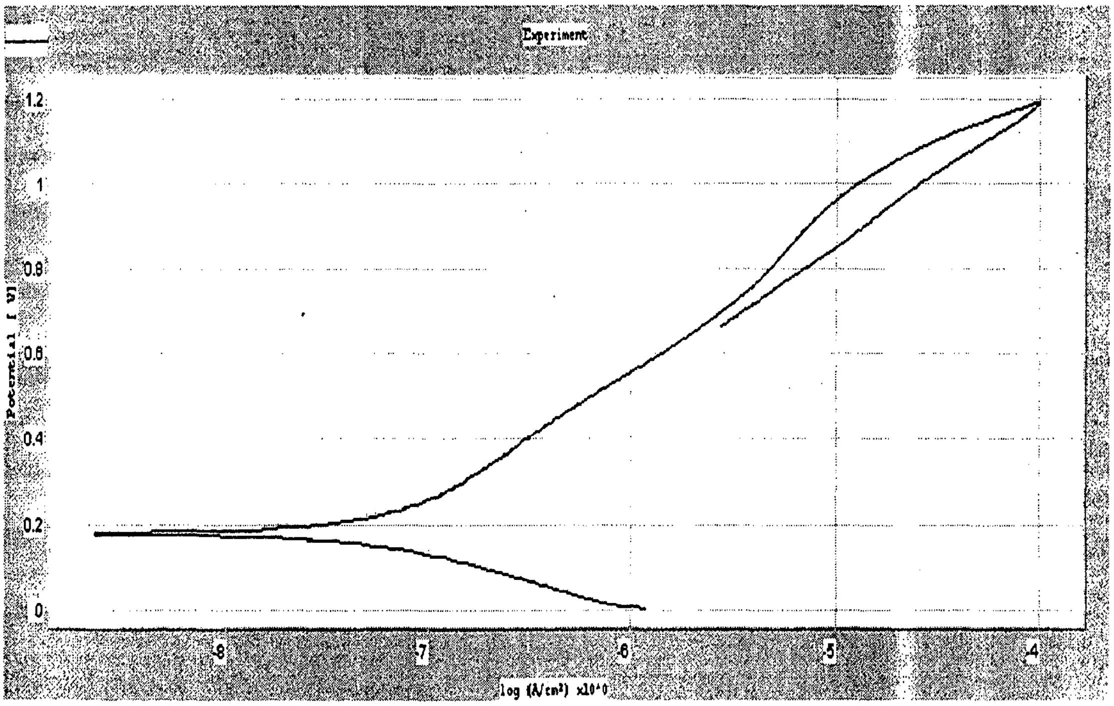

Fig. 5.4 : Cyclic polarization curve of SS 304L in P_x solution, without Cl^-, having pH = 6

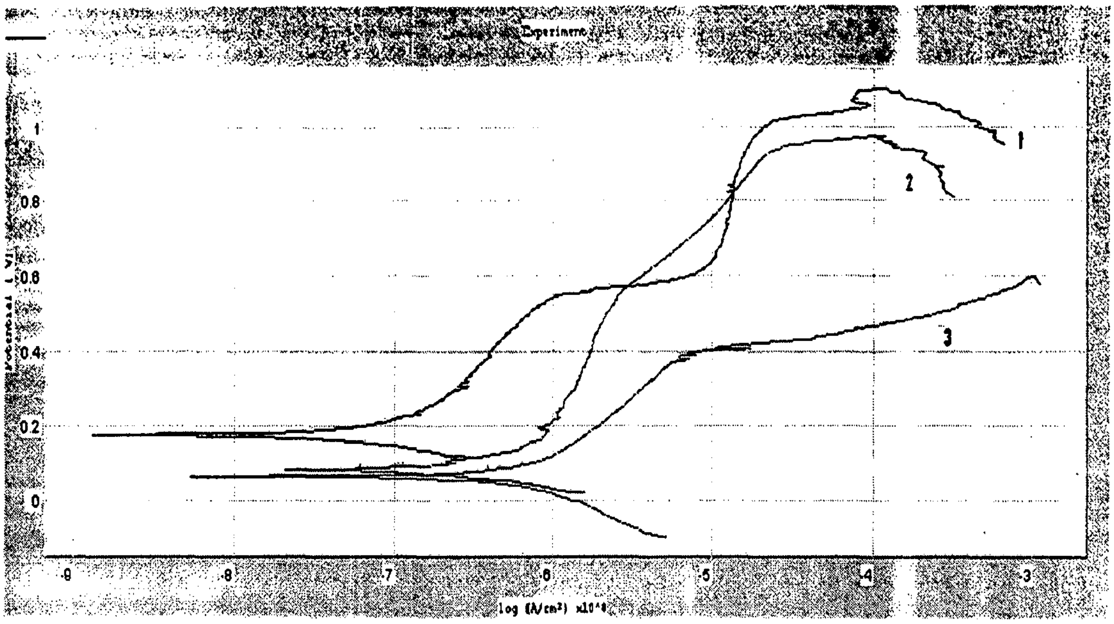

Fig. 5.5 : Cyclic Polarization Curves exhibiting non-passive nature of pits. Curve 1 and 2 : SS 304L and 316L in P_x solution having pH = 6, and Cl^- = 1000 ppm, Curve 3 : Duplex stainless steel 2205 in P_a solution having pH = 9 and Cl^- = 1000 ppm.

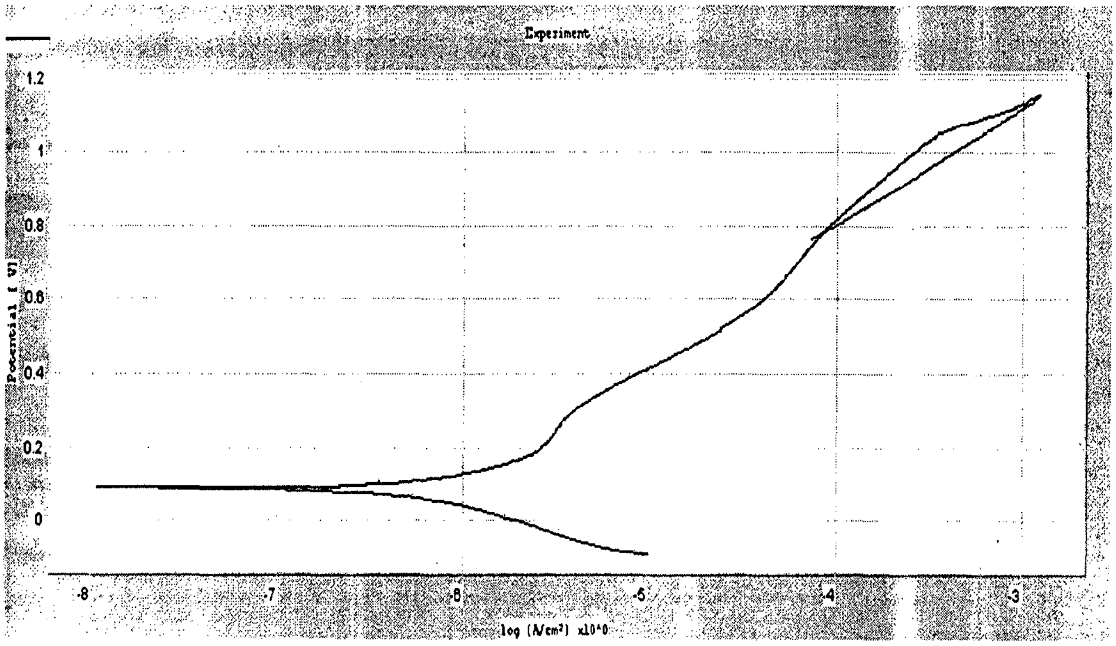

Fig. 5.6 : Cyclic Polarization Curve of Avesta 254SMO in Pa solution having pH = 9 and Cl^- = 1000 ppm.

Chapter : 6

Conclusion and Recommendations

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This chapter describes the conclusions drawn on the basis of laboratory and in-plant corrosion tests performed on steels in different corrosive media/conditions. The description has been given in the same order as the investigations described in chapters 3, 4 and 5. This is followed by the recommendations about the future work that should be done related to corrosion in pulping and bleaching section.

6.1 Corrosion in Solutions having Sulfur Compounds :

Corrosion test and their investigations in alkaline solutions having sulfur compounds (as described in Chapter 3) were undertaken in order to mitigate the corrosion problems faced by the digesters in the paper mills. To understand the problems from the basics of corrosion phenomenon, to begin with, E-pH diagrams for S-H_2O and Fe-S-H_2O systems were constructed and long term immersion test was performed in the alkaline solutions having sulfur compounds in proportion as normally observed in pulping liquor. Following conclusion can be drawn on the basis of analysis of above results:

1. The E-pH diagrams for S-H_2O system show that within the pH range likely to be observed for the pulping liquor, sulfur species present in the solution could be HS^- and to some extent S^{2-}, $S_2O_3^{2-}$ and SO_3^{2-} depending upon the potential, which will in turn be governed by the nature of material exposed e.g. mild steels or stainless steels

2. Fe-S-H_2O diagrams constructed for considering above sulfur species and concentrations. Thus if the liquor consists of $S_2O_3^{2-}$, 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 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 $S_2O_3^{2-}$ increases. It indicates that if the amount of $S_2O_3^{2-}$ is higher, the steel is likely to experience localized corrosion.

3. In long term immersion test, the metallic samples were exposed for six months in sulfide solutions. After the exposure, the corroded test materials were analyzed for uniform and localized type attack. The results of this test showed no significant corrosion on the tested stainless steels. Mild steel experiences uniform corrosion and crevice corrosion. Corrosion rates increased with the increased amount of $S_2O_3^{2-}$ content in the solution. This behavior becomes more pronounced in the presence of Cl^- ions.

4. Measurement of redox potential of 304L and 2205 in pH ~14 solution having sulfidity, as considered in E-pH diagram, shows that sulphur species near 304L electrode will be mainly SO_3^{2-} and $S_2O_3^{2-}$ while those near the 2205 electrode will be mainly HS^-. Accordingly, E-pH diagram of $Fe-S-H_2O$ shows that corrosion products forming on 304L will be pyrite or iron oxide and on 2205 it could be pyrrhotite/ troilite/ mackinawite depending upon the potential. Except mackinawite and troilite, other sulfides /oxide provide protection. This could be the reason for observing lesser corrosion rates in these stainless steels.

6.2 In-Plant Corrosion test of Steels in Digester of Paper Mill :

In - plant corrosion test was conducted by exposing different steels near the middle part in kraft digester of a nearby paper mill. The aim was to observe their performance against corrosion attack and to correlate same with conditions inside digester. After the six month exposure, the corroded coupons were analyzed for uniform corrosion, pitting, crevice corrosion and weld related attack. Following conclusions can be drawn on the basis of this analysis:

1. Varying degree of uniform corrosion and pitting is observed on different steels. Crevice corrosion is observed but is non measurable while no weld related attack has been observed on these coupons.

2. Mild steel is observed to experience maximum uniform corrosion. While pitting is maximum in case of 304L whereas duplex stainless steel do not show any pitting attack. The attack can be correlated with the amount of Cr and N present in steels. At these pH (~14), Mo content of stainless steel does not provide protection as it gets dissolved as MoO_4^{2-}.

3. For the lower sulfidity levels, mild steel may be suitable for cylindrical section of the batch digester. However, for cooking liquors with increased sulfidity and /or for parts of the digester which are affected by the erosive action of the liquors (e.g. bottom cone, liquor heater tubes etc.), one may have to opt for duplex stainless steels with Cr and N as preferable alloying elements.

4. An overall view of the corrosion attack indicates that all the materials, including mild steel, tested have sufficient corrosion resistance in the tested media. However, since the liquor composition is likely to change in future so as to have higher sulfidity, thiosulfate and polysulfide content because of advantages associated with high sulfide pulping, it is likely that mild steel will no more be considered suitable and one may have to opt for duplex stainless steels.

5. Findings of the present in-plant test could be compared with those of Swedish test. Comparisons of the results reveal the following. In general, the Swedish mills (having a sulfidity of ~40%) show a higher corrosion rate of mild steels (1.7-5.9 gm/m^2.cook with an average of 3.3 gm/m^2 cook). The amount of silicon in the tested mild steel varies between 0.06 - 0.1 %. In the present test, mild steel shows lesser corrosion rate (~0.74 gm/m^2.cook, considering ~ 500 cooks in the test duration of 6 months). This could be due to lesser Si content (~0.4%) in the mild steel and less (~19%) sulfidity in the digester liquor. Both these factors have been suggested to affect corrosion rate. Lesser sulfidity probably is also responsible for lower corrosion rates in case of stainless steels as compared to those in Swedish mill. Unlike the case of Swedish mill, mild steel does not show non uniform attack. Pitting is observed on SS-304L and 316Lcoupons while other coupons showed no visible pitting. The steel coupons do not show any crevice attack. Non- observance of crevice attack could be due to highly alkaline nature of the digester liquor.

6.3 Corrosion Study of Steels in Peracid Bleach Solutions :

Peracid bleach solutions may be potential non-chlorine chemicals for future bleach plants. It is therefore necessary to check as to how the metallurgy of bleach plant machinery will behave in the presence of peracids. Accordingly, electrochemical and weight loss test were conducted on steels in peracid solutions to investigate the corrosivity of the chemicals and performance of test materials against corrosion attack in the test solutions. Conclusion were drawn on the basis of results obtained from the electrochemical polarization tests and weight loss tests performed on mild steel and stainless steels 304L, 316l, 2205 and 254SMO in solutions of peracetic acid (P_a), caro's acid (P_x) and mixture of P_a and P_x (P_{xa}) having Cl^- upto 1000 ppm and pH between 6 – 9. These conclusions are given below :

1. OCP's of different steels are higher than their respective E_{corr}. E_{corr}/OCP of steels is higher for pH=6.0 solutions than pH=9.0. Also increase in Cl^- and decrease in pH decrease passivation range

2. Electrochemical measurements on stainless steels in per acid solutions with Cl^-, show high degree of localized corrosion whereas it is less severe in case of solutions without Cl^-. In general, corrosivity of the solutions increases in following order : $P_x < P_{xa} < P_a$.

3. Performance of mild steel is observed very poor against corrosion attack in these solutions. Stainless steel, tested in the present investigations, can be put in

following order of increased resistance against corrosion:

304L<316L<2205<254SMO.

4. Corrosion investigation in peracids, reported in chapter 5, concludes that peracetic acid is most corrosive whereas caro's acid is least corrosive. The comparison of performance of different test materials showed Avesta254SMO to be most resistant while 304L least resistant against corrosion attack.

5. It is concluded that Avesta254SMO is appropriate for handling Cl^- containing peracid solutions and duplex stainless steel 2205 for handling these solutions without Cl^- on the basis of degree of attack alongside comparison of cost vis-à-vis strength of different stainless steels.

6.4 Recommendations for future work :

The work carried on the corrosivity of sulfur containing solutions included immersion test at room temperature only while E-pH diagrams were constructed without considering polysulfides and for room temperature only. In order that the analysis of corrosion test results is complete and laboratory tests and E-pH diagram can correlate with the actual conditions faced by the material of construction of digester, following needs to be done further as an extension of this work:

- Electrochemical polarization (AC/DC) and Immersion tests of different steels in alkaline solutions having different sulfur compounds including polysulfides and with varying sulfidity. The test should be done at room temperature and at high temperatures upto 160°C, as observed in digesters globally.

- Construction of E-pH diagrams for $S-H_2O$ and $Fe-S-H_2O$ systems considering varying sulfidity and polysulfides as one of the sulfur containing compounds at temperatures varying up to 120°C and 160°C, because polysulfides are unstable beyond 120°C.

In the in-plant test, described in Chapter 4, coupons of different steels were fixed in digester nearby strainer, where the effect of erosion due to flow of pulp slurry at the end of the batch is not significant. Consequently, one of the reasons for not observing high corrosion even on mild steel coupon was assigned to almost absence of the effect of erosion. However, bottom cone of the digesters in the mills, where erosive effects are maximum, have been found to show excessive corrosion, hence a better idea about the suitable material of construction can be obtained if an in-plant corrosion test is conducted where the coupons of the steels are fixed in bottom cone. Similarly, for top part of the digester and other parts which are affected by caustic cracking, an in-plant test needs to be conducted where coupons are fixed in top and other parts of the digester that are prone caustic cracking.

Corrosion investigations in peracids, reported in the present thesis, are related to fixed amount of active oxygen and Cl^- content. Further, in the present tests only synthetically prepared solutions were considered for the test. In comparison to these conditions of the laboratory tests, the mill conditions will have varying amount of active oxygen and Cl^- content, also the corrosive media will be pulp slurry instead of just solution of

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