CORROSION INVESTIGATION ON MATERIALS IN BLEACH MEDIA OF PAPER INDUSTRY

A THESIS

Submitted in fulfilment of the
requirements for the award of the degree
of
DOCTOR OF PHILOSOPHY

By

GAYAAN SINGH

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Candidate's Declaration

I hereby certify that the work which is being presented in the thesis entitled "**Corrosion Investigation on Materials in Bleach Media of paper industry** " in fulfillment of the requirements for the award of the degree of Doctor of Philosophy and submitted in the "**Indian Institute of Technology – Roorkee**" is an authentic record of my own work carried out during the period from August 1998 to June 2003 under the supervision of Dr. A.K.Singh.

I have not submitted the matter presented in this thesis for the award of any other degree of any other university.

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This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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ABSTRACT

The thesis starts with introducing the process of paper making in general and discussing the process conditions with a view to have an idea about the corrosivity of the liquors and possible candidate materials of construction. Emphasis has been given on the bleach plant as it is widely believed to be most corrosive section in a paper mill. In this endeavor, a review of the literature has been done and presented dealing with corrosion aspects and material performance in bleach plant and related liquors. The next chapter deals with the experimental aspects of the various laboratory and in-plant tests done as a part of present thesis work. Next three chapters discuss and analyse the work of the present thesis. The work presented in this thesis pertains to the corrosion behavior observed on commercial grades of mild steel and stainless steels in liquors of bleach media of paper industry. Besides this, attempt has been done to explore the mechanism of corrosion in the existing and future bleach plant conditions. Attempt has also been made to suggest possible materials of construction. The studies presented in this thesis involved laboratory and in-plant tests. The last chapter deals with the conclusion and recommendations on the work that needs to be done in future The summary of the thesis is presented now in the following paragraphs.

CHAPTER-1 : Introduction

This chapter introduces briefly about paper making process and gives an account of corrosion prevailing in various section of paper mill. Bleach plant, being the more corrosive section, has been dealt with in greater detail. A survey of the literature has been done to show various attempts made, in past, for controlling corrosion in bleach

plant by appropriate material selection or otherwise. The prevailing process condition in bleach section indicate it to be most corrossive and the losses are maximum in bleach washer. It is mainly due to the application of oxidizing bleaching chemicals e.g. chlorine, hypochlorite etc. But mills are finding it hard to use them more as these chemicals produce carcenogenic compounds. As such mills are either decreasing their use of chlorine and/or switching over to alternative bleach chemicals which are eco-friendly. As such elemental chlorine free (ECF) and total chlorine free (TCF) bleaching processes are finding wider acceptability. Accordingly, chlorine dioxide, hydrogen peroxide, peracids, ozone etc. are being projected as the futuristic bleach chemicals. Whereas the ECF bleaching uses chlorine dioxide as major bleach chemical, the TCF process, bleaches pulp without using chlorine dioxide. It uses peracids, peroxide, ozone, enzyme etc. as bleaching agents. Switching over from conventional bleach chemicals to newer chemicals is likely to affect the corrosivity of the liquor and as such suitability of conventional materials, for bleach plant fabrications, has become questionable. Consequently following was proposed for investigation-

1. To conduct in-plant corrosion tests, in chlorination (C), chlorine dioxide (D) and C_D washers, on advanced grade of stainless steels e.g. 317L, 904L, 2205 and 254SMO including conventional SS316L to investigate the extent of corrosion attack, its correlation with process parameters, suitability of the test materials and economic viability in replacing conventional material with the tested ones.

2. To test the candidate materials in chlorine dioxide solutions simulating to those of D-washer by electrochemical polarisation and long term immersion tests. The aim was

to understand the mechanism of corrosion and effects of changing the process variables on the materials performance.

3. To conduct the electrochemical polarisation and long term immersion tests on possible materials of construction e.g. mild steel and stainless steels 304L, 316L, 317L and 2205 in peracid solutions simulating to those likely to be observed in peracid bleach plant stage. The aim was to understand the corrosivity of peracid solutions, suitability of the test materials and mechanism of corrosion in these solutions. Peracids are being projected as important bleaching chemical for future bleach plants using ECF and TCF bleaching sequence.

CHAPTER:-2 Experimental Procedure

Various experimental techniques, brief technical discussion of experimental equipment's and formulae used have been described in this chapter. For mill tests, the coupons of different stainless steels were obtained and their surface preparation was done as per ASTM specification. The coupons were mounted on the racks and fitted into vat, on washer drum and near shower pipes of bleach washers so that they get exposed to liquid, wet/dry and gas phase respectively. The coupons were collected after six months of exposure and were analysed for corrosion rate and extent of localised corrosion attack.

In the electrochemical polarisation tests, cyclic polarisation, E vs time curve and potentiostatic (current vs time curve) were performed on cylindrical samples of SS-304L, 316L, 317L, 254SMO and duplex stainless steel 2205. Electrochemical polarisation techniques were used to investigate the corrosion mechanism and effect of process variables on corrosion behavior of steels. Experiments were also conducted to find critical pitting and critical crevice temperatures (CPT and CCT respectively) for the tested stainless steels to compare their performance with their respective CPT and CCT values alongside PRE numbers.

CHAPTER :- 3 In-Plant Corrosion Investigations

This chapter deals with the results of in-plant corrosion tests on stainless steels exposed in different bleaching stages. The in-plant tests were conducted in two kraft pulping mills. The bleaching sequence for mill A was $CE_1D_1E_2D_2$ and for mill B, it was C_DE_0HED. Autogenously welded corrosion coupons of austenitic (316L, 317L, 904L and 254SMO) and one duplex stainless steel 2205 were exposed for approximately 200 days in bleach washers inside the vat (liquid media) and hood (gaseous media) in both mills. Additionally, racks of the test coupons were also exposed on the drum (wet/dry media) in mill A. The exposed coupons after the mechanical/chemical cleaning were weighed to calculate corrosion rate and analysed for the extent of pitting , crevice attack and weld related corrosion.

The corrosion rate data and analyses of the corroded coupons indicated the gaseous media of C washer to be most corrosive. The corrosivity is lesser in D-washer's liquid and gaseous media. The corrosion environment experienced by the coupons by alternative exposure to gaseous and liquid media in D washer is still less harmful but similar to that experienced by the coupons in the liquid media of C washer. Alternate exposure in liquid/gaseous media in C washer is least corrosive in mill A. in mill B, C_D washer is likely to pose more corrosion problems than D washer to the tested materials.

Various stainless steels can be put in the following order of increasing resistance on the basis of degree of uniform and localised corrosion attack :

316L< 317L < 904L≤ 2205 < 254SMO

The above order of corrosion performance has also been compared with that obtained on the basis of pitting resistance equivalent (PRE) no. and critical pitting temperature (CPT) and critical crevice temperature (CCT). The importance of alloying elements N and Mo in providing the localised corrosion resistance has been observed. On comparing corrosion attack, mechanical strength, cost and fabrication aspects, duplex stainless steel 2205 appears to be an appropriate material for most media with a few exceptions.

CHAPTER:- 4 Corrosion Investigations in Chlorine- dioxide Solutions

In this chapter, the electrochemical and weight loss test results have been discussed. The electrochemical tests (E vs t, cyclic polarisation and potentiostatic) were conducted on stainless steel 316L, 317L, 2205 and 254SMO in chlorine dioxide solution simulating to those of D-washer. The pH of the solutions 3 and 5 and Cl^- in them varied from 500 to 3000 ppm. Long term immersion tests on the autogenously welded coupons of above stainless steels were also conducted in chlorine dioxide solutions of similar compositions. Both the above tests were conducted at room temperature. After the exposure, the coupons were analysed for the uniform corrosion, degree of pitting and crevice attack and weld related attack. Only crevice attack was found on the steels. No pitting or weld related attack was observed. This was different from the observations of the in-plant tests and may be attributed to more aggressive conditions due to comparatively higher temperature of the liquors in the mills. On the basis of various electrochemical equations, thermodynamic data and the consequent E-pH diagram, it was concluded that the corrosion of stainless steel samples in chlorine dioxide solutions is governed by the reduction of ClO_2, ClO_2^- and ClO_3^- mainly. In general, the resistance to uniform and localised corrosion of the tested stainless steels was in the following order : 316L< 317L < 904L ≤ 2205 < 254SMO. A comparison of degree of corrosion attack as observed in laboratory tests has been made with that observed in the in plant tests. Consideration of the corrosion performance alongside the mechanical properties, fabrication aspects, and material cost, alloy 2205 would be the most appropriate material of construction for the D-stage bleach plant machinery. Alloy 254SMO may be a good option but is likely to be a cost effective option.

CHAPTER:-5 Corrosion Studies in Peracid solutions:

In this chapter, the electrochemical and weight loss test results in peracid solutions have been discussed. Peracids are among the potential non-chlorine bleach chemicals for paper making process. The peracids considered in the present investigations are peracetic acid (P_a), Caro's acid (P_x) and mixture of the peracetic and Caro's acid (P_{xa}). The electrochemical polarisation tests (E vs t, cyclic polarisation and potentiostatic) were performed, at room temperature, on mild steel, stainless steels 304L, 316L, 317L, and 2205 in peracid solutions simulating to those observed in peracid bleach washer. The pH of the solutions was fixed at 5 and Cl^- content was varied from 0 to 2000 ppm. The long term immersion tests on above steels, in above mentioned solutions, were conducted at room temperature and at 50^0 C. After the exposure, the samples were analysed for uniform corrosion, pitting, crevice attack. Results of both the tests indicated peracitic acid (P_a) is most corrosive followed by P_{xa} and P_x (Caro's acid). With increased level of Cl^- concentration, localised corrosion attack increases on stainless steel samples. Mild steel showed extremely high level of uniform corrosion, hence is not suitable for handling these liquors. Stainless steel showed crevice attack but not pitting. Among the stainless steels, SS-304L can be used for handling liquors under lesser corrosive conditions (P_a solution without Cl^-, P_x and P_{xa} solution with Cl^- up to1000 ppm at least up to 50^0C). SS-316L for more corrosive conditions (P_{xa} having Cl^- beyond 1000 ppm for temperature up to 50^0C, P_a solution up to1000 ppm Cl^- at room temperature). For still more corrosive conditions 317L or 2205 may be used.

CHAPTER:- 6 Conclusions and Recommendations:

Conclusions drawn on the basis of work done in mill as well as in laboratory are discussed in this chapter. The mill test showed the gaseous media of C washer to be most corrosive. Other washer media show varying degree of corrosivity. Replacement of chlorine by chlorine dioxide seems to increase crevice corrosion as compared to a washer having only chlorine. Performance of the test materials have been compared on the basis of extent of uniform and localised corrosion. On comparing corrosion attack, mechanical strength, fabrication aspects and cost, 2205 turns out to be appropriate

material for most media except in some environment of mill A namely (i) C-hood where 654SMO is expected to perform better (ii) D-vat where 254SMO seems a better choice.

The laboratory tests in chlorine dioxide indicated, the corrosion on stainless steel samples is governed by the reduction of ClO_2, ClO_2^- and ClO_3^- mainly. The corrosivity of the solution increase by the reduction of pH and increasing concentration of ClO_2 and Cl^-. In electrochemical polarisation tests, stainless alloys 316L and 317L showed susceptibility to localised attack in these solutions whereas alloys 2205 and 254 SMO remained passive. In the long term immersion tests, these alloys exhibited only crevice attack but no pitting. In general, the tested stainless steel show degree of corrosion resistance in the following order : 316L< 317L < 2205 < 254SMO. The comparison of corrosion resistance alongside the mechanical properties, fabrication aspects and material cost, indicates alloy 2205 to be the most appropriate material of construction for the D-stage bleach plant machinery. The laboratory tests in peracid solutions indicated mild steel can not be used in these solutions, even at room temperature. For the lesser corrosive solutions, SS-304L may be useful material but for more corrosive solution 317L or 2205 is better option.

This thesis reports corrosion investigations carried on stainless steels in D and C_D stage of mills. As an extension of this work, laboratory corrosion tests are required to be conducted in liquors having varying amount of chlorine (C) and chlorine dioxide (D) to see dependence of corrosivity of liquor on the extent of replacement of chlorine by chlorine dioxide and the performance of the candidate materials in these liquors. This will be a useful data to mills in material selection while considering partial replacement

of chlorine by chlorine dioxide. Further, to corroborate these findings and to demonstrate them in actual plant conditions, an in-plant tests in mills having bleach plant with up to 90% chlorine dioxide substitution should be done to find out the corrosivity of the media and suitability of the material in these washers.

Corrosion investigation in peracids, reported in presented thesis, pertains to solutions at low pH. However, a pH range of 5-9 has been suggested for peracid bleaching. Accordingly, it is also equally important to investigate the corrosion effects in peracids at higher pH's involving the same grades of steels and stainless steels as tested for lower pH solutions. It is also necessary to peform electrochemical tests at higher temperatures (upto 50C) in peracid solutions. Peracids have been suggested for use as delignification agent, activating agents for lignin before oxygen and peroxide stage, as a replacement for chlorine and in the oxidation stage as a replacement for hypochlorite and chlorine dioxide. It is therefore also important to perform corrosion investigations in solutions having peracid as one component and one of the oxygen, chlorine, hypochlorite and chlorine dioxide as the second component to see the effect of substitution on corrosivity of the solutions and material performance of the candidate materials.

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5. Corrosion Studies of Steels in Peracid Bleach Solutions

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CORROSION is the destructive attack upon a metal by its environment and it is probably the commonest electrochemical phenomenon that is experienced in day- to-day living. Common examples of corrosion include the rusting/staining of iron and steel, tarnishing of silver and copper, blistering and bubbling of chromium plating and paint work on cars, discharge of colored water from domestic taps and many similar occurrences such as seizure of nuts and bolts, frequent painting of steel furniture etc. In industry, corrosion is serious in that it can lead to weakening of metal structures, premature failure of plant, pollution of process liquors and contamination/decoloration of products. Corrosion is an insidious phenomenon which adversely affects those properties of metal e.g. strength, ductility, composition etc, that are to be preserved, as a result of chemical or electrochemical reaction with surrounding environment. The losses due to purely mechanical forces are not called corrosion but are known as wear, fretting etc.. In some cases, chemical or electrochemical attack may be accompanied by these mechanical forces and are described as stress corrosion cracking, corrosion-erosion, corrosion fatigue or fretting corrosion. Such disease of metal affects the production by unwanted shutdowns due to sudden failures, excessive leakage etc. 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. Unexpected failures, due to corrosion, of pressure vessels have resulted in to loss of life thus making the working environment less safer. Consequently industry has lost considerable amount of money on account of corrosion. Several studies 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 (1-6). The report of the committee on corrosion and protection by T.P. Hoar in 1971 concluded that the corrosion in the United Kingdom was 3.5% of GNP (1). Battelle and the Specialty Steel Industry of North America estimated in 1996 that the annual cost of metallic corrosion in the United States economy is approximately US $300 billion (1). The report estimates that about one-third of the cost of corrosion (US$100 billion) is avoidable and could be saved by broader application of corrosion resistant materials and application of proper anti-corrosive methods. This forced the scientists and technologists to develop necessary preventive measures against corrosion and thereby reduce the revenue loss.

Paper industry is no exception to corrosion problems. Corrosion problems in this industry are more serious, as it is using wide variety of corrosive chemicals like chlorine, chlorine dioxide, sodium sulfide, caustic soda, etc. and generating several 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 type (pH~1-2). Additionally, the process involves high pressure as well as high temperatures in some stages. Corrosion is responsible for huge losses in terms of repair and replacement. A survey conducted by the National Bureau of Standard (U. S. department of commerce) in 1984 estimated annual cost of corrosion in American pulp and paper industry at $ 525 -1170 million or 4.4% of the value of the goods produced by the industry (2,3). Similar survey in 1989 showed the corrosion cost $ 300 millions by Canadian pulp and paper industry (3). NPC (National Productivity Council) in 1985 has reported that the loss due to corrosion at Rs.160 millions by Indian paper industry (3,4). Moreover, human costs associated with catastrophic failure of corrosion-damaged equipment's are beyond measure. Chandler (5) showed that every year several billion dollars are spent to repair and maintain reinforced concrete structures.

The paper industry is undergoing rapid changes in the process to meet the demands of market and government regulations. Developments are aimed at improvement in paper quality, reduction of manufacturing costs, more environmental friendly and energy efficient paper production and introduction of new and modified paper products. The changes coming up in production of the bleached Kraft pulp includes reduction in overall water use, recycle of as much of the bleaching effluents as possible, more delignification during the pulping stage, reduction and elimination of chorine and its compound 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, it therefore, is likely to alter the corrosion vagaries in industry.

The bleach section of the paper industry is most corrosive accounting for roughly 50% of total corrosion cost. Further bleaching process is undergoing significant changes to make it more environment friendly and to meet consumer demands on paper. It is important to investigate the effects of these changes on the corrosion behavior of materials. As such, this dissertation deals with studies carried on corrosion and its control by suitable measures in changed strategy of bleach plant. The work presented in this thesis, have been performed in Indian mills as well as in the laboratory by simulating the environment as prevails in bleach plant. To introduce the reader with subject of the thesis, a brief is given about paper making process. This is followed by a short general description of corrosion then a review of corrosion in paper industry. Finally, justification of the problem with objectives has been outlined.

1.1 Paper Making Process :

Paper is an important material in the economic development of a country. It is used by the world community to satisfy various needs. It provides an essential component in the process of business and communication through newspapers, periodicals, magazines and books. It contributes to industrial development with improved packaging for protection and conservation in transport and storage of goods. In fact, the extent of paper usage is a parameter 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. In order for fibers to be useful to paper making, they must be conformable i.e. capable of being matted into uniform sheet. They must also develop strong bonds between fibers at the point of contact. Paper making process essentially involves the pulping of wood/ non-wood species, which is followed by bleaching, stock preparation, paper making and finishing (Fig.1.1) (7,8). Recovery of chemicals from spent cooking liquor from the pulping process and realization of energy from incineration of organic chemicals are accomplished in a separate section called recovery section. Pulping is the process by which wood is disintegrated into individual or small agglomerate fibers. This can be done mechanically, thermally, chemically or by combination of these treatments. The Kraft process (chemical pulping) is most popular among the pulping processes. Pulping is carried out in a vessel called 'digester', by chemical reaction between lignin and (constituents of wood chips) and cooking liquor at a pressure around 6.5 -7 Kg/cm2 and temperature 165 -170°C. The cooking liquor is composed of sodium hydroxide and sodium sulfide in the approximate proportion ($5\ NaOH + 2Na_2S$), $Na_2S_2O_3$, Na_2SO_3 etc. and has pH of 13.5 to 14.0. The resulting pulp is transferred to 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 sodium hydroxide ($NaOH$) which is recirculated to form cooking for pulping. Organic constituents from black liquor are burnt in recovery boiler to recover energy. The washed pulp is sent to bleaching section for brightening the pulp by removal of remaining lignin and other coloring material. Bleaching is generally carried out in a multistage process. Commonly used bleaching stages are chlorination (C), alkali extraction (E), hypochlorite (H), chlorine dioxide (D), peroxide oxygen (O), ozone (Z), peracetic acid (P_a) 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. This mixture, called stock is passed over paper machine comprising of head box, fourdrinier, couch roll, suction roll, press rolls and lastly dryers and calendering for making the final product paper.

1.2 Corrosion :

Corrosion has been defined in several ways by different authors (9,10). It can be satisfactorily described as an "Undesired chemical and/or electrochemical reaction on materials with its environment that leads to destruction or deterioration of material resulting in the reduction of their economic value".

1.2.1 Types of Corrosion (11) :

Various forms of corrosion have been observed on materials exposed to different environment and operating conditions. The are schematically depicted in Fig.1.2 and briefly discussed in following paragraph:

1.2.1.1 Uniform Corrosion :

When a material is attacked uniformly over its surface, due to the surrounding media (Fig.1.2 a), the type of attack is known as uniform or general corrosion.

1.2.1.2 Bimetallic Corrosion (Galvanic corrosion) :

It is a common practice in industry to use two different type materials in contact with each other. In such cases one of the materials may be anodic while other may be cathodic relatively. The two materials form a galvanic cell in which anodic material preferentially corrodes. This is called as bimetallic corrosion (Fig.1.2 b).

1.2.1.3 Pitting (Pinhole attack) :

It is an extremely localised type of attack resulting into formation of pits over metal (Fig.1.2 c) and its perforation in extreme case. The chances of pitting are more if pH is lower, temperature of the media higher and media having more oxidising chemicals. References (12-14) are some of the studies related to electrochemical aspects of pitting, prediction of pitting and its control.

1.2.1.4 Crevice Corrosion :

This type of corrosion is experienced by the part of materials where liquid media gets trapped because of formation of crevices (Fig. 1.2 d) (15). This a particular form of concentration cell corrosion and is more of concern if media is acidic and Cl^- containing.

1.2.1.5 Weld Decay (Inter Granular Corrosion) :

Every material consists of large number of areas on microscopic scale which differ in composition, structure or orientation. These are known as grains. The interface between the grains is called 'grain boundary'. The area in the vicinity of the grain boundaries are sometimes corroded preferentially ((Fig. 1.2 e), thereby weakening the material as a whole. This in turn is due to depletion of Cr (<12%) in the grain boundary area as a consequence of formation Cr23C6 when stainless steel is heated beyond about 550C. It is called as inter granular corrosion(IGC). Ref. 16 is among the many references related to inter-granular corrosion.

1.2.1.6 Stress Corrosion Cracking :

This type of attack occurs when a material under stress is exposed to a specific corrosive media. The attack is manifested in the form of cracks which propagate inside material (Fig. 1.2 f). For material–environemnt combination susceptible to stress corrosion cracking, please refer to reference 11.

1.2.1.7 Erosion Corrosion :

It is caused by the erosive action of the flowing liquids and gases. The wearing action removes the protective oxide film causing fresh metal surface to expose to corrosive liquor thereby increasing the attack ((Fig. 1.2 g),. Pipe systems, bends, tees, pump impellers etc. are exposed to the vagaries of this type of attack.

1.2.1.8 Corrosion Fatigue :

This type of attack occurs when material is subjected to recurring stresses in the presence of corrodent (Fig.1.2 h),. Thus it is similar to SCC except that stress is cyclic in nature. Thus drum washers, driers in the paper industry are susceptible to corrosion fatigue.

1.2.2 Corrosion Testing :

Evaluation of corrosion on a material in given environment is required so as to (i) predict the probable life of equipment or a part of machinery (ii) selecting the optimum alloy and minimise corrosion losses (iii) compare the different means of corrosion control and economise a given process e.g. paper making by choosing most economical means (iv) monitor in-service corrosion for avoiding sudden and catastrophic failures (v) study corrosion mechanism, (vi) develop new and more resistant materials etc. For estimating corrosion, one needs to know about various corrosion testing procedures because a properly conducted corrosion test can mean savings of millions of rupees, through minimising or avoiding corrosion. Most common corrosion tests are given below:

1.2.2.1 Weight Loss :

Quantitative evaluation of corrosion depends on whether material is experiencing uniform corrosion or localised corrosion. In the uniform corrosion, the metal is lost uniformly with time from its surface exposed to corrosive environment. Change in the weight or thickness gives the good estimation of the severity of corrosion. This is denoted by a parameter called as 'corrosion rate' , defined in two ways. Firstly, as 'weight loss per unit exposed surface area of metal per unit exposure time in a corrosive environment'. It is commonly represented as 'mdd' i.e. milligram/dm^2.day. Secondly, it has been defined, from engineering point of view, as rate of metal penetration (due to corrosion) or rate of thinning of material per unit time. Corrosion rate is represented as 'mpy' i.e. mils per year. For details, please refer to chapter 2.

1.2.2.2 Localised (Pitting/Crevice) Corrosion :

Mass loss is generally not a good indication of the extent of localised attack e.g. pitting and crevice corrosion unless uniform corrosion is slight and pitting in fairly severe. Hence generally these are not evaluated by the methods used for uniform corrosion. A sample exposed in a solution for long duration is cleaned off the rust and then analysed for extent of pitting . Pit depth measurement is done with the help of optical microscope. Test for determining resistance against crevice corrosion is same as that for pitting except that serrated washers (crevice formers) of non metals e.g. PTFE, acrylic plastic etc., are attached to the metal specimen. Test duration is kept roughly same as in pitting. After the sample has been exposed for a predecided duration, the crevice formers are removed. The pits formed under crevices are evaluated in similar manner as in the case of pitting corrosion. For details, please refer to chapter 2.

1.2.2.3 Stress Corrosion Cracking :

The tests on stress corrosion cracking (scc) involves exposing specimens under stressed conditions to corrosive liquor at a given temperature. Important aspects in scc testing is, therefore, the manner in which the specimens are stressed. Thus U-bend, C-ring and bent beam stressed coupons are used in these tests (Fig. 1.3). U-bend specimens may be formed into U-shape from any ductile metal alloy without mechanical cracking. It is most easily made from strip, sheet or wire specimens. C-ring specimens are used in scc tests on all types of alloys in a wide variety of product form. It is particularly suitable for making specimens from tubes and rods. Bent beam specimen is designed for determining stress corrosion behavior of alloy sheets and plates in variety of environments. Axially loaded tension specimen provide one of the most versatile methods of preforming a stress corrosion test due to the flexibility permitted in the choice of type and size of specimen, stressing procedure and range of stress levels. The stressed specimens, are put in corrodent simulating to environment for which resistance against scc has to be tested. The specimen should be inspected daily for the appearance of cracks. Uncertainty in crack, appearing sometimes due to deposits of corrosion products, may be overcome by chemically cleaning the specimen to facilitate the adequate inspection. During testing, it is desirable to record time required to initiate cracking , rate of crack growth and time to failure. For some of these recordings, it may become necessary to remove specimen from corrodent periodically. For detecting cracks, microscopic examination of affected surface is done. To determine types of cracking, transgranular, intergranular or mixed type, metallographic examination of exposed surface and of polished and etched cross sections is required at higher magnification.

1.2.2.4 Electrochemical Testing :

The electrochemical tests have its wider acceptance for rapid determination of material performance in given corroding environment in laboratory, for in plant monitoring of corrosion and understanding corrosion mechanism. Following electrochemical tests have been described in brief in forthcoming paragraphs.

- Corrosion potential measurement
- Tafel plot
- Linear polarisation
- Anodic polarisation/ cyclic polarisation
- Potentiostatic measurement

(i) Corrosion Potential Measurement :

For corrosion potential measurements, one has to record a potential versus time curve until a reasonable steady state value is achieved. Time taken to achieve this value depends upon material-solution system and could vary from a few hours to even days. This potential sometimes also tells about whether the material is in passive state or is in localised corrosion prone region.

(ii) Tafel Plot :

This is a potentiodynamic polarisation measurement of potential against current on the material, whose corrosion behavior is to be investigated, in the given liquid media.

In the determination of Tafel plot, metal electrode is polarised within ±250 mv around its corrosion potential (E_{corr}). Tafel plots are used to evaluate Icorr, ßa and ßc – anodic and cathodic Tafel slopes and hence corrosion rate.

(iii) Linear Polarisation :

The basis of this method is the approximation when E does not differ very much from E_{corr} i.e. $\delta E = E - E_{corr} \leq 10 - 25$ mv. In this condition, variation between potential ,E, and current ,i, is approximately linear . From Tafel equations, under approximation that E does not differ much from E_{corr}, one gets

$$\frac{\delta E}{\delta i} = \frac{1}{(2.3)\ I_{corr}} \quad \frac{\beta_a \times \beta_c}{\beta_a + \beta_c}$$

$\delta E / \delta i$ – slop of E versus i curve

I_{corr} – corrosion current density

From E versus i curve, one calculates $\delta E/\delta i$. β_a and β_c are known from Tafel plots hence I_{corr} can be calculated from above equation. One then calculates corrosion rate from I_{corr} value.

(iv) Anodic Polarisation / Cyclic Polarisation :

In these tests, the sample is polarised in anodic direction with a certain scan rate and the corresponding value of current density is recorded for each preselected potential. From anodic polarisation curve one obtains information about nature and extent of corrosion. It is known that such a curve is devided into three zones – active (uniform) corrosion, passivation and localised corrosion i,e. pitting / crevice corrosion. The potential at which the passivation film is broken down is called breakdown potential or pitting potential (E_p). A slight modification of anodic polarisation behaviour, called as 'cyclic polarisation', is if external applied potential of metal is made to decrease after reaching some value in transpassive region. The curve then cuts somewhere in passivation region or it does not cut at all. The former is a case when material experiences crevice corrosion whereas in later case, metal does not experience crevice corrosion. The potential where curve cuts the passivation region is called as repassivation potential (E_c).

(v) Potentiostatic measurement :

This test is an alternate test to determine E_p and E_c – breakdown and repassivation potential respectively, which indicate resistance of material to pitting and crevice corrosion in the test solution. In this test, first of all the sample is polarized to a potential slightly different than E_p (breakdown potential known from potentiodynamic anodic polarisation curve), so that pitting is stimulated. This is observed as increase in current with time. Then the potential is lowered down below E_p and one observes change of current with time. The two variations indicate about the range of potential within which the E_p lies.

1.2.2.5 In-Service Testing :

Even though the materials of plant machinery have been selected carefully after undergoing laboratory and simulated service testing, it is important to monitor the progress of corrosion of the process equipment while in service so as to take safeguard measures from ill effects of sudden and unexpected failures. In selecting test methods for monitoring plant corrosion, few points are to be checked (i) The test period should be determined as per the requirements of corrosion experiments and it should not be set by production or maintenance requirements (ii) It should be possible to record changes in corrosion behaviour due to varying process conditions particularly those which may not be important from process point of view and hence are not recorded, but very vital in affecting corrosion performance of the material of the equipment (iii) There may be occuring some rapid changes in process resulting in corrosponding change in corrosion severity. The corrosion test method should be sensitive and quick enough to record these changes. Based on above aspects, one of the following techniques could be used for corrosion monitoring .

- Linear Polarisation Resistance Method
- Electrical Resistance Method
- Potential Monitoring
- Radiography
- Ultrasonics
- Sentinel Holes

1.2.3 Corrosion Control :

Corrosion can be minimised/controlled in several ways. These are (i) alteration of the media composition/ process parameters (ii) appropriate material selection (iii) application of protective layer e.g. coating; lining, cladding and weld overlaying (iv) application of inhibitors (v) electrochemical corrosion control. Selection of control procedure depends overall on cost-effectiveness. First of all it is tried to control the composition of media so that it is lesser corrosive. However, this alternative is practically not possible many times. One then opts for appropriate material selection. Many reports have appeared in literature on the evaluation of various materials for corrosion behavior in the test media with this aim (17-19 are few of these references). The most cost- effective method for corrosion protection is often proper material selection that includes a coating. However, many times a corrosion resistant material may be very costly or it may not have other acceptable properties. In such cases, one of the options is to consider a protective layer over a material which may be acceptable otherwise but for corrosion resistance. This protective layer could be of an organic paint/ ceramic coating (20), rubber/plastic/polymer (21) or corrosion resistant metals e.g. stainless steel, brass, Ti, Sn etc. Film-forming inhibitors are essentially a barrier between the material and environment. Inhibitors are compounds that will effectively decrease the corrosion rate when used in small amounts. Inhibitor studies (22-24) have shown corrosion control of stainless steels, inter-relation among hydrogen absorption, mechanical strength and inhibition efficiency and role of Cl^- ion during pickling of steel. Electrochemical protection includes anodic protection and cathodic protection. Anodic protection includes maintaining the passivity of metal (that is to be protected) with an external current source. The protected structure is to be deliberately polarised to the anodic direction. Cathodic protection is production of surplus anodic current by sacrificial anodes or external current source to satisfy the needs of cathodic reaction (9).

1.3 Corrosion in Pulp and Paper Industry :

This section presents an overview of corrosion problem and selection of material of construction in pulp and paper industry. The corrosion problem in paper industry is more serious as compared to any other industry because paper industry uses wide variety of very corrosive chemicals like sodium thiosulfate , polysulfides, chlorine, chlorine dioxide, hypochlorite, peroxide, sulfuric acid, hydrochloric acid etc. (25,26). In fact the paper industry was the first to utilize molybdenum bearing stainless steels more than 60 years ago and also it has shown enthusiastic acceptance of FRP construction. Paper making technology is experiencing continuous changes due to (i) shortage of fibrous raw material (ii) ecological restriction (iii) demand of quality paper (iv) 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. Due to diversified type of environment, various forms of corrosion are experienced in different sections of a paper mill e.g. chipper house, digester house, washing and screening section, bleaching plant, stock preparation, paper machines, power generation and recovery plant. Uniform corrosion, galvanic corrosion, pitting and crevice corrosion, intergranular corrosion, stress corrosion cracking, high temperature corrosion cracking, corrosion fatigue, hydrogen embrittlement, caustic embrittlement and microbial corrosion are the various forms of corrosion which commonly occur at various stages of pulp and paper manufacture. Various factors affecting corrosion are type of raw material, cooking liquor concentration, digester operation, bleaching chemicals and sequence of bleaching, temperature, pH, dissolved gases differential aeration, bacteria, existence of stresses, dissolved oxygen etc. However, nature of chemicals , process parameters and hence degree of attack differ in different sections.

Consequently, a brief discussion of corrosion problems, generally observed in various sections of this industry is given in following sections –

1.3.1 Pulping Section :

1.3.1.1 Chipper House :

In chipper house wear and erosion/corrosion occurs in log handling system, chain conveyers, feed chute, and cyclone and chips blow line. However, corrosion is not of very serious nature and minor repair, proper selection of materials of construction, proper preventive mainten[redacted] incorporation of impact boxes in chips blow lines have helped in reducing corrosion problem (27).

1.3.1.2 Digester House :

Generally two types of digesters are in use in paper industry (a) continuous and (b) batch types. 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 Indian mills, mostly batch digesters are used. It is used to cook the wood chips with kraft cooking liquor. The kraft cooking liquor contain sodium hydroxide, sodium sulfide, sodium sulfite, sodium carbonate, sodium chloride, sodium thiosulfate. sodium sulfate etc.. Cooking is usually performed at pH ~ 13.5 -14 and temperature of 170°C. Digester, preheater, circulation pump, white liquor storage tanks, cooking liquor feeding line, digester blow line and blow tanks are the various units which are seriously affected by corrosion. Many reports have been published / presented in conferences in past years. Olsson reported the corrosion rate of digester approximately 5 (0.1 mm) mils after 3 years in service, where selective phase corrosion occurred (28). 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(29). The acids for cleaning, such as sulfamic acid and formic acid , are less corrossive to digesters (30). Crowe suggested on line corrosion monitoring in kraft white liquor clarifier (31). 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 differential, galvanic effect, violent agitation of pulp and blowing causing erosion of passive film, presence of thiosulfate in white liquor, presence of lignin compounds chloride etc. (27,32). 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 thiosulfate activate corrosion and act to impair passivation. The corrosion is dependent on the equilibrium of the following reaction (33).

$$S^{2-} + S_2O_3^{2-} \leftrightarrow SO_3^{2-} + S^{2-}$$

The $S_2O_3^{2-}$ / SO_3^{2-} molar ratio can be used as a corrosion factor of the liquor (33). Corrosion increases with the increasing concentration of thiosulfate in the digester. Lignin has a passivating effect in shell and decreases corrosion (34). 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 (35). Mueller (36) 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 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. Digesters blow bends, blow tank at the top are also getting corroded very rapidly and their rates have increased substantially with the use of more and more hard wood and high 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(37). In other digesters it is worst in the bottom cone, in yet others, in 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) and Type 304L (18-20% Cr) can experience rapid corrosion, up to 40 mpy (1mm/y)(37). Work by Audouard 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 (38-42).

1.3.1.3 Brown Stock Washer :

The cooked pulp from the digester is washed by displacing the black liquor, containing organic material and residual alkali compounds from the sheet as the drum continue to rotate. Although the black liquor in its usual form of concentration and temperature does not pose any serious corrosion problem to standard material of construction. However corrosion of washer backing plates and vacuum pipes especially at grouting places due to pitting has been experienced, Presence of sand and other foreign material causes erosion of wire mesh, repulper and washer vat,

1.3.1.4 Ancillary Equipments (43) :

Stainless steels have been used as a material of construction for much of the equipment ancillary to digesters. This includes piping, valves and pumps. Some of the major ancillary equipments are discussed below:

(i) Liquor Heater :

For many of the years welded type 304L stainless steel tubes have been the "standard" material of construction in liquor heaters. Unfortunately, austenitic stainless steels Types 304L and 316L are susceptible to both chloride and caustic SCC, which has caused many tube failures. Duplex stainless steels such as 3RE60 (S31500), Alloy 2205 (S32205), and Alloy 2507 (S32750) are resistant to SCC in liquor heater service but are also susceptible to thinning, specially at higher temperatures. High nickel alloys such as Alloy 600 (N06600) and Alloy 800 (N08800) are resistant to SCC and have improved resistance to acid cleaning damage.

(ii) Chip Conveyors :

Chip conveyors, which bring chips from the wood yard to the chip feeders, use type 304 for bends and other components subject to chip abrasion. Chip feeders for continuous digesters are typically made from centrifugally cast, precipitation hardened stainless steel Alloy CB-7Cu-1(J92180), in the solution anealed and aged (H925) condition, for best abrasion resistance.

(iii) Steaming Vessels :

Chips are usually presteamed in a steaming vessel prior to introduction into the cooking vessel through a rotary type high-pressure feeder. The steaming vessel is horizontal cylindrical vessel which has conventionally been constructed from carbon steel with partial cladding of type 304L stainless steels on the side. In 1980s several steaming vessels were constructed from solid Type 304L stainless steel. Most of these vessels experienced external SCC beneath the insulation when the insulation became wet from the liquor spills. These vessels also had internal SCC in the steaming nozzles. Duplex stainless steels such as Alloy 2304 (S32304) and Alloy 2205 have superior resistance to SCC and wear and are preferred for the internal lining, particularly the wear plate. Some steaming vessels have been constructed from clad duplex stainless steel (roll-clad or explosion clad) and are relatively maintenance-free.

(iv) Flash Tanks, Blow Tanks, Valves and Pumps :

In a continuous digester there are typically two flash tanks for the liquor extracted from the digester. The flash tanks were typically made from carbon steel, but there have been many reports of severe corrosion or erosion corrosion of these vessels. Types 304L and 316L were rated as marginal and duplex Alloy 2205 is preferred (44). Thermal spray coating or lining with type 304L stainless steel has extended the life of corroding flash tanks. Replacement of flash tanks with solid duplex Alloy 2205 is a solution to the corrosion problem. The blow tank for batch digesters may be of carbon steel, Type 304L, or for larger tanks, Alloy 2205 construction. Blow valves are usually CF-3 (J92500) cast stainless steel, CD-4McuN (J93372) or CD-6MN (J93371). Cast duplex stainless steels are preferred for pumps due to abrasion from sand and grit loadings.

1.3.2 Recovery System :

Various corrosives and environment which are responsible for corrosion in various sections of recovery plants are chloride, thiosulfate, sulfide, polysulfide, CO_2 , high temperature, dissolved oxygen etc. Corrosion problems, usually, occurs in the following section of recovery system –

1.3.2.1 Evaporators :

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. Stainless steels 304 or 316 are frequently used as evaporator tubes. The use of closed cycle systems, however augments the risk of SCC occurring in the evaporator tubes. To avoid the SCC, duplex stainless steels 3RE60 or SAF2205 are suitable alternatives. These grades also eliminate the risk of pitting on the steam side of the tubes in the bottom part of the heat exchanger where chloride containing condenses and deposits may occur.

1.3.2.2 Recovery Boiler :

The operating pressure of boiler ranges from 10 Kg/cm^2 to a maximum value of 60 Kg/cm^2. Aside the general corrosion of the lower furnace tube walls of the recovery boiler, strong corrosion of local spots on the surface wall outside and inside the primary air ports is observed frequently. This increases further when sulfidity level exceeded 45%, previously varying between 28-35%, shown by Scandinavian Kraft mill with the use of ClO_2 bleaching and increase in recycled ash (45). The wastage of water wall tube is aggravated by higher tube wall temperature associated with higher pressure. Composite tube offers considerable resistance to fireside corrosion, but at considerable expenses. Carbon steel tube in recovery boiler experiences extensive corrosion in certain areas as a result of reaction by the furnace gases (CO_2, O_2, H_2S, and SO_2) and reaction with ash. Type SS-304 clad carbon steel tubes appears to provide a solution to these problems (45).

Tube temperatures are highest in the superheated section. The superheated steam temperature at the outlet can be as high as 510 °C. Outside tube metal temperature make the superheater metal vulnerable to high rate of corrosion. Exposed surfaces of superheater are subjected to corrosion by the flue gases. Type 31 or 22 composite tubes are finding continuous use in Canadian and other boilers worldwide, to help offset corrosion in the superheater sector (46).

1.3.2.3 Recausticizing Plant :

The function of recausticizing plant is to convert sodium carbonate (Na_2CO_3) into active sodium hydroxide (NaOH). The operation starts with the smelt flowing out from the furnace and dissolved into water (green liquor) and is clarified and causticized with lime to produce cooking liquor for pulping. In recausticizing plant, plain carbon steel storage tanks, clarifiers, piping, lime and slurry pumps, lime kiln scrubbers components. etc. suffer severe corrosion attack due to lime-mud slurries and lime-mud wash water, particularly in zones where liquor level fluctuate frequently. The corrosion rates as high as 20-30 mpy are experienced on the walls and trays of the storage tanks and clarifiers where liquors are relatively stagnant. In piping and other locations where liquor velocity is considerably higher, corrosion rate as high as 200 mpy can be encountered (25). The corrosion of carbon steel is strongly influenced by the concentration of polysulfides and thiosulfate present in cooking liquor (25). Anodic protection has been shown to be effective and economic corrosion control measures to protect storage tank and clarifiers. Several other alternatives to control the corrosion are stainless steel fabrication, specification of thick wall carbon steel at critical sites, controlling thiosulfates, and polysulfides. In some cases storage tanks and clarifiers have been lined with epoxy or glass/ epoxy composites. Although these have fair resistance to direct attack by corrosive liquor, a more severe problem is penetration of liquor behind the epoxy.

1.3.2.4 Electrostatic Precipitators and Deaeraters :

Electrostatic precipitators are used in recovery furnaces to recover the chemical ash (salt cake) generated during the combustion of black liquor. Principal cause of corrosion of precipitator is that temperature lower than the temperature (50°C) at which sulfur trioxides gas combines with moisture and condenses out of the process gas stream as a sulfuric acid. Precipitators made of mild steel are susceptible to sulfuric acid attack hence should be operated above 50°C, the dew point temperature (26). Area of localized corrosion in precipitators, generally, are test port expansion joints, access doors, damper seals and rapper rods. In order to minimize precipitator shell corrosion, insulation of side wall and elimination of in leakage of cool air appear to be beneficial. Organic coatings such as vinyl ester can be used to reduce corrosion rate. Deaerator system conventionally operate at pressure between 30-75 psi and corresponding temperature of 175-205°C. A wide spread cracking is the reason of failure of feed water deaerators and deaerator storage tanks. Remedial measures have included vessel replacement, weld repair, short peening or stress relief.

1.3.3 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 found to increase when one adopts 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, Cl^- etc. in bleach plant. Average process conditions prevailing in bleach plant are shown in Table- 1.1

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 to minimize the localized corrosion in this area.

1.3.3.1 Corrosion in Different stages :

(i) Chlorination (C) Stage :

The highly acidic and oxidizing (containing residual chlorine) environment prevails in chlorination washer (Table-1.1) is mainly responsible for corrosivity of this section. Chloride ions (Cl^-) in the process, due to reduction of chlorine and also there presence in local water, facilitate the propagation of localized attack. Corrosion in the gaseous phase has generally been more serious than that of liquid or wet dry phase exist in the washer (47-54). This attack is caused by condensation of chlorine gas in droplets on non-wetted components e.g. shower pipes and metal above the stock level. The condensed droplet contains high concentration of oxidants and Cl^- with very low pH. The common mode of localized failure of stainless steel in this sections are crevice corrosion on shielded metal surfaces, pitting attack on unshielded areas of metal surfaces, weld associated corrosion on heat affected zone of weld, and stress corrosion cracking. Perel (55) showed that Hastelloy C22, an alloy developed to resist the corrosion of mill weldments in conditions of hot, saturated, wet chlorine.The introduction of water reuse or recycling, to reduce energy and water demand is found to change the chlorination washer environment. One study apprehends (52) that the vat temperature of this stage has increased from 25 to 44°C and average residual chlorine level was down to 49 from 120 ppm but the occasional excursion was observed high enough e.g. 200 ppm. Vat chloride concentration has almost tripled (920 to 2950 ppm). Although the average vat pH remains at 2. These environmental changes tend to enhance corrosivity of this washer.

(ii) Chlorine-Dioxide (D) Stage :

Corrosion in chlorine dioxide bleach washer mainly depends upon concentration of ClO_2 but it, alone, can not corrode acid proof stainless steel until Cl^- is present in the solution (56). Though, the pH of the solution is lesser acidic and concentration of residual Cl_2/Cl^- is also lower than in C-washer (Table-1.1). Nevertheless, higher rate of corrosion have been reported (47,51) in this stage than C-stage while some (50) suggests otherwise. Higher temperature is considered beneficial as the bleaching reaction and thus consumption of ClO_2 is accelerated, which increases actual life of filter drum (53).

In-plant tests in Swedish bleach plant (51) showed good performance by austenitic stainless steels containing 6% molybdenum. High nickel alloys were also proved corrosion resistant in the liquid media, however, only titanium has resisted corrosion in gaseous phase. Garner observed (57) copious corrosion products of ferrous oxide deposited on 316L, 317L, and 904L coupons exposed to liquid phase. These deposits have the effect of promoting widespread corrosion on the stainless steel since it served as a self forming crevice pad, under which additional pitting and crevice occurred. This mode of corrosion was particularly severe since it resulted in very high rates of penetration of the steel.

Recycling of filtrates (e.g. recycling D_1 stage filtrate to D_2 stage showers) can compound corrosion problem. In the first D-stage (D_1), bleaching is performed at pH= 3.5 - 4.0 for optimal chemical usage. However, a somewhat higher pH (= 5.5-6.0) is found to provide the highest brightness in second D-stage (D_2). It was suggested (57, 58) that recycling of D_1 or D_2 stage filtrate to the C-stage should be avoided completely, since the more acidic C-stage filtrate regenerate ClO_2 from chlorite ions, making showers more corrosive to stainless steels. Addition of SO_2 before D_2 washer to the washing filtrate which contains residual ClO_2, may reduce corrosion up to some extent. In some cases, SO_2, additions are also made before D_1 washer for the purpose of corrosion control, however excessive addition might contribute to corrosion in gaseous phase of D- washer.

The laboratory tests (59) were performed to study the effect of chemical composition on the corrosivity of the chlorine-dioxide solution and the corrosion resistance dependence of stainless steel on the Mo and Si content. In laboratory immersion test performed in D-washer media (60,61), Ni base alloys, unwelded and when welded autogeneously / with Ni-base fillers show general corrosion. Increasing the iron content in these alloys shifts the transition to transpassivity to higher potentials(61). Stainless steels having high resistance to localised corrosion perform satisfactorily (60) while lower alloyed stainless steels fail by pitting/crevice corrosion (61). Their welded area shows localised attack or no attack depending upon iron filler composition, while distinctive localised corrosion was observed when Ni-base fillers were used (60). Another test performed in near neutral D-bleach media (62), shows the importance of Mo content in resisting crevice attack both on stainless steels and Ni alloys. In a test conducted to observe the performance of super-austenitic stainless steels (63) under service conditions (Temp. 64, pH 2.4-3, ClO_2 42-160ppm, Cl^- 312-483ppm), SS904L shows breakdown of passivation even for lowest Cl^- and 50^0C temperature while 254SMO shows passivation even at Cl^- level that is 12 times that found in service conditions and at 65^0C thus exhibiting the beneficial effect of Mo. Only at 80^0C, the pitting is observed in 254SMO.

Immersion and electrochemical test (64) performed on Ni alloys exposed to C+D mixer media with chlorine dioxide substituting chlorine from 0-100%, shows general and localised corrosion. Another test (65,66) shows that Ni-base alloys do not have adequate corrosion resistance in these media. However, C-276 Ni alloys perform better than stainless steels in chlorination (0% D-substitution), the latter material not acceptable in these applications. Titanium has been suggested ideal choice for C+D media provided efforts are made to exclude dry Cl_2 in mixer environment which attacks titanium.

In the earliest performed in-plant test related to D-stage washer (67), 6%Mo containing SS is observed to be best among the tested SS. While Ni base alloys and Ti performed even better. In case of coupons exposed to inlet box and hood of D-stage washers (68), extensive localised corrosion is observed even on 6% Mo-stainless steel while Ni alloys show acceptable performance. Another test (69) in C and D stage bleach plant shows Ti suitable for mixer-to-tower piping in case of D and solid or clad Ni base alloys in case of C bleaching, solid or clad Ni base alloys are suitable for tower to vat section piping and 6%Mo alloy with alloy 625 or higher Mo content filler metal are excellent candidate for washers and filtrate piping. In the latest reported (70) in-plant test, the materials were exposed in tanks for spent acid from chlorine dioxide production, bleach plant scrubbers, bleach tower inlets and bleach washer. Two highly alloyed materials 904L and 2205 proved to be unsuitable for any of these environments. 254SMO was resistant in all except bleach tower inlet where its welded area was attacked. Stainless steel 2750 (25%Cr,7%Ni, 4%Mo) experienced pitting in weld area in spent acid tank while 654SMO and Ti was resistant in all cases. Ni alloys were also resistant except in inlet of bleach tower where it experienced extensive uniform corrosion.

Charles J. (71) showed the performance of super austenitic stainless steel UR B66 is equivalent or better than Ni based alloys. Wensley (72), showed 317L stainless steel is no longer recommended whereas 6% Mo super austenitic SS family have improved corrosion resistance overtype 317L but may not be reliably superior unless the Pitting resistance equivalent number PREN>48. For super duplex SS this PREN > 42. Troselius (73) indicated duplex stainless steel type 5B1803 is an optimal material for use in ClO_2 pulp bleaching service. Hakkarainen (74) indicated the effects of main variables controlling pitting of stainless steels under wet deposits in atmosphere containing ClO_2 can be investigated quantitatively. Feng (75) indicated the diffusion coefficient of ClO_2 in resin 199 and life of resin coating when the consistency of ClO_2 was 10g/L.

(iii) 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 (76). Pitting and crevice are the dominant forms of corrosion, usually, occur 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 (OCl^-) to hypochlorous acid (HOCl) (76) 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. A significant reduction of corrosion rate may be obtained by maintaining pH in the range of 10.0 - 11.0 (51). The liquid phase corrosion is more severe than in gaseous phase generally higher rate is observed when residual chlorine concentration is higher at pH (50). Stainless steel 316L and 317L are the principal construction material of washer drum, piping and mixing equipments.

(iv) Peroxide (P) Stage :

Corrosion data pertaining to peroxide washer is not much. Peroxide is a strong oxidizer and can create a aggressive condition to candidate material in presence of equate chloride concentration. Hydrogen peroxide is degradable by some metal ions ferric, cupric, magnese etc., which might enter in the solution through corrosion reaction with washer materials (77) and thereby reducing bleaching efficiency. Though the corrosion reactions due to peroxide appears less severe as compared to those due to chlorine and chlorine-di-oxide yet zirconium and titanium have been suggested for the construction materials of peroxide washer (77). Application of these metals may also reduce degradation of peroxide. Been (78) studied the corrosion of grade 2 titanium in alkaline hydrogen peroxide environements and found calcium and pulp were as corrosion inhibitors. Been (79) showed that in hydrogen peroxide stage calcium and pulp are as corrosion inhibitors . Yang (80) indicated the corrosivity of m-benzol unsaturated polyester resin containing filler in H_2O_2 was studied. 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. Presently stainless steel 316L is generally used for construct of washer equipments.

(v) Oxygen (O) Stage :

High pH (~11), significant amount of chloride along with high temperature 266^0F (130^0C), in this washer, increase the possibilities of stress corrosion cracking (SCC). study (81) has shown that at pH = 13 and 10 gpl NaCl, cracking occurs in both liquid. well as in gaseous phase. It also has concluded that the invariable presence of carbon 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 2Ocb3 to guard against chloride cracking. Wensley (82) studied about external stress corrosion cracking of stainless steel vessels (oxygen reactor, concentrators, evaporators, steaming vessels and tanks).

1.3.3.2 Later Developments in Bleaching and Consequential Changes in Corrosivity and Material Performance :

It has become a common practice in pulp bleaching to substitute some chlorine with chlorine dioxide to keep control on pulp quality and pollution due to effluent discharge from chlorination washer. The use of chlorine dioxide in chlorination stage reduces the amount of chloride produced. Consequently the aggressiveness of environment should thereby reduce. Whereas experimental report (83) 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.

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. Table 1.2 (84) 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.

In recent years, developments are being directed towards the use of ozone, peracids, enzymes and biological treatments for delignification and bleaching of pulps. Peracids such as peracitic acid (P_a), caro's acid (P_x) and mixed peracids (P_{xa}) containing both P_a and P_x have been evaluated as a dilignification agents or bleaching agents for chemical pulp and textile since the early 1950's (85). Baily and Dence (86) published a research paper describing the use of peracitic acid for both delignification and brightening of chemical pulp. This initial work found that minimum pulp degradation occurred in the pH range of 5 to 9, 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. According to a study (87) on corrosion in ozone and peracetic 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 1g/L Cl^- at 80^0C. Bio-bleaching requires longer reaction time and yet to be recognized. The liquors of the new bleaching stages may not have Cl^-, and therefore expected to be less corrosive than chlorine and chlorine containing bleaching stages (88,89). 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.

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 (52).

1.3.3.3 Corrosion Prevention in Bleach Plant :

Corrosion prevention in bleach plant is usually accomplished in three ways: (i) by controlling the process environment (ii) through the use of suitable resistant material and (iii) by applying electrochemical protection system. Selection of a particular protection measure, depends upon its cost effectiveness.

(i) Environment Control :

Control or modification of environment, particularly the residual oxidant level, is a way of preventing corrosion. This, however, avoids the elevation of corrosion potential of alloys in transpassive regions, above which the localized failures of metal occurs. This is especially critical for residual chlorine or chlorine dioxide. Higher the residual chlorine level more susceptible is material to localized attack. The threshold value of residual chlorine level for chlorination and chlorine dioxide washer are identified around 25 ppm (50). Temperature, chloride, and pH are also important factors in determining the corrosiveness of bleaching environment. Increasing temperature and chloride ion concentration make the alloy/metal more susceptible to localized corrosion (84) while decrease in pH (to more acidic value) increases the aggressivity of environment. Vapor phase corrosion is increasingly severe when high level of oxidants prevail at low pH of washer environment. Excess addition of SO_2 antichlor ahead of C and D washer to remove residual oxidants can also make the vapors more corrosive (50). In this case the cost of antichlor treatment usually makes antichlor addition too costly to be a cost-effective.

(ii) Material Selection :

Materials for bleach plant have undergone major changes over the past 30 years. In the 1970s recycling of wash water and approaching to closure of the wash water cycle increased corrosivity. Changes in bleaching process and reduction in time available for maintenance, together with recycling of wash water, required upgrading to more highly alloyed, more resistant materials in the late 1970s and 1980s. More recently, the need to reduce dioxins has resulted in replacing chlorine with chlorine dioxide. Substituting chlorine dioxide for elemental chlorine is known as elemental chlorine-free (ECF) bleaching. Substituting oxygen, ozone, peracids and hydrogen peroxide for both chlorine and chlorine dioxide is known as totally chlorine free (TCF) bleaching. TCF bleaching requires less highly alloyed materials than ECF bleaching. Types 316L (S31603), CF-3M (J92800) and CF-8M (J92900) (37) are quite adequate for most applications in TCF bleaching.

Suitable material selection involves intelligent use of metal as well as non-metal including polymers and composites. This requires the ranking of corrosion resistant materials by doing laboratory testing followed by long-term in-service testing. To rank the corrosion resistance of different alloys in bleach plant, tests have been conducted on various grades of stainless steels (47,48,49,51). Bleach washer drums have traditionally been constructed of 317L stainless steels (for acidic Cl_2 and ClO_2 containing process streams) and 316L (for alkaline extraction and hypochlorite), which until recently has given reasonably good service. But with more extensive reuse of wash water in the plant, 317L is no longer adequate. One study (90) showed that the austenitic stainless steels with more than 6% Mo like 254SMO, 654SMO, Cronifer 1925HMO, AL-6X and ferrite with 4% Mo appears to provide acceptable corrosion resistance in all of C, D and H stage liquid phase even in welded condition. One in-plant study (91) showed the duplex stainless steel 2205 as the appropriate material for

C, D, and H liquid media. In addition, the superior corrosion resistance of nickel based alloys (C-276, G-3, 625, and 20Mo-6) and titanium was demonstrated for bleach plant service. However, these more exotic metals and alloys are relatively expansive and especially in the case of titanium, extra care in fabrication and welding is required. It is also useful to determine the threshold residual oxidant levels for corrosion for various metal-environment combinations.

Faced with increasingly corrosive bleaching solutions many mills are turning to non metallic material of construction in critical areas. These ranges from inorganic material e.g. brick, tile, cement through organic polymers to composite materials e.g. fiber glass reinforced plastic (FRP) and polymer concrete. The polyvinyledene fluoride (Knyar) piping and lining serve well even in high concentration of bleaching chemicals and offers alternative to Ni-based alloys (92) FRP stock lines and hood, for bleach washers, when properly designed are usually competitive with those of stainless steels. FRP coated drum washers have been used successfully in highly corrosive environment. But premature failure of coated drums have been associated with poor quality fabrication (92).

(iii) Electrochemical Protection :

Increasing corrosivity with premature failures of polymer/ FRP equipments due to incorrect fabrication procedures have led many mills to select electrochemical protection as a cost effective alternative in corrosion control strategy. This is evident from one survey (52) that around 50% of the surveyed Canadian mills are using this system, though it is available commercially only since about a decade (47, 93) or so.

There are two way of protecting the system electrochemically (i) cathodic protection and (ii) anodic protection.

In the cathodic protection method, the system that is to be protected is made cathode either by imposed negative potential from external battery or by the use of sacrificial anode. In the former case, negative terminal of power supply is connected to the system that to be protected and the positive to the inert anode such as graphite or duriron. The electric lead to the system and inert electrode are carefully insulated to prevent current leakage. In the latter case, a sacrificial anode, which corrodes preferentially, is electrically connected to the system to be protected so that the working system acts as a cathode e.g. magnesium is anodic to steel and hence will corrode preferentially when galvanically coupled. Niemmlainen(94) investigated the cathodic protection can prevent corrosion of metal surfaces on bleaching equipment . Another studies (95-96) also indicated the cathodic protection of the equipments.

Anodic protection is achieved, usually, by making the equipment as anode by polarising the specimen in anodic (positive) direction, so that it passivates. During passivation, metal/ alloy corrodes with minimum corrosion rate. The system to be protected is polarized to potential well below the crevice and critical pitting potential. Therefore, this method is applicable only for those alloys/metals which experience passivation such as stainless steels, Ni-based alloys, etc. Electrochemical system for oxidizing chloride environment (chlorination, chlorine-dioxide etc.) is achieved by the polarization of stainless steels surface in the cathodic direction to a predetermined controlled potential (97- 100). It was differentiated from cathodic protection since the controlled potential for electrochemical system falls out side the potential range for cathodic protection. Owing to less operational cost, simplicity of operation and its acceptability to already existing system, the anodic protection system is more compatible to bleach washers. A study reveals (101) that the installation and running cost of electrochemical protection system are small as compared to the resulting cost savings. Capital cost savings are such that if the life of washer is extended from five to ten years by protection, the system will have a pay back period of about one year.

1.3.4 Paper Machine:

The paper machine section of the paper industry also is very corrosive. Different parts of paper machine section suffering serious corrosion include machine head boxes, suction and couch rolls, machine framework and supporting structures, hydrapulpers, external surfaces in dryer section, machine and water pumps. Paper machine environment is acidic (≈ 4-6), temperature 40°C to 55°C, very high humidity and contains 300 to 2000 ppm dissolved solids. Sulfate and chloride in the process increase the corrosivity of environment. In recent years thiosulfate anions have also been identified for promoting pitting and crevice corrosion of stainless steel components (102).

The concentration of cell activity due to microbiological organism causes localised failures of headboxes, white water storage tanks, stock lines and pipes. Steel losses passivity under the effect of sulfate reducing bacteria and gets locally attacked. Critical equipments such as headbox internals are often electropolished to minimize hang up of fibers and adhesion of deposits which initiates microbiological attack. FRP construction effective in reducing crevice corrosion in piping and chests. Modern headboxes are hydraulic in design with the elemination of air pads and other components. Common headbox construction is of type 316L with a specified minimum

2.5% molybdenum. Type 317L stainless steel and more highly alloyed materials have been used occasionally in headboxes to reduce or eliminate potential corrosion problems in more corrosive mill (38).

Fourdrinier wire (paper machine wire) made of phosphor bronze and brass, usually attacked by crevice corrosion, pitting corrosion, dezincification and direct surface corrosion. The factors which accelerate the corrosion in this section are low pH, chlorides, and/ or sulfates and high temperature. Addition of organic inhibitor and organic polymers (30) has been shown to reduce corrosion of wires, these inhibitors are also used to minimize corrosion incidence on circulating pumps and bronze impellers. With advent of synthetic wire as monofilament polyester wire, the life of wire has been greatly enhanced. But, however, corrosion on suction couch rolls is increased considerably since it is believed that metallic wire acts as a sacrificial anode to protect the suction couch rolls (26). The area around the suction rolls is subjected to splash from stock and white water, and deposit of paper fibers are also present in the crevice. Bacterial growth can also occur especially in areas that are difficult to treat with biocide chemicals. Suction rolls are also subjected to corrosion from chemicals and water used in showers around the rolls and from felt treatment chemicals. Some laboratory studies (102) have shown that $Na_2S_2O_3$ in stock and white water system results in the severe pitting of less resistant martensitic stainless steels and it also promotes cracking of suction rolls shell. Holton showed (103) the occurrences of head to shell corrosion on yankee dryers have increased over the past decade. Anon (104) suggested the safety of yankee dryers. Perdomo (105) investigated corrosion fatigue of heat treated duplex stainless steel in paper machine white water. Cracking of suction rolls is favored by corrosion fatigue induced by the fluctuating stresses that are imposed during routine operations. Though stainless steels were introduced for suction rolls metallurgy in 1969 but later new duplex stainless steel alloy such as VK-A378, KCR-A682 and A-86 were, introduced between 1978 and 1986 have much greater resistance to cracking than alloys used previously. Most suction roll vacuum boxes on older paper machines have been manufactured from epoxy painted cast iron (38). More recently, manufacturers have used weld fabricated type 316L (S31603) stainless steel suction boxes to better resist corrosion and deterioration.

Corrosion of paper machine becomes, further, a matter of great concern with introduction of system closure, either directly or after treatment. The degree of closure can be expressed as the amount of water consumed per air dried ton (adt) of paper produced. Closure results in increasing the concentration of dissolved inorganic and organic solids, decrease in pH and increase in temperature. Closure is considered detrimental from corrosion standpoint, however there is no clear relationship between increasing closure and paper machine corrosion. This can only serve to decrease the "margin of safety" for localized corrosion free service with a given stainless steel. Beyond a certain degree or closure, spontaneous pitting of less resistant stainless steels (type 304 and 321) may occur due to shrinking of "margin of safety" region.

1.4 Statement of Problem:

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, high temperature bleaching and displacement bleaching.

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 concentration of corrosive chemicals e.g. Cl^-, residual oxidants and temperature. In addition, sometimes it also brings down the pH of the media towards more acidic value. The process is now becoming fully closed or 'zero discharge' process, thus making the liquors all the more aggressive. Closure not only enhances the corrosivity of bleach plant but also of other sections e.g. chemical recovery by increasing the Cl^- concentration in different liquors.

Bleaching by chlorine dioxide (D-stage) was started with a view to make brighter paper. Also it discharges less hazardous chlorine compounds to the downstream and hence was preferred over Cl_2 in order to control pollution. However, chlorine dioxide bleaching is costlier so an alternative was adopted where Cl_2 was replaced partially by ClO_2 giving rise to C/D stage bleaching. This was an acceptable compromise between the cost, pollution aspects and the paper properties. Some countries are averse to the idea of using Cl_2 so those countries started adopting new technology for its bleaching stage. Consequently, the elemental chlorine free (ECF) or total chlorine free (TCF) bleaching came into existence (106,107). As such, ClO_2 in ECF and much lesser toxic bleach chemicals e.g. peracids, hydrogen peroxide, ozone, enzyme etc. in TCF process are likely to play an important role in bleaching. Among these, peroxide and ozone are widely accepted while trials have been undertaken to improve the enzyme bleaching. Bio-bleaching needs sufficient reaction time and therefore is yet to be recognized globally for commercialization.

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.

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. Investigations on corrosion of materials in bleaching process e.g. C-, D-, H- etc. have been made earlier. Corrosivity is expected to vary in different mills due to differences in process conditions, degree of closure and types of fibrous raw materials. One such study conducted earlier in Indian mills (58) found that the environment is very corrosive although they were not recycling bleach plant effluents. Stainless steel was found unacceptable in C- and H- washers and other media also do not guarantee the cost effective utilisation of all tested commercial stainless steels including 316L. The studied bleach washers were not covered as such they may be effecting the environment of bleach plant due to emanation of Cl_2 gas from chlorinated pulp hence the material performance. The above test did not include investigation in D-stage as the same were not existing at that time. Some Indian paper mills have adopted replacement of Cl_2 by ClO_2 since last 8-9 years. Peracids have not been adopted by Indian paper industry up to now but these are the futuristic bleach chemicals. Also the author has not come across work on corrosivity in peracids solutions.

Keeping in mind the above, there is a requirement of investigation of corrosivity of bleach plant further and possible measures to reduce the corrosion losses. For this purpose, the following tests were proposed.

1. In-plant corrosion tests, in chlorination (C), chlorine dioxide (D) and C_D washers, on advanced grade of stainless steels e.g. 317L, 904L, 2205 and 254SMO including conventional SS 316L to investigate the extent of corrosion attack, its correlation with process parameters, suitability of the test materials and economic viability in replacing conventional material with the tested ones.

2. The electrochemical polarisation and long term immersion tests on advanced grade of stainless steels e.g. 317L, 904L, 2205 and 254SMO including conventional SS 316L in chlorine dioxide solutions simulating to those of D-washer. The aim was to understand the mechanism of corrosion and effects of changing the process variables on the materials performance.

3. The electrochemical polarisation and long term immersion tests on possible materials of construction e.g. mild steel and stainless steels 304L, 316L, 317L and 2205 in peracid solutions simulating to those likely to be observed in peracid bleach plant stage. The aim was to understand the corrosivity of peracid solutions, suitability of the test materials and mechanism of corrosion in these solutions.

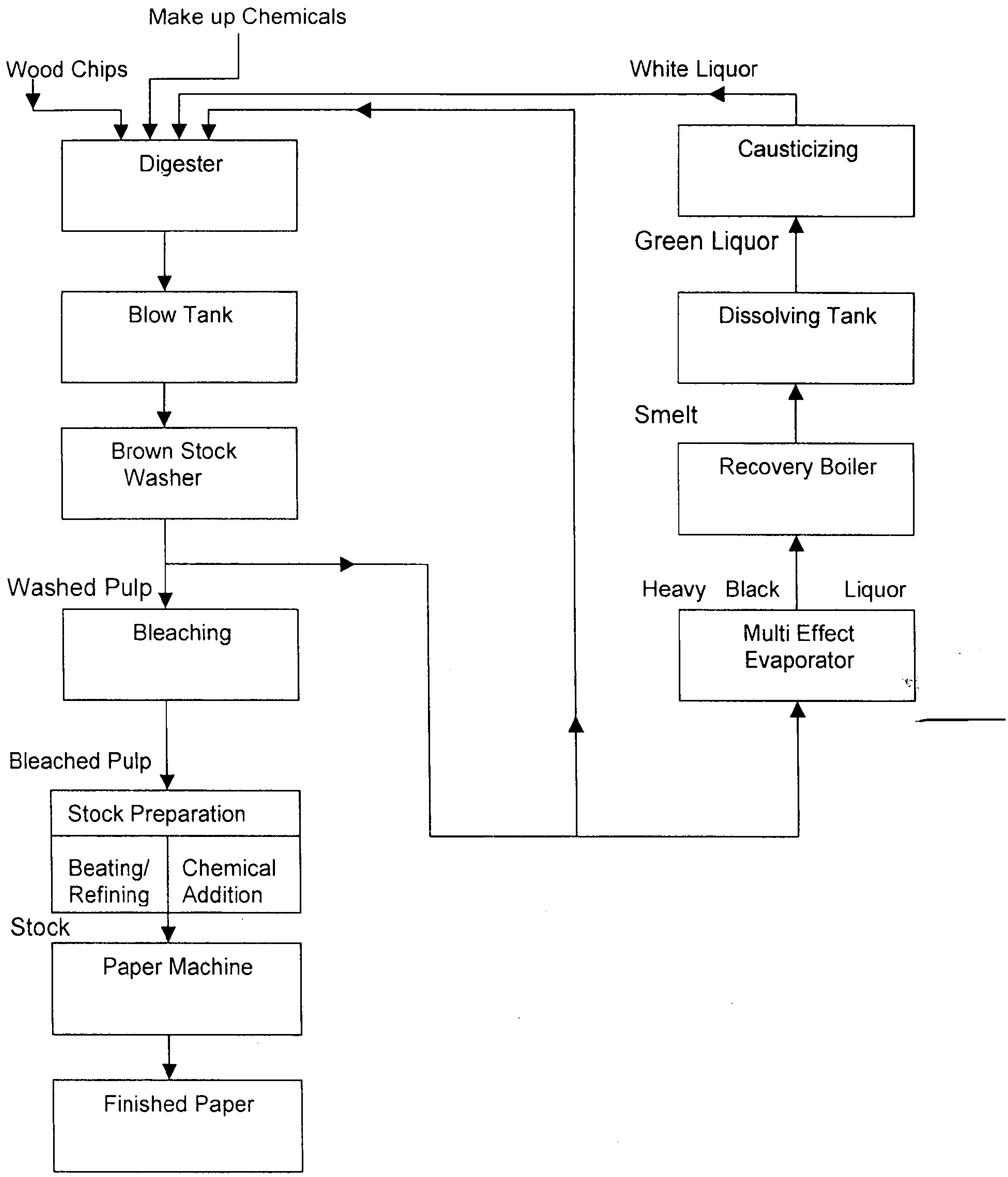
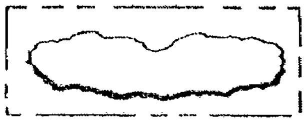


FIG. 1.1: KRAFT PAPER MAKING PROCESS

Appearance

Loss of metal on all exposed surfaces.



(a) UNIFORM CORROSION

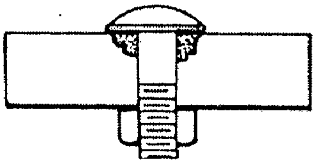
Two dissimilar metals (A&B) corrode at Junction of (A&B)

(b) GALVANIC CORROSION

Holes in the exposed surface.

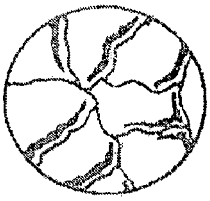
(c) PITTING ATTACK

Holes in the shielded area.



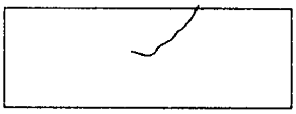
(d) CREVICE ATTACK

Microscopic attack along grain boundaries



(e) INTERGRANULAR

Dynamic Stress

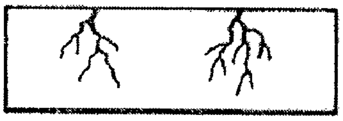


(f) CORROSION FATIGUES

Smooth, wavy pattern indicative of flow direction.

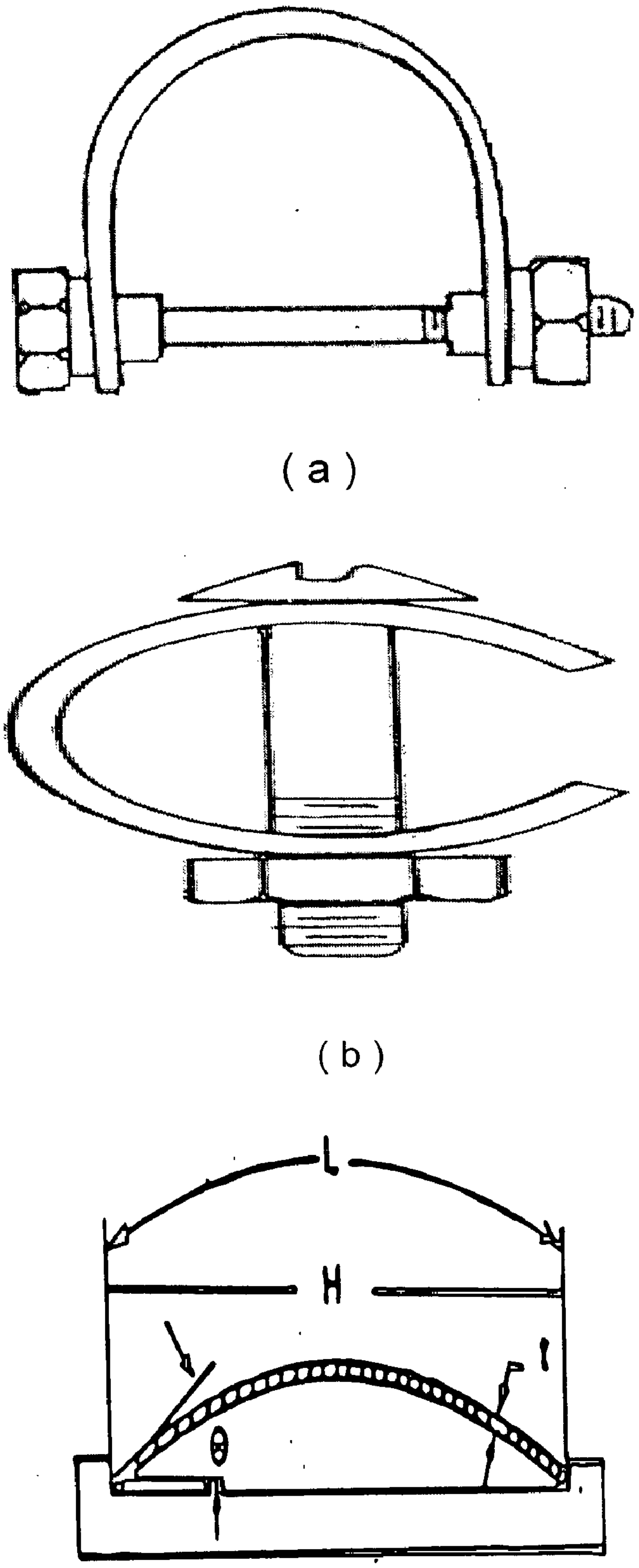
(g) EROSION CORROSION

Static Stress



(h) STRESS CORROSION CRACKING

Fig.1.2: DIFFERENT FORMS OF CORROSION



(a)

(b)

(c)

Fig. 1.3 : STRESSED COUPONS FOR STRESS CORROSION CRACKING

Stage	pH	Temperature ($^\circ C$)	Residual Cl_2 (ppm)	Chloride (ppm)
C	2.0	35	90	1250
D_1	2.4	58	56.5	576
D_2	4.2	73	21.7	360
E	10.3	48	-	850
H	10.0	37	1.2 Kg/ton	1450

TABLE 1.1: AVERAGE FILTRATE CONDITIONS IN BLEACH WASHERS

Process Conditions	In 1971 survey	Proposed closed bleach plant
Chloride (ppm)	1000 ± 500	3000 - 5000
pH	2.0 ± 0.5	2.0
Temperature(oC)	25 ± 2	60 -75
Residual Cl_2 and ClO_2 (ppm)	100 ± 50	?

TABLE 1.2: CHLORINATION FILTRATE COMPOSITION

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CHAPTER : 2

EXPERIMENTAL PROCEDURES

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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 (108). Thus in order to select a better resistant material or opt for suitable protective measures for bleach plant, the present study was carried out through (i) in-plant tests and (ii) laboratory based tests. 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. Also even the field tests can only imperfectly evaluate localized corrosion, environmental cracking, heat transfer effects and intermittent process contamination. This way of 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 service (field) testing. They can also be use 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 covers a spectrum ranging from simple immersion test to sophisticated electrochemical tests. Standardized tests methods, especially electrochemical testing 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 testing and can give idea of material's life on]y in relative sense. In the following paragraphs are given the details of the procedures adopted to performed the proposed work.

2.1 Material Selection :

It has been documented that the austenitic group of stainless steels possesses a wide spectrum of corrosion resistance including suitability for the bleach plant service (109). Low carbon steel (mild steel) is not suitable for bleach plant due to its poor corrosion resistance in oxidizing media. Although the newer generation of 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 (97). Also these steels are not easy to weld as austenitic and are prone to embrittlment when thick sections are welded. The austenitic stainless steels generally have good strength and high ductility alongside corrosion resistance. Consequently, austenitic stainless steels namely 316L, 317L, 904L and 254SMO and a duplex steel were selected for in-plant studies in two mills. They contain higher amount of chromium, nickel and comparatively lesser amount of molybdenum and nitrogen. An elevated nickel amount increases the resistance of austenitic stainless steels to stress corrosion cracking and higher molybdenum content imparts better resistance against pitting, crevice and stress corrosion cracking (110, 111). Presence of nitrogen ensures high tensile and yield strengths. Duplex steel, 2205, is generally known for considerable resistance to chloride stress corrosion cracking (112). The yield strength of duplex stainless steel is two to three times greater than conventional steels. These were subjected to test to offer a better material of construction for most corrosive washers e.g. chlorination and chlorine dioxide. For weight loss and electrochemical tests in laboratory, mild steel, austenitic stainless steel 304, 304L, 316L, 317L and 254SMO and a duplex stainless steel 2205 were selected.

2.2 Specimen Preparation :

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 capacity of available analytical balance, and by the problem of effective entry into the operating equipment. The most common shape of coupons, preferred for the test purpose, is rectangular. Circular and disk type shapes are also used but rectangular is common because most alloys are available in p]ate or sheet form. Also mostly materials are used such that their major exposed area to corrosive media is their surface. Their thickness is much smaller as compared to surface area hence they are tested in plate or sheet form. Other shapes are used when there are restrictions on available product forms or when a specific material condition is required. For the mill test and weight loss test in chloride solutions, coupons of the size 2"x 3/4"x1/8" with a hole of diameter 0.375" at its center of austenitic stainless steels 316L, 317L, 904L, 254SMO and one of duplex stainless steels 2205 were procured from Nickel development Institute, Canada. For in plant test, these coupons were mounted on a rack (described in a later section) which in turn was fixed at different location in washer for exposing the coupons. For weight loss test in peracids solution, the coupons of rectangular shape of the size 1.5" x 1" x 0.12", with a hole at the center, were cut from plane sheet of SS - 304L and mild steel. Chemical composition of the test materials have been given in Table: 2.1.

For electrochemical measurements, austenitic stainless steel 316L, 317L and 254SMO and duplex stainless steel 2205 (each 1.2 cm. long and 0.94 cm diameter) were supplied by Metal samples, USA. Cylindrical sample of mild steel and austenitic stainless steel 304L of length 2.5 cm were cut from the rods of 1.5 cm diameter. The samples were threaded on one plane surface by drilling machine. Chemical composition of all these samples are 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. Otherwise the test results can lead to wrong predictions in terms of relative corrosion resistance due to metal composition. Standard surface conditions are therefore desirable and necessary in order to compare the corrosion resistance of different materials. Also it helps in analyzing 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 (unless the use of temporary protective film such as grease or lacquer would form a part of the service usage) (113, 114).

For the present work, polishing machine with two different speed 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 SiC paper with grit sequence starting from coarse towards fine i.e. 120, 240, 320, 600 and 800 fitted on 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 and to maximize the life of emery paper. 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 physical balance and dimensions were measured by vernier calipers. These coupons were exposed for in-plant study and weight loss study.

2.3 Exposure Details :

2.3.1 In-plant tests :

The in-plant tests were conducted on stainless steel coupons in the bleach plant of two mills, Mill A: APPM, Rajamundary and Mill B: Bilt, Ballarshah, Andhra Pradesh.

These coupons were mounted on a rack having serrated washers to avoid bimetallic corrosion (Fig.2.1). The metal coupons in duplicate were fitted in a rack consisting of two SS-3l6 rods so as to support the specimens rigidly. These racks were fitted on different location in washers namely liquid, wet/dry and gaseous media (Fig.2.2). The bleaching sequences employed in the mill A and Mill B were $CE_1D_1E_2D_2$ and C_DE_oHED respectively. All the racks were removed after six months exposure for analyzing the corroded coupons.

2.3.2 Laboratory Tests :

In laboratory for weight loss test in chlorine dioxide solution simulating to D-stage bleach washer, the austenitic stainless steel 316L, 317L and 254SMO and a duplex stainless steel 2205 were selected. The serrated washers also were used for crevice corrosion. The test duration of these tests was six months. After the exposure, the above coupons were analysed for degree of uniform and localised corrosion. For electrochemical tests in chlorine dioxide solution, the cylindrical samples of above mentioned steels were used. The weight loss tests in peracid solutions were conducted on mild steel, austenitic stainless steel 304L, 316L, 317L and a duplex stainless steel 2205 for six months duration. For crevice corrosion, serrated washer also were used in these tests. The electrochemical tests were performed on cylindrical samples of 304L, 316L, 317L and a duplex stainless steel 2205 in peracid solutions.

2.4 Analysis of liquors :

Analysis of bleach washer liquors, where the specimens were exposed in in-plant test, has been described first. It is well known that process conditions e.g. residual oxidants, chloride, pH, temperature, etc. affect corrosion attack on materials predominantly. Earlier studies (47, 81,115) have reported that whenever corrosion of bleach washer was severe, the washer filtrate exhibited (i) chloride ion level significantly higher than the average . It indicates that regular monitoring and control of this parameter is essential to check the corrosivity of medium.

2.4.1 Residual Chlorine Dioxide Determination (116) :

Reagents

Potassium iodide (KI) 10% Solution

Sodium Thiosulfate ($Na_2S_2O_3$) 0.1N

Starch solution (5 gpl)

Sulfuric Acid (H_2SO_4) N

Chlorine Dioxide Solution Strength :

10.00 ml of the stock solution is pipetted into a 250 ml conical flask containing about 50 ml of water and 25 ml of potassium iodide solution. Be careful that the tip of the pipet extends below the surface of the KI solution. Titrate with 0.1N sodium thiosulfate (0.1N $Na_2S_2O_3$) to a colorless endpoint. Note volume of thiosulfate used and designate as A. Add 25 ml of normal sulfuric acid (N H_2SO_4). Continue titration with thiosulfate to colorless endpoint using starch as an indicator . Note volume of thiosulfate used and designate as B.

Calculations:

Grams per liter ClO_2 = (B – A) x 0.169

Grams per liter Cl_2 = $[B - (B - A) \times 1.25] \times 0.355$

2.4.2 Chloride Ion Determination :

The chloride containing 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 indicator to observe end point (47, 81, 115).

2.4.3 pH Determination :

This was determined by pH meter. The pH meter was calibrated by 0.05 M potassium hydrogen pthalate and 0.01M sodium tetra borate (borax) for pH = 4 and 9.0 respectively at room temperature.

2.5 Solution preparation for Laboratory Tests :

2.5.1 Chlorine Dioxide Solution :

Chlorine dioxide can not be safely handled in concentrated form. For example, chlorine dioxide air mixtures above 10% ClO_2 by volume are explosive (124) . It is well known that chlorine dioxide explodes at : (i) high temperature, (ii) high concentrations, (iii) in the presence of spark, (iv) in the presence of easily reduced material (v) in commercial generators when rust, scale and foreign material inadvertently enter the generator. The sensitivity to explosion is reduced by dilution of chlorine dioxide with either gas or water, and by lowering the temperature. A pure chlorine dioxide solution in laboratory was prepared by slowly adding dilute H_2SO_4 to sodium chlorite ($NaClO_2$) (125). It was then passed into distilled water at very low temperature. Chlorine dioxide water of high concentration, thus obtained, was further diluted to required level and pH was adjusted by adding HCl and NaOH. Desired chloride level was maintained by A.R. grade sodium chloride (NaCl) crystals.

2.5.2 Peracids solutions (117) :

The peracids (P_a - Peracitic acid, P_x - Caro's acid, P_{xa} - mixture of P_a and P_x) are prepared by H_2O_2 , CH_3COOH and H_2SO_4. Peracitic acid was prepared by adding glacial acetic acid to hydrogen peroxide containing the sulfuric acid catalyst. The mixture was then warmed to 45^0C, 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 $30\text{-}35^0C$. P_{xa} samples were prepared by adding the required amount of glacial acetic acid to the cold solution of P_x. Then these solutions were analysed to determine their active oxygen content prior to use and diluted to a required level. pH was increased by adding diluted NaOH. Desired chloride level was maintained by A.R. grade sodium chloride (NaCl) crystals.

2.6 Analysis of Test Liquors of Lab Test :

2.6.1 Chlorine Dioxide Solutions :

The laboratory tests done in chlorine dioxide solutions were synthesized on the basis of their composition normally observed in bleach washers. Accordingly they were also analysed for their pH and chlorine dioxide and Cl- content using same methods as mentioned in section 2.4 above.

2.6.2 Peracid Solutions (117) :

These solutions were analysed for active oxygen content. For this purpose, about 0.3- 0.4 g of the Caro's acid was added to a 500 ml Erlenmayer flask containing 100 ml of distilled water and 10 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 ml of 25% potassium iodide was then added to the Erlenmayer 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, 2-3 ml, was added at this point and the titration was continued until the the dark blue color disappeared to a pale reddish-orange color end point. The concentration of peracids active oxygen were determind by using the following formula:

$$\% \text{ A.O.} = \frac{(V_{\text{thio}} \times 0.1 \times 0.8)}{\text{Sample Weight}}$$

2.7 Weight-Loss Determination :

In this test, the weight of the metal is lost uniformly with time from its surface 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 as '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' (1 mil = 10^{-3} inch).

In the estimation of weight loss and corrosion rate determination, corroded coupons are cleaned off the rust, mechanically and by chemical cleaning procedures (118). It was performed by light brushing of the specimen to remove lose bulky corrosion products. After that coupons were treated with cold solution of concentrated HCl acid + 50gpl $SnCl_2$ + 20gpl $SbCl_3$ which has been specifically suggested for cleaning corroded steel surfaces (118). Following formula was used for corrosion rate calculations (9).

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

W = weight loss in grams

D = density of metal in gm/cm^3

A = area in cm^2

T = exposure time in hours

2.8 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 localised corrosion. Thus on the basis of maximum pit / crevice depth, corrosion resistance against pitting/ crevice corrosion of various alloys can be categorized by the table is given below (119).

	Max. Pit depth	
	Base Plate pits	Pits Under Crevice
Superior	< 0.13 mm	< 0.13 mm
Useful	< 0.13 mm	< 0.39 mm
Unsatisfactory	> 0.13 mm	> 0.39 mm

Pit depth measurements can be accomplished in several ways namely graphic examination, machining, by use of micrometer or depth gauge. In present study, the cleaned coupons were examined 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 focussed at the top of pit by fine focussing 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 (120).

2.9 Electrochemical Measurements :

2.9.1 Basics

Metal undergoes 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 this, 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 the test solutions and acts as one of the three electrodes of cell. The other two electrodes are a counter electrode (graphite rods) and a reference electrode. With the help of potentiostat, one measures for the test material (i) electrode potential (ii) current - potential relationship where potential is changed in predetermined manner (potentiodynamic/cyclic polarisation) (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:

2.9.1.1 Corrosion Potential Measurement :

On dipping a metal in solution, the former tries to aquire an equilibrium potential value 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, simulating actual service conditions as closely as possible, and records a potential versus time (E vs time) curve until a reasonable steady state value is achieved. This potential sometimes also tells about whether the material is in passive state or is in localised corrosion prone region.

2.9.1.2 Potentiodynamic / Cyclic Polarisation :

These are the polarization charecteristics 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.2.3). 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 localised i.e. pitting , crevice corrosion and (iv) the corrosion rate. This plot can be described in following way:

Region A in Fig. 2.3 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, the current, hence corrosion rate decreases rapidly to minimum value as the passivating film is formed over the surface of specimen , termed as passivation region . As one proceeds to potential beyond passivation region, the current again increases (region D). This high current behaviour 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 in the potentiodynamic polarisation plot, called as 'cyclic polarisation', is if external applied potential of metal is made to decrease after reaching some value in the transpassive region. The polarization curve then crosses the passive region somewhere or it does not cut at all (Fig. 2.3). The former is a case when material experiences crevice corrosion whereas in later case, metal does not experience crevice corrosion. The potential where the reverse scan crosses the forward scan is called as repassivation or protection potential. Growing pits passivate at this potential. The more noble this potential, obtained at fixed scan rate, the less susceptible is the alloy to initiate crevice corrosion. In general, once initiated the localised corrosion can propagate at any potential value lies within the hysteresis loop.

To record polarization curves, clean polished specimen was immersed in the test solution for an hour so as to reach he steady state before initiating polarization. Potential was scanned at the rate of 0.116 mV / sec. The change of current with potential was recorded in IBM computer loaded with corrosion software (soft-corr). 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 or more than this (121). The scanning is continued until reverse scan curve crosses the forward scan curve or until the corrosion potential is reached (Fig. 2.3).

2.9.1.3 Potentiostatic :

Although the tendency of pitting/ crevice corrosion can be measured by potentiodynamic 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 (97, 122). Potentiostatic method is solely designed for determining pitting/ crevice potential more accurately than can be done with potentiodynamic tests.

In this method (123), active pits are initiated at the potential more noble than pitting potential (E_p) (as 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 500 μA/cm^2. After stimulation of localized corrosion, the potential is returned as rapidly as possible to preselected value e.g. E_1 ($E_1 \geq E_{corr}$.) 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. 2.4 a). 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. 2.4 b), 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. 2.4 b. 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.

2.9.2 Experimental Equipments :

The equipments used in present study, to perform the variety of electrochemical measurements is computer controlled potentiostat / Galvanostat with basic operating system and corrosion measurement software soft-corr and corrosion cell (Fig.2.5). These are summarized below:

2.9.2.1 Corrosion Cell :

The corrosion cell selected for the present study is versatile, contaminants 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). The working electrode is internally threaded cylinder of the alloy being tested. It is seated against the tubular glass holder using a threaded metal rod and a teflon gasket to avoid crevices. The reference electrode (saturated calomel electrode, SCE) rests in a luggin capillary which is adjusted so that the tip is closed 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.

2.9.2.2 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 time and temperature (dE/dT -7.6×10^4 V/ °C). The electrode consist of pool of mercury 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 eqn at 25^{0}C is

$E_{calomal} = E^0{}_{Hg2\,Cl\,2\,/Hg} - 0.0592 \log (a_{Cl^-})$

$E_{calomal}$ (for saturated KCl solutions) = 0.242 V.

The value of E^0 at 25^{0}C for the calomel half cell has been found to be 0.2677. Consequently, above eqn. becomes

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

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

2.9.2.3 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 (Model 273 of EG&G Princeton Applied Research, USA make) 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 between the highest vertex potential minus the lowest potential can not exceeded 4V. Current is specified as a fraction of the selected current range up to maximum of two times the current range exception of 1 A scale.

The corrosion curves were recorded and analysed with the help of software (soft-corr). It can perform as many as nine different types of corrosion experiments including E vs time, Tafel plots, linear polarization, anodic polarisation, cyclic polarization, potentiacstatic etc. A most useful feature of this software is that it can do any of these techniques or any combination of them up to nine different potentiostat simultaneously, using only one IBM or compatible computer and GPIB card. The routine automatically select the data that lies within Tafel region. It then calculates corrosion current, corrosion rate, Tafel slopes, etc and display the results. The results (except for area and peak) are stored with data, making storage and retrieval, simply a matter of serving and recalling the data.

Some electrochemical measurements in peracid solutions were recorded by Potentiostat / Galvanostat (Model 173 of EG&G Princeton Applied Research, USA make) at Aligarh Muslim University. The model 173 Potentiostat / Galvanostat offers complete flexibility in potential or current control for electrochemical applications.

This model uses an X-Y Recorder and Model 175 Universal Programmer to recoed polarisation curves. Following sections describe the calibration of X-Y recorder.

Before calibration, a sheet of 5-cycle semi-log paper is fitted on the recorder bed. The paper should be oriented such that the log scale numbers are at the top, i.e. cycle increase from left to right. For X-axis calibration, BNC cable is not connected initially from the 'S/A output' at the back of Model173. The pen should coincide with the right most vertical line of semi-log paper, if it does not, adjust by calibration knob of X-axis of X-Y recorder. Then we connect the BNC cable from Model 173 to the x-axis of X-Y recorder. The center conductor of the S/A output should connect to the recorder "-" x input. The outer conductor of the S/A output should connect to the "+" input. Model 173 settings are as follows:

Applied potential: - 4.999 V

"A" Light "ON"

Operating Mode: Contr. E

Cell Selector : Dummy Cell

The pen should coincide with the left most vertical line, if it does not, adjust the recorder 'calibrate' knob on the Range switch so that the pen coincides with the leftmost vertical line.

For Y-Axis Calibration, move the cable from the x input to the y input maintaining the polarity described previously. If the pen coincide with 5 inch at y-axis at 1000 mv (say). Then by A initial potential knob of Model 175 programmer we change the potential to 1100 mv (say) from 1000mv and if the pen coincide with 6 inch at y-axis. In this case scale of y-axis would as such 1100 -1000mv = 6 - 5 inch or 100mv/ inch. We can change the scale by varying the position of calibrate knob of y axis.

2.9.2.4 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. of the 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.

2.9.2.5 Metallurgical Microscope :

The metallurgical microscope has been used to examine etched metalographic or polished specimens. 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 refer to orientation of the face of the polished sample that is being examined. The microscope used in present study is upright type (Fig.2.6) 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:

2.9.2.5.1 Illuminating System :

Tungsten-halogen filament lamps are used in the microscope (EpiStar 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 5 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.

2.9.2.5.2 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.

2.9.2.5.3 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.

2.9.2.5.4 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

$$NA = n \sin \alpha$$

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 or bright field and polarised 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 standardised 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 planochromatic objectives 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 of the objective to the specimen surface. Working distance decreases as magnification of the objective increases. All the objectives in this microscope are perfocal, 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 parcentered 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.

2.9.2.5.5 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. EpiStar 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

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

2.9.2.5.6 Microstructure Examination :

The stainless steel samples were polished for etching and microscopical 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 MeF3 optical microscope (Cambridge Instruments Company, Austria make). The table indicates materials, their respective time and chemicals for etching, is given below.

Materials	Time of Etching	**Etchants**
Mild steel	10 seconds	HNO_3 (1 - 5 ml) mixing in 100 ml methanol
Stainless steels 304L, 316L	10 -15 seconds	Solution of 100gm of oxalic acid (A.R. grade) crystals in 900 ml of distilled water.
Stainless steels 317L, 904L and 2205,	45 seconds	Solution of 20 ml glycerin , 20 ml HCl, 10 ml HNO_3 and 10 ml $H_2 0_2$.
Avesta 254SMO	80 - 90 seconds	Solution of 0.5 gm chromic acid in 50 ml of conc. HCl .

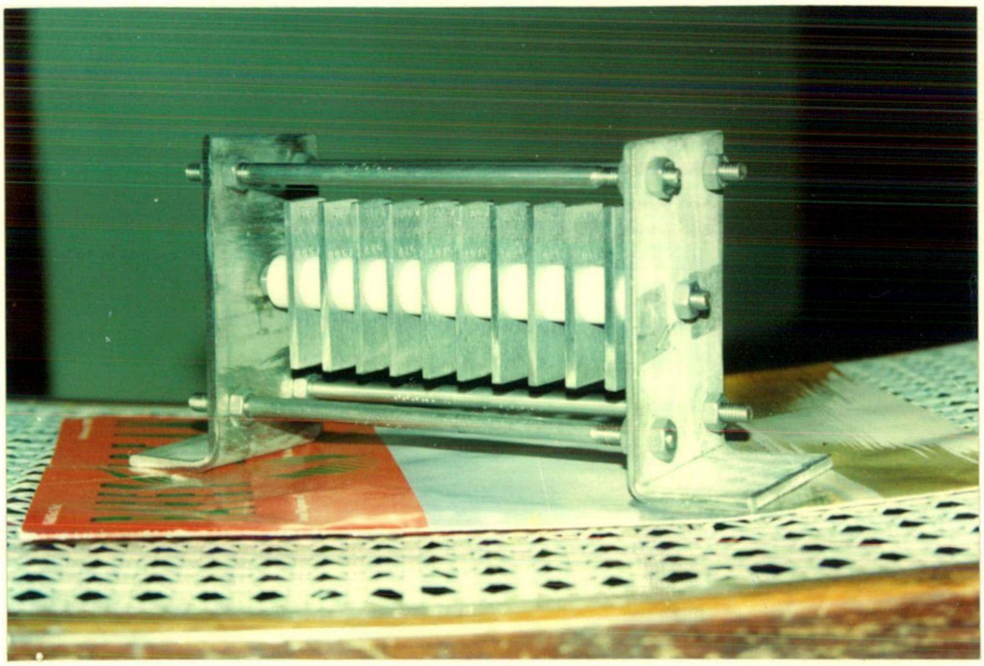

FIG. 2.1 : TEST RACK USED IN MILL A AND B, ANDHRA PRADESH

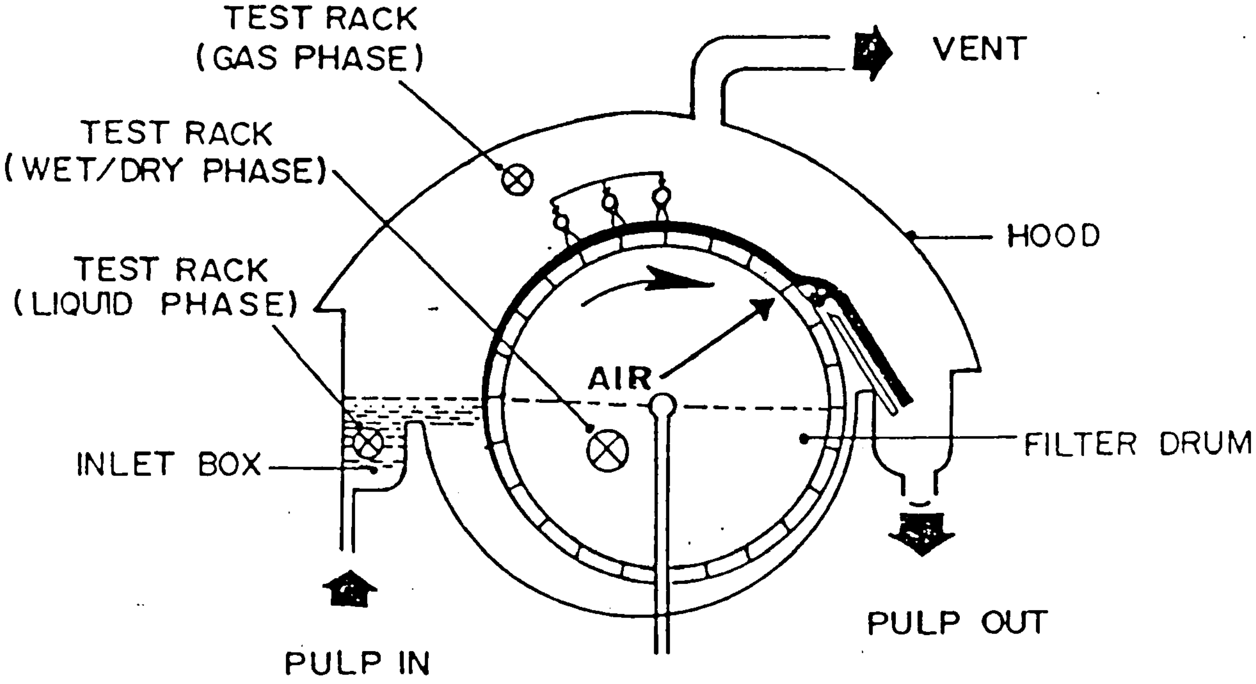

FIG. 2.2 : LOCATION OF COUPON TEST RACK

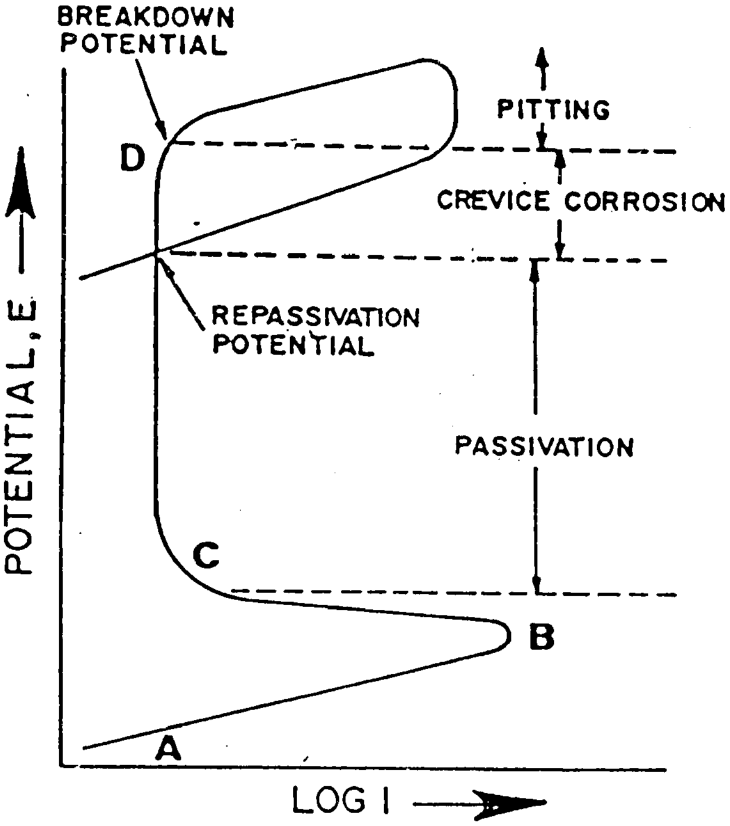

FIG. 2.3 : ACTIVE PASSIVE TRANSITION

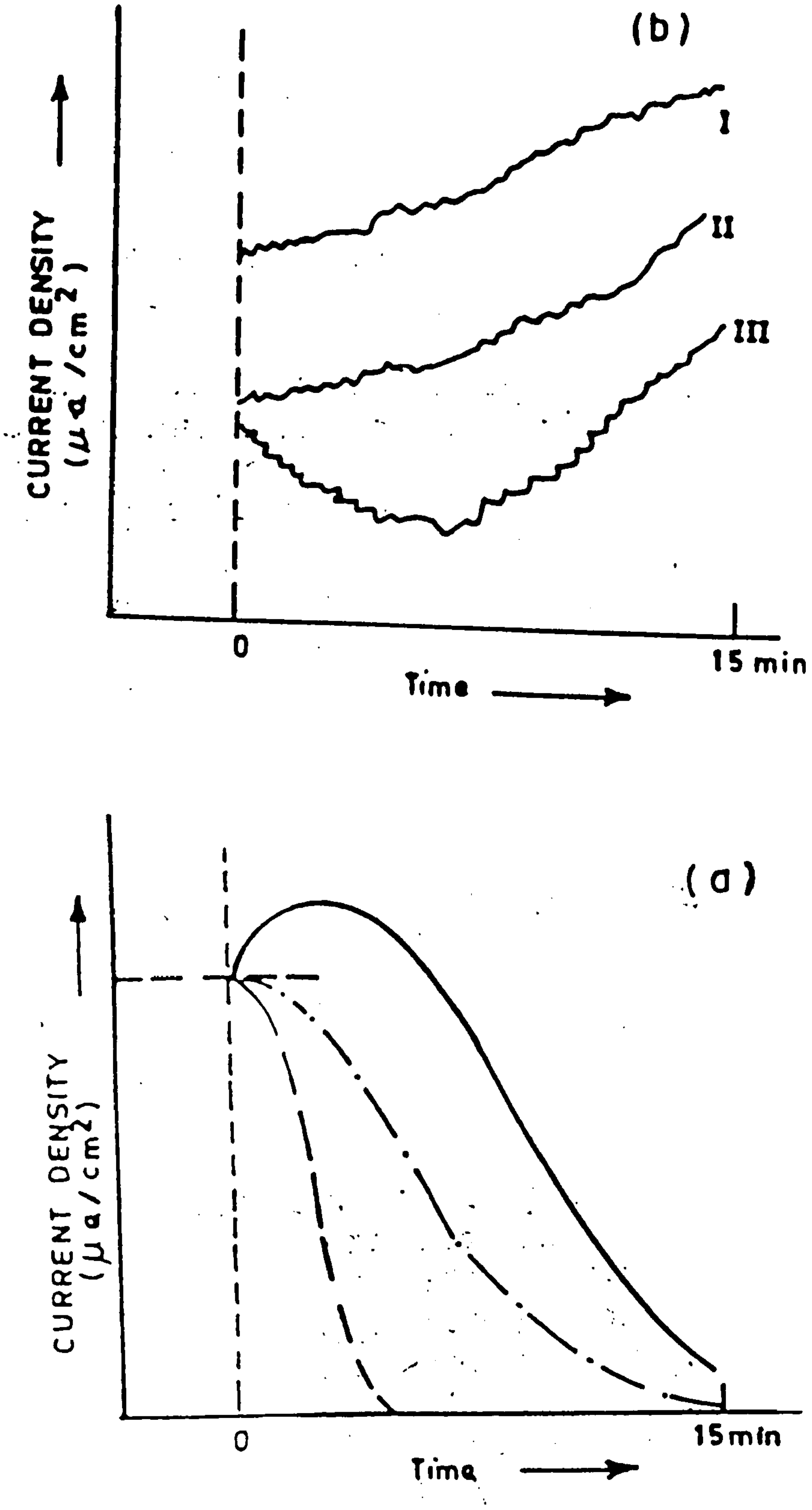

FIG. 2.4 : POTENTIOSTATIC CURVES (I VS TIME)

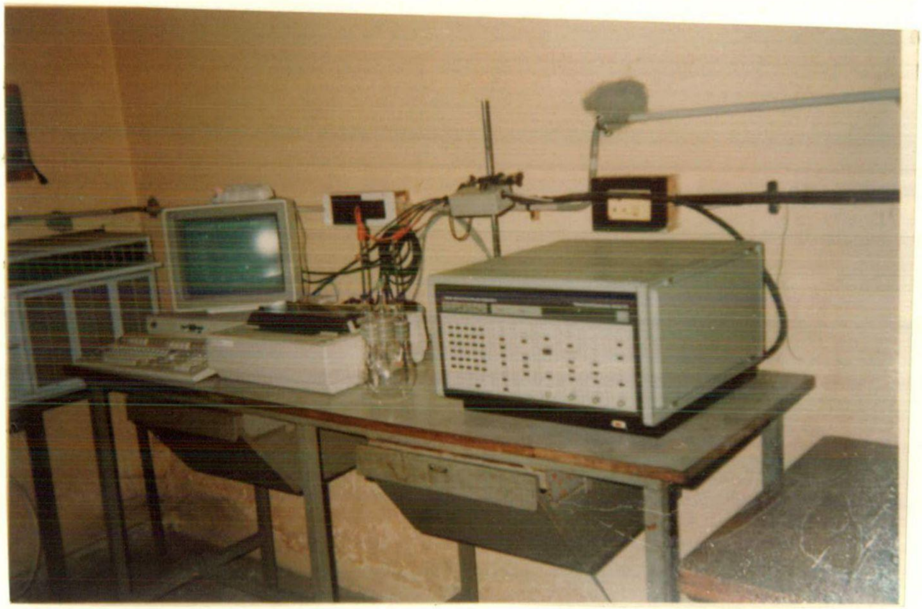

FIG. 2.5 : ELECTROCHEMICAL EXPERIMENTAL SET- UP FOR CORROSION MEASUREMENTS

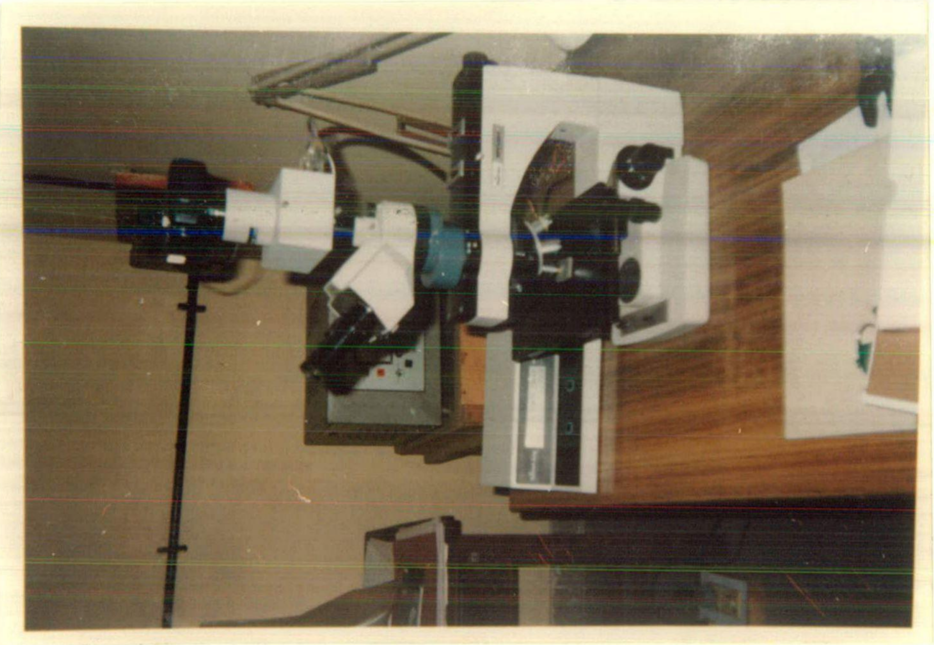

FIG. 2.6 : METALLURGICAL MICROSCOPE USED FOR MICROSCOPICAL OBSERVATIONS

Alloy	C	Cr	Ni	Mo	Cu	Mn	P	S	Si	N
MS	0.18					1.66			0.04	
304L	0.02	18.10	11.52	-	-	1.92	-	-	0.59	-
316L	0.016	16.45	10.22	2.11	0.25	1.75	0.026	0.008	0.44	0.03
317L	0.019	18.19	13.23	3.11	0.42	1.78	0.031	0.001	0.55	0.047
904L	0.009	19.7	24.1	4.26	1.40	1.52	0.02	0.001	0.28	0.045
2205	0.025	22.00	5.700	3.01	0.29	1.44	0.022	0.001	0.48	0.154
254SMO	0.011	19.9	17.9	6.07	0.67	0.43	0.024	0.001	0.31	0.203

TABLE : 2.1 : COMPOSITION OF MILD STEEL AND STAINLESS STEELS (PLATE SAMPLES)

Alloy	**C**	**Fe**	**Ni**	**Co**	**Mn**	**P**	**Cr**	**Mo**	**S**	**Cu**	**N**	**Si**
304L	0.02		11.52		1.92		18.10					0.59
316L	0.020	BAL*	10.87	0.18	1.69	0.030	17.44	2.16	0.030	0.31	0.04	0.69
317L	0.016	BAL*	13.44		1.75	0.026	18.80	3.37	0.004			0.50
2205	0.020	BAL*	5.480		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 : 2.2 : COMPOSITION OF STAINLESS STEELS (CYLINDRICAL SAMPLES)

CHAPTER : 3

IN-PLANT CORROSION INVESTIGATIONS

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3.1 Introduction :

Globally, the paper industry is undergoing major changes in their paper making process for several reasons - controlling water and air pollution within stipulated limits is the most important of them. Accordingly, as a part of pollution controlling exercise, the paper mills are renovating their bleach sequences by introducing chlorine-dioxide (D) bleach stage and/or substituting chlorine partly by chlorine-dioxide (C_D). Changes in the bleach chemicals affect the corrosivity of the liquid media which in turn may affect the credibility of metallurgy of bleach plants. To understand this aspect of corrosion, several laboratory and in-plant tests have been performed on stainless steels, Ni-based alloys and Titanium in D and C+D bleaching stage or in environment observed in these bleach plant conditions.

Several studies (47 – 75) indicate that chlorine-dioxide is equally or in certain conditions more corrosive than chlorine, hence D and C_D stages are expected to be more aggressive than C stage. It is therefore of immense importance if experimental data is generated on the corrosion performance of the presently used material and the possible candidate materials in the bleach plants using chlorine dioxide. Since the process parameters for bleaching depend on the fibrous raw material and the pulping conditions, it was considered necessary to generate data on corrosion performance in the local mills which have only recently started using chlorine dioxide and have reported corrosion failures apprehended because of this change. Consequently, an in-plant test was conducted to suggest suitable material of construction for bleach washers and related machinery of C, D and C_D stages. To achieve this objective, coupons of five stainless steels were exposed for about six months in bleach plants of two Indian mills. These coupons were analysed for uniform, localised and weld related corrosion.

3.2 Experimental Details :

3.2.1 Materials :

Corrosion test coupons, size 2"x $^{3}/_{4}$"x $^{1}/_{8}$" with a hole of diameter 0.375" at its centre, of austenitic and one of duplex stainless steels were selected for the present tests. The compositions of these stainless steels have been given in Table 2.1 in chapter 2. All the samples were solution annealed as per ASTM spec A240. They were welded on one side autogenously using GTAW (TIG) and then ground smooth using 120 grit. Before exposure, the coupons were degreased using acetone solution and weighed. Duplicate coupons of all the five stainless steels were fixed in a rack made from SS-316 stainless steel plates, rods and nuts. The coupons were insulated from each other and from the stainless steel rod with the help of teflon shoulder washers, spacers and tape. The covering of metal by shoulder washer provided the sites for initiating crevice corrosion. The coupons in the racks were tightened to a fixed torque using torque wrench so that position of coupons is not disturbed during the exposure so as to avoid any mechanical wearing. These racks were welded at different locations in bleach washers for corrosion exposure as detailed below.

3.2.2 Test - Sites and Environment :

In-plant tests were conducted in two kraft pulping mills (named as mill A and B). Mill A uses 10 - 20 % bamboo and rest hardwood for making pulp. Their bleaching sequence is $CE_1D_1E_2D_2$ type which help them achieve 84% pulp brightness. Mill B uses 67% bamboo and rest hardwood as fibrous raw material. The bleaching sequence is C_DE_OHED for achieving 86 - 87 % pulp brightness. Both mills recycle their filterates and use SO_2 as antichlore in D washer.

The racks of test coupons (Fig. 2.1) were exposed in washers of C and D_1 stage of Mill A and of C_D and D stage of Mill B. The process conditions in these washers are given in Table 3.1. The coupons were exposed by welding the racks in vat and on the hood (inside washer) in both the mills while, in addition, over the rotating drum in Mill A (Fig. 2.2). Thus the metals corroded due to liquid, gaseous and wet/dry phases of the media respectively. Duration of exposure of the coupons was 202 to 206 days.

3.2.3 Test Method For Determining CCT and CPT (126, 127):

In this method serrated washers have been used for providing teflon to metal crevices to the stainless steels. The testing method adopted is an extension of the technique which proved successful for the quantitative evaluation of pit initiation resistance. Samples of austenitic stainless steel (316L, 317L, 904L and 254SMO) and duplex stainless steel 2205 had been exposed to 10% $FeCl_3$ for 24 hours at fixed temperature in Teflon to metal crevice configuration. At the end of one such exposure period, the stainless steel was examined visually. If no corrosion attack of any type could be observed, the sample was considered to be immune at that temperature and was then exposed for a further 24 hours at a 2.5°C higher temperature. This procedure was continued until attack of any kind was observed.

The CPT value for all steels were also calculated by same procedure except serrated washers not used.

3.3 RESULTS :

After the exposure, the corroded coupons e.g. in test racks (Fig.3.1 and 3.2) were cleaned by light brushing and by treating with cold solution of concentrated HCl with 50 gpl $SnCl_2$ and 20 gpl $SbCl_3$ (128). The cleaned coupons were weighed to calculate the corrosion rates (Table-3.2). They were also analysed for the extent of pitting, crevice corrosion and weld related corrosion. For knowing these parameters, depths of the pits formed on (i) open surface, (ii) under crevices (part of coupons covered under shoulder washers) and (iii) on welded area of the coupons respectively were measured under the microscope. Depth of the deepest pit (maximum pit depth), formed under different conditions, has been considered as a parameter representing the degree of attack. On this basis and the criteria adopted earlier (68), the materials have been classified in three categories namely unacceptable, satisfactory and superior. This categorisation is shown in Tables- 3.3, 3.4 and 3.5.

The microstructures of tested stainless steels are shown in Fig. 3.3. The microstructure of these steels shows austenitic matrix. The microstructure of 316L austenitic stainless steel is a single phase structure, consisting of grains of austenite. Twins are also visible. The extent of twinning is less than the alloy 304L and grains are also finer as compared to the alloy 304L (Fig.5.1). The microstructures of 317L is also a single phase structure, shows austenite grains. Twins are also visible. Grains are finer as compared to 304L. The structure of 904L is also a single phase structure, consisting austenite. Twins are also visible. Grains are coarser than 316L and 317L. Dual phases i.e ferritic phase with austenitic is observed in the structure of 2205. This is a banded structure. Twinning are visible only in the austenite grains. A single phase austenite is also present in the structure of 254 SMO. Due to higher amount of alloying elements, grains are not homogeneous. This is revealed by etching. Some grains are etched lightly and some are heavily etched. Twins are also visible across the grains.

3.4 Discussion :

3.4.1 Corrosivity of Washers :

The coupons exposed to gaseous phase in C-washer have been attacked most (Fig 3.1, Fig. 3.4, Fig. 3.5 and Fig. 3.6), predictably due to presence of gaseous Cl_2 along with moisture which together create highly corrosive media of pH ~ 1-2 with dissolved Cl_2 and Cl^- (50).The next corrosive stage is D-vat. This is probably due to higher oxidising power of ClO_2 as compared to Cl_2, higher concentration of residual oxidant (129) as compared to C-vat although liquor in D-vat is less acidic. Pitting attack on coupons exposed to gaseous phase of D-washer is of the same order as in D-vat. The attack is lesser as compared to C-hood due to lesser concentration of ClO_2 (in gaseous phase of D-washer) as its solubility, in water, is more than Cl_2.

Coupons exposed on washer drum experience lesser corrosion as they undergo immersion in D-vat in cyclic manner thus alternating between liquid and gaseous media. Liquor in C-vat poses similar degree of corrosivity under crevices as D-drum.The corrosivity of liquor in C-vat is comparatively less, although its pH is more acidic than that of D-vat's liquor. Crevice attack on coupons exposed on C-drum is slightly less. The media in C_D-washer (Mill B) are more corrosive as compared to D-washer. This may due to (i) lower pH (ii) more oxidising nature of the liquors being mixture of Cl_2 + ClO_2. Under some conditions, this may be equally corrosive as the liquor of C-washer.

Overall, the conditions in Mill A appear more corrosive than in Mill-B. This could be attributed to higher concentration of residual oxidants and lower pH in some cases in Mill A.

3.4.2 Performance of Materials :

Corrosion rates of various stainless steels are not high except for the coupons exposed in C-stage gaseous phase (barring 254SMO) for instance 316L coupon was overwhelmingly `eaten' (No.2 in Fig.3.4) and 317L showed unacceptably higher attack (No.0 in Fig.3.5). The different stainless steels may be put in following order of increasing degree of resistance against uniform corrosion :

316L < 317L < 904L and 2205 < 254SMO

However, in the Cl^- containing acidic oxidising media, more cases of materials' failure have been reported due to localised corrosion, as such it will be better to assess the extent of localised corrosion on the tested materials for estimating their suitability. The results (Table 3.3) show pitting on 316L as maximum followed by 317L, 904L, 2205 and 254SMO . In some cases, 317L and 904L show equivalent performance. The present results are in accordance with the latest reported in-plant test (70) according to which 904L experiences high degree of localised attack while 254SMO was resistant in D-washer having less than 100 ppm of residuals. In present case, 904L exposed in D-washer of mill-A experiences high degree of pitting where amount of residuals are quite high in comparison to the observations in Mill-B. In an earlier reported in-plant test results (68), extensive localised corrosion is observed even on 6% Mo-stainless steel exposed in hood of D-washer which is an attribute of high temperature and residual oxidant. In both the mills (A, B), where presently reported tests were conducted, the temperatures and amount of residual oxidant were comparatively low and the localised attack on 254SMO was also negligible. This significantly different observation on corrosion performance all the more justifies performing in-plant tests in different mills because of substantial differences in process conditions.

Figure 3.7 and Figure 3.8 show severity of crevice corrosion in Mill B (C_D - liquid stage). In Fig. 3.7, coupons of SS-316L, 317L and 904Lare denoted by No. 1, 2 and 3. These indicate unacceptable, satisfactory and suitable material of construction respectively. Fig. 3.8 shows the severity of crevice corrosion also by Scanning Electron Photomicrograph at 25x in same media and for same materials. On comparing crevice corrosion (Table 3.4), in most cases 316L shows least resistance, followed by 317L, 904L, 2205, 254SMO. Some exceptions are observed however. Thus in case of coupons exposed in C-hood (Mill A)- attack on 904L is much more than at 317L (may be due to inconsistent or unequal flow of Cl_2 gas) (904L coupons were at the middle of rack so Cl_2 gas may easily pass around these coupons as compared to 317L). On the basis of pit density on the surface under the crevice, one observes that, in D-washer of mill-A, 317L, 904L and 2205 are attacked to same degree and they show lesser resistance than 316L (Table 3.4) when exposed to liquid media of this washer. It seems, in D washer of mill A, conditions are such which makes SS with higher Mo more vulnerable to attack than SS-316L. However, presence of higher N (in 254SMO) seems to nullify this.

The microstructure of welded part of the tested stainless steels (316L, 317L, 904L, 2205 and 254SMO) are shown in Fig.3.9. The grains are not cleared in the structure of SS 316L due to some defect of etching or polishing process. The structure of 317L and 904L are a typical cast structures. Dendrites are visible in both structures. Dendrites are coarser as compared to 317L. The interdendritic region which is appearing black, is due to segregation of alloying elements like Mn, Mo, Cu etc.. This segregation is due to coring phenomena. Due to difference in chemical composition, etching characteristics is different. The structure of 2205 is a single phase structure but due to some etching or polishing defect, black areas is appearing. This black region is not a phase. It has to be further investigated. In the structure of 254SMO, dendrites are visible. Basically it is a single phase structure.

Higher degree of weld area attack as compared to pitting is observed in more corrosive media (Table 3.5). Thus coupons exposed in C-hood of Mill A have become totally porous in their weld areas (Fig.3.4 – 3.6, a rectangular strip on all the sample except 316L, which is overwhelmingly eaten). Mill B does not show these type of attack. In almost all cases, 316L shows maximum attack and 254SMO shows minimum. In majority of the cases, the attack on 2205 appears more than on 317L followed by 904L. It is known that welding practices result into microsegregation and coring. The materials showing higher degree of attack may have larger fraction of dendritic phase (Cr~14%, Mo~1.8%), which in turn may be the result of the composition (130). It is also expected that more richly alloyed stainless steels (Mo >

4%) may show higher degree of attack on their welded areas due to (i) alloy depleted region (ii) precipitation of intermetallics like sigma (σ) phase (131). Although all the coupons were autogeneously TIG welded, the strange behaviour of weld area attack on 317L/904L/2205 coupons could be attributed to the variation in their composition particularly Ni, Mo and N.

On the basis of all the above type of corrosion attacks, following can be suggested (i) In general, 316L is least while 254SMO is most resistant material.
In one of the earliest performed in-plant test related to D-stage washer (67), 6%Mo containing SS is observed to be best among the tested stainless steels.(ii) corrosion resistance is in the order : 316L<317L<904L ≤ 2205<254SMO.

The observations on pitting and crevice corrosion can also be checked with the help of pitting resistance equivalent (PRE) no. (130,131), critical pitting temperature (CPT) and critical crevice temperature (CCT) values. PRE no. indicates resistance of a material against pitting attack while CPT and CCT, in °C, are the lowest temperatures at which pitting and crevice corrosion respectively occurs on the steel surface. The PRE numbers of the tested materials were calculated by the formulas, are given below:

(1) PRE =% Cr + 3.3 x %Mo + 16 x N

(2) PRE =% Cr + 3.3 x %Mo + 30 x N

The CPT and CCT values were determined using methods described in section on experimental details. These are observed to be similar to those reported in literature (131,132) with slight difference which could be related to the composition of stainless steels. PRE nos., CPT and CCT values for the tested materials have been given on next page.

Material	PRE No. (130)	PRE No. (131)	CPT °C	CCT °C
316L	23.893	24.313	5 -10	<5
317L	29.205	29.863	33	<5
904L	34.478	35.108	45	10 -12
2205	34.397	36.553	52 - 54	15
254SMO	43.179	46.021	75	45

Accordingly, 316L is expected to show least resistance while 254SMO the highest resistance to pitting. Pitting resistance of 317L should be better than that of 316L. According to PRE no. (131) and CPT value, 904L should pit more than 2205. This is observed in the test results also. Better assessment of the pitting resistance on the basis of PRE no.(131), appears to emphasis the inclusion of N vis-à-vis Mo in enhancing pitting resistance of the stainless steels.

By and large, CCT values of the tested stainless steels and the predicted resistance against crevice corrosion is in accordance with the test results. This shows the importance of Mo and N together in imparting resistance against crevice corrosion. Another test performed in near neutral D-bleach media (62), however, shows the importance of Mo content in resisting crevice attack. Beneficial effect of Mo in imparting pitting resistance has also been demonstrated in another study (63), which suggests breakdown of passivation in case of 904L even at lowest Cl level and 50C while 254SMO still showing passivation even for higher Cl and upto 65C in service conditions of D-washer. The present in-plant test, however, show 254SMO also experiencing localised attack although to a lesser degree than 904L in temperatures range 50-60C.

3.4.3 Material Selection :

Material selection involves not only the comparison of corrosion resistance of the materials but also their mechanical properties and cost along with their fabrication aspect so as to provide a maintenance free long life. As such, effort has been made to propose about material selection considering their mechanical properties and cost (Table 3.6 and 3.7) also.

3.4.3.1 Mill A :

C-washer :

For exposure in gaseous phase e.g. for pipings, valves and other equipment, one should consider a material more resistant than 254SMO for instance 654SMO which has been observed to show required corrosion resistance (133). This material is also less costlier than the Nickel based alloys which could also be potential resistant materials. For vats, 254SMO will be the premium brand. In order that types of fabrication materials are limited to as low as possible, all except 316L will be suitable choice. A comparison of strength and cost (Table 3.6 and 3.7), makes 2205 better (for equal strength requirement) because of its superior strength in comparison to 317L and 904L and lower cost with respect to 904L. Similarly, for washer drum and machinery to be exposed to wet/dry environment, 2205 will be better choice.

D-washer :

For liquid media in vat, crevice corrosion tendency on all the tested stainless steels except 254SMO is on the higher side, although in satisfactory limit. Hence, 254SMO will be better material for vat and related process equipments. For hood or equipment exposed to gaseous media, 316L onwards could be suitable materials. However, 2205 is suggested on the basis of strength and cost. For drum washer and related machinery likely to expose to wet/dry environment, all except 316L are acceptable though only 254SMO is in premium range. Since crevice attack on 317L is lower than that on 904L and 2205, the former will be better acceptable. Initially it may be a little more costlier than 2205 but may turn out cost-effective in longer duration.

3.4.3.2 Mill B :

C_D - washer :

For C_D-vat, the premium brand will be 254SMO. However 2205 should be preferred on the basis of cost, strength and degree of attack. For hood and other equipment likely to be exposed to gaseous media, 2205 will be best acceptable material. This material experiences least attack and is cheapest if compared for equal strength barring 254SMO.

D – washer :

For vat, hood and process equipment likely to be exposed to gaseous and liquid media 2205 is best material on comparing degree of attack, strength and cost.

In nutshell, one observes the suitability of duplex stainless steel 2205 in most of the environment except for exposure in (i) C-hood, (ii) C-vat and (iii) D-drum in Mill A. An additional advantage in using 2205 is in its having better resistance for chloride stress corrosion cracking (CSCC), due to lesser Ni content.

From fabrication aspect, welding of 2205 is not much different than the conventional material 316L except that cost of welding consumables in former case is higher. This is balanced by considering thinner gauges of 2205 (for equal strength), which will require less welding consumables and lesser efforts in edge preparation. Fabrication of 254SMO is more costly due to restricted heat input at welding and more time consuming machining. Overall, the proposition on material selection for different bleaching stages as per the conditions prevailing in the present studied plants, is given in Table-3.8.

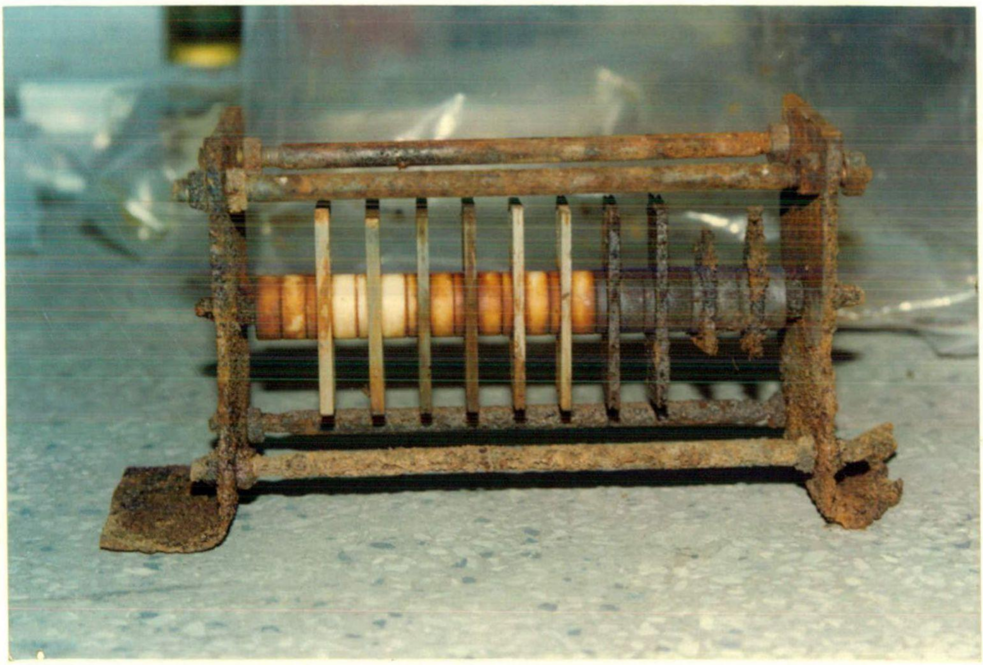


FIG. 3.1 : TEST RACK (AFTER SIX MONTHS EXPOSURE) OF MILL A (C-WASHER, GASEOUS PHASE).

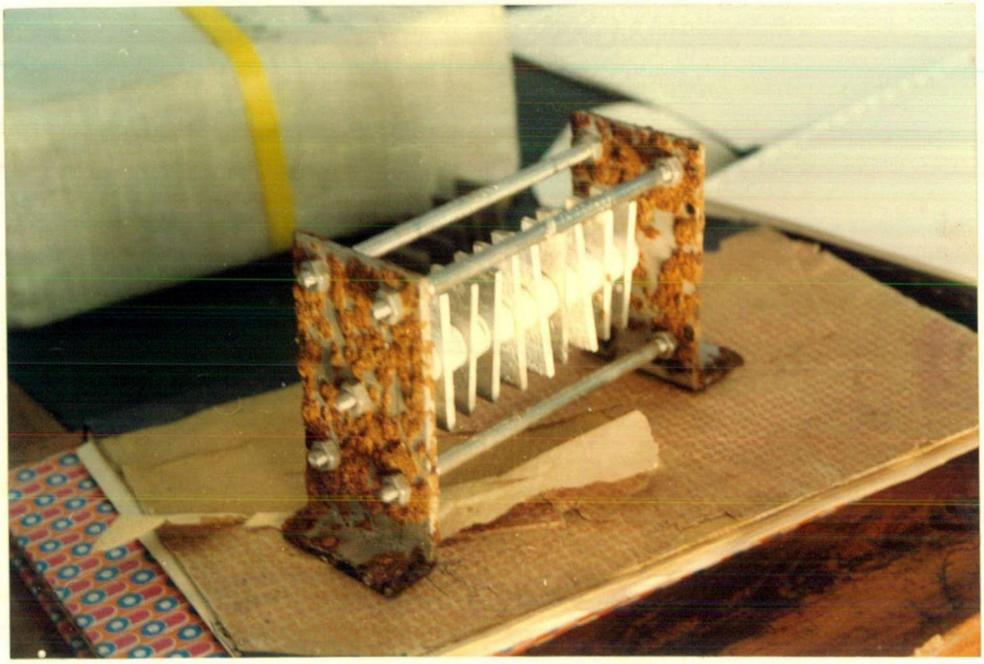
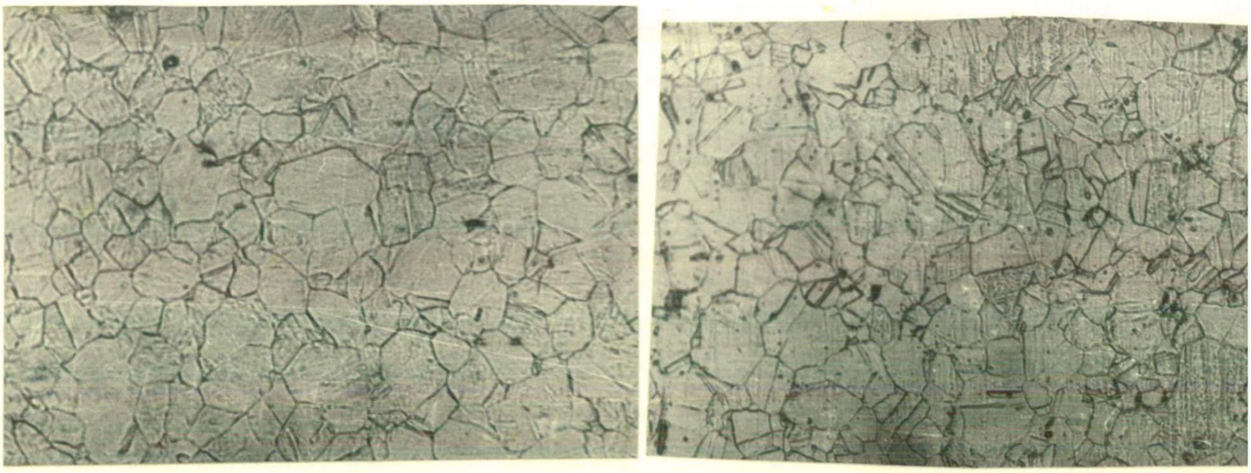


FIG. 3.2 : TEST RACK (AFTER SIX MONTHS EXPOSURE) OF MILL B (H - LIQUID PHASE).



(a) SS 316L (x 200)

(b) SS 317L (x 200)

(c) SS 904L (x 200)

(d) Duplex SS 2205 (x 200)

(e) 254 SMO (x 200)

FIG. 3.3 : MICROSTRUCTURE OF STAINLESS STEELS (BASE METALS)

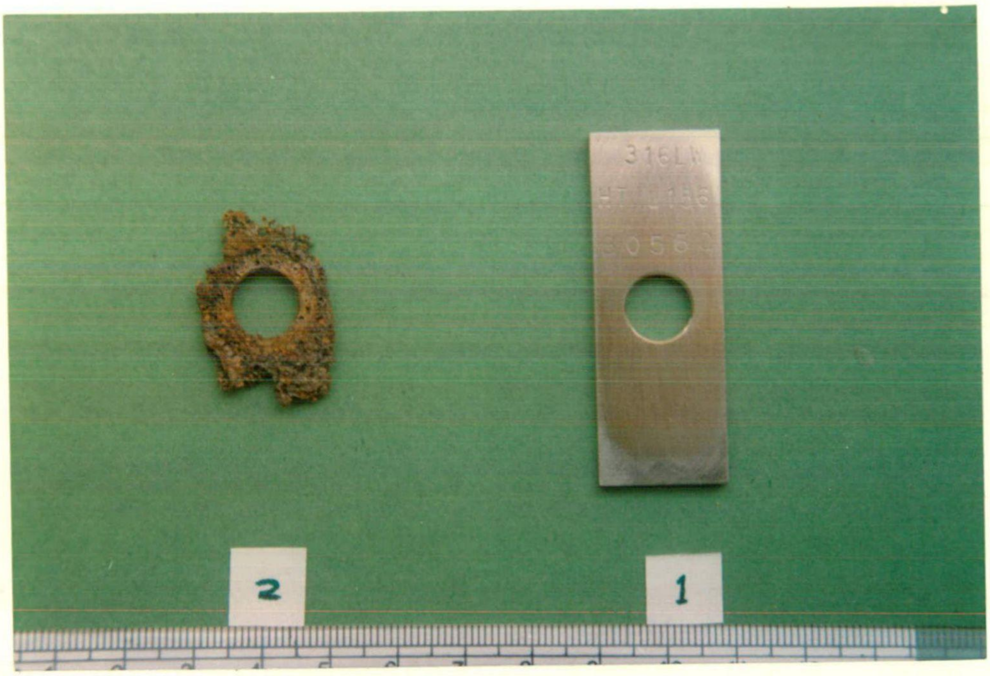
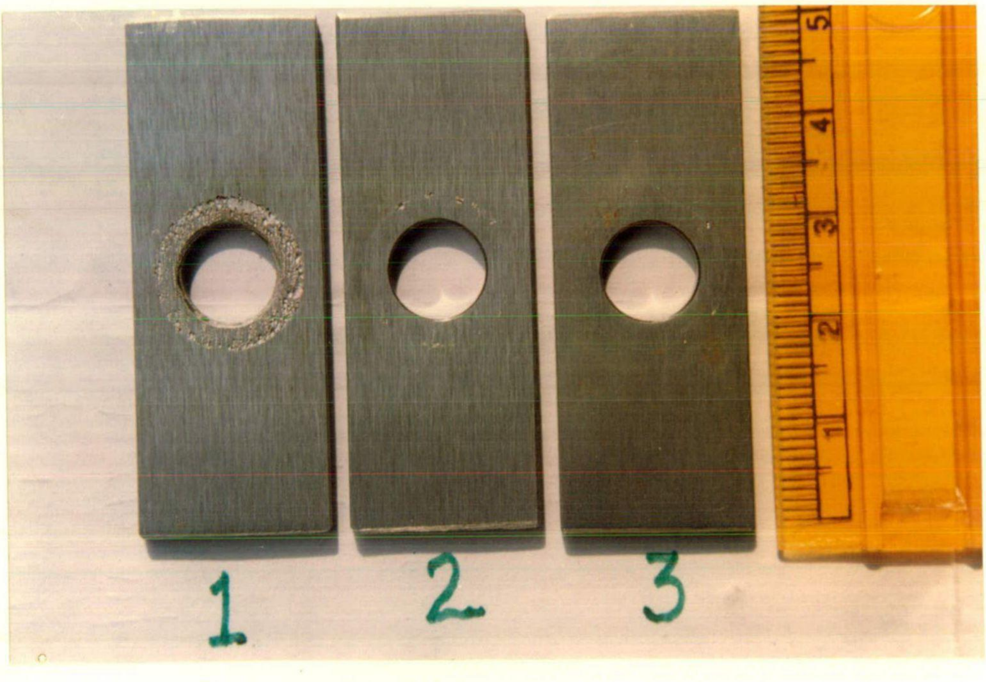


Fig. 3.4 : CORRODED (NO.2) AND FRESH (NO.1) COUPONS OF SS 316L
MILL A (C-WASHER, GASEOUS PHASE)

Fig. 3.5 : CORRODED COUPONS OF SS 317L (NO.0) AND SS 904L(NO.01)
MILL A (C-WASHER, GASEOUS PHASE)

Fig. 3.6 : CORRODED COUPONS OF 2205 (NO.4) AND 254 SMO (NO.5)

MILL A (C-WASHER, GASEOUS PHASE)



SS 316L (no.1) SS 317L (no.2) SS 904L (no.3)

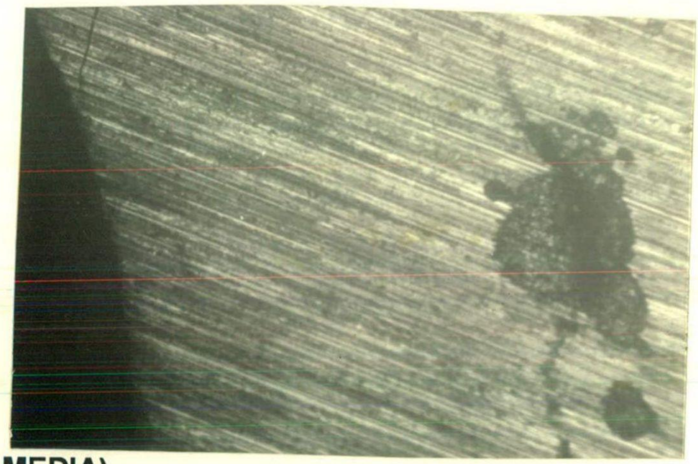
Fig. 3.7 : SEVERITY OF CREVICE CORROSION BY NORMAL PHOTOGRAPH

MILL B (C_D-WASHER LIQUID MEDIA)

(a) UNSATISFACTORY

SS 316L (X 25)

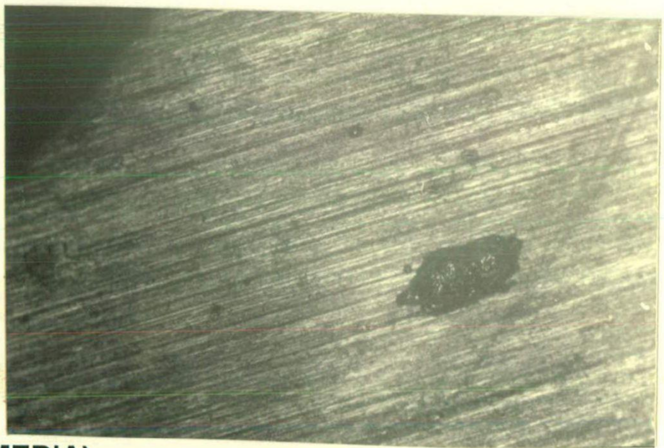
MILL B (C_D-WASHER LIQUID MEDIA)



(b) SATISFACTORY

SS 317L (X 25)

MILL B (C_D-WASHER LIQUID MEDIA)

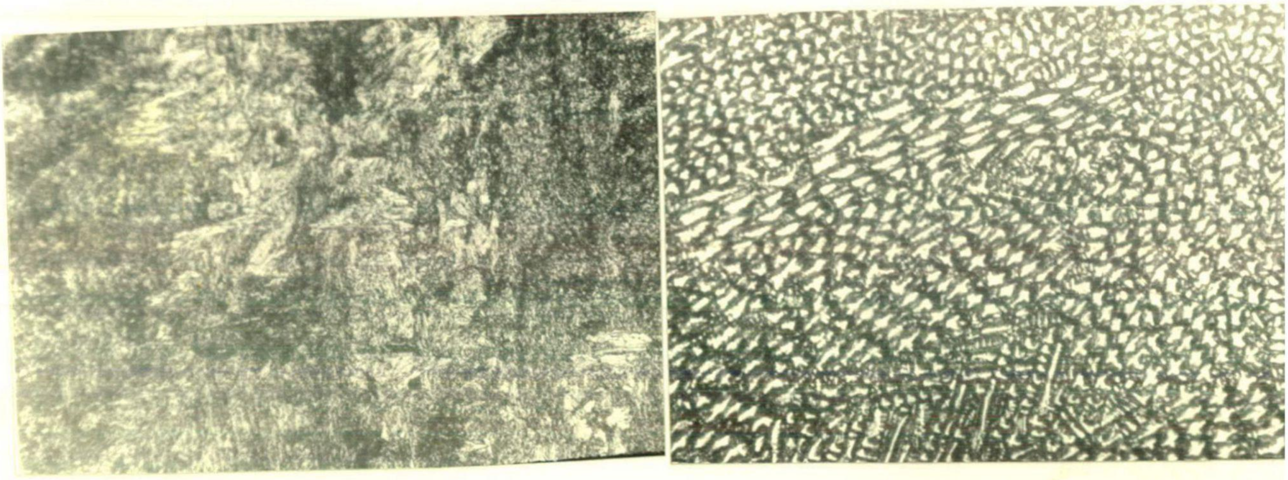


(c) SUITABLE

SS 904L (X 25)

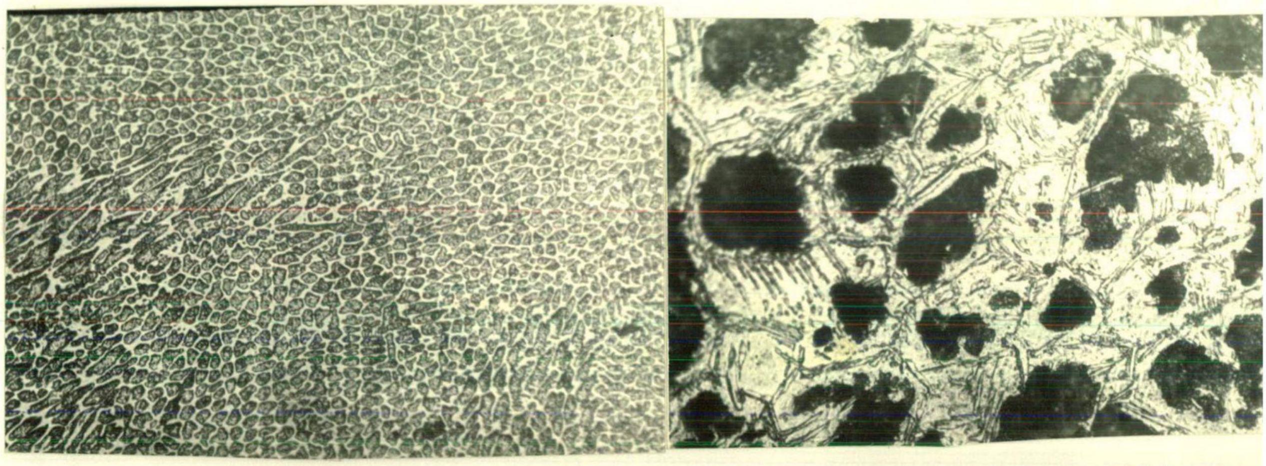
MILL B (C_D-WASHER LIQUID MEDIA)

Fig. 3.8 : SCANNING ELECTRON MICROPHOTOGRAPHS SHOWING SEVERITY OF CREVICE CORROSION



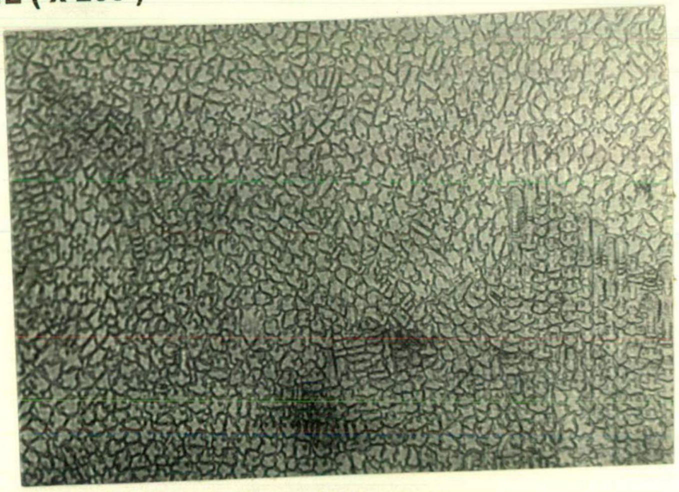
(a) SS 316L (x 200)

(b) SS 317L (x 200)



(c) 904L (x 200)

(d) Duplex SS 2205(x 200)



(e) 254 SMO (x 200)

Fig. 3.9 : MICROSTRUCTURE OF STAINLESS STEELS (WELD METALS)

Mill	Bleach Stage	Temperature (°C)	pH	Residual Oxidant (ppm)	Chloride (ppm)
Mill A	C	39±1.5	2.1 ± 0.4	88.5 ± 53.5	951±150
	D_1	53±3.0	2.4 ± 0.3	136.6 ± 90.4	490±40
Mill B	C_D	35.5 ± 2.5	1.8 ± 0.1	57 ± 14	3000 ± 500
	D	55 ± 5	2.9 ± 0.1	33 ± 23	550 ± 100

TABLE : 3.1: PROCESS CONDITION IN BLEACH WASHERS

	Mill A						Mill B			
Materials	C			D			C_D		D	
	vat	hood	drum	vat	hood	drum	vat	hood	vat	hood
316L	0.07	*	0.02	1.52	0.06	1.09	0.04	1.25	0.004	N
317L	0.07	13.47	0.02	0.65	0.11	0.33	0.05	0.35	0.003	0.004
904L	0.05	4.27	0.02	0.40	0.06	0.21	0.01	0.10	0.009	N
2205	0.06	4.00	0.09	0.43	0.03	0.20	0.02	0.07	0.001	N
254SMO	0.04	0.07	0.04	0.30	N	0.11	N	N	N	N

* samples were corroded completely to brittle pieces.

N - No measurable/visible attack.

TABLE : 3.2 : CORROSION RATES OF STAINLESS STEELS

	Mill A						**Mill B**			
Materials	***C***			***D***			C_D		***D***	
	vat	**hood**	**drum**	**vat**	**hood**	**drum**	**vat**	**hood**	**vat**	**hood**
316L	*	***	*	***	*	***	*	***	*	*
317L	*	***	*	*	*	*	*	***	*	*
904L	*	***	*	*	***	*	*	*	*	*
2205	*	***	*	*	*	*	*	*	*	*
254SMO	*	*	*	*	*	*	*	*	*	*

TABLE : 3.3 : MATERIAL EVALUATION FOR PITTING RESISTANCE

	Mill A						**Mill B**			
Materials	***C***			***D***			C_D		***D***	
	vat	**hood**	**drum**	**vat**	**hood**	**drum**	**vat**	**hood**	**vat**	**hood**
316L	**	***	**	*	*	**	***	**	**	*
317L	**	***	*	**	*	*	**	**	**	*
904L	**	***	*	**	*	*	*	**	*	*
2205	**	***	*	**	*	*	**	*	*	**
254SMO	*	**	*	*	*	*	*	*	*	*

TABLE : 3.4 : MATERIAL EVALUATION FOR CREVICE CORROSION RESISTANCE

	Mill A						Mill B			
Materials	C			D			C_D		D	
	vat	hood	drum	vat	hood	drum	vat	hood	Vat	hood
316L	*	***	*	***	*	*	*	**	*	*
317L	*	***	*	**	*	**	*	**	*	*
904L	*	***	*	*	**	*	*	*	*	*
2205	*	***	*	**	*	**	*	*	*	*
254SMO	*	***	*	*	*	**	*	*	*	*

***- unacceptable (high degree of attack), **- satisfactory (medium degree of attack),

*-superior (negligible/no visible attack)

TABLE : 3.5 : MATERIAL EVALUATION FOR RESISTANCE AGAINST WELD AREA ATTACK

Materials	316L	317L	904L	2205	254SMO
TensileStrength*	490	515	500	680	650
0.2% proof stress*	210	220	220	480	300

* Values measured at 20°C, in MPa

TABLE : 3.6 : MECHANICAL PROPERTIES OF BLEACH PLANT MATERIALS

Materials	**316L**	**317L**	**904L**	**2205**	**254SMO**	**654SMO**
Plates*	1.0	1.4	2.0	1.4	2.5	3.5
Tube(seamless)*	1.0	1.2	1.6	1.2		
(welded)*	0.5	0.6	1.3	0.6		
General**	1.0			0.85		

* cost for equal weight , ** cost for equal strength

TABLE : 3.7 : COST OF BLEACH PLANT MATERIALS

		vat	2205
	C	hood	654 SMO
Mill A		drum	2205
		vat	254 SMO
	D	hood	2205
		drum	317L
	C_D	vat	2205
Mill B		hood	2205
	D	vat	2205
		hood	2205

TABLE : 3.8 : SUGGESTED MATERIAL OF CONSTRUCTION FOR BLEACH WASHER

CHAPTER : 4

Corrosion investigation in Chlorine Dioxide Solution

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4.1 Introduction :

The chemicals used in the bleaching process are highly corrosive in nature. Additionally, the use of chlorine enhances the pollutants level in nearby streams through discharge of malignant chloro-organics. As a result, chlorine is being replaced increasingly by chlorine dioxide. Changes in the bleach chemicals are likely to influence the corrosivity of the liquid media, which in the worst cases may affect the integrity of the materials of construction of bleach plants. As such, the metallurgy of plants using chlorine dioxide is likely to change. In-plant corrosion tests that were conducted in the past addressed the corrosion behaviour of highly alloyed stainless steels, 6% Mo (Molybdenum) containing stainless steels, Ni base alloys and Ti and exhibited a variable degree of corrosion resistance, (68, 69, 70). In a recently conducted in-plant tests, stainless steel alloy 316L, which until recently was considered as the normal material of construction for paper plants, was found to experience excessive attack, as compared to the higher Mo- containing stainless steels (91). The tests also showed that solutions containing chlorine-dioxide, in certain conditions, could be more corrosive than was chlorine. In consequence, it appeared appropriate to investigate corrosion of stainless steels in chlorine dioxide solutions under controlled conditions.

Previous laboratory tests evaluated the effects of chemical composition on the corrosivity of chlorine dioxide solution and performance of stainless steels vis-à-vis their Mo and Si content (66), the importance of Mo in resisting crevice attack in near-neutral D-bleach media (62), and the effect of Cl^- and the beneficial effect of Mo in improving corrosion resistance (63). The present investigation includes a study on the corrosion of stainless steels in acidic chlorine dioxide solutions with bleach liquor compositions. In this study, three austenitic and one duplex stainless steel samples were subjected to electrochemical and long-term immersion testing at room temperature. The results of the tests were evaluated with reference to Pourbaix diagrams to gain a better understanding of corrosion behaviour , and to estimate the degree of resistance of the tested materials against localised attack and its dependence on the composition of the solutions. The results were compared with in-plant test data reported previously (91). The objective of the work was to investigate the corrosion reactions prevailing in chlorine-dioxide solutions and to test the suitability of the candidate materials for bleach stages involving chlorine-dioxide environments.

4.2 Experimental Details :

4.2.1 Materials :

Austenitic stainless steel 316L, 317L and 254SMO and duplex stainless steel 2205 samples, each 1.2 cm. long and 0.94 cm diameter, were supplied by Metal Samples, USA. The composition of the test samples is given in Table 2.2. The samples were solution annealed as per ASTM standard A240 and ground smooth using 320 to 800 grit emery paper. Before testing, the samples were degreased with acetone solution.

4.2.2 Solutions :

The basis of the test solution composition (Table 4.1) was the composition of liquors in bleach plant washers of the chlorine dioxide stage. Thus, the solutions had pH = 3 and 5, ClO_2 = 50 and 100 ppm and Cl^- ion contents between 500 to 3000 ppm. The amounts of the various chemicals in the prepared solutions were within the limits as indicated in Table 4.1. To prepare the test solutions, first stock solution of chlorine-dioxide was prepared by dissolving chlorine dioxide gas in distilled water to saturation limit. This stock solution showed chlorine dioxide concentration of about 3 gpl, which was diluted until the target concentration of chlorine dioxide was achieved. The amount of Cl^- ion in these solutions was adjusted by mixing appropriate amount of NaCl. The pH of these solutions was adjusted by adding HCl or NaOH as per the requirement.

4.2.3 Experiments :

The electrochemical tests were conducted on computer controlled EG&G PARC corrosion measurement system using Greene type corrosion cell and saturated calomel electrode (SCE) as reference electrode. Potential (E) vs. time curves were recorded for knowing the corrosion potential (E_{corr}) (Fig.4.1). Anodic polarisation tests were performed to investigate the passivation characteristics of the stainless steels. Potentiostatic tests, specifically current (I) vs. time curves were performed at pre-selected potentials to ascertain if the steel was experiencing localised corrosion and to determine the pitting potential (E_p) of the material in the test solution (Fig. 4.2 and 4.3). Cyclic polarisation curves for 2205 and 254SMO (Fig. 4.4) were measured to identify the repassivation potential (E_c) and the passivation current density (I_{pass}). In the polarisation experiments, the samples were immersed in the solution for 1 hour before scan were started, and a scan rate of 0.6 V/hour was employed, as per ASTM standard G5-87 (134). In cyclic polarisation experiments, the scanning direction was reversed when the value of the potential was 140±10 mV above the pitting potential. The repassivation potential was considered to be the potential at which reverse scan crossed the forward scan trace. The corrosion current density, (I_{corr}) expressed in amp/cm^2 was determined from the polarisation experiments using Model 352 Softcorr^{TM} II software, and the PARCalc routine was used to perform a non-linear square fit of the data to the Stern and Geary equation. The software was used to calculate corrosion rates using the following equation :

Corrosion rate (in mils per year) = 1.287×10^5 (EW/d) I_{corr}

Where EW – equivalent weight (gms), and d – density (gms/cm^3)

In the long - term tests, the samples were immersed for 6 months in similar solutions to those used in electrochemical tests. The samples were fitted with serrated washers, which provided a multiple crevice assembly. Maximum pit depths were measured under the crevices, as per ASTM standard G78-89 (135), to give an estimate of the rate of crevice corrosion attack on the sample. The maximum pit depth on the open surface indicates the degree of pitting attack. During the tests, the pH, ClO_2 and Cl^- contents of the solutions were checked twice every day and were maintained within the specified limits. After exposure, the coupons were cleaned mechanically by brush followed by chemically treating with a solution of concentrated HCl with 50 gpl $SnCl_2$ and 20 gpl $SbCl_3$.The cleaned coupons were re-weighed and the overall corrosion rate was calculated. Samples were examined microscopically to estimate the degree of pitting and crevice corrosion. To further compare the resistance of the tested stainless steels to pitting and crevice corrosion, critical pitting temperature (CPT) and critical crevice temperature (CCT) values (obtained as indicated in Chapter 3) of the steels were compared.

4.3 Results :

Table 4.2 presents the results for E_{corr}, E_p, E_c, corrosion rate, passivation range and passivation current that were derived from the electrochemical tests. Accordingly, E_{corr} generally was observed to increase with increasing ClO_2 content. It also increased slightly with any decrease in the pH of the solution. E_{corr} for different materials in the test solutions increased in the order : 316L < 317L < 2205 < 254SMO, indicating that 316L was the most susceptible to corrosion, and 254SMO was the most resistant of the tested materials. Corrosion rates, obtained from the polarisation curves, for 316L and 317L were observed to be high, whereas those of 2205 and 254SMO were much lower (Table 4.2). These results indicated that in these solutions, 316L and 317L, can be expected to perform poorly, whereas 2205 and 254SMO are more resistant to general (i.e. 'uniform') corrosion.

In case of 316L and 317L, the anodic polarisation tests, did not indicate clearly if the steels were passivating or were experiencing localised corrosion. In consequence, potentiostatic tests were conducted which revealed that their pitting potentials were lower than was the corrosion potential, thereby indicating that both of the stainless steels were sustaining localised corrosion. Cyclic polarisation curves were recorded only for stainless steel 2205 and 254SMO. Two of the curves recorded in chlorine dioxide solutions (solutions 1 and 3 respectively) are shown in Figure- 4.4. The E_p values for 316L and 317L, as determined from potentiostatic curves, appeared to be lower than E_{corr} values for both of the steels, while those for 2205 and 254SMO were higher than their respective E_{corr} values (Table 4.2). It may be concluded that the E_c's for 2205 and 254SMO were higher than were their respective E_{corr} values. Thus, the results of the electrochemical tests suggest that 316L and 317L are likely to experience localised corrosion in these solutions, whereas 2205 and 254SMO were resistant to pitting and crevice corrosion and were passive. The almost identical values of E_c for 2205 and 254SMO suggest that they should exhibit similar resistance to crevice corrosion. The passivation range (Table 4.2), which is an indicator of the margin of safety (MOS) against pitting and crevice corrosion, was marginally higher for 2205 than was the case for 254SMO. However, for practical purposes, they may be considered to be quite similar. The passivation current density of 2205 was greater than was that of 254SMO, the difference being more significant in comparatively acidic solutions (Table 4.2). Overall, 254SMO appeared to be more resistant than was 2205 against localised corrosion, the more so when the solution was more acidic.

The long-term exposure test showed a decrease in the pH of solutions when tested after every 12 hours during the exposure, (though the solution pH was routinely readjusted to the specified value). The results of these tests are shown in Table 4.3. These results suggest that corrosion rate was highest for 316L, followed by 317L, 2205 and 254SMO. Similarly, crevice attack was found greatest in the case of 316L, followed by 317L, 2205 and 254SMO. Pitting attack was not observable in the studied solutions. The table in chapter 3 in section 3.4.2, shows CPT and CCT values measured for the tested stainless steels.

4.4 Discussion :

4.4.1 The Electrochemistry of Test Solutions :

This discussion is based on the E-pH diagram shown in (Figure 4.5), which was drawn on the basis of the various reactions possible in chlorine-water system and their electrochemical data (136). The numbers assigned to different reactions in the text below and in Figure 4.5 are same as in the referred literature (136). As ClO_2 dissolves in distilled water, it undergoes following reactions (136, 137).

$$2ClO_2 + H_2O \rightarrow ClO_2^- + ClO_3^- + 2H^+ \qquad \text{(a)}$$

$$ClO_2 + H_2O \rightarrow ClO_3^- + 2H^+ + e^- \qquad \text{(54)}$$

Reaction 54, an oxidation reaction, is accompanied by the reduction of oxygen, that is dissolved in the chlorine dioxide solutions, since $(E)_{O2/H2O}$ for both pH=3 and 5 solutions is higher than is $(E)_{ClO2/ClO3-}$. Both the above changes cause a decrease pH of the ClO_2 solution. It was observed that when ClO_2 was dissolved in water, in the amount 50 -100 ppm, the pH of resulting solution decreased to between 4 and 5. Thus, the solutions (pH=3 and 5) should have ClO_2 together with ClO_2^- and ClO_3^-.

H^+ and ClO_2^- may combine to give $HClO_2$ by following reaction

$$H^+ + ClO_2^- \rightarrow HClO_2 \qquad \text{(2)}$$

According to the electrochemical data for the reaction (136), at the pH of the tested solutions, the amount of ClO_2^- will be dominant, in comparison to $HClO_2$, (Figure 4.5). Therefore, chlorine based components in the solutions are most likely to be ClO_2, ClO_2^- and ClO_3^-.

Considering various reactions and their electrochemical data for the chlorine-water system (136), (some of which are drawn in Figure 4.5), the measured values of the corrosion potential of the stainless steels and pH's of the test solutions, the following reduction reactions seem to be responsible for corrosion of stainless steel

$$ClO_2^- + 4H^+ + 4e^- \rightarrow Cl^- + H_2O \qquad (7)$$

$$ClO_3^- + 6H^+ + 6e^- \rightarrow Cl^- + 3H_2O \qquad (8)$$

$$ClO_2 + 4H^+ + 5e^- \rightarrow Cl^- + 2H_2O \qquad (48)$$

When a stainless steel sample is immersed in these solutions, it oxidises as per following reaction (138):

$$Fe + Cl^- \rightarrow FeCl^+ + 2e^- \qquad (b)$$

The associated reduction reactions will be 7, 8 and 48. Further, considering the aspects of the E-pH diagrams for the Fe-Cl-H_2O system (138), and that the pH of the solution is observed to decrease with time in long term experiments, the two following additional reduction reactions are proposed :

$$2FeCl^+ + ClO_2 + 2H_2O + 3e^- \rightarrow 2\alpha FeOOH + 3Cl^- + 2H^+ \qquad (c)$$

$$2FeCl^+ + ClO_2^- + 2H_2O + 2e^- \rightarrow 2\alpha FeOOH + 3Cl^- + 2H^+ \qquad (d)$$

Reactions (7), (8) and (48) will result in an increase in pH, whereas reactions (c) and (d) will be responsible for decreases in pH, such that the net change in pH causes the solution to be more acidic as the reactions proceed.

E_{corr} increases with ClO_2 and decreases in pH of the solution. This is expected, considering the E-pH equation for reduction reactions ClO_2/Cl^- (48 and c) given below

$$(E)_{ClO2/Cl^-} = 1.511 - 0.047pH + 0.0118 \log (a_{ClO2}/ a_{Cl^-})$$

$$(E)_{ClO2/Cl^-} = 2.03 + 0.039 (pH + \log a_{FeCl^+}) + 0.0196 \log (a_{ClO2}/ a_{Cl^-}^{3})$$

and that (i) as pH of solution decreases, proportion of ClO_2 increases with respect to ClO_2^- as per reaction (a), (ii) the effect due to change in the amount of ClO_2 may be dominant, in comparison to that due to the decrease in pH. Accordingly, the effect of both changes is to increase the redox potential of the reduction reactions (48) and (c). The net effect will be an increase in E_{corr}, as was observed experimentally.

For more acidic solutions, the E_p's for respective steels are lower, and E_{corr} increases. The net effect for more acidic solutions, is a reduction in the margin of safety, and a lower resistance to pitting, as is evident in Table 4.2, showing passivation range. Any increase in ClO_2 decreases the E_c's of the respective steels. However, no clear dependence of E_c was observed in relation to the pH of the solutions. In every solution the passivation current density for 254SMO was lesser than for 2205. I_{pass} was observed to increase with lowering of pH. An increase in Cl^-, from 500 to 3000 ppm, decreased the passivation range from 755 to 407 mv for

2205 and from 509 to 352mV for 254SMO. Overall, therefore, the corrosivity of these solutions increased with any decrease in pH, or increase in ClO_2 or Cl^- content.

4.4.2 Performance of Materials :

The comparison of E_{corr} of the tested materials in different solutions, confirmed 316L to be most active, followed by 317L, 2205 and 254SMO. This trend indicated that the former was the most vulnerable to general corrosion, and this tendency decreased from 316L to 254SMO. In general, this finding was supported by the trend observed in corrosion rates for different materials in these solutions. However, even the maximum corrosion rate for 316L of 7.5 mpy, was not alarmingly high. Hence, the primary problem in using these materials tends to be localised corrosion.

The cyclic polarization and potentiostatic measurements indicated that if 316L and 317L were exposed in these solutions they would experience pitting and crevice corrosion. Alloys 2205 and 254SMO both were observed to passivate in the test solutions. The E_p for 254SMO was higher than that was the case for 2205. The passivation range for 254SMO was approximately the same, or was slightly lower than that of 2205. However, the passivation current for 254SMO was lower than in the case of 2205, thereby indicating that if both steels were passivating in a solution, 254SMO will corrode at lower rate. Thus in these test solutions, 254SMO is expected to show better resistance against pitting than 2205. Roughly same values of E_c suggest both these steels to show similar degree of resistance against crevice corrosion. Since resistance against localised corrosion of stainless steels is adversely affected by increased amount of Cl^-, the performance of 2205 and 254SMO was checked in the solutions having Cl^- upto 3000 ppm. Both materials even with highest Cl^- content showed passivation. Passivation range decreases and I_{pass} increases for higher Cl^- content. Passivation range of 2205 is more or less same as that of 254SMO. Although increase in I_{pass} for 254SMO is more than for 2205 for an equivalent degree of increased Cl^-, I_{pass} is always less for the former steel. This indicates better performance of 254SMO than 2205 in solutions with higher Cl^- content. Thus, a ranking of the overall corrosion resistance of the tested stainless steels, considering both uniform and localised attack, has the following order:

254SMO > 2205 > 317L > 316L

This is in accordance with the PRE nos. (131) calculated for these materials, on the basis of the % amount of Cr, Mo and N, which is highest for 254SMO and lowest for 316L. The relationship of localised corrosion resistance to PRE no. indicates the importance of Cr, Mo and N in stainless steel. Also, CPT and CCT values (in section 3.4.2) measured for these materials were highest (CPT>54°C, CCT = 45°C) for 254SMO and lowest for 316L (CPT = 5-10°C, CCT<5°C).

4.4.3 Comparison With Long Term Laboratory and In-Plant Tests :

4.4.3.1 Long Term Lab Test :

According to the results (Table 4.3), corrosion rates and degree of crevice corrosion (for the tested stainless steels) were generally observed to increase with increasing ClO_2 concentration and decreasing pH. Accordingly, a more acidic chlorine dioxide solution having higher ClO_2 concentration is expected to be more corrosive. This was observed to be in accordance with the electrochemical tests results.

On the basis of the extent of corrosion rate, the tested stainless steels can be ranked in the following order of increasing resistance to uniform corrosion : 316L< 317L< 2205 < 254SMO.

No pitting was observed on any of the tested materials. However, corrosion attack under crevices was observed widely. Alloy 316L showed the greatest susceptibility to crevice corrosion, whereas alloys 317L and 2205 exhibited crevice attack only to lesser degree. Alloy 254SMO did not show any measurable attack in crevices. Thus, the resistance of these materials was of the same order as was observed for uniform corrosion, and this was in accordance with the results of electrochemical polarisation experiments.

When compared with the results of reference (68), it was observed that the extent of crevice corrosion for alloy 316L in all the solutions, and for alloy 317L in the most corrosive solution, would make them unsuitable for handling the respective liquors, as a result of their inadequate resistance to crevice corrosion. Only alloys 2205 or 254SMO could be used for such liquors.

4.4.3.2 In-Plant Tests (91) :

These in-plant tests were carried out at two mills that had recently adopted chlorine dioxide bleaching and have been described in Chapter 3. The corrosivity of the liquid media and comparative material performances were determined by exposing the alloys in the chlorine dioxide bleach washer for a period of six months. The samples were analysed for general corrosion, pitting attack, and crevice corrosion damage.

It was observed that the higher concentration of oxidant (ClO_2 in this case) and lower pH of the solutions during the chlorine dioxide stage were responsible for its increased corrosivity. The corrosion rate of alloy 316L was highest, whereas that the corrosion rates of alloys 317L, 2205 and 254SMO were progressively lower. In one mill, there was no measurable attack on 254SMO.

Pitting and crevice corrosion was observed on all of the samples. The extent of pitting attack was unacceptable on only alloy 316L, whereas on the other alloys, the attack was negligible. Crevice corrosion attack was negligible on alloy 254SMO, but the degree of attack was higher on the other materials. Overall, the corrosion resistance of materials could be ranked in following order : 254SMO > 2205 > 317L > 316L, the same as was concluded on the basis of every other test conducted by the authors on these four materials.

While in-plant test showed pitting on all the materials, the electrochemical test showed pitting on alloys 316L and 317L only and long term immersion test did not show pitting on any of the tested materials. This variation in the corrosion performance could be attributed to the higher service temperature (up to 60°C) of the bleach washer. However, conducting the laboratory experiments at room temperature is still useful as they help in short listing the probable materials for the in-plant tests planned with the aim of selecting the appropriate material for actual service conditions. Additionally, one can also understand the dependence of corrosivity on the liquor composition and compare the performance of the candidate materials from room temperature laboratory tests.

4.4.4 Material Selection :

In undertaking materials selection for use with corrosive media, corrosion resistance aspects alone should not be considered. Instead, mechanical properties, fabrication aspects and overall cost must also be taken into account. Alloy 2205 material has the highest tensile strength and 0.2% proof stress of the materials tested, (91). In terms of cost, 316L is the least expensive, whereas alloys 317L and 2205 are approximately 1.4 times, and 254SMO is 2.5 times more costly than alloy 316L on a per unit weight basis. However, for equal design stress, the cost on equal strength basis should be compared. On this basis, alloys 316L and 317L are costlier than is alloy 2205 (316L is about 20% more costly). Whereas, considering fabrication aspects, 317L is equally costly as alloy 2205. Alloy 254SMO will be the costliest of all materials. Additionally, alloys 2205 and 254SMO have similar resistance against chloride cracking (CSCC), which is better than that of alloys 316L and 317L. Considering the above aspects alongside the corrosion resistance, alloy 2205 is the more appropriate material of construction for the D-stage bleaching vat and related process equipment in bleach plant, even for Cl^- contents up to 3000 ppm level.

Solution	**pH**	**ClO_2(ppm)**	**Cl^- (ppm)**
Solution1	3±0.1	50±10	500±20
Solution2	3±0.1	100±10	500±20
Solution3	5±0.1	50±10	500±20
Solution4	5±0.1	100±10	500±20
Solution5	3±0.1	100±10	1000±20
Solution6	3±0.1	100±10	2000±20
Solution7	3±0.1	100±10	3000±20

TABLE : 4.1 : COMPOSITION OF SOLUTIONS

	Corrosion Potential (mV_{sce})				Corrosion Rate (mm per year)			
	Sol1	**Soln2**	**Soln3**	**Soln4**	**Soln 1**	**Soln2**	**Soln3**	**Soln4**
316L	120	156	113	146	0.03	0.19	0.09	0.13
317L	117	140	161	158	0.01	0.04	0.06	0.04
2205	470	620	488	617	0.01	$<10^{-5}$	0.01	$<10^{-3}$
254SMO	716	710	595	680	$<10^{-3}$	$<10^{-5}$	0.01	$<10^{-2}$
	Pitting potential (mV_{sce})				Repassivation Potential (mV_{sce})			
316L	<50		<50					
317L	75		125					
2205	1225		1275		1208		1122	
254SMO	1225		1375				1139	
	Passivation range (mV_{sce})				Passivation current (µa/cm^2)			
2205	755		787		3.97		2.12	
254SMO	509		780		1.45		1.41	

TABLE : 4.2 : CORROSION DATA FROM ELECTROCHEMICAL TESTS

Solution	Materials	Corrosion Rate(mm/y)	Max Pit Depth (under crevice) (mm)
pH- 3 ± 0.10 ClO_2^- -50 ±10ppm Cl^- -1000±20ppm	316L	5.84 x10^{-3}	0.25
	317L	1.5 x10^{-3}	0.09
	2205	1.27 x10^{-3}	0.04
	254SMO	2.54 x10^{-4}	NA
pH-5± 0.10 ClO_2^- -50 ±10ppm Cl^- -1000±20ppm	316L	5.08 x10^{-3}	0.16
	317L	2.03 x10^{-3}	0.07
	2205	1.27 x10^{-3}	NA
	254SMO	2.54 x10^{-5}	NA
pH-3± 0.10 ClO_2^--100±10ppm Cl^- -1000±20ppm	316L	1.01 x10^{-2}	0.17
	317L	1.14 x10^{-2}	0.22
	2205	7.62 x10^{-4}	NA
	254SMO	5.08 x10^{-4}	NA
pH-5± 0.10 ClO_2^--100±10ppm Cl^- -1000±20ppm	316L	5.84 x10^{-3}	0.20
	317L	5.58 x10^{-3}	0.07
	2205	5.08 x10^{-4}	NA
	254SMO	5.08 x10^{-4}	NA

NA - No measurable pitting attack on samples.

TABLE : 4.3 CORROSION DATA FROM LONG-TERM TESTS

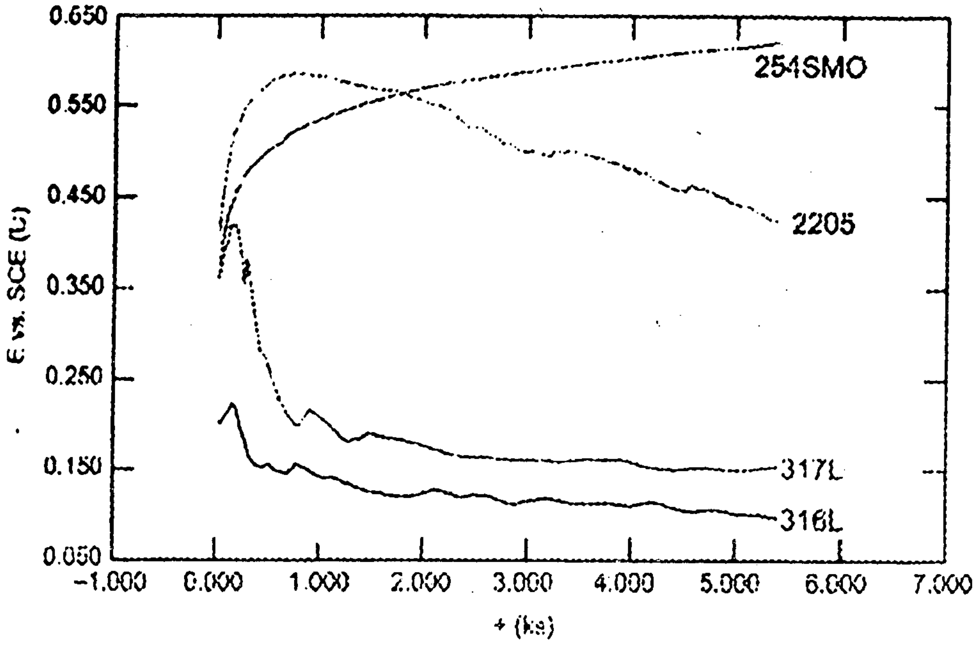

Fig. 4.1 : POTENTIAL VS TIME CURVES FOR TESTED ALLOYS IN SOLUTION 3

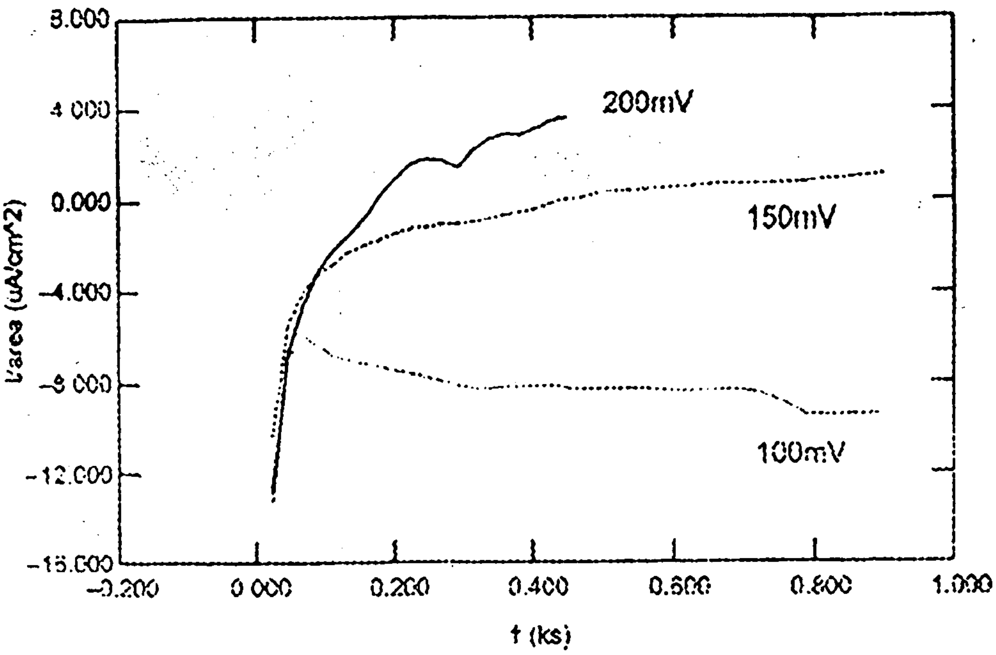

Fig. 4.2 : POTENTIOSTATIC (I VS TIME) CURVES FOR SS 317L IN SOLUTION 3

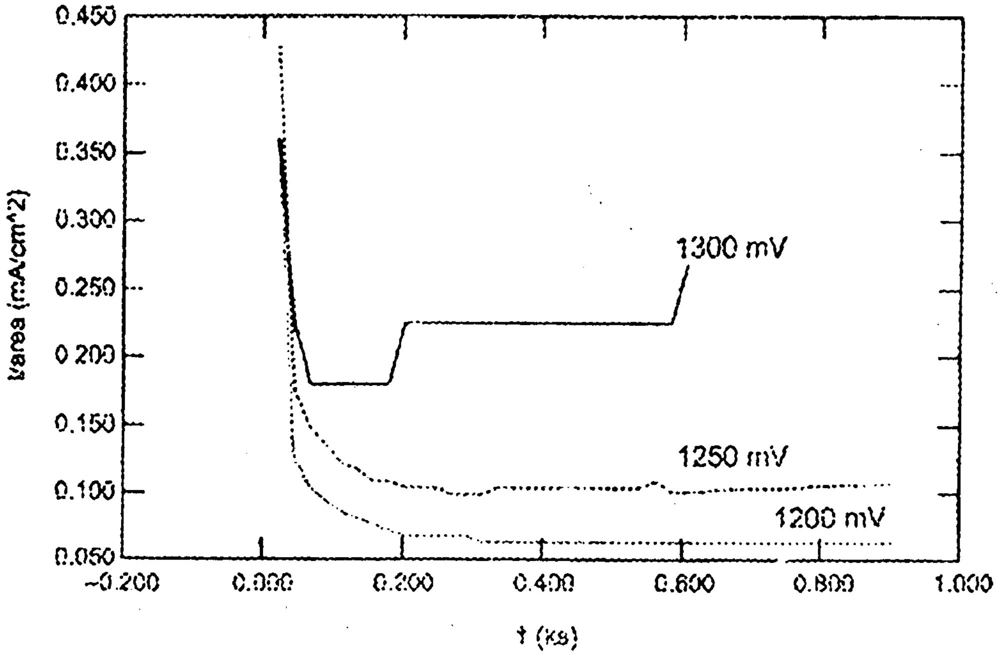

Fig. 4.3 : POTENTIOSTATIC (I VS TIME) CURVES FOR STAINLESS STEEL 2205 IN SOLUTION 3

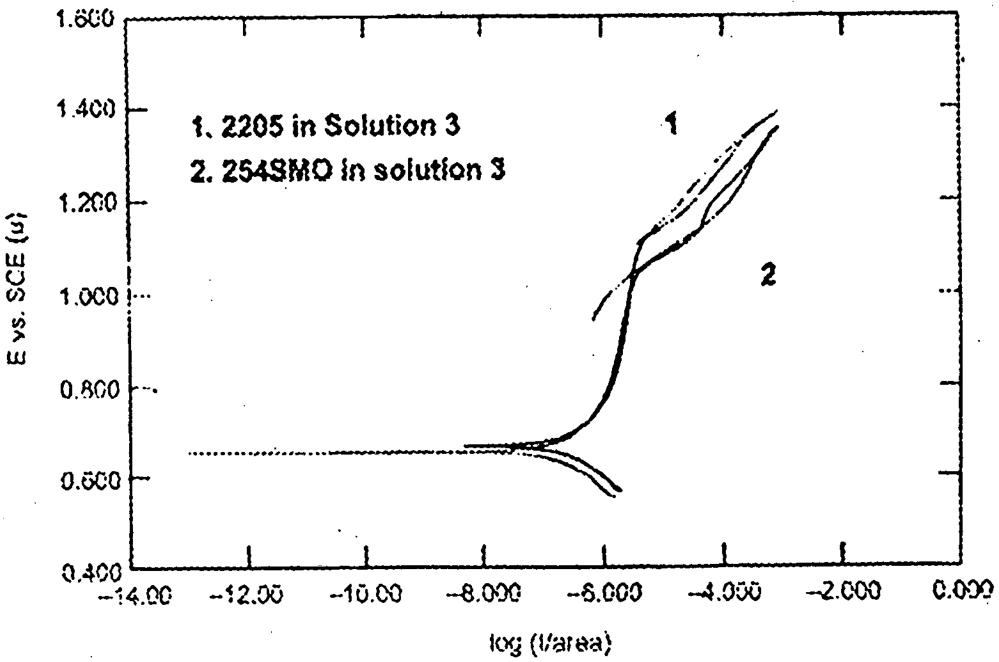

Fig. 4.4 : CYCLIC POLARISATION CURVES OF STAINLESS STEEL 2205 AND 254SMO IN SOLUTION 3

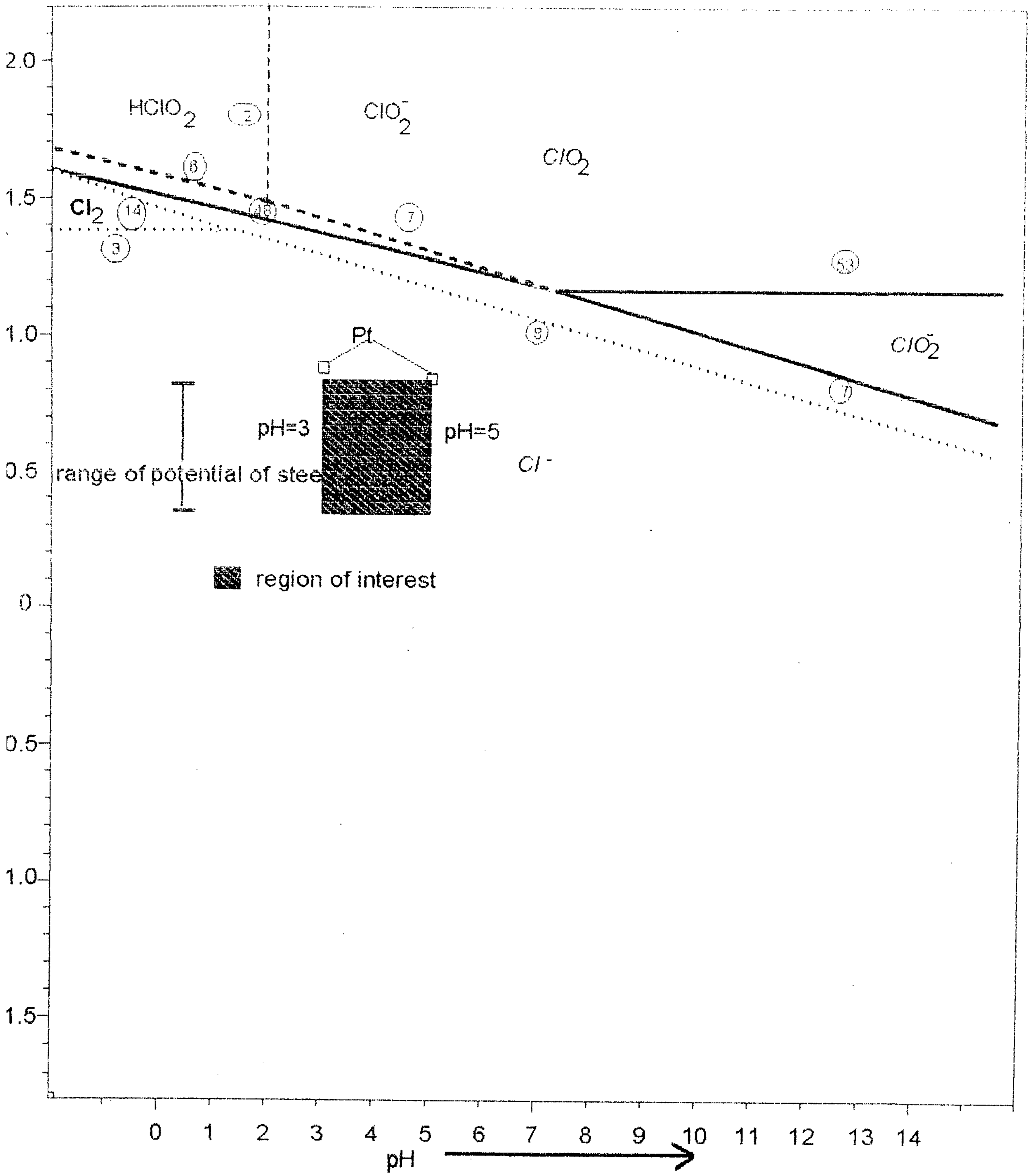

Fig. 4.5 : E-pH DIAGRAM FOR ClO2 - H2O SYSTEM

CHAPTER : 5

CORROSION INVESTGATION IN PERACID SOLUTION

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5.1 Introduction :

Paper industry is slowly but surely adopting new technologies for its bleaching process because chlorine and its compounds, which were quite popular with the industry for this purpose until few years' ago, have been observed to pollute the environment. These are, therefore, to be replaced by the bleach processes which involve non-chlorine chemicals. Hydrogen peroxide, peracids, oxygen, ozone etc. are some of the potential non-chlorine bleach chemicals for possible applications in paper mills. Out of these, the peracids [peracetic acid (P_a), Caro's acid (P_x) and (P_{xa}) (mixture of P_a and P_x)], may prove viable for use in chlorine and in chlorine free, both elemental chlorine free - ECF and total chlorine free – TCF, bleaching sequences. When compared with ozone (139), not only are the quality parameters as good or better in the case of peracids, but the low capital and operating costs are attractive particularly as mill assess the viability of ozone. Peracids have been used as activating agents for lignin before oxygen or a peroxide stage and as brightening agent in later oxidation stages. With the possibility of using peracids in the bleach section, one also needs to know the corrosion effects on the mill machinery and hence its credibility due to change in the nature of chemicals. Literature survey on corrosion in peracids does not show any work except two (87, 140) on peracetic acid. Accordingly, experiments were planned to investigate the corrosion effects on mild steel and stainless steels while they were exposed to peracid liquors. The corroded samples were then analysed for localised and uniform corrosion and evaluated for their possible use in peracid bleach plant. To the best knowledge of the author, the present work on peracids is the first ever reported of its kind on investigations on the suitability of materials of construction in the corrosive media of peracid bleach liquor.

5.2 Experimental Details :

5.2.1 Material :

Corrosion test coupons of mild steel, austenitic stainless steel 304L, 316L and 317L and duplex stainless steel (2205) were selected for the present tests, because of their being the candidate materials for plant fabrication. Mild steel was considered for the test because, as a part of TCF bleaching process, the liquor is not likely to have a significant amount of Cl^- and so it may as well be a strong candidate. Further, duplex stainless steel was considered because this steel has recently been predicted as a very useful material as a replacement of 304L and 316L because of its useful properties and lesser cost per unit strength. The composition of these steels is given in Table 2.1 and 2.2.

All the samples were solution annealed as per ASTM spec A240. For long term immersion tests, the coupons were polished up to 800 grit emery paper and finally by self adhesive cloth. Before the exposure, the coupon were degreased using acetone solution so as to remove any grease or dirt. This surface prepared and cleaned coupons were weighed. For the weight loss test, the coupons were fixed each with a serrated washer of teflon at the center. These serrated washer provided the sites for initiating crevice corrosion. This arrangement, thus, helped in giving the data on crevice corrosion. For electrochemical tests, the cylindrical samples of steel were used . The compositions of the samples have been shown in Table 2.2.

5.2.2 Solutions :

In both the long term immersion test and the electrochemical polarisation test, the samples were exposed to three peracid solutions namely peracetic acid (P_a), Caro's acid (P_x) and P_{xa} (mixture of P_a and P_x). All the solutions were prepared as described by Amini and Webster (117). Accordingly, P_a was prepared by adding glacial acetic acid to hydrogen peroxide (1 molar ratio) containing sulfuric acid as catalyst. The mixture was then warmed to 45°C, 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 30-35°C. P_{xa} solution was prepared by adding the required amount of glacial acetic acid to the cold Caro's acid. pH of these solutions was kept as 5 since in one study on the possible use of peracids as delignifying and brightening agent, Bailey et.al. (86), found that minimum pulp degradation occurred in the pH range of 5-9 and temperature and consistency did not have an effect on pulp properties in this pH range. Further, maximum corrosion is expected in solutions with lowest pH in this range i.e. 5. Table 5.1 gives the composition of the solution and the test conditions.

5.2.3 Tests :

In the long term test, the steel coupons were exposed for a duration of six months at 50°C and room temperature. Each coupon was immersed in the solution (Table 5.1) with serrated washers fitted on both the sides at its center so as to provide site for initiating crevice corrosion. During the test, the composition and pH of the solutions were monitored and maintained each day. After the exposure, the corroded coupons were first cleaned by light brushing, then they were treated with cold solution of concentrated HCl with 50 gpl $SnCl_2$ and 20 gpl $SbCl_3$ to remove the more adherent corrosion products. The cleaned corroded coupons were weighed for determining corrosion rate and were viewed under the metallurgical microscope (Leica make) for estimating the extent of localised attack.

The electrochemical polarisation tests e.g. potentiodynamic and cyclic polarisation measurements were conducted using Green's cell connected to computer controlled EG&G PARC Potentiostat / Galvanostat (Model 273) and saturated calomel electrode (sce) as reference electrode. These tests helped in evaluating E_{corr}, pitting potential, passivation current density and repassivation potential for the different metal samples at room temperature.

The cyclic polarisation tests were conducted on 173 Potentiostat / galvanostat, which had different modules for current programming and logarithmic current converter and was connected with an X-Y plotter and a programmer (EG&G PARC MODEL 175 UNIVERSEL PROGRAMMER). The model 175 Universal programmer produce a wide variety of complex waveforms of up to four segments, which are suitable for such varied applications as:

- Programming voltage-controlled instruments
- Programming electrochemical systems
- Evaluating frequency dependent characteristics of systems
- Testing system responses

In fact, the Model 175 is valuable in any application requiring precise and independent control of slope or interval and vertex or set point potentials.

Features :

- ► Four independent potential controls
- ► Scan slope and amplitude completely independent
- ► Pulse duration and amplitude completely independent
- ► Single or repetitive waveforms with up to four differing segments
- ► Scan rates from 1 mV / sec to 10,000 V/sec
- ► Pulse widths from 100 micro sec to 1,000 sec
- ► Option 175/99 permits scan rates of 0.1 mV/sec and pulse widths of 10, 000 seconds
- ► Negative and positive slopes independently variable over 10 :1 range
- ► Versatile controls for synchronizing, starting, stopping and reversing waveforms either manually or with peripheral devices

The programmer has different settings of potentials by different potential knobs e.g. initial potential (A), upper limit (B), lower limit (C) and final potential (D). The following steps are followed for cyclic polarisation tests :

(1) Give some initial potential (by 175 universal programmer) 100 mv lower than the E_{corr} .

(2) Choose initial direction +ve.

(3) Select upper limit (vertex potential)100 - 200 mv more than pitting potential.

(4) Select final potential between E_{corr} and pitting potential.

(5) Choose final scan direction as –ve and cell selector knob towards D switch.

5.3 Results :

The microstructures of mild steel and SS 304 L are shown in Fig. 5.1. The structure of mild steel shows two phases. The black portion is pearlite whereas white is ferrite phase. The structure of austenitic SS 304L, is a single phase structure. Grains consist of austenite. Twins are also visible across the grains.

The results of long term immersion test at room temperature and 50°C are shown in Table 5.2. The results indicate corrosion rate and corrosion attack under crevices. These tests did not show any pitting attack on the coupons.

In the electrochemical tests, first of all potential (E) vs. time (t) measurements were done so as to obtain the value of E_{corr}. E vs, t curves for different materials (304L, 316L and 317L) are shown in Fig.5.2 and 5.3. Values of E_{corr} obtained from these curves are given in Table 5.3. Values of E_{corr} help in knowing the tendency of the materials to corrode and also help in deciding working parameters for electrochemical polarization measurements. Cyclic polarization curves were then recorded in order to know the pitting potential (E_p), repassivation potential (E_c) and other associated passivation characteristics. However, it was observed that in many of the cases the reverse scan curve was not cutting the forward scan curve thereby posing problem in the estimation of E_c. On analyzing it was found that the kink observed in the polarization curve (Fig.5.4), which was considered as due to onset of pitting, was actually due to O_2 evolution reaction

$$2\ OH^- \leftrightarrow O_2 + H_2O + 2e^-$$

$$E_{(O2/OH^-)} = 814\ V - 0.0295\ pH + 0.02\ \log\ (a_{O2}/a^2_{OH^-})$$

Visual observation of the polarization curves of some of the materials (Fig.5.5 and 5.6) show kink around this potential and these are also the cases where estimation of E_c was not possible. This observation is likely to occur in cases where E_p of the material is expected to be higher (more anodic) than O_2 evolution potential. This situation will occur in the solutions which have highly oxidizing chemicals e.g. peracids in the present case and the material has a comparatively better localized corrosion resistance.

Potentiostatic curves were recorded, therefore, to know the value of pitting potential, E_p, which will help in deciding the modified parameters, particularly the vortex potential, for recording cyclic polarization curves. The values of E_p for different material-liquor system are given in Table 5.3.The cyclic polarization curves were again measured with the help of modified parameters. In all these cases, the reverse scan curve was cutting the forward scan curve so it was possible to determine E_c. Some of these curves had two kinks (Fig.5.5 and Fig.5.6), one appearing for O_2 evolution and other representing the onset of pitting. The values of E_p and E_c obtained from these curves are given in Table 5.3. In some of these cases, E_c is found to be more than E_p which seems to contradict the theory. However, E_c is obtained from the cyclic polarization curves (Fig.5.5 - 5.16) whereas E_p is from potentiostatic measurements (5.17 – 5.24). It is well known that values of E_p obtained from potentiostatic measurements are lesser than those obtained from potentiodynamic polarisation measurement. So if E_p is only slightly higher than E_c in a particular case, one is likely to come across the situation as above i.e. $E_c > E_p$. A better comparison of E_p and E_c, for a particular metal-liquor system, can be done only from the values obtained from same type of measurements. Accordingly, Table 5.3 gives E_p obtained from potentiosatic as well as that obtained from cyclic polarization curves. Also while discussing the results, use of E_p, obtained from either measurement, has been made depending upon the requirement.

These results, obtained from the long term immersion tests and electrochemical polarization measurements, form the basis for comparing the corrosivity of the solutions, performance of the materials and the selection of appropriate material of construction for the media in question.

5.4 Discussion :

5.4.1 Corrosivity of Solutions :

Corrosion rate, at room temperature, on mild steel is maximum in P_a solution followed by P_x and P_{xa} (Table 5.2). On stainless steel samples too, uniform corrosion is highest in P_a solutions followed by P_x and P_{xa}. Analysis of pits under crevices, in case of stainless steel samples, shows pit depth to be higher for P_a solutions than others.

From electrochemical polarisation data, E_{corr} of both 304L and 316L is highest in P_x solution but their values in other two solutions are lower and very close to each other. Thus P_x seems to be the least corrosive of them. All parameters relating to pitting and crevice corrosion e.g. E_p, E_c, passivation range for 304L shows P_{xa} to be more corrosive than P_x. While these parameters for stainless steel 316L shows that P_a is most corrosive followed by P_{xa} and P_x. So overall, one can put these solutions in the order of increasing corrosivity as given below :

$$P_x < P_{xa} < P_a$$

Increase in Cl^- is found to decrease E_p (potentiostatic) for all the stainless steels in all the solutions. While for 317L, E_p (cyclic), E_c and passivation range, in P_a solution, are observed to decrease with increase in Cl^-. This is as per the expectations because increase in Cl^- makes stainless steel more vulnerable to localized corrosion.

5.4.2 Material Performance :

Mild steel experiences very high degree of general corrosion in all the tested solutions, as is evident from extremely high values of corrosion rates. In case of P_x2 and P_a1 at room temperature while in case of $P_{xa}1$ and $P_{xa}2$ at 50^0C, 316L shows lesser crevice attack than 304L. In case of $P_{xa}2$ and P_a1, 316L shows higher corrosion rate and crevice attack than 317L at 50^0C. While 2205 shows intermediate resistance between 316L and 317L on the basis of corrosion rate and crevice attack in P_a2 solution. In general, wherever possible, the comparison shows 304L to be least resistant to corrosion followed by 316L, 317L and 2205.

The corrosion performance of 304L and 316L was compared in P_x2, $P_{xa}1$, $P_{xa}2$ and $P_a(0)$ solutions because either of these can be suitable material for handling these liquors. All the electrochemical parameters namely E_p, E_c and passivation range show 316L to be more resistant against pitting and crevice corrosion than 304L. Better resistance of 316L can be assigned to ~2% Mo content in it whereas 304L does not have any Mo (Table 2.2).

Behavior of SS-316L and 317L was compared in case of P_a solutions because in them 304L was not expected to perform well. E_p of 316L from potentiostatic test is observed to have very low value in both P_a1 and P_a2 solutions. These values are very close to the E_{corr} values in the respective cases. Cyclic polarization measurements were not taken in these cases since the materials were expected to lie in the transpassive region. Stainless steel 317L, however, shows much higher E_p and E_c and passivation range. As such, 317L shows better resistance than 316L. This can be attributed to higher amount of Cr (18.8%) and Mo (3.37%) in 317L than 316L (Table 2.2) which are known to provide resistance to steel in oxidising environment in the presence of Cl^- (49).

Duplex stainless steel shows higher values (Table 5.3) of E_p, E_c and passivation range in P_a2 solution thereby showing its better resistance in comparison to 317L. Higher amount of Cr, similar amount of Mo and presence of N in 2205 (Table 2.2) may be attributed to the better resistance of 2205 in these media. In fact, Cr, Mo and N all three provide localized corrosion resistance in oxidizing media having Cl^- (please refer to Chapter 3) which is evident from its higher PRE No. and CPT value than 317L.

5.4.3 Material Selection :

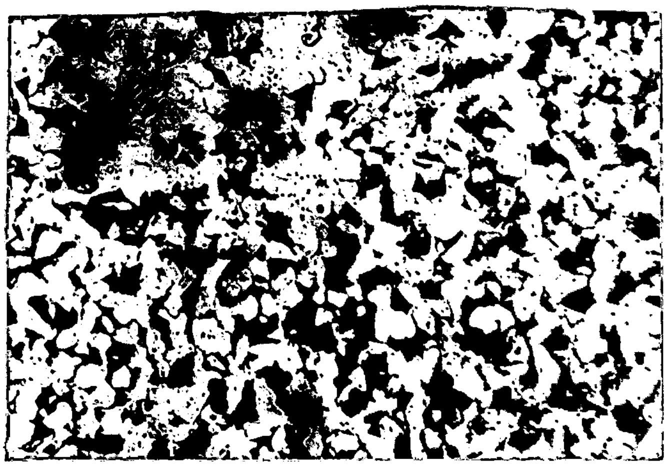
An extremely high degree of corrosion rate of mild steel in peracid solutions makes this steel totally misfit for handling these liquors. In case of stainless steel samples, the corrosion rates are quite low (maximum observed rate ~ 4 mpy), hence the basis of selection of the material of construction for handling peracid liquors can be considered as the pitting/crevice corrosion attack.

A comparison of electrochemical parameters indicate that values of E_p, E_c and passivation range of 304L and 316L are quite high in case of P_x, P_{xa} and P_a0

solutions so they expect to show good resistance against pitting and crevice corrosion in these solutions. 316L, however, shows very low values of E_p (potentiostatic) and very close to the respective E_{corr} values in P_a1 and P_a2 solutions. This stainless steel is, therefore, likely to experience localised attack in these solutions. Stainless steel 317L shows acceptable performance in P_a1 and P_a2 solutions. Duplex stainless steel shows even better resistance in these solutions.

Now one tries to support this information from the results of weight loss tests. Since no observable pitting has been noticed in any of these samples in weight loss tests, the criterion of the material selection has been considered as the degree of crevice corrosion and its comparison with the in-plant data of Tuthill (141), providing guidelines for acceptability of material (please refer to Table in section 2.8). On this basis, material of constructions suitable for handling peracids of varying composition have been proposed. Thus for P_x1, $P_{xa}1$ and P_a0, 304L is acceptable at room temperature and 50^{0}C, while for $P_{xa}2$ it is acceptable only for room temperature but not for 50^{0}C and for P_x2 and P_a1, it is not acceptable even at room temperature. Stainless steel 316L is acceptable for handling P_x2 and $P_{xa}2$ at room temperature and 50^{0}C both, while it is not acceptable for P_a1 at 50^{0}C and for P_a2 at even room temperature. 316L shows marginal performance for P_a1 at room temperature and $P_{xa}2$ at 50^{0}C. For P_a1 and P_a2 stainless steel 317L is acceptable at both room temperature and 50^{0}C. 2205 is also acceptable for P_a2 even at 50^{0}C.

The proposed scheme of materials acceptable for handling different liquors is given in Table 5.4.



MILD STEEL (x200)

SS 304L (x 200)

Fig. 5.1 MICROSTRUCTURE OF MILD STEEL AND SS 304L

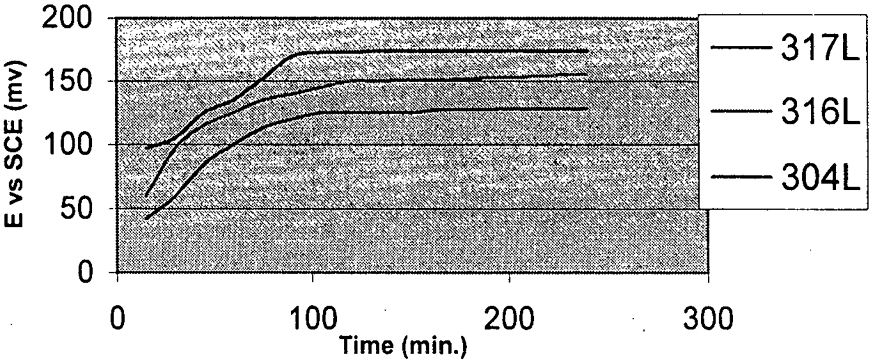


Fig. 5.2 : E vs TIME CURVE IN P_{xa} SOLUTION

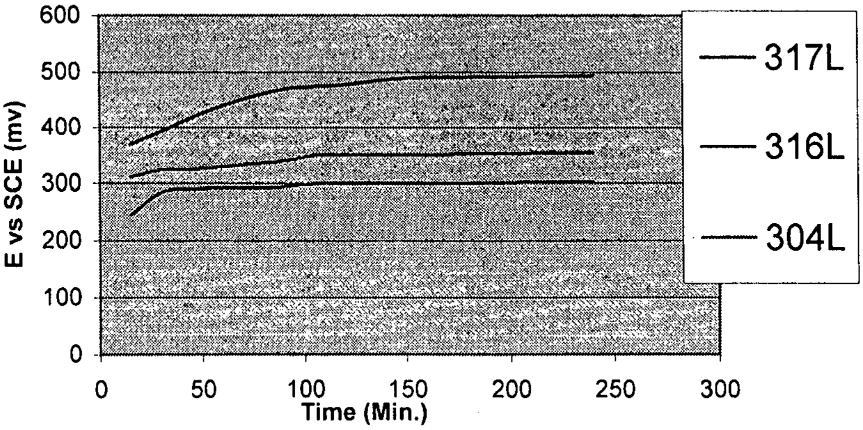


Fig. 5.3 : E vs TIME CURVE IN $P_a(0)$ SOLUTION

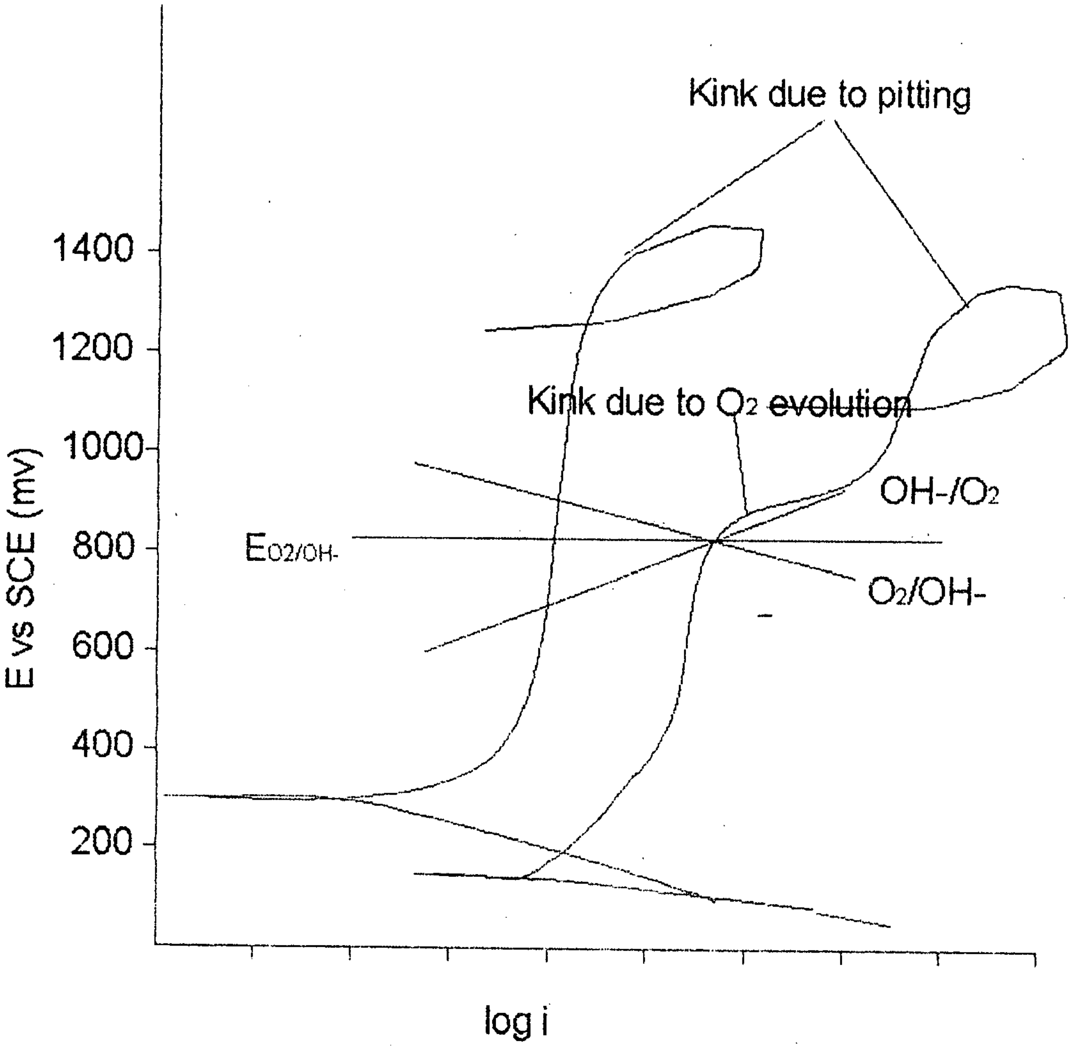


Fig. 5.4 : CYCLIC POLARISATION CURVE SHOWING TWO KINKS.

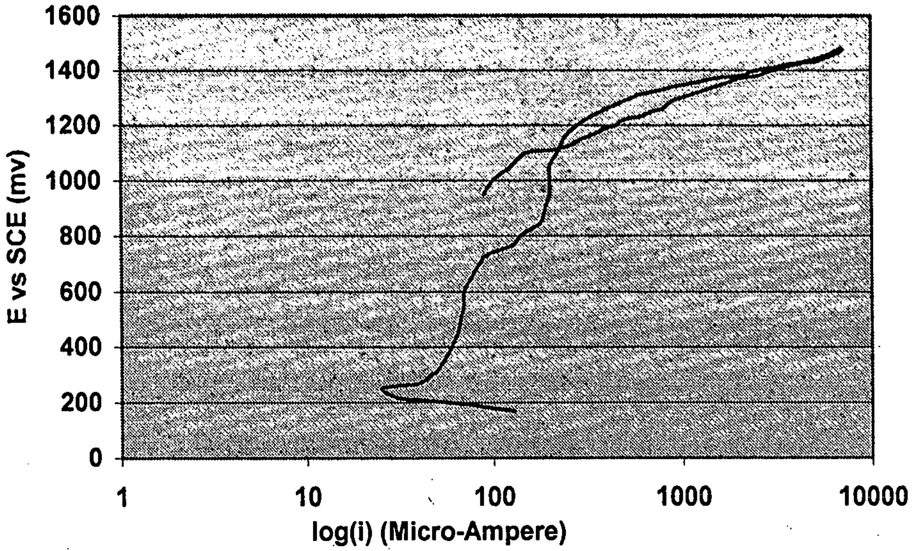


Fig. 5.5 : CYCLIC POLARISATION CURVE IN P_a1 FOR SS 317L

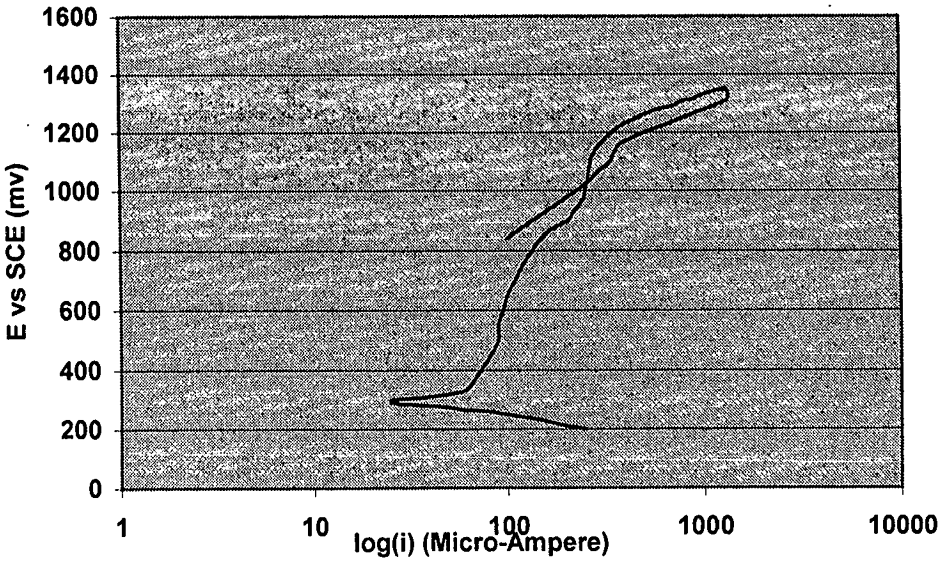


Fig. 5.6 : CYCLIC POLARISATION CURVE FOR SS 317L IN P_a2

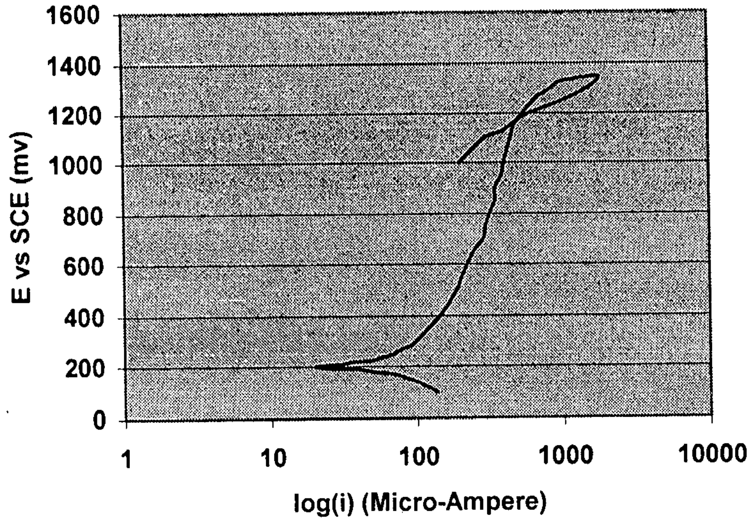


Fig. 5.7 : CYCLIC POLARISATION CURVE FOR SS 2205 IN P_a2

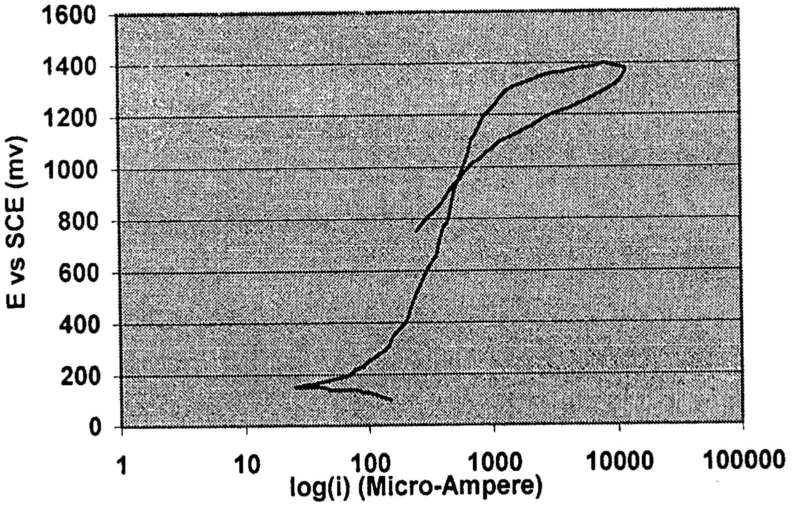


Fig. 5.8 : CYCLIC POLARISATION CURVE FOR SS 304L IN Pa (0)

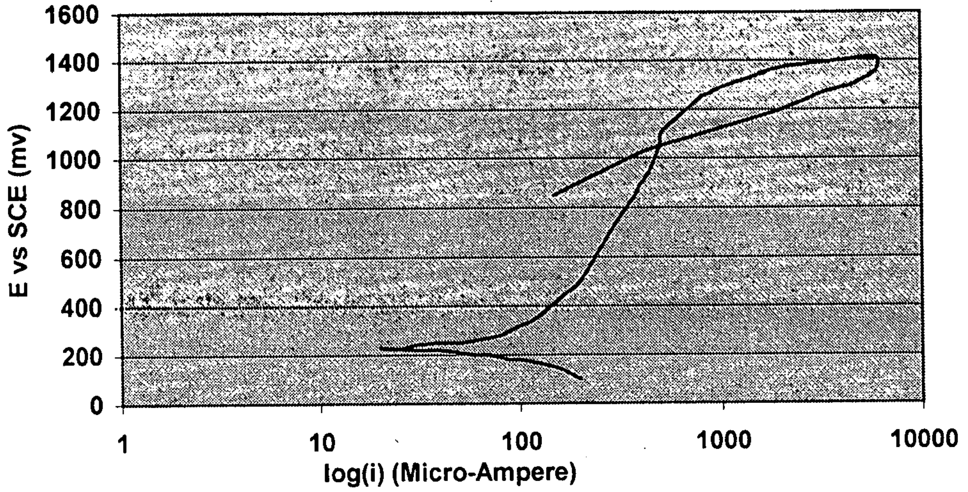


Fig. 5.9 : CYCLIC POLARISATION CURVE FOR SS 316L IN $P_a(0)$

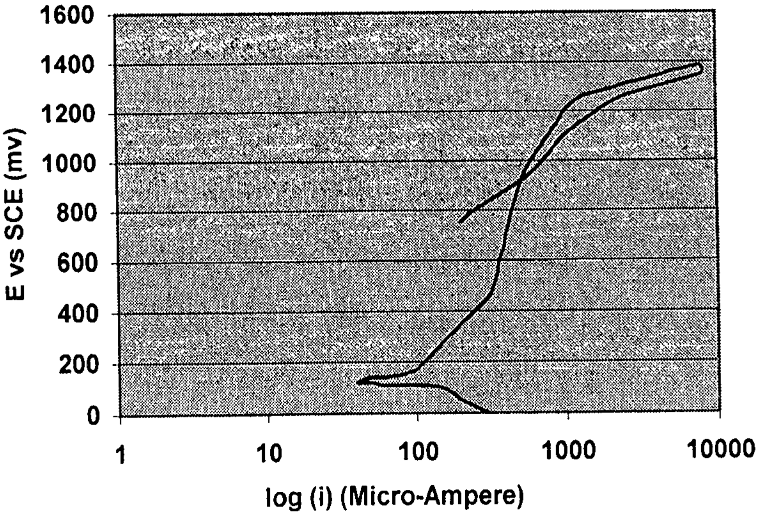


Fig. 5.10 : CYCLIC POLARISATION CURVE FOR SS 304L IN P_x1

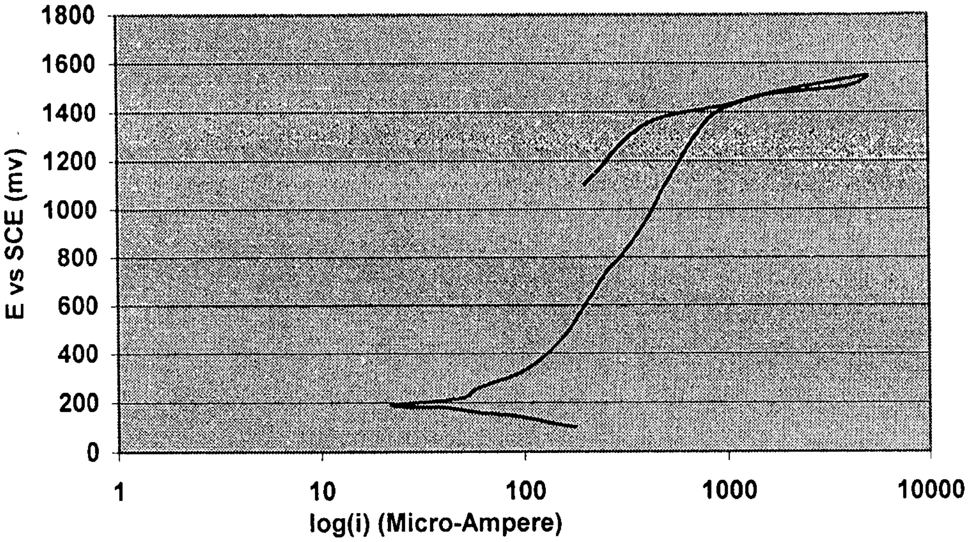


Fig. 5.11 : CYCLIC POLARISATION CURVE FOR SS 304L IN P_x2

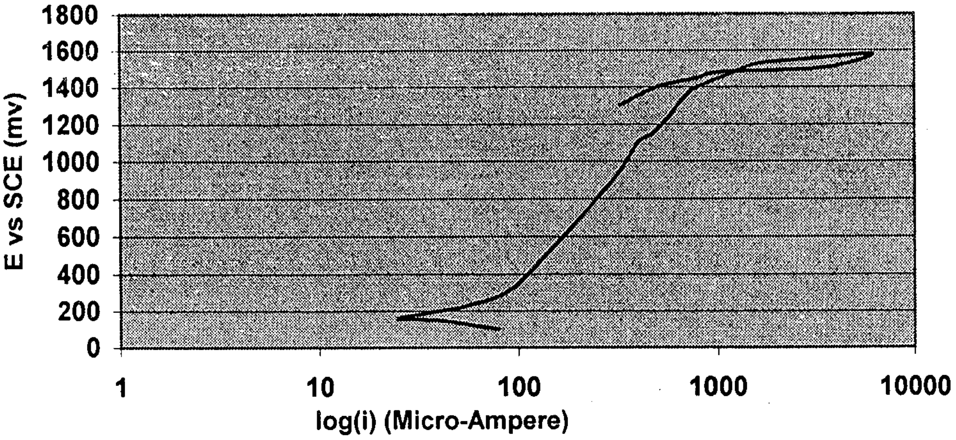


Fig. 5.12 : CYCLIC POLARISATION CURVE FOR SS 316L IN P_x2

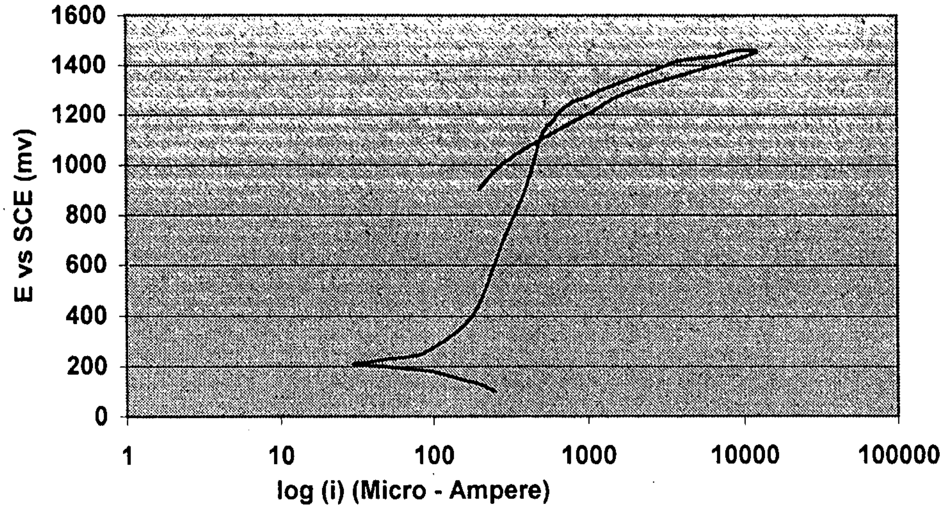


Fig. 5.13 : CYCLIC POLARISATION CURVE FOR SS 316L IN $P_{xa}1$

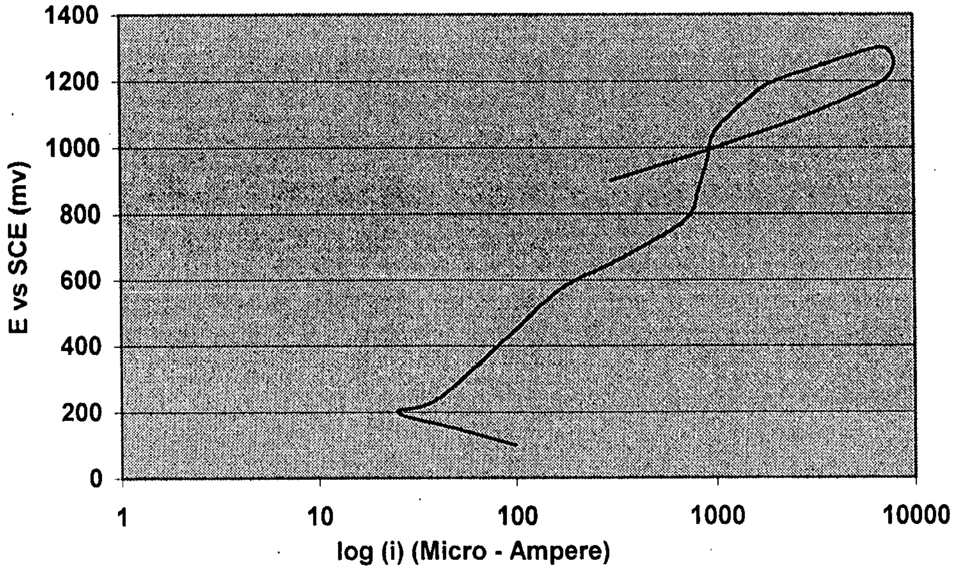


Fig. 5.14 : CYCLIC POLARISATION CURVE FOR SS 304L IN $P_{xa}1$

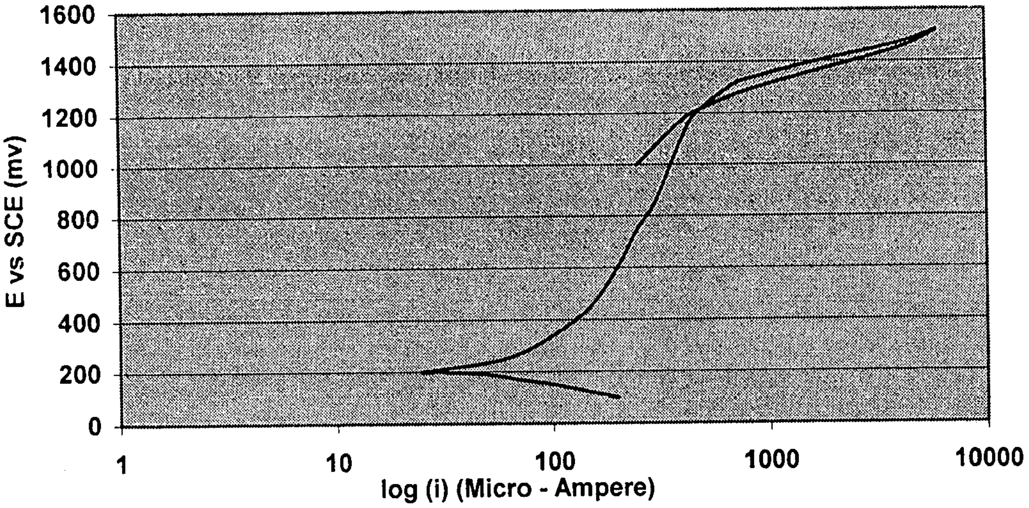


Fig.5.15 : CYCLIC POLARISATION CURVE FOR SS 304L IN Pxa2

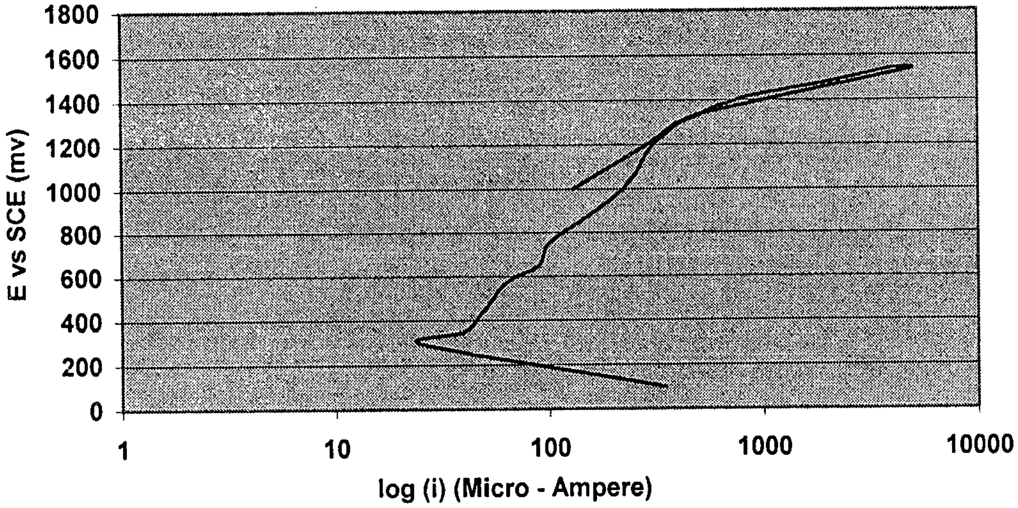


Fig. 5.16 : CYCLIC POLARISATION CURVE FOR SS 316L IN Pxa2

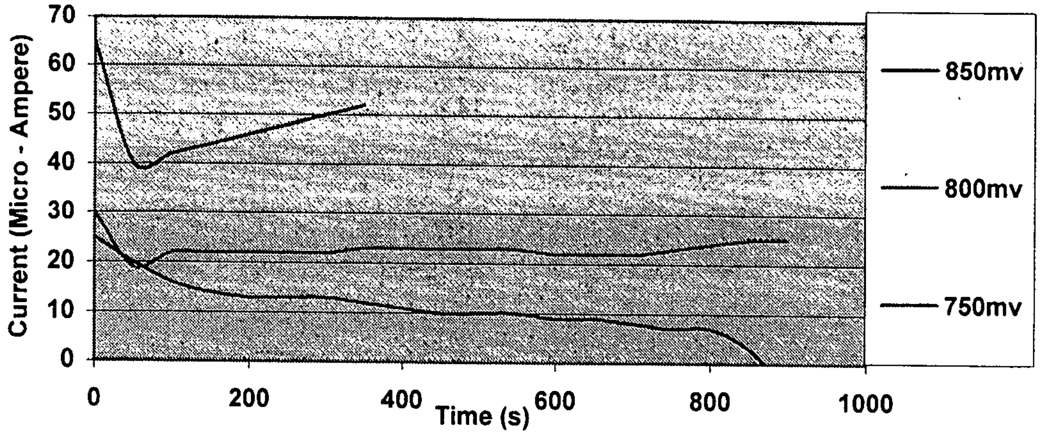


Fig. 5.17 : POTENTIOSTATIC CURVE FOR SS 317L IN Pa1

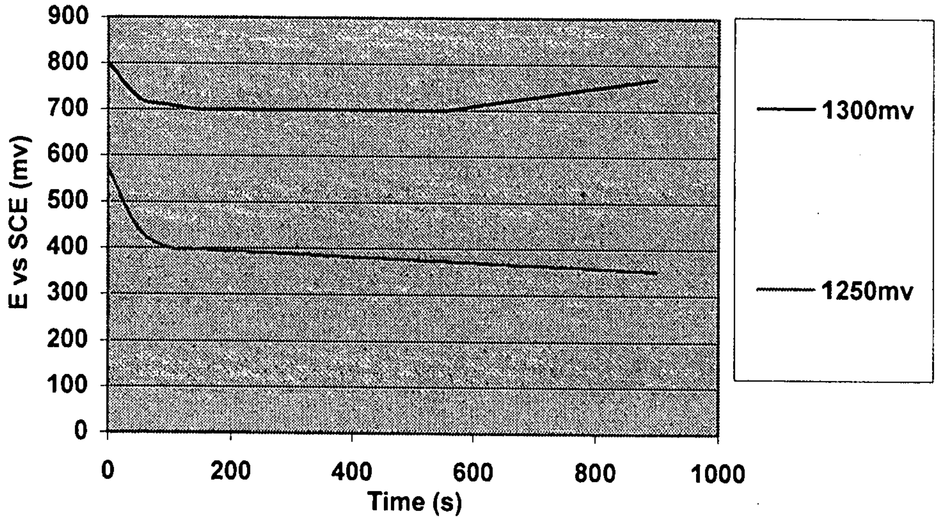


Fig.5.18 : POTENTIOSTATIC CURVE FOR SS 304L IN P_a 0

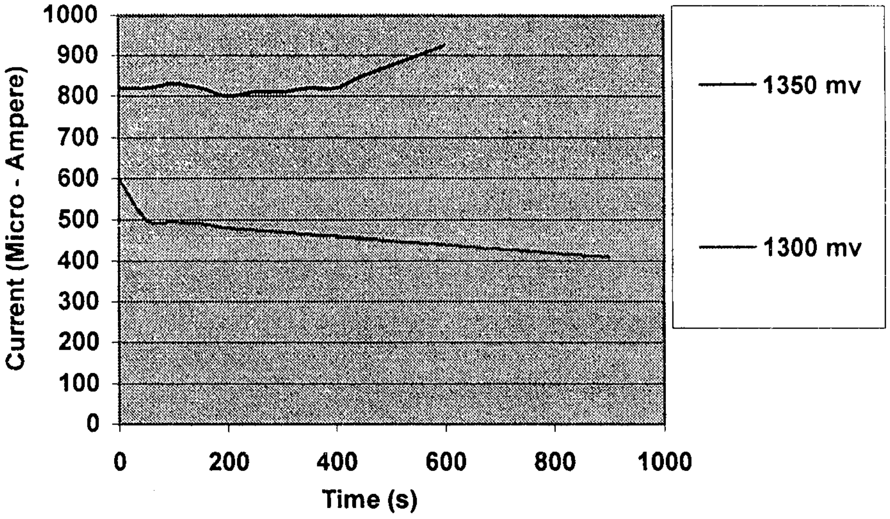


Fig. 5.19 : POTENTIOSTATIC CURVE FOR SS 316L IN P_a0

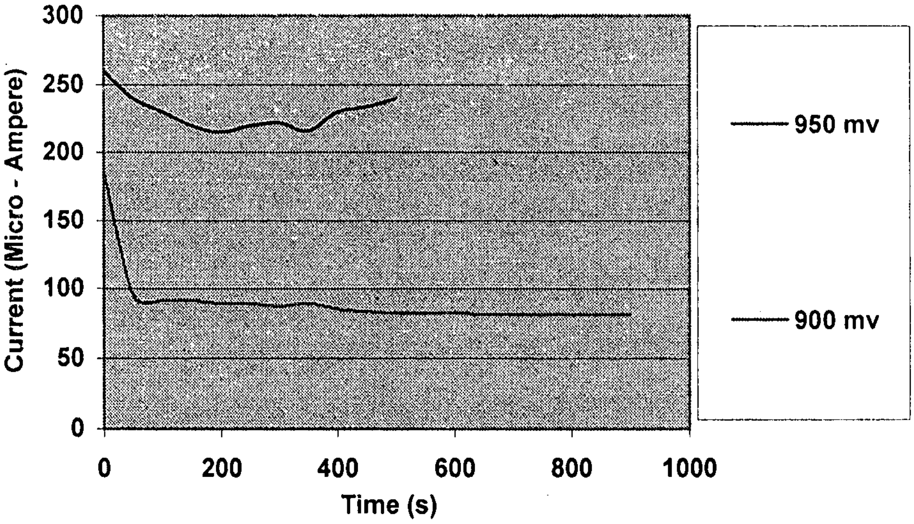


Fig. 5.20: POTENTIOSTATIC CURVE FOR SS 316L IN $P_{xa}2$

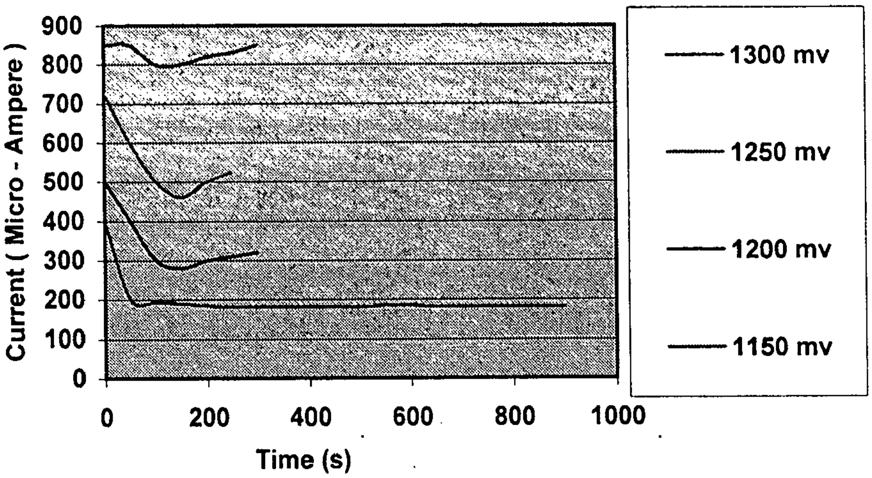


Fig. 5.21 : POTENTIOSTATIC CURVE FOR SS 317L IN $P_{xa}2$

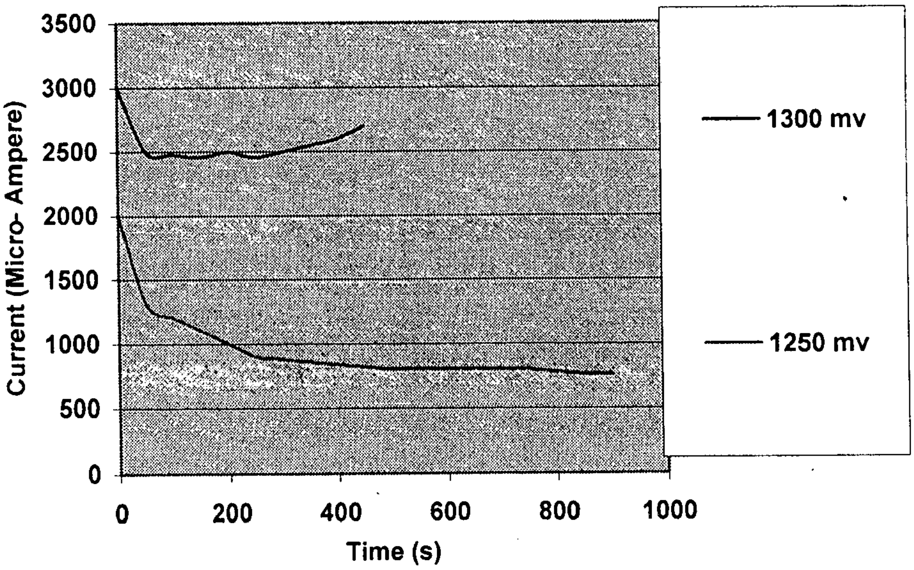


Fig. 5.22 : POTENTIOSTATIC CURVE FOR SS 316L IN $P_{xa}1$

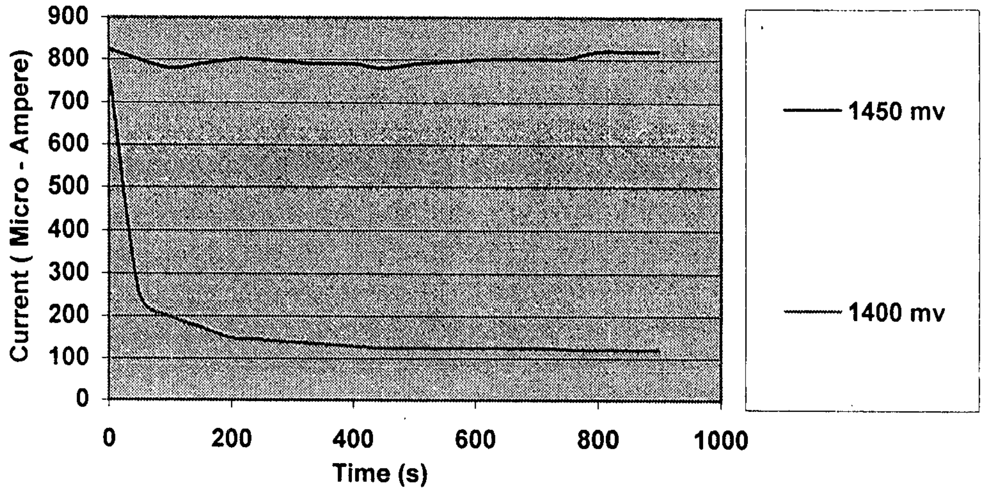


Fig. 5.23 : POTENTIOSTATIC CURVE FOR SS 316L in P_x2

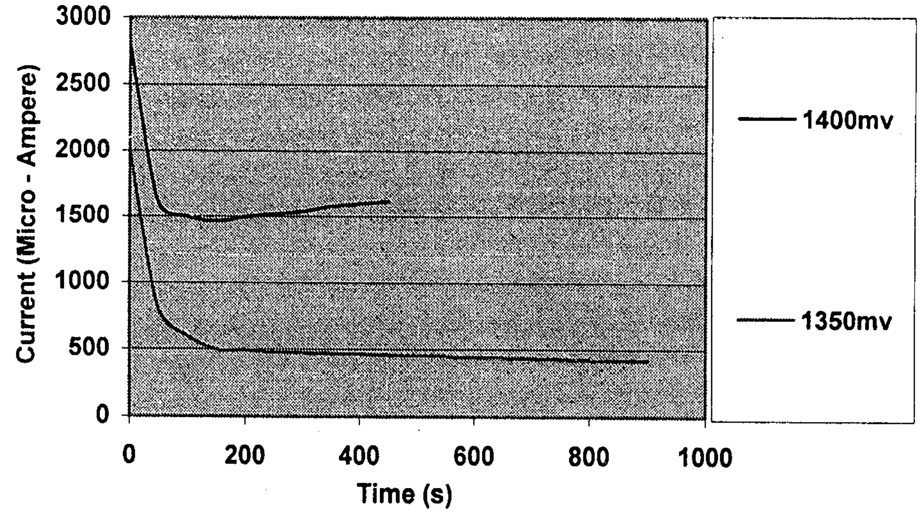


Fig. 5.24 : POTENTIOSTATIC CURVE FOR SS 304L IN Px1

Solution	Chemical Charge (as % A.O.)	pH	Cl^-(ppm)
P_x 1	0.47±0.05	5±0.10	1000±0.20
P_x 2			2000±0.20
P_{xa} 1	0.94 ±0.05	5±0.10	1000±0.20
P_{xa} 2			2000±0.20
P_a 1	0.47±0.05	5±0.10	1000±0.20
P_a 2			2000±0.20
P_a 3			0

TABLE 5.1 : CHEMICAL COMPOSITION OF THE SOLUTIONS

Solution	Materials	Corrosion rate(mpy)		Pit depth under crevices(mm)	
		RT	50°C	RT	50°C
				Max	Max
P_x 1	Mild Steel	382.16			
	304L				0.08
P_x 2	Mild Steel	210.49			
	304L	0.45	0.71	0.21	0.29
	316L	0.12	1.71	0.06	NVA
P_{xa} 1	Mild Steel	128.10			
	304L	0.37	0.70	NVA	0.05
P_{xa} 2	304L	0.03	0.03	0.09	0.15
	316L	0.23	0.31	0.09	0.11
	317L		0.18		0.08
P_a 0	Mild Steel	953.82			
	304L		0.12		0.03
P_a 1	304L	0.52		0.15	
	316L	1.64	1.77	0.12	0.21
	317L	0.02	0.02	NVA	NVA
P_a 2	316L	4.24		0.54	
	317L	0.09	0.023	NVA	NVA
	2205	0.44		0.09	0.06

NVA – No visible attack

TABLE 5.2 : CORROSION PARAMETERS IN PERACID SOLUTIONS (LONG TERM IMMERSION TEST)

Solutions	Materials	E_{corr} (mv)		E_c (mv)	E_p(potentiostatic) (mv)	E_p(cyclic) (mv)
		E vs t	Cyclic			
P_x1	304L	335	120	900	1375	1250
P_x2	304L	335	190	1470	1125	1400
	316L	360	100	1480	1425	1400
P_{xa}1	304L	100	200	1000	1225	1200
	316L	125	210	1100	1275	1270
P_{xa}2	304L	100	200	1220	825	1330
	316L	125	300	1290	925	1420
	317L	135	210	1400	1125	1430
P_a0	304L	293	160	950	1275	1300
	316L	330	225	1100	1325	1320
P_a1	316L	330			325	
	317L	440	250	1150	775	1250
P_a2	316L	330				
	317L	440	300	1020	625	1180
	2205		200	1170	1225	1370

TABLE 5.3 : ELECTROCHEMICAL RESULTS

Solutions	P_x1	P_x2	P_{xa}1	P_{xa}2	P_a1	P_a2	P_a0
RT	304L	316L	304L	304L	316L ?	317L	304L
50°C	304L	316L	304L	316L ?	317L	317L	304L

TABLE 5.4 : MATERIALS OF CONSTRUCTION FOR PERACID BLEACH PLANT

CHAPTER : 6

CONCLUSIONS AND RECOMMENDATIONS

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6.1 In - Plant Test :

Corrosion study on stainless steels 316L , 317L, 904L and 254SMO and a duplex stainless steel 2205 in C, D and C_D bleach washers of two Indian mills who have recently introduced chlorine-dioxide bleaching, forms the subject matter of chapter 3. The conclusions drawn on the basis of in-plant test performed on above stainless steels considering the extent of pitting, crevice and weld related corrosion vis-a-vis the cost and strength of the tested materials are as follows:

(1) The gaseous media of C-washer appears most corrosive.

(2) The corrosivity is lesser in D-vat and D-gaseous media.

(3) The corrosion environment experienced by alternative exposure to gaseous and liquid media in D-washer is still lesser but of the same degree as experienced by coupons in liquid media of C-washer.

(4) Alternate exposure in liquid/gaseous media in C-washer is least corrosive in this mill (Mill A).

(5) In mill B, C_D washer seems to pose more problems than D-washer. Replacement of chlorine by chlorine-dioxide seems to increase crevice corrosion as compared to a washer having only chlorine.

(6) The degree of corrosion resistance shown by various stainless steels is in following order of increasing resistance :

316L < 317L < 904L ≤ 2205 < 254SMO.

(7) On comparing corrosion attack, mechanical strength, cost and fabrication aspect, duplex stainless steel 2205 turns out to be appropriate material for most media except in some environment of Mill A namely (i) C-hood where 654SMO is expected to perform better (ii) D-vat where 254SMO seems a better choice.

(8) The results of some of the tests performed earlier show 254SMO to be the more resistant material for washer and filtrate piping of bleach plants using chlorine dioxide. But a comparison of cost and other properties along with the corrosion resistance may suggest a lesser resistant material e.g. 2205 for many of the media present in these plants.

6.2 Corrosion Investigation in Chlorine Dioxide Solutions :

Chapter 4 reports the electrochemical polarisation and long term immersion measurements performed on stainless steels 316L, 317L, 2205 and 254SMO in chlorine dioxide solutions to observe localised corrosion. The results have been analysed with reference to Pourbaix diagrams, constructed for this purpose for $ClO_2 - H_2O$ system, taking into account the various chemical species present in the bleach solutions. Conclusions drawn from electrochemical tests have been compared with those from long-term laboratory and in-plant tests. Effort has also been made to coroborate the results and conclusions with the CPT and CCT values, determined as a part of this work, and PRE values of the different tested materials . Materials options are also proposed on the optimal choice of materials for bleach plants, in a context of probable corrosion performance, capital cost and mechanical strength.

Electrochemical tests and long term immersion tests were conducted on stainless steel alloys 316L, 317L, 2205 and 254SMO in chlorine dioxide solutions, simulating the service environments observed in a chlorine dioxide bleach plant. The results obtained from these tests have been compared with those from in-plant tests reported (91). On the basis of the above, the following conclusions can be drawn:

1. The corrosion of stainless steel samples, in chlorine dioxide solutions, is governed by the reduction of ClO_2, ClO_2^- and ClO_3^-.

2. E_{corr} becomes less noble with increasing ClO_2 content and with decreasing pH of the solution.

3. The corrosivity of the solutions increases with decreasing pH, and increasing concentration of ClO_2 and Cl^-.

4. In electrochemical polarisation tests, stainless steel alloys 316L and 317L were observed to experience pitting and crevice corrosion in these solutions whereas alloys 2205 and 254SMO remained passive.

5. In Long-term immersion tests, these alloys exhibited only crevice corrosion but no pitting whereas in-plant tests, all stainless steels showed pitting and crevice corrosion.

6. In general, the resistance to uniform and localised corrosion of the tested stainless steels was in the following ranking order : 316L < 317L < 2205 < 254SMO. This finding was consistent with the expected behaviour, based on PRE number and CPT and CCT values for the tested steels.

7. Comparison of pitting and crevice corrosion resistance with the CPT, CCT and PRE values of the respective stainless steels vis-à-vis their composition indicate the importance of N in providing resistance against localised corrosion in synergy with the effect of Cr and Mo.

8. The comparison of corrosion resistance, observed in laboratory tests, and degree of corrosion attack as observed in the in-plant tests, taken in conjunction with the mechanical properties, fabrication aspects and material cost, indicated that alloy 2205 would be the most appropriate material of construction for the D-stage bleach plant machinery. Alloy 254SMO probably could deliver better performance, but it would be unlikely to be a cost-effective option.

6.3 Corrosion Investigation in Peracid Solutions :

Peracids are among the potential non-chlorine bleach chemicals for paper making. The present corrosion study (in chapter 5) reports the corrosion effects on machinery materials and their suitability in liquors likely to be observed in peracid bleaching. To the best of information available to author, this is the first work of its kind ever reported. For this purpose, electrochemical polarisation and immersion tests were performed on steels including stainless steel in these solutions. Three types of peracid solutions were considered for this investigation. Peracitic acid (CH_3COOOH)

- P_a, Caro's acid (H_2SO_5) – P_x and mixture of Peracitic acid and Caro's acid – P_{xa}. On the basis of corrosion investigation on mild steel and austenitic stainless steel in peracid solutions following conclusions have been drawn :

(1) Peracetic acid (P_a) solutions are most corrosive, followed by P_{xa} (mixture of peracetic acid and Caro's acid) and P_x (Caro's acid) solution. The increasing order of the corrosivity of the solutions can be writen in the following order :

$P_x < P_{xa} < P_a$

(2) With increased level of Cl^- concentration, localised corrosion attack increases on stainless steel samples.

(3) The comparison of corrosion resistance among the steels, on the basis of weight loss and electrochemical tests , The following increasing order of the corrosion resistance is given below :
M.S. < 304L < 316L < 317L < 2205.

(4) Mild steel experiences extremely high level of uniform corrosion, hence is not suitable for handling these liquors.

(5) Among the stainless steels, SS-304L can be used for handling liquors under lesser corrosive conditions (P_a solution without Cl^- and P_x and P_{xa} solution with Cl^- up to 1000 ppm at least up to 50°C).

(6) SS-316L for more corrosive conditions (P_{xa} solutions having Cl^- beyond 1000

ppm for temperatures up to 50°C, Pa solution up to 1000 ppm Cl^- at room temperature).

(7) The performance of 316L is marginal in $P_{xa}2$ solution at 50 degree and in P_a1 solution at room temperature

(8) For still more corrosive conditions (Pa solution, having Cl^- up to 2000 ppm and temperature 50 ^0C), 317L or 2205 are suitable materials of construction.

6.4 Suggestions For Future Work :

In the in-plant tests, described in chapter 3, corrosion study shows 316L is unacceptable material for C-stage. If we do inhibitor study in this stage, this material may be suitable and hence this could be a cost effective option. In the C_D (Cl_2/ClO_2) stage a long term immersion test should be done for knowing uniform corrosion , degree pitting attack and degree of crevice attack in C_D solutions up to 90% substitution. For complete study an in-plant tests up to 90% substitution and the electrochemical tests also should be done to find out the suitability of the material in C_D solutions. The E-pH diagram for Fe-Cl_2/ClO_2 system also should be formed to know about the corrosion mechanism. A long-term immersion tests and electrochemical tests in chlorine dioxide at higher temperature (about 70 ^0C) will give the information about corrosion in D-stage at higher temperature.

In future, in-plant tests should be done in peracid solutions to know the actual corrosion behavior of steels in these solutions. The work reported in this thesis, mild steel is found not suitable in peracid solutions. It may be suitable at higher pH in peracid solutions so it needs corrosion study at higher pH varying 6 to 9. An electrochemical and weight loss studies for mild steel also should be done at higher pH for complete study. To see the effect of temperature on corrosion of stainless steels in these solution, weight loss test and electrochemical tests should be done at higher temperature having pH-5. Another tests should be at higher pH and temperature both. An inhibitor study also may be favourable for mild steel in these solutions. The E-pH diagram for Fe-CH_3COOOH and Fe-H_2SO_5 system should be formed to know the species present in these solutions, which are responsible for corrosion of steels.

In each of the above cases, corrosion investigation should be performed in the respective solution having fibers / extractives from fibers also. This will correspond to the actual plant conditions. Since plant machinery in many cases exposed to pulp slurry which has fibers and their chemicals. Whereas, the present study relates to the effect of bleach chemicals only, it needs to be supplemented by considering the effect of pulp fibers also. In this manner, the data obtained may differ significantly and may be more useful for local mills due to variation in the characteristics of fibers from one plant specie to another.

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