### CAUSTIC CRACKING SUSCEPTIBILITY OF SAE A 516 Gr. 70 STEEL

### IN ALKALINE SULPHIDE SOLUTIONS

by

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#### ABSTRACT

The stress corrosion cracking (SCC) of A516 Gr. 70 steel was investigated in three solution composed of 3.35 m NaOH, 2.5 m NaOH + 0.42 m Na<sub>2</sub>S, and 3.35 m NaOH + 0.02 m Na<sub>2</sub>S. The electrochemical potential for maximum susceptibility was assessed by the slow strain rate testing technique (SSRT), and was found to reside in the active passive transition zone in each solution (-1 V<sub>SCE</sub> in the 3.35 m NaOH solution, and -0.88 V<sub>SCE</sub> in the solution containing sulphide ions). Some secondary cracking was visible at potentials corresponding to the passive zone in the 3.35 m NaOH + 0.42 m Na<sub>2</sub>S solution, indicating that the material was mildly susceptible to stress corrosion cracking at anodic protection potentials.

Since most industrial failures have occurred, in the vicinity of welds, a series of tests with a weld incorporated in SSRT specimen was conducted to ascertain whether or not changes in microstructure affected stress corrosion susceptibility. The fusion zone of a single pass weld was found to be most susceptible to cracking in alkaline sulphide solutions, at potentials corresponding to the active-passive transition.

The fracture mechanics technique, utilizing fatigue precracked to study the effects of stress intensity, electrochemical potentials, microstructure, and heat treatment, on crack propogation rates in the  $3.35 \text{ m NaOH} + 0.42 \text{ m Na}_2\text{S}$  solutions. Both stress intensity dependent (regions I and III) and stress intensity independent (region II) cracking propogation behavior was observed. Region II crack velocities of the order of 4 x  $10^{-10}$  m/sec were observed at -0.88 V<sub>SCE</sub>, and 2 x  $10^{-10}$  m/sec at -0.75 V<sub>SCE</sub>. No significant change in region II crack velocity was observed when the base material was subjected to a simulated stress relief anneal (650°C for 1 hr.) and tested at -0.88 V<sub>SCE</sub>. The region II crack velocity through a material with a dendritic microstructure (fusion zone of a weld) was found to be approximately 1 x  $10^{-10}$  m/sec.

A mechanism for failure due to coalescence of cracks and not due to the penetration of a single crack through the wall, has been suggested. The applicability of anodic protection in prolonging the service life of digesters has been examined.

Although no experiments were conducted to determine the mechanism of crack propogation, hydrogen embrittlement has been ruled out as a possible mechanism contributing to failure.

The results obtained are expected to find applications in the pulp and paper industry.

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## LIST OF SYMBOLS AND ABBREVIATIONS

## SYMBOLS

a	Crack length
В	Thickness of fracture mechanics specimen
Е	Potential
н	Fracture Mechanics specimen height
κ <sub>I</sub>	Stress intensity factor for mode I opening
κ <sub>I</sub>	Critical stress intensity factor
<sup>K</sup> ISCC	Treshold SCC stress intensity factor
Ρ	Load
v	Crack velocity
V <sub>SCE</sub>	Potential with respect to a standard saturated calomal electrode
W	Fracture mechanics specimen length
	Applied stress
ys	Yield stress

### ABBREVIATIONS

COD	Crack opening displacement gauge
DCD	Double contilever Beam fracture mechanics specimens
FCP	Free Corrosion potential
HAZ	Heat affected zone.
LEFM	Linear Elastic Fracture Mechanics

- MIG Metal Inert gas welding
- PTFE Poly Tetra fluo ethylene (PTFE)
- SAW Submerged Are Welding
- SCC Stress Corrosion Cracking
- SEM Scanning metal are welding
- SMAW Shielded metal are welding
- SSRT Slow strain rate testing technique

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Discussion of Paper by Hodge, J.C. and Miller, J.L., Trans of ASM, <u>28</u> (1940).

#### CHAPTER 1

#### INTRODUCTION

### 1.1 Stress Corrosion Cracking

Stress corrosion cracking (SCC) could be defined as the penetration and cracking of a metal under the conjoint action of a tensile stress and a corrosive environment, at a rate in excess of that produced by either factor acting singly.<sup>2</sup> One wishes that Brooks' forecast appearing in the frontpiece of this thesis had been correct. for industrial surveys show that SCC is reponsible for approximately 33% of the failures in the chemical industry,  $^3$  and continues to occur at unsuspected locations, a fact that was brought home by the recent catastrophic failure of a pulp and paper mill digester at Pine Hill, Alabama, 4,5 which managed to shake the industry out of it's present state of complacence. SCC is particularly dangerous because it is not readily detectable, and the first inkling that a stress corrosion problem exists is often the catastrophic failure of a piece of equipment. In addition to the prohibitive cost of repair and/or replacement of a valuable piece of equipment, and the attendant loss of production, the risk of injury to the operating personnel, makes the phenomenon particularly distasteful.

SCC was once associated with specific metal-environment systems like brass in ammoniacal solutions, austenitic stainless steel in brine, high strength steel in moist  $H_2S$  environments, and environments as innocuous as distilled water.<sup>6</sup> It is now recognised that the phenomenon is more widespread and no single theory can account for all occurrences of SCC.

A large number of variables could interact synergistically to affect the stress-corrosion reaction. In addition to specific metal-environment combinations, the microstructure, the metallurgical history of the metal in solution, presence of damaging ions in solution, nature of the oxide film formed on the metal, nature of the kinetics of the competing electrode reactions, and the presence of residual stresses on the metal, could affect the stress corrosion behaviour. Furthermore, the stress, and the environment at the tip of a stress corrosion crack could differ significantly from the bulk conditions frequently used to characterize SCC.

### 1.2 Origin of the Present Work

Several industries deal with highly alkaline solutions on a regular basis. One of these is the pulp and paper industry. In the Kraft process, which is the most widely used pulping process, and where SCC has become a serious problem, a solution primarily containing 1-4 m NaOH + 0.2 - 0.6 M Na<sub>2</sub>S, termed as white liquor, is used to dissolve lignin from the wood chips, leaving behind cellulose fibres, or pulp. The chips and white liquor came into contact with each other in large pressure vessels termed digesters (currently made of A516 Gr. 70 steel plates welded together, and illustrated in Fig. 1), where they encounter temperatures between 100 - 165°C, and pressures of 687 - 1,200 kPa.

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Figure 1 - A typical continuous Kraft digester.

When digestion is complete, the spent liquor containing lignin and other soluble residue from the wood chips and oxidized sulphur species, is separated from the pulp. The spent liquor, or 'black liquor', as it is now called, is subjected to a series of rejuvenating operations to restore its original NaOH and S<sup>--</sup> ion concentrations, and remove impurities from solution. Besides NaOH and Na<sub>2</sub>S, white liquor also contains impurities like Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub>, NaCl and other organic impurities which cannot be removed by the rejuvenating process.<sup>7</sup>.

Most SCC problems in the process were encountered in the digester. A digester is essentially a cylindrical pressure vessel, with an internal cone at the top. During September 1980, in an accident involving a digester at Pine Hill, Alabama, the entire 18 ft base diameter upper cone, welded to the cylindrical base was blown away. The failure was attributed to intergranular Stress Corrosion Cracking.<sup>8</sup>

The problem encountered in the Pine Hill, Alabama, digester was not unique, but served to focus attention on the problem. Significant shell corrosion was experienced in a continuous digester at a mill in Vancouver Island, as far back as 1967. In 1977, cracking of the transition zone welds of a continous digester in Mackenzie, B.C. was accidentally discovered when the level indicator was being installed.<sup>9</sup> Severe cracking was encountered when a soda process (utilizing only NaOH for pulping) continuous digester at Pennsylvania, in 1978. This was subsequently controlled by installing at anodic protection system.<sup>9</sup>,<sup>10</sup>. In 1980, the fillet welds attaching the centre-pipe support plates to the shell in a digester at Grande Prarie, Alberta, were found to be cracked.

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Continuous neglect of this problem culminated in the accident at Pine Hill. Subsequent careful investigations conducted by the TAPPI continuous Digester cracking task force found that 65% of digesters and impregnation vessels contained some cracking.<sup>7</sup>

Several authors<sup>11-13</sup> have suggested that the active-passive range of potentials, as defined by the anodic polarization curve, was the region where the metal was most prone to SCC in, alkaline environments. The present work was undertaken to determine whether or not

- (i) welded structures are more prone to SCC; and
- (ii) anodic protection would be a useful tool in controlling SCC in continuous digesters.

#### 1.3 Theories of Stress Corrosion Cracking

No unified theory of SCC exists that can explain all occurrances of cracking. A number of 'simplistic' models have been advanced to explain specific situations. However, there are a number of features common to all SCC problems.<sup>14</sup>

- The existance of a tensile stress, either applied, or present as a residual stress.
- (11) The alloy usually shows good resistance to general corrosive attack by the environment causing cracking.
- (iii) The microscopic appearance of stress corrosion fracture in brittle, although the metal itself may exhibit significant ductility in a mechanical test.

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- (iv) In order for SCC to occur, a threshold stress must be exceeded.
- (v) There exists a potential, or range of potentials where the metal is most prone to SCC.

Three distinct schools of thought exist among researchers attempting to model SCC. The electrochemically based models require that the sides of a crack become passivated, whereas the material at the crack tip actively dissolves. Vermilyea and Diegle<sup>15,16</sup> and Stachle<sup>17</sup> consider that dissolution at the crack tip occurs because of the localized rupture of the passive film. Thus, the development of a crack is controlled by a balance between the rate of passivation, and the rate of dissolution at the crack tip. In contrast to this view, Scully, <sup>18,19</sup> Parkins, <sup>20</sup> and Hoar and Jones<sup>21</sup> consider the material at the crack tip to be constantly active. The absence of passivation can be explained either by assuming the existance of regions that are difficult to passivate or by supposing that a material under plastic deformation is more difficult to passivate than the surrounding non-deforming material. In all cases, the specific effect of agressive ions is explained on the basis of their influence on the rate of repassivation.

In the SCC theory proposed by Uhlig,  $^{22-24}$  the formation of cracks is considered to be a phenomenon of mechanical fracture, rather than a corrosive problem. The theory assumes cracking to be caused by the adsorption of the SCC provoking anions onto those regions which are in a state of sub-critical tension. By this adsorption, the surface

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energy is lowered so greatly that the material will fracture at a stress level below the nominal yield limit. This theory is presumably applicable only in a small number of SCC systems. However, Scully<sup>18,19</sup> has pointed out that adsorption of anions can be regarded as important in SCC by virtue of their influence on the rate of electrochemical dissolution.

The Hydrogen-embrittlement mechanisms, the third group of model used to explain SCC, has been considered by some workers to be a different phenomena from SCC. However, since cathodic reactions (which could produce hydrogen under the proper conditions) are as much a part of the cracking processes as anodic reactions, it would be inappropriate to exclude hydrogen embrittlement from a discussion of SCC. The hydrogen embrittlement model postulates that fracture results from the production of a brittle region at the crack tip because of the introduction of hydrogen into the alloy, via cathodic processes. The production of brittle regions has been attributed to decohesion, 14 new phase formation, 25, 26 and pinning of dislocations. 28 The environment can affect the process by influencing the rate of production of hydrogen ions, and by enhancing or inhibiting the rate of entry of hydrogen into the metal, by the interposition of adsorbed, or reaction layer films. In aqueous systems, the potential and pH at the crack tip determine whether or not it is thermodynamically feasible to evolve hydrogen.

The observation of Benedicts<sup>28</sup> that hydrogen gas was evolved when iron filings were immersed in white liquor, caused workers to speculate as to whether hydrogen embrittlement could, in fact, be

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responsible for brittle failure in the pulp and paper industry. However, this observation has not been independently confirmed. It has been observed that hydrogen enters steel more readily from sulphide solutions, when the pH is below 5. This may be a consequence of increased hydrogen ion activity, or may be a result of the change in stable species as the pH decreases. Biernat & Robins<sup>29</sup> report that dissolved  $H_2S$  is stable at a low pH, but is transformed into the HS<sup>-</sup> species when the pH is about 5 ( $H_2S/HS$  has a pk of 6.7). At still higher pH values, the stable species is the  $S^{-1}$  ion. It appears that the sulphur species must be present as  $H_2S$  in an acid medium for significant hydrogen embrittlement to occur. The digesters are usually in contact with highly alkaline solutions (pH = 12-13) for most of their The only time a solution of a lower pH could be in contact lifetime. with the digester wall is during acid cleaning of the screens within the digester. The impregnation zone, where most of the stress corrosion cracks are observed<sup>30</sup> is not immersed in the acid, but some condensation of the vapours could occur on the walls of the impregnation zone. It is highly unlikely that the pH could be lowered into the region where  $H_2S$  is the stable species, due to condensation. If the moisture that condensed on the walls to be acidified, most cracking would be expected in the region around the screen. However, no SCC cracks are observed in this region.<sup>7</sup> The aforementioned facts estabish that Hydrogen Embrittlement could be ruled out as a cause of SCC occurs in Kraft digesters.

Other authors have attempted to model specific aspects of SCC of

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mild steel in alkaline solutions, based on anodic dissolution theories. Bignold,<sup>31</sup> Doig & Flewitt,<sup>32</sup> and Melville,<sup>33</sup> have all examined the effects of a change in potential down the crack length on SCC, and Mogensen et  $al^{34}$  have investigated the dissolution and repassivation kinetics of oxide formation at various potentials.

It must be noted that none of the mechanisms in any of the three groups of models specify, or imply, an intergranular or transgranular crack path. Examination of SCC cracks by traditional methods have shown that SCC of mild steel follows a predominantly integranular path in alkaline solutions, <sup>11,35</sup> although transgranular cracking has been reported in some instances.<sup>36</sup>

The correlation of SCC with passive film behavior has led to several investigations of the properties of these films. Cyclic voltammetry experiments,<sup>37</sup> have shown that initial film formation occurs in the active region as an adsorbed layer of  $Fe(OH)_2$ . At higher potentials, further oxidation of iron occurs and the passive film oxidation to either FeOOH or  $Fe_3O_4$ . This occurs at the active-passive transition. At still higher potentials, the FeOOH or  $Fe_3O_4$  oxidizes to form  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>.<sup>38</sup> It has been shown that the films formed at the SCC susceptible potentials are more brittle than the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> films formed at higher potentials, and therefore more likely to rupture under the application of a tensile stress.<sup>39</sup> Other studies<sup>16,21,38</sup> have shown that film rupture at SCC susceptible potentials produces large current transients before repassivation can occur. At other potentials, rupture

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of the passive film causes little, or no increase, in the anodic current density. This behaviour has been related to the thermodynamic stability of the soluble iron species,  $HFeO_2^-$  (dihypoferrite), in the potential range where these transients are produced, and the rate of repassivation of the exposed metal. The passivation process involves the following two-step sequence.<sup>36</sup>

$$HFeO_2^- \rightarrow Fe(OH)_2 \rightarrow passive film$$

In the presence of  $CO_3^{--}$  or S<sup>--</sup> ions, the dihypoferrite ions may combine with the carbonate (or sulphide) ions to form ferrous carbonate (or ferrous sulphide) which is less soluble, and more stable than ferrous hydroxide. The intermediate step in the passivation process becomes relatively stabilized, and a complete layer of  $\gamma$ -FeOOH becomes more difficult to form. The range of conditions for possible SCC is therefore extended.

### 1.4 Structure and Properties of Welds

Since all the cracking problems in the digester occur in the vicinity of welds, it would be prudent to examine the structure and properties of various region in the weld. Fig. 2 indicates the front view of a digester, and the locations of various fusion welding processes used in its construction.

The weld can be divided into the fusion zone and the Heat



Figure 2 - Location of different welds in a continuous digester.

Affected Zone (HAZ). The fusion zone is the result of solidification of the molten metal pool. The heat from the molten metal would affect the base material adjacent to the deposited molten metal. This region comprises the HAZ.

The process of soldification of the molten weld pool is fundamentally similar to ingot solidification. Conditions which promote constitutional supercooling, i.e. fast growth rates, high alloy contents, and extreme values of the solute distribution coefficient, exist in the weld pool. This promotes breakdown of the fusion boundary interface,<sup>40</sup> which results in the development of a dendritic structure. Dendritic growth is associated with segregation, either as coring, or accumulation of solute in the interdentritic spaces.

The original columnar structure of the weld may be refined in grain size, and becomes equiaxed by heating to above the  $A_3$ temperature, or between the  $A_1$  and  $A_3$  temperatures. Such refinement takes place when multiple passes are deposited. The heat of each succeeding bead reheats the previously deposited beads, refining the grains of those portions of the weld layers that are reheated to the critical temperature range.

The HAZ is comprised of a narrow band of material adjacent to the fusion line, which has been heated to peak temperatures ranging from the initial plate temperature, to the melting point of the metal, at the fusion boundary. Depending upon the maximum temperature attained at any point in the HAZ, and the cooling rate at that point, a wide variety of microstructures ranging from coarse pearlite, bainite, to even martensite could be produced. In multipass welds, the structure of a

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given region can be altered substantially by the localized heating caused by subsequent weld passes. The local heating and cooling accompanying weld cycles, causes local strains, which in turn produces residual stresses.

Thus, in terms of the SCC behaviour of a welded joint, we are confronted with two possibilities:

- (i) regions with high residual tensile stress which serves to initiate SCC; or
- (ii) microstructural changes which play a more dominant role than residual stresses in the phenomenon of SCC.

If the first scenario were true, digestors which have been subjected to a full stress relief anneal would be immune to SCC. However, in practice, cracking problems have been encountered even in digesters which have been subjected to a full stress relief anneal.<sup>9</sup>

Furthermore, dense networks of stress corrosion cracks have been observed in the fusion zones of welds in digesters, whereas fewer stress corrosion cracks were observed in either the HAZ or the base material.<sup>41</sup> Hurst and Cowen have also reported cracking in the fusion zone of welds exposed to strongly alkaline environments. Also no correlation has been obtained between the SCC susceptibility and welding procedure.<sup>7</sup>

All the above suggests that residual stresses do not play a dominant role in SCC. This prompted the author to follow testing techniques which completely eliminate the effect of residual stresses, and allowed examination of the susceptibility of various microstructures to SCC.

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### 1.5 Effect of Heat Treatment on SCC Susceptibility

During the weld cycles, the base material adjacent to the fusion zone could be heated to a temperature which approaches its melting point. In addition the microstructure of the parent material in the HAZ would be altered. Furthermore, after welding, the parent material surrounding the weld is subjected to a stress relief anneal at approximately 650°C for 1 hr. It is possible that different microstructures would exhibit susceptibility to SCC to varying degrees. However, very little work has been done on the effect of heat treatment and/or thermal history on the stress corrosion susceptibility in alkaline environments. Bohnenkamp<sup>50</sup> reported that dead loaded specimen quenched and tempered at 400 - 700°C failed faster, by a factor of 2 - 4, than specimen quenched and tempered at 300 - 400°C.

Bohnankamp also suggested that the distribution of carbon, rather than the absolute carbon content, plays a more important role in determining the SCC resistance of a material. He reported a higher rate of dissolution of carbides in NaOH solutions, which accounts for the intergranular attack which has been observed in low carbon steels. Furthermore, observations that steels with sufficiently low carbon and nitrogen contents are immune to intergranular attack<sup>51</sup> provide additional support to this.

### 1.6 SCC Testing Techniques

Due to the large number of variables which affect SCC, many

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different techniques have been used to study the phenomenon. They range from relatively simple tests which monitor the lifetime of a stressed sample exposed to corrosive environments, the sophisticated tribo-ellipsometric experiments, where passive film growth kinetics and current density are measured with time.<sup>42</sup>

Since SCC can be a relatively slow process, by laboratory standards, many SCC tests are performed by increasing the relative aggressiveness of the environment, vis a vis, the test specimen. This could be done by increasing the concentration of the aggressive species in the environment and/or increasing the temperature, or introducing a notch or precrack in the test specimen. This serves to

- (i) decrease the time required for initiation of a stress corrosion crack; and
- (ii) increase the rate of propogation of the stress corrosion crack;

so that results could be obtained within a reasonable period of time. The two relatively new methods of particular interest to this study are the Slow Strain Rate Technique (SSRT) and the fracture mechanics approach. These compare favourable with the traditional accelerated SCC tests, and yield information without having to increase the aggressiveness of the environment.

The primary advantages of the SSRT are

(a) it provides a rapid laboratory method for evaluating SCC susceptibility in solution of laboratory or industrial

interest. Usually a test never lasts for more than 48 hrs, compared to the 60+ days for constant load, or constant strain tests; and

(b) the results are positive, i.e., a failure always occurs, either in the ductile (overload) manner, or prematurely, due to SCC, in the brittle mode.

The SSRT tests demonstrates the fact that SCC is dependent on the local strain rate produced at the crack tip, rather than the tensile stress per se. Parkins<sup>43</sup> postulated that creep or strain rate is the controlling parameter in SCC. He suggested that cracks will propagate only if electrochemical conditions which cause cracking were established before creep in the plastic zone ahead of the crack tip was exhausted.

Studies have shown that there is an upper and lower limit of strain rate that will produce SCC. Both above and below this range, the material will fail by ductile, microvoid coalescence. The upper limit occurs as a result of insufficient crack advance, with respect to the amount of strain occurring, while the lower limit is thought to be due to a protective film which establishes itself over the crack tip faster than it can be ruptured by the strain. The optimum strain rate for producing SCC varies with the metal, environment, electrochemical potential, and temperature, and must be experimentally determined for each system.<sup>8,44</sup>.

A typical SSRT test consists of pulling apart, to failure, a cylidrical tensile specimen exposed to the appropriate environment, at a low, constant, extension rate. Since the onset of SCC will affect the

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Figure 3 - Stress-strain curves for specimen tested in SCC susceptible and inert environments using SSRT, where  $A_0$  and  $A_{SCC}$  are the areas under the respective curves.

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relative ductility of the test specimen, as illustrated in Fig. 3, SCC susceptibility can be characterized by mechanical parameters which include % elongation, % reduction in area, or even time to failure. Visual confirmation of secondary cracks on the specimen surface could be used to reinforce the conclusion obtained from this test.

The SSRT has been found to be a more severe test of SCC than other traditional tests, and has produced SCC for metal-environment combinations where SCC was difficult to intitiate.<sup>43,45</sup> Semi-quantitative data, in the form of apparent crack growth rates has also been obtained from the slow strain rate tests.<sup>46</sup>

The fracture mechanics approach to the study of SCC is an extension of Linear Elastic Fracture Mechanics (LEFM) which is used to quantify fracture in materials of limited ductility.<sup>48</sup> This technique follows the growth of a crack as a function of the stress intensity at the crack tip, which is characterized by  $K_I$  for a mode I crack opening. The stress intensity is directly proportional to the applied load, and the square root of the crack length, all other factors being equal. At sufficiently high values, the stress intensity approaches  $K_{IC}$ , when spontaneous unstable crack growth occurs.

In most fracture mechanics experiments, the crack growth rate, v, is measured as a function of the stress intensity. A plot of log v VS stress intensity usually shows three distinct regions. In region I, at low  $K_I$  values the crack propogation rate is stress-intensity dependent. Region II, where the rate of crack propagation is independent of stress-intensity, and finally region III where crack

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propagation becomes  $K_I$  dependant at high stress intensities. At very high stress intensities, when  $K_I = K_{IC}$ , unstable crack propagation occurs. On the other end of the  $K_I$  spectrum, for values of  $K_I$  below a particular threshold stress intensity denoted by  $K_{ISCC}$ , no crack propagation is detectable. A schematic log  $V-K_I$  plot is provided in Fig. 4. The complex interaction of stress intensity and environment variables in regions I and II, makes it difficult to treat data mechanistically. However, the presence of the relatively stress independent region II is useful in determining the effects of temperature, solution composition, viscosity etc., on crack propagation, which eventually help elucidate the rate controlling mechanism of crack propagation.

Moreover, fracture mechanics allows separation of the initiation from the crack propagation stages, which makes it a useful tool for kinetic studies.<sup>49</sup>





#### CHAPTER 2

#### EXPERIMENTAL

### 2.1 Scope of the Present Work

During the course of this work, two test methods, namely the Slow Strain Rate Technique (SSRT), and the Fracture Mechanics technique, were conducted with three different alkaline solutions. The SSRT experiments were employed to determine the conditions where the test material was most prone to SCC, in solutions composed of 3.35 moles/kg NaOH, 2.5 moles/kg NaOH + 0.42 moles/kg Na<sub>2</sub>S, and 3.35 moles/kg NaOH + 0.42 moles/kg Na<sub>2</sub>S. This technique has been used successfully by other workers to study SCC in alkaline solutions.<sup>11,38,44</sup> The material used was a A516 Gr. 70 steel, obtained as hot-worked plates 1/2" (1.27cm) and 1" (2.54cm) thick, whose composition is indicated in Table 1. Since hot-worked plates are used directly in the construction of digesters in pulp and paper plants, tests were conducted in the as-received condition.

Based on the SSRT results, specific potentials were chosen for the fracture mechanics study, to investigate the effect of stress-intensity and potential on v, the crack propagation rate. Detailed fractography was conducted on the fracture surfaces produced by both test techniques.

The solutions used were prepared under nitrogen purged conditions, using singly distilled water and reagent grade chemicals (NaOH pellets, and Na<sub>2</sub>S • 9H<sub>2</sub>O crystals).

	Yield Strength	Tengile Strength	Hardness No.	Cł	nemical	L Compo	osition	(%)
Material	MPa	MPa	VHN	С	Si	Mn	P	S
A516 Gr. 70 0.5 in plate	308	525	171	0.18	0.22	1.12	0.021	0.007
A501 Gr. 70 l in. plate	343	498	-	0.19	0.23	1.16	0.021	0.008
E70S Welding electrode	-	572	189	-	-	-	-	-

## Table 1 - Yield Strengths and Chemical Composition of Steels

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#### 2.2 Specimen

Tensile SSRT specimen, were machined from the 1/2" plate, with the tensile axis parallel to the Rolling Direction. The configuration and dimensions of these specimen are indicated in Fig. 5.

In addition, tests were conducted in tensile SSRT specimen incorporating both the fusion zone, and the HAZ of a weld, in the gauge section, as illustrated in Fig. 5(b). This ensured that a wide variety of microstructures were simultaneously in contact with the environment. Welds were made by machining 3/8" (9.5mm) deep groves into the plate, perpendicular to the rolling direction, and depositing weld metal into the groove with an automated MIG welding machine, and a E70S wire electrode. Prior to use, these specimen were polished with 300 grit paper, degreased with chlorothane, and dried with ethanol.

Double Cantilever Beam (DCB) specimen, machined from the 1" (25.4mm) plate whose geometry is shown in Fig. 6, were used for the Fracture Mechanics experiments. The Beam height (H) for these specimen was 11.6 mm, specimen length from the loading line (W) was 66.7 mm, and the specimen thickness (B) was 25.4 mm. The length of the initial machined notch from the loading line was 25.4 mm, and the beams were threaded to receive grips for the application of a load. The faces perpendicular to the crack plane were polished to a 0.3  $\mu$ m finish, washed with water, then dried with ethanol, and stored in a dessicator until further use.

Brown and Srawley<sup>54</sup> have shown that the  $K_I$  calibration for the DCB geometry is given by



Figure 5 - SSRT specimen geometry.



Figure 6 - DCB specimen geometry.

$$K_{I} = \frac{p}{RH^{3/2}} (3.45 + 2.415 \frac{H}{a})$$

The above calibration equation is valid only when  $a/w \leq 0.6$  and  $W/H \geq 5$ .

In order to compare the crack propagation rates of the as-cast dendritic structure (as in the fusion zone of a weld) vis a vis the hot-worked microstructure DCB specimen with a machined notch incorporated in the fusion zone of a weld were utilized. This was done by machining a 3/8" deep groove parallel to the rolling direction, on the 1/2" thick plate, and depositing molten metal into the groove with a MIG

welding machine. The above is illustrated in Fig. 7. Subsequently  $\frac{1}{8}$  (3.2mm) of the base metal was ground way, suitable sections were cut out, and notches were incorporated within the fusion zone. As in the previous case, the beam height was 11.6 mm, the specimen length from the loading line was 66.7 mm, but the specimen thickness was 9.53 mm.

# 2.3 Equipment and Apparatus

SSRT experiments were carried out on a modified, vertically mounted hounsfield tensometer, capable of achieving a cross-head speed of .00015 in /min, corresponding to a strain rate of 2.5 x  $10^{-6}$ /sec. The cross-heads were pulled apart by a motor rotating at 12 rev./hour, whose drive shaft is coupled to a reducing gear system. A schematic diagram of the cell used is provided in Fig. 8. The cell was

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constructed of FEP or PTFE fluocarbon polymers, and the solution within the cell was heated by an externally wrapped, resistance heated tape. Temperature control of ±1°C was maintained by connecting the heating tape, through a Variac power transformer, to a YSI model 71 temperature controller. A FEP coated thermistor probe (YSI model 400) was inserted into the cell. Two spectrographic grade graphite counter electrodes were positioned at opposite ends of the cell, as were a Nitrogen purge line, and a reflux condenser. An external, saturated calomel electrode, maintained at room tempeature, was connected to the cell via a luggin capillary, which was positioned approximately 1 mm from the gauge section of the specimen. A cotton thread was run through the luggin capillary to ensure stable potential control. Potential control was maintained by a Wenking Model 68 Potentiostat.

A few tests were conducted with 0.5 - 1 mm of the surface of the gauge section removed electrochemically in a solution comprising of 25 gms. chromium trioxide, 135 ml acetic acid and 7 ml water. These tests were performed to ascertain the influence of residual stresses on the surface, on secondary cracking.

DCB specimen were fatigue precracked by a Sonntag SF-1-U fatigue testing machine. Fatigue grips were constructed of high speed tool steel. A universal grip was used to ensure loading along a single plane. The maximum  $K_I$  value during fatigue was maintained below the  $K_I$  value for subsequent SCC tests. The DCB specimen were self-loaded by opposing bolts. A calibration curve of deflection of the beams VS load acting along the loading line for the DCB specimen was generated,

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and is illustrated in Fig. 9. Deflection of the beam was measured by a MTS model 632 COD gauge.

Fracture mechanics tests were conducted in a Teflon basin, heated from the outside by a resistance heated tape. A nitrogen purge line, FEP coated thermistor probe, luggin capillary, and a FEP coated thermometer were inserted into the Teflon basin. Temperature was controlled in the same manner as in the SSRT experiments. Low carbon steel wires were used as counter electrodes. The text specimen were connected in parallel to ensure that all the specimen were maintained at the same potential.

Polarization curves were generated by a EG & G Model 135 potentiostat using a scan rate of 1 mv/sec.

Fracture surfaces were examined with an ETEC Autoscan Scanning Electron Microscope (SEM), using a secondary electron imaging mode and 20 keV excitation.

# 2.4 Experimental Procedures

#### 2.4.1 Slow Strain Rate Test Experiments

The test cell was assembled as illustrated in Fig. 8, and mounted on the modified hounsfield tensometer. About 500 ml of test solution was poured into the cell. A small tensile load was applied as the specimen was brought up to a temperature of 92°C. When the test temperature was attained, a potential of -1.3  $V_{\rm SCE}$  was applied to the



Figure 9 - Calibration curve for DCB specimen

specimen for a period of 10 minutes, in order to reduce all the oxides present on the surface of the gauge section. A preselected potential was subsequently applied to the specimen, after which the sample was pulled apart at a strain rate of  $2.5 \times 10^{-6}$ . Temperature and potential were maintained constant throughout the test, and nitrogen was continually bubbled through the cell in order to provide a stirring action and minimize oxidation of S<sup>--</sup> ions. In order to reduce the surface area of the metal exposed, and consequently, the amount of current supplied by the potentiostat, and changes in the solution concentration due to dissolution of iron, the entire specimen, with the exception of the gauge section, was covered with Teflon tape.

At the conclusion of each test, the two halves of the test specimen were cleaned, first with distilled water, and then with ethanol, and dried. The reduction in cross-sectional area of the fracture region was measured with a travelling microscope. The oxide scale present on the failed halves were removed by suspending them in an inhibited acid solution composed of 4ml 35% 2 butyne-1,4 diol + 3 ml HCl + 50 ml H<sub>2</sub>O, in an ultrasonic cleaner for 2-3 minutes. The failed ends were subsequently examined under the SEM. Secondary cracking was observed at some potentials. The frequency of these cracks was measured by longitudinally sectioning the failed halves through the centre, polishing to a 0.06 µm finish, etching with 2 vol. % Nital, and observing the sample under an optical microscope. The regions where the welded samples failed, were also examined in a similar manner.

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# 2.4.2 Fracture Mechanics Experiments

DCB samples utilized for fracture mechanics experiments on the base metal, both in the as-received condition and after a 650°C anneal to simulate industrial stress relief. Most specimen were precracked at a maximum stress intensity of 20 MPa  $\sqrt{m}$ , but test specimen which were loaded to a low K<sub>I</sub> level were recracked at a maximum K<sub>I</sub> level of 15 MPa $\sqrt{m}$ , until the machined notch was extended by 3-4 mm.

Test specimen in the as-received conditon were loaded with opposing bolts. The deflection required to maintain a particular  $K_I$ level was extrapolated from the calibration curve, fig.9, and the specimen was bolt-loaded till the desired deflection was obtained. Nickel wires were spotwelded onto the sample prior to loading. The spotwelded joint was coated with an epoxy resin to minimize degradation of the joint within the corrosion cell. Several specimen were connected in parallel to one Potentiostat. The schematic diagram of the fracture mechanics corrosion cell is provided in Fig. 10.

DCB specimen in the heat treated condition (annealed for 1 hr at 650°C), and the specimen incorporating the fusion zone of a weld in the crack plane, were loaded in a hounsfield tensiometer.

Iron wires were used as counter electrodes, as both graphite and platinum electrodes were observed to erode during the course of the test, which lasted for 3 weeks. Potential and temperature control were effected in a manner explained previously.

At the conclusion of each test, the samples were broken open in liquid nitrogen. The corrosion deposits in the crack were removed with



Figure 10 - Fracture mechanics test cell

an inhibited acid solution, and crack extension was measured with a travelling microscope. All measurements were made with respect to a fiducial/reference line. Due to the small crack extensions, the crack growth increment was verified when the sample was viewed in the SEM. The path of the secondary cracks (i.e., cracks branching from the microcrack) was determined by sectioning the sample longitudinally, polishing to a 0.06 µm finish, etching with a 2 vol. % Nital solution, and finally viewing the polished face in a SEM.

### 2.4.3. Anodic Polarization Curves

All polarization curves were generated potentiodynamically. Small square sections were cut from the plates, and Ni wire was spotwelded to one of the ends. The sample was mounted in an epoxy mould. Before the commencement of each test, the specimen was ground to a 300 grit finish.

All polarization tests were conducted in a Teflon cell, provided with graphite counter electrodes, as illustrated in Fig. 11. Temperature control at 92°C was maintained in a manner explained in section 2-3, and N<sub>2</sub> was continually bubbled through the cells.

Just before the commencement of each test, the specimen was polarized to, and held at  $-1.2V_{SCE}$  for 15 mintues, after which an anodic polraization scan was initiated. No attempt was made to correct for any small potential differences due to thermal and concentration gradients in the salt bridge.



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#### CHAPTER III

#### RESULTS

#### 3.1 Anodic Polarization Tests

The anodic polarization curves generated for this work were similar to those presented by other authors.<sup>12,13,51</sup>. Figures 12 and 13 show the anodic behaviour for the as-received material in 2.5 m NaOH + 0.42 m Na<sub>2</sub>S; and 3.35 m NaOH and 3.35 m NaOH + 0.42 m Na<sub>2</sub>S respectively. All the curves show a distinct and well defined active peak, and a transition from an active to a passive behaviour. The important differences between the anodic behaviour of the metal in NaOH, and the NaOH + Na<sub>2</sub>S solutions were:

- (i) a shift in the onset of passive behaviour from -1  $V_{SCE}$  in the NaOH solution, to -900 mV<sub>SCE</sub> in the solution containing S<sup>--</sup> ions.
- (i1) a much higher current density attained by the sulphide solution (simulated white liquor), both at the active peak, and in the passive zone.
- (iii) an increase in current density in the presence of S<sup>--</sup> ions at potentials above -725  $mV_{SCE}$ , due to the oxidation of S<sup>--</sup> ions to higher oxidation states.<sup>12</sup>

The Free Corrosion Potential (FCP) was found to reside in the active zone at approximately  $-1.1 V_{SCE}$  in the deaerated simulated white liquor solution. However, the FCP was raised when the liquor was







Figure 13 - Anodic polarization curves of A516 Gr 70 steel in 3.35 m NaOH and 3.35 m NaOH + 0.42 m Na<sub>2</sub>S solutions at 92°C





aerated. Thus, the FCP in digesters utilizing improperly prepared and stored white liquor would be greater than -1.1 V<sub>SCE</sub>, and could conceivably reside in the active-passive transition zone.

Increases in the Fe<sup>++</sup> ion concentration from  $10^{-6}$  M to  $10^{-4}$  M did not affect the potential for the onset of the active-passive transition, as illustrated in Fig. 14.

#### 3.2 Slow Strain Rate Testing Technique

# 3.2.1 2.5 m NaOH + 0.42 m Na<sub>2</sub>S

Fig. 15 shows the result of the SSRT experiment superimposed on the anodic polarization curve of the steel in the same caustic sulphide environment. The results are plotted as % Reduction in area VS Potential, as illustrated in Fig. 15. The minimum reduction in area occurs in the region of transition from the active to the passive behaviour. The Active-Passive Transition (APT) has been reported to be the region most prone to SCC.<sup>13</sup> However, the % reduction in area of the failed samples in the APT zone differed from that in other regions of the anodic polarization curve by only 13%. This, combined with the fact that no secondary cracking was observed in the failed specimen, appeared to suggest that the steel was not very prone to SCC in the white liquor with a caustic concentration of 2.5 m NaOH.

SSRT tests conducted after removal of the outer 0.5 - 1 mm by electropolishing yielded similar results. This established that the



Figure 15 - Effect of potential upon reduction in area in 2.5 m NaOH + 0.42 m Na<sub>2</sub>S superimposed upon the anodic polarization curve obtained in the same solution.

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formation of secondary cracks were not impeded by residual stresses introduced by machining.

# 3.2.2 3.35 m NaOH

In order to determine if the OH<sup>-</sup> ion concentration had any influence on the SCC behaviour, a series of SSRT tests were conducted in the 3.35 m NaOH solution. the minimum reduction in area occurred in the active-passive transition zone, as illustrated in Fig. 16 and tabulated in Table 2. Once again, the % reduction in area of the failed samples at the potentials corresponding to the Active-Passive transition of the anodic polarization curve was not very marked. However, the presence of secondary cracks penetrating the surface of the specimen near the region where failure occurred, confirmed SCC as the cause of premature failure, as illustrated in Fig. 17. When the failed halves were viewed by the SEM, an annulus of material affected by the environment was observed. No secondary cracking was observed in samples tested at potentials corresponding to either the active, or the passive regions.

### 3.2.3 3.35 m NaOH + 0.42 m Na<sub>2</sub>S

### 3.2.3.1 Base Material

Since it was apparent that the stress corrosion susceptibility of the steel was affected by the  $OH^-$  ion concentration, a series of SSRT tests were conducted in 3.35 m NaOH + 0.42 m Na<sub>2</sub>S solutions. Minimum

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Potential (V <sub>SCE</sub> )	% Reduction in Area		
0	47.7		
-0.500	46.8		
-0.750	47.4		
-0,950	34.4		
-0.980	34.1		
-1.05	41.8		
-1.2	40.8		

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Table 2 - SSRT Test Results in 3.35 m NaOH



Figure 16 - Effect of potential upon reduction in area for 3.35 m NaOH superimposed upon the anodic polarization curve obtained in the same solution.



Figure 17 - Secondary cracking at -0.98 V<sub>SCE</sub> in a 3.35m NaOH environment at 92°C. reduction in area was obtained at potentials corresponding to the Active-Passive transition, as illustrated in Fig. 18. Also, extensive secondary cracking was observed at these potentials, as illustrated in Fig. 19. Some secondary cracking was observed at potentials corresponding to the passive zone, as illustrated in Fig. 20, and at less noble potentials where hydrogen is expected to be evolved. The apparent crack velocities, i.e., the ratio of the largest crack length, to the duration of the test was found to be  $1.85 \times 10^{-9}$  m/sec in the active passive transition zone, 8.1 x  $10^{-10}$  m/sec is in passive zone, and  $1.31 \times 10^{-9}$  m/sec at -1.8 V<sub>SEC</sub>, as illustrated in Tables 3 and 4. Thus the presence of S<sup>--</sup> ions enhanced SCC at potentials, other than the active-passive transition region.

### 3.2.3.2 Welded Samples

SSRT tests were conducted on tensile samples with a weld incorporated in the gauge section. Failure occurred in the parent material at potentials residing in the Active and Passive zones. However, in samples which were tested at potentials corresponding to the Active-Passive transition zone, failure was observed to occur in the fusion zone of the weld. Extensive secondary cracking was observed at these potentials, with most of the cracks occurring in the fusion zone. The apparent crack velocity of the secondary cracks in the base metal was found to be 1.88 x  $10^{-9}$  m/sec which is comparable to that obtained in the SSRT tests conducted on samples fabricated from the as-received material, under the same conditions (Table 3). The apparent crack

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Potontial	% Reduction in Area		
V <sub>SCE</sub>	2.5 M NaOH + Na <sub>2</sub> S	3.35 M NaOH + Na <sub>2</sub> S	
0	47.7	47.5	
-0.5	47.9	-	
-0.6	-	47.0	
-0.7	-	47.5	
-0.75	47.4	46.5	
-0.88	35.5	35.5	
-0.85	34.1	35.7	
-0.906	43.9	-	
-1.0	· _	45.5	
-1.05	41.8	-	
-1.20	-	44.2	
-2.10	-	18.2	

Table 3 - SSRT Test results in simulated White Liquor

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Potential <sup>V</sup> SCE	Frequency of Secondary Cracks*	Apparent Crack Velocity m/sec
-0.50	8	9.2 x $10^{-10}$
-0.65	6	$8.5 \times 10^{-10}$
-0.70	7	8.1 $\times 10^{-10}$
-0.75	6	8.3 $\times 10^{-10}$
-0.85	18	$1.85 \times 10^{-9}$
-0.88	19	$1.9 \times 10^{-9}$
-1.05	3	$3.9 \times 10^{-10}$
-2.1	14	$1.3 \times 10^{-9}$

.

Table 4 - Secondary Cracking in the base material in the  $3.35 \text{ m NaOH} + 0.42 \text{ m Na}_2\text{S}$  environment.

\*Total number of secondary cracks on sectioned sample.







0.8 mm

Figure 19 - Secondary cracking at -0.88  $V_{\rm SCE}$  in a 3.35m NaOH + 0.42 m Na2S environment



Figure 20 - Secondary cracking at -0.750  $V_{\rm SCE}$  in a 3.35m NaOH + 0.42 m Na2S environment



Figure 21 - Oxide scale on a SSRT specimen at -0.88  $V_{SCE}$  in a 3.35 m NaOH + 0.42 m Na<sub>2</sub>S environment.

Potential	BASE MATERIAL		HAZ		FUSION ZONE	
VSCE	Freq. of Cracks	V m/sec	Freq. of Cracks	V m/sec	Freq. of Cracks	V m/sec
-0.650	4	6.5 x $10^{-10}$				-
-0.750	6	6.2 $\times 10^{-10}$	-	-	-	. –
-0.850*	4	$1.88 \times 10^{-9}$	12	$7.4 \times 10^{-10}$	36	$1.38 \times 10^{-9}$
0.880*	5	$1.85 \times 10^{-9}$	8	$7.1 \times 10^{-10}$	32	$1.24 \times 10^{-9}$
-1.3	1	$6.94 \times 10^{-10}$	-	$7.1 \times 10^{-10}$	32	$1.24 \times 10^{-9}$

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Table 5 - Secondary Cracking in the welded specimen in the  $3.35 \text{ m NaOH} + 0.42 \text{ m Na}_2\text{S}$  environment.

\*Failure in the fusion zone.

velocity in the HAZ and fusion zone was 7.4 x  $10^{-10}$  m/sec and 1.38 x  $10^{-9}$  m/sec respectively. However, the apparent velocities of most of the cracks in the fusion zone was 6.4 x  $10^{-10}$  m/sec., i,e., numerous long cracks were obtained.

The apparent crack velocity, and the frequency of cracking results for both types of specimen, i.e. those made of the as-received material, and those incorporating the weld, are tabulated in Tables 4 and 5 respectively.

# 3.3 Fracture Mechanics Results

# 3.3.1 General Comments

Fracture mechanics tests were conducted in a 3.35 m NaOH + 0.42 mNa<sub>2</sub>S environment, since it was found to interact more severely with the base material.

When the DCB specimen were split open in liquid nitrogen after exposure to simulated white liquor for a period of three weeks, it was possible to visually distinguish the boundaries betwen the fatigue precrack, stress corrosion crack, and the brittle overload regions. Both, the fatigue precrack, and the stress corrosion cracks were observed to trail at the edges of the specimen. This was possibly due to the presence of residual compressive stresses at the surface layer, after the rolling operations, due to changes in stress state, or subtle differences in the crack liquid composition at the free surface.

The average crack velocity was the mean increment of the stress corrosion crack growth, measured at a minimum of 15 locations. Since very small crack increments were obtained during each test, there was little change in the  $K_{I}$  value during testing. Hence, for practical considerations, the fracture mechanics tests could be considered to be under constant  $K_{T}$  conditions.

# 3.3.2 Effect of Stress Intensity

The log of the crack velocity is plotted against the stress intensity in Fig. 22. the log v V/S K<sub>I</sub> plot exhibits three distinct regions. The stress independent crack velocity, i.e., the stage II crack propagation rate was found to be approximately 4 x  $10^{-10}$  m/sec at -0.88 V<sub>SCE</sub> (corresponding to the active-passive transition region of the anodic polarization curve). The threshold stress intensity for SCC was approximately 20 MPa/m. An increase in the stress intensity above 30 MPa/m indicates the onset of region II crack propagation, as illustrated in Fig. 22.

# 3.3.3 Effect of Potential

DCB specimens were tested at -0.88  $V_{SCE}$  and -0.75  $V_{SCE}$ , i.e., potentials corresponding to the active-passive transition zone, and the passive zone of the anodic polarization curve respectively. The threshold stress intensities for SCC, at both the above mentioned potentials were found to be approximately 20 MPa/m. The stage II crack propagation rate was found to be approximately 4 x 10<sup>-10</sup> m/sec at -0.88



Figure 22 - Effect of stress intensity on crack growth in a 3.35 m NaOH + 0.42 m Na<sub>2</sub>S environment at  $-0.88 V_{SCE}$ 



Figure 23 - Effect of potential on crack growth in a 3.35m NaOH + 0.42 m Na<sub>2</sub>S environment.
$V_{SCE}$  and 1.5 x  $10^{-10}$  m/sec at -0.75  $V_{SCE}$ , as illustrated in Fig. 23. Thus, the ratio of the stage II velocities at -0.88  $V_{SCE}$  and -0.75  $V_{SCE}$  was found to be 2.6, which compared favourably with the ratio of the apparent crack velocities at the aforementioned potentials, obtained from the SSRT tests, which was found to be 2.35. Also, the threshold stress intensity for crack propagation was not significantly affected by a change in potential.

These results suggest that digester cracking rates could be reduced by at least a factor of 2, by imposing an anodic protection potential of -0.75  $V_{SCE}$ , where the current requirement is not excessive.

#### 3.3.4 Effect of Microstructure

Failure was observed to occur preferentially in the fusion zone of the weld, in SSRT tests conducted at potentials corresponding to the APT zone. Hence DCB crack velocity measurements were made with the crack plane situated in the fusion zone of the weld, at a potentials corresponding to the active-passive transition zone, to help explain this phenomenon. The stage II crack velocity in the fusion zone was found to be approximately  $1 \times 10^{-10}$  m/sec. Thus the preferential failure in the fusion zone during SSRT cannot be attributed to higher crack rates.

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## 3.3.5 Effect of Stress-Relief Anneal

In order to relieve stresses generated during fabrication, the regions around the welded joints are subjected to a stress relief anneal at temperatures as high as 650 °C for 1 hour. The heat treatment does not cause any significant spheroidization of carbides, or grain growth. The stage II crack velocity of the heat treated material, at -0.88  $V_{\rm SCE}$ , did not differ significantly from the stage II velocity of the base material, as illustrated in Fig. 24.

## 3.4 Fractography

#### 3.4.1 General Comments

All fractography of the stress corrosion cracks were taken as close to the leading edge as possible, in order to minimize the effect of general corrosion on topography.

The test specimen were covered with a black layer of corrosion product when they were removed from the test solution, at the conclusion of each experiment. The corrosion product was thicker on the machined notch, and fatigue precrack, as compared to the stress corrosion crack. The surface films were removed with an inhibited acid solution, which produced no pitting, nor introduced any artefacts onto the fracture surface.

The fatigue zone and the zone of overload failure were easily



Figure 24 - Effect of microstructure and heat-treatment on crack propagation in a 3.35m NaOH + 0.42m Na<sub>2</sub>S environment.

discernable from the SCC crack. The fatigue surface was featureless, and had retained its original banded structure. Evidence of etching of the surface by the environment was visible, as illustrated in Figure 25. In contrast, the zone of overload failure showed a brittle, transgranular mode of failure, as illustrated in Fig. 26.

All photographs have been mounted, such that cracks propogate from left to right.

# 3.4.2 Effect of Stress Intensity and Potential

The crack surfaces of all the specimen tested at -750 mV<sub>SCE</sub> exhibited, the roughened surface characteristics of the general dissolution phenomenon, obliterating most of the fine fractographic features. Hence, the crack path could not be readily identified, as illustrated in Fig. 27 (a-d). Examination of stereographic photographs (Fig. 28a-b) did not reveal any intergranularly faceted regions. Hence it was concluded that the crack path was transgranular. Deep secondary cracks were observed. Longitudinal sectioning of the sample revealed that these secondary cracks followed a transgranular path, as illustrated in Fig. 29. The amount of dissolution occurring at the secondary cracks appeared to increase with increasing stress intensity. This suggests that dissolution is a dominant mechanism for crack propagation.

The crack front of the specimen tested at -880°C also exhibited dissolution effects, as illustrated in Fig. 30a-c. However the crack path was found to be intergranular by metallographic examination of the

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Figure 25 - Fatigue surface, on the DCB specimen, showing evidence of etching



Figure 26 - Brittle overload failure zone, showing a transgranular mode of failure



Figure 27a -  $K_I = 25 \text{ MPa/m}$ 



Figure 27b -  $K_I = 35 \text{ MPa/m}$ 



Figure 27c -  $K_I = 40 \text{ MPa/m}$ 



Figure 27c -  $K_I = 50 \text{ MPa/m}$ 

Figure 27 - Variation of fractography with stress intensity in a 3.35 m NaOH + 0.42 m Na\_2S environment at -0.750  $\rm V_{SCE}$ 



(a)



(b)

Figure 28 - Stereographic photographs of crack front at 40 MPa/m, -0.75  $V_{\rm SCE}$ 



Figure 29 - Transgranular secondary cracks at 40 MPa/m,  $-0.75~\rm V_{SCE}$ 



Figure 30a -  $K_I = 25 \text{ MPa/m}$ 



Figure 30b -  $K_I = 35 \text{ MPa/m}$ 



Figure 30c -  $K_{I}$  = 50 MPa/m

Figure 30 - Variation of fractography with stress intensity in a 3.35 m NaOH + 0.42 m Na\_2S environment at -0.88  $\rm V_{SCE}$ 



Figure 31 - Intergranular crack path at 40 MPa/m, -0.88  $V_{\rm SCE}$ 



(a)



Figure 32 - Stereographic photographs of crack front at 40 MPa/m, -0.88  $V_{\rm SCE}$ 



Figure 33 - Intergranular secondary cracks at 40 MPa/a,  $-0.88~V_{\rm SCE}$ 

primary and secondary crack perpendicular to the crack plane, before the sample was fractured in a liquid Nitrogen environment, as illustrated in Fig. 31. Examination of stereo photographs of the stress corrosion crack front revealed a mildly faceted topography, as illustrated in Fig. 32a-b. secondary cracks, which were intergranular in nature were visible, as illustrated in Fig. 33.

#### 3.4.2 Effect of Stress Relief Anneal

Samples which had been annealed were exposed to the test solution for only 2 weeks at a potential of -880 mV<sub>SCE</sub>. Since, all fine features had not been obliterated to a very great extent, by general dissolution, it was possible to discern that the crack had propagated in an intergranular manner, as illustrated in Fig. 34. However, the possibility that the heat treatment could have promoted a more pronounced intergranular failure cannot be ruled out.

#### 3.4.3 Effect of Microstructure

The stress corrosion crack appeared to propagate along the interdendritic spaces, in the specimen where the crack was incorporated in the fusion zone of the weld, as illustrated in Fig. 36-37. Interdendritic spaces are regions of solute segregation. Hence, this result was not unexpected.

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Figure 34 - SCC crack front in the heat treated specimen at 40 MPa/m, -0.88  $\rm V_{SCE}$ 



Figure 35 - Intergranular secondary cracks in heat treated specimen at 40 MPa/m, -0.88  $\rm V_{SCE}$ 



Figure 36 - Fractograph of DCB specimen incorporating a weld, indicating the crack front and the overload region.

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Figure 37 - SCC crack front in the DCB specimen incorporating a weld

# CHAPTER IV

#### 4.1 Slow Strain Rate Testing

The SSRT has proved to be a remarkably versatile technique in assessing the SCC susceptibility of the steel, under any set of environmental conditions. It was a relatively rapid test, which yielded a great deal of information. This technique, however, exhibited some drawbacks.

An annulus of metal at the surface was affected during the SSRT tests, where cracks formed and grew radially inwards. This annulus effectively reduces the load carrying capability of the specimen. In metal-environment conditions where the rate of crack growth was low, the annulus was of a small depth, and consequently, the load carrying capability of the sample was affected to a very small degree. When the percentage reduction in area is the only parameter used to gauge SCC susceptibility, misleading, or at best, inconclusive results were obtained. In such situations, results were better interpreted by combining data on the frequency of secondary cracking with that of the percentage reduction in area. Specimen which were thought to be immune to SCC based on area reduction (as in the passive region in simulated white liquor environmnts) were found to exhibit a small definite, degree of susceptibility to SCC when results were interpreted in terms of these other parameters.

Since the secondary cracks in failed SSRT specimens were

distributed uniformly, the frequency of secondary cracking on the specimen surface, was related to the frequency of cracks along the intersection of any longitudinal section with the surface (drawing an analogy with the principles of quantitative optical microscopy).

$$i.e. N_0 = K N_p (1)$$

N<sub>0</sub> = frequency of secondary cracks/unit area of the surface of the specimen.

Merely measuring the % reduction in area, as a gauge of SCC susceptibility, tended to overestimate the immunity of the base material from susceptibility to SCC at anodic protection potentials. The presence of a few secondary cracks at potentials corresponding to the passive zone, indicated a small degree of susceptibility to SCC at these potentials. Use of a combination of secondary cracking data, and data on the % reduction in area, to interpret SSRT test results has not been reported in the literature.

The ratio of the apparent crack velocities obtained from the SSRT specimen, tested under different environments, was approximately equal to the ratio of the stage II crack velocities. Hence, for the steel examined in this study the SSRT tests were a rapid test method for the comparison of the the relative region II crack velocities under different conditions. Such a situation could apply to other metal/environment systems.

## 4.2 Cracking in Digesters

Cracking has been observed in the fusion zone of welds in Kraft

digesters. Since the tensile strength of the fusion zone is usually greater than that of the base material, failure in this region is clearly due to environmental interaction. Failure occured in the fusion zone, during SSRT tests, only at potentials corresponding to the active-passive transition zone. The free corrosion potential (FCP) was found to reside in the active zone. However, aeration of industrial white liquor due to improper preparation, and/or storage,<sup>53</sup> would lead to oxidation of the S<sup>--</sup> ions, according to equation 2.

$$2x S^{2-} + (x - 1) O_2 + 2(x - 1) H_2 O + 2 S_x^{2-} + 4(x - 1) OH^-$$
(2)

In practice, an equilibrium which controls the  $S_x^{2-}$  concentration is established between the  $S_x^{2-}$ ,  $S^{2-}$  and  $S_2O_3^{2-}$  ions in solution, according to equation 3.

$$4 S_{x}^{2-} + 6(x - 1) 0H^{-} \rightarrow 2(x - 1) S^{2-} + (x - 1) S_{2}O_{3}^{2-} + 3(x - 1) H_{2}O$$
(3)

The effect of adding  $S_x^{2-}$  to white liquor has been shown to raise the corrosion potential.<sup>54</sup>

Therefore, during commercial pulping, the FCP could be raised to the active-passive transition zone where cracking problems in the weld fusion zone could be encountered.

#### 4.3 Analysis of Partial Surface Cracks

#### 4.3.1 General Comments

Failure of digesters could result from the growth of stress corrosion cracks, radiating radially outwards, from the inside of the digester wall. The stress intensity,  $K_{\rm I}$ , for a partial surface crack of elliptical shape subjected to a tensile stress is given by  $^{52}$ 

$$K_{T} = Y \sigma/a/Q$$
(4)

$$\mathbf{Y} = \sqrt{\pi} \tag{5}$$

Q = 
$$f(a/2c) = [\phi^2 - 0.212 (\sigma/\sigma ys)^2]$$
 (6a)

$$\phi = \int_{0}^{\pi/2} \sqrt{\left[1 - \frac{c^2 - a^2}{c^2}\right]} \sin^2 \theta \, d\theta$$
 (6b)

where 'a' is the crack depth, and '2c' is the crack length at the surface.

# 4.3.2 Leak Before Catastrophic Failure

Consider the scenario where a single partial surface crack nucleates at a region of local breakdown of passivity, and propagates as an approximately semi-circular flaw, as illustrated in Fig. 38a. Under these conditions,  $K_{\rm I}$  is given by

$$K_{I} = \frac{2}{\pi} \sigma \sqrt{\pi a}$$
 (7)<sup>55</sup>

The driving force for the propagation of this flaw would be provided by a tensile, hoop stress,



Figure 38 - Proposed mode of propagation of flaws in the digester wall

$$\sigma_{\rm HOOP} = \frac{PD}{2t} \tag{8}^{55}$$

(For vessels with a large diameter to thickness ratio)

P = internal pressure

D = internal diameter of vessel

t = wall thickness of vessel

The Hoop stress was found to be 245 MPa and 123 MPa for the 2.54 cm and 5.08 cm thick vessels respectively, utilizing a typical internal pressure of 1130 KPa (165 psi), and wall thickness of 2.54 cm (1") and 5.08 cm (2").

The K<sub>I</sub> value of the flaw, at penetration of the semi-circular crack through the vessel with a 2.54 cm wall thickness was found to be 44.05 MPa /m. For a 5.08 cm thick vessel, the K<sub>I</sub> value of the flaw was found to be 31.28 MPa/m, at the point of penetration through the wall. The above values of stress intensity correspond to the stage II of the log v - K<sub>I</sub> plot. Such flaws could cause the digesters to leak, but would not cause catastrophic failure of the type experienced at Pine Hill, Alabama.

# 4.3.3 Catastrophic Failure Before Leak

Consider the situation where 'n' equally spaced partial surface cracks nucleate, and propagate as semi-circular cracks, coalesce to give an approximately elliptical crack, as illustrated in Fig. 38b. Applying the condition  $K_I = K_Q$ , equation (4) may be employed to determine the total crack length (2c) of coalesced crack, at which catastrophic failure would occur for specific crack penetration values, 'a', that are

Penetration 'a' cm.	a/2 C		2C (cm.)			n	Frequency	K <sub>I</sub> of
	No Residual Stress	With Residual Stress*	No Residual Stress*	With Residual Stress	No Residual Stress*	With Residual Stress	of Flaws** m	Single Flaw MPa√m
1.71	-	0.005	<u>-</u>	343.0		199	59	36.1
1.78	-	0.03	-	60.0	-	32	56	36.8
1.9	-	0.1	-	19.0	-	9	53	38.1
2.03	-	0.125	_	16.25	-	7	49	39.4
2.16	-	0.16	-	13.5	-	5	46	40.6
2.29	0.01	0.18	228.6	12.7	99	5	44	41.8
2.35	0.02	0.2	117.5	11.74	49	4	42	42.3
2.41	0.04	0.21	60.3	11.5	24	4	41	42.9

# Table 6 - Critical Coalsced Crack Data

\*Residual Stress = 35 MPa.

**\*\*Frequency of Flaws = 1/a.** 

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less than the wall thickness of 2.54 cm. The Hoop stress is considered to be the only driving force for crack propagation. The results of the above caculation are listed in Table 5. Since a valid  $K_{IC}$  value could not be determined from the 1" (2.54 cm) plate, a typical  $K_Q$  value of 70 MPa/m for the material has been assumed.

Also, from the model, 'n', the minimum number of flaws which would have to coalesce to produce a flow of critical dimensions, could be determined from the condition:

$$(n + 1) = 2c/a$$
 (9)

SSRT test results indicate that the phenomenon of initiation of cracks is potential dependant, and is most pronounced in the fusion zone of the weld, at potentials corresponding to the APT. The frequency of cracks in the failed SSRT specimen incorporating a weld, tested at the APT was found to be 72/cm. Although the SSRT test results cannot be directly applied to a practical situation, it illustrates the fact that an extremely high frequency of nucleation points per unit length could be obtained in the fusion zone. This could cause catastrophic failure after a penetration considerably smaller than the wall thickness.

#### 4.4 Effect of Residual Stresses

Residual stresses are introduced in the vessel due to the welding operations. These stresses provide an increased driving force for crack propagation in longitudinal welds. Utilizing the analysis which has ben enunciated in Section 4.3, and applying a residual stress of 35 MPa, a coalesced flaw was found to attain critical dimension, after a

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penetration of 1.71 cm, i.e., the minimum depth of penetration for catastrophic fracture was less than that calculated in the absence of a residual stress. Thus, if crack nucleation is sufficiently frequent for coalescence to occur, the presence of residual stresses could significantly reduce the lifetime of a structure.

However, it must be recognized, that in addition to the hoop stress, the flaw is also acted upon by a tensile, longitudinal stress (normal to the hoop stress) which could affect the crack propagation. The effect of the longitudinal stress has been neglected in the calculations conducted above. Thus, the results displayed in Table 6 are all very conservative in nature, and could be used only as a guidelines.

Consistent with the coalescence hypothesis, numerous cracks have been observed in digesters. For e.g. a discontinuous network, 1/8" deep has been observed to run approximately 360° around the circumference of the digester. Also, several small cracks have been observed transverse to the weld, 1/8" long and 1/16" deep, with 2" long cracks in the vicinity, suggesting a coalescence of smaller cracks.<sup>56</sup>

#### 4.5 Anodic Protection of Digesters

The lifetime of digesters can be increased by either:

(i) decreasing the rate of penetration of the flaw; or

(ii) reducing the frequency of nucleation of cracks.

A slower rate of penetration could enable the operator to detect the presence of a flaw, before it attains critical dimensions, during the periodic inspections which a digester is subjected to. A reduction

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of the frequency of nucleation of flaws would serve the same purpose. It would necessitate an increased depth of penetration before the crack can attain a critical length. This increases the chances of detection of the flaw before it attains critical dimensions.

Polarization of the A516 Gr.70 steel to potentials in the passive zone brings about a two fold reduction in the crack propogation rate, and a marked reduction in the frequency of nucleation of cracks (lower frequency of cracking in SSRT tests). As a consequence, a flaw could be more easily detected before it could attain critical dimensions. Although anodic protection might not completely eliminate the problem of cracking in digesters, it could control the problem, and greatly reduce the attendent risks of catastrophic failure.

#### CHAPTER V

#### CONCLUSIONS

The results of the present work on MIG welded A516 Gr. 70 steel in a 3.35 m NaOH, 2.5 m NaOH + 0.42 m Na<sub>2</sub>S, and 3.35 m NaOH + 0.42 m Na<sub>2</sub>S solutions support the following conclusions:

(i) The base material is mildly susceptible to SCC at higher caustic concentrations. The potentials of maximum susceptibility resided in the active-passive transition zone of the anodic polarization curve.

(ii) The fusion zone of the weld in the steel plate exhibited a preferential susceptibility to SCC at potentials corresponding to the active-passive transition zone. At all other potentials, the weld (both the fusion zone and the HAZ) exhibited no preferential susceptibility to SCC.

(iii) Anodic polarization was found to decrease the frequency of cracking in simulated white liquor solutions.

(iv) The steel exhibited both stress intensity dependent, and potential dependent cracking. The region II crack velocity at -0.75  $V_{SCE}$  (corresponding to the passive zone) was lower than the region II cracking velocity at -0.88  $V_{SCE}$  (corresponding to the active passive transition) by a factor of 2.

(v) The region II crack velocity in the fusion zone (dendritic microstructure) was found to be significantly lower than that in the as-received, hot rolled material. Annealing the base material for 1 hr. at 650°C (simulating a thermal stress relief anneal) however did not

result in any change in the stage II velocity, as compared to the as-received material.

(vi) A hypothesis that crack growth occurs by coalescence of stress corrosion cracks has been advanced.

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