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IN KRAFT DIGESTER LIQUORS**

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STRESS CORROSION CRACKING OF CARBON STEEL
IN KRAFT DIGESTER LIQUORS

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ABSTRACT

The susceptibility of carbon steel (A516 Gr.70) to stress corrosion cracking at typical digester operating temperature was studied using liquors sampled from four kraft continuous digesters. Slow strain rate tests were conducted at controlled potentials to delineate the zone for stress corrosion cracking. Additional tests were performed in synthetic liquors with the same major inorganic species as the mill liquors to determine whether the behavior could be attributed to these species alone. Liquors with high NaOH, Na₂S and Na₂S₂O₃ concentration increased the susceptibility and narrowed the cracking range. Organics or trace inorganics appeared to be beneficial in reducing the severity of stress corrosion.

KEYWORDS: kraft digester, stress corrosion cracking, slow strain rate tests.

INTRODUCTION

Stress corrosion of carbon steel kraft continuous digesters has been thoroughly investigated in the past several years (1-9). An early history of the cracking problem including summaries of engineering details was published by Bennett (2). Cracking has plagued a large proportion of digesters, but there has been no correlation with the pulping chemistry, wood species pulped, process or cleaning practice, among other factors. A survey (10) of cracking at a number of mills identified only a few conditions which significantly increased the risk of cracking, including

larger digester sizes, lack of stress relief and pulping of southern pine or mixed hardwood/ softwood. Yeske (3) surveyed three mills with cracking problems and three without, but there were no clear differences to account for the different susceptibilities to cracking.

As Singbeil and Tromans (1,11) demonstrated, stress corrosion cracking in alkaline sulfide solutions is most probable within a range of electrochemical potential at the transition from the active to the passive state. They noted that the critical potential would change with solution composition because the active/ passive transition potential is affected by the solution composition. Whether or not a particular digester has a corrosion potential in the cracking range would depend on the liquor composition, and especially on the concentrations of oxidants such as polysulfide. Organic species may also put the corrosion potential in the cracking range (9) or inhibit cracking (12). Based on polarization data, Singbeil and Garner (4) thought that stress corrosion would be most strongly influenced by concentrations of NaOH and Na_2S_x but independent of Na_2CO_3 , NaCl and $\text{Na}_2\text{S}_2\text{O}_3$. Cracking was strongly related to the NaOH concentration of the liquor, becoming less severe as the NaOH concentration was decreased. A minimum of 8 to 20 g/L NaOH in the presence of 13 to 20 g/L Na_2S was required to cause stress corrosion. They found that, although cracking was less severe in the cooking zone liquor than in more concentrated solutions, the cracking occurred over a wider range of potential (6). The most severe cracking occurred in impregnation zone liquor obtained from a mill which pulped predominantly pine.

Yeske and Guzi (13) conducted in-situ studies of stress corrosion cracking of a continuous digester. The cracking range was determined using slow strain rate tests, and although the corrosion potential was generally outside of this range, excursions into the cracking range occurred during digester upsets.

The extent of stress corrosion cracking in kraft continuous digesters is observed to vary from vessel to vessel and various reasons for these differences have been found, but much of the research has been done

using synthetic kraft liquors. The objective of this work has been to compare behavior in actual liquors from different mills to determine the influence of liquor chemistry on the differences in behavior and to establish the range of cracking susceptibility in real liquors. Slow strain rate tests of digester steel have been performed in real mill liquors to determine susceptibility to stress corrosion cracking for comparison purposes. Additional tests were performed in synthetic liquors with the same major inorganic species as in the mill liquors to determine whether the behavior could be attributed to these inorganic species alone.

STRESS CORROSION CRACKING AND SLOW STRAIN RATE TESTS

The slow strain rate method is a widely accepted technique for determining susceptibility to stress corrosion cracking (14). A cylindrical tensile specimen is pulled at a very slow rate in the environment of interest, until fracture occurs. If a specimen does not experience stress corrosion cracking (SCC), it will elongate, neck down and finally fail in a ductile mode. The percent reduction in its diameter will be large. On the other hand, if cracking occurs during the test, the specimen will fail early in the test at a primary crack in its surface. The fracture will be brittle and many secondary cracks will be present. The specimen will not have necked down, so its diameter will be closer to the original and the percent reduction in diameter will be low. Thus the percent reduction in diameter will provide a measure of susceptibility to SCC. The number of cracks in the failed specimens provides another measure of SCC susceptibility.

EXPERIMENTAL

The carbon steel used for this study was A516 Grade 70. The slow strain rate specimens had a gauge section 25.4 mm in length and 3.2 mm diameter. Tests were performed in a pressurized autoclave at 130 C. The autoclave was mounted on a slow strain rate tester which was used to pull the specimen vertically through a seal in the top of the autoclave (15). The strain rate was $2.5 \times 10^{-6} \text{ sec}^{-1}$. Potential of the test specimen was

measured and controlled via a potentiostat. A silver/ silver sulfide reference electrode was located in the test cell. Load and potential were recorded throughout the test using a strip chart recorder. The percent reduction in cross-section at final fracture was measured using a traveling microscope. Specimens were also cross-sectioned, polished and examined metallographically. The relative number of cracks was estimated by counting the number intersecting the surface of a cross-section of one half of the failed slow strain rate specimen. Cracks longer than 12 μ m were counted. Polarization tests were conducted on unstrained specimens at a scan rate of 1 mV/sec by means of a Princeton Applied Research Model 350 Corrosion Measurement System.

Liquor samples were obtained from four mills located in the southeastern United States. Mills M and P produce kraft linerboard, mill H is a kraft mill and mill E produces uncoated printing and writing paper. Digester liquor was obtained from the top separator/ top circulation lines of Kamyr continuous digesters at the mills by drawing off liquor through a cooled coil and collecting it in a plastic container. Care was taken to prevent oxidation of the liquor in sampling, shipment and storage. Liquor analyses are summarized in Table 1. Slow strain rate tests have been completed in the liquor from these mills plus synthetic liquors with the same concentrations of inorganic constituents as the mill E and mill P liquors. The objective of testing with the synthetic liquors was to determine whether the major inorganic species control stress corrosion susceptibility, or whether organic species and trace inorganics have a significant effect.

RESULTS

Polarization curves of steel in the mill liquors and the synthetic liquors are plotted in Fig. 1 - 6. The polarization curves differed in shape in the various mill liquors. In mill M and H liquors, relatively small current peaks were observed, as would be expected for liquors with low concentrations of sulfide and hydroxide. Polarization curves in liquor

from mills P and E had large active/ passive current peaks typical of more concentrated liquors. The peak was smaller in the synthetic mill E liquor, indicating some difference between the real and synthetic liquors. On the other hand, the polarization curve in the synthetic mill P liquor was similar to that in the real liquor.

Table 1. Digester Liquor Composition

	Mill M	Mill P	Mill E	Mill H
NaOH, g/L	14.1	39.5	50.7	25.4
Na ₂ S, g/L	11.1	18.9	21.6	14.5
Na ₂ CO ₃ , g/L	30.7	16.6	26.6	17.3
Na ₂ S ₂ O ₃ , g/L	2.5	2.5	6.8	2.8
Na ₂ SO ₃ , g/L	1.3	2.6	4.8	1.5
Na ₂ SO ₄ , g/L	3.4	2.2	7.7	3.3
NaCl, g/L	1.2	1.5	0.5	0.4
Na ₂ S _x , g/L	0.7	0.2	-	0.6

Data from slow strain rate tests in mill liquors and the synthetic liquors are also plotted in Fig. 1 - 6. Cracking susceptibility was measured by the percent reduction in diameter of the test specimen and by the number of cracks in a cross-section. The number of cracks in failed specimens, and the percent reduction in diameter were used to indicate the zone of SCC. The ranges of potential for brittle failure and for cracking were sometimes different at an individual mill and also varied from mill to mill. In mill M liquor, Fig. 1, extensive cracking occurred in the range from +10 to -120 mV and the cracking range corresponded to the SCC range as measured by percent reduction in diameter. On the other hand, in mill P liquor, fewer cracks were observed at potentials where the percent reduction in diameter indicated SCC susceptibility, Fig. 2, although percent reductions in diameter were similar to mill M. In mill P liquor, cracking was most severe at -40 mV with cracking at all potentials below 20 mV. There were two minima in the percent reduction in diameter values in mill M liquor; perhaps the two cracking zones are based on different dissolution reactions at those potential ranges. The number of cracks was low in mill E liquor, Fig. 3 and the cracking range

spanned +20 to -40 mV, with severe cracking at -40 mV as measured by percent reduction in diameter. As shown in Fig. 4, the cracking range measured in mill H liquor was very distinct, spanning -20 to -55 mV, with the cracking ranges defined by the percent reduction in diameter and the number of cracks in good agreement.

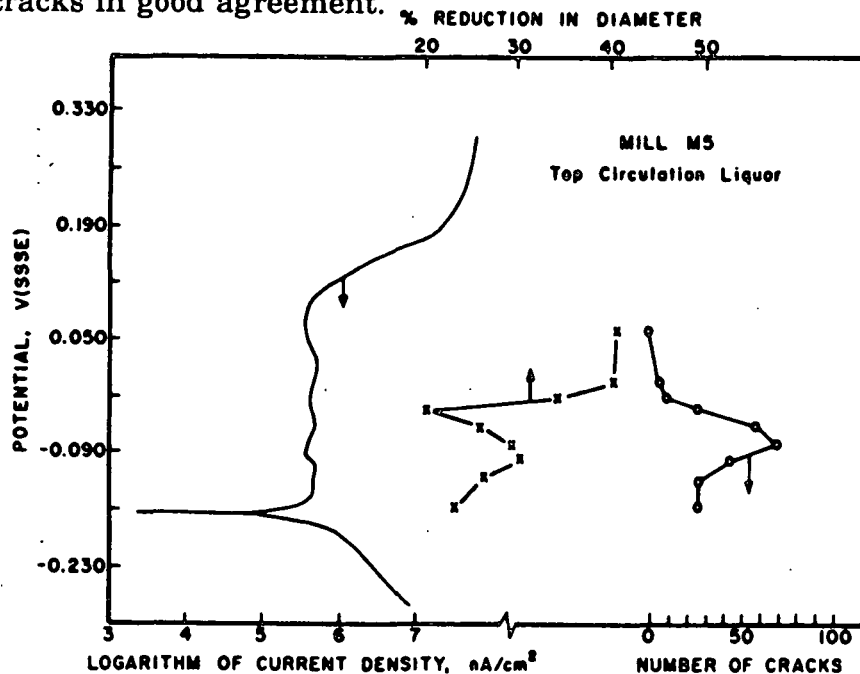


Figure 1. Polarization curve and percent reduction in diameter of stress cracks in test samples as a function of potential for mild steel in mill M liquor, illustrating the susceptibility to stress corrosion in the active/passive range.

The differences between mills may be related to different concentrations of inorganic species, mainly NaOH and Na₂S. The Na₂S, NaOH and Na₂S₂O₃ concentrations were highest at mill E, where cracking was most severe. The mill E liquor had a high thiosulfate concentration which may have contributed to severe SCC. The cracking zone correlated with the active/passive peak of the polarization curve. The Na₂S concentration was high at mill P, but the NaOH and Na₂S₂O₃ were lower relative to mill E. In the weaker liquors at mills M and H, the cracking zone was wider. The ranges of cracking for mill H were similar to those for mill M which had similar liquor composition. In mill liquors M and H, the active/passive peak was not pronounced. The variation in

cracking zone appears to be related to the liquor composition and the polarization curve also reflects the differences in liquor composition.

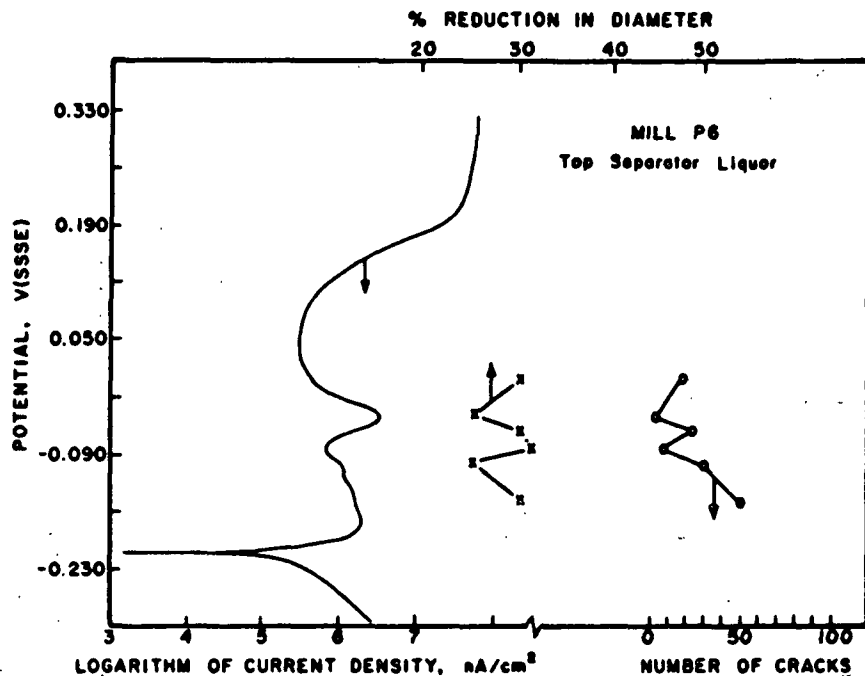


Figure 2. Polarization curve, percent reduction in diameter and number of cracks in test samples as a function of potential for mild steel in mill P liquor.

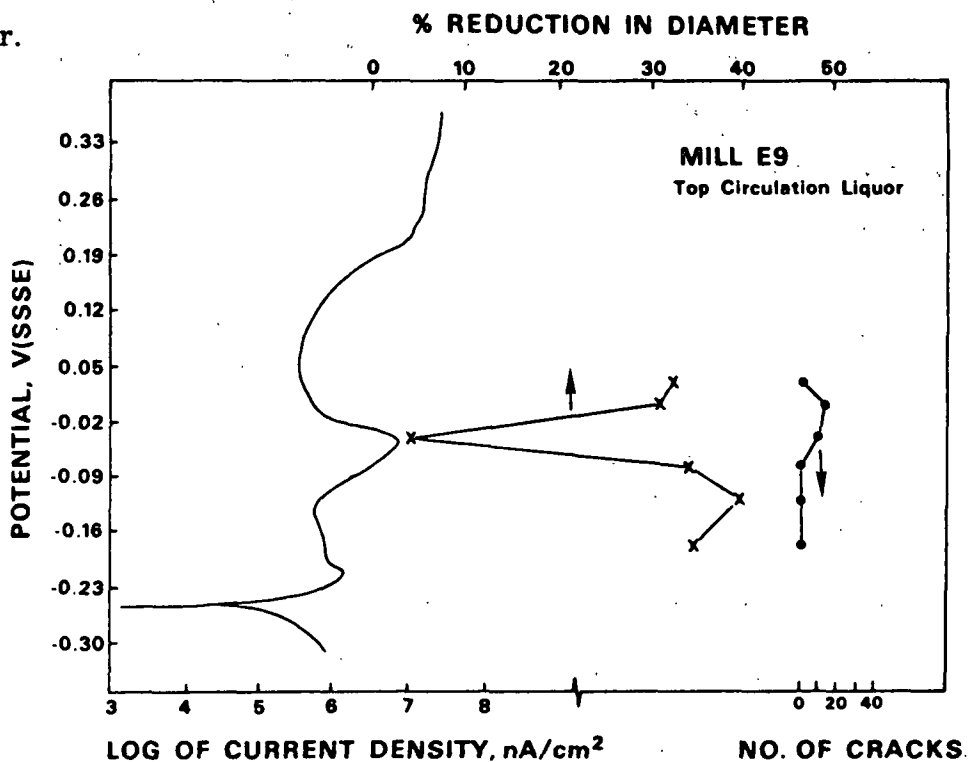


Figure 3. Polarization curve, percent reduction in diameter and number of cracks in test samples as a function of potential for mild steel in mill E liquor.

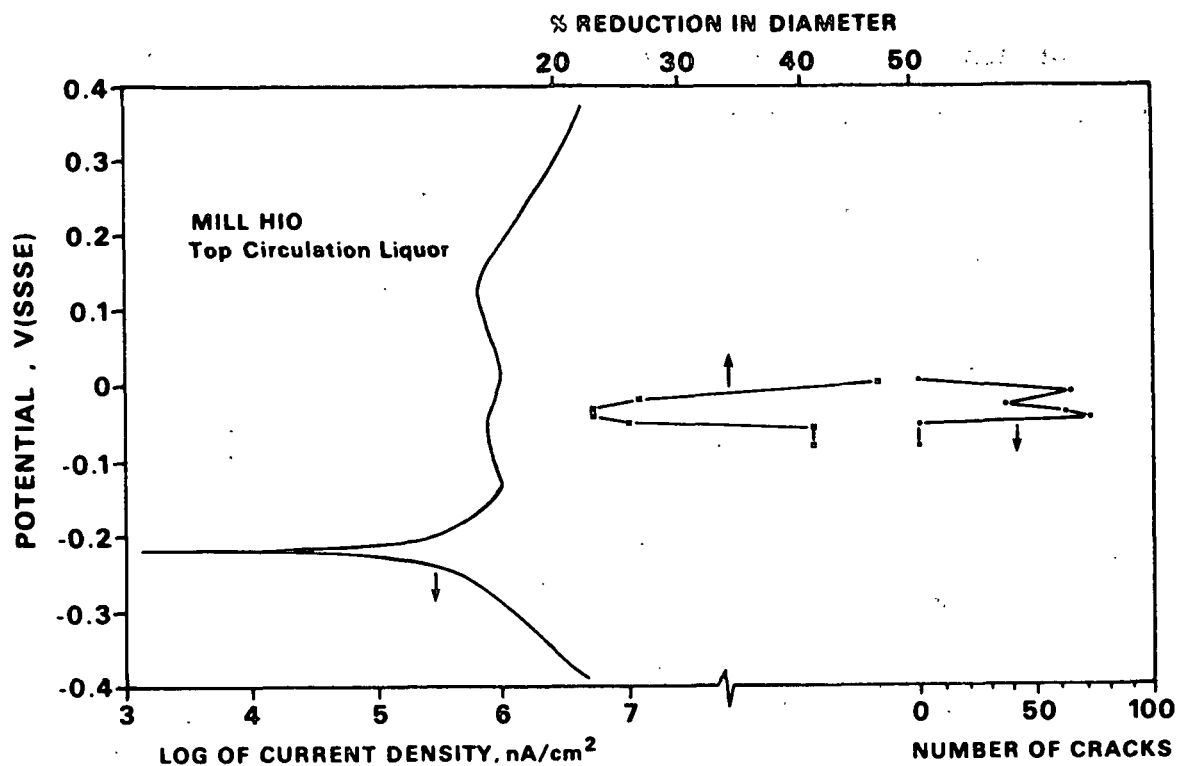


Figure 4. Polarization curve, percent reduction in diameter and number of cracks in test samples as a function of potential for mild steel in mill H liquor.

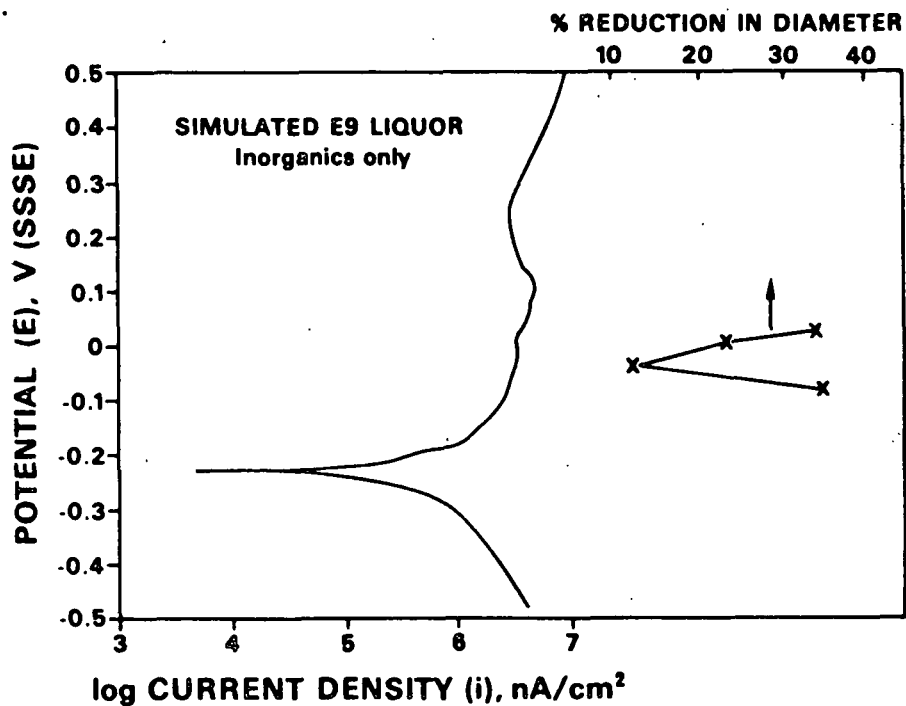


Figure 5. Polarization curve, percent reduction in diameter in test samples in synthetic mill E liquor containing the major inorganic species of the mill E liquor.

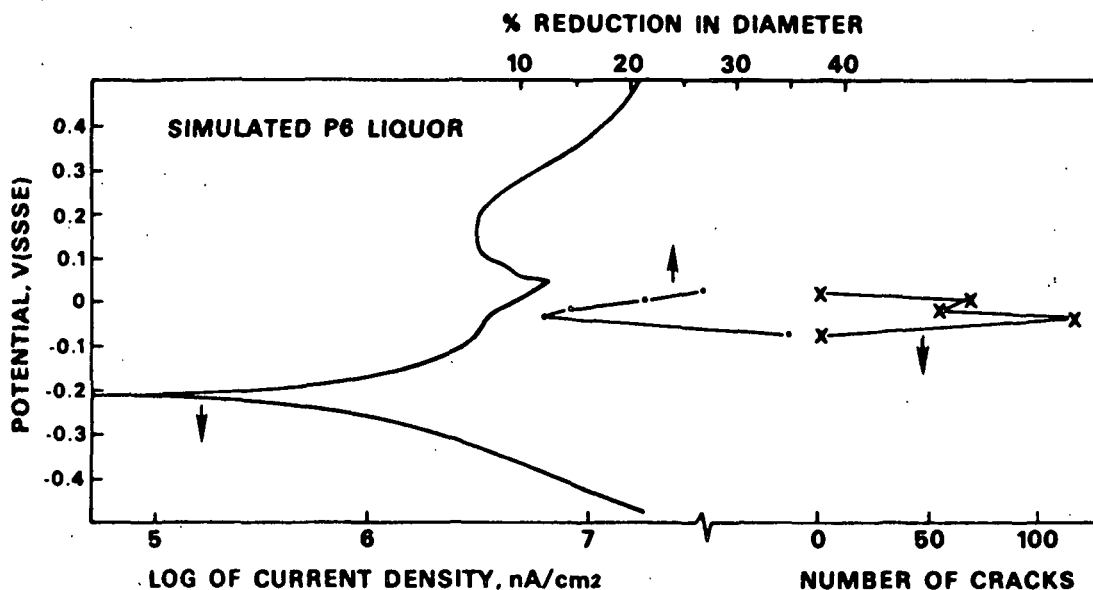


Figure 6. Polarization curve, percent reduction in diameter and number of cracks in test samples in synthetic mill P liquor containing the major inorganic species of the mill P liquor.

Slow strain rate tests were performed at free corrosion potentials. The test sample in mill M liquor attained a potential of 55 mV and no secondary cracking was observed. In the test in mill P liquor, the free corrosion potential started at -60 mV and increased to 0 mV where it stayed throughout most of the test. A tight black film was formed on the surface; stress corrosion cracks were jagged in appearance, and in contrast to the cracks in the mill M liquor. In the mill E liquor, the free corrosion potential was 23 mV and there was no evidence of stress corrosion cracking. A test at the free corrosion potential was not performed in the mill H liquor. On the basis of the corrosion potentials, cracking would be expected at mill P, and indeed cracking has been observed there. Cracking has not been observed at mill E or mill M, although the top section of the digester at mill E is stainless steel clad. Thus, the tests at the free corrosion potential corresponded with mill experience, and results were in agreement with tests at controlled potentials.

Behavior in synthetic liquors was different from real liquors. Synthetic mill P liquor, Fig. 6, caused more severe cracking than the real mill liquor. Likewise, innumerable cracks were observed on the samples in the synthetic mill E liquor, Fig. 5, suggesting that organics in the real liquor may have inhibited crack initiation. There were in excess of 175 cracks per specimen and so the numbers were not plotted. In general, cracks were longer in the synthetic liquors. In the synthetic liquors, Fig. 5 and 6, there was good agreement between SCC ranges defined by the percent reduction in diameter and the frequency of cracking. The synthetic mill P liquor caused fewer cracks than synthetic mill E liquor, probably due to the lower concentrations of constituents. The cracking range in the synthetic mill E liquor was the same as for the real mill liquor. The lack of organics in the synthetic mill E liquor did not appear to affect the range for stress corrosion. This suggests that the major inorganic species determine the range for cracking, but not necessarily the severity.

In an effort to determine the effect of the thiosulfate on the cracking in the mill E liquor, a few tests were done using a synthetic mill E liquor without thiosulfate. At -40 mV, in the liquor without thiosulfate, the percent reduction in diameter was much larger than in the liquor with thiosulfate (26 % vs. 13 %) meaning that the steel was more susceptible in the liquor containing thiosulfate. This is limited evidence that the thiosulfate contributes to the cracking susceptibility or severity.

DISCUSSION

It has been shown that the anodic currents at the active passive potential are larger in liquors with higher concentrations of sulfide and hydroxide (16). These higher currents reflect higher dissolution rates which could increase the chance of crack initiation and growth, and thus the severity of stress corrosion cracking. The present results confirm that stress corrosion is more severe in more concentrated liquors. In an operating digester, the most concentrated liquor is present in the impreg-

nation zone before the chemical has been depleted in the cooking reaction. Thus the greatest chance of cracking occurs in the impregnation zone. The wider SCC zone, with less severe cracking, in weaker liquors confirms the results of Singbeil (6) for cooking zone liquors.

The present results are consistent with the film rupture and dissolution mechanism of SCC. Higher dissolution currents in more concentrated solutions may lead to faster crack rates and more cracks.

Based on the results obtained in synthetic liquors, the stress corrosion cracking susceptibility depends on more than the concentration of the major inorganic species. The organics or trace inorganics present in the real liquors apparently reduced the severity of cracking. This confirms the observation by Singbeil and Garner (9,12) that organic species can play a role in the cracking susceptibility. This was especially striking when the number of cracks in real liquors was compared with the much larger number in the synthetic liquor. It has been suggested that pulping of southern pine may increase SCC susceptibility. The present results, obtained in liquors from mills which pulp predominantly pine, indicate that at a given potential, the organics do not increase SCC. However, the pine may increase cracking if it moves the corrosion potential into the cracking range. Alternatively, other species may provide more inhibition than pine does.

The range for stress corrosion cracking will be shifted as the active/passive peak is shifted. Due to differences in the polarization curve from mill to mill, the range for cracking will also differ. If the free corrosion potential resides in the cracking range, then the probability of cracking is greatly increased, but still depends on the presence of stress in the digester shell. Various liquor constituents will influence the corrosion potential. Polysulfide is known to move the corrosion potential upward, placing it in the active/passive range. At high concentrations of polysulfide, the steel is passivated (1,17,18). Polysulfide concentration was low in the liquors tested. Thiosulfate is also known to increase the corrosion potential into the active/passive range, where high corrosion

rates can result (18). In the mill E liquor, thiosulfate concentration was high enough to place the corrosion potential at the active/ passive peak, but the material passivated for unknown reasons. (Other work at mill E showed that potential increased during pulping of pine.) There was some evidence that in synthetic mill E liquor without thiosulfate, stress corrosion cracking susceptibility was lessened.

The reason for high cracking rates at mill P is related to the free corrosion potential being in the active/ passive range, but the factors controlling the potential are not clear.

CONCLUSIONS

Differences in kraft liquor compositions in real mill liquors have been shown to have a considerable effect on the susceptibility to SCC. Liquors with higher NaOH, Na₂S and Na₂S₂O₃ concentration increase SCC susceptibility and narrow the cracking range. It appears that the organics or trace inorganics in real liquor are beneficial in reducing the severity of SCC.

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