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CORROSION OF CARBON AND STAINLESS STEELS IN CONDENSED BLACK LIQUOR VAPORS

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ABSTRACT

Condensate of black liquor vapors is known to cause corrosion in pulp mill equipment like digesters, flash tanks, storage tanks, evaporator domes, and other equipment handling black liquor condensate. This type of corrosion typically occurs in parts of equipment where the black liquor vapors can condense on a metal surface. Generally organic acids and other wood extractives in the condensate are thought to be responsible for the vapor phase corrosion of pulp mill equipment. Different wood species have different extractives at varying concentrations. Black liquor from softwood and hardwood were used in this study to characterize the corrosive constituents in different condensates. Seven alloys were tested in this study. Carbon steel corrodes at higher rates in the softwood condensate compared to the hardwood condensate. Austenitic stainless steel coupons experienced localized attack in both condensates. Chemical analysis of condensates have shown that although the hardwood condensate had more total organic acids than softwood condensate, the pH of the softwood condensate was always lower than that of the hardwood. Significantly higher concentrations of thiosulfate ions were present in the hardwood condensate than in the softwood condensate. This study indicates that presence of the organic acids is not be the only reason for the overall corrosivity of black liquor condensates.

Keywords: Stainless steel, carbon steel, duplex stainless steel, black liquor, vapor phase corrosion, condensate, softwood, hardwood, thiosulfate ion, hydrogen sulfide, methyl mercaptan, corrosion.

INTRODUCTION

Condensed vapors of black liquors are reported to cause corrosion in equipment like digesters, storage tanks, flash tanks, evaporator domes or vapor heads, and equipment used to handle black liquor condensate ⁽¹⁻⁷⁾. Materials commonly used to build these pieces of equipment include carbon steel, austenitic stainless steels and duplex stainless steels. The corrosion attack on these materials is mainly concentrated in areas where vapors from the black liquor can condense at the equipment surface. Failures in these equipment in vapor phase areas indicates that the condensed vapors or condensate

from the black liquor contains corrosive species. Lankenau et al. ⁽²⁾ reported that carbon steel used in the evaporator effects, and other equipment handling lower temperature and lower percentage solid liquors experience accelerated corrosion in the vapor areas. Artem'eva et al. ⁽⁵⁾ studied corrosion in the secondary steam condensate from multieffect evaporators and stated that hydrogen sulfide and methyl sulfur compounds in the condensate cause corrosion and stress corrosion cracking of carbon steel. Condensates of bisulfite chemimechanical pulping (BCMP) were reported to be acidic due to sulfur trioxide vapors ⁽⁸⁾. The amount of acid in BCMP condensates depends upon the pH of liquor as well as on the oxygen present in the reactors.

Other researchers have attributed vapor phase corrosion attack in black liquor containing equipment to volatile organic extractives and organic acids in the condensate. Maclean and Gardner ⁽¹⁾ studied vapor space corrosion in western red cedar pulping and attributed corrosion to presence of isomeric isopropyl tropolones, α , β , and γ thujaplicin compounds. These compounds contain unsaturated seven-membered carbon rings and form stable chelate complexes with ferric iron salts. These compounds are steam distillable and rapidly attack iron in the absence of alkali ⁽¹⁾. Clarke and Stead ⁽³⁾ carried out tests in which candidate alloy specimens were exposed in the flash tanks in two different softwood mills. They reported that caustic concentration in the test areas were very low to cause any significant corrosion at the temperature of 120°C. They speculated that the presence of organic acids was the most likely cause for the observed general corrosion of carbon steel and titanium, and pitting corrosion of stainless steels in the flash tanks that they monitored. There is anecdotal evidence that shows that the corrosivity of condensates can vary with wood species pulped as well as pulping conditions. Organic acids are also known to cause corrosion in the chemical and refinery industries. Organic acids, as part of organic solvents, were the subject of extensive research by Heitz ⁽⁹⁾, who indicated that the corrosive organic solvents can serve as carriers for aggressive reagents and corrosion products. Organic acids are generally weaker than the inorganic acids because they are only slightly ionized ⁽¹⁰⁾. Formic acid is one of the strongest organics and is the most corrosive. Stainless steel 316 corroded at lower rate (< 0.508 mm/y [20 mpy]) in formic acid (80%) than stainless steel 304 (> 1.27 mm/y [50 mpy]).

The main objective of the present study was to characterize the chemical constituents in the black liquor condensates from softwood and hardwood that may be responsible for the corrosion of steels in different condensates. Another objective of the study was to compare the corrosion behavior of commonly used alloys in black liquor condensates at different temperatures. Two separate black liquors, from softwood and hardwood, were used in this study.

EXPERIMENTAL WORK

Collecting Black Liquor Condensate

The black liquor (1000 mL) was placed in the kettle of a distillation setup and heated to its boiling temperature ($\sim 102.5^\circ\text{C}$). All connections and joints were sealed to prevent any vapors from escaping out or air leaking in. Condensed vapors were collected in a clean flask. Condensate was collected until 650 mL of black liquor remained in the kettle. This simulates the concentration process of black liquor from about 30% solids to about 50%. The pH of the condensates was measured, and the condensates poured into a collection jar that was then sealed to prevent any air from oxidizing the condensate. Condensate from both hardwood and softwood liquors were collected following the above procedure.

Specimen Preparation

Seven alloys were chosen from commonly used materials of construction as candidates for testing in this work. Materials tested included two carbon steels, two austenitic stainless steels, two duplex steels, and one superaustenitic stainless steel. The chemical compositions of the tested alloys are given in Table I. Specimens were cut out of sheet into 1" x 1" [25.4 mm x 25.4 mm] test coupons with a hole in the middle. All specimens were polished to a 120-grit paper finish. The area of each specimen was measured. Specimens were degreased using acetone, and the initial weight of each specimen was recorded. Test coupons were individually wrapped in plastic bags and stored in a dessicator. Test racks with one coupon from each material were assembled such that each specimen was exposed to the same environment. The metal rods used to assemble coupon racks were covered with a Teflon sleeve to avoid any galvanic contact with the test coupons. The ends of the assembly rod and tightening nuts were covered with silicone rubber to prevent their corrosion. Serrated

Teflon washers were placed on either side of specimens in order to create artificial crevices. These washers also prevented galvanic corrosion.

Exposure Testing

Individual test racks, containing one coupon from each material, were exposed to 2000 ml of condensate. Tests were conducted in a high-density polyethylene container with a lid. Test coupons were completely submerged in the test solution. Candidate materials were exposed for 8, 24, 72 hours in one container and for 168, and 360 hours in another. Temperature was maintained within 2°C of the test temperature by keeping the test containers in a constant temperature bath. The pH of the condensate was measured at the end of each time interval. Once the rack was removed, the specimens were washed with acetone and weighed. Each specimen was examined under the microscope to confirm the mode of corrosion. After that the specimens were cleaned by sand blasting, and weighed after washing with acetone. This final weight was used to calculate the corrosion rates for each specimen.

Chemical Analysis of BL Vapors and Condensates

Condensate vapor samples for chemical analysis were collected from the vapor line. Analysis of condensate vapors was performed using gas chromatography. The gas chromatograph was specially designed to analyze for light gases including H₂, CO₂, O₂, N₂, CH₄, and CO as well as for various sulfur-bearing gases including H₂S, methyl mercaptan (MM), dimethyl sulfide (DMS), dimethyl disulfide (DMDS). This method does not analyze for the water vapors, therefore the gas composition is reported as for a dry sample. Volatile organic compounds present in the condensate were analyzed by taking a liquid condensate sample and analyzing by headspace method using an automatic headspace sampler and capillary gas chromatograph. In this method, a measured amount of condensate liquid is injected into vials, samples are fully evaporated in the vials, and the vapor phase is analyzed. Although this method uses gas chromatography, the analysis is for the liquid introduced in the vial, which is condensate liquid in the present study. Headspace method is a well-established method to analyze volatile organic compounds from black liquor ⁽¹¹⁾. Liquid condensate samples were also characterized by using capillary electrophoresis method coupled with mass spectroscopy. This method was used to analyze inorganic constituents as well as low-molecular weight organic acids present in the condensates.

RESULTS AND DISCUSSION

Coupon Exposure Tests

Results for the materials tested in both softwood and hardwood condensates at room temperature (22°C) are listed in Table II. In both condensates, carbon steel coupons showed higher general corrosion rates than other austenitic or duplex stainless steels tested. Figure 1 shows corrosion rates for carbon steel, A516-70, and A 569, as a function of exposure time in the hardwood and softwood condensates. Corrosion rate for the carbon steel was 0.203-0.305 mm/y [8-12 mpy] in the hardwood condensate compared to 0.508-0.61 mm/y [20-24 mpy] for the softwood condensate after 8 hours of exposure. Corrosion rates of carbon steel dropped with time. However, after 168-hour test the corrosion rates were 0.102-0.127 mm/y [4-5 mpy] for both carbon steels in the two condensates. As expected, corrosion rates of carbon steels increased with an increase in test temperature, as shown in Figure 3. After 8 hours of exposure at 70°C, corrosion rates for carbon steel were 0.61-0.762 mm/y [24-30 mpy] in the hardwood and 1.143-1.422 mm/y [45-56 mpy] in the softwood condensates. Even after 72 hours of exposure the corrosion rates were ~0.305 mm/y [12 mpy] in hardwood and ~ 0.4826 mm/y [19 mpy] for the softwood condensates. Results from coupon exposure tests carried out at 70°C are listed in Table III.

As expected, all stainless steel alloys (austenitic and duplex) corrode at very low rate at room temperature and 70°C in both types of condensate. Each specimen was examined for the localized corrosion attack and the results are listed in Table II and III. Stainless steel alloys showed very low corrosion rates even at early stages of testing and for all stainless steels tested the rates became negligible at longer times. However, general corrosion of stainless steels was expected to be negligible. Their resistance to localized corrosion in condensate environment was of prime concern.

304-L stainless steel specimens had pitting and crevice attack in both softwood and hardwood condensates at both tested temperatures. In softwood condensates, the first signs of localized attack appeared after 24 hours of exposure whereas it took about 72 hours for visible localized attack to appear in hardwood condensates. 316-L stainless steel performed better than 304L. 316L SS coupons did not show any signs of localized attack in hardwood condensate at room

temperature even after 360-hour exposure. However, small pits were observed on the surface of coupons after 360 hours in softwood condensate. The performance of 2205, 2304, and SMO254 specimens was better than the 304 and 316 stainless steels in both types of condensates at both tested temperatures as is shown by the results in Table II and III.

Black liquor pH for both softwood and hardwood was ~13.5. However, the pH of condensates was much lower, around 7.2 for the hardwood and 6.2 for the softwood condensate. Changes in pH with time were monitored during coupon exposure tests, as shown in Figures 2 and 4. Figure 2 shows that at room temperature the pH decreased with time up to 72 hours then started to increase. However, at 70°C the change in pH shows a different trend in softwood condensate than at room temperature. At 70°C, the pH increased to a maximum at 24-hours and then decreased. The pH trend in hardwood, however, showed a similar trend to that at room temperature. Exact mechanisms are not clear yet but the pH change may arise from the oxidation of sulfur compounds and corrosion reactions in the test environment.

To investigate the changes in condensate corrosivity, tests were performed in which A-569 carbon steel specimens were exposed for 24 hours in hardwood and softwood black liquor condensates during a 7-day test (168-hour) at 70°C. Table III shows that the carbon steel specimen exposed to hardwood in the last 24 hours of this test had corrosion rate of 0.194 mm/y compared to 0.821 mm/y for the specimen exposed in the first 24 hours (in fresh condensate). Similarly for the softwood, the corrosion rates were 0.077 and 0.331 mm/y for the old and fresh condensate, respectively. These results clearly indicate that the corrosivity of condensate decreases with time. This may explain why the corrosion rates decrease with time in the present study. However, mill equipment is exposed to fresh condensate most of the time. Thus the corrosion rates from short exposure times (say 8 to 24 hours) in the present study may be more relevant to predict the corrosivity of condensates in mill equipment.

Characterization of Chemical Species in Black Liquor Condensate

Vapor phase characterization. Chemical analyses of the vapor samples, carried out by using gas chromatography method, is shown in Table IV. Typical chromatograms obtained by this method are shown in Figures 5 and 6. Results show that the vapor phase is rich in sulfur bearing gases like H₂S, methyl mercaptan, carbonyl sulfide, and dimethyl disulfide. However, hydrogen sulfide and methyl mercaptan are the major sulfur-bearing gas species in both type of condensate vapors. Water was not quantified in this analysis though the majority of gas is expected to be water vapors. These sulfur bearing gases, especially H₂S and CH₃SH are responsible for bad-odor problems in condensates [6]. Condensates from BCMP reactor has also been reported to contain sulfur-bearing gas species which further react and change condensate compositions⁽⁸⁾. Gas sample were taken when the solids content was ~30% and ~50% solids. Results in Table IV indicate that the sulfur bearing gases were produced throughout the concentration process. Although the composition of minor sulfur gases change with time, hydrogen sulfide and methyl mercaptan were in high concentration in both samples. This implies that the condensates from different parts of the black liquor line, from digester to evaporators, may have dissolved sulfur-bearing gases in them, which may form more stable sulfur compounds in the condensate. H₂S dissolved in aqueous media can react with oxygen to form thiosulfate ion (S₂O₃²⁻) and other sulfur compounds⁽¹²⁾. Thiosulfate ion is an aggressive anion and known to cause accelerated general corrosion of carbon steel and localized attack on stainless steels in the oil refinery industry, the nuclear power industry, and the pulp and paper industry⁽¹²⁻¹⁴⁾.

Liquid condensate characterization. Inorganic species, organic acids, condensable volatile organic compounds (VOC), and some of the sulfur-bearing species present in the liquid condensate were analyzed using capillary electrophoresis and headspace gas chromatography. In this technique, a measured amount of condensate liquid is injected into a vial, and the sample is fully evaporated and the vapors analyzed by gas chromatography. The headspace method shows the presence of methanol in both condensates, although hardwood had higher concentrations than softwood, as shown in Table V. Small amounts of acetone and methyl ethyl ketone were also found in the two condensates. Hydrogen sulfide, methyl mercaptan, and dimethyl disulfide were also dissolved in both types of condensates.

Results from capillary electrophoresis (CE) showed the presence of organic acids (mainly formic and acetic acids). However, the concentrations of these acids were low, as shown in Figures 7 and 8 and summarized in Table VI. The total concentration of organic acids was higher in the hardwood condensates than the softwood condensates. If organic acids were the only reason for corrosion in condensate, the hardwood condensates should have been more corrosive. However, our results listed in Tables II and III show that softwood condensate is more aggressive than hardwood condensate. Organic acids may contribute to the corrosivity of condensates but they are not the only corrosive species present in these environments.

Capillary electrophoresis data indicates presence of high concentrations of thiosulfate ions in both softwood and hardwood condensates, as is shown in Figure 7 and 8. The presence of thiosulfate ions was also confirmed using iodimetric titration. This is a standard test for thiosulfate ions ($\text{S}_2\text{O}_3^{2-}$) where KI/I_2 solution oxidizes $\text{S}_2\text{O}_3^{2-}$ to $\text{S}_4\text{O}_6^{2-}$ and produces I^- ions.

Gas chromatographic analysis of gases from the condensates indicates that H_2S and CH_3HS were the predominant absorbed gases in this liquid. In aqueous environments containing oxygen, hydrogen sulfide is metastable and reacts with the oxygen to form sulfur compounds including $\text{S}_2\text{O}_3^{2-}$ ⁽¹²⁾. Thiosulfate ions ($\text{S}_2\text{O}_3^{2-}$) can be formed in the presence of O_2 (air) through the following reaction in aqueous solution;



Hydrosulfide ions (HS^-) are formed whenever hydrogen sulfide or methyl mercaptan is passed through water. The large negative value of Gibb's free energy in reaction (1) indicates the stability of thiosulfate ion in the solution.

It was confirmed that the hydrogen sulfide and methyl mercaptan can produce thiosulfate ions in water in the presence of oxygen by passing hydrogen sulfide gas through deionized water for 20 minutes. The resulting solution contained significant amount of thiosulfate ions, which was then confirmed by standard iodimetric titration. Similar effect was seen when methyl mercaptan gas was used instead of hydrogen sulfide. Once $\text{S}_2\text{O}_3^{2-}$ ions are formed in the condensate, they are very stable. This was also confirmed by passing hydrogen sulfide gas through deionized water for 20 minutes and then heating the resulting solution to boiling the remaining volume of solution was reduced to half. The resulting concentrated solution was used for iodimetric titration and showed that $\text{S}_2\text{O}_3^{2-}$ ions were still present without any change. These results confirm that thiosulfate ions can be formed when hydrogen sulfide and/or methyl mercaptan gases dissolve in aqueous solutions in the presence of oxygen. Once formed, thiosulfate ions are very stable even at temperatures as high as the boiling temperature.

Thiosulfate ions are well known as an aggressive pitting agent, especially for stainless steels that do not contain molybdenum. Thiosulfate pitting, unlike chloride pitting, occurs below a certain critical potential (the thiosulfate reduction potential). Reduction of thiosulfate in the presence of hydrogen ions produces an adsorbed sulfur monolayer on the metal surface. The adsorbed sulfur activates the anodic dissolution of the metal and hinders repassivation ⁽¹³⁾. Laboratory studies have shown that $\text{Na}_2\text{S}_2\text{O}_3$ in white water results in severe pitting corrosion of martensitic stainless steels as well ⁽¹⁴⁾.

Condensates are corrosive. Corrosion does not correlate with the concentration of organic acids in present results as was reported before ^(1,3). There is a significant difference in the chemical composition, condensate pH, and the corrosivity of softwood and hardwood condensates. Thiosulfate ion concentration differences can not explain the discrepancy in corrosion rates of the two condensates. However, the softwood condensates have lower pH and are more corrosive than hardwood condensates. The reason for this is not clear and further investigation is required to correlate the chemical composition and pH of condensates to their corrosivity. Higher Cr and Mo containing materials, in general, perform better in black liquor condensate environments.

CONCLUSIONS

1. Corrosion rate of carbon steels is more rapid in the softwood condensate than in the hardwood condensate. The rate of carbon steel corrosion increases with an increase in the test temperature.
2. General corrosion rates of carbon steels are higher than austenitic and duplex stainless steels tested in this study.
3. 304L stainless steel shows signs of pitting and crevice attack in both softwood and hardwood condensates.
4. 316L stainless steel performed better than 304L coupons. Small pits were observed on the surface of 316-L coupons after 168 hours at room temperature in softwood condensate, but no attack was observed after 360 hours of exposure in hardwood condensate.
5. 2205 duplex steel showed small pits under crevices in softwood condensate. However, in hardwood condensate 2205 did not show any signs of localized corrosion.

6. 2304 and SMO254 specimens performed better than the 304L and 316L stainless steels in both types of condensates in both temperatures.
7. In the present study, softwood condensate was always more corrosive than hardwood condensate.
8. Corrosivity of black liquor condensate decreases with time.
9. Although total organic acids, as detected by capillary electrophoresis technique, in softwood condensates were less concentrated than in hardwood condensates but the initial pH of the softwood condensate was always lower than that of hardwood condensate.
10. Much higher concentrations of $S_2O_3^{2-}$ ion were present in the hardwood condensates than in the softwood condensates and may have raised the pH of the hardwood condensates.
11. From the present results, pH of the condensate seems to be one of the predominant factors in determining relative corrosiveness of black liquor condensates. Further characterization of condensates is required to correlate pH with chemical composition and their corrosivity.

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TABLE I
CHEMICAL COMPOSITION (%) OF STEEL ALLOYS USED IN THIS WORK (WITH FE BAL.)

Alloy	C	Si	Mn	P	S	Cr	Ni	Mo	others
A 516-70	0.230	0.26	1.11	0.007	0.010	0.02	0.01	0.004	0.01 Cu, 0.036 Al, 0.019 V, 0.003 Nb
A 569	0.15		0.60	0.035	0.035	0.15	0.20	0.06	0.20 Cu, 0.008 V, 0.008 Nb
SS-304L	0.018	0.44	1.79	0.032	0.015	18.2	8.29	0.36	0.086 N, 0.11 Co
SS-316L	0.018	0.58	1.67	0.031	0.002	16.39	10.27	2.1	0.033 N, 0.44 Cu
SS-2205	0.021	0.43	1.56	0.02	0.001	21.9	5.8	3.05	0.168 N
SMO254	0.014	0.31	0.43	0.025	0.001	20.2	17.9	6.0	0.183 N, 0.69 Cu
SS-2304	0.018	0.41	1.46	0.023	0.000	22.9	4.8	0.49	0.103 N, 0.31 Cu

TABLE II
CORROSION RATE OF STEEL ALLOYS IN CONDENSATE FROM HARDWOOD AND SOFTWOOD BLACK LIQUOR TESTED AT ROOM TEMPERATURE OF 22°C.

Alloy	Test Time, Hr	CR in HW Condensate, mm/y (mpy)	CR in SW Condensate, mm/y (mpy)	Comments
A 516-70	8	0.2845 (11.2)	0.5969 (23.5)	General Corrosion
	24	0.1778 (7)	0.254 (10)	General Corrosion
	72	0.1067 (4.2)	0.1905 (7.5)	General Corrosion
	168	0.094 (3.7)	0.1143 (4.5)	General Corrosion
	360	0.1067 (4.2)	0.1041 (4.1)	General Corrosion
A 569	8	0.2032 (8)	0.541 (21.3)	General Corrosion
	24	0.1626 (6.4)	0.254 (10)	General Corrosion
	72	0.1168 (4.6)	0.193 (7.6)	General Corrosion
	168	0.1067 (4.1)	0.1117 (4.4)	General Corrosion
	360	0.0914 (3.6)	0.1016 (4)	General Corrosion
SS-304L	8	0	0	
	24	0	0.01 (0.4)	
	72	0.0025 (0.1)	0	
	168	0	0	Few small pits (HW), Pitting (SW)
	360	0	0	Few pits in crevice (HW), Pitting (SW)
SS-316L	8	0	0.0228 (0.9)	
	24	0	0	
	72	0.0025 (0.1)	0.0051 (0.2)	
	168	0	0	Small pits (SW)
	360	0	0	Small pits (SW)

SS-2205	8	0	0	
	24	0	0.0051 (0.2)	
	72	0	0	
	168	0	0	Few pits in crevice (SW)
	360	0	0	Few pits in crevice (SW)
SMO254	8	0.0102 (0.4)	0	
	24	0	0	
	72	0	0	
	168	0.0025 (0.1)	0	
	360	0	0	
SS-2304	8	0.0381 (1.5)	0	
	24	0	0.0279 (1.1)	
	72	0	0.0051 (0.2)	
	168	NA	NA	Not tested at this time period
	360	NA	NA	Not tested at this time period

TABLE III
CORROSION RATE OF STEEL ALLOYS IN CONDENSATE FROM HARDWOOD AND SOFTWOOD
BLACK LIQUOR TESTED AT 70°C.

Alloy	Test Time, Hr	CR in HW Condensate, mm/y (mpy)	CR in SW Condensate, mm/y (mpy)	Comments
A 516-70	8	0.742 (29.2)	1.419 (55.9)	General Corrosion
	24	0.389 (15.3)	0.701(27.6)	General Corrosion
	72	0.32 (12.6)	0.478 (18.8)	General Corrosion
	168	NA	0.389(15.3)	General Corrosion
	360	NA	0.277 (10.9)	General Corrosion
A 569	8	0.597(23.6)	1.130(44.5)	General Corrosion
	24	0.31 (12.2)	0.546 (21.5)	General Corrosion
	24*	0.821 (32.6)	0.331 (13.0)	General Corrosion
	24**	0.194 (7.7)	0.076 (3.0)	
	72	0.295(11.6)	0.47 (18.5)	General Corrosion
	168	0.269 (10.6)	0.348 (13.7)	General Corrosion
	360	NA	0.2845 (11.2)	General Corrosion
SS-304L	8	0.0406 (1.6)	0.0432(1.7)	
	24	0	0	
	72	0.0025 (0.1)	0.0051 (0.2)	
	168	0.0051 (0.2)	0.0025 (0.1)	
	360	0.0025 (0.1)	0	

SS-316L	8	0	0.0635 (2.5)	
	24	0	0	
	72	0	-0.0025 (-0.1)	
	168	0.0051 (0.2)	0.0025 (0.1)	
	360	0.0025 (0.1)	0	
SS-2205	8	0.033 (1.3)	0.0838 (3.3)	
	24	0	0	
	72	0	0.0025 (0.1)	
	168	0.0025 (0.1)	0.0025 (0.1)	
	360	0.0025 (0.1)	0	
SMO254	8	0.0102 (0.4)	0.061 (2.4)	
	24	0	0	
	72	0	0	
	168	0.0025 (0.1)	0.0025 (0.1)	
	360	0.0025 (0.1)	0	
SS-2304	8	0	0.125 (4.9)	
	24	0	0	
	72	0.0051 (0.2)	0.0025 (0.1)	
	168	0	0	
	360	0	0	

*; first 24 hours in corrosivity test of 168 hours

**; last 24 hours in corrosivity test of 168 hours

TABLE IV
GC-1 ANALYSIS OF VAPORS, AS DRY SAMPLE, FROM VAPOR LINE DRAWN DURING HEATING OF
BLACK LIQUOR (HEATING ELAPSING TIME IN BRACKETS).

Black Liquor Type [time, hr]	H₂S, %	COS, %	MM, %	DMS, %	PM, %	DMDS, %
Hardwood [after 1 hr]	53.6097	0.4808	36.7009	0.4987	0	8.7098
Hardwood [after 5 hr]	71.3276	1.4263	25.8028	0	0	1.4432
Softwood [after 1 hr]	34.0882	2.4191	54.7346	0.0923	0	8.6659
Softwood [after 5 hr]	65.7219	2.0467	32.2239	0	0.0073	0.0049

MM - methyl mercaptan; DMDS - dimethyl di-sulfide; MEK - methyl ethyl ketone; PM - propyl sulfide

TABLE V
GC-2 ANALYSIS OF CONDENSATES COLLECTED DURING HEATING OF BLACK LIQUOR (IN PPM).

Type of Black Liquor	H ₂ S	MM	DMS	DMDS	Methanol	Acetone	MEK
Hardwood	29	21	<1	54	1307	4.5	0.9
Softwood	30	20	<1	49	916	6.1	1.6

MM - methyl mercaptan; DMDS - dimethyl disulfide; MEK - methyl ethyl ketone

TABLE VI
CHEMICAL ANALYSIS OF LIQUID CONDENSATE COLLECTED DURING HEATING OF BLACK LIQUOR AND ANALYZED USING CAPILLARY ELECTROPHORESIS METHOD.

Ion	Hardwood Condensate, mg/L	Softwood Condensate, mg/L
Chloride, Cl ⁻	0.08	0.04
Sulfate, SO ₄ ²⁻	3.67	2.55
Thiosulfate, S ₂ O ₃ ²⁻	164.51	15.62
Carbonate, CO ₃ ²⁻	25.81	2.68
Organic Acids (Formic + Acetic)	74.5	1.25

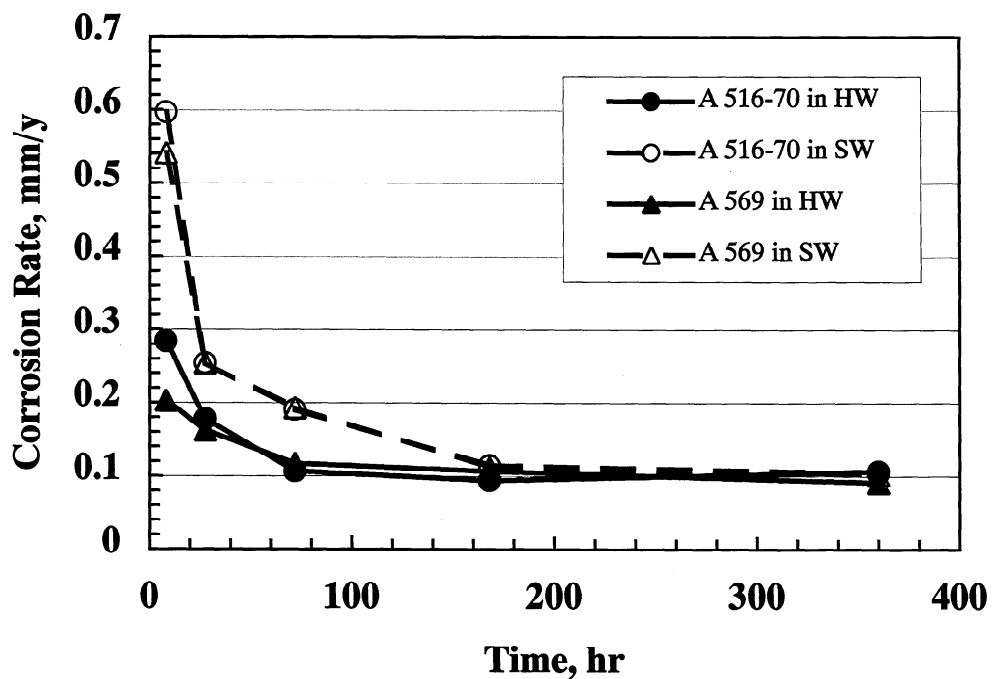


FIGURE 1. Corrosion rates of carbon steel alloys in black liquor condensate at room temperature of 22°C.

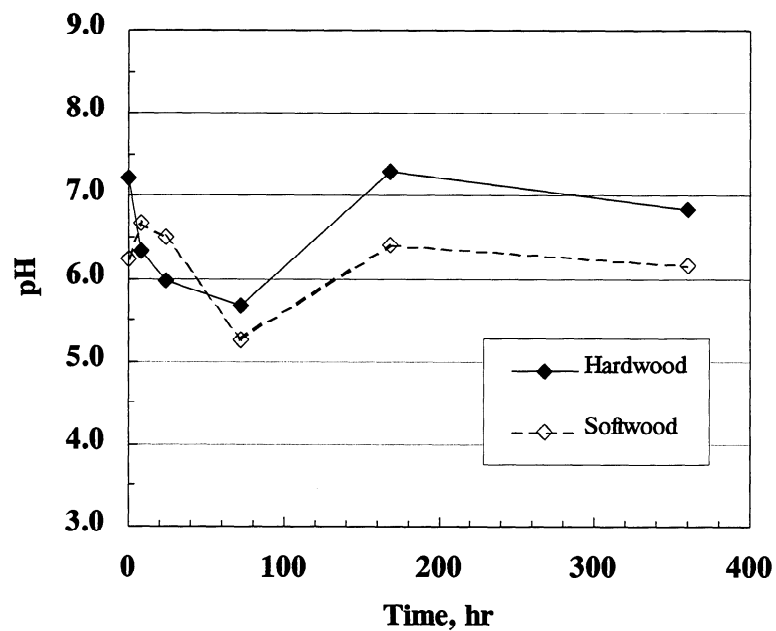


FIGURE 2. The change in pH of condensate with time of testing for tests carried out at room temperature of 22°C.

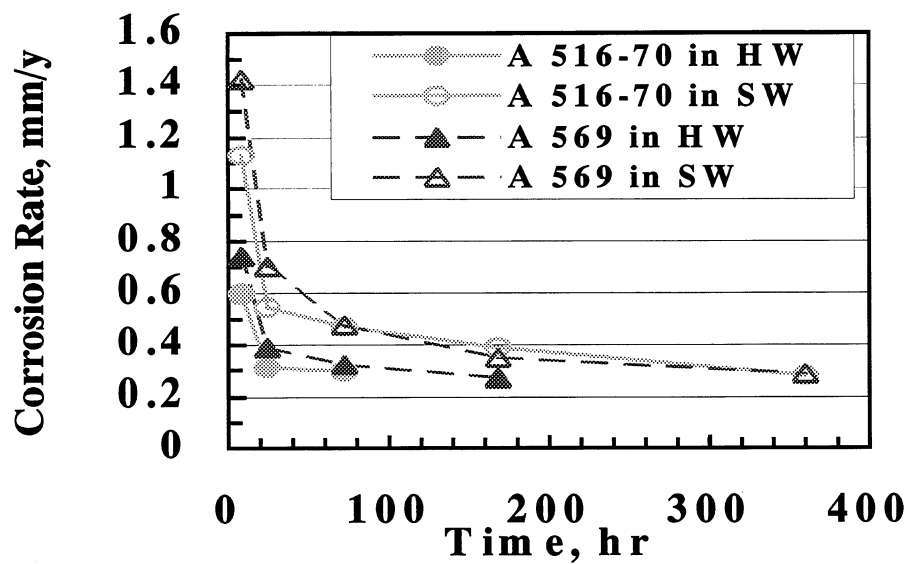


FIGURE 3. Corrosion rates of carbon steel alloys in black liquor condensate at room temperature of 70°C.

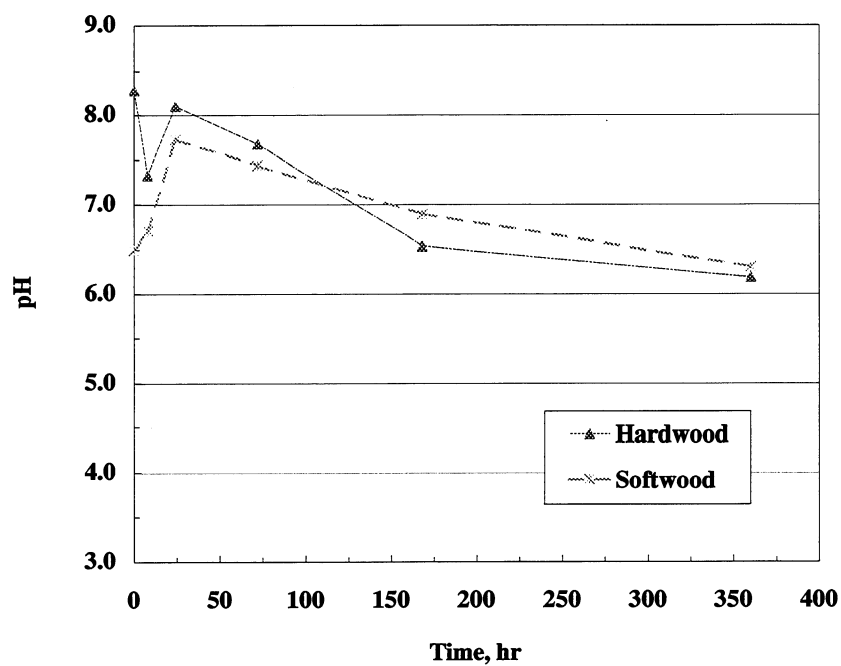


FIGURE 4. The change in pH of condensate with time of testing for tests carried out at room temperature of 70°C.

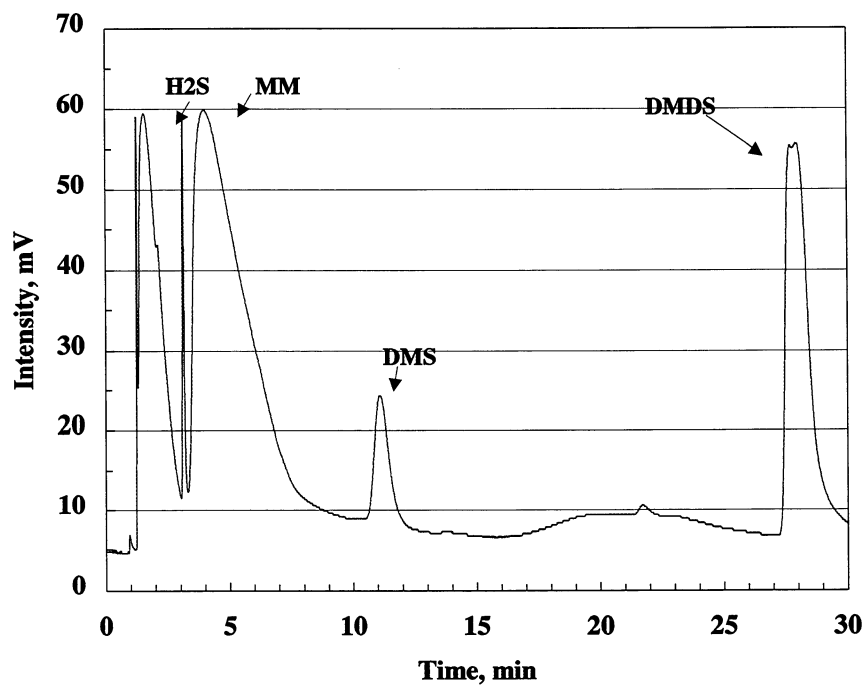


FIGURE 5. Sulfur-bearing gases (dry) chromatogram of hardwood black liquor vapors. MM is methyl mercaptan, DMS is dimethyl sulfide, and DMDS is dimethyl disulfide.

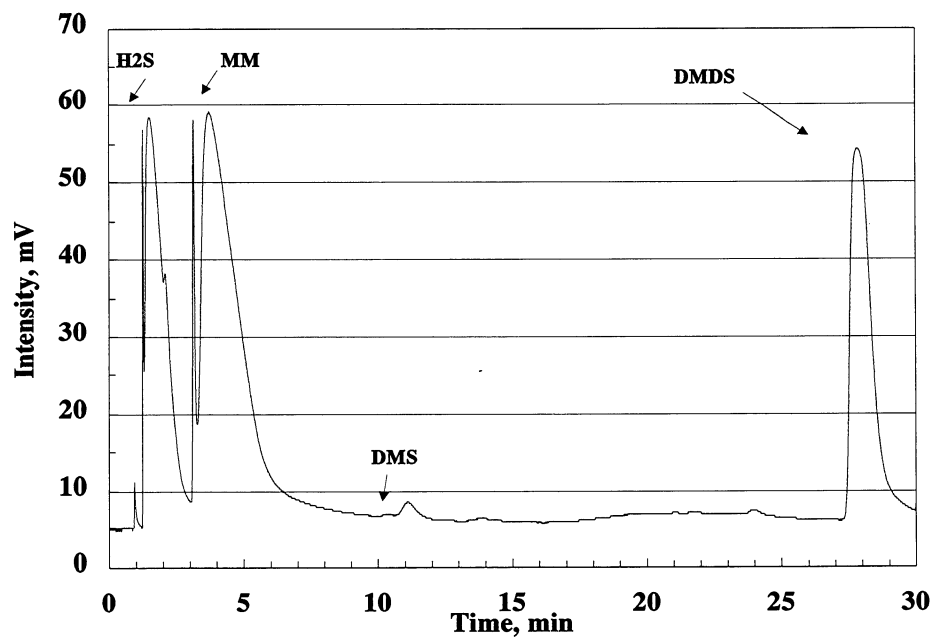


FIGURE 6. Sulfur-bearing gases (dry) chromatogram of softwood black liquor vapors. MM is methyl mercaptan, DMS is dimethyl sulfide, and DMDS is dimethyl disulfide

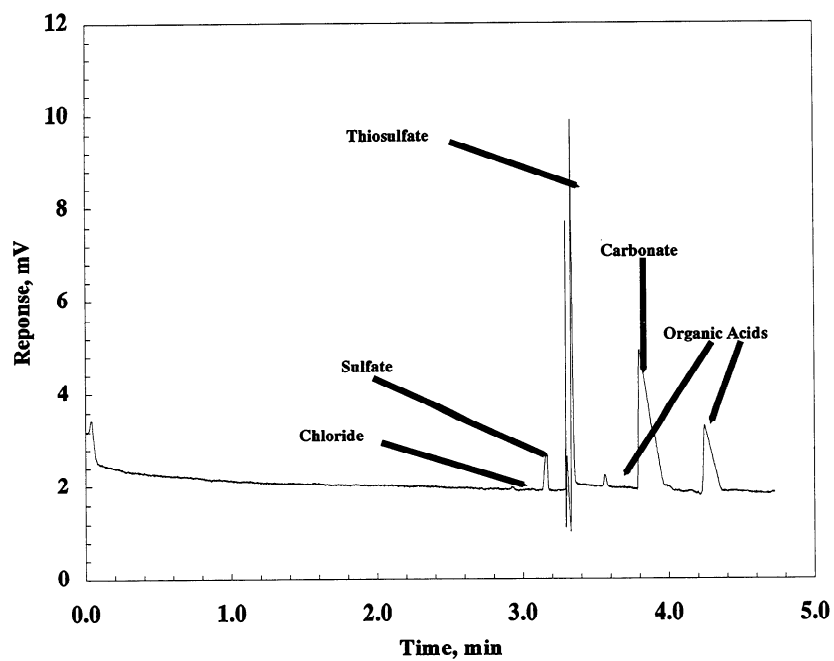


FIGURE 7. Capillary Electrophoresis analysis of hardwood condensate.

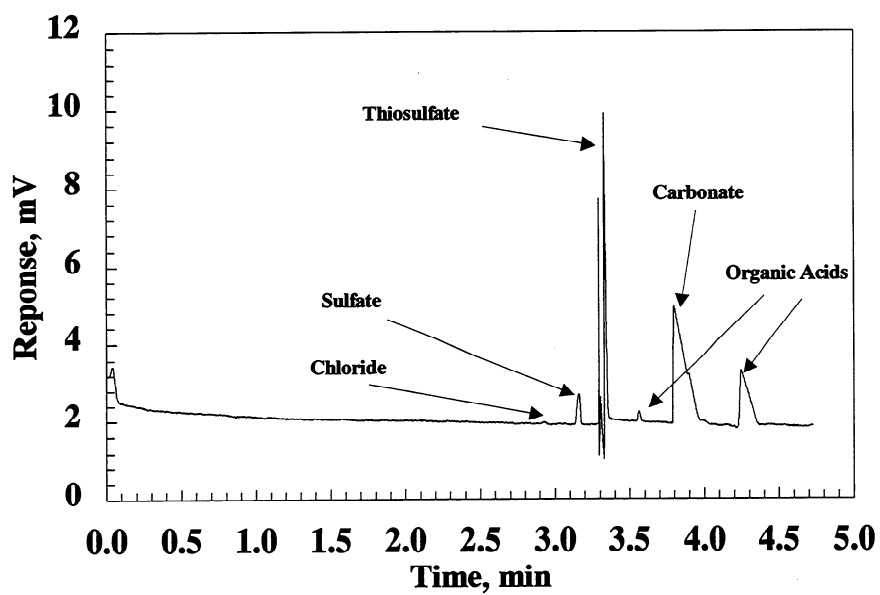


FIGURE 8. Capillary Electrophoresis analysis of softwood condensate.

