Evaluation of cast bronze alloys in paper mill white waters

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ABSTRACT *Corrosion resistance and corrosion fatigue performance of 1N Bronze and aluminum bronze were determined in two laboratories. The 1N Bronze exhibited corrosion rates greater than or equal to those of aluminum bronze after both exposure to white waters simulated in the laboratory and exposure to white waters in an actual mill. Severe surface roughening occurred on both alloys after long-term exposure to simulated and actual white waters. Corrosion fatigue performance, determined by the reverse plate bending method (TIS 0402-09) in TAPPI I and modified TAPPI I white waters, revealed the same behavior for both alloys. Thiosulfate ion (at a concentration of 15 mg/L) reduced the corrosion fatigue performance of both alloys. Aluminum bronze was susceptible to dealloying in actual white water in the paper mill.*

KEYWORDS
Bronze
Corrosion
Materials testing
Suction rolls
White water

Centrifugally cast 1N Bronze is used extensively throughout the world as a material for suction roll shells. This material has lasted for extended periods in a wide variety of paper mill rolls. However, in recent years and in certain aggressive white water environments, 1N Bronze has undergone more rapid degradation from corrosion (*1*).

Susceptibility to various forms of corrosion has resulted in premature failure of suction roll shells and excessive wear of fabrics or felts (*2*). The shorter life of paper machine clothing and roll shells has increased papermaking costs. Various ionic species responsible for this more rapid degradation have been identified (*3, 4*), and the corrosive effect of thiosulfate ion on bronze alloys has been documented (*1, 3–5*). In the future, the move toward closed water systems in mills will undoubtedly lead to higher concentrations of corrosive ionic species and subsequently to more corrosion-related problems.

An aluminum bronze alloy has recently been offered as an alternative to 1N Bronze in suction rolls. Reportedly, this material is more resistant to corrosion than 1N Bronze and has improved resistance to corrosion fatigue. In two separate laboratories, we examined how semi-continuously cast aluminum bronze compares with centrifugally cast 1N Bronze in its resistance to corrosion and corrosion fatigue.

Experimental procedures

Materials

We evaluated three production castings of 1N Bronze and a single production casting of aluminum bronze. The 1N Bronze heats were centrifugally cast and the aluminum bronze was cast semi-continuously. **Table I** shows the chemistry of each bronze test variable evaluated, and **Table II** lists the corresponding mechanical properties.

Laboratory immersion testing

Specimens for laboratory immersion studies were machined cylinders with nominal dimensions of 7.9 mm in diameter by either 25.4 mm or 12.7 mm in length. The 25.4-mm-long cylinders (1 in. long) were wet-ground with 180-grit SiC paper. The 12.7-mm specimens were wet-ground with 600-grit SiC paper. Each specimen was washed, rinsed, degreased in acetone and methanol, and wiped dry. Specimens were desiccated prior to weighing and immersion.

Immersion studies were conducted in two separate laboratories. In one laboratory, a six-week immersion test program was undertaken. The purpose of this test was to compare the corrosion resistance of two bronze alloys in simulated white water solu-

I. Chemical composition by weight percent

Alloy	Heat no.	Cu	Sn	Pb	Zn	Al	Ni	Fe	Mn
1N Bronze	171945	84.95	4.58	5.03	4.56	...	0.65	...	...
1N Bronze	168131	85.01	4.54	5.09	4.58	...	0.56	...	...
1N Bronze	166002	85.10	4.74	5.05	4.40	...	0.58	...	...
Aluminum bronze[a]	77-55895	81.5–83.5	...	...	...	9.0–9.5	4.0–4.5	3.0–3.5	0.5–1.0

[a]Chemistry data obtained from Kabelmetal brochure.

tions of increasing concentrations of thiosulfate ion. Simulated white water solutions were prepared using reagent-grade chemicals in deionized water, resulting in ionic concentrations listed in **Table III**. Each solution was monitored daily with appropriate chemical additions to maintain ionic strength. Duplicate specimens were withdrawn after 21 and 42 days.

In a second laboratory, a one-year immersion test program was completed. The purpose of this program was to compare the corrosion resistance of two bronze alloys in a corrosive solution simulating white waters containing thiosulfate ions. This solution was prepared using reagent-grade chemicals in distilled water, resulting in ionic concentrations listed in Table III. The solution was changed twice daily to maintain ionic strength. Duplicate or triplicate specimens were withdrawn after 30, 91, 178, and 365 days of exposure.

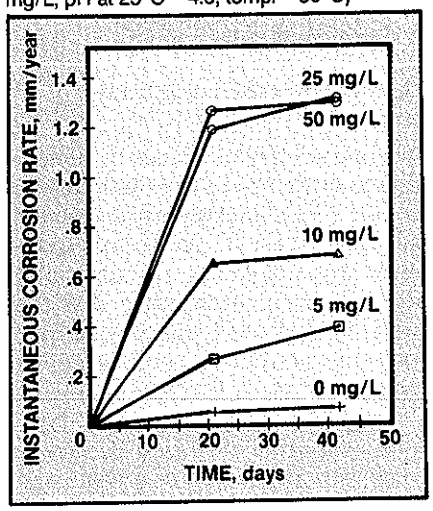
In both laboratories, acidification of the simulated white water solutions was achieved by sulfuric acid addition. Solutions were continuously aerated to achieve oxygen saturation, simulating paper mill operating conditions for suction rolls. In both laboratories, spent solutions were analyzed to ascertain which ionic species played a major role in the corrosion process. The corrosion products were removed chemically from specimens after each exposure period. The extent of localized corrosion was documented. Weight loss as a function of exposure time was determined. Instantaneous corrosion rates of each alloy were calculated and graphed.

II. Mechanical properties

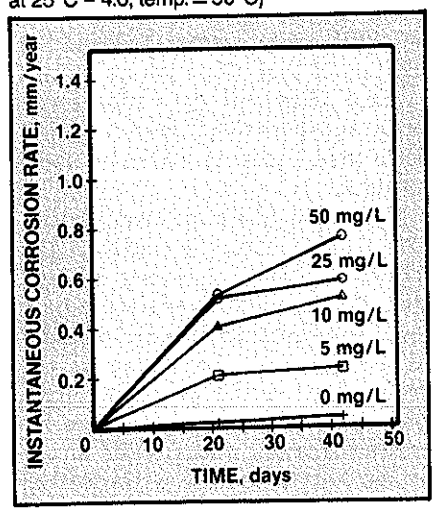
	Heat no.	0.2% offset yield strength	Tensile strength	Elongation in 50 mm, %
1N Bronze	171945	...	243 (35.2)	23
1N Bronze	168131	...	234 (33.9)	24
1N Bronze	166002	...	269 (39.0)	39
Aluminum bronze[a,b]	77-55895	245 (35.5)	600 (87.0)	20

[a]Mechanical properties data obtained from Kabelmetal brochure.
[b]Average values.

1. Instantaneous corrosion rates of 1N Bronze vs. thiosulfate concentration as measured in the 6-weeks laboratory immersion test (chloride = 50 mg/L, sulfate = 500 mg/L, pH at 25°C = 4.0, temp. = 50°C)



2. Instantaneous corrosion rates of aluminum bronze vs. thiosulfate concentration as measured in the 6-weeks laboratory immersion test (chloride = 50 mg/L, sulfate = 500 mg/L, pH at 25°C = 4.0, temp. = 50°C)

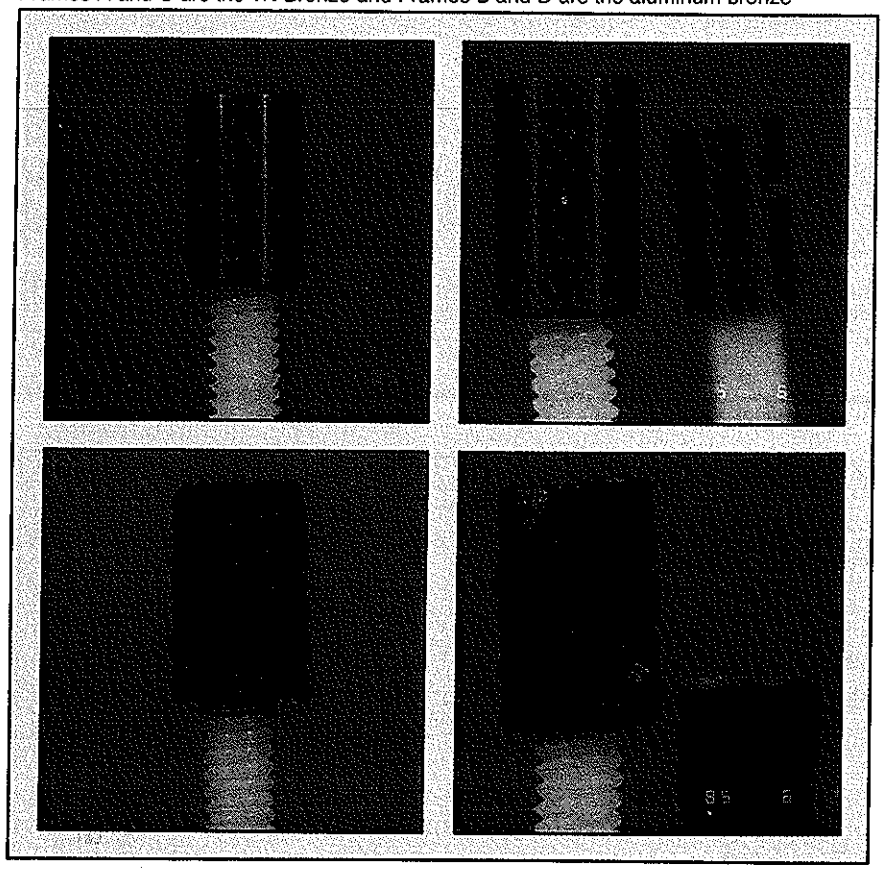


Corrosion fatigue testing

Rectangular bars typically measuring 184.15 mm by 15.875 mm by 6.35 mm were cut and machined from actual production castings. The long axis of each bar coincided with the longitudinal direction of the casting. A single, 3.97-mm-diameter, drilled and reamed hole was centered in the width of the bar, 25.4 mm from one end. The remaining surfaces of the rectangular bar were ground to a typical finish of 0.8μm R_a (average roughness value). Specimens were washed and rinsed in deionized water prior to testing.

Corrosion fatigue testing was performed according to TAPPI TIS 0402-

3. Bronze alloys after six weeks of exposure to thiosulfate and thiosulfate-free environments; Frames A and C are the 1N Bronze and Frames B and D are the aluminum bronze



09, the reverse plate bending method. TAPPI I white water (Table I) and modified TAPPI I white water were prepared with reagent-grade chemicals in deionized water. Modification of TAPPI I white water involved the addition of thiosulfate ion at 15 mg/L. Test solutions were monitored daily, and necessary chemical additions were made to maintain ionic strength.

We used reverse plate bending with deflection control to evaluate the corrosion fatigue resistance of each alloy (*6*). This method results in a fully reversed (zero mean stress) sinusoidal stressing pattern occurring at the drilled hole periphery during each load cycle. To account for the increased stresses which occur at the drilled hole periphery, a theoretical stress concentration factor (*Kt*) was included in maximum stress calculations. Time to crack initiation was determined at three stress levels: 138, 172, and 207 MPa (20, 25, and 30 ksi). Individual specimens were inspected twice daily with a five-power magnifying glass to determine the number of cycles to crack initiation. Cyclic frequency was maintained at 1725 cycles/min. The corrodent was wicked into the drilled hole. Corrosion fatigue resistance was determined by recording time to crack initiation as a function of stress amplitude.

Exposure to white water spray in the mill

Specimens were machined to typical dimensions of 57.15 mm in diameter by 4.70 mm in thickness with a center hole 11.11 mm in diameter. Specimens were mounted on racks and insulated from each other and the rack by Teflon™ spacers. Fiber washers were placed between Teflon spacers and metal surfaces to provide a creviced area. Surface finish typically measured 1.3-1.4μm R_a. Specimens were degreased in acetone and methanol prior to weighing and rack assembly.

Racks containing disc specimens were situated on a paper machine downstream from the couch position. In this manner, specimens were exposed to a completely aerated white water spray, the result of centrifugal action as white water was thrown from the couch. Chemical analysis and other characteristics of the white water are listed in **Table IV**. Duplicate specimens of each alloy were exposed for 336 days of actual machine running time. Upon completion of the test, specimens were removed from racks, corrosion products were removed chemically, and the type and extent of localized corrosion was documented. Weight loss was determined, and corresponding corrosion rates were calculated.

Results and discussion

Laboratory immersion testing

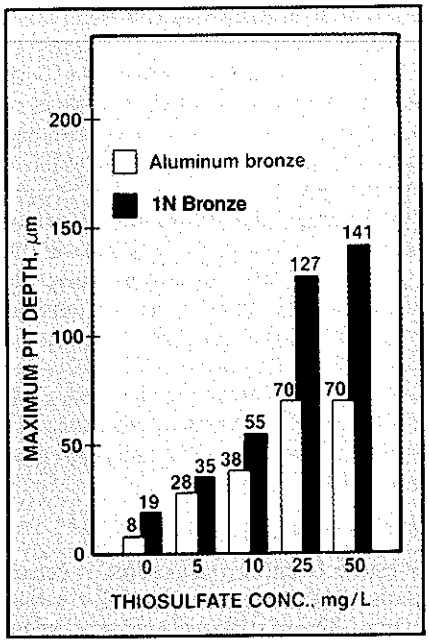
We analyzed spent solutions in both laboratories to ascertain which ionic species played a major role in the corrosion process. In all tests, concentrations of hydronium and thiosulfate ion were reduced. Conversely, chloride and sulfate ions were not measurably consumed.

Figure 1 shows profiles of instantaneous corrosion rates of 1N Bronze as a function of time and thiosulfate ion concentration. Instantaneous corrosion rate is derived from the slope of the line tangent to the curve of weight loss vs. time at a specific time. It expresses the rate of change in corrosion at that time. Typical corrosion meters actually measure instantaneous corrosion rate, and it is this value more than weight loss that has significance in design engineering.

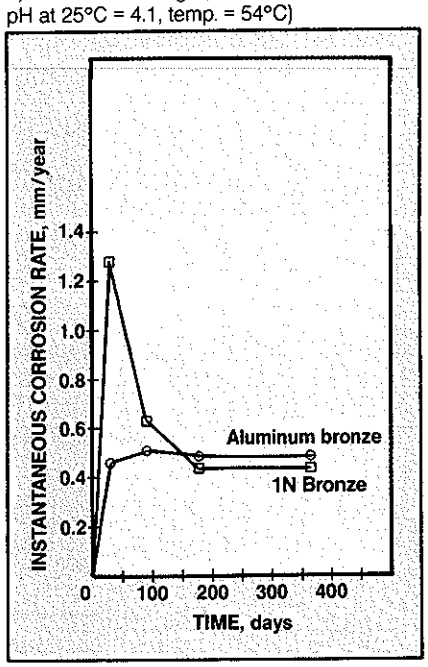
In the 42-day exposure period, the corrosion rate of 1N Bronze is negligible in the thiosulfate-free environment, as the figure shows. Its instantaneous corrosion rate reached steady state as early as 21 days into the test. These low instantaneous corrosion rates for 1N Bronze in this environment indicate that the corrosion product is protecting the base metal.

However, with as little as 5 mg/L of thiosulfate ion present, the corrosion rate of 1N Bronze increases dramatically. A further increase in thiosulfate ion to 10 mg/L results in a proportionately higher corrosion rate. Between 25 and 50 mg/L, there is no further increase in the corrosion rate. Furthermore, corrosion products that formed on 1N Bronze in the presence of thiosulfate ion spalled off readily compared with behavior in the absence of thiosulfate. Such spalling indicates that the corrosion product is not protecting the base metal, result-

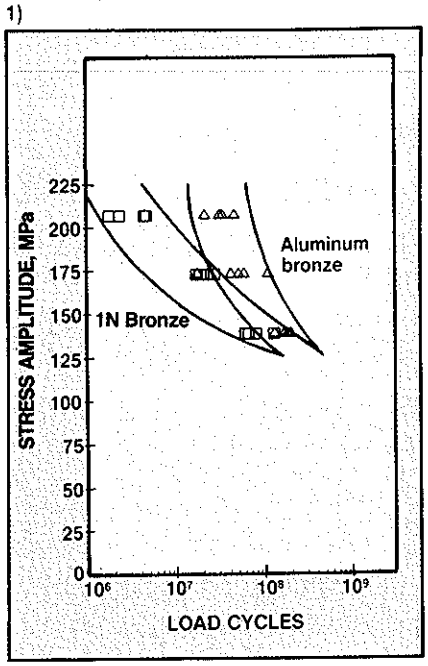
4. Maximum pit depth vs. thiosulfate concentration as measured in the 6-weeks laboratory immersion test



5. Corrosion rates of 1N Bronze and aluminum bronze as measured in the 1-year laboratory immersion test (chloride = 400 mg/L, sulfate = 800 mg/L, thiosulfate = 35 mg/L, pH at 25°C = 4.1, temp. = 54°C)



6. Stress amplitude as a function of cycles to crack initiation in TAPPI I white water (chloride = 100 mg/L, sulfate = 1000 mg/L, pH at 25°C = 3.5, temp. = 24°C, frequency = 1725 $R = -1$)



ing in continuous dissolution of the base metal.

Figure 2 shows corresponding profiles of instantaneous corrosion rates for aluminum bronze as a function of time and thiosulfate ion concentration. The instantaneous corrosion rate of aluminum bronze is negligible, like that of 1N Bronze in the thiosulfate-free environment. Again, like 1N Bronze, the corrosion rate of aluminum bronze increased dramatically in the presence of only 5 mg/L of thiosulfate ion. Increasing thiosulfate to 10 mg/L resulted in a proportionate increase in the corrosion rate of aluminum bronze. Between 10 and 25 mg/L of thiosulfate ion, there is little increase in the corrosion rate, but a noticeable increase in the corrosion rate of aluminum bronze did occur when the thiosulfate ion concentration increased to 50 mg/L. Corrosion products that formed on aluminum bronze in the presence of thiosulfate continuously spalled off specimens during the test, while this did not take place in the thiosulfate-free environment. As with 1N Bronze, this spalling indicates that the corrosion product is not protecting the base metal.

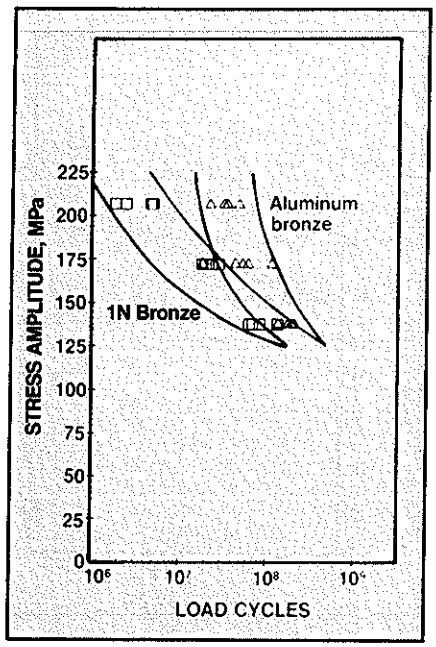
Figure 3 shows the difference in appearance of both bronze alloys after six weeks of exposure to thiosulfate-free and thiosulfate-containing environments. The 1N Bronze and aluminum bronze were observed to form a thin, tightly adhering, blue-green corrosion product in the thiosulfate-free environment (Figs. 3A and 3B). In comparison, a thick, spalling (nonadhering), black corrosion product readily formed on 1N Bronze in all thiosulfate environments even at a concentration of only 5 mg/L of thiosulfate ion (Fig. 3C). A nonuniform, spalling, black corrosion product together with a few white nodules was observed on corroding aluminum bronze specimens exposed to all thiosulfate-bearing environments, even as low as 5 mg/L of thiosulfate ion (Fig. 3D). Pitting occurred directly beneath the white nodules. Both alloys exhibited undesirable corrosion rates above the level of 10 mg/L of thiosulfate ion.

More importantly, localized corrosion was observed on both alloys in the thiosulfate environments. Each alloy experienced undesirable, nonuniform corrosive attack that resulted in a roughened surface. The maximum depth of attack for each alloy is illustrated in **Fig. 4**. Incremental

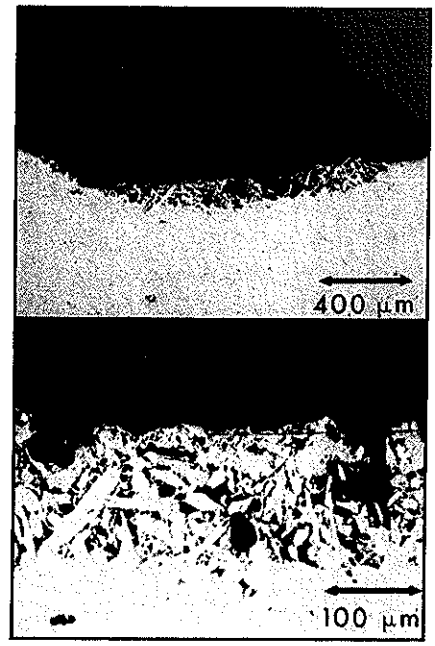
III. Characteristics of the simulated white water

	Immersion test		*Corrosion fatigue*	
Ionic species	*6-weeks, mg/L*	*1-year, mg/L*	*TAPPI I, mg/L*	*TAPPI I modified mg/L*
Chloride	50	400	100	100
Sulfate	500	800	1000	1000
Thiosulfate	0, 5, 10, 25, 50	35	. . .	15
Test temp.	50	54	50	50
pH at 25° C	4	4.1	4	4
Conductivity at 25°C, microsiemens/cm	1500–1550	2900	2780	2800

7. Stress amplitude as a function of cycles to crack initiation in modified TAPPI I white water (test conditions as in Fig. 6 with the addition of 15 mg/L thiosulfate ion)



8. Regions of dealloying at the base of a pit, for aluminum bronze after 336 days' exposure to actual white water in the mill



IV. Characteristics of the actual white water in the paper mill

Ionic species	*Conc., mg/L*
Chloride	335
Sulfate	1670
Thiosulfate	4
Test temp.	48
pH at 25° C	4.5
Conductivity at 25° C, microsiemens/cm	2500

V. Corrosion rates after 336 days' exposure to white water spray in an actual paper mill

Alloy	*Heat no.*	*Rate mm/year*	*Rate MPY**
1N Bronze	168131	0.2	7.0
Aluminum bronze	77-55895	0.2	5.0

*mils per year

increases in thiosulfate ion concentration generally resulted in increases in the depth of nonuniform attack.

Examination by energy dispersive spectrophotometry (EDS) of corroded aluminum bronze specimens after six weeks' exposure to the 25-mg/L thiosulfate environment revealed immediate surface layer dealloying. We detected significant reduction in major alloying elements. This phenomenon of surface dealloying was not observed in 1N Bronze.

Figure 5 shows values of instantaneous corrosion rate as a function of time as taken from the study conducted in the second laboratory. This figure illustrates the instantaneous corrosion rate of both alloys in an aggressive thiosulfate environment. The instantaneous corrosion rate for both alloys rapidly increased during the first 30 days of exposure. After 30 days, the corrosion rate of aluminum bronze reached a maximum value and remained constant for the duration of the test. Although 1N Bronze reached a greater maximum corrosion rate after 30 days of exposure, it reached a corrosion rate equal to that of aluminum bronze after 150 days of exposure. Both alloys continued to corrode at an equivalent constant rate for the remainder of the test. Similarly, both alloys produced the continuously spalling corrosion products indicative of nonprotective behavior.

More importantly, the extent of localized corrosion observed on both metals was severe after 365 days of exposure. Each metal experienced unacceptable, nonuniform corrosive attack that caused a severely roughened surface. The maximum depth of attack on 1N Bronze was 914μm (36 mils). The form of attack was the same, and it ran to an equivalent depth on aluminum bronze, measuring 813μm (32 mils). This behavior has occurred in service on suction roll shells of 1N Bronze, resulting in reduced endurance in rolls, fabrics, and felts.

Corrosion fatigue testing

Figure 6 shows the results of corrosion fatigue tests in TAPPI I white water. The number of cycles to crack initiation is longer for aluminum bronze than for 1N Bronze at the 207-MPa(30 ksi) stress amplitude (for applied stress). This performance reflects the fatigue resistance of the aluminum bronze and not its resistance to corrosion fatigue, as indicated by the uncorroded appearance of specimens at the end of testing.

At greater load cycles to crack initiation (lower stress amplitudes), the specimens did corrode. This effect is observed in the decrease in corrosion fatigue performance. At the relatively short time to crack initiation of 100 million load cycles, the corrosion fatigue scatter bands of both alloys begin to converge, revealing approximately equivalent behavior. For a modern suction roll measuring 1372 mm (54 in.) in outside diameter and operating at 914 m/min (3000 ft/min), 100 million cycles represents approximately 11 months of actual running time.

Corrosion fatigue test results for both bronze alloys in modified TAPPI I white water are shown in **Fig. 7**. The increased aggressivity of 15 mg/L of thiosulfate is demonstrated by a reduction in the number of load cycles to crack initiation at the lower stress of 138 MPa (20 ksi). This is further supported by the extent of corrosion observed on test specimens. Both alloys were similarly affected.

Exposure to white water spray in the paper mill

Analysis of mill white water revealed the same aggressive ionic species as contained in simulated white waters prepared in the laboratory, though to a lesser extent. Data from these analyses are listed in **Tables III and IV.** Corrosion rates for both alloys are listed in **Table V.** Similarities between the results at the two laboratories and those for the actual exposure are noteworthy. Corrosion rate values for both alloys are 2.5 times lower, supporting the less aggressive nature of the actual white water. Corrosion rates of 1N Bronze and aluminum bronze are equal. Comparisons between laboratory and paper mill exposure indicate good correlation of corrosion rate data.

The 1N Bronze experienced nonuniform corrosion to a maximum depth of 229μm (9 mils), resulting in slight surface roughening. This alloy did not exhibit dealloying. Conversely, aluminum bronze experienced exposed surface pitting to a maximum depth of 457μm (18 mils) and nonuniform corrosive attack to a maximum depth of 298μm (12 mils), resulting in a more roughened surface than the 1N Bronze.

More importantly, we observed dealloying of the aluminum bronze at the base of many pits. Dealloying, as suspected in laboratory testing, was confirmed after exposure to the actual white water spray on the paper machine. Dealloying was documented by cross-sectioning a specimen and viewing the polished surface with an optical microscope.

Figure 8A is a photomicrograph at 50-times magnification, documenting the extent of dealloying associated with pitting. **Figure 8B** is a photomicrograph at higher magnification (200X), showing the dealloyed region. Dealloying is the selective removal from a metal of most or all major alloying additions, leaving behind a porous metal matrix which has a dramatically reduced strength. Under cyclic loading conditions, this reduction in strength could lead to premature suction roll failure.

Conclusions

Aluminum bronze and 1N Bronze alloys demonstrated high corrosion rates and susceptibility to severe localized forms of corrosion when exposed to simulated and actual corrosive white waters containing thiosulfate ion. Also, aluminum bronze showed dealloying associated with pitting after exposure to an actual mill white water containing thiosulfate ion.

Laboratory tests indicate that white water containing as little as 5 mg/L of thiosulfate ion (5 ppm) may reduce the service of aluminum bronze and 1N Bronze suction roll shells, particularly in press rolls. Laboratory corrosion rates correlated well with paper mill corrosion rates. However, localized corrosion attack did not correlate well for aluminum bronze, thus necessitating long-term coupon exposure in the mill.

The corrosion fatigue resistance of both alloys was equivalent after 100 million load cycles. Addition of thiosulfate to TAPPI I white water at 15 mg/L reduced the corrosion fatigue resistance of both alloys.

Recommendations

TAPPI I white water (TIS 0402-09) should be modified to contain thiosulfate ion, to properly evaluate the corrosion fatigue performance of materials in recognized aggressive environments. Mill white water analyses, including thiosulfate measurements, must proceed proper material selection. Finally, an economic evaluation of the cost/life factors on bronze vs. stainless steel alloys is necessary when thiosulfate ions are present in the environment.

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