Electrochemical corrosion testing of duplex stainless steel suction roll alloys

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Duplex stainless steel suction roll alloys can be evaluated for pitting and crevice corrosion resistance with electrochemical techniques.

Since the 1950s, paper machine suction roll alloys have undergone a metallurgical evolution from bronze to martensitic stainless steels to duplex stainless steels and precipitation hardening duplex stainless steels. This evolution occurred to meet demands for increased strength as paper machine size and speed increased, as well as for improved corrosion fatigue resistance as recycle made paper machine white waters more corrosive (*1*).

Many failures of martensitic stainless steel rolls had been attributed to corrosion fatigue which began with pitting or crevice corrosion within suction holes. Centrifugally cast duplex stainless steels were thus introduced to provide both strength and increased corrosion resistance. However, one of the first of these alloys, Sandusky Alloy 63[1] (the 63 refers to the year of introduction), suffered several premature failures. The water quench required for corrosion resistance produced excessive residual stresses which promoted corrosion fatigue failure (*2*). A similar water quenched material, Valmet-Kubota VK-A171,[2] has also experienced several failures.

Succeeding duplex stainless steel suction roll alloys—Sandusky Alloy 75, Valmet-Kubota VK-A378, and Sandusky Alloy 86—were heat treated to reduce residual stress.

In 1979 MacMillan Bloedel began electrochemical testing for localized corrosion resistance as a screening test for duplex stainless steel suction rolls. Assuming equivalent residual stress levels, casting quality and suction hole surface smoothness, it was believed that localized corrosion resistance could become a deciding factor in corrosion fatigue initiation. Pits and crevices within suction holes could promote crack initiation by providing both stress raisers and local high acidity environments.

Localized corrosion was a particular concern for West Coast paper mills because ocean transport and storage of logs produced significant chloride ion concentrations in paper machine white water. Chloride ion concentrations exceeding 180 ppm were not unusual. Increasing recycle was raising white water temperature and lowering its pH. In addition, brightening reactions were producing significant concentrations of thiosulfate ion, which is now recognized as a promoter of localized corrosion in chloride containing white waters (*3*).

Laboratory and mill electrochemical corrosion testing, as well as immersion testing, showed VK-A171 had superior corrosion resistance in aggressive white water. Thus VK-A171 was chosen for West Coast service. Similar electrochemical testing in 1983 showed that the precipitation hardening duplex stainless steel, Valmet-Kubota VK-A378, also possessed superior localized corrosion resistance.

More recently, additional duplex stainless steels have become available:

- Centrifugally cast Sandusky Alloy 86
- Forged Pasco PM-2-1804M[3]
- Forged Pasco PM2-2106MC.

This paper presents the results of electrochemical corrosion testing of these alloys, as well as VK-A378 and Alloy 75.

Experimental procedures

Simulated white water was made up using reagent grade chemicals and distilled water to duplicate the relevant inorganic content of paper machine white water. **Table I** gives the synthetic white water composition. **Table II** gives the compositions of the alloys tested.

Potentiodynamic polarization was used to determine each alloy's crevice corrosion breakdown potential, E_b, in deaerated simulated white water. Potential monitoring was then performed for several days in aerated simulated white water to determine the alloy's stable corrosion potential, E_c. Crevice corrosion resistance, CCR, was expressed as $E_b - E_c$. CCR>200 mV offers a desirable margin of safety.

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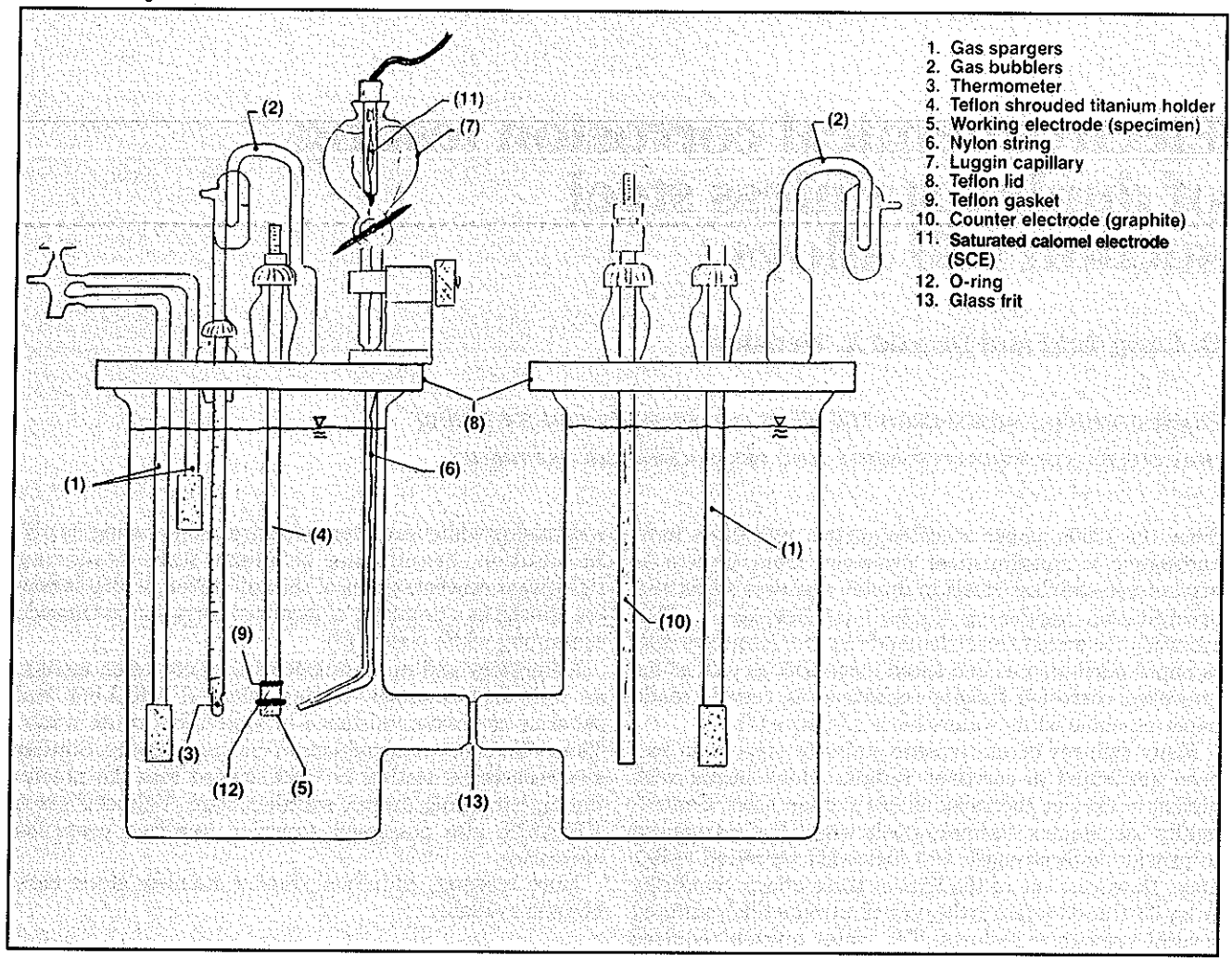
[1]Sandusky Foundry and Machine Co., Sandusky, Ohio.
[2]Valmet Corp., Jyvaskyla, Finland; Kubota Ltd., Osaka, Japan.
[3]Pacific Steel Mfg. Co. Ltd., Toyama, Japan.

1. H-cell configuration



Potentiodynamic polarization

Electrodes. Cylindrical electrodes (2 cm^2 exposed surface area) were prepared for each alloy by machining (where necessary) to 0.25 in. diameter followed by mechanical polishing to 600 grit. Each electrode was drilled and tapped [5-40 national coarse (NC)] so that it could be threaded onto an electrode holder.

Viton O-rings (0.25 in. inside diameter) were fitted around the cylindrical test electrodes to create a reproducible crevice. This O-ring crevice enhances reproducibility, gives a relatively distinct breakdown potential, and makes the test more severe than a simple pitting breakdown test.

An insulating glyptal[4] varnish was painted on the top surface of the electrode to prevent crevice corrosion at the nonreproducible junction between the test electrode and the electrode holder.

Polarization cell. An H-Cell was employed. It included a graphite rod counter electrode and a saturated calomel reference electrode (SCE) maintained at room temperature in a reservoir above the Luggin capillary

[4]Canadian General Electric G-1202, Glyptal Varnish.

I. Synthetic white water composition

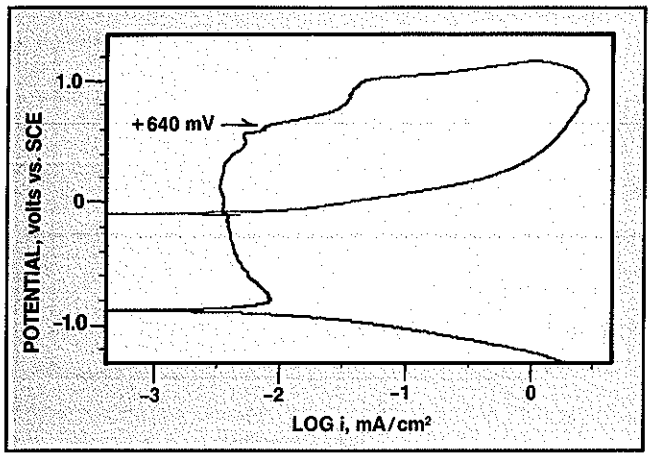
NaCl	300 ppm
Na_2SO_4	900 ppm
$Na_2S_2O_3$	15 ppm
Temperature	50°C
pH	4.0

II. Suction roll alloy compositions

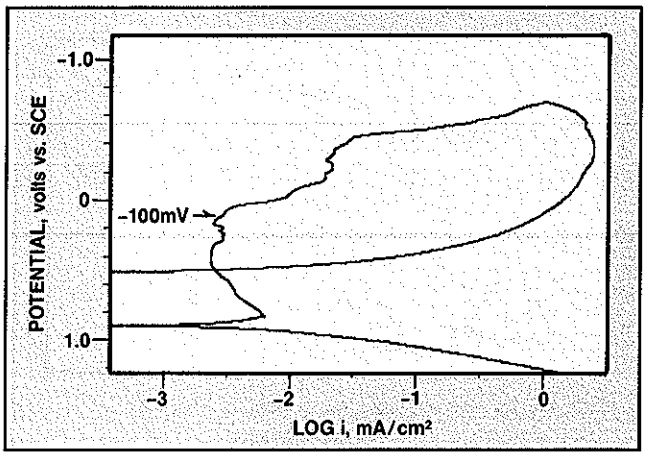
	Composition					
Alloy	*C*	*Cr*	*Mo*	*Ni*	*Si*	*Cu*
VK-A378*	0.06	20.3	2.03	5.5	1.01	3.5
Alloy 86	0.01	26.2	0.04	6.7	0.72	1.77
PM-2-1804M	0.08	19.2	2.7	4.2	0.93	...
PM-2-2106MC	0.07	21.5	1.90	6.05	0.62	...
Alloy 75	0.02	26.0	...	6.8	0.5	...

*Also contains proprietary additions of tungsten and nitrogen.

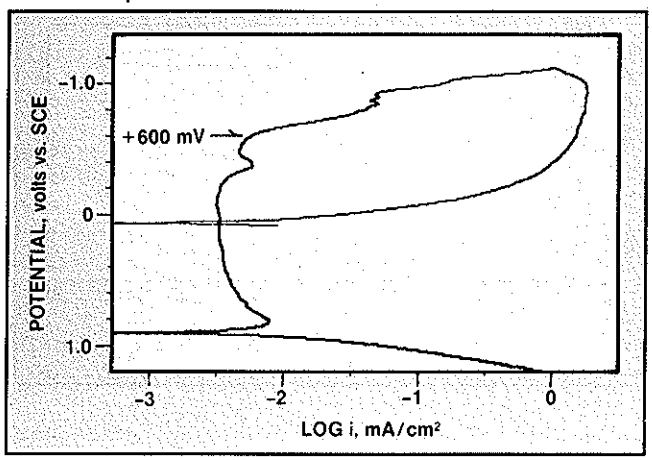
2. Alloy 86 polarization curve



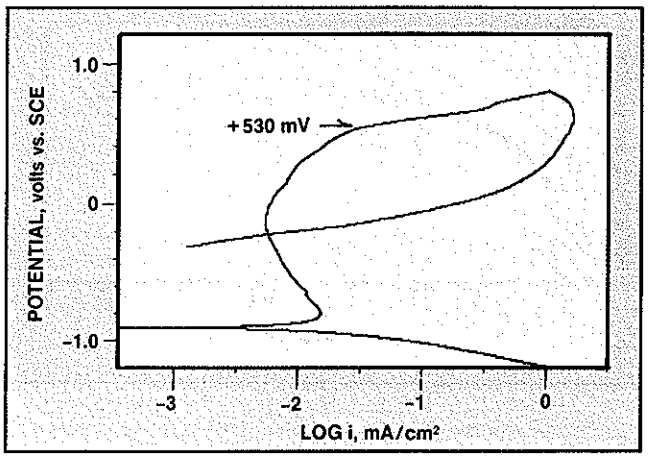
3. Alloy 75 polarization curve



4. VK-A378 polarization curve.



5. PM-2-1804M polarization curve.



(**Fig. 1**). The test solution was continuously purged with K-grade nitrogen bubbled through an O_2 scavenging column.

Instrumentation. A PAR[5] Model 273 Potentiostat/Galvanostat equipped with a software controlled Model 351 Corrosion Measurement System was used to perform polarization scans.

Procedure. All scans were performed using a rapid/slow potentiodynamic scan technique developed for use in mildly acidic electrolytes. The general procedure was as follows:

1. The test solution was deaerated for about one hour. The test electrode was then introduced into the H-cell under open circuit conditions and the corrosion potential monitored for about 45 min.
2. The test electrode was then placed under potentiodynamic control and scanned at 16.7 mV/s in the negative direction from the corrosion potential. The scan was reversed at a current density of -10 mA/cm². When the potential rose to -1.4 volts, potentiostatic control was temporarily stopped so the cathodic curve could be stored. The purpose of this initial negative scan was to remove surface oxides and contaminants, thus yielding a reproducible surface for testing.
3. The test electrode was then scanned at 0.2 mV/s in the positive direction, starting at -1.5 volts.
4. The positive scan was continued past the breakdown potential E_b until a current density of 1 mA/cm² was reached. The scan was then reversed and continued in the negative direction (still at 0.2 mV/s). The scan was stopped and the polarization curve stored when the repassivation potential was reached.

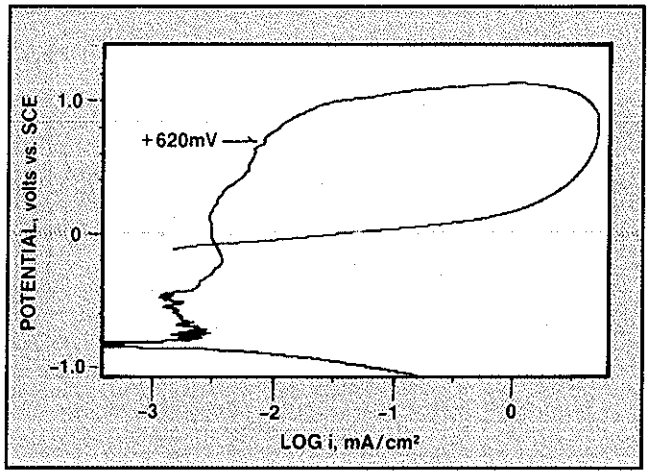
Potential monitoring

An electrode specimen of each alloy was placed in a test cell containing aerated simulated white water of the same composition used for the polarization scans. The potential of each alloy vs. a Lazaran[6] reference electrode (silver/silver chloride) was monitored over time. A saturated calomel reference electrode was not used during this test since it would add additional chloride ion to the test cell. The saturated calomel reference electrode generates a potential of +43 mV vs. the Lazaran reference electrode; for convenience all results are reported vs. the saturated

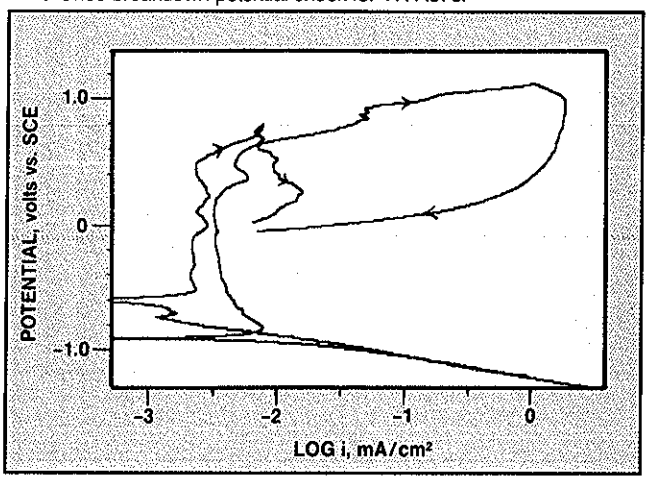
[5]EG&G Princeton Applied Research, Princeton, N.J.

[6]Beckman Industrial Corp., Cedar Grove, N.J.

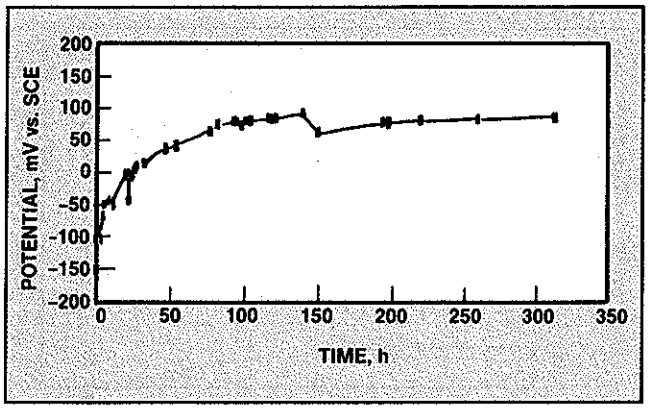
6. PM-2-2106MC polarization curve.



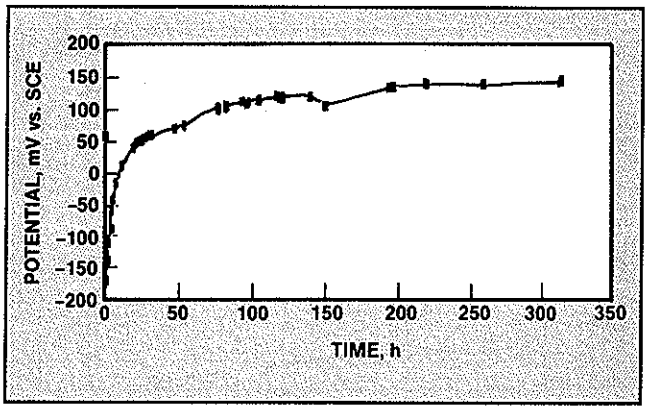
7. Crevice breakdown potential check for VK-A378.



8. Alloy 86 open circuit potential in aerated simulated white water



9. VK-A378 open circuit potential in aerated simulated white water



calomel reference electrode. The simulated white water was periodically analyzed and its composition adjusted as necessary to compensate for thiosulfate ion depletion.

When the open-circuit potential had stabilized (indicating passive film formation), the specimens were removed (total immersion time of 13 days). The final open circuit potential E_c was recorded. Each electrode was visually inspected for localized corrosion.

Results

Polarization curves

Figures 2–6 show typical polarization curves. Crevice breakdown potentials are indicated by arrows. Once breakdown occurred, all alloys experienced severe crevice corrosion beneath the O-ring.

Even with the O-ring crevice, the breakdown potential was sometimes indistinct. To ensure breakdown had actually occurred, scans for each alloy were reversed at potentials below the apparent breakdown potential. If crevice corrosion had occurred, a "hysteresis loop" would be generated on the backscan; if crevice corrosion had not occurred, the backscan would follow the upscan.

Figure 7 is an example of the procedure for VK-A378. The full polarization curve and a breakdown check curve are superimposed. It is clear that crevice breakdown occurred in the neighborhood of 600 mV vs. SCE. After all tests, the electrodes were carefully inspected for crevice corrosion beneath the O-ring. Crevice corrosion was always found when a hysteresis loop had been generated.

Potential monitoring

Figures 8–11 show the potential monitoring results. Alloy 86, VK-A378, and PM-2-1804M exhibited stable passive potentials. Alloy 75 exhibited a more negative, erratic corrosion potential indicative of localized corrosion. The electrode was found to have suffered both crevice corrosion and pitting during the test. Alloy 86, VK-A378 and PM-2-1804M did not experience localized corrosion. A PM-2-2106MC sample was not available for the potential monitoring test.

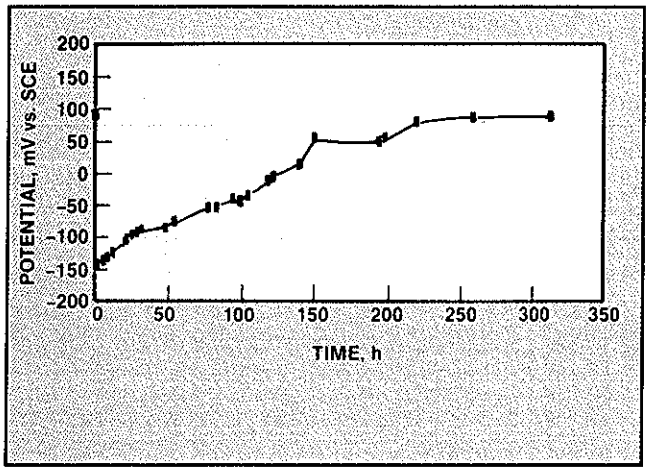
Table III summarizes the E_b, E_c, and CCR values. Alloy 86, VK-A378 and PM-2-1804M had CCR>200 mV.

Discussion

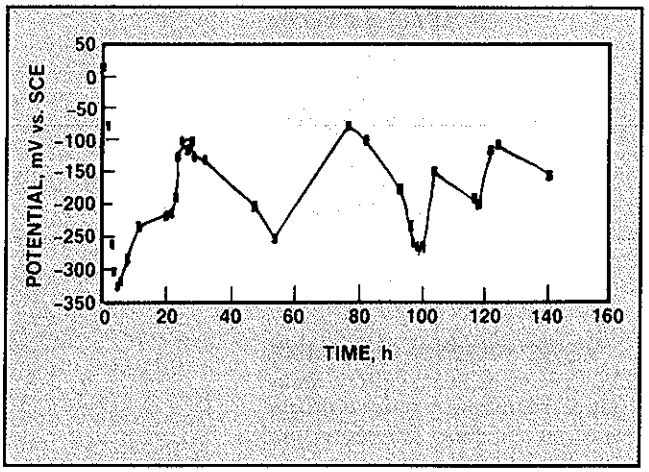
The polarization curves for VK-A378 and Alloy 75 were in good agreement with curves obtained in 1983. This confirmed our faith in electrochemical corrosion testing as a practical, reproducible technique for alloy evaluation.

Electrochemical corrosion testing is performed on a sample from each new suction roll purchased as a check on roll-to-roll variability. Several VK-A378 shells have all shown similar high localized corrosion resistance.

10. PM-2-1804 open circuit potential in aerated simulated white water



11. Alloy 75 open circuit potential in aerated simulated white water



III. Crevice corrosion resistances of suction roll alloys

Alloy	E_b (mV vs. SCE)	E_c (mV vs. SCE)	CCR (mV)
Alloy 86	640	85	555
VK-A378	600	144	456
PM-2-1804M	530	89	441
PM-2-2106MC	620	nd	nd
Alloy 75	-100	...	None

nd = not determined

The localized corrosion resistance of Alloy 86 and PM-2-1804M is essentially equal to that of VK-A378. All three alloys possess CCR>200 mV. Thus the choice among these alloys can now be made on other grounds, such as:

- Maximum tensile residual stresses
- General service record
- Quality; for example, forged is unidirectional and cast has more porosity
- Price
- Delivery time.

Recent work at the Institute of Paper Chemistry (IPC) indicates that the threshold stress intensity range for corrosion fatigue crack growth may also be useful in characterizing suction roll alloys (*4*). An alloy with a high threshold could tolerate larger manufacturing defects and more severe localized corrosion before corrosion fatigue set in.

The IPC work showed that Alloy 75 has a relatively high threshold and thus theoretically could tolerate relatively severe localized corrosion. This may explain Alloy 75's excellent service record.

It should also be noted that Alloy 75 would not be expected to suffer localized corrosion in low NaCl white waters. In-situ potentiodynamic polarization work in machine white water containing only 150 ppm NaCl failed to produce crevice corrosion of Alloy 75. The machine white water was otherwise similar to that used in the laboratory studies.

Conversely, in more aggressive white waters, even the more corrosion resistant alloys would have a reduced margin of safety. For example, E_b for VK-A378 is 280 mV vs. SCE in synthetic white water containing 300 ppm NaCl and only 275 ppm Na_2SO_4.

Conclusions

Electrochemical corrosion testing is a practical, reproducible technique for assessing localized corrosion resistance in paper machine white waters. Three duplex stainless steel suction roll alloys have been shown to possess satisfactory localized corrosion resistance in a relatively aggressive white water.□

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Received June 1, 1988.

Accepted Oct. 10, 1988.

Presented at the 1988 Engineering Conference.