The corrosion behavior of titanium (grade 2) in alkaline peroxide bleach liquors

William E.Wyllie II, Barbara E. Brown, and David J. Duquette

ABSTRACT: An experimental program to determine the effects of hydrogen peroxide (H_2O_2) and of potential corrosion inhibitors on the corrosion behavior of titanium has been developed. Corrosion rates less than 0.25 mm/year were observed in laboratory bleach liquor at pH 12 to which 5 g/L of H_2O_2 were added. At pH 13, with 10 g/L H_2O_2, the corrosion rates were unacceptably high in both sodium hydroxide (NaOH) and laboratory bleach liquor solutions (>8.38 mm/year). The preliminary results of inhibitor studies indicated that the addition of 3.7 g/L sodium silicate or 0.01 g/L calcium nitrate [$Ca(NO_3)_2$] effectively inhibited the corrosion of titanium exposed to 5 g/L of H_2O_2 in NaOH solutions of pH 12. It was also found that in simulated paper mill chemistries, i.e., basic solutions containing 3.7 g/L sodium silicate and 0.6 g/L EDTA (ethylenediaminetetraacetic acid), corrosion rates increased markedly with the addition of 5 g/L H_2O_2. However, subsequent additions of peroxide resulted in corrosion rates which were even lower than those found in NaOH. This is believed to be due to the formation of a black scale on the surface of the sample. The addition of magnesium sulfate ($MgSO_4$) in the 0.1–0.5 g/L range also was shown to inhibit corrosion in the NaOH solution, but only after prior exposure to H_2O_2.

KEYWORDS: Corrosion, corrosion inhibitors, hydrogen peroxide, peroxide bleaching, pH, titanium compounds.

In light of the continued pressure to reduce the use of chlorine dioxide for bleaching purposes in the production of pulp and paper, due to the presumed environmentally hazardous by-product, dioxin, alternative bleaching agents such as hydrogen peroxide are being considered.

The effect of these alternative bleaching agents on the corrosion behavior of materials for systems which may be converted to hydrogen peroxide bleaching, or which may alternate between peroxide and chlorine dioxide bleaching, are presently being studied in both laboratory and in-plant systems. Titanium is one of the materials which is of great interest in these studies because of its typically high corrosion resistance in oxidizing chlorine environments and its wide use in the pulp and paper industry. However, the technical literature reports high corrosion rates of titanium exposed to alkaline hydrogen peroxide *(1, 2).* Under standard operating conditions in a bleaching mill, the mixer can be expected to experience the worst conditions of pH of 12–13 with up to 10 g/L of H_2O_2. However, less severe conditions should exist for the washer, with pH values near 10 and residual H_2O_2 around 2 g/L. Corrosion rates in the washer region must remain less than 0.025 mm/year in order to be acceptable.

This report presents the results of a series of experiments designed to examine the effects of hydrogen peroxide on the corrosion rates of unalloyed titanium ASTM Grade 2

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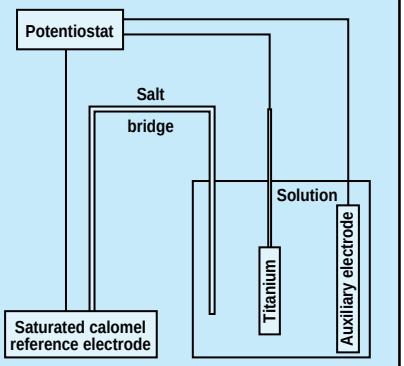
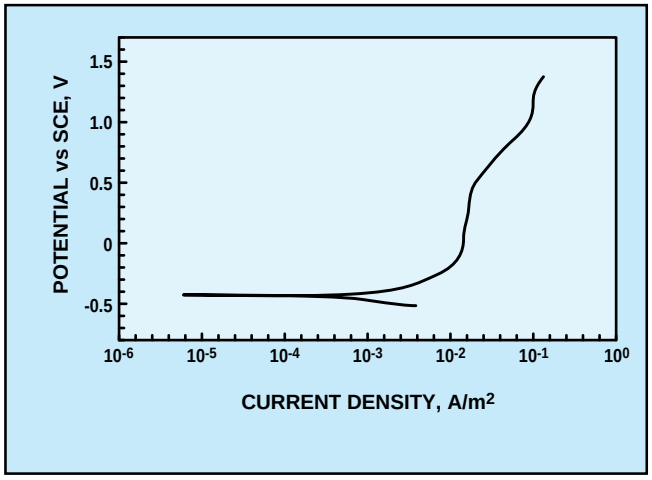
I. Nominal composition of titanium grade 2

Element	*N*	*C*	*H*	*Fe*	*O*	*Ti*
Limits, wt%	0.03 max.	0.10 max.	0.015 max.	0.20 max.	0.18 max.	Balance
Actual, wt%	0.012	0.020	0.0011	0.10	0.120	Balance

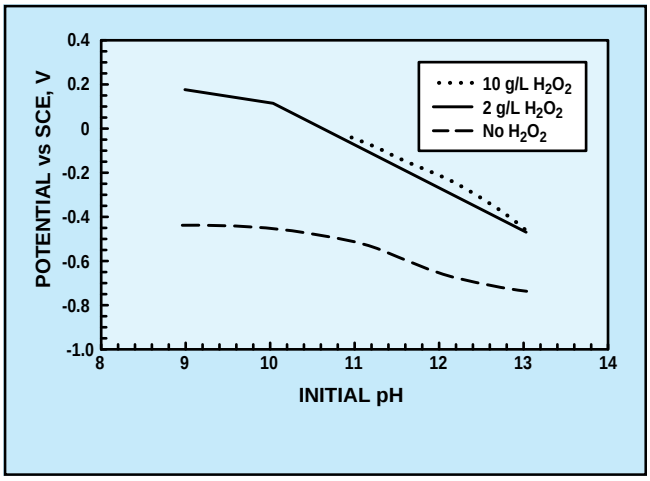
1. Electrochemical setup



2. Polarization curve of titanium in deaerated solution A at pH 9, 76°C



3. The effect of hydrogen peroxide additions on the corrosion potential of titanium in deaerated solution A at varying initial pH levels, 76°C



(UNS R50400)* in laboratory reference solutions of NaOH, in simulated bleach liquor, as well as in laboratory bleach liquor which had been exposed to pulp. The effects of potential corrosion inhibitors are also reported.

Experimental procedure

The nominal composition of unalloyed titanium, ASTM Grade 2, is shown in **Table I**. Samples of titanium Grade 2 were prepared by cutting a 0.19-cm thick sheet into 1.25- x 4.44-cm specimens, with a hole drilled near one end of the sample. The samples were ground through 600 grit SiC, ultrasonically cleaned in ethanol, and then rinsed with distilled water. A Grade 2 titanium wire was inserted through the hole in order to suspend the sample in the test solution while maintaining electrical contact. The sample/wire connection was wrapped with Teflon™ tape to prevent possible galvanic interactions in the solution. Samples were then immersed approximately 2.2 cm into a 300-mL solution, in a Teflon electrochemical cell. An external saturated calomel electrode (SCE) was used as a reference electrode (**Fig. 1**) and connected to the cell with a salt bridge. The offset potential for SCE is +0.242 V vs. SHE (standard hydrogen electrode).

The hydrogen peroxide used in these tests was reagent grade 30% H_2O_2, stabilized with sodium stannate (manufacturer's proprietary concentration).

Experiments were carried out in a laboratory reference solution, con-

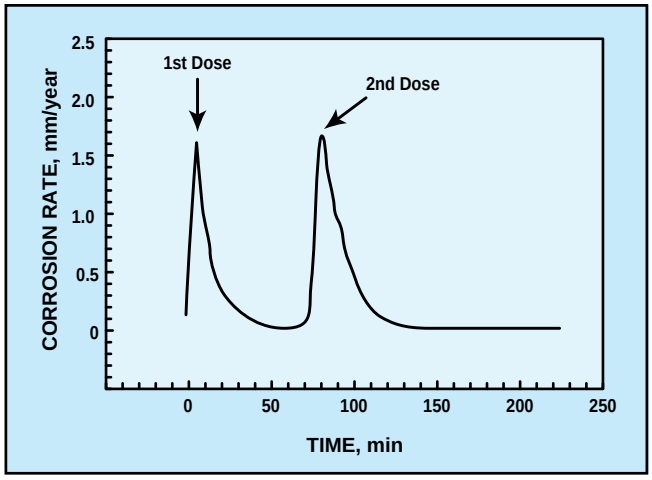
*UNS numbers are listed in *Metals and Alloys in the Unified Numbering System,* published by the Society of Automotive Engineers (SAE) and co-sponsored by ASTM.

II. Composition of the three solution types used in corrosion testing in alkaline solutions of pH 10 - 13

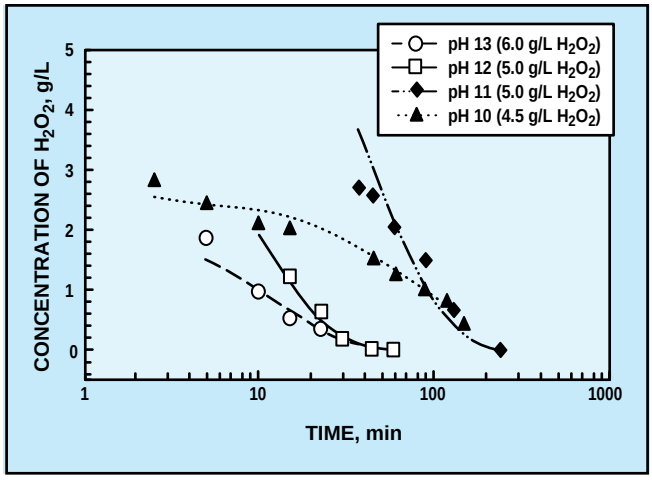
Solution	NaOH	Cl^-	Chelating agents		$Na_2O \cdot xSiO_2$ (x = 3 - 5)	Residual lignin + organic acids	Other
			DTPA[a]	EDTA[b]			
A	As req'd for pH	2 g/L	—-	—-	—-	—-	—-
B	As req'd for pH	2 g/L	—-	0.6 g/L	3.7 g/L	—-	—-
C	As req'd for pH	—-	0.6 g/L max.	—-	—-	Yes	0.05 g/L $MgSO_4$

[a] DTPA = diethylenetriaminepentaacetic acid
[b] EDTA = ethylenediaminetetraacetic acid

4. Typical double dose experiment. Solution A at an initial pH of 12 with 5 g/L of H_2O_2 added for each dose. E_{SET} = +300 mV vs. SCE, deaerated, 76°C.



5. The dependence of H_2O_2 decay on the initial pH of solution A, deaerated, 76°C



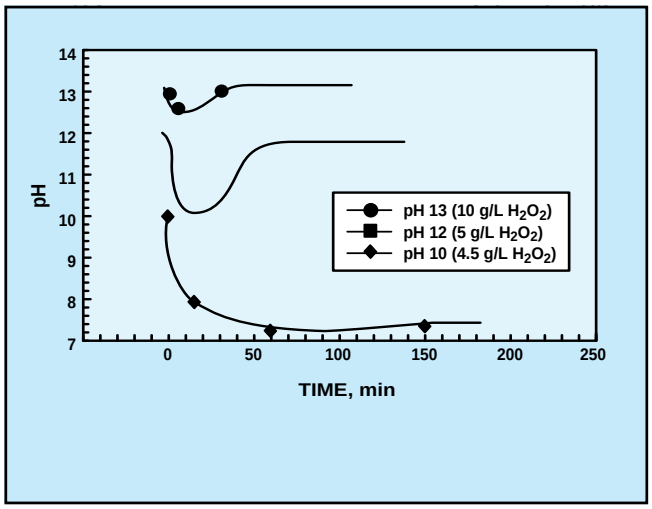
taining only sodium hydroxide of pH 9–13, to which 2 g/L of Cl was added as NaCl (solution A), as well as in laboratory bleach liquor solutions (solution B) and in solutions of simulated bleach liquor that had been exposed to pulp (solution C). The chemistries of solutions A, B, and C are shown in **Table II**. Solution was the filtrate obtained from a laboratory bleaching operation at Kamyr, Inc. located in Glens Falls, NY. The specific conditions of the bleaching operation are shown in **Table III**.

When chemical additions were added to the respective solutions, they were added prior to the introduction of peroxide. Calcium nitrate and magnesium sulfate were tested as possible inhibitors at concentrations of 0.1–0.5 g/L. These chemicals and concentrations were chosen from a list of titanium corrosion inhibitors based on the results of Clerbois *et al. (2)*. The concentrations of chemical additions were also determined to be near the maximum allowable in conventional pulp bleaching plants *(3)*.

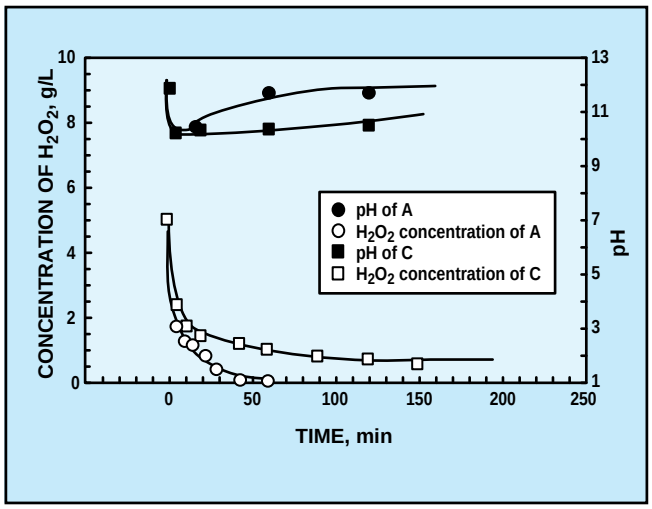
The pH of each solution was fixed prior to immersion of each sample. It was also monitored during each experiment by periodically measuring the pH of 5 mL "grab" samples at room temperature. These samples were returned to the cell afterwards.

Solutions were deaerated with ultra-high-purity argon and heated to 76°C before testing. The purpose of deaeration was to minimize the effects of any reactions in solution, other than the peroxide reactions, on the electrochemical data. Hydrogen peroxide was added in doses of 10 g/L for pH 13 experiments because the rate of peroxide decomposition at high pH values was too rapid to obtain meaningful results with lower doses. For solutions of pH 12,

6. The decomposition and recovery of pH in solution A, deaerated, 76°C



7. Comparison of solutions A and C of initial pH 12 with the addition of 5 g/L H_2O_2. Note the slower decay of peroxide and recovery of pH in solution C. Deaerated, 76°C.



peroxide was introduced in doses of 5 g/L. In order to monitor the decay of the hydrogen peroxide in the solutions, 5-mL "grab" samples were taken at specific time intervals or before a second addition of peroxide, and placed in 3.3% H_2SO_4 to stabilize the hydrogen peroxide. The concentrations of the samples were later determined by using a potassium permanganate titration method *(4)*.

Steady state corrosion potentials were measured at the beginning of each experiment. The potential was then shifted anodically into the passive range and the current was allowed to stabilize. For pH values of 10–13, a potential of +300 mV vs. SCE was selected as a set potential, while for pH 9 a value of +500 mV was selected. **Figure 2** shows that for pH 9, this potential is approximately 900 mV noble to the normally observed corrosion potential in a deaerated solution, and is in the passive current density range. The reason for using such a noble potential is that early experiments show that the addition of peroxide causes the potential to shift noble to the steady-state corrosion potential by 250–610 mV, with the larger potential shifts occurring at lower pH values (**Fig. 3**). The set potential was

III. Conditions of the laboratory bleaching operation from which solution C was produced *(9)*

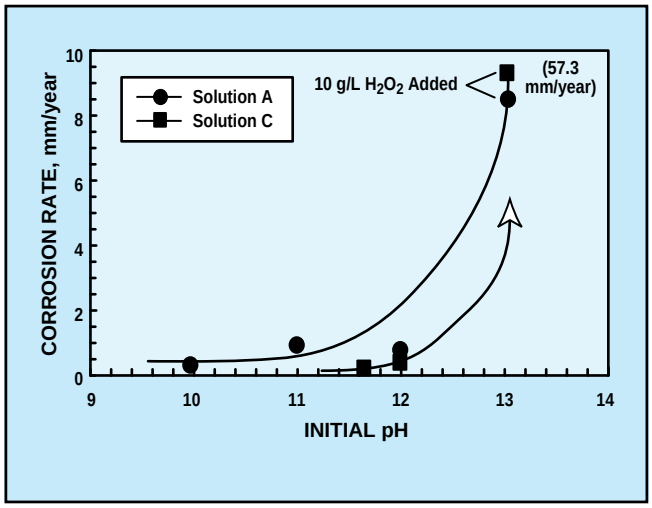
Initial Pulp	
Pulp Sample	*Oxygen delignified softwood pulp*
Pulp weight (oven-dried)	260 g
Initial kappa number	8.8
Initial viscosity	19.1 mPa· s
Bleaching Conditions	*(Bleached twice)*
Consistency, %	10
Temperature, °C	90
Time, min	120
H_2O_2 charge, % on pulp	3.0
NaOH charge, % on pulp	1.2
$MgSO_4$ charge, % on pulp	0.05
Final pH	10.4
Final kappa number	6.2
Final viscosity	15.7 mPa· s
Pulp brightness	60.9% ISO
Approx. lignin removed from pulp, %	0.4

IV. Exponential decay functions[a]

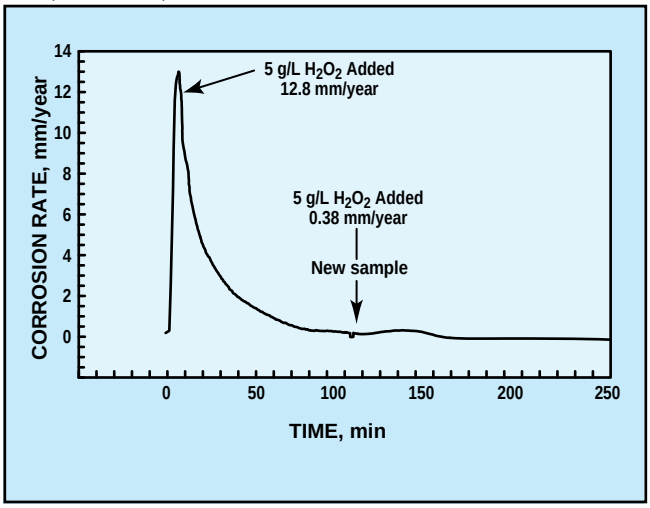
Initial pH	*Function*
11 (5 g/L H_2O_2)	$C = 5.231\exp -0.019797t$
12 (5 g/L H_2O_2)	$C = 5.349 \exp -0.10197t$
13 (10 g/L H_2O_2)	$C = 1.174 \exp -0.13802t$

[a]Functions are not valid for $t < 5$ min
C = Concentration of H_2O_2, g/L
t = Time, min

8. The effect of initial pH on titanium corrosion rates in solution A and C when exposed to 5 g/L H_2O_2. (Note increase in corrosion rate at pH 13 when 10 g/L H_2O_2 added.) Deaerated, 76°C.



9. The corrosion rate of titanium in solution B of initial pH 12 exposed to 5 g/L H_2O_2 in a double dose experiment in which the sample is changed between peroxide additions. E_{SET} = +300 mV vs. SCE, deaerated, 76°C.



V. Effects of repeated doses of H_2O_2 on the corrosion rates of titanium in NaOH solutions of pH 12

Solution (pH=12)	*Corrosion rate, mm/year*	
	1st Dose, 5 g/L H_2O_2	*2nd Dose, 5 g/L H_2O_2*
Solution A	1.27[b]	1.83
Solution B	25.8	0.382
Solution A + 0.6 g/L EDTA	7.26	2.94
Solution A + 3.7 g/L sodium silicate	0.382	0.152
Solution A + 0.01 g/L $Ca(NO_3)_2$	0.508	0.304
Solution B + 0.01 g/L $Ca(NO_3)_2$ [a]	29.8	0.178
Solution B + 0.1 g/L $Ca(NO_3)_2$	27.2	[c]
Solution B + 0.5 g/L $Ca(NO_3)_2$ [a]	[c]	0.280
Solution A + 0.1 g/L $MgSO_4$	1.50	[c]
Solution A + 0.5 g/L $MgSO_4$ [a]	[c]	0.406
Solution A + 0.01 g/L $Ca(NO_3)_2$ + 0.005 g/L $MgSO_4$	0.610	0.686
Solution B + 0.5 g/L $MgSO_4$ + 0.5 g/L $Ca(NO_3)_2$ [a]	21.6	0.356
Solution C	0.050	0.076

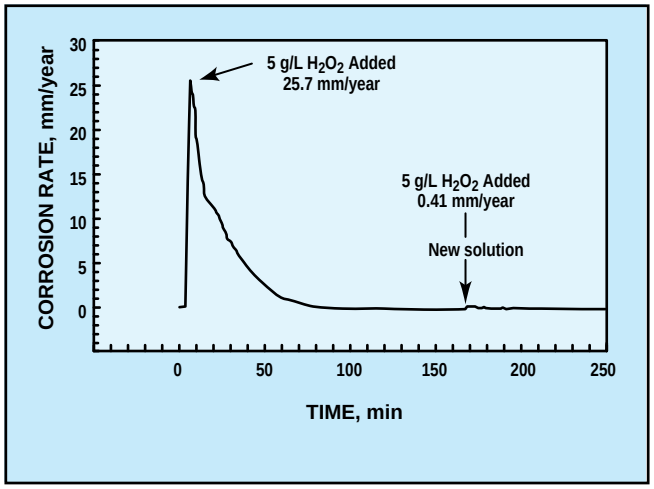
[a] Precipitate formed in solution
[b] Average value
[c] Value not obtained

selected such that it would be noble to the corrosion potential after the addition of peroxide, and therefore remain in the passive current density region.

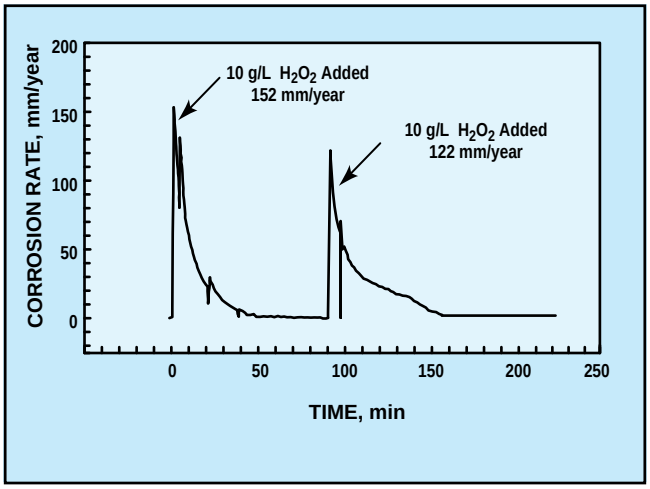
The current was monitored continuously during subsequent additions of peroxide. Spontaneous increases in the current upon the addition of peroxide were used to monitor the effects of peroxide additions on the corrosion rates. After each experiment was completed, the sample surface area that had been immersed in the solution was measured. Using the exposed surface area, the current values were converted to current densities and subsequently to corrosion rates using a titanium valence of 2 *(5, 6)*. The corrosion rates reported for specific peroxide concentrations were derived from the maximum current peaks which were observed upon the addition of peroxide. In general, the current measurements are net values of the anodic and cathodic currents which result from the series of reactions which occur in the presence of peroxide.

For inhibitor studies, the effects of additions of magnesium sulfate and calcium nitrate to laboratory reference solutions (solution A), and to solutions representing typical mill

10. The corrosion rate of titanium in solution B of initial pH 12 exposed to 5 g/L H_2O_2 in a double dose experiment in which the solution is changed between peroxide additions. E_{SET}= +300 mV vs. SCE, deaerated, 76°C.



11. The corrosion rate of titanium in solution B of initial pH 13 exposed to 10 g/L H_2O_2 in a double dose experiment in which the sample had been previously exposed to 5 g/L H_2O_2 in solution B at pH 12. E_{SET}= +300 mV vs. SCE, deaerated, 76°C



chemistries (solution B) were investigated. The concentrations of the mill chemicals used were based on average values *(3)*. Potential inhibitors, $Ca(NO_3)_2$ and $MgSO_4$, as well as the mill chemicals, sodium silicate ($Na_2O{\cdot}xSiO_2$, x = 3 – 5) and EDTA, were tested alone and in combination. Inhibitor testing was carried out in solutions of initial pH values of 12 and 13.

In the inhibitor studies, hydrogen peroxide was added in two doses, of 5 g/L and 10 g/L for pH 12 and 13, respectively. The second dose of peroxide was added after the passive current had restabilized, indicating that the effects of the first dose of peroxide had dissipated. **Figure 4** shows a plot of a typical response of titanium to multiple peroxide additions. The purpose of the second dose was to determine the effect of initial peroxide exposure on titanium and the subsequent corrosion behavior of the alloy when more peroxide was added.

VI. Effects of repeated doses of H_2O_2 on the corrosion rates of titanium in filtrate solutions of pH 13

Solution *(pH=13)*	Corrosion rate, mm/year: 1st Dose, *10 g/L*	Corrosion rate, mm/year: 2nd Dose, *10 g/L*
Solution A	8.16	[a]
Solution C pH 13	57.3	46.2
Solution C pH 13 + 0.6 g/L $Ca(NO_3)_2$	33.8	108
Solution C pH 13 + 0.33 g/L $CaCO_3$	83.2	[a]

[a] No data was obtained for these values

Results

H_2O_2 Decomposition and pH effects

In neutral and acidic solutions, hydrogen peroxide decomposes by the following reaction *(1)*:

$$H_2O_2 \rightarrow OOH^- + H^+ \qquad (1)$$

In alkaline solutions the decomposition reaction is *(1)*:

$$H_2O_2 + OH^- \rightarrow OOH^- + H_2O \qquad (2)$$

With the intermediate perhydroxyl ion (OOH^-) subsequently decomposing according to:

$$OOH^- \rightarrow OH^- + 1/2O_2 \qquad (3)$$

This leads to a net decomposition, Reactions 2 + 3, of:

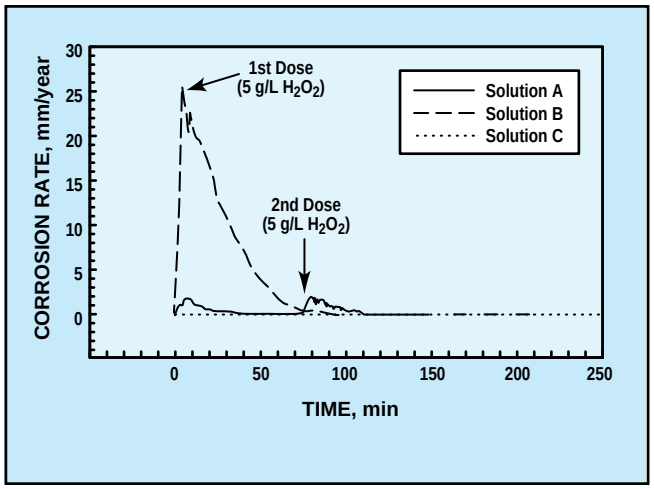
$$H_2O_2 \rightarrow H_2O + 1/2O_2 \qquad (4)$$

Increasing the pH of the solution increases the rate of decomposition Reaction 2 in accordance with Le Chatelier's principle, by increasing the supply of OH^- which drives the reaction forward. **Figure 5** shows the rapid decay of the H_2O_2 as the initial pH of the NaOH solutions was increased from 10 to 13. Immediately after the addition of peroxide, the decay rate is extremely rapid. After about 5 min, the hydrogen peroxide concentration decay follows an approximate exponential decay function (**Table IV**). The exception to this occurred at a pH of 10, where the data did not fit the exponential model very well.

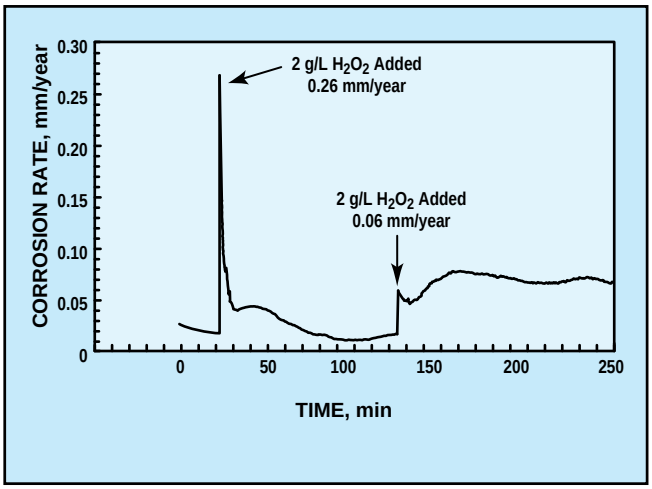
In the presence of peroxide in alkaline solutions, the overall anodic reaction for titanium may be expressed as *(1)*:

$$Ti + OOH^- + 3OH^- \rightarrow Ti(OH)_2O_2 + H_2O + 4e^- \qquad (5)$$

12. Instantaneous corrosion rate data for solutions A, B, and C at initial pH 12, subject to a double dose of hydrogen peroxide. Deaerated, 76°C



13. The corrosion rate of titanium in solution A with initial pH 9 exposed to 2 g/L H_2O_2 in a double dose experiment. E_{SET} = +500 mV vs. SCE, deaerated, 76°C.



In all tests a decrease in pH occurred upon addition of the H_2O_2 **(Fig. 6)**. No attempt was made to readjust the pH immediately after the H_2O_2 was added, although the pH was monitored during testing. This pH decrease is readily explained by the consumption of OH^- in the H_2O_2 decomposition shown in Reaction 2 and to some extent in Reaction 5. However, the pH recovered to nearly its initial value at the end of the H_2O_2 decomposition for most experiments, indicating that Reaction 3 was occurring simultaneously. Based on the time period for the solution pH to recover to its initial value, it appears that Reaction 2 occurs much more rapidly than Reaction 3 in all cases. It was also found that, in the system examined here, H_2O_2 decomposition and the resulting pH decay and recovery were independent of the presence of titanium (i.e., titanium did not appear to catalyze the reactions).

Experiments performed in a laboratory bleach liquor solution which had been exposed to pulp (solution C) showed that the decomposition of H_2O_2 was greatly reduced compared to the laboratory reference solution A of the same initial pH (**Fig. 7**). This is due to the presence of $MgSO_4$ in solution C, which is known to be an H_2O_2 stabilizer. It was also noted that the pH in solution C did not recover to its initial value after the addition of the H_2O_2, even after several days. It is believed that, during the corrosion test, the hydrogen peroxide bleached the lignin in solution C, breaking it down into organic acids such as formic and acetic acids *(3)*.The presence of acids in solution neutralizes the OH^- forming during reaction (3), and explains the persistently lower pH.

From Reaction 5, the corrosion rates are expected to increase with increasing initial pH and hydrogen peroxide concentration (**Fig. 8**). As the pH and/or hydrogen peroxide concentration increase, the availability of OOH^- and OH^- for destabilization of the passive film and for the oxidation reaction is greater, leading to higher corrosion rates.

Effects of chemical additions on the corrosion rate of titanium in solutions A and B

The results of the multiple additions of 5 g/L H_2O_2 to solutions A, B, and C at pH 12 indicate that certain chemical additions to the laboratory reference solution act to inhibit corrosion, reducing the corrosion rates upon subsequent exposure to peroxide. The results of these experiments are shown in **Table V**.

The steady-state corrosion rates of titanium in solutions A and B, prior to the addition of H_2O_2, were 0.041 and 0.048 mm/year, respectively. The addition of 5 g/L H_2O_2 to a pure hydroxide solution at pH 12 (solution A) resulted in a corrosion rate of approximately 1.27 mm/year. After allowing the sample to repassivate, a second addition of peroxide resulted in a similar corrosion rate of 1.83 mm/year. In solution B (simulated mill chemistry), the initial addition of H_2O_2 resulted in a corrosion rate of approximately 25 mm/year; however, a second addition of H_2O_2 resulted in a corrosion rate of only 0.38 mm/year, or only 20% of the corrosion rate observed in solution A, the reference solution.

In the cases where a high corrosion rate was observed upon the application of an initial dose followed by a low corrosion rate for the application of a second dose, it is believed that a highly protective film formed due to the combined reaction of the H_2O_2 and the inhibiting species. H_2O_2 reacting in solution A alone produced a less protective film on titanium, as indicated by the observation of essentially the same corrosion rate upon the application of a second dose of peroxide.

The presence of EDTA in solution A at pH 12 resulted in a corrosion rate of approximately 7.36 mm/year compared to 1.27 mm/year without the addition of EDTA. The second dose of H_2O_2 resulted in a decrease in corrosion rate to approximately 2.5 mm/year, which is larger than the corrosion rates observed in solution A alone. This decrease could be due to a decrease in the available EDTA from interactions during the first peroxide addition.

EDTA alone is ineffective as an inhibitor. EDTA and DTPA (diethylenetriaminepentaacetic acid) are chelating agents which are introduced into the bleaching process in order to react with metal ions, forming complexes which nullify the ability of metal ions to react. It is believed that EDTA actually destabilizes the protective film, perhaps by complexing the metal ions produced at the surface of the material, or directly complexing the film. The EDTA also acts as a catalyst for the higher initial corrosion rates noted for potential inhibitors in combination with the components of solution B.

Sodium silicate is a very effective inhibitor of corrosion for titanium in solutions of pH 12 *(1, 2)*. Table V shows that the corrosion rate observed upon adding 5 g/L H_2O_2 to a basic silicate solution is approximately 0.38 mm/year, and decreases to 0.152 mm/year upon the addition of a second dose of peroxide. In basic silicate solutions with EDTA, solution B, the first exposure of titanium to peroxide apparently results in very high corrosion rates. However, it also appears to result in enhanced corrosion resistance which is retained for subsequent exposures. It is hypothesized that sodium silicate reacts with titanium to form a protective silicate film. However, it has been reported that sodium silicate may result in scale formation in closed water bleaching systems *(1)*. Thus, caution should be exercised in the application of silicates as inhibitors.

The addition of 0.01 g/L of calcium nitrate provides inhibition against corrosion of titanium in reference solution A, the corrosion rate being decreased by a factor of 2.5 after a first dose of peroxide and by a factor of 6 after a second dose. However, if EDTA and silicate are also present, the initial corrosion rate is increased to 29.7 mm/year (approximately the same value as that which is observed in the absence of the nitrate in solution B). When a second dose of peroxide is added the corrosion rate decreases to approximately 0.176 mm/year, a value essentially the same as that observed without the calcium nitrate addition. Increasing the nitrate concentration to 0.1 and 0.5 g/L yields similar results, although at 0.5 g/L a precipitate was observed in the solution; presumably calcium silicate which is insoluble at 76°C. Thus it appears that, while calcium nitrate is effective in inhibiting corrosion of titanium in basic solutions, the complexing agents (EDTA or DTPA) which are present in mill chemistries significantly enhance the corrosion of titanium upon initial exposure to H_2O_2.

At a concentration of 0.1 g/L in solution A, $MgSO_4$ showed no inhibiting effects after initial exposure to H_2O_2, maintaining the same corrosion rate as solution A after the first dose. However, upon a second exposure, with 0.5 g/L of $MgSO_4$ present, the corrosion rate was reduced by a factor of 5. This shows that $MgSO_4$ is also an effective inhibitor on subsequent exposure to peroxide.

Combining $MgSO_4$ and $Ca(NO_3)_2$ in solution A, at concentrations of 0.01 and 0.005 g/L, or in solution B at concentrations of 0.5 g/L each, did not result in a significant improvement over the addition of each component separately. In solution A, the corrosion rates for both the first and second peroxide addition were approximately 0.635 mm/year, while in solution B the corrosion rates were the same as in solution B with no additions present.

Calcium and magnesium provide some corrosion inhibition in solutions of pH 12, which is enhanced for subsequent exposures of H_2O_2. It is believed that the formation of $Mg(OH)_2$ or $Ca(OH)_2$ on the sample surface may decrease the corrosion rate upon the second addition of peroxide. The combination of these two inhibitors provides little improvement over the addition of each independently. It should be noted that the effects of either calcium or magnesium are minor when compared with the inhibiting effect of silicate for periodic exposure of titanium to peroxide solutions.

Determining the cause of lower 2nd dose corrosion rates

In order to determine the mechanism causing a decrease in corrosion rate upon a second addition of H_2O_2 in solution B at pH 12, a fresh titanium sample was substituted between peroxide additions. **Figure 9** shows that the corrosion rate of the new sample, in a solution which had been previously exposed to H_2O_2, was about 0.38 mm/year upon the addition of 5 g/L of H_2O_2 compared to a corrosion rate of 12.8 mm/year of the original sample. EDTA was present in solution B and, as mentioned previously, was considered to promote higher corrosion rates via its action as a complexing agent. The lower corrosion rate for the new sample shows that EDTA was consumed upon the first peroxide addition, so that little or no uncomplexed EDTA was present at the second peroxide addition to promote higher corrosion rates on the new sample.

In order to verify the effect of EDTA on the corrosion rate of titanium, an experiment was carried out in which the test solution was changed between peroxide additions. The original sample was used in both solutions. The results of this experiment are shown in **Fig. 10**. It can be seen that the sample showed an initially high corrosion rate upon the first addition of H_2O_2; however, the

second addition of peroxide in a fresh solution caused the corrosion rate to decrease to 0.41 mm/year, similar to prior double dose experiments. Upon removal of the sample after both exposures, a black scale was evident on the submerged portion of the sample. This scale was also observed in the previous experiments in solution (B) after multiple exposures of H_2O_2. These results indicate that the scale present on the sample, probably due to sodium silicate, protected it from the effects of the newly introduced EDTA in solution.

It appears that exposure to peroxide in pH 12 solution B resulted in the formation of a protective scale, which imparted corrosion resistance upon subsequent peroxide exposures. Another experiment was performed in order to determine if this scale could withstand the worst case scenario of 10 g/L hydrogen peroxide in pH 13 solution B. A sample was exposed to 5 g/L of peroxide in pH 12 solution B, then transferred into a solution of pH 13 and exposed to 10 g/L of peroxide. As can be seen in **Fig. 11**, the scale does not withstand the extreme conditions of elevated pH and peroxide levels. In addition, the scale is easily scraped off, and may fail to protect titanium even at pH 12 under service conditions of pulp abrasion.

Effects of chemical additions on the corrosion rate of titanium in bleach liquor

It is significant to note that in the pH 12 solution C, the corrosion rate which is measured at the introduction of a second dose of H_2O_2 is essentially the same as that measured after the introduction of the first dose, and is significantly lower than any other corrosion rate values in Table V. In other studies, it has been shown that the corrosion rates of titanium during in-plant testing conditions (pH = 11.2) are actually much lower than what has been predicted by testing in laboratory reference solutions of sodium hydroxide (solution A) alone *(8)*. This effect has also been observed in experiments conducted in laboratory bleach liquor exposed to pulp (solution C) at pH 12, in which the corrosion rates were much less than what was observed in solutions A or B (**Fig. 12**). It is hypothesized that the corrosive action of H_2O_2 on titanium at pH 12 is less in the presence of pulp [in-plant tests *(8)*] or the lignin that results from exposure to pulp (solution C tests) because H_2O_2 is consumed in the bleaching process. Other chemicals also are present in the in-plant tests *(9)*, which may act to inhibit corrosion. For example, solution C contains $MgSO_4$, which has been shown in the present program to inhibit the corrosion of titanium in solutions of pH 12 upon subsequent exposures to H_2O_2.

However, **Table VI** shows that in solution C at pH 13, with 10 g/L H_2O_2 additions, the corrosion rates are extremely high. The corrosion rate of the titanium in pH 13 solution C was measured as 7–8 times that of solution A at the same pH, and showed only a small decrease when a second dose of peroxide was admitted to the solution. The presence of neither lignin nor $MgSO_4$ appear to be sufficient to inhibit corrosion. The addition of 0.33 g/L of calcium carbonate, as a possible inhibitor, resulted in a measurable increase in the corrosion rate, whereas the addition of 0.6 g/L of calcium nitrate decreased the corrosion rate for the first dose, but resulted in a significant increase in the corrosion rate for a subsequent peroxide dose. In any event, the inherent corrosion rates are so large that neither calcium carbonate or calcium nitrate could be used as inhibitors for the corrosion of titanium in solution (C) at pH 13.

Determination of a lower bound operating condition

One goal of this study was also to see if there was a "lower bound" operating condition which would produce corrosion rates of less than 0.025 mm/year in a washer environment. Experiments in pH 9 solution A (NaOH with 2 g/L Cl^-) showed that the first addition of 2 g/L H_2O_2 caused a corrosion rate of 0.26 mm/year and the second addition caused a factor of 4 decrease in the corrosion rate (**Fig. 13**). It is of interest that the second addition of peroxide caused a lower corrosion rate than the first addition, as this effect was not found at higher pH values in solution A. It should be noted that the corrosion rates presented in this paper show the general trends rather than absolute rates under different conditions of pH, inhibitors, and H_2O_2 concentration. It is possible that the corrosion rates reported here are actually higher than what might be found under actual operating conditions, due to the measurement of net current. Titanium may actually experience the "lower bound" corrosion rates of 0.025 mm/year or less in a pulp bleaching operation at pH 9 after being pre-conditioned by initial exposure to H_2O_2.

Conclusions

Some preliminary conclusions based on these results are as follows:

1. Hydrogen peroxide added to a basic solution decays exponentially as a function of time. The reactions that follow its decay cause the pH of the solution to initially decrease by a large amount, then recover with time.
2. Magnesium and/or calcium salts provide some inhibition of titanium corrosion in solutions of pH 12 containing 5 g/L of H_2O_2; however, silicate is a much more effective inhibitor. EDTA appears to be a corrosion accelerator.
3. Sodium silicate appears to provide inhibition in the case of periodic doses of peroxide at or below pH 12 by the formation of a black scale. However, inhibitor treatments with silicates must be care-

fully considered to minimize heavy silicate buildup, especially in closed water systems. In addition, it is possible that this scale may be abraded off by pulp during the bleaching operation and result in a return to elevated corrosion rates.

4. In laboratory bleach liquor solutions that had been exposed to pulp, and in reference solutions of NaOH at nominal pH 12, titanium shows low corrosion rates upon exposure to 5 g/L H_2O_2. However, in the same solutions at pH 13, titanium shows unacceptably high corrosion rates when exposed to 10 g/L H_2O_2.
5. Neither calcium nitrate or calcium carbonate is an effective inhibitor in laboratory bleach liquor solution at pH 13.
6. Results in solution A indicate that pH 9 is possibly a lower bound operating condition for a washer environment after pre-conditioning, especially in the presence of pulp or residual pulp filtrate.

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