

Practical windows and inhibitors for Grade 2 titanium use in alkaline peroxide bleach solutions

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ABSTRACT: *The authors present a corrosion database for Grade 2 titanium using laboratory weight-loss testing in uninhibited and inhibited alkaline 0.2-0.3% H_2O_2 solutions at 65–80°C. Despite titanium's limited resistance to uninhibited peroxide solutions, useful resistance dramatically expands in solutions containing inhibiting species commonly existing in bleach plant processes. Effective inhibitors are Ca^{+2} , Mg salts, and silicate. Using this corrosion database provides expanded application guidelines for acceptable use of Grade 2 titanium in Ca^{+2} ion-inhibited solutions containing 0.3% maximum H_2O_2 by weight at 65°C, 70°C, and 80°C.*

KEYWORDS: *Alkaline earth metals, bleaching, calcium, chelating agents, chemical properties, complexing agents, corrosion inhibitors, corrosion resistance, inhibitors, ions, oxidative bleaching, peroxide bleaching, pH, titanium.*

Unalloyed titanium has been a traditional material of construction for critical equipment in pulp and paper bleach plants (1–3). It has superior resistance to highly oxidizing, chlorine-based bleaching chemicals. Typical applications include drum washers; diffusion (displacement) bleacher and washer systems; diffusion mixers; chlorine dioxide generators; bleach storage

tanks; and transfer piping systems in C, D, and E stages of the Kraft bleach plant.

Driven by environmental constraints, alkaline, peroxide-bleaching reagents are replacing many chlorine-based bleach processes worldwide. Although they are more costly, the alkaline peroxide bleaches do not form chlorinated organics (dioxins) and decompose to environ-

mentally safe water and oxygen by-products.

Previous work has recognized the limited, uniform, corrosion resistance of titanium to uninhibited alkaline peroxide solutions (4, 5). This phenomenon raises serious concern about the compatibility of emerging peroxide bleaching processes with existing titanium bleach plant equipment and the selection of titanium for future plant equipment. This is particularly true where bleach process flexibility (“swing” capability between both bleaching systems) is desirable. Although increasing pH, temperature, and H_2O_2 concentration exacerbate titanium corrosion (4), several common background ions such as Ca^{+2} (5–8) are potent corrosion inhibitors in these peroxide solutions. Silicates and magnesium salts intentionally added to stabilize peroxide bleach solutions may also inhibit titanium corrosion at higher levels (4, 6, 8). Although their influence in titanium corrosion has not been defined to date, chelating agents such as ethylenediaminetetraacetic acid (EDTA) and diaminetriethylenepentaacetic acid (DTPA) are typically added as well to thwart accelerated peroxide decomposition by complexing unwanted catalytic metal ions of iron, copper, nickel, manganese, and molybdenum.

Our laboratory study established a useful corrosion database on Grade

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I. Matrix of test conditions for corrosion evaluation of Grade 2 titanium samples in hot, alkaline-peroxide solutions

H_2O_2 concentration, % by weight	Temperature, °C	pH	Inhibitor addition	Chelating agent addition, molar ratio, X:Ca ⁺²
0.2–0.3	65	12.0	None	None
	70	10.0–12.5	None	None
	75	12.0	None	None
	80	9.5–12.0	None	None
	65	12.5	1 ppm Ca ⁺²	None
	70	11.0–12.0	1–100 ppm Ca ⁺²	None
	80	10.0–12.0	1–200 ppm Ca ⁺²	None
	70	12.0	50–200 ppm Mg ⁺²	None
	70	12.0	100 ppm Ca ⁺²	None
			+100 ppm Mg ⁺²	
	70	12.0	100–10,000 ppm SiO ₃ ⁻²	None
	70	12.0	100 ppm Ca ⁺²	EDTA (2.5:1, 1:1, 1:2)
	70	12.0	100 ppm Ca ⁺²	DTPA (2.5:1, 1:1, 1:2)
0.3–0.4	70	12.5	None	None
	80	12.5	None	None
	70	12.5	200 ppm Ca ⁺²	None
	70	12.5	100 ppm Ca ⁺²	EDTA (1:1, 1:2)
	80	12.5	200 ppm Ca ⁺²	None
	80	12.5	100 ppm Ca ⁺²	EDTA (1:1, 1:2)

2 titanium in uninhibited and inhibited alkaline peroxide solutions typically used in pulp and paper bleaching processes. The practical alloy corrosion performance windows are 0.2–0.4% H₂O₂ solutions over the pH range of 9.5–12.5 and temperatures of 65–80°C. The study evaluates the effects of various naturally-occurring and intentionally-added corrosion inhibitor species and chelating agents within these peroxide bleaching process parameters to formulate guidelines for successful titanium use.

Experimental

Test plan

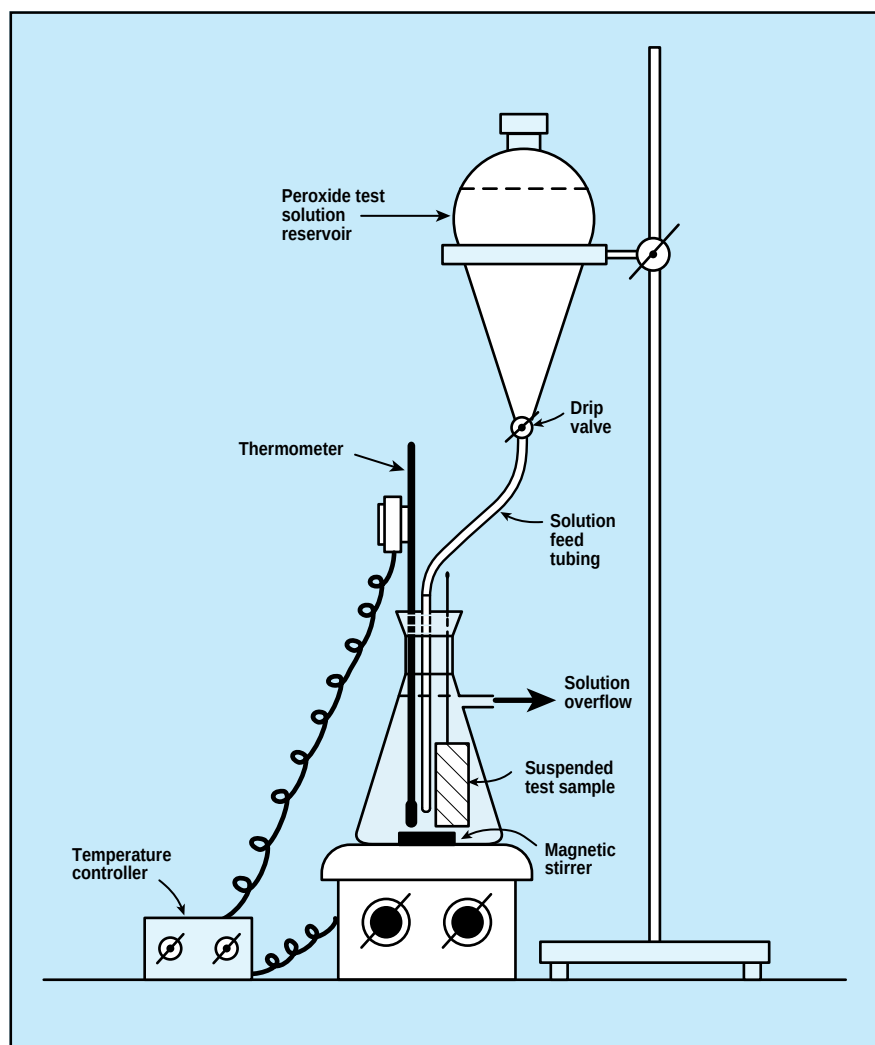
Table I presents the detailed laboratory corrosion test plan. The plan shows the general (uniform) corrosion resistance of Grade 2 titanium within a window of hydrogen peroxide solution concentrations, pH levels, and temperatures typically encountered in pulp and paper peroxide bleach plants. The specific test-solution conditions are H₂O₂ concentrations of 0.2–0.3% by weight, pH levels of 9.5–12.0, and temperatures of 65–80°C. To account for infrequent but possibly severe process upset conditions in actual bleaching

systems, the study also evaluated peroxide levels of 0.3–0.4% combined with an elevated pH of 12.5 at 70°C and 80°C.

After measuring baseline corrosion rates in these uninhibited peroxide solutions, the authors examined additions of common, naturally-occurring (Ca⁺²) and intentionally-added (MgSO₄ and Na₂SiO₃) corrosion inhibitors in this framework of conditions. The evaluation of Ca⁺² and Mg⁺² ion solution additions was over the range of 1–200 ppm. Assessment of silicate addition was at 100–10,000 ppm.

Due to the strong inhibition of Ca⁺² ions observed in these tests, the final stage of corrosion testing focused on

1. Schematic of laboratory test for weight-loss corrosion testing of titanium samples in hot alkaline peroxide solutions



identifying possible interactions between the chelating agents EDTA or DTPA and the inhibiting Ca^{+2} ion in alkaline peroxide solutions. Investigation of several molar ratios of EDTA or DTPA: Ca^{+2} used ion levels of 100 ppm and 200 ppm at pH levels of 12.0 and 12.5 with temperatures of 70°C and 80°C.

Short-term weight-loss tests conducted in continuously refreshed peroxide solutions determined all corrosion rate data.

Test material

Typical mill-annealed 1.5 mm (0.063 in.) Grade 2 (unalloyed) titanium sheet stock was the test material. This product contained 0.12% oxy-

gen and 0.10% iron. The sheet underwent shearing, deburring, and pickling in 35% by volume HNO_3 and HF mixture to produce a test coupon size of 64 x 18 x 1.5 mm (2.5 x 0.7 x 0.060 in.). After deionized water rinsing and drying, the coupons were weighed to ± 0.0001 g accuracy before exposure. Weighing after testing was to the same degree of accuracy.

Test solution preparation

The peroxide test solution was distilled and deionized water containing appropriate additions of certified ACS grade 30% H_2O_2 solution. Addition of concentrated NaOH solution adjusted this solution to the desired

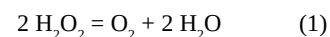
pH using a calibrated pH meter at room temperature. For inhibited peroxide solution makeup, Ca^{+2} , Mg^{+2} , and silicate ion species additions were with granular reagent grade $\text{Ca}(\text{OH})_2$, MgSO_4 , and Na_2SiO_3 compounds. Thorough mixing after these additions into the solution before final pH adjustment ensured maximum solubilization. EDTA was added in the form of a 39% solution by weight of a commercially available tetrasodium ethylenediaminetetraacetate. The DTPA was added in the form of a 40% solution by weight of commercially available pentasodium diethylenetriaminepentaacetate.

Corrosion testing

Figure 1 shows a schematic of the weight-loss corrosion test. The test sheet coupon was suspended and exposed to the H_2O_2 test solution contained in a 300 mL PTFE Erlenmeyer flask. A hot plate heated the flask to maintain solution temperature to $\pm 1^\circ\text{C}$. A magnetic stirring bar rotating at the flask bottom continuously agitated this solution at a vigorous rate. A valve continuously fed unheated, fresh peroxide solution from a 2 L PTFE reservoir. The premixed feed solution entered the test flask through a dip tube near the bottom where it mixed instantaneously with the heated bulk solution. This essentially eliminated solution temperature and H_2O_2 concentration gradients within the test flask. Excess solution continuously overflowed and drained from the flask side-arm.

Corrosion test procedure

A serious challenge with laboratory test exposures in alkaline peroxide solutions is rapid decomposition of H_2O_2 according to the following reaction:



This requires continuous and rapid refreshment and replenishment of test solutions with additional peroxide to achieve steady-state test con-

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ditions. Since sustained, long-term test conditions are extremely difficult to maintain in the laboratory at these high pH, temperature, and peroxide levels, this program selected more manageable, short-term, weight-loss exposure tests. The tests in this program were 1 h duration at solution temperatures at or below 70°C and 30 min duration above this temperature with higher peroxide levels of 0.3–0.4%.

Test solutions were prepared with H_2O_2 concentrations significantly higher than the desired test level. During test solution heating, the peroxide concentration gradually decayed. After reaching the desired peroxide level, the titanium test coupons were immersed in the test solution to begin each test. To counteract the rapid peroxide decomposition, fresh reservoir solution continuously dripped into the flask. Despite solution refreshment, it was not possible to maintain a single, accurate value of H_2O_2 concentration in the 0.5–1.0 h test period. Instead, the H_2O_2 concentration was controlled within a 0.1% by weight window. The data tables report the range.

The key to control of these corrosion test conditions is the frequent measurement of solution pH and H_2O_2 level. In these tests, both parameters were measured at 10 min intervals. A classic, wet redox titration method determined the peroxide concentration. This wet analytical method involves a concentrated KI solution containing starch indicator to which there is addition of a specific aliquot of test solution. Back-titration with a standardized $Na_2S_2O_3$ solution follows. A port in the lid of the test flask allowed rapid withdrawal of solution samples for analysis.

Due to the short-term test exposures, it was vital to expose sufficient coupon surface area to achieve significant coupon weight loss for accurate corrosion rate determinations. Weighing and exposing three

II. Corrosion rate of Grade 2 titanium as a function of pH in 0.2–0.3% H_2O_2 solutions at 70°C and 80°C

Temperature, °C	pH	Corrosion rate	
		mm/y	mils/year
70	10.0	0.07	2.7
	10.3	0.28	11
	10.6	0.91	36
	10.9	2.44	96
	11.2	0.48	19
	11.3	1.55	61
	11.5	2.06	81
	12.0	8.89	350
	12.1	8.43	332
	12.2	10.90	429
	12.4	10.62	418
80	9.5	0.12	4.7
	10.0	1.73	68
	11.2	5.56	219
	12.0	13.78	543

test coupons per test provided a single corrosion rate determination.

Results

Uninhibited peroxide solutions

Table II shows the corrosion rate values for Grade 2 titanium exposed to uninhibited 0.2–0.3% H_2O_2 solutions over the pH range of 9.5–12.5 and temperatures of 70°C and 80°C. **Figure 2** depicts these results graphically as a function of solution pH. The data confirms that both increasing pH and temperature dramatically increase titanium corrosion rate in alkaline peroxide solutions. For these totally uninhibited solutions, acceptable corrosion rates are less than 0.127 mm/year or 5 mils/year. Corrosion only occurred at pH levels below 10.0 at 70°C and well below pH 10.0 at 80°C. The plot in Fig. 2 suggests that corrosion rates at 70°C gradually increase up to pH 11.5 and then rapidly increase above this pH value.

The plot in **Fig. 3** shows the effect of temperature on titanium corrosion rate in 0.2–0.3% H_2O_2 solution at pH 12.0. The results indicate low acceptable corrosion rates at 65°C with values that rise rapidly and level off within the 70°C and 75°C win-

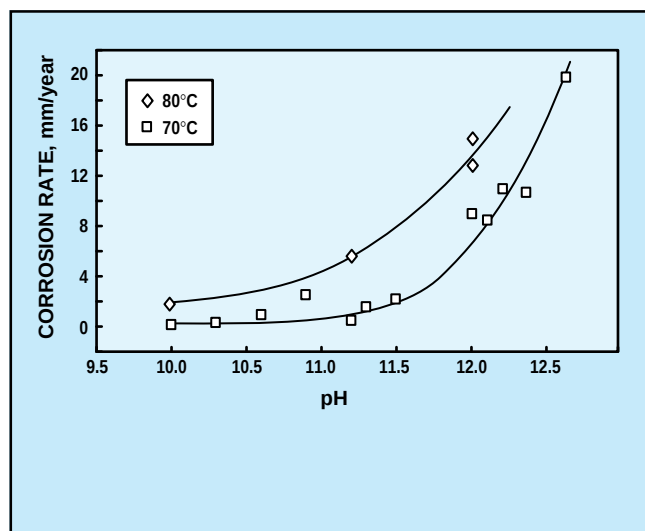
dow. Rates rise steeply again between 75°C and 80°C.

Inhibited peroxide solutions

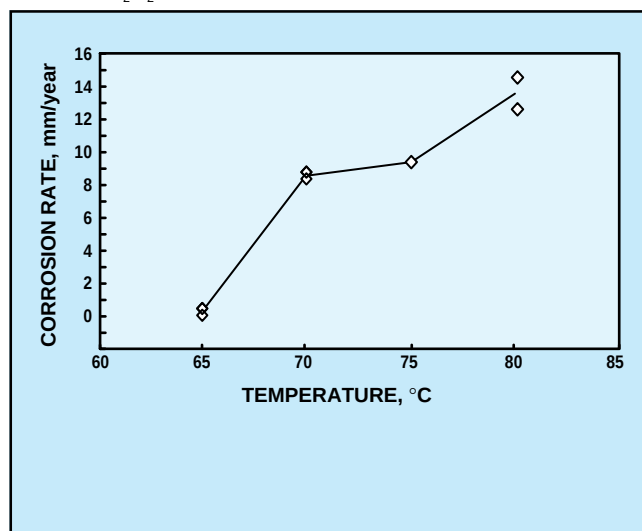
Table III lists corrosion rate values for Grade 2 titanium exposed to alkaline 0.2–0.3% H_2O_2 solutions containing various Ca^{+2} ion additions at 70°C and 80°C. **Figures 4 and 5** show these results plotted as a function of Ca^{+2} ion concentration. The results dramatically demonstrate the high potency of Ca^{+2} ion as a titanium corrosion inhibitor even at trace levels of concentration. At 70°C, Ca^{+2} ion concentrations as low as 1 ppm effectively thwarted corrosion in 0.2–0.3% H_2O_2 solutions at pH levels of 11.0 and 12.0 to rates below 0.25 mm/year (10 mils/year). There is some corrosion rate scatter at these very low corrosion rates from error derived from minimal coupon weight loss and exposure time and variable solution composition. Although Ca^{+2} ion-inhibited rates were above acceptable corrosion rates in pH 12.0 solutions at 80°C, there was a similar dramatic inhibition effect at Ca^{+2} ion additions greater than 1 ppm.

Figure 5 reveals the influence of Mg^{+2} ion additions on titanium corrosion rate in 0.2–0.3% H_2O_2 solutions at pH 12.0 and 70°C. At Mg^{+2}

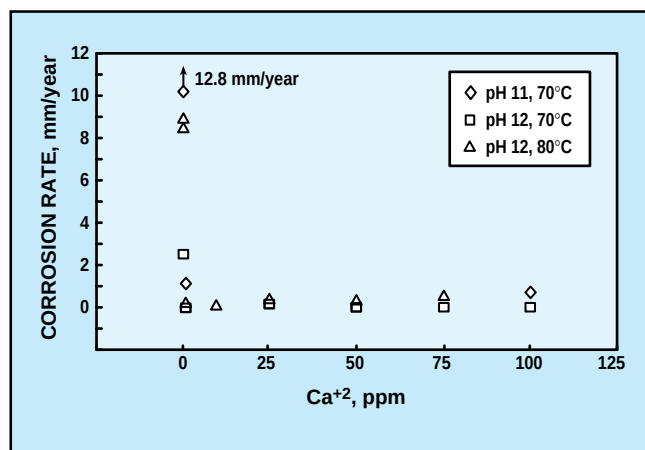
2. Dependence of Grade 2 titanium corrosion rate in 0.2–0.3% H_2O_2 solutions on pH at 70°C and 80°C



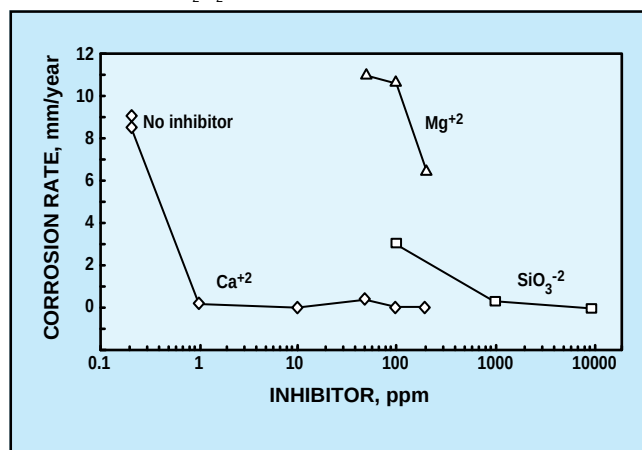
3. Influence of temperature on Grade 2 titanium corrosion rate in 0.2–0.3% H_2O_2 solution at pH 12.0



4. Corrosion rate of Grade 2 titanium in alkaline, 0.2–0.3% H_2O_2 solutions as a function of Ca^{+2} ion addition at 70°C and 80°C



5. Relative potency of various inhibitor species on titanium corrosion in 0.2–0.3% H_2O_2 solutions at pH 12.0 and 70°C



ion levels at or below 100 ppm, there is no significant corrosion inhibition. Some reduction in corrosion rate does occur at the 200 ppm level. One test conducted with a solution containing both 100-ppm Ca^{+2} and 100-ppm Mg^{+2} ions still produced a low corrosion rate. This indicates there is no significant interaction between these species.

Figure 5 also reveals the inhibiting influence of Na_2SiO_3 additions on titanium corrosion in 0.2–0.3% H_2O_2 solutions at pH 12.0 and 70°C. The silicate species is a more potent and effective corrosion inhibitor than the Mg^{+2} ion below 200 ppm. It does

not reduce corrosion rates to acceptably low levels (<0.127 mm/year) under these conditions until reaching concentrations of approximately 1%.

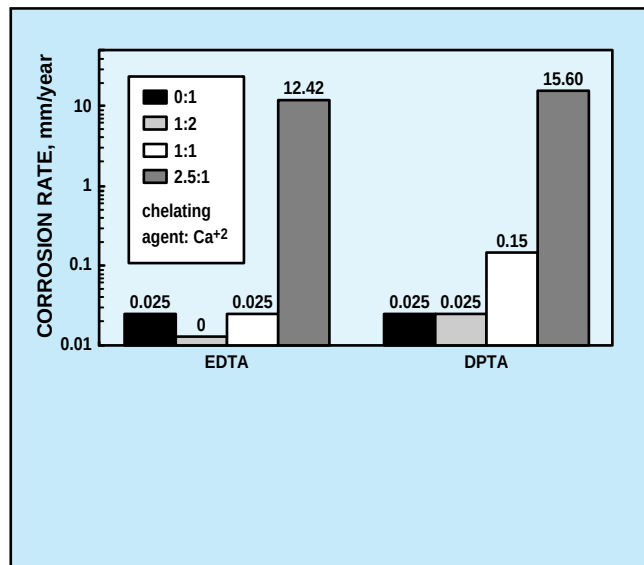
Inhibited solutions containing chelants

Figure 6 graphically presents the effect of varying EDTA or DTPA chelating agent addition to 0.2–0.3% H_2O_2 solutions containing 100 ppm Ca^{+2} ion at pH 12.0 and 70°C. The results reveal that addition of EDTA or DTPA to these solutions at or below chelant: Ca^{+2} ion molar ratios of 1:1 have little influence on tita-

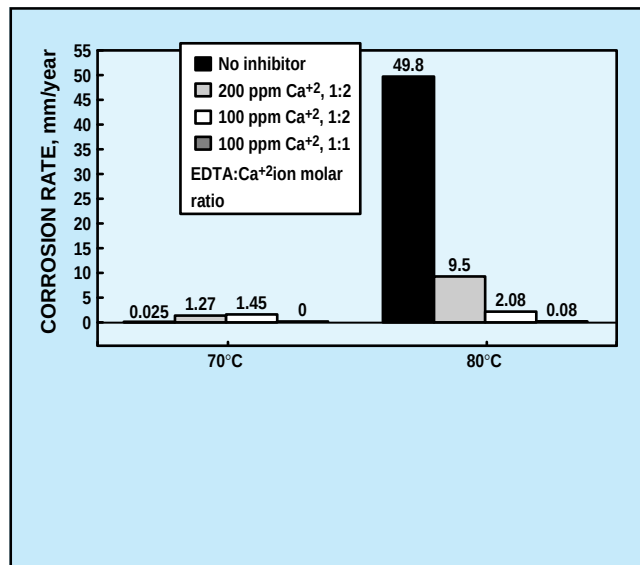
nium corrosion inhibition derived from the Ca^{+2} ion. At the molar ratio of 2.5:1, the excessive chelate concentration resulted in elevated corrosion rates and no significant corrosion inhibition. Figure 7 demonstrates that the potent inhibiting influence of 100–200 ppm Ca^{+2} ion, when chelated with EDTA at 1:2 and 1:1 molar ratios, persists in solutions at elevated pH (12.5) and H_2O_2 levels (0.3–0.4%) at 70°C and 80°C. Under these more severe conditions, the 1:1 molar ratio was more inhibiting than the 1:2 ratio at both temperatures. The 1:2 ratio, however, produced lowest corrosion rates in

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6. Influence of chelating agent:Ca²⁺ ion ratio on the corrosion of Grade 2 titanium with 0.2–0.3% H₂O₂ solution containing 100 ppm Ca²⁺ ion at pH 12.0 and 70°C



7. Influence of EDTA chelant additions to 0.3–0.4% H₂O₂ solutions containing 100–200 ppm Ca²⁺ ion at pH 12.5 on Grade 2 titanium corrosion inhibition at 70°C and 80°C



0.2–0.3% H₂O₂ solution at pH 12.0 as Fig. 6 indicates.

Discussion

Influence of test parameters

This study fixed the solution H₂O₂ concentration at 0.2–0.3% by weight while pH and temperature varied over the ranges of 9.5–12.5 and 65–80°C, respectively. One can therefore assume that the trends and guidelines derived are valid for H₂O₂ concentrations below 0.3%. The test procedure used could not maintain a precise single value of H₂O₂ level with time but only a range of 0.2–0.3%. Typical H₂O₂ levels evaluated in this lab study were actually within the 0.24–0.28% window.

Earlier corrosion studies in alkaline peroxide solutions have shown the highly aggravating influence of increasing H₂O₂ concentration, temperature, and pH or combinations of these factors on titanium corrosion rate (4, 6, 7). Increasing pH and temperature also significantly enhanced titanium corrosion in the uninhibited and inhibited peroxide solutions tested in this study. The influence of pH does not appear very gradual or

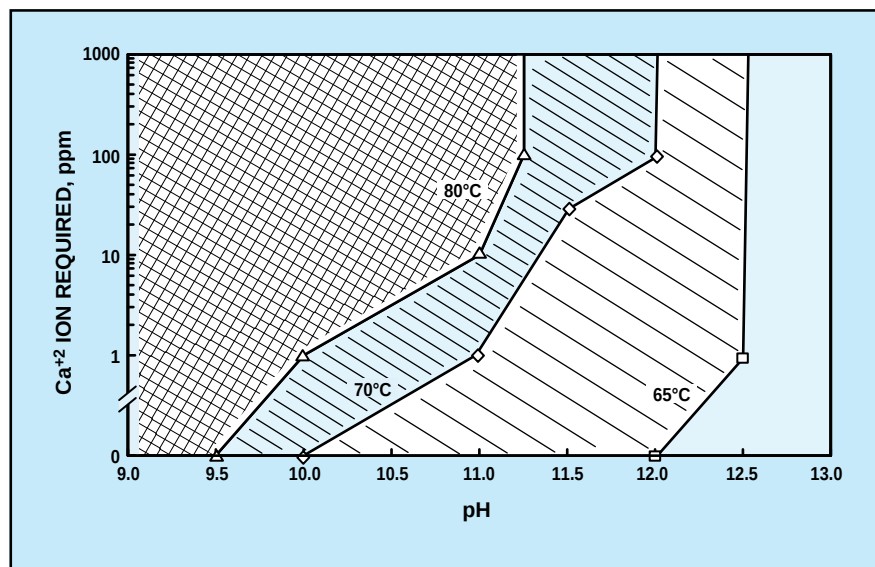
linear. It may exhibit a discontinuous “threshold” type behavior. Figure 2 shows this behavior. Small increases in corrosion rate occurred up to pH 11.5 at 70°C but rapidly increased above this pH value. At 80°C, this apparent pH “threshold” occurred below 11.0 in these uninhibited solutions. In Ca²⁺ ion inhibited solutions at 70°C or 80°C, increasing solution pH from 11.0 to 12.0 had a small negative influence on titanium corrosion ratios as Fig. 4 shows.

Increasing test temperature from 65°C to 80°C highly accelerated titanium corrosion in uninhibited alkaline peroxide solutions. As Fig. 3 reveals, the influence of temperature also appears abrupt and discontinuous. There is a rapid increase in corrosion rate between 65°C and 70°C and between 75°C and 80°C. There is little negative influence of temperature in the 70–75°C range and between 75–80°C. The 70–75°C window also has little negative influence from temperature. Figures 4 and 7 show that the aggravating effect of increasing temperature on corrosion is highly mitigated and much more subdued in Ca²⁺ ion-inhibited solutions.

It becomes obvious from this study that the variable with the greatest and most dramatic effect on titanium corrosion in alkaline peroxide solution is the addition of Ca²⁺ ion. As Figures 4 and 5 reveal, as little as 1 ppm Ca²⁺ ion effectively mitigates and inhibits corrosion at 70°C and 80°C. Ca²⁺ ion inhibition in these solutions is not unusual according to earlier studies (5–8). What is surprising is the extremely low concentration of Ca²⁺ ion that can effectively inhibit corrosion. The Mg²⁺ ion and silicate additions also were highly significant corrosion inhibitors, but they were much less potent and required higher concentrations to be effective as Fig. 5 indicates.

Figures 6 and 7 show that the addition of EDTA or DTPA chelating agents to the Ca²⁺ ion-inhibited solutions did little to compromise the inhibiting quality of Ca²⁺ ion provided molar ratios remained at or below 1:1. Additions of chelate above this ratio, however, appear to counteract this beneficial effect of Ca²⁺ ion resulting in elevated corrosion rates.

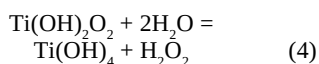
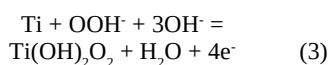
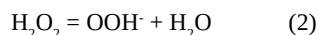
8. Approximate limits for useful corrosion resistance of Grade 2 titanium in Ca^{+2} inhibited solutions containing a maximum of 0.3% by weight H_2O_2 at 65°C, 70°C, and 80°C



Corrosion mechanism

Corrosion of Grade 2 titanium in hot alkaline peroxide solutions manifests itself as general (uniform) corrosion and not as localized attack. Examination of cross-sectioned, corroded sample microstructures reveals an unselective attack with no intergranular corrosion. There is also an absence of absorbed hydrogen indicated by no hydride surface films and precipitates. Corroded metal surfaces may often exhibit gold or dark brown colors.

Three reactions (4) describe the basic mechanism of titanium corrosion exposed to alkaline H_2O_2 solutions:



Equation 2 is the common dissociation of H_2O_2 in alkaline solutions to form the very unstable but highly oxidizing perhydroxyl species used for pulp and paper bleaching. Note that increasing pH shifts this reaction to the right with concomitantly

increasing perhydroxyl ion concentration. This perhydroxyl ion has a high affinity for titanium and readily forms the stable, highly soluble titanium peroxide complex of Eq. 3. These soluble titanium complexes may become unstable as peroxide concentration decreases. They can hydrolyze to form insoluble titanium hydroxide or oxide precipitates as Eq. 4 shows. The discoloration often observed on corroded titanium surfaces may stem from growth of thin, hydrolyzed titanium oxide corrosion products.

The fact that Eq. 3 produces a highly soluble corrosion product and not a highly protective titanium oxide film explains why corrosion of titanium occurs. Anodic polarization studies on titanium in alkaline H_2O_2 solutions (4, 8) suggest that significant anodic polarization occurs at high passive currents noble to the corrosion potential. This is possibly due to formation of a semi-protective film by Eq. 4 such that the corrosion process is in anodic control. The rapid reduction of the peroxide ion fully depolarizes the cathodic process. This explains the lack of hydrogen absorption by the corroding metal surface. Because of these ca-

thodic and anodic processes, typical corrosion potentials for titanium actively corroding in alkaline peroxide solutions lie in the -100 to -400 mV range (4, 8, 9). Grade 7 and Grade 12 titanium alloys that are normally more resistant to reducing acids and that rely on ennoblement for improved passivity offer no performance advantages under these conditions (4).

The mechanism for the corrosion inhibition by Ca^{+2} , Mg^{+2} , and silicate species has not been investigated and is not well understood. Observations of reduced oxygen gas bubble formation and peroxide decay measurements in inhibited peroxide test solutions suggest that these inhibiting species may act as peroxide stabilizers. A stabilizer diminishes the generation of perhydroxyl ion in Eq. 1 and reduces the critical reactant in Eq. 2 to quell corrosion. This hypothesis requires further evaluation, and more diagnostic investigations are necessary to identify the actual mechanism involved.

Practical implications and application guidelines

Peroxide pulp and paper plant bleaching processes generally operate within an H_2O_2 concentration range of 0.1–0.5% by weight, pH levels of 10.0–12.0, and temperatures of 60–90°C. This lab corrosion study focused on a fixed H_2O_2 window of 0.2–0.3 wt.%, pH levels of 10.0–12.0, and temperatures of 65–80°C. Using the corrosion rate data generated within this finite operating window, it is possible to formulate several practical application limits for titanium for both uninhibited and inhibited peroxide bleach solutions. If a maximum corrosion rate of 0.13 mm/year (5 mils/year) represents an acceptance criterion for alloy corrosion resistance, the corrosion data suggest the following limits in pure, uninhibited solutions containing 0.3% H_2O_2 maximum:

- At 65°C, titanium is resistant at or below pH 12.0.

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- At 70°C, titanium is resistant at or below pH 10.0.
- At 80°C, titanium is not resistant at or above pH 10.0.

These worst-case limits represent a narrow window of useful performance for Grade 2 titanium in uninhibited alkaline peroxide solutions at temperatures above 70°C and H₂O₂ concentrations up to 0.3%. Much wider, useful pH ranges are possible at temperatures below 65°C.

In actual bleach plant processes, it is fortunate that one or more species known to inhibit titanium corrosion in alkaline peroxide media will inevitably be present. These beneficial species include the following:

- Ca⁺² ions that are present in all hard and natural waters
- MgSO₄ often used in stock peroxide solutions as a stabilizer
- Na₂SiO₃ also used in some bleach streams to stabilize peroxide and enhance fiber brightness.

Background levels of Ca⁺² ion in bleaching process streams are typically in the 150 ppm range depending on pH and other solution constituents. MgSO₄ concentration may be as high as several hundred ppm. Na₂SiO₃ additions are over several thousand ppm. Although the presence of Ca⁺² and Mg⁺² in these process streams usually occurs, there may be no silicate addition for scaling reasons. Silicate is not present in most peroxide bleaching processes.

This study generated corrosion rate data in 0.2–0.3% H₂O₂ solution at 65°C, 70°C, and 80°C inhibited with 1–100 ppm Ca⁺² ion, 50–200 ppm Mg⁺² ion, or 100–10,000 ppm silicate ion. With Ca⁺² ion-inhibited 0.3% H₂O₂ maximum solutions, the following limits result using the greater than 0.13 mm/year corrosion-rate acceptance criteria:

III. Corrosion rate of Grade 2 titanium as a function of both pH and Ca⁺² ion concentration in 0.2–0.3% H₂O₂ solutions

Temperature, °C	pH	Ca ⁺² ion concentration	Corrosion rate	
			mm/year	mils/year
65	12.0	0	0.08	3
		1	0.05	2
	11.0	0	2.44	96
70	11.5	1	0.03	1
		25	0.18	7
		50	0.04	2
		25	0.36	14
		30	0.13	5
		0	8.66	341
	12.0	1	0.18	7
		10	0.05	2
		25	0.33	13
		50	0.46	18
		75	0.56	22
		100	0.03	1
80	10.0	1	0	0
		10	0	0
		11.5	0.25	10
		200	0.18	7
	12.0	0	10.16	400
		1	1.09	43
		50	0.41	16
		100	0.76	30

- At 65°C, titanium is resistant above 1 ppm Ca⁺² at pH 12.5.
- At 70°C, titanium is resistant above 1 ppm Ca⁺² at pH 11.0, titanium is resistant above 30 ppm Ca⁺² at pH 11.5, and titanium is resistant above 100 ppm Ca⁺² at pH 12.0.
- At 80°C, titanium is resistant above 1 ppm Ca⁺² at pH 10.0, and titanium is resistant above 10 ppm Ca⁺² at pH 11.0.

Although Mg⁺² up to 200 ppm provided inadequate inhibition, a 1% silicate addition did provide adequate inhibition at pH 12.0 and 70°C.

Figure 8 plots these titanium corrosion limits for uninhibited and inhibited solutions containing a maximum of 0.3% by weight H₂O₂ to provide some approximate application guidelines at 65°C, 70°C, and 80°C. It is interesting to note the large expansion of allowable solution pH when the temperature drops a mere five degrees from 70°C to

65°C. The pH limit diminishes substantially for the ten-degree temperature drop from 80°C to 70°C indicating that increasing temperature seriously aggravates any Ca⁺² ion-inhibited peroxide corrosion of titanium nonlinearly. The addition of only 1–10 ppm Ca⁺² ion effectively expands the safe, allowable pH window by 0.5–1.5 units over the 65–80°C temperature range. In addition, the corrosion boundary condition at 80°C and 10 ppm Ca⁺² correlates well with the very small titanium corrosion measured during in situ exposure in operating peroxide bleach plant streams (7).

It is important to note that the guidelines depicted in Fig. 8 do not include or address possible effects of and interactions with chelating agents or silicate additions. Corrosion test results for various EDTA and DTPA additions to Ca⁺²-ion inhibited peroxide solutions indicate a relatively minor influence on corrosion rate when chelant:Ca⁺² ion molar ratios remain at or below 1:1.

These results were developed at 100 and 200 ppm Ca^{+2} ion levels, however. It will be necessary to determine whether these relationships are valid at the lower Ca^{+2} -ion levels. Figure 8 guidelines may still be valid within the range of EDTA or DTPA additions typically made to pulp slurries—0.005–0.04% by weight of slurry. Recent data (8) suggest that EDTA by itself or in excess may accelerate titanium corrosion in these solutions. Additional testing within this range of chelant additions is necessary for peroxide solutions inhibited with 1–50 ppm Ca^{+2} ion.

Although it appears that the presence of MgSO_4 will not adversely affect Ca^{+2} -ion inhibition, it is possible that significant silicate additions may compromise Ca^{+2} -ion benefits. Earlier work (8) indicated this effect with implication of the formation of insoluble calcium silicate precipitates. More studies are clearly necessary to evaluate the effect of silicate or chelants at the low Ca^{+2} ion levels anticipated in bleaching service. Future corrosion studies will focus on these chelant ratio and silicate issues. They will also develop guidelines for temperatures in the 80–90°C window used in certain bleach plants.

Conclusions

It is possible to draw the following conclusions from the work reported in this presentation:

- The laboratory weight-loss test-

ing has developed a corrosion database for Grade 2 titanium in uninhibited and inhibited alkaline 0.2–0.3% H_2O_2 solutions at 65–80°C.

- There is limited corrosion resistance of titanium in uninhibited alkaline peroxide solutions particularly at temperatures at or above 70°C with pH levels exceeding 10.5.
- Titanium corrosion resistance dramatically expands in inhibited solutions compared to uninhibited solutions at temperatures of 65–80°C. Effective corrosion inhibitor species include Ca^{+2} ions, Mg salts, and silicates.
- The order of decreasing corrosion inhibitor potency and effectiveness within the range of conditions tested is $\text{Ca}^{+2} > \text{SiO}_3^{-2} > \text{Mg}^{+2}$. Ca^{+2} ion inhibition at 65–80°C occurs as low as 1 ppm depending on solution pH.
- The addition of EDTA or DTPA chelating agents to Ca^{+2} ion-rich peroxide solutions has small effect on titanium corrosion inhibition at chelant: Ca^{+2} ion molar ratios of 1:1 or less. Excessive chelant additions may compromise inhibition and exacerbate corrosion.
- Use of the corrosion database can derive expanded application guidelines for acceptable use of Grade 2 titanium in Ca^{+2} ion-inhibited solutions containing a maximum of 0.3% by weight H_2O_2

at 65°C, 70°C, and 80°C.

- Additional corrosion testing is necessary to define chelant: Ca^{+2} ion interactions at typical bleach process concentrations and possible interactions with the silicate added in some plants. Development of corrosion behavior and use guidelines for titanium at service temperatures as high as 90°C would also be of commercial interest. 

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