HYDROGEN UPTAKE RATES FOR GRADE 12 TITANIUM
IN HOT ALKALINE BRINE MEDIA

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## INTRODUCTION

Applications of grade 12 titanium in concentrated brine media are numerous and diverse throughout the CPI.[1] Many of these applications are due to the extended regime of corrosion resistance offered by grade 12 titanium, as compared with unalloyed titanium.[2] In particular, the excellent crevice corrosion resistance of grade 12 titanium has made it very attractive to salt producers. Salt crystallizers, with near saturated brine feed material, and temperatures over 105°C, have experienced crevice corrosion failures of unalloyed titanium. Grade 12 titanium, however, is resistant to crevice attack in these near neutral (pH 5-8) brine solutions to temperatures in excess of 250°C[3], and has provided years of trouble-free service in this application.

A recent application of grade 12 titanium tubing involved use in a triple-effect evaporator, producing salt from a concentrated natural brine. A pretreatment process on the brine raised the alkalinity of the brine to around pH 12. Due to the high pH and temperatures (about 115°C) involved, concerns were raised about possible hydrogen embrittlement of the titanium. Although published pH-temperature guidelines exist for alkaline hydrogen uptake[2,4], they were developed on unalloyed titanium. The addition of nickel as an alloying agent in grade 12 titanium raises concerns for increased hydrogen uptake in alkaline solutions.[5] The addition of nickel stabilizes beta phase in titanium, which is known to be more susceptible to hydrogen uptake.[6] Also, the guidelines were developed in pure NaCl; the effect of salt mixtures had not been determined.

The intent of this work was to generate guidelines specific to grade 12 titanium for avoiding deleterious hydrogen uptake in caustic brine media. Several factors were assessed as to their effect on hydrogen uptake. These included brine pH, temperature, and composition, as well as alloy surface condition and exposure time. A predictive model was also developed to offer some insight into long-term hydrogen uptake on grade 12 titanium exposed to hot alkaline brine solutions.

## EXPERIMENTAL

ASTM grade 12 titanium (Ti-0.3Mo-0.8Ni) mill-produced strip material was utilized for this study. Analyzed composition of the material (0.29% Mo, 0.73% Ni, 0.13% O, 0.12% Fe) fell well within ASTM specifications. All exposure test coupons extracted from the 0.89mm gage sheet material, were 51mm x 19mm. Analyzed base level hydrogen content of the sheet material was 39 ppm. Prior to exposure, all samples were immersed in an ambient temperature 35 vol. % $HNO_3$/5 vol. % HF solution for approximately 5 minutes. The samples were then rinsed in distilled water and air dried. This procedure constituted the "as-pickled" surface condition. The "thermally oxidized" surface condition involved subsequent air annealing at 650°C ± 10°C for 5 minutes, air-cooled.

Two brine compositions were tested; saturated NaCl, and a simulated natural brine feedstock for a salt evaporator process. The natural brine, as it will be henceforth designated, consisted of 21% NaCl, 5% KCl, and 3.7% $Na_2SO_4$, all by weight. NaOH was used to adjust pH, whose values are reported at 25°C. Balance of all solutions was de-ionized water. All chemicals were of reagent grade purity.

Brine exposure temperatures were 107°C (boiling) and 121°C. The 107°C exposures were carried out in 1 liter test vessels constructed from titanium. This minimized solution contamination, most notably from glass. These caustic solutions tend to etch glass vessels, producing undesirable silaceous deposits on the titanium specimens. These vessels did however utilize glass reflux condensers to prevent solution evaporation. Boiling solutions were refreshed every seven days. The 121°C exposures utilized 2 liter titanium-lined autoclaves. These solutions were refreshed once each month. All test specimens were suspended in test solutions on titanium wire hangers. Each wire was Teflon® tape wrapped to provide electrical isolation between specimens.

Linear polarization studies were performed on an EG&G Princeton Applied Research Model 273 computer controlled potentiostat/galvanostat. Model 342 corrosion software was utilized to conduct the polarization tests. Grade 12 titanium described above was used as the test material, with 1 $cm^2$ surface area exposed to the solutions. All tests were carried out at 107°C. A one liter titanium vessel was used to minimize contaminant interference during testing.

Hydrogen uptake efficiency (HUE) testing, which has been described elsewhere[7] was also performed in the specially constructed titanium vessels described above. Galvanically controlled charging tests were performed with an EG&G Princeton Applied Research Model 273 potentiostat/galvanostat. Current density was varied between 0.05-1.00 $mA/cm^2$, with charging times inversely proportional to current density, so as to maintain a constant hydrogen production rate. All HUE tests were carried out at 107°C.

Post exposure specimen evaluation consisted of bulk hydrogen analysis. Hot vacuum extraction was utilized for hydrogen analysis. Samples were analyzed in duplicate unless results differed by more than 10%, in which case a third analysis was made. In either case, average hydrogen uptake (ΔH) is reported, which is the difference between average post-test hydrogen and the aforementioned base-line hydrogen content.

## RESULTS

Hydrogen uptake results for grade 12 titanium immersion exposures in caustic brine media are shown in Tables 1-3. The data are reported according to brine media, temperature, pH, and surface condition. Tables l and 2 represent data from exposures in natural brine at 107°C and 121°C, respectively. Saturated NaCl results are reported in Table 3.

Linear regression plots of selected [ΔH versus exposure time] results were prepared to more clearly see effects of the variables studied (see Figures 1-3). Figure 1 illustrates uptake rates for as-pickled and thermally oxidized grade 12 titanium in pH 12.0 and 12.5 natural brine at 107°C. A small but finite uptake rate appears to occur for pH 12.5 brine exposure specimens in the as-pickled surface condition. The pH 12 as-pickled specimens exhibit a parallel slope to the pH 12.5 specimens, but with a reduced offset. Thermally oxidized specimens exhibit relatively flat hydrogen uptake rates, suggesting little or no time dependence.

Figure 2 reveals, somewhat surprisingly that the 121°C natural brine exposures produced slightly lower hydrogen uptake than the 107°C exposures. The as-pickled specimens appear to exhibit a small positive uptake rate, while thermally oxidized specimens have little or no time dependent uptake rates. Interestingly, as-pickled specimens exposed at pH 13, although not plotted, exhibited significantly higher hydrogen uptake rates as compared to those at 107°C (see Tables l and 2).

Figure 3 illustrates the hydrogen uptake characteristics of grade 12 titanium in saturated NaCl at 107°C. From comparing Tables 1 and 3, one can deduce that pure NaCl has a much greater effect on hydrogen uptake than the simulated natural brine. This difference is also exemplified in Figure 3, which illustrates for instance, the very high hydrogen absorption rates for as-pickled specimens in pH 12.5 brine. Thermal oxidation appears to provide much less benefit in saturated NaCl brine. uptake rates for thermally oxidized specimens at pH 12.5, although diminished somewhat from the as-pickled specimen rates, represent unacceptable hydrogen absorption in terms of eventual metal embrittlement.

Hydrogen absorption rates calculated from the linear regression analysis equations of data in Figures 1-3, is presented in Table 4. The values given are for thin wall strip material, 0.89mm gage, and assume that only one side of the titanium is exposed to the hot caustic brine media. This analysis indicates almost a six-fold increase in hydrogen absorption rates for grade 12 specimens in pH 12.5 saturated NaCl, as opposed to the simulated natural brine. For comparison, the actual one year hydrogen uptake results (yearly average based on 52 and 78 week data) are shown as well. The numbers are halved to reflect a single side exposure, so that direct comparison can be made with the regression calculated rates.

Table 5 contains information on the predictive hydrogen uptake model developed using hydrogen uptake efficiency (HUE) testing and corrosion rates determined via linear polarization. The predicted rates were determined on as-pickled grade 12 titanium specimens, in saturated NaCl and the simulated natural brine, at 107°C. Brine pH values of 12.0 and 12.5 were used in developing the model. Since the predictive model yields uptake data for single sided exposures, the actual uptake results were halved for the sake of comparison, as above for the regression analysis comparison.

## DISCUSSION

The mechanism of hydrogen absorption by grade 12 titanium in hot alkaline brine media is based on finite general corrosion attack of the alloy in these high pH solutions. This slow anodic dissolution of the titanium oxide film allows cathodic breakdown of water at the metal surface, generating nascent hydrogen. The nascent hydrogen then reacts to form titanium hydride. At temperatures above 8O°C, the hydrogen diffuses into the titanium, causing eventual embrittlement of the metal.

Hydrogen absorption in this study was quite variable, as evidenced by the tabulated uptake results. Since the formation of titanium hydride occurs at the metal surface, compositional variations in the surface film will affect hydrogen absorption. Thus, oxide film growth during high temperature solution exposure, which is known to occur[2], could quite likely be the major cause of uptake variations. It most likely also produces the "leveling off" of hydrogen uptake data observed for many of the conditions plotted in Figures 1-3. As the oxide film increases in thickness, the corrosion rate of titanium is diminished, thus increased exposure times lead to a static level of hydrogen uptake.

Thermal oxidation, which has been shown to be an effective barrier to hydrogen absorption in reducing acid environments[8], appears to have a neutral to positive effect on hydrogen uptake in alkaline media, depending on brine make-up and pH. At pH ≥ 12.5, the thermal oxide serves to diminish the uptake rate somewhat. However, in saturated NaCl, the uptake rate is not reduced sufficiently to eliminate eventual hydrogen embrittlement. This is not the case in the natural brine at pH 12.5, in which thermal oxidation lowered the uptake rate by 50%, putting it into a regime of innoccuous hydrogen absorption. Uptake rates at pH 12 were not significantly affected by thermal oxidation. The most likely explanation being due to the oxide film buildup occurring during solution exposure, negating the effect of any pre-existing thermal oxide film.

Temperature had mixed effects on hydrogen uptake of grade 12 titanium. Increasing temperature lowered uptake rates at pH ≤ 12.5, yet increased the uptake rate at pH 13. The explanation for this is possibly due to more rapid oxide film growth during solution exposure at 121°C when low corrosion rate conditions prevail (pH 12 and 12.5). While at higher corrosion rate, such as pH 13, the corrosion (and subsequent hydrogen absorption) overwhelms the faster oxide film buildup.

Brine composition appears to influence hydrogen uptake only at pH levels above 12.5. At these higher pH levels, saturated NaCl significantly increased hydrogen absorption rates on grade 12 titanium. The cause of the increased uptake rates is due to much higher corrosion rates at pH 12.5, in saturated NaCl. In fact, at pH 12.5, the corrosion rate more than doubles for grade 12 titanium in saturated NaCl, compared with natural brine. However, at pH 12, the corrosion rates were identical.

Linear regression of the hydrogen uptake data was utilized as a conservative approach for data analysis. Generally, good line fits were obtained only on the highest uptake rates (> 20 ppm/yr). Lower uptake rates, in which data exhibited the "leveling off" effect described earlier, tended to best fit logarithmic curves. Despite this, the calculated absorption rates from regression equations correlated very well with observed uptake.

The predictive model for hydrogen uptake rates was intended to supplement regression analysis data in determining long-term effects of grade 12 titanium exposure to alkaline brine solutions. The model also revealed that it is increased corrosion rates, rather than HUE, responsible for the significantly higher uptake rates in saturated NaCl at pH ≥ 12.5. The predictive model confirms actual uptake results that suggest long-term pH 12.5 brine solution exposure poses a hydrogen embrittlement concern for grade 12 titanium.

### Practical Guidelines

Hydrogen embrittlement, in terms of measurable loss of mechanical integrity, has been found to occur in grade 12 titanium at levels above about 300 ppm.[9] Assuming a base level hydrogen content of about 50 ppm, the critical threshold level of hydrogen uptake can be targeted at about 250 ppm. Thus, to ensure 20 year service life, hydrogen uptake rates should be no higher than about 12.5 ppm/yr for a thin wall (0.89mm) sheet or tube. Hydrogen uptake rates are inversely proportional to wall thickness, so as wall thickness increases, absorption rates fall. For example, at a 6.35mm wall, the hydrogen uptake rate for grade 12 titanium exposed to natural brine at pH 12 and 107°C, drops to 1.5 ppm/yr. Thus, the concern for excessive hydrogen uptake and possible embrittlement will generally be limited to thin wall material. From this study, it is clear that grade 12 titanium will perform well in brine solutions at pH ≤ 12.0. Above this pH level, grade 12 titanium can be subject to excessive hydrogen uptake and possible embrittlement. Thermal oxidation may inhibit hydrogen uptake in pH 12.5 brine, allowing successful application of grade 12 titanium in natural brines. However, in saturated NaCl, thermal oxidation offers no real benefit.

## CONCLUSIONS

1. Grade 12 titanium exhibits on the order of 10 ppm/yr (1mm gage) hydrogen uptake rates in brine solutions with pH ≤ 12.0. Increasing wall thicknesses will reduce the uptake rate proportionately.

2. Brine solutions with pH ≥ 12.5 appear to significantly increase hydrogen absorption rates for grade 12 titanium, rendering it susceptible to long-term hydrogen embrittlement. Thermal oxidation may effectively inhibit against hydrogen uptake, however, its effectiveness is dependent on brine composition.

3. Predicted hydrogen uptake rates based on short-term electrochemical tests, offer reliable assessments for long-term performance of grade 12 titanium in hot alkaline brine solutions.

4. Corrosion rates of grade 12 titanium increase by over a factor of 2 when the alloy is exposed to saturated NaCl at pH ≥ 12.5, as opposed to a natural brine at the same pH levels.

## ACKNOWLEDGEMENT

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## Table 1

### Hydrogen Uptake Results for Grade 12 Titanium in Natural Brine[1] at 107°C

| Exposure Time (Wks) | Media pH | Avg. Hydrogen Uptake ($\Delta H$) As-Pickled (ppm) | Avg. Hydrogen Uptake ($\Delta H$) Thermally Oxidized (ppm) |
|---|---|---|---|
| 4 | 12.0 | 3 | 12 |
| 4 | 12.5 | 23 | 6 |
| 4 | 13.0 | 20 | 17 |
| 6 | 12.0 | 8 | 9 |
| 6 | 12.5 | 22 | 11 |
| 6 | 13.0 | 44 | 12 |
| 8 | 12.0 | 4 | 11 |
| 8 | 12.5 | 20 | 11 |
| 8 | 13.0 | 69 | 21 |
| 26 | 12.0 | 21 | 30 |
| 26 | 12.5 | 46 | 16 |
| 52 | 12.0 | 25 | 16 |
| 52 | 12.5 | 47 | 13 |
| 78 | 12.0 | 29 | 26 |
| 78 | 12.5 | 56 | 22 |

[1]Composition: 21% NaCl, 5% KCl, 3.7% $Na_2SO_4$.

Table 2

Hydrogen Uptake Results for Grade 12 Titanium in Natural Brine[1] at 121°C

| Exposure Time (Wks) | Media pH | Avg. Hydrogen Uptake (ΔH) As-Pickled (ppm) | Thermally Oxidized (ppm) |
|---|---|---|---|
| 4 | 12.0 | 7 | 8 |
| 4 | 12.5 | 11 | 15 |
| 4 | 13.0 | 81 | 3 |
| 8 | 12.0 | 15 | 3 |
| 8 | 12.5 | 15 | 9 |
| 8 | 13.0 | 62 | 33 |
| 26 | 12.0 | 18 | 3 |
| 26 | 12.5 | 19 | 0 |
| 52 | 12.0 | 18 | 16 |
| 52 | 12.5 | 27 | 27 |
| 78 | 12.5 | 33 | 8 |

[1]Composition: 21% NaCl, 5% KCl, 3.7% $Na_2SO_4$.

Table 3

Hydrogen Uptake Results for Grade 12 Titanium in Saturated NaCl at 107°C

| Exposure Time (Wks) | Media pH | Avg. Hydrogen Uptake ($\Delta H$) As-Pickled (ppm) | Avg. Hydrogen Uptake ($\Delta H$) Thermally Oxidized (ppm) |
|---|---|---|---|
| 4 | 12.0 | 16 | - |
| 4 | 12.5 | 36 | - |
| 4 | 13.0 | 376 | - |
| 12 | 12.0 | 12 | 15 |
| 12 | 12.5 | 84 | 8 |
| 12 | 13.0 | 773 | 12 |
| 26 | 12.0 | 17 | 9 |
| 26 | 12.5 | 98 | 26 |
| 26 | 13.0 | 891 | 30 |
| 52 | 12.0 | 23 | 25 |
| 52 | 12.5 | 440 | 180 |
| 78 | 12.0 | 31 | 11 |
| 78 | 12.5 | 324 | 108 |

Table 4

Hydrogen Absorption Rates for Grade 12 Titanium From Regression Analysis of Caustic Brine Exposure Results

| Brine Media | Temperature (°C) | pH | Surface Condition | Hydrogen[3] Absorption Rate (ppm/yr) | Actual Uptake[4] After 1 Yr (ppm) |
|---|---|---|---|---|---|
| Natural Brine[1] | 107 | 12.0 | As-Pickled | 12 | 11 |
| " | 107 | 12.5 | As-Pickled | 24 | 21 |
| " | 107 | 12.0 | T.O.[2] | 11 | 8 |
| " | 107 | 12.5 | T.O. | 9 | 7 |
| " | 121 | 12.0 | As-Pickled | 10 | 9 |
| " | 121 | 12.5 | As-Pickled | 13 | 12 |
| " | 121 | 12.0 | T.O. | 7 | 8 |
| " | 121 | 12.5 | T.O. | 7 | 8 |
| Saturated NaCl | 107 | 12.0 | As-Pickled | 12 | 11 |
| " | 107 | 12.5 | As-Pickled | 141 | 164 |
| " | 107 | 12.0 | T.O. | 8 | 8 |
| " | 107 | 12.5 | T.O. | 50 | 63 |

[1]Composition: 21% NaCl, 5% KCl, 3.7% $Na_2SO_4$.

[2]Thermally Oxidized.

[3]Calculated from linear regression analysis equations. Assumes 0.9mm wall thickness and single side exposure.

[4]Yearly average based on 52 and 78 week results, corrected for single size exposure.

## Table 5

Predictive Model for Hydrogen Uptake Rates in Grade 12 Titanium

| Brine Media (107°C) | pH | HUE (%) | Corrosion Rate (Linear Polarization) (mm/yr) | Predicted Uptake (ppm/yr) | Actual Uptake[2] After 1 Yr. (ppm) |
|---|---|---|---|---|---|
| Natural Brine[1] | 12.0 | 27 | $5.1 \times 10^{-4}$ | 13 | 11 |
| Natural Brine | 12.5 | 26 | $1.3 \times 10^{-3}$ | 31 | 21 |
| Sat. NaCl | 12.0 | 24 | $5.1 \times 10^{-4}$ | 12 | 11 |
| Sat. NaCl | 12.5 | 26 | $2.8 \times 10^{-3}$ | 69 | 164 |

[1]Composition: 21% NaCl, 5% KCl, 3.7% $Na_2SO_4$.

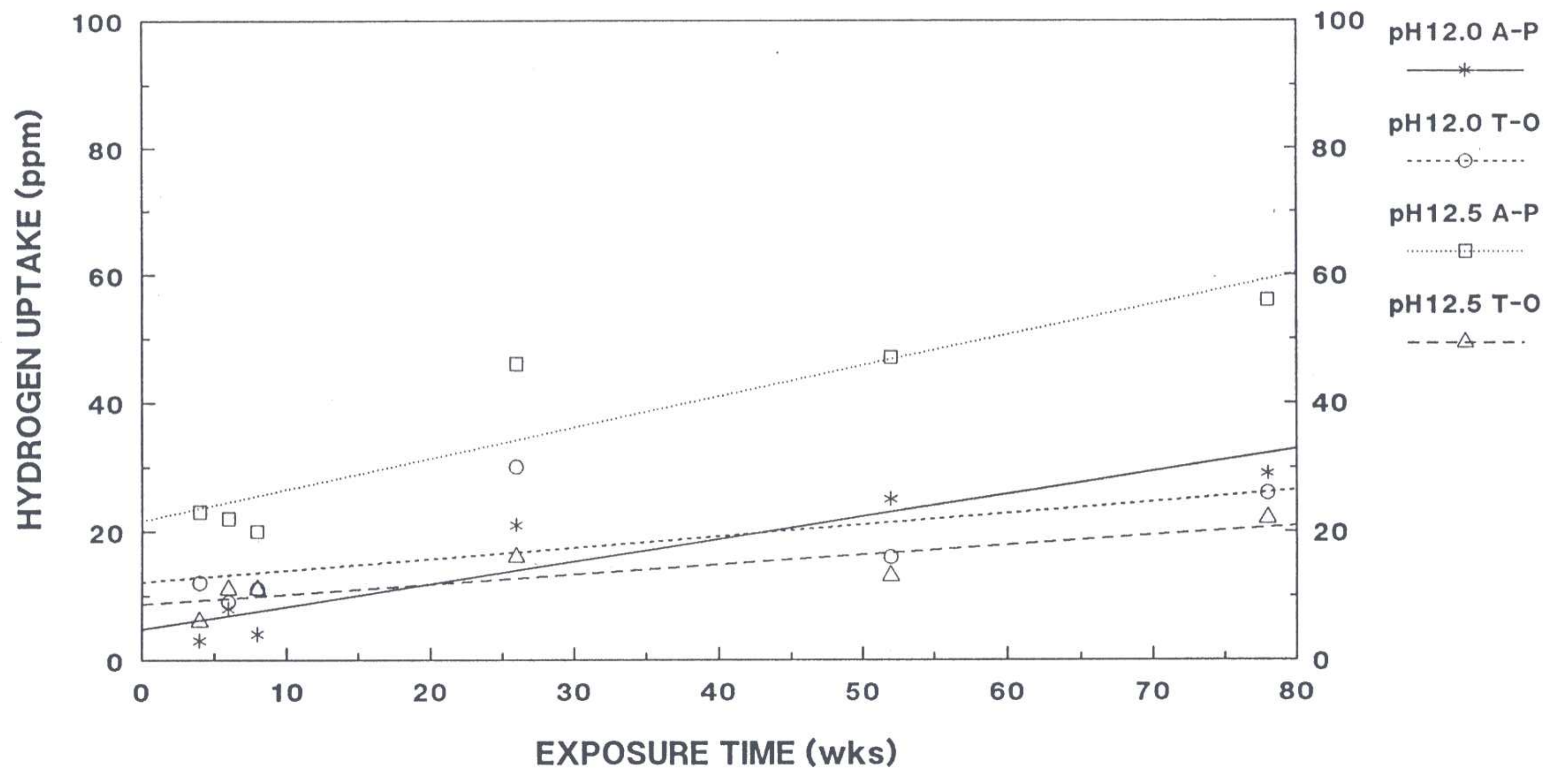
[2]Yearly average based on 52 and 78 week results, corrected for single side exposure.

Figure 1

# HYDROGEN UPTAKE ON GRADE 12 TITANIUM

## IN NATURAL BRINE AT 107 C

## LINEAR REGRESSION ANALYSIS




A-P : AS PICKLED SURFACE COND.

T-O : THERMALLY OXIDIZED SURFACE COND.

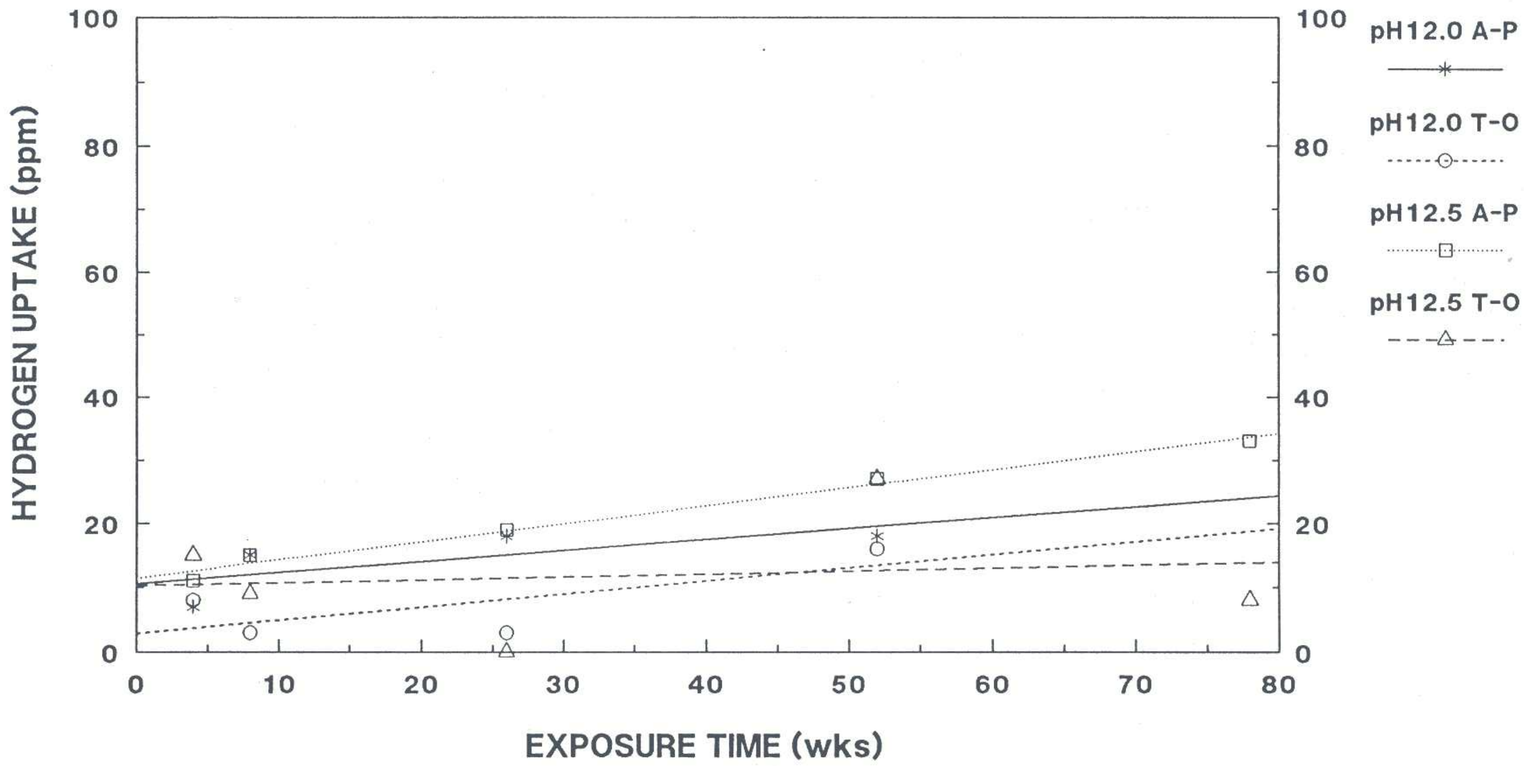
BRINE COMP.: 21%NaCl, 5%KCl, 3.7%$Na_2SO_4$

Figure 2

# HYDROGEN UPTAKE ON GRADE 12 TITANIUM

## IN NATURAL BRINE AT 121 C

## LINEAR REGRESSION ANALYSIS




A-P : AS PICKLED SURFACE COND.

T-O : THERMALLY OXIDIZED SURFACE COND.

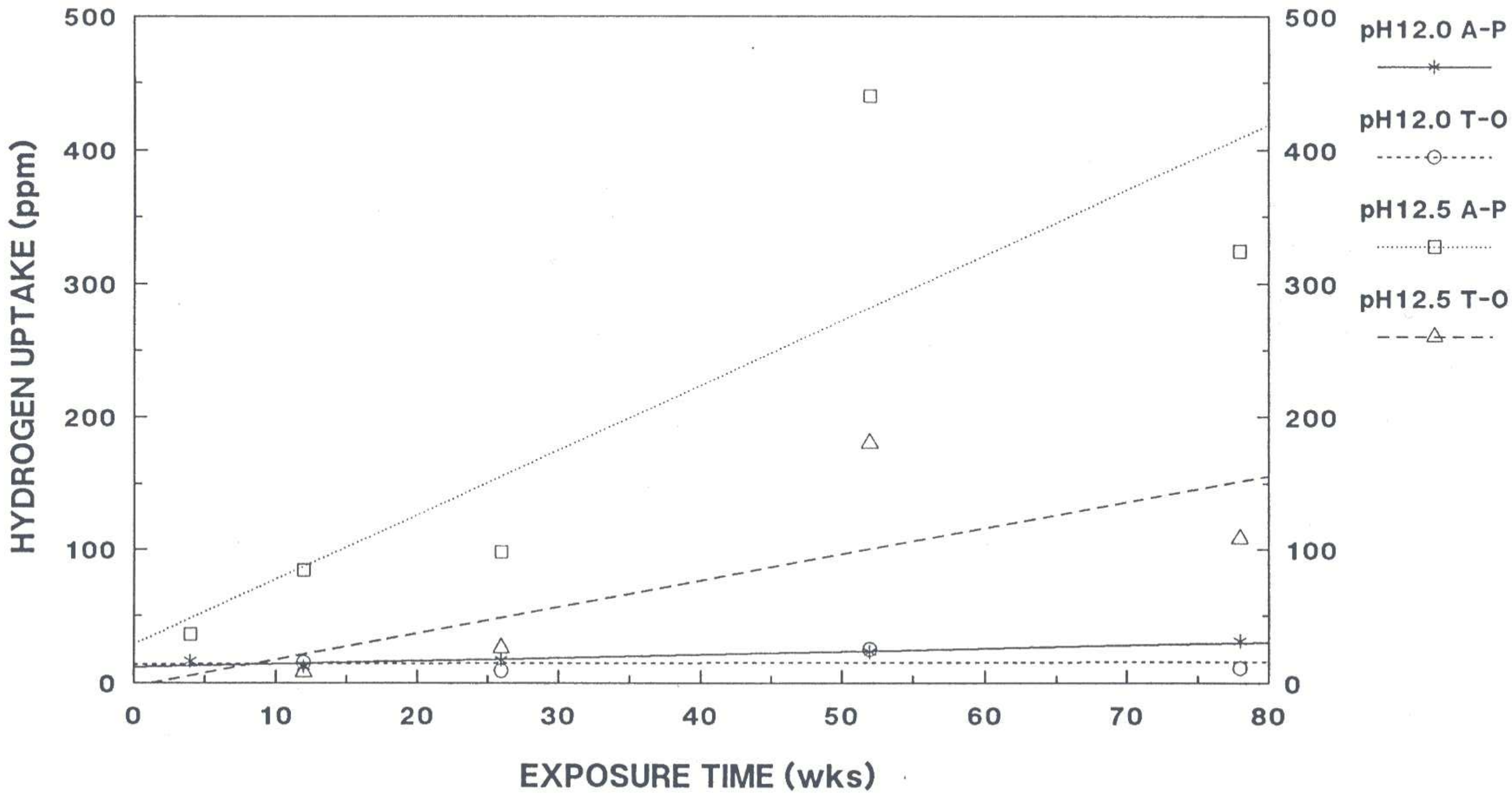
BRINE COMP.: 21%NaCl, 5%KCl, 3.7%$Na_2SO_4$

Figure 3

# HYDROGEN UPTAKE ON GRADE 12 TITANIUM

## IN SATURATED NaCl AT 107 C

## LINEAR REGRESSION ANALYSIS




A-P : AS PICKLED SURFACE COND.

T-O : THERMALLY OXIDIZED SURFACE COND.