

# **CORROSION BEHAVIOR OF TITANIUM METAL IN PRESENCE OF INHIBITED SULFURIC ACID AT 50°C<sup>1</sup>**

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## **ABSTRACT**

Titanium metal has been used extensively for heat exchanger tubes in MSF type desalination plants in Middle East countries. This is mainly due to its excellent erosion-corrosion resistance and good heat transfer properties. In an MSF plant, during desalination process progressive build up of scales occurs inside the tubes and the cleaning of tubes by descaling is an essential maintenance operation. The scales are mainly constituted of  $\text{CaCO}_3$  and  $\text{Mg}(\text{OH})_2$ . The descaling is usually carried out by using an inhibited acid. This paper presents the results of a study aimed to determine the feasibility of using inhibited  $\text{H}_2\text{SO}_4$  as an effective and trouble free descalant.

An investigation has been undertaken to study the corrosion behavior of titanium metal in  $\text{H}_2\text{SO}_4$  solution inhibited with CP-20, a  $\beta$  ethyl phenyl ketocyclohexyl amino hydrochloride based commercial inhibitor. The studies were carried out at 50 °C under deaerated and atmospheric exposure conditions applying immersion and potentiodynamic polarization and Tafel plot techniques. The possibility of hydrogen absorption or hydride formation in titanium metal was also considered under test conditions. For comparison, the corrosion behavior of carbon steel (flash chamber material) and aluminum bronze (tube sheet and water box material) have also been studied under identical conditions.

The results of immersion tests show a zero corrosion rate for titanium under normal or deaeration condition since no perceptible weight change was observed. The electrochemical tests show corrosion rates below 0.1 mpy (0.0025mm/y) which

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indicates outstanding resistance of the metal. Extremely low corrosion rates of titanium in inhibited  $\text{H}_2\text{SO}_4$  under testing conditions (50 °C, normal/deaerated, 0.5%  $\text{H}_2\text{SO}_4$ , dynamic) indicate virtually no hydrogen absorption in the metal. Also, the analytical determination of hydrogen absorption in acid treated titanium under aforementioned conditions shows no hydrogen pick up.

## 1. INTRODUCTION

In recent years, titanium tubes have found increasing applications in heat exchangers of desalination plant due to the excellent resistance of the metal towards general pitting and crevice corrosion and stress corrosion cracking [1,2,3]. The titanium tubes can withstand erosion-corrosion and impingement of flow velocities as high as 20m/s and are unaffected by seawater. However, a serious shortcoming with titanium is its characteristics of absorbing hydrogen which is greatly affected by the temperature, metal in contact or service medium. Titanium alone in contact with seawater does not undergo hydrogen absorption but during cathodic protection, excessive cathodization allows the discharge of hydrogen on Ti and formation of  $\text{TiH}_2$ . This causes loss of ductility and cracking of tubes [4].

In an MSF plant, during desalination process progressive build up of scales occurs inside the tubes and the cleaning of tubes by descaling is an essential maintenance operation. The scales are mainly constituted of  $\text{CaCO}_3$  and  $\text{Mg}(\text{OH})_2$ . The descaling is usually carried out by using an inhibited acid. Sulfamic acid with IBIT (Asahi Chemical) inhibitor is commonly recommended due to its good cleaning action and safe operation.  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$  may also be considered as descalants due to their more efficient and rapid action and cost effectiveness. However, under certain conditions, titanium undergoes corrosion in presence of  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$  and may absorb hydrogen or form hydrides.

In a typical modern seawater desalination plant where titanium (heat transfer tubes), copper alloys (tubes plate) and steel or Fe-9% Ni alloy (sacrificial anode) are the common construction materials, sulfamic acid containing IBIT inhibitor has been recommended as the most preferred chemical for descaling [5]. It saves the metallic

materials against corrosion and hydrogen absorption. Amongst the other acids tested for descaling of titanium tubes, 4% H<sub>2</sub>SO<sub>4</sub> containing 0.1% HNO<sub>3</sub> for IBIT inhibitor has been found to suppress corrosion and hydrogen absorption. Addition of HNO<sub>3</sub> to 4% HCl solution inhibits corrosion and hydrogen absorption of Ti but IBIT has no preventive effect because of its instability in HCl solution.

## **2. AIMS & OBJECTIVES**

The main aim of the present studies was to study the viability of using sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) with an inhibitor based on β-ethyl phenyl ketocyclohexyl amino hydrochloride for cleaning titanium heat transfer tubes in desalination plants.

The objectives of the studies were: (1) to determine corrosion rates of titanium in inhibited H<sub>2</sub>SO<sub>4</sub> at 50 °C under deaerated and atmospheric exposure conditions and dynamic state and compare it with the corrosion rates of carbon steel and aluminum bronze obtained under similar conditions and (ii) to assess the possibility of hydrogen absorption or hydride formation in titanium metal under test conditions.

The techniques used during the studies include immersion in seawater and electrochemical potentiodynamic polarization.

## **3. METHODOLOGY**

Immersion and electrochemical tests were carried on carbon steel (0.3% C), aluminum bronze (7% Al, 2% Fe, 1% Mn) and titanium metal (50 A, grade 2) in acidified seawater (0.5% H<sub>2</sub>SO<sub>4</sub> solution in seawater) with and without inhibitor (25 ppm) under aerated and deaerated conditions (10 < ppb dissolved oxygen). All the tests were carried out under dynamic condition. The dynamic condition was achieved by shaking the solution electrically using a magnet capsule. The immersion tests were of 5 hours duration.

The electrochemical potentiodynamic tests were carried out on an EG & G 342-2 Soft Corr measurement system. All the experiments were carried out using a corrosion cell

kit (EG &G K0047) with a saturated calomel reference electrode (SCE) and a graphite counter electrode.

The hydrogen absorption in titanium metal was determined analytically by LECO RH-404 Hydrogen Detector using ASTM E 1447 method [Courtesy: Japan Titanium Society]. The determination was carried out in three samples comprising of titanium metal (50A Grade 2) powder, titanium treated with 0.5% H<sub>2</sub>SO<sub>4</sub> and titanium treated with inhibited acid at 50 °C.

#### **4. RESULTS**

For both electrochemical and immersion tests, a 0.5% solution of H<sub>2</sub>SO<sub>4</sub> in seawater containing 25 ppm of inhibitor was used during testing at 50 °C under dynamic condition. The corrosion rates were determined from Tafel plots using potentiodynamic polarization technique.

The results of electrochemical testings are summarized in Table 1 and electrochemical potentiodynamic plots representing some typical experiments are given in Figures 1 and 2. Table 2 provides the summary of the results of immersion tests.

Figure 1 shows potentiodynamic polarization curves for carbon steel, aluminum bronze and titanium in inhibited acid and uninhibited acid under deaerated condition. The Log I Vs. potential plots for carbon steel and aluminum bronze show significant lowering in corrosion current values on inhibition indicating thereby the positive effect of addition of inhibitor on the corrosion rates of metals. Titanium metal shows a comparatively small shift in current value on inhibition. Figure 2 shows log I vs. E plots for titanium, aluminum bronze and carbon steel in deaerated inhibited acid solution. Carbon steel has the highest corrosion current value followed by aluminum bronze. Titanium has the lowest value indicating the highest corrosion resistance of titanium amongst the three metals under investigation.

## **Carbon Steel**

In bare H<sub>2</sub>SO<sub>4</sub> solution, the corrosion rates as determined electrochemically are in the range of 92-107 mpy which are lowered to 60-68 mpy on addition of CP-20 inhibitor under open atmospheric conditions. Under atmospheric or deaerated condition, the carbon steel in inhibited acid has similar corrosion rates. The corrosion rates in inhibited acid appear to be independent of oxygen concentration due to the formation of passive film of iron oxide. In uninhibited H<sub>2</sub>SO<sub>4</sub>, the growth of oxide film on steel goes uninterrupted as appeared from high corrosion rates.

The corrosion rates of carbon steel in bare H<sub>2</sub>SO<sub>4</sub> solution, as determined from immersion tests using weight loss method are high, the results are inconsistent due to the growth of uninterrupted and uneven oxide film. On addition of inhibitor, the average corrosion rate which is 176 mpy under open atmospheric condition goes down to 22 mpy under deaerated condition.

The corrosion rates of carbon steel, in inhibited H<sub>2</sub>SO<sub>4</sub>, under deaerated condition, as determined electrochemically, are much higher than those determined from immersion tests. This could be attributed to insufficient time available for the passive oxide film to be developed on steel during polarization test whereas under immersion test, sufficient time is available for the growth of passive oxide film.

## **Aluminum Bronze**

In bare H<sub>2</sub>SO<sub>4</sub> and under open atmospheric condition, the corrosion rates of metal as determined electrochemically, are around 19 mpy which are lowered to 13 mpy on addition of inhibitor. Under deaerated condition, the corrosion rates are further lowered to 2 - 5 mpy, which are quite low.

The results from immersion tests indicate that the corrosion rates of aluminum bronze under normal condition (open atmosphere) are considerably lowered on addition of inhibitor (41.4 mpy to 9.8 mpy).

Under deaerated condition, the corrosion rates are further lowered, 8.2 mpy (without inhibitor) to 2.3 mpy (with inhibitor).

### **Titanium Metal**

Corrosion rates of titanium metal, as determined from electrochemical technique are very low. The rate decreases further with the addition of inhibitor and on deaeration. The corrosion rates of titanium in H<sub>2</sub>SO<sub>4</sub> solution under aerated, aerated inhibited and deaerated - inhibited conditions are 0.12, 0.096 and 0.082 mpy, respectively.

Immersion tests under normal test condition with or without inhibitor do not show any perceptible weight change and therefore, the corrosion rate is found to be zero.

The surface condition of the metal does not show any change on acid treatment, as indicated by visual and metallographic examinations. The extremely low corrosion rates for titanium, obtained from electrochemical and immersion studies, indicate that virtually there would be no absorption of hydrogen gas by the titanium metal or formation of titanium hydride(s). Following relationship has been reported between corrosion rate and hydrogen absorption of titanium in acids (4 and 6% HCl or H<sub>2</sub>SO<sub>4</sub>) at 40 °C exposed for 100 hours [6].

$$H(\text{ppm}) = 1430 \times \text{CR} (\text{mm/y})$$

This relationship can conservatively be applied in our case and provides hydrogen absorption of 4 ppm which is negligible. The analytical determination of hydrogen absorption in titanium powder and titanium powder in uninhibited and inhibited acids gives a value of 25 ppm in all cases, thus indicating no hydrogen pick up in acid treated titanium. The results are summarized in Table 3. The corrosion resistance ranking of the materials, based on their allowable corrosion rates, is given in Table 4.

## **5. DISCUSSION**

The electrochemical polarization and immersion studies carried out on titanium, carbon steel and Al-Bronze in CP-20 inhibited H<sub>2</sub>SO<sub>4</sub> are aimed at to determine the corrosion

behavior of titanium tubes during acid cleaning. The titanium tube bundles in desalination plant are encased in a carbon steel shell with Al-Bronze tube sheet and naval brass tube support. There is no direct contact between carbon steel and titanium metal which often become cause of H<sub>2</sub> absorption. The results of corrosion studies of Ti, cupronickel steel in 4% H<sub>2</sub>SO<sub>4</sub> reported by Satoh [5] showed that Ti in contact with Cu-Ni reduces the corrosion rate and hydrogen absorption less because the potential of Ti is shifted to a more noble direction by galvanic coupling. When a couple of Ti and Cu-Ni touched steel, the corrosion rate and hydrogen absorption did not change while contact with steel causes hydrogen absorption. Studies carried out by Japanese investigators [6] confirmed that Ti immersed in 6% NaCl itself or even in contact with a copper alloy or stainless steel did not absorb hydrogen up to a temperature of 120°C. However, when Ti is in contact with steel, it absorbs hydrogen at temperatures greater than 80°C.

From the available data in literature [5], the corrosion of Ti in 4% H<sub>2</sub>SO<sub>4</sub> at 50°C is about 1.9 mm/y (76 mpy). Sufficient data are lacking regarding the corrosion rates of Ti at lower acid concentrations but we do believe that at these concentrations the corrosion rates should be significant. Keeping in view the reactivity of H<sub>2</sub>SO<sub>4</sub> towards Ti and application of acid for cleaning of Ti tubes in the plant, only lower concentrations of acid (<1%) were tried. Preliminary studies showed that lower concentrations of H<sub>2</sub>SO<sub>4</sub> around 0.5% were good enough for corrosion free satisfactory cleaning of Ti tubes. A combination of 0.5% H<sub>2</sub>SO<sub>4</sub> and 25 ppm inhibitor appears to be promising for acid cleaning operation of titanium tubes due to negligible corrosion and no hydrogen pick up. Studies are in offing on the electrochemical behavior of Ti metal in contact with different metals in acid and/or chloride media which could provide useful information regarding the role of galvanic corrosion and hydrogen absorption in desalination plants.

## **6. CONCLUSIONS**

1. Using 0.5% H<sub>2</sub>SO<sub>4</sub> in seawater and 25 ppm inhibitor at 50 °C, and under dynamic condition, the behavior of metals relevant to evaporator cleaning is as follows:

- (i) Corrosion rate of carbon steel under normal condition (open atmosphere) is 62 mpy which is slightly higher than permissible limit, however, under deaerated condition, the corrosion rate is 22 which is well under permissible limit.
  - (ii) Corrosion rate of aluminum bronze under normal condition (open atmosphere) is about 10 mpy which is further lowered to about 3 mpy under deaeration condition. The corrosion rates are well under permissible limit.
  - (iii) The immersion tests show a zero corrosion rate for titanium in  $\text{H}_2\text{SO}_4$  solution under normal or deaerated condition since no perceptible weight loss was observed. The electrochemical tests show corrosion rate below 0.1 mpy which indicates outstanding resistance of the metal.
2. Corrosion rates of carbon steel and titanium metal in inhibited  $\text{H}_2\text{SO}_4$  as determined by electrochemical method, are higher than those obtained from weight loss method. This can be attributed to the insufficient time available for the formation of passive oxide film during electrochemical polarization measurements.
3. Under normal or atmospheric conditions, the corrosion resistance of the materials in inhibited  $\text{H}_2\text{SO}_4$  may be ranked as:

CS(Poor), Aluminum Bronze (Good) and Titanium (Outstanding)
4. Under deaerated conditions, the corrosion resistance of the material in inhibited  $\text{H}_2\text{SO}_4$  may be ranked as:

CS(Fair), Aluminum Bronze (Excellent) and Titanium (Outstanding)
5. Extremely low corrosion rates of titanium metal in inhibited  $\text{H}_2\text{SO}_4$  under testing conditions (50 °C, normal/deaerated, dynamic, pH ~ 1.2) indicate virtually no hydrogen absorption in the metal [2].

6. Analytical determination of hydrogen absorption in acid treated titanium show no absorption.

**Table 1. Corrosion rate of carbon steel, aluminum bronze and titanium in 0.5% H<sub>2</sub>SO<sub>4</sub> in seawater with and without inhibitor at 50 °C under dynamic condition as determined by electrochemical experiments.**

S.No	Material	Corrosion rates					
		H <sub>2</sub> SO <sub>4</sub>		Inhibited H <sub>2</sub> SO <sub>4</sub>		Inhibited H <sub>2</sub> SO <sub>4</sub> under deaeration	
		mpy	mmy	mpy	mmy	Mpy	mmy
1	Carbon steel	92	2.3	68	1.7	61	1.52
2	Al-Bronze	18.65	0.466	12.57	0.314	2.02	0.050
3	Titanium	0.12	0.003	0.096	0.0024	0.0822	0.0020

**Table 2. Corrosion rate of carbon steel, aluminum bronze and titanium in 0.5% H<sub>2</sub>SO<sub>4</sub> in seawater with and without inhibitor at 50 °C under dynamic condition as determined by immersion test method.**

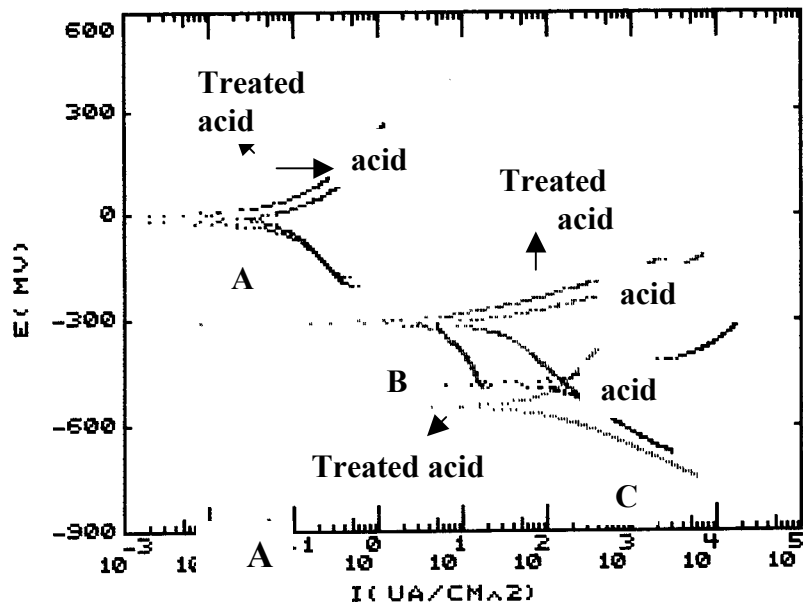
S. No.	Material	Corrosion rates							
		H <sub>2</sub> SO <sub>4</sub>		Inhibited H <sub>2</sub> SO <sub>4</sub>		H <sub>2</sub> SO <sub>4</sub> under deaeration		Inhibited H <sub>2</sub> SO <sub>4</sub> under deaeration	
		mpy	mmy	mpy	mmy	mpy	mmy	mpy	mmy
1	Carbon steel	200	5.0	62	1.55	176	4.4	22	0.55
2	Al-Bronze	41.4	1.035	9.8	0.245	8.2	0.205	2.33	0.058
3	Titanium	0	0	0	0	0	0	0	0

**Table 3. Analytical determination of absorbed hydrogen in titanium**

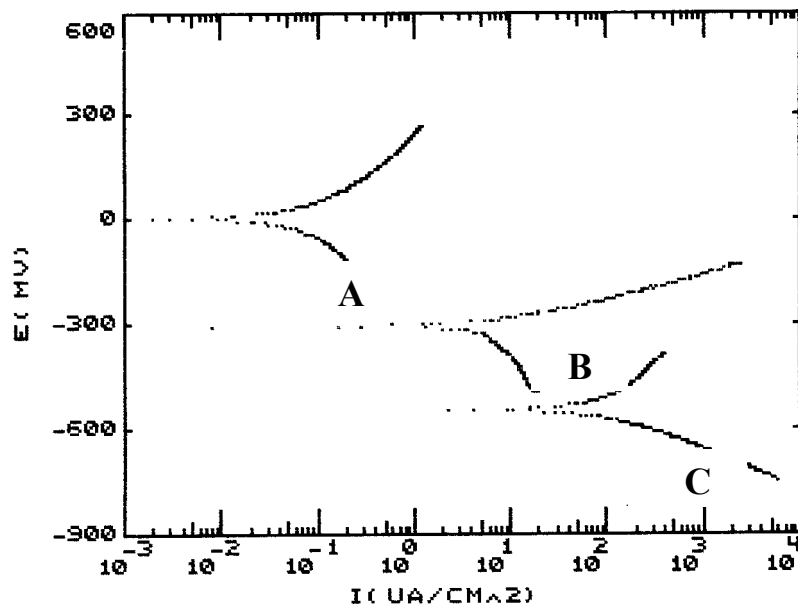
Sample	Condition	H (Weight %)
1	Ti powder	0.0025
2	Ti powder treated with 0.5% H <sub>2</sub> SO <sub>4</sub> solution for 5 hours at 50 °C	0.0025
3	Ti powder treated with inhibited H <sub>2</sub> SO <sub>4</sub> for 5 hours at 50 °C	0.0025

**Table 4.** Corrosion resistance performance of material during acid cleaning with inhibited H<sub>2</sub>SO<sub>4</sub> [7,8].

S.No.	Test Condition	Alloy	Corrosion Rate (mpy)		Rank
			Found	Max. Allowance	
1	Normal	Carbon steel	62	50-200	Poor
2	Deaerated	Carbon steel	22	20 – 50	Fair
3	Normal	Al-Bronze	9.8	5 – 20	Good
4	Deaerated	Al-Bronze	2.3	1 – 5	Excellent
5	Normal	Titanium	<0.1	< 1	Outstanding
6	Deaerated	Titanium	<0.1	<1	Outstanding



**Figure 1.** Potentiodynamic polarization curves of Titanium (A), Aluminum Bronze (B) and Carbon Steel (C) metals in deaerated inhibited acid solution and in untreated acid solution.



**Figure 2.** Potentiodynamic polarization curves of Titanium (A), Aluminum Bronze (B) and Carbon Steel (C) metals in deaerated inhibited acid solution at 50°C under dynamic condition.

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