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Hazardous waste reduction from mixed acid titanium etching

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Abstract This paper presents the findings of a technical study performed by the New York State Pollution Prevention Institute at Rochester Institute of Technology to evaluate process modifications that would reduce hazardous waste generated from the manufacture of titanium alloy turbine blades. This study focused on the acid etch process step in which titanium alloy turbine blades are immersed in a mixed nitric and hydrofluoric acid solution to chemically mill the blades; which is one of a sequence of finishing steps. The spent acid is a hazardous waste that is sent off-site for disposal. A pollution prevention approach identified several process and operational improvements that would significantly reduce the amount of hazardous acid waste generated. Implementation of process improvements identified in this study resulted in reducing the quantity of hazardous waste generated from 502 tons/year in the Baseline year to less than 210 tons/year in Year 2, thereby resulting in a cost savings of nearly 43% per year. Full implementation of the study recommendations are expected to reduce the hazardous waste quantity to 71 tons/year, thereby achieving a cost savings of nearly 70% due to an 86% reduction in waste generation and a 66% reduction of total acid purchase and disposal costs.

Keywords Titanium · Etch · Cost savings · Process improvement

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Introduction

TECT received assistance from the New York State Pollution Prevention Institute (NYSP2I) at Rochester Institute of Technology to determine the potential to reduce the quantity of hazardous waste generated from their titanium etch tank operation. Titanium alloy turbine blades are etched in a mixture of nitric and hydrofluoric acids to chemically mill the blades at a controlled rate as part of the sequence of finishing steps. Spent acid from the etch operation is pumped to a 6,000 gal storage tank and periodically sent off-site for disposal via tank truck. Since the spent acid is a hazardous waste, there is a significant cost for its disposal. A pollution prevention approach was utilized to determine operational changes that would reduce the quantity of acids used and, therefore, the hazardous waste generated from the etch process. When implemented, these changes will result in cost savings from both reduced acid purchase and waste disposal fees. It also reduces the environmental impact of the etch process.

The initial acid concentrations in an etch tank and the criteria for boosting the acids after a series of etch operations were specified by the customer. During the initial evaluation phase of this study, it was determined that the etch tanks were not operated consistently with regard to acid boosting or the end point at which the tank contents were discharged and a new acid solution was made up. Initially, the etch tanks were discharged for disposal after approximately 14 working days. If the life of the etch tanks could be extended, even by only doubling the current life, it would have a significant impact on reducing both the acid purchase and waste disposal costs. This study focused on extending the etch tank life since this process step has the most significant costs.

Etch bath chemistry

Reactions with titanium metal

An initial approach to extend the etch tank life was to consider systems that would remove dissolved titanium species from solution. A previous study conducted by NYSP2I at TECT determined that treatment of the acid baths with an anionic additive was not effective in removing titanium from solution. It was concluded from the study that titanium was present as an anionic complex and that a cationic additive would be needed but was not available. Before proceeding to evaluate other techniques to remove the titanium species in solution, it was important to define the chemistry involved in the etch process to better understand it.

A literature review located studies that described the chemistry of titanium when exposed to a mixed nitric-hydrofluoric acid solution (Sutter and Goetz-Grandmont 1990; Bijlmer 1970). Interestingly, unlike the single-step reaction involved when metals such as zinc are treated with hydrochloric acid, a series of reactions occur with titanium. The series of reactions are described below.

Titanium exhibits excellent corrosion resistance in many dilute acids, except in the presence of hydrofluoric acid in which it readily reacts as follows:

$$2Ti + 6HF \rightarrow 2Ti^{+3} + 6F^- + 3H_2 \tag{1}$$
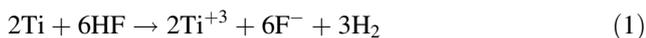
However, using only hydrofluoric acid for etching is unacceptable because hydride formation at the metal surface causes subsequent metal embrittlement that can result in unacceptable stress failure characteristics in the turbine blades. However, etching titanium in a mixed nitric and hydrofluoric acid solution reduces hydride formation to an acceptable level.

When titanium is immersed only in nitric acid, TiO_2 is produced which forms a protective surface coating that blocks further reaction since TiO_2 does not react with nitric acid. This reaction is referred to as passivation and is shown as:

$$Ti + 2HNO_3 \rightarrow TiO_2 + 2HNO_2 \tag{2}$$

When titanium is immersed in a mixed acid solution, any TiO_2 coating present is readily dissolved by the HF acid according to reaction (3):

$$TiO_2 + 6HF \rightarrow 2H^+ + TiF_6^{-2} + 2H_2O \tag{3}$$
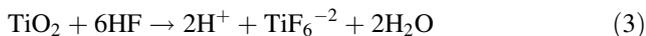
After removal of the oxide coating, the exposed titanium metal reacts with nitric acid to form Ti^{+3} according to reaction (4):

$$2Ti + 3HNO_3 + 6H^+ \rightarrow 2Ti^{+3} + 3HNO_2 + 3H_2O \tag{4}$$
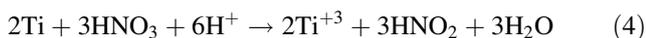
The Ti^{+3} subsequently reacts with nitric and hydrofluoric acids according to reaction (5) to yield the final oxidation product TiF_6^{-2} according to reaction (5):

$$2Ti^{+3} + HNO_3 + 12HF \rightarrow 2TiF_6^{-2} + HNO_2 + H_2O + 10H^+ \tag{5}$$
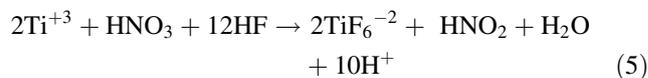
The net result of titanium treatment in a mixed nitric and hydrofluoric acid solution is the formation of titanium hexafluoride anion (TiF_6^{-2}). Combining reactions (4 and 5) yields the following:

$$Ti + 6HF + 2HNO_3 \rightarrow 2H^+ + TiF_6^{-2} + 2HNO_2 + 2H_2O \tag{6}$$
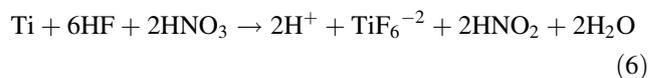
However, since nitrous acid (HNO_2) is unstable in solution it decomposes as follows:

$$2HNO_2 \rightarrow HNO_3 + {}^1/_2N_2O + {}^1/_2H_2O \tag{7}$$
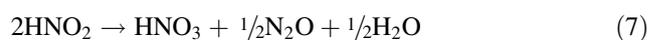
Combining reactions (6) and (7) gives the overall reaction of Ti in a mixed acid solution as shown in reaction (8):

$$Ti + 6HF + HNO_3 \rightarrow 2H^+ + TiF_6^{-2} + {}^1/_2N_2O + 2{}^1/_2H_2O \tag{8}$$
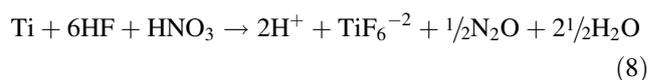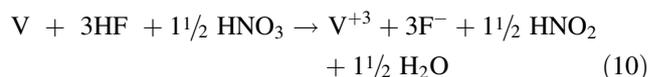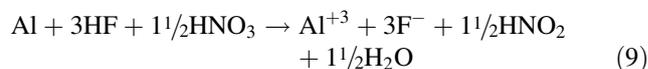
Reactions with titanium alloy

The metal used to manufacture turbine blades is not pure titanium but is a specified alloy composed of 90% titanium, 6% aluminum, and 4% vanadium by weight (Ti–6Al–4V). Since aluminum and vanadium also react with nitric and hydrofluoric acids, the presence of these additional metals needs to be taken into account to precisely define the process chemistry. The mol percent of each metal in the alloy is determined as:

$$(90g\,Ti/g\,alloy)/48g\,Ti/mol = 1.88\,mol\,Ti/g\,alloy$$
$$= 86\,mol\%\,Ti$$
$$(6g\,Al/g\,alloy)/27g\,Al/mol = 0.22\,mol\,Al/g\,alloy$$
$$= 10\,mol\%\,Al$$
$$(4g\,V/g\,alloy)/51g\,V/mol = 0.08\,mol\,V/g\,alloy$$
$$= 4\,mol\%\,V$$

The reactions of aluminum and vanadium in the mixed acid solution are as follows:

$$Al + 3HF + 1{}^1/_2HNO_3 \rightarrow Al^{+3} + 3F^- + 1{}^1/_2HNO_2 + 1{}^1/_2H_2O \tag{9}$$

$$V + 3HF + 1{}^1/_2HNO_3 \rightarrow V^{+3} + 3F^- + 1{}^1/_2HNO_2 + 1{}^1/_2H_2O \tag{10}$$

Therefore, combining reactions 8, 9, and 10 gives the net reaction of the titanium alloy as:

$$\begin{aligned} \text{Ti} + 0.12\text{Al} + 0.05\text{V} + 6.5\text{HF} + 1.1\text{HNO}_3 \\ \rightarrow 2\text{H}^+ + \text{TiF}_6{}^{-2} + 0.12\text{AlF}_3 + 0.05\text{VF}_3 + 0.6\text{N}_2\text{O} \\ + 2.8\text{H}_2\text{O} \end{aligned}$$

$$(11)$$
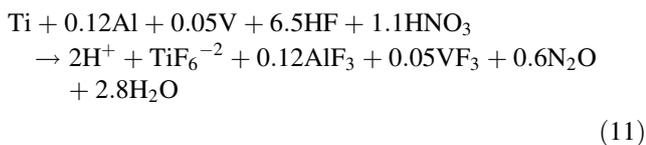
Reaction rates

Although the reaction rate coefficients of reactions 1, 4, and 5 are not known, the reaction rate equations can be written as:

$$v_1 = k_1 [\text{HF}]^6 [\text{related to Eq. 1}]$$

$$v_4 = k_4 [\text{HNO}_3]^{1.5} [\text{H}^+]^3 [\text{related to Eq. 4}]$$

$$v_5 = k_5 [\text{Ti}^{+3}] [\text{HNO}_3]^{0.5} [\text{HF}]^6 [\text{related to Eq. 5}]$$

The reaction rates are dependent on both solution temperature and acid concentrations and will determine the predominant chemistry in the etch process. For example, if v_1 is significantly higher than v_5, Ti^{+3} will be generated at a higher rate than it is removed from solution and would initially increase in concentration in the etch solution. As the reaction proceeds and the HF concentration decreases, v_5 will eventually become greater than v_1 and the Ti^{+3} concentration will decrease as it is converted to $\text{TiF}_6{}^{-2}$. However, if v_5 is greater than v_1, the Ti^{+3} concentrations will always remain low since it is more rapidly converted to $\text{TiF}_6{}^{-2}$ than it is generated. No evaluation was conducted in this study to determine the reaction rate coefficients.

When the HF acid concentration is relatively low, reactions (1 and 5) slow significantly. Reaction (4) is then the primary reaction, continuing the dissolution of titanium with the generation of Ti^{+3} instead of $\text{TiF}_6{}^{-2}$. An incident was described by the staff at the facility in which an etch tank operated in an HF-starved condition for a prolonged period. When the tank was boosted with HF and HNO_3, a vigorous exothermic reaction occurred along with the generation of a brownish gas. The exothermic reaction rapidly increased the temperature in the 250 gal tank by approximately 50°F. The reaction that occurred in the etch tank is the rapid reaction of Ti^{+3} with both hydrofluoric and nitric acids shown as follows:

$$\text{Ti}^{+3} + 3\text{F}^- + 3\text{HF} + \text{HNO}_3 \rightarrow 2\text{H}^+ + \text{TiF}_6{}^{-2} + \text{NO}_2 + \text{H}_2\text{O}$$

$$(12)$$
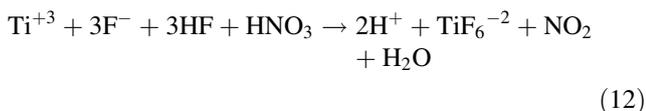
A calculation of the exothermic energy released from the oxidation of the Ti^{+3} estimated to have been in the etch tank accounted very closely with the temperature increase observed in the tank. Further anecdotal evidence was related from a vendor familiar with titanium pickling operations who noted that the generation of the brownish gas is commonly referred to as "burning off", indicating that this is a condition that has been encountered elsewhere.

When an etch bath is operated in an HF-starved mode, boosting the HF acid concentration requires more than the normal calculated amount. The reason is that some of the added HF reacts with the residual Ti^{+3} that is present in solution. Therefore, it is important to measure the HF concentration after boosting in order to determine that the proper amount of HF is present before continuing the etching process.

Etch process operation

General process description

The titanium etch process is conducted in etch tanks where the initial acid concentrations are customer specified at 9% HF and 12% HNO_3 (by volume). Concentrated acids are purchased in bulk and added to water in the etch tanks. The concentrated acids used are:

49% Hydrofluoric acid (HF) : 28.9 M, density 1.19 kg/l

70% Nitric acid (HNO_3) : 15.8 M, density 1.42 kg/l.

The quantities of acids in a new 100 l etch solution would be:

9 l HF + 12 l HNO_3 + 79 l H_2O = 100 l total

In a 100 l solution, the molar quantities of HF and HNO_3 are:

$9 \, l \times 28.9 \, \text{mols/l} = 260 \, \text{mols HF}$

$12 \, l \times 15.8 \, \text{mols/l} = 190 \, \text{mols HNO}_3$

Since the acids react during the etch process, they are periodically boosted to return them to the original 9 and 12% concentrations by removing liquid from the etch tank and adding an equivalent total combined volume of concentrated acids. The customer specification is that the HF acid concentration remains above 7%. Based on the stoichiometry in reaction (11), HF is the limiting reactant in etch tank solutions. When the HF is 100% depleted, the nitric acid is only $\sim 25\%$ utilized.

General operating parameters

The etch tanks are operated with the target of maintaining an etch rate of 0.001 inch/min. The etch rate is determined by suspending a test titanium alloy coupon in an etch tank for 10 min while maintaining a bath temperature between 70 and 75°F. The thickness loss of the coupon is measured with a micrometer to calculate the etch rate per minute. If

the etch rate is not within the specification range, consideration is given to either adjusting the acid concentrations or pumping the tank contents to the waste storage tank and preparing a new batch. If an entire etch tank is dumped, when adjusting the acid concentrations would have extended the tank's use, this unnecessarily adds incremental cost for both wasted raw materials (from preparing a new batch) and disposal fees (from the dumped tank volume).

In addition to monitoring the etch rate, both the nitric and hydrofluoric acid concentrations are routinely measured. When they are below their specified concentrations, they are boosted to the original concentrations by removing a calculated quantity of liquid from the tank and replacing it with an equal combined quantity of both acids.

Laboratory scale testing

Lab scale tests were conducted to simulate an etch bath. The tests were performed in a 1-l Nalgene beaker using an etch solution volume of 500 ml that was continuously stirred. One or more titanium alloy coupons were suspended in the etch solution and periodically weighed on an analytical balance to determine the quantity of metal oxidized. Since the reaction of nitric and hydrofluoric acids with titanium is exothermic, the beaker was placed in an ice bath to maintain the etch solution within the desired temperature range.

The primary purpose of the lab-scale testing was to determine whether the chemistry, previously described in "Etch bath chemistry" section, properly represents this titanium alloy etching process. Once confirmed, the knowledge of the chemistry allows conclusions and recommendations to be made to reduce the amount of waste acid that is generated.

A test was conducted in which the beaker contents were maintained at approximately 80°F, the mid-point of the 70–90°F full-scale operating range specification. The initial acid concentrations were at the customer specified concentrations of 9% HF and 12% HNO_3 (by volume). Titanium coupons were suspended in the beaker and etched until ∼90% of the HF acid was utilized. At that point, the acids were boosted to the initial concentrations and the etch process continued. The data for the etch test is shown in Appendix 1 and is discussed below.

Total metal etched

Since the weight loss of the titanium alloy coupons was accurately measured using an analytical balance, this was the primary data from which the theoretical acid consumption was calculated for comparison with actual acid used. Based on the weight loss from the titanium alloy
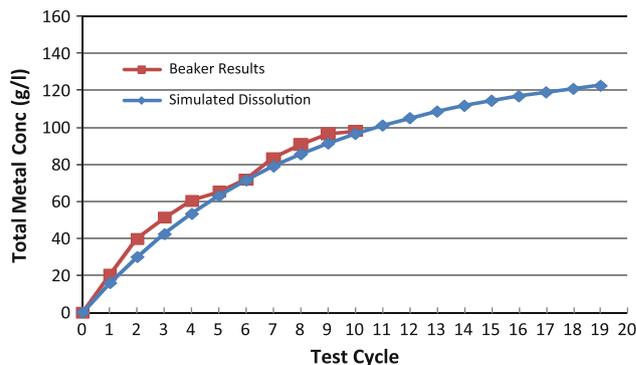

Fig. 1 Total metal dissolution

coupons, the increase in total metal concentration in the etch tank during the test is shown in Fig. 1 (see Beaker Results curve). As expected, the total metal concentration in solution follows an exponential curve that will eventually reach a steady state value with additional etch cycles.

The average mass of metal in solution and the volume of boost acid per cycle were used as input to a mathematical model to simulate the beaker. As shown in Fig. 1, the total metal concentration predicted by the model simulation closely matched the test data. Although the beaker test was ended prior to reaching steady state, the model simulation shows that the steady state metal concentration would have been ∼132 g/l. There were no signs that, up to a total metal concentration of 110 g/l, the saturation concentration had been exceeded. This is important with regard to considering how long the etch tanks could be operated before they need to be dumped and a new etch solution prepared.

The total metal concentration reaches a steady state level based on the specific operating conditions in an etch bath. This occurs because the total metal concentration increases to the point where an equal amount of metal is removed in the fluid withdrawn for acid boosting as is added from each subsequent etch cycle. The steady state concentration in the test series was calculated from a mass balance equation to be ∼132 g/l, thereby matching the simulation model results.

Acid utilization

Based on the quantity of titanium alloy etched and the chemistry described in Eqs. 8 and 11, the theoretical amounts of HF and HNO_3 acids used were calculated and compared to the actual amounts of acids utilized. The comparative results for both HF and HNO_3 acids are shown in Figs. 2 and 3, respectively.

The results show that the actual and theoretical acid utilization values correlate closely with each other for both acids, thereby confirming the chemistry described in "Etch bath chemistry" section. A comparison of the molar ratios
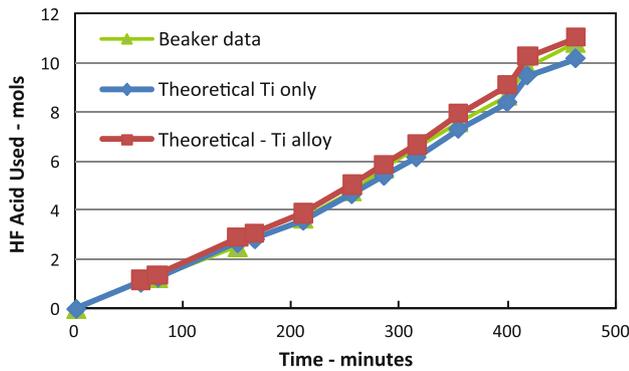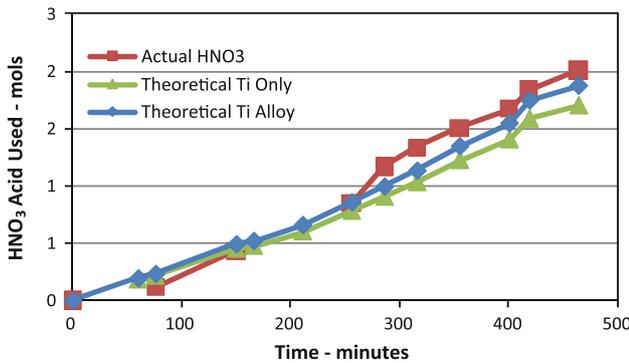
Fig. 2 HF acid use

Fig. 3 HNO$_3$ acid used

Table 1 Comparison of actual and theoretical values

Evaluation method	Molar ratios		
	HF:Ti	HNO$_3$:Ti	HF:HNO$_3$
Theoretical equation (titanium only)	6.0	1.0	6.0
Theoretical equation (titanium alloy)	6.5	1.1	5.9
Actual results (Beaker test—with titanium alloy)	6.4	1.2	5.4

obtained from the beaker test versus Eqs. 8 and 11 are shown in Table 1. The results demonstrate that the molar ratios obtained compare well with the theoretical values but the fit is closest when compared to the titanium alloy.

Effect of etch tank temperature

A series of tests were conducted in which temperature was varied to evaluate its effect on the etch rate. Although the tests were conducted using only HF acid, the results shown in Fig. 4 demonstrate that temperature has a significant effect on the etch rate over the 70–90°F range evaluated. The results showed that the etch rate increased by a factor of ~1.6 times for a 10°F increase.
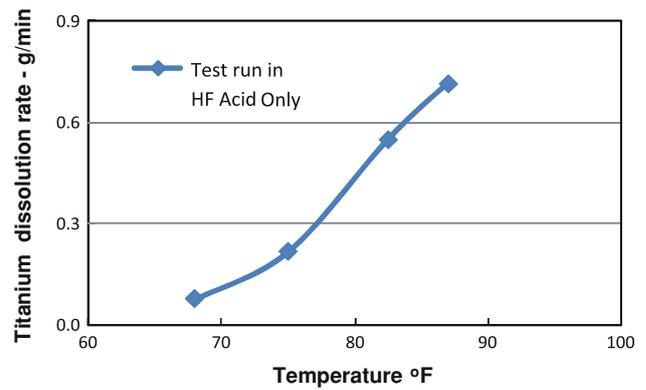

Fig. 4 Titanium dissolution rate

Since the etch tank temperature tests were conducted in an etch solution that contained only HF acid, they may not represent the results that would be obtained in a mixed HF and HNO$_3$ solution. However, if the temperature effect is similar, these results point out the importance of temperature control in the etch tanks since a small change in operating temperature significantly affects the time to achieve the desired removal of titanium during an etch cycle. Also, in regard to the initial coupon test, if the etch tank temperature is lower than the specified set point, the lower etch rate may incorrectly be interpreted as the tank not having an appropriate etch rate and could result in the tank being unnecessarily dumped.

Etch rate

The etch rates in the beaker tests were determined by calculating the grams of titanium oxidized per minute in each test cycle. Although the temperature and exposed titanium coupon surface area were not equal run-to-run, they were considered to be sufficiently consistent for comparison purposes. It was found that the etch rate remained essentially constant throughout the series. This result is in agreement with the study conducted by Sutter and Goetz-Grandmont (1990) where consistent etch rates were reported when the acids were properly maintained in the etch solution.

Another important result from this evaluation was that the etch rate was not adversely affected as the concentration of titanium alloy increased to 110 g/l at the end of the 11th etch cycle. This is in contrast to the information reported by equipment vendors that the etch rate was significantly reduced when the total metal concentration in solution exceeded 40–50 g/l. This result demonstrates further that when the appropriate balance of acids is maintained in the etch solution, the etch rate remains constant at the original rate. Given that result, the potential existed that the etch baths could be operated indefinitely

without periodically dumping the tank. If so, that would significantly reduce the waste generated from the process.

Process improvement opportunities

An important result determined in this study was that the etch rate remained constant for multiple etch cycles when the chemistry in the bath was properly maintained even though the total metal concentration in solution reached 110 g/l. Based on this knowledge, an optimum operating condition was defined and several process improvements were determined which would allow this condition to be reached. Interestingly, the information learned in this study contradicted both vendor information about the etch process as well as what was widely considered by the process operators. Yet, implementation of the changes in the full-scale equipment has continued to support the fundamental learnings that were obtained in this study.

During Year 1, most of the operational changes were related to improvements in the analytical procedures and the consistency of operating conditions maintained by the operators. Some of the wet chemistry methods used to determine acid concentrations were determined to give interferences as the total metal concentration in solution increased, whereby the chemistry in the etch tanks drifted away from that most effective for etching. This frequently resulted in the decision to dump etch tanks that would have run much longer if the proper chemistry had been maintained. The solution was that alternate, probe-based analytical methods were determined to be effective for these measurements and were substituted for them. Secondly, a significant effort was made to provide more technical information to the operators and to encourage them to operate the etch process based more on this information rather than on intuitive patterns that had developed over time. These changes also resulted in increasing the average life of the etch tanks.

In Year 2 the focus was to implement operation of the etch tanks such that they would not be dumped and the only waste would be from withdrawal of the volume needed to boost the acids. A more complete description of this operating change is given below in "Minimum etch tank acid waste generation" section. Significant progress was made to implement this change by the time the study was ended. A significant capital improvement program for the etch process area has temporarily slowed further implementation but is expected to be continued when that work is completed.

An additional recommendation was to develop a computer-based system by which the chemistry in each etch tank could be tracked based on the number and extent to which turbine blades had been etched. Based on the etch rate and the time of etching, the quantity of titanium alloy oxidized can be calculated. From this, the quantity of acid utilized could be calculated. This approach would provide an improved level of quality control in regard to avoiding operating at HF acid concentrations below the customer specified levels.

Minimum etch tank acid waste generation

The theoretical operating condition that represents the minimum waste generation is when the etch tanks are never dumped and the only waste generated is from the volume removed for acid boosting. Under these conditions, the boost volume equals the waste acid generation volume.

To illustrate the quantity of waste generated, consider a 200 gal etch tank with 9% HF and 12% HNO_3. If acid boosting is done when the HF concentration decreases to 7, 3.2% of the tank volume (6.4 gal) will need to be removed and replenished with 4.4 gal of concentrated HF and 2.0 gal of HNO_3 to return it to the initial acid concentrations.

To evaluate the effect of the etch tank life on the amount of waste generated using a 3.2% boost rate, a mathematical model was prepared to simulate the 200 gal tank for 100 boost cycles. The worst case would be if the tank was dumped after each etch cycle. In that case the total quantity of waste generated during 100 etch cycles would be 20,000 gal [100 × 200]. If the tank were dumped only after every two etch cycles, the total amount of waste generated would be reduced to 10,320 gal [(6.4 + 200) × 50]. If it was dumped every three cycles, the waste is 7,093 gal; every five cycles the waste is 4,512 gal, etc. When the tank is operated for the full 100 etch cycles without dumping until the last cycle, the total quantity of waste generated is only 833 gal. If it was not necessary to dump the tank after 100 cycles, the total waste would be only 640 gal.

As shown in Fig. 5, the decrease in the quantity of waste generated is initially very steep as the number of etch cycles/dump increases. When there are five etch cycles/dump, the total waste quantity is reduced by 77% compared to the worst case situation of dumping after each cycle. For 10 etch cycles/dump the waste generated is reduced by ∼90% compared to dumping after each cycle. This illustrates the importance of minimizing the dumping of the etch tank and maximizing the number of etch cycles.

Testing frequency

In order to avoid operating the etch process below the minimum specified HF acid concentration of 7%, it is important to understand the operating criteria that would cause this situation to occur. Using a 200 gal etch tank as
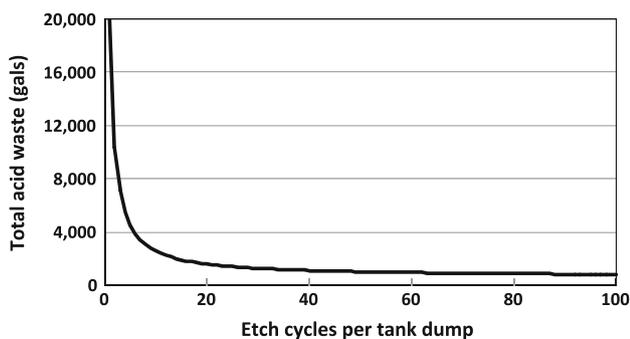
Fig. 5 Acid waste generation

an example with 9% HF acid (by volume), it contains ∼1,970 mols HF. If all the HF acid was utilized, 328 mols (15,750 g) of titanium would be oxidized and results in ∼21 g/l of titanium in the tank. The results obtained in the beaker test yielded the same titanium concentration when the HF acid was fully depleted.

Data provided by TECT shows that approximately 42,000 g of titanium are etched during a "typical" day for a 180 gal etch tank when 0.01 inch of metal are removed from the turbine blades. At this rate, the HF acid would be completely utilized after ∼8 h of operation (assuming an even processing rate during the day).

The customer specification stipulates that the HF concentration will not be less than 7%. For the 180 gal etch tank, the HF acid concentration would be less than 7% in approximately 2 h. Therefore, diligence is required by the operations staff to routinely monitor and boost the acid concentrations to maintain proper operating conditions.

Hazardous waste reduction and cost savings

Reductions achieved from actual operation modifications

The primary focus of this study was to evaluate the potential to reduce both the amount of hazardous waste generated and the total operating cost of the acid etch process. The Baseline cost and operating conditions were determined from the data for the year preceding this study since this was considered to be normal operation prior to any improvements being implemented. All of the improved cost and process operating conditions are in comparison to those of the Baseline.

Due to the sensitivity of disclosing confidential operating cost information for the etch process at TECT, the data are presented such that the highest individual cost in the Baseline year (i.e., acid transportation and disposal) has been normalized to $100. All of the remaining costs for the Baseline year and subsequent years are relative to this normalization factor. This approach allows the percent reduction in costs to be calculated for the improvements that were implemented so that the magnitude of the cost savings from the improvements can be demonstrated.

Several etch tank operational changes were made in Year 1 that resulted in reduced waste generation and cost savings. These were largely related to improvements in the analytical procedures and consistency of process steps followed by the operators. In Year 2, additional operational changes, largely based on the technical information obtained in this study, were implemented. The operating changes implemented through Year 2 resulted in extending the average etch tank life from a Baseline value of less than 14 days to over 26 days. The results of these changes are shown in Table 2 in which a reduction in the Total Operating Costs of 43% was achieved.

The results in Table 2 do not take into account changes in the level of production compared to the Baseline. Since production volumes change year-to-year, it is important to account for these changes in the cost evaluation. By adjusting the production values to a normalized value of 1.0 for the Baseline year, the production adjusted costs are shown in Table 3. The values for Years 1 and 2 are then divided by the Normalization Factor for that year to obtain the revised cost values. With this adjustment, the improvement in Total Operating Cost is reduced to 30% and reflects the effect of a constant production level.

The cost savings shown in Table 3 are primarily due to lower hazardous waste generation disposal fees resulting from a reduction of the volume of waste generated. Even

Table 2 Hazardous waste reduction and cost savings		Baseline	Year 1	Year 2
Hazardous acid waste generated (tons/year)		502	321	210
Normalized cost of acid disposal (transportation and disposal)		$100.0	$66.1	$36.4
Normalized acid purchase cost (HF and HNO_3)		$87.0	$94.4	$87.5
Normalized hazardous waste generator fee		$65.0	$19.5	$19.5
Normalized quarterly hazardous waste generation fee		$4.9	$5.5	$2.2
Total normalized cost		$257	$185	$146
Annual normalized savings compared to Baseline			$71	$111
Percent reduction in cost			27.8	43.3

Table 3 Values normalized to Baseline production level

	Baseline	Year 1	Year 2
Production normalization factor	1.00	1.02	0.79
Hazardous acid waste generated (tons/year)	502	315	266
Normalized cost of acid disposal (transportation and disposal)	$100.0	$65.0	$46.2
Normalized acid purchase cost (HF and HNO$_3$)	$87.0	$93.0	$111.0
Normalized hazardous waste generator fee	$65.0	$19.5	$19.5
Normalized quarterly hazardous waste generation fee	$4.9	$5.5	$2.2
Total normalized cost	$256.9	$183.0	$178.8
Annual normalized savings compared to Baseline		$73.9	78
Percent reduction in cost		28.8	30.4

Table 4 Waste reduction and cost savings for potential state

	Baseline	Year 1	Year 2	Potential
Hazardous waste generated (tons)	502	321	210	71
Hazardous waste generated (gal)	106,706	68,274	44,681	15,000
Total acid used (gal)	30,578	26,598	18,603	12,000
Waste volume (% of total acid used)	29	39	42	80

Table 5 Values normalized to Baseline production level

	Baseline	Year 1	Year 2	Potential
Production normalization factor	1.00	1.02	0.79	1.00
Hazardous acid waste generated (tons/year)	502	321	210	71
Normalized cost of acid disposal (transportation and disposal)	$100.0	$65.0	$46.2	$12.3
Normalized acid purchase cost (HF and HNO$_3$)	$87.0	$93.0	$111.0	$43.7
Normalized hazardous waste generator fee	$65.0	$19.5	$19.5	$19.5
Normalized quarterly hazardous waste generation fee	$4.9	$5.5	$2.2	$0.7
Total normalized cost	$257	$183	$179	$76
Annual normalized savings compared to Baseline		$74	$78	$181
Percent reduction in cost		28.8	30.4	70.3

though the amount of acids used decreased, the total acid cost increased because the raw material costs increased during this 2-year period, 38 and 31%, respectively, for HF and HNO$_3$. If the acid costs had remained steady at the Baseline levels, the cost savings would have been greater.

Reductions achievable at optimum operating conditions

In order to evaluate the maximum potential cost savings due to implementing all the process improvements identified in this study, a "Potential" operating state was created. In this state, the etch tank is operated with an unlimited tank life as discussed previously in the paper, thereby minimizing acid use and hazardous waste generation.

The operating parameters for a "Potential" operating state were determined by examining the total acid and hazardous waste data. As shown in Table 4, the efficiency of acid use improved from a Baseline value of 29 up to 42% in Year 2 (calculated by dividing the total acid used each year by the total volume of hazardous waste generated each year). The increased efficiency clearly demonstrates that the process improvements implemented through Year 2 produced less waste per gallon of acid used. By operating with an unlimited tank life, an acid use efficiency of 80% was considered to be a practically achievable condition for the "Potential" state. The quantity of acid used is then calculated to be ∼12,000 gal. This is based on the assumption that the Year 2 quantity used will be reduced by 50%, followed by normalizing it to the 2007 production level. The total amount of hazardous waste generated is then obtained by dividing the acid use by 80% to yield 15,000 gal hazardous waste generated per year. Using the conversion of 9.4 lbs/gal, 71 tons/year of hazardous waste

would be generated per year in the "Potential" state. These values are summarized as follows in Table 4.

Based on the values in Table 4, the Total Operating Cost in the "Potential" state can be determined and is shown in Table 5. The evaluation has been done whereby the production rate for the "Potential" state is normalized to the Baseline year. The cost evaluation shows that when operating at the conditions defined for the "Potential" state, there is an opportunity for a total annual cost savings of more than 70% compared to the Baseline.

Conclusions

Based on laboratory scale testing

1. The proposed etch chemistry described in this report has been defined and validated through experimental testing.
2. The total metal concentration in an etch solution reached ∼110 g/l without causing precipitation of any material in the solution.

3. Based on a mathematical model of the lab test data, the steady state total metal concentration would be ~130 g/l for the operating conditions defined in this study.
4. The etch rate remained constant through 11 etch cycles by properly maintaining the process chemistry
5. The etch rate is affected by temperature; increasing approximately 1.6 times for a 10°F increase in temperature between 70 and 90°F.

Implications for full scale etch tank operation

1. The etch rate will remain constant when the solution chemistry is properly maintained.
2. If the total metal saturation concentration is greater than 130 g/l, the etch tanks can be operated indefinitely without dumping because the metal concentration will remain below the saturation concentration.

3. Continuous operation without dumping the tanks represents the minimum possible hazardous waste generation condition because waste is generated only from the volume of material removed for acid boosting.
4. If the efficiency of acid use increased to a reasonably expected level of 80% (compared to 42% in Year 2), this would result in reduced hazardous waste generation and disposal and a consequent savings of ~70% compared to the Baseline.

Appendix 1: Laboratory test results

Time (min)	Dissolved metal							Scanacon readings			WCM
	g	g/min	End of last test (g)	Added by test (g)	Removed by boost (g)	Before boost (g/l)	After boost (g/l)	HF (vol%)	HNO$_3$ (vol%)	Metal (g/l)	HNO$_3$ (vol%)
0	0			0.00		0.00	0.0				0
60	9.43	0.16	0.00	9.43	0.00	18.86	18.9				
76	11.27	0.11	9.43	1.84	1.01	22.54	20.5	0.21	12.2	18.2	10.5
150	23.75	0.17	10.26	12.48	2.87	45.48	39.8	0.15	12.1	51.4	7.76
166	25.14	0.09	19.88	1.39	0.00	42.53	42.5				
211	31.84	0.15	21.27	6.70	2.35	55.93	51.2	0.8	16.6	55.1	13
256	41.37	0.21	25.62	9.53	4.92	70.29	60.5	1.22	17.1	66.6	6.43
286	47.98	0.22	30.23	6.61	4.20	73.67	65.3	2.46	20.6	67.2	7.76
316	54.67	0.22	32.63	6.69	3.37	78.64	71.9	3.12	25.4	55.9	9.75
355	64.93	0.26	35.95	10.26	4.53	92.43	83.4	1.65	35	43.9	10
400.5	74.57	0.21	41.69	9.63	5.96	102.65	90.7	1.43	34	61.9	8.58
419	84.20	0.52	45.37	9.64	6.74	110.00	96.5	0.68	30.6	80.3	8.58
464	90.38	0.14	48.26	6.18	5.44	108.89	98.0	2.22	31.7	71.2	9.21

Initial soln: 395 ml water, 45 ml HF (1.28 mol HF, 4.8 wt%, 9 vol%), 60 ml HNO$_3$ (0.9 mol HNO$_3$, 10.7 wt%, 12 vol%), 500 ml in total

Time (min)	Boost (ml)		Cum boost (ml)		Cum HF (ml): HNO$_3$ (ml)	Total dissolved metal (g)			Total dissolved metal (mols)		
	HF	HNO$_3$	HF	HNO$_3$		Ti	Al	V	Ti	Al	V
0	45	60				0.000	0.000	0.000	0.000	0.000	0.000
60		0				8.487	0.566	0.377	0.177	0.021	0.007
76	44.7	0	45	0		10.143	0.676	0.451	0.212	0.025	0.009
150	45	18	90	18	5.0	21.375	1.425	0.950	0.446	0.053	0.019
166						22.626	1.508	1.006	0.472	0.056	0.020
211	42	0	132	18		28.656	1.910	1.274	0.598	0.071	0.025

Table continued

Time (min)	Boost (ml)		Cum boost (ml)		Cum HF (ml): HNO$_3$ (ml)	Total dissolved metal (g)			Total dissolved metal (mols)		
	HF	HNO$_3$	HF	HNO$_3$		Ti	Al	V	Ti	Al	V
256	40	30	172	48	3.6	37.233	2.482	1.655	0.777	0.092	0.032
286	34.1	23	206	71	2.9	43.182	2.879	1.919	0.902	0.107	0.038
316	30.8	12	237	83	2.9	49.203	3.280	2.187	1.027	0.121	0.043
355	38	11	275	94	2.9	58.439	3.896	2.597	1.220	0.144	0.051
400.5	39	19	314	113	2.8	67.110	4.474	2.983	1.401	0.166	0.058
419	42.6	19	356	132	2.7	75.782	5.052	3.368	1.582	0.187	0.066
464	35	15	391	147	2.7	81.346	5.423	3.615	1.698	0.201	0.071

Time (min)	Total metal (mol)	Reaction 2				HF:Ti	HNO$_3$:Ti	HF:HNO$_3$	Reaction 1	
		Theoretical	Measured	Theoretical	Measured				HF used	HNO$_3$ used
		HF used (mol)	HF used (mol)	HNO$_3$ used	HNO$_3$ used (mol)				Non-alloy equation	
0	0.000	0.000	0.000	0.000	0.000				0.000	0.000
60	0.206	1.134		0.195					1.063	0.177
76	0.246	1.355	1.250	0.233	0.113	5.90	0.53		1.271	0.212
150	0.518	2.856	2.509	0.491	0.431	5.62	0.96	5.83	2.677	0.446
166	0.548	3.023		0.520					2.834	0.472
211	0.694	3.829	3.675	0.658		6.14			3.589	0.598
256	0.902	4.975	4.782	0.855	0.848	6.15	1.09	5.64	4.664	0.777
286	1.046	5.770	5.712	0.992	1.166	6.34	1.29	4.90	5.409	0.902
316	1.192	6.574	6.548	1.130	1.335	6.37	1.30	4.90	6.163	1.027
355	1.415	7.808	7.593	1.342	1.504	6.22	1.23	5.05	7.320	1.220
400.5	1.625	8.967	8.670	1.541	1.673	6.19	1.19	5.18	8.406	1.401
419	1.835	10.125	9.853	1.740	1.841	6.23	1.16	5.35	9.493	1.582
464	1.970	10.869	10.817	1.868	2.010	**6.37**	**1.18**	**5.38**	10.189	1.698

Reactions: #1 $Ti + 6HF + HNO_3 \Rightarrow TiF_6^{-2} + 2H^+ + 0.5N_2O + 2.5H_2O$

#2 $Ti + 0.10Al + 0.04V + 6.4HF + 1.1HNO_3 \Rightarrow TiF_6^{-2} + 2H^+ + 0.1AIF_3 + 0.04VF_3 + 0.6N_2O + 2.8H_2O$

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