# Metal Finishing Workshop

## Rochester Institute of Technology
## March 4, 2010

# Acid Etching of Titanium Alloy Case Study

# Overview

- Introduce TECT Power Corporation
- Define Problem
- Understand the chemical reactions
  - Conduct research
  - Propose stoichiometric solution
  - Test proposed solution on bench scale
  - Confirm veracity of proposed solution
- Develop process alternative consistent with proposed stoichiometric solution
- Implement process alternative
- Measure results

# Introduction to TECT Power Corp.

- Based in Utica, New York
- Manufactures turbine blades to stringent specifications
- Incurred large expenses in disposing of hazardous waste
  - Generated 502 tons of hazardous waste in 2007 from chemical etching operations
  - Spent $395K on purchase and disposal of etching acids
- Contacted local RTDC (MVATC) to find a P2 solution
- MVATC contacted NYSP2I, and a collaborative effort between TECT, MVATC, and NYSP2I was initiated

# Define Problem

- Uses corrosive acids to mill blades to specifications
- Turbine blades are very expensive - $40K per blade
- TECT changes out acid baths frequently (once per week) so as to maintain reasonably constant acid etching rates; doesn't want to overetch (and ruin) turbine blades
- TECT wanted to identify a means of reducing etching costs and waste, but did not replace process due to customer specification requirements

# Understand Stoichiometry

Conduct Research

- Conduct literature search
- Determine chemical reactions of hydrofluoric acid (HF) and nitric acid ($HNO_3$) on titanium

Combine above reactions to obtain overall chemical reaction

$$\mathbf{Ti + 6HF + HNO_3 \rightarrow 2H^+ + TiF_6^{-2} + \tfrac{1}{2}N_2O + 2\tfrac{1}{2}H_2O}$$

Note that molar ratio of HF to $HNO_3$ is 6:1!

# Propose Solution

- Next, determine composition of alloy by weight
  - 90% titanium
  - 6% aluminum
  - 4% vanadium
- Determine chemical reactions of hydrofluoric acid (HF) and nitric acid ($HNO_3$) on vanadium and aluminum
- Combine above reactions using molar composition of alloy to obtain overall chemical reaction

$$\mathbf{Ti + 0.12Al + 0.05V + 6.5HF + 1.1HNO_3 \rightarrow}$$

$$\mathbf{2H^+ + TiF_6^{-2} + 0.12AlF_3 + 0.05VF_3 + 0.6N_2O + 2.8H_2O}$$

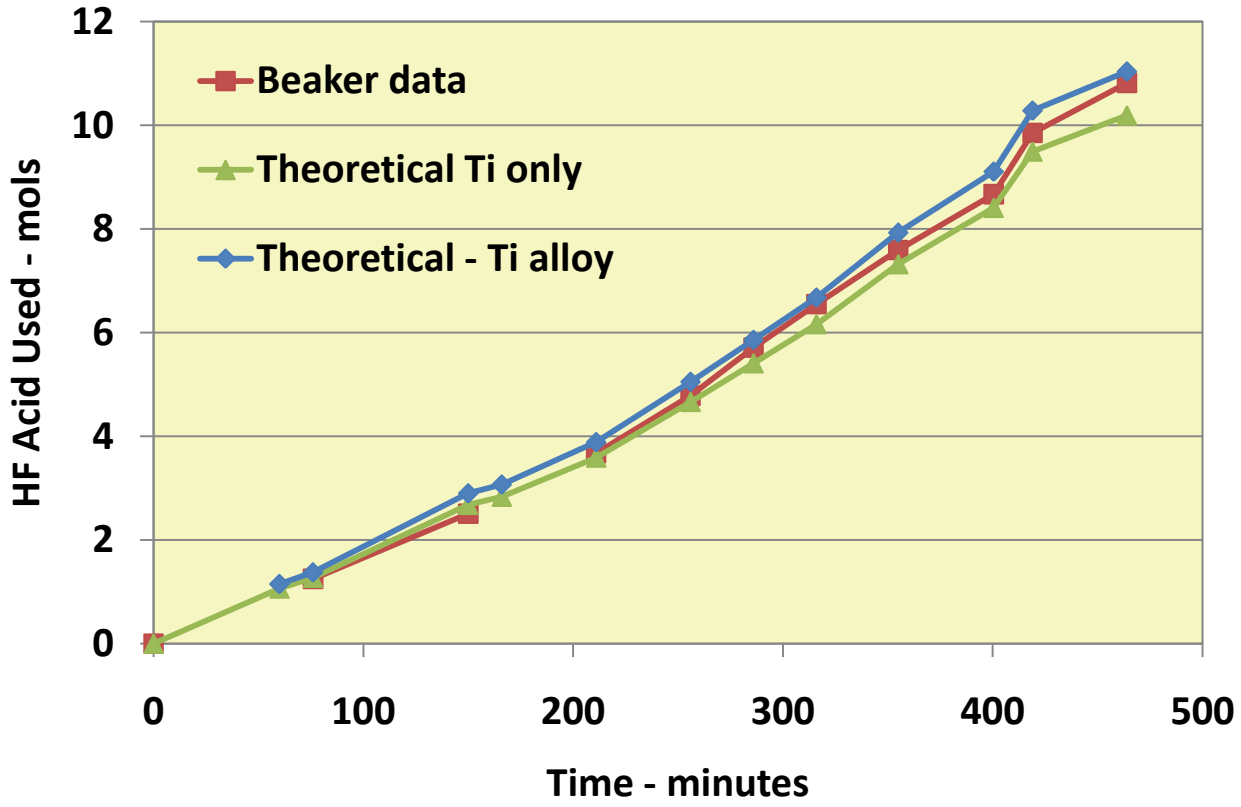
Note that molar ratio of HF to $HNO_3$ is still about 6:1!

# Conduct Bench-Scale Testing


Test Conditions:

- 500 ml test volume in 1-liter beaker
- Initial acid concentrations at 9% HF and 12% $HNO_3$ as per customer specifications
- Etch titanium coupon for prescribed time period and boost to return acid concentrations to 9% and 12%
- Control temperature with ice bath at 80 deg F
- Run each etch cycle to nearly deplete HF
- Dissolved metal mass determined by weighing coupon on analytical balance

# Confirm Veracity of Proposed Solution



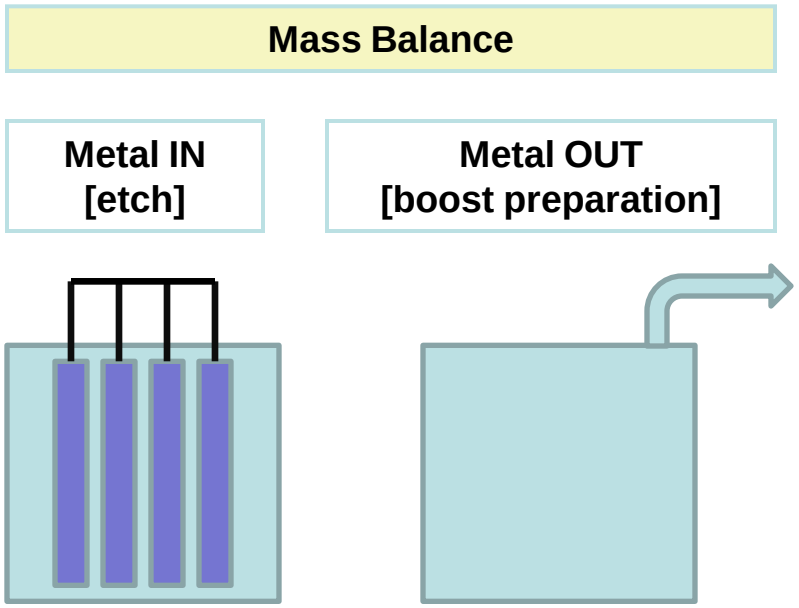
# Application of Beaker Test Results

**An understanding of the stoichiometry allows us to:**

- Determine maximum waste generation
- Determine maximum total metal concentration
- Identify and avoid potentially unacceptable operating conditions

# Determine Maximum Dissolved Metal Concentration

1. Titanium is added during etching
2. Dissolved titanium is removed with liquid to prepare for boosting

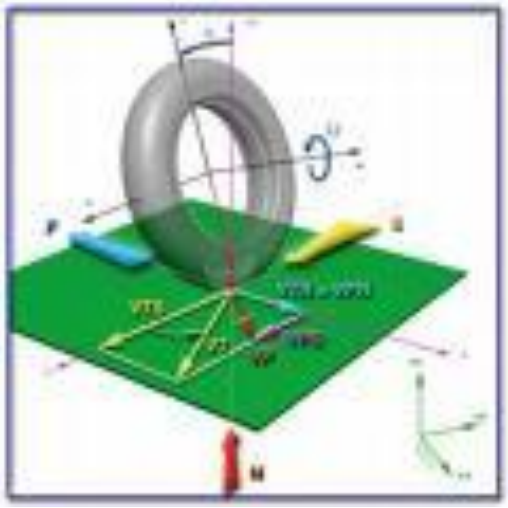



➔ **At Steady State: Metal In = Metal Out**

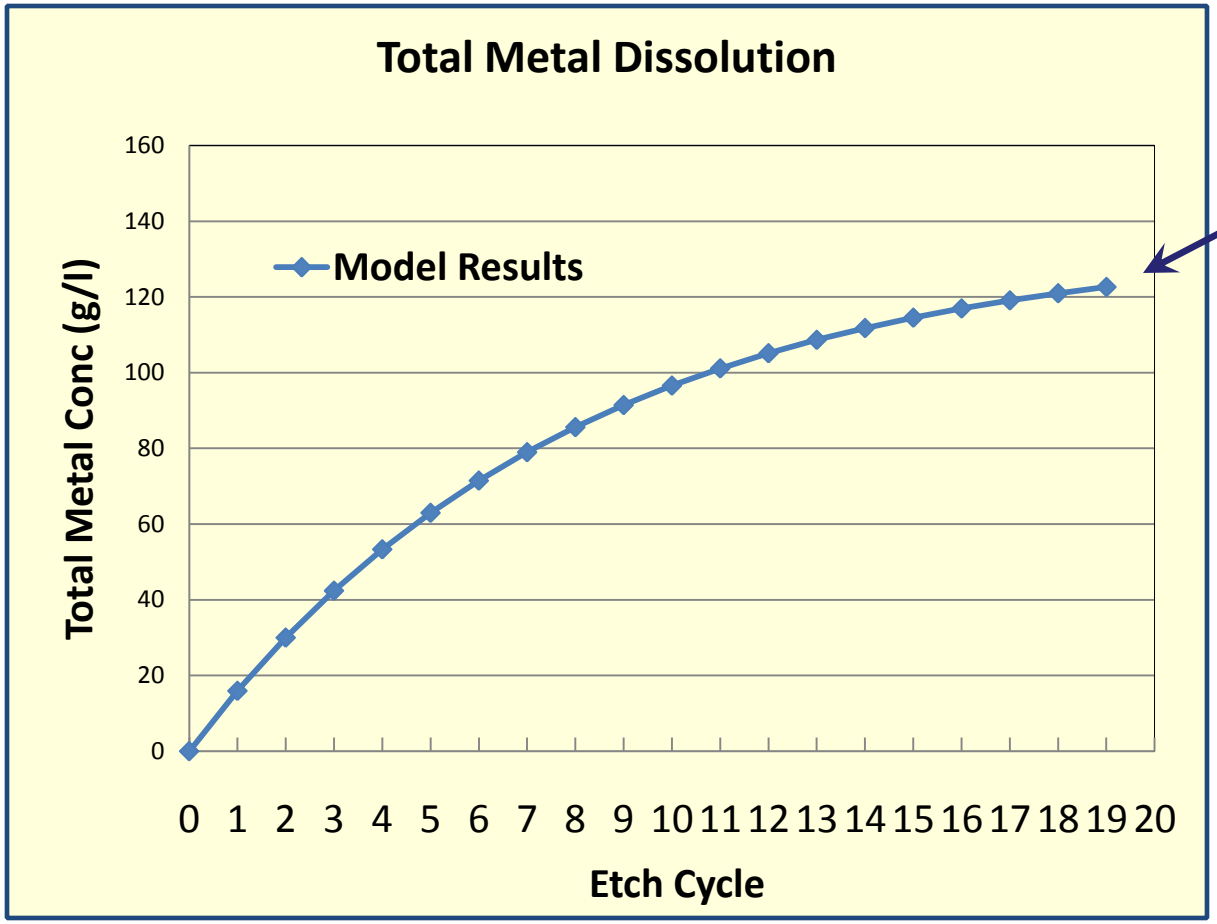
# Develop Mathematical Model

Mathematical Model Formulated to Simulate Beaker Test:

- Titanium dissolution – 6.5 moles HF per mole of Ti
- HF and $HNO_3$ acid concentrations initially set at 9% and 12%, respectively
- HF and $HNO_3$ acid concentrations are boosted at the end of each etch cycle to return to 9% and 12%, respectively

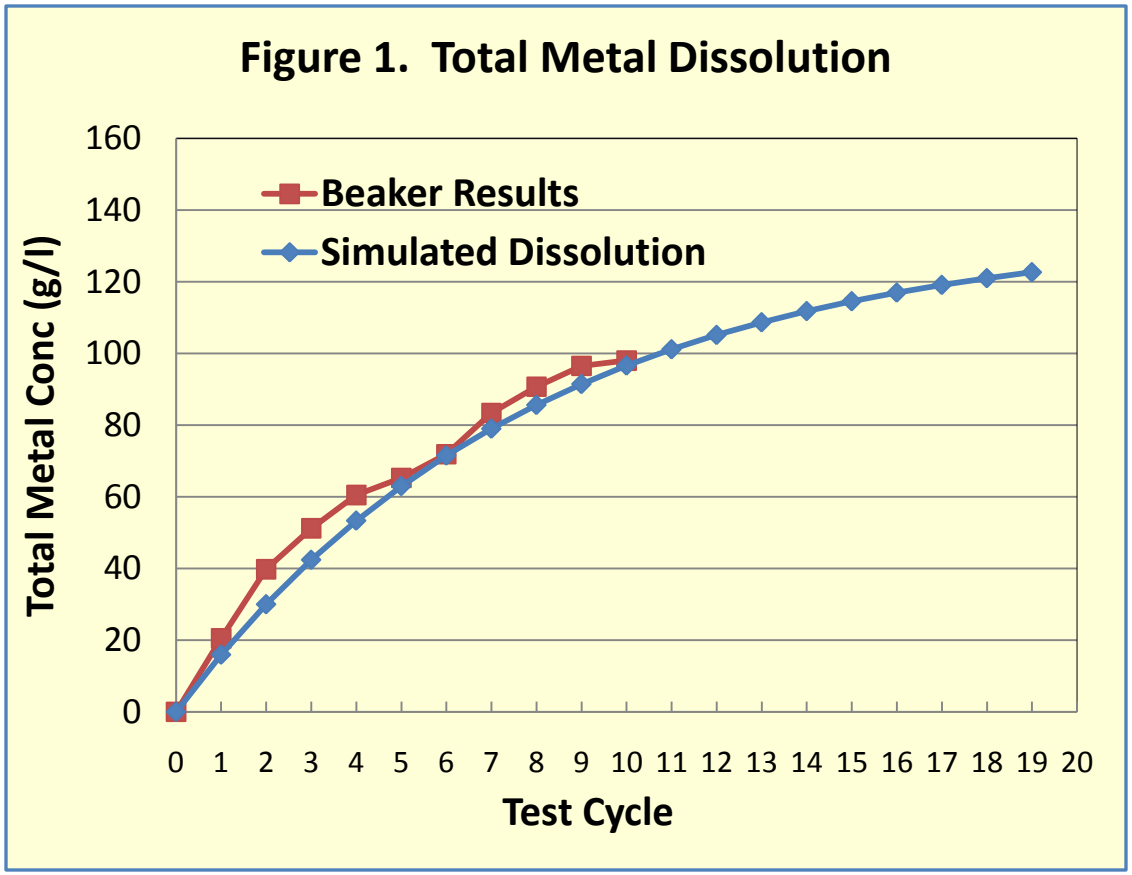


# Model Predictions of Etch Process




Steady State
~130 g/l

# Comparison of Model with Beaker Test Results



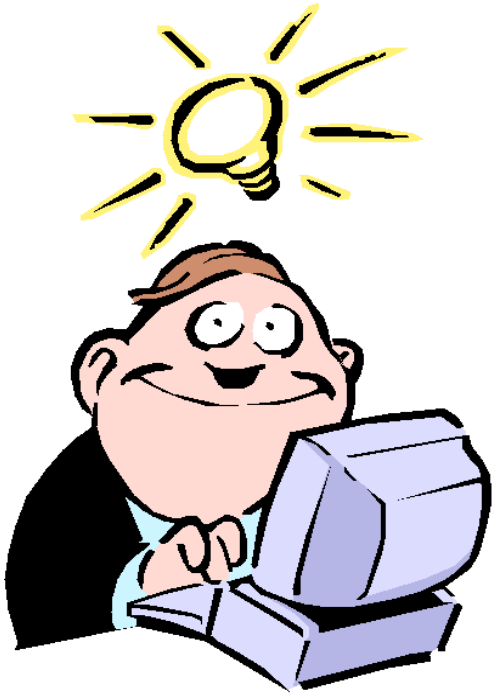

**Math model and beaker data show good correlation**

# Outcome of Steady State Evaluation

- Total metal concentration reached approximately 110 grams/liter at the end of the last beaker etch cycle
- If the saturation concentration of dissolved titanium is greater than 130 grams/liter, then the etch bath could operate indefinitely without dumping (other than for maintenance needs), provided acid boosts were performed correctly
- Operating in this mode reduces the quantity of hazardous waste generated to its minimum level because all tank dumping is eliminated

# Key Learnings from Lab Testing

- Proposed stoichiometric solution is correct
- No precipitation occurred up to 110 grams/liter of dissolved metal
- Etch rates remain constant over multiple boosts
- Multiple etch batches can be run without dumping when the acid boosts are properly conducted, so there is no need to dump acid baths so frequently!



# Actual Results for 2009

- Proposed solution was partially implemented at TECT during the latter half of 2009
- Actual reductions in hazardous waste from chemical etching operations amounted to 292 tons per year in 2009 when compared to the baseline year of 2007
- This 58% reduction represents savings of $178,000 per year, and reflects both implemented P2 process improvements as well as decreased production.

# Potential Results for 2010

- If TECT fully implements NYSP2I's recommendations for all of 2010, hazardous waste from chemical etching operations can be potentially reduced by 431 tons (86%) if production volume returns to 2007 levels
- This represents annual savings of $290,000 for the purchase and disposal of etching acids, due to the longer acid bath lives

# Questions and Discussion