

Microwave Corrosion Testing of Alloys for Autoclaves

Shawn M. Allan*

Morgana Fall, Inessa Baranova, Dr. Holly Shulman

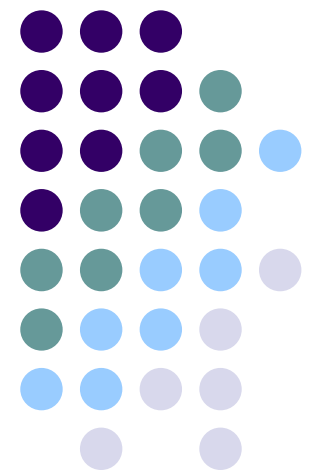
Ceralink Inc.

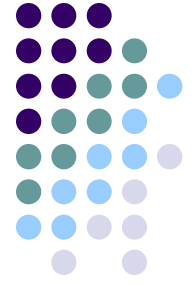
Dr. Lawrence Shore, BASF Catalysts

October 18, 2010, 3:40 PM

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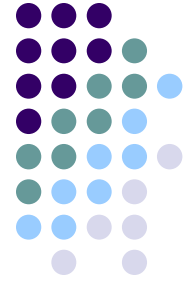
High Temperature Corrosion Session
Houston, Texas





Outline

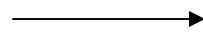
- Background
 - Need for an autoclave for strong acid solutions
 - Technical difficulties in materials selection
- Study
 - Microwave digestion system for determining suitable materials
 - Materials selection and autoclave building
 - Autoclave testing in corrosive environment
- Summary



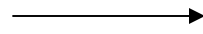
Polymer Fuel Cells

5 layer Membrane Electrode Assembly

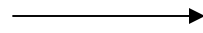
Gas Diffusion Layer



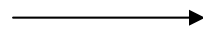
Anode Catalyst Layer



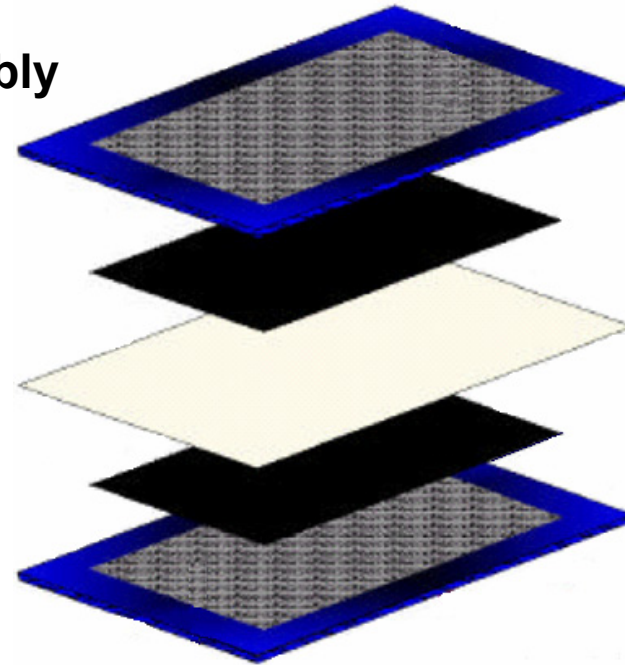
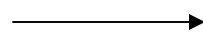
Nafion® Membrane



Cathode Catalyst Layer



Gas Diffusion Layer

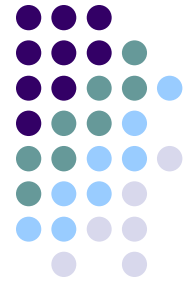


Recycling Project Goals:

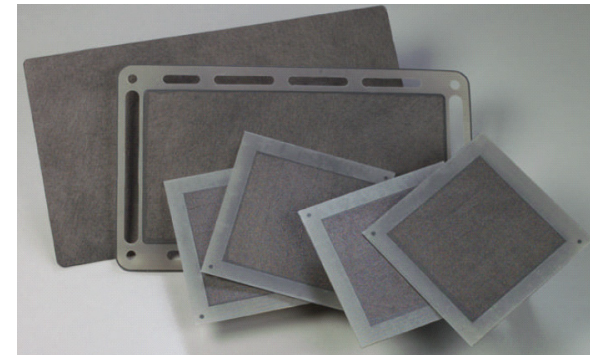
- Digest platinum catalyst into solution
- Avoid burning Nafion membrane

Precious Metal Recovery

Microwave Digestion

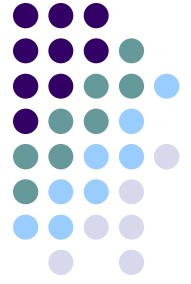


- Ceralink assisted BASF → \$5 mil from DOE to develop a method for precious metal recovery from used fuel cell membranes.
- Current method is ashing:
 - Fluoropolymer + flame → **HF** → costly environmental problem
 - And... **Platinum** → **\$511 /m²**
Nafion® → **\$2,400 /m²**
- Microwave digestion → up to **99% Pt recovery**
 - Improved yield
 - Avoid HF generation
 - Easier to manage by-products
 - Simultaneous recovery of metal and polymer
- Uses for recycled Nafion®

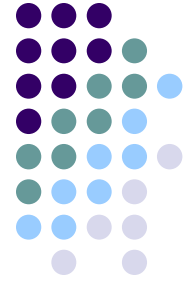


Microwave Autoclaves

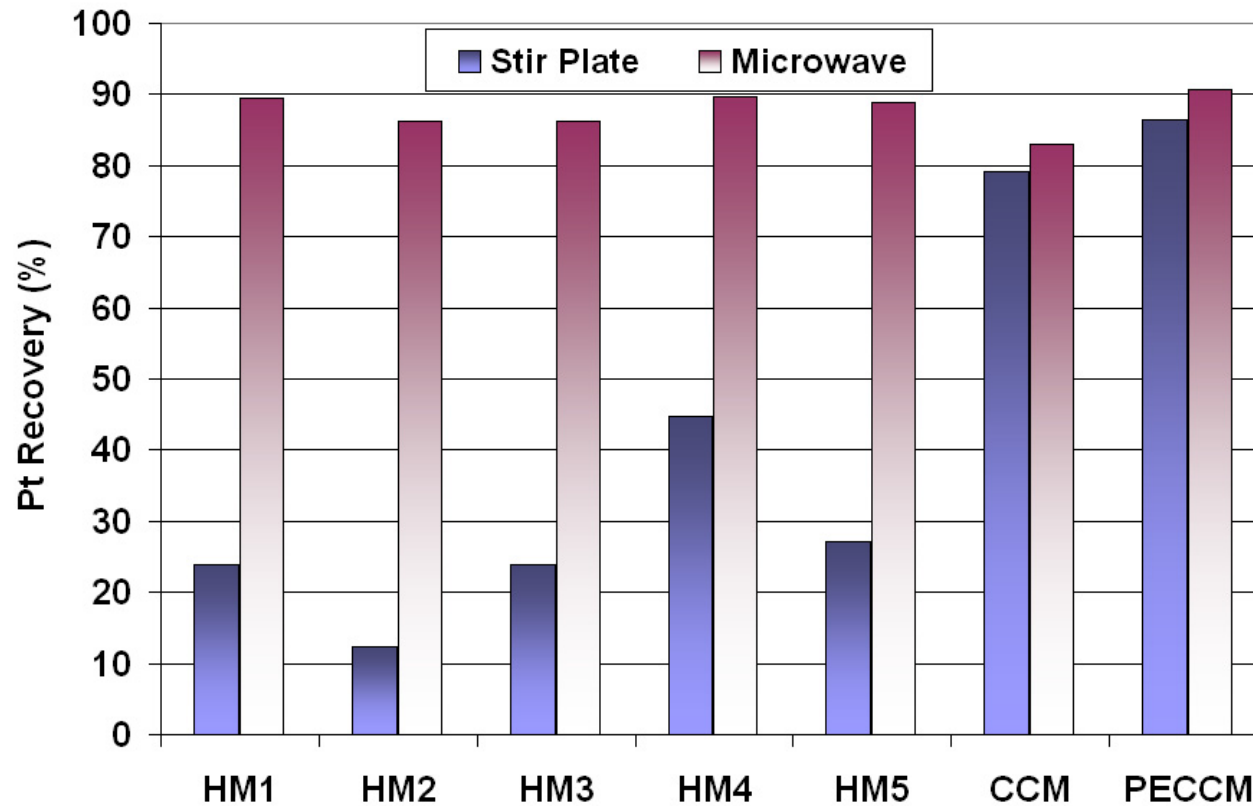
- Short cycle times → Quick process development
- Accelerated reactions (microwave superheating)
- Safety: no physical contact with heat source
- Allows high T-P research without exhaustive materials search
- Significantly lower cost vs. specialty alloy autoclaves
- Cold walls – less system corrosion



Ceralink inc



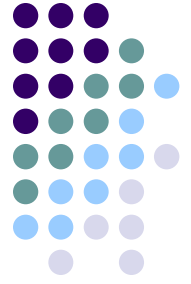
Microwave vs. BENCHTOP



Stir plate ~70 °C
1 atm
stirred

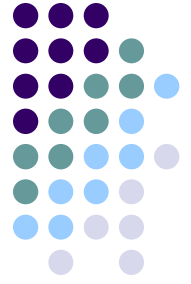
Microwave ~200 °C
20-40 atm
30 minute soak
no agitation

Effects →
Temperature,
Pressure,
Stirring,
Containment



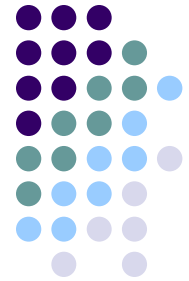
Corrosion testing summary

- Highly corrosive environment – strong demand on the system
 - Vessel valves, fittings, safety devices (e.g., rupture discs)
 - Fluid pumps, motors
- Over 60 corrosion tests were performed
 - Stainless Steel T316
 - Hastelloy B
 - Hastelloy C
 - Inconel
 - Tantalum
 - Zirconium 702
 - Titanium Grade 2 & 4
- Identified silicon coating – Silcotek’s Silcolloy (formerly Restek Silcosteel-CR)
- Results are being prepared for publication



Corrosion study - materials

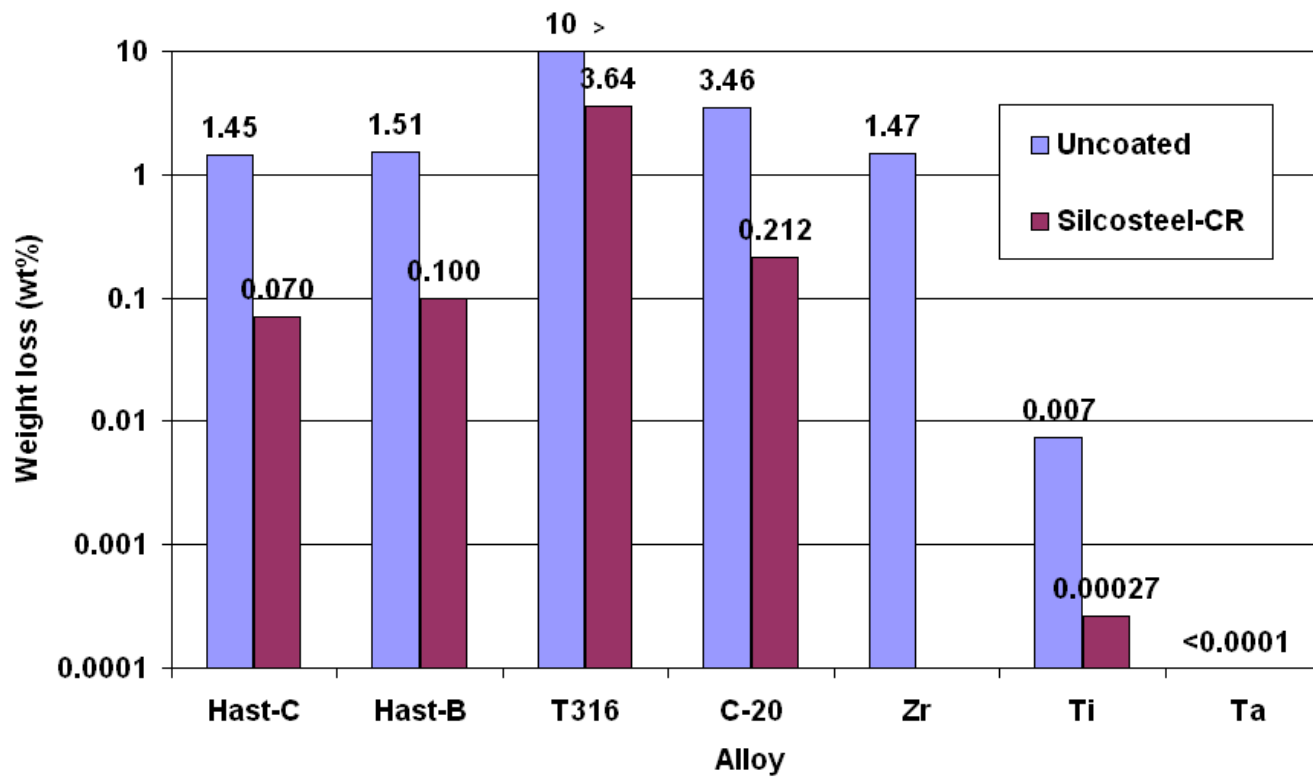
- Stainless steel and nickel alloys (Hastelloy, Inconel, Monel, Zirconium)
 - Poor resistance to aqua regia and HCl + peroxide
- Tantalum
 - Best chemical resistance
 - Exorbitant cost & severe supply issues
 - Rupture discs available in tantalum
 - Stable oxide prevents Ti-interaction from oxidation potential differences
- Titanium
 - Acceptable resistance to both reagent systems
 - Cost similar to nickel alloys
 - Lighter weight system – easier to handle
 - Low pressure rupture discs not available



Silcotek™* silicon coating

- Silcosteel-CR silicon coating reduced corrosion 20-fold for each alloy

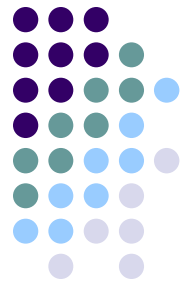
Impact of Silcosteel-CR coating on corrosion
16.5 mL HCl + 5 mL H₂O₂, 125 °C, 10 min dwell
Gravimetric loss to 0.01%. Smaller changes by ICP-OES.



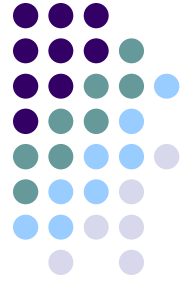
*Silcotek, formerly Restek Performance Coatings

Corrosion testing of titanium

- Corrosion testing performed in Milestone microwave system
- Same system as for MEA digestion
- Teflon vessel and lines
- Tested several reagent combinations
 - HCl + H₂O₂
 - Aqua regia (3.3 HCl : 1 HNO₃)
 - Reduced aqua regia (3.3 HCl : 0.1 HNO₃)
- Investigated corrosion inhibitors
 - Boric acid
 - Iron chloride
 - **Copper sulfate**
- Investigated corrosion resistant coating – Silcosteel CR

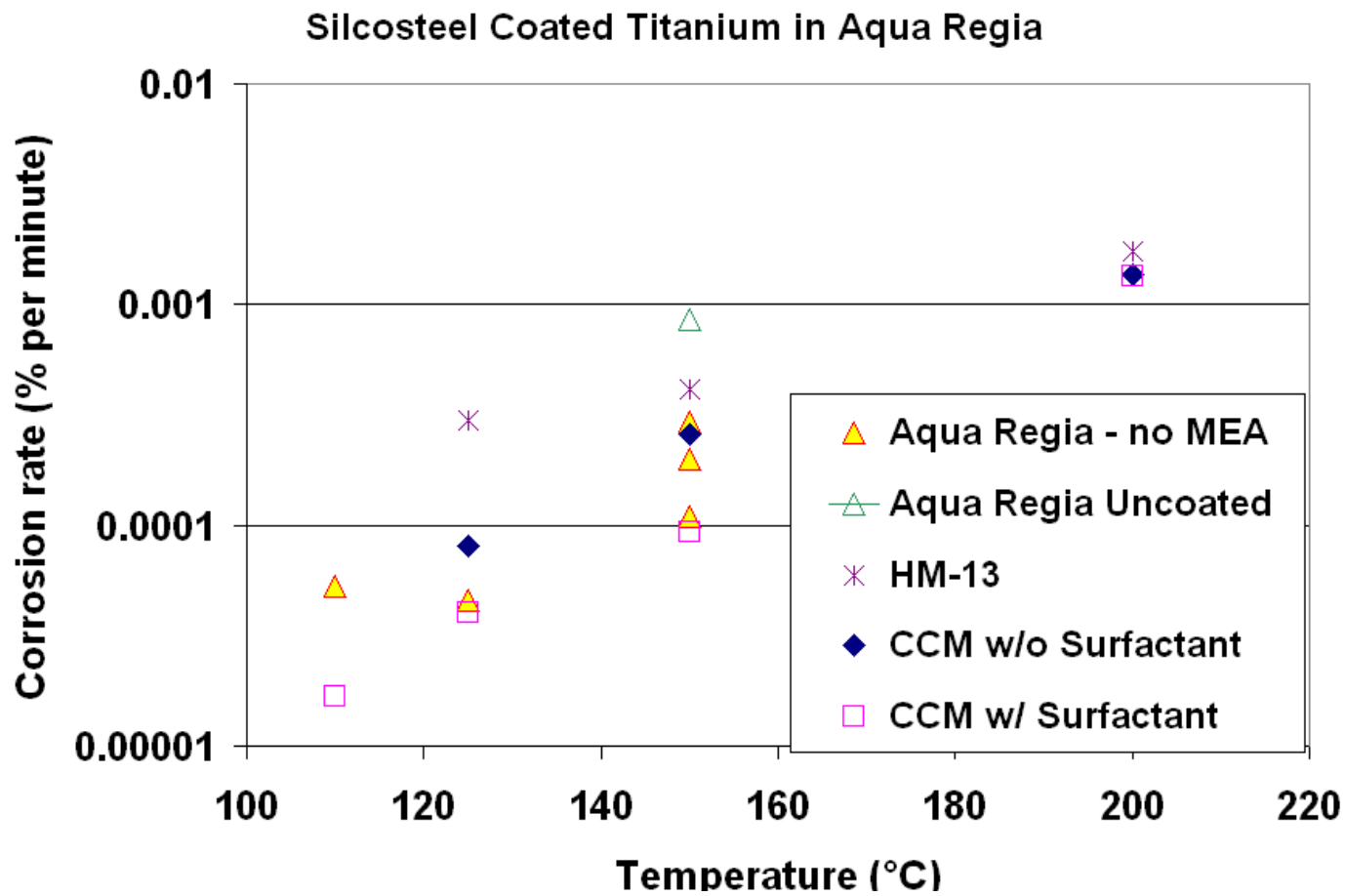
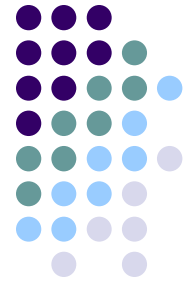


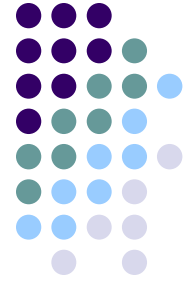
Titanium resistance to digestion reagents



- Ti attacked by reducing acids – HCl, HF
- Ti protected by oxidizers – wet Cl_2 (HClO), HNO_3
 - Timet reports 1% HNO_3 provides strong resistance to boiling HCl
 - Testing found
 - Aqua Regia (3.3 HCl : 1 HNO_3) → Ti has good resistance
 - $\text{HCl}:\text{H}_2\text{O}_2$ → Ti has good resistance at low temperature < 0.01 % at 100 – 125 °C
 - $\text{HCl}:\text{H}_2\text{O}_2$ → Severe reaction occurred at 200 °C → **58% loss of Ti!!**
- Corrosion results indicate order of acid addition may be important with Ti
- Corrosion testing contributed to selection of Aqua Regia for scale up.
- Increased Ti corrosion with reduced nitric aqua regia (3.3 HCl : 0.1 HNO_3)
- 29 experiments showing 0.01 % or less corrosion of Ti with various reagent combinations, MEA, and inhibitors

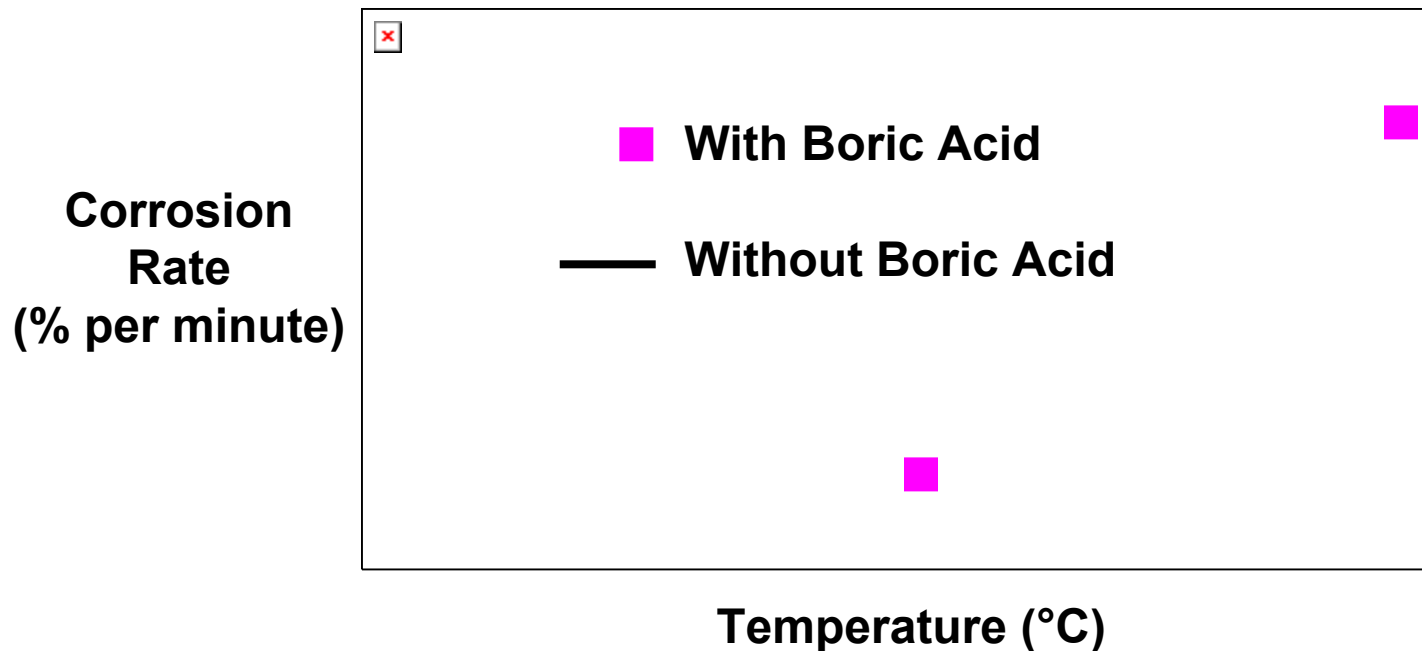
Corrosion resistance with Silcosteel-CR coating

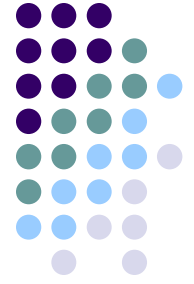




Boric acid data

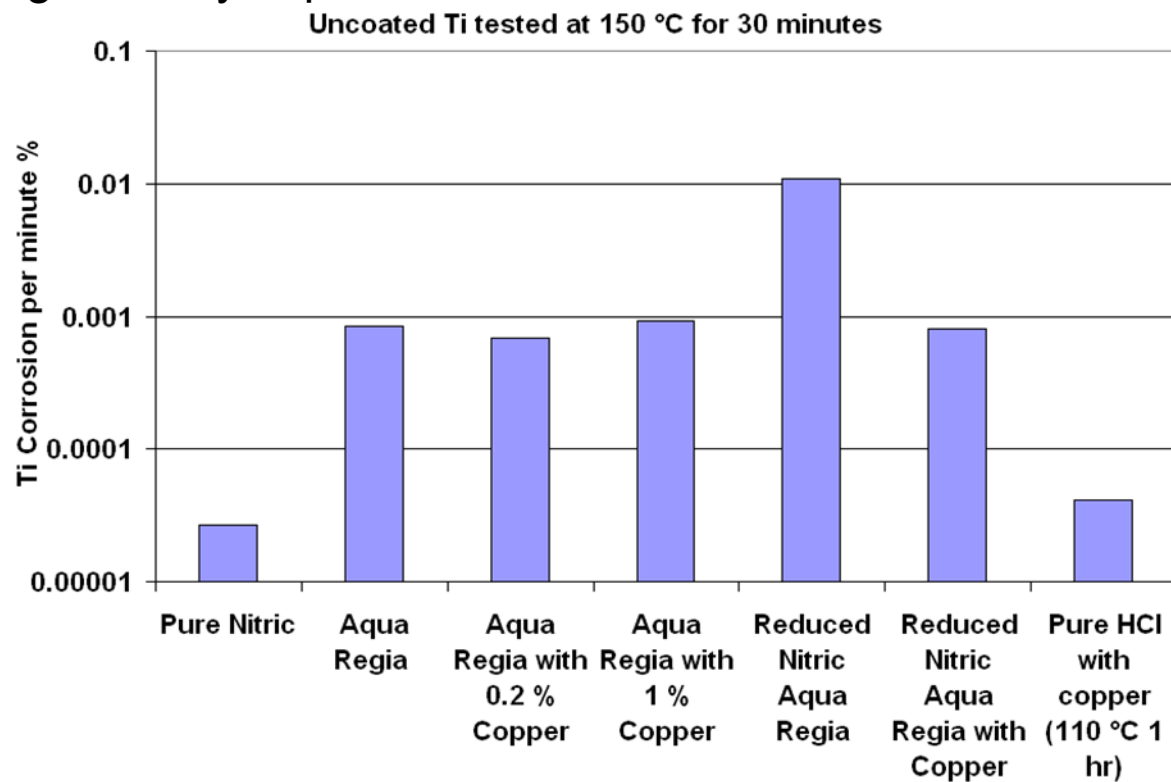
- Nafion releases some fluoride (ppm level) into solution during digestion
- Fluoride expected to attack silicon coating and titanium
- Expected boric acid to getter fluoride
- Boric acid increased corrosion rate of Ti

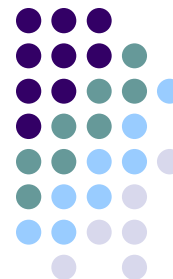




Ti protection by CuSO_4 addition

- Copper sulfate identified by Timet as inhibitor of HCl corrosion on Ti
- Concentrations as low as 0.2% in HCl provide high temperature protection
- CuSO_4 significantly improved Ti resistance to Reduced Nitric Aqua Regia





Parr autoclave

Basic Parr Instruments System

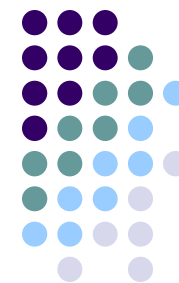
- **Titanium** vessel Magnetic drive stirrer
- Sampling ability

Ceralink additions

- Silcosteel-CR coating
- **Tantalum** rupture disc
- High pressure **titanium** valves and tubing
- **PFA** and **Teflon** low pressure tubing and fittings
- Toxic gas detection system
- Recirculating cooling water
- Acid gas scrubbing system



Parr autoclave

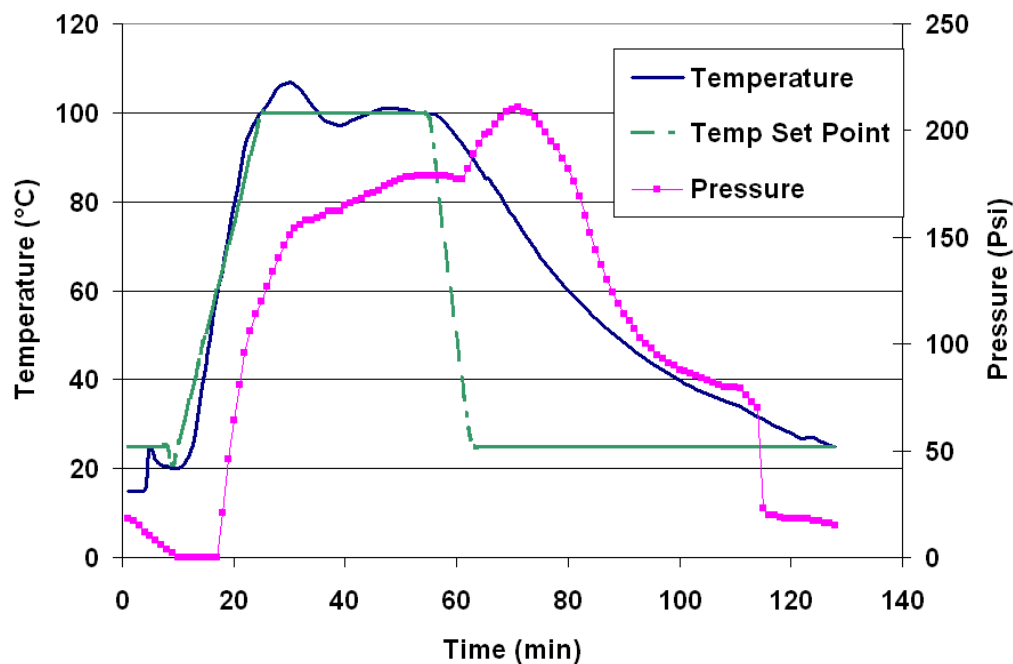


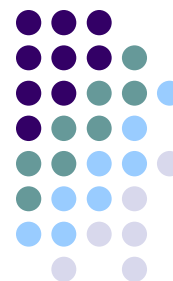
- Detailed Standard Operating Procedure developed
- Vacuum filtration system for rapid sample collection
- Computer controlled with data acquisition
- Some difficulty with <100 °C temperature control

Temperature & Pressure Profile for Run PAR-009

Aqua Regia + CuSO_4
NE-17-08
100 °C for 30 minutes
~350 rpm stirring

99.5% Pt Recovery





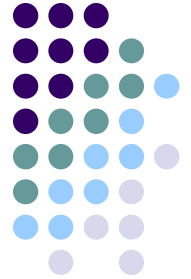
Parr initial data summary

All initial testing performed at 100 °C, 30 minutes, ~300-350 rpm
Using Aqua Regia and 0.2 % CuSO₄

| MEA | Run No. | Solids loading (g) | Pt % Recovery |
|----------|---------|--------------------|---------------|
| HM-4 | PAR-007 | 3.649 | 56.6* |
| HM-9 | PAR-008 | 3.651 | 98.6 |
| NE-17-08 | PAR-009 | 3.654 | 99.5 |
| NE-18-08 | PAR-010 | 3.660 | 99.5 |
| NE-17-08 | PAR-011 | 7.303 | 99.5 |

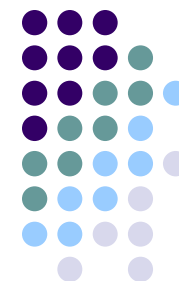
*HM-4 result was significantly higher than Iselin method, but less than 200 °C microwave method

External Benefits of Development



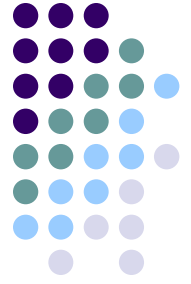
- Identified application of Restek (now Silcotek in PA) coating to Titanium for high temp
- Parr (IL) now sends components to Silcotek for coating
- Collins Inst. (TX) supplied Ti ball valves, now also working with Silcotek
- Fike (OK) developed low pressure Ta rupture disc

Reagent System Pros & Cons



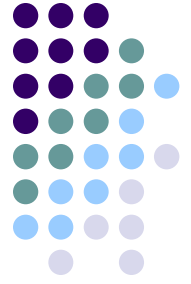
| System | Pt Recovery | Ti System |
|--|---|--|
| HCl & H ₂ O ₂ 3.3 HCl : 1 H ₂ O ₂ | Rapid reaction of reagents High pressure Good recovery rates | Potential for rapid corrosion at 200 °C Low temperature – ok corrosion resistance. Coating greatly improves resistance even at low T |
| Aqua Regia 3.3 HCl : 1 HNO ₃ | Slower decomp. Lower Pressure Good recovery rates | Ti has inherently good corrosion resistance |
| Low Nitric Aqua Regia 3.3 HCl : 0.1 HNO ₃ | Lowest pressure Process prefers HCl added first for non-agglomerated Agglomerated – no impact of Equivalent Pt recover rates Less reagent expense Higher % HCl recycling Less Cl ₂ and NOCl emission | Less corrosion resistance, especially if HCl added first Inhibitors more useful in this system Ti prefers HNO ₃ added first |

Project Outcomes & Conclusion



- Microwave digestion systems provided excellent opportunity for fast, safe corrosion testing
- Successful lab demonstration of platinum and Nafion® recovery
- A patent applied for PEM recovery process
- A microwave and non-microwave autoclave designed and built
- Titanium autoclave built to study high P-T without microwave
 - Aqua regia and wet Cl₂ resistant without use of Teflon liner
 - Microwave autoclave used for extensive corrosion testing
 - **Need better alternative to Si-coating on Ti in hot zone**
- BASF designed pilot plant facility
- **HF emissions from PEM fuel cell recycling will be avoided** – when polymer fuel cells become ubiquitous

Thank you! Questions?



www.Ceralink.com



Contact: Shawn Allan
Sr. Materials Engineer
(518) 283-7733
shawn@ceralink.com

