

Platinum Group Metal Recycling Technology Development

Dr. Lawrence Shore

BASF Catalysts LLC

Iselin, NJ 08830

5/21/2009

fc_33_shore



The Chemical Company

This presentation does not contain any proprietary, confidential or otherwise restricted information

Timeline

- Start - 11/2003
- Finish – extended to 10/2009
- 98% Complete

Budget

- Total project funding
 - DOE share = \$4.03MM
 - BASF share = \$1.01MM
- \$536k received in FY08
- \$517k budgeted for FY09

Barriers

- N (Cost)
 - O (Stack Material and Manufacturing Cost)
- \$45/kw for transportation
 - \$400-\$700kw for stationary

Current Partners - Ceralink

Interactions/Collaborators

- W.L. Gore, 3M, Pemeas (MEAs)
- Parr Company, De Dietrich/Rosenmund (reactor design)
- Hosakawa Polymer Systems (milling)
- B.F. Enterprizes (sonication)

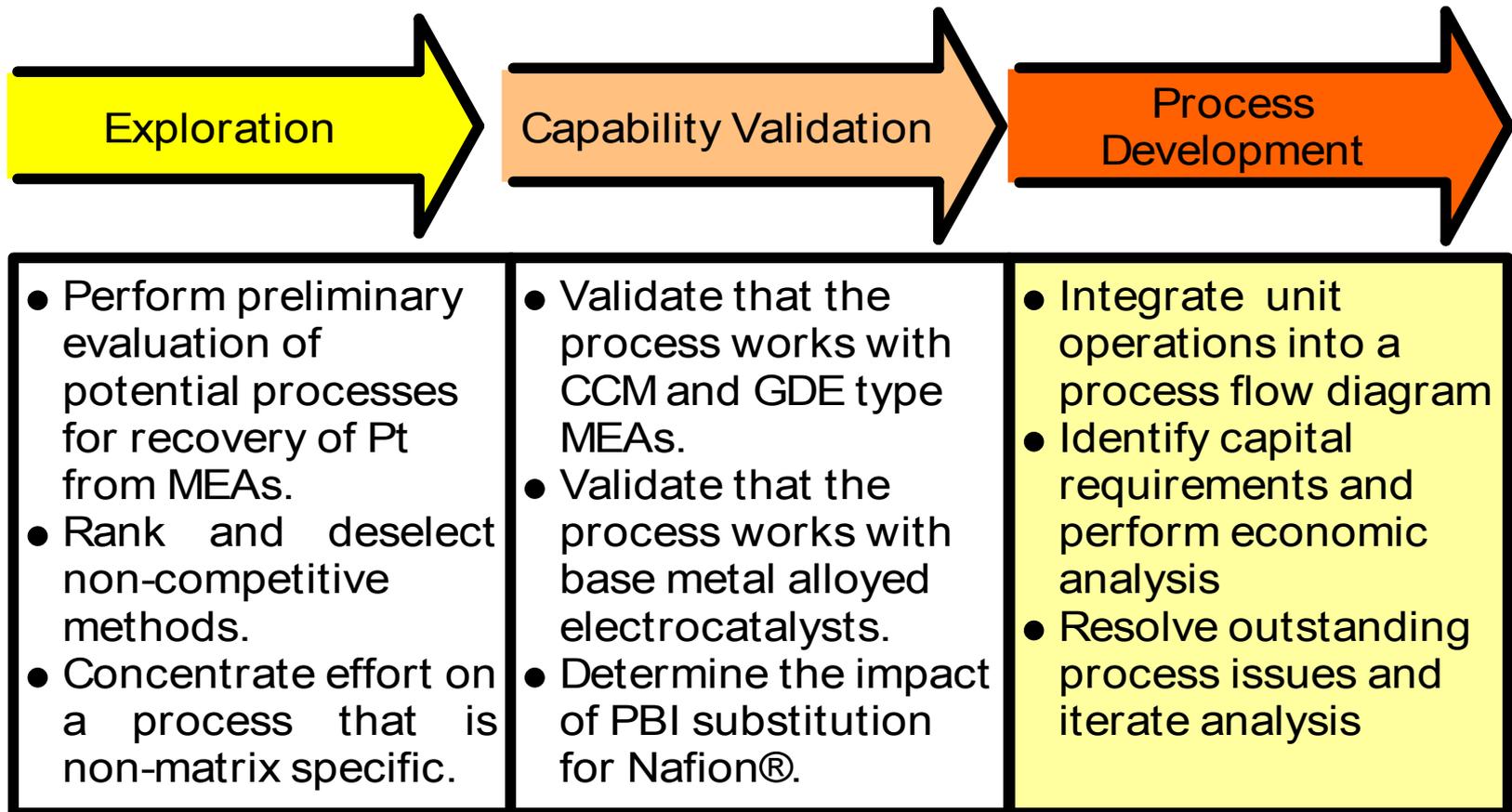
Objectives for 2008-2009 - Relevance

- Achieve Pt recovery rate of 98%
 - To lower the effective cost of Pt used in the MEA
- Simplify process so that Pt recovery is achieved using a single leach
 - To reduce the cost of Pt recovery by increasing throughput
- Determine chemistry and reaction conditions to optimize Pt leaching
 - To reduce reagent usage, reducing process cost
 - To reduce cost of construction for the reactor vessel by identifying the most appropriate reactor liner

Milestones for 2008-2009

Date	Milestone
Oct-08	✓ Evaluate hot-melt agglomeration as a substitute for MEA surfactant wetting
Oct-08	✓ Demonstrate feasibility of pre-embrittlement with LN ₂
Oct-08	✓ Complete evaluation of Laser ablation-ICP for QC testing
Dec-08	✓ Determine preferred order of reagent addition in leaching
Mar-09	✓ Reduce reagent consumption
Mar-09	✓ Re-examine reactor materials of construction
Mar-09	✓ Recalculate process economics

Approach - Overview



Technical Accomplishments (Summary)

- Achieved the objective of 98% Pt recovery without HF release
- Simplified the process so that leaching can be performed in one step in one vessel
- Identified room-temperature alternatives to milling requiring cryogenic cooling
- Reduced the reagent usage required for Pt leaching
- Calibrated the laser ablation-ICP method as an at-line QC test for leach efficiency (supplemental slides)
- Validated a process for pre-leaching of PBI MEAs to remove H_3PO_4 (supplemental slides)

Technical Accomplishments

- Achieved the objective of 98% Pt recovery
 - Determined that a limiting factor is low HCl concentration
 - Minimizing HNO₃ used increases HCl excess
 - Using azeotropic HCl (21%) lowers Pt yield compared to using concentrated (37%) HCl by ~4%
 - Order of addition of reagents is also important
 - Highest Pt yield achieved when HCl is added to MEA powder first, followed by HNO₃
 - This information impacts the selection of reactor materials of construction

Titanium resistance to digestion reagents (Evaluated at Ceralink, Troy, NY)

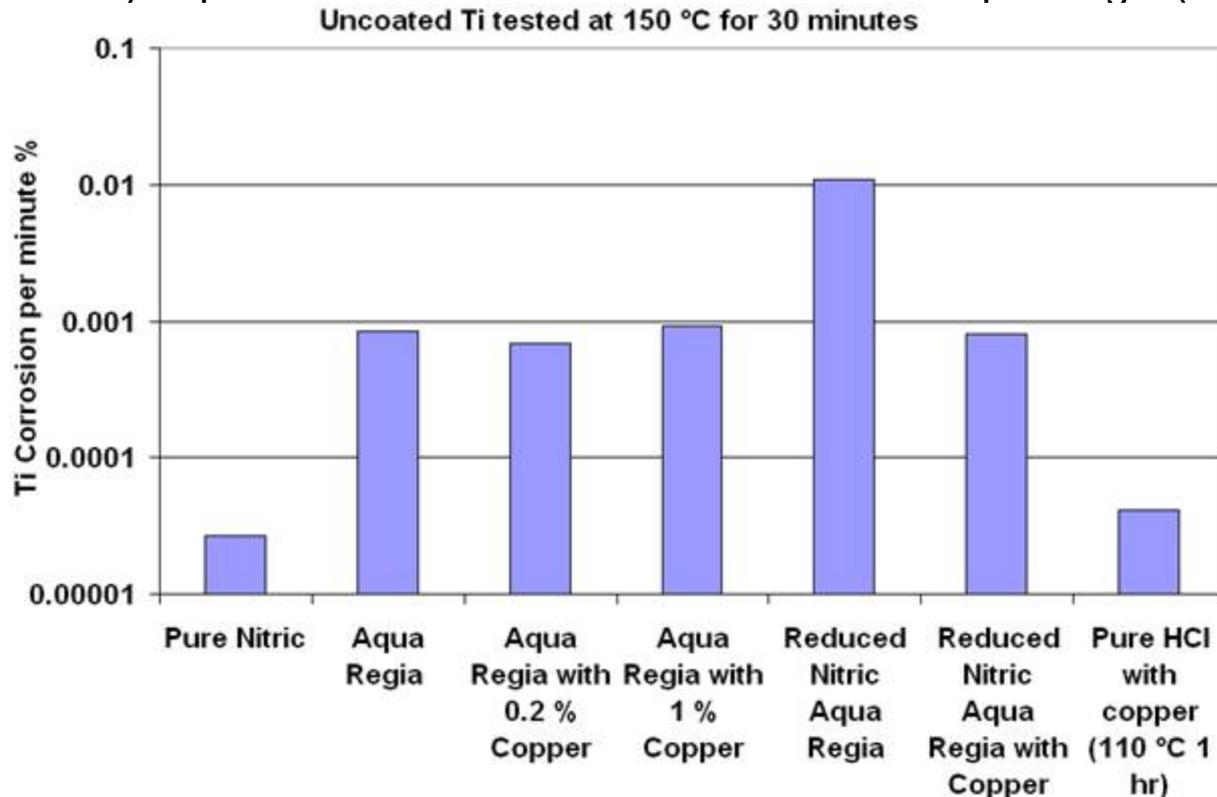
- Ti attacked by reducing acids – HCl, HF

- 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)

Ti protection by CuSO_4 addition (Compiled by Ceralink, Troy, NY)

- Copper sulfate identified by Timet as an inhibitor of Ti corrosion by HCl
- Concentrations as low as 0.2% in HCl provide high temperature protection
- CuSO_4 significantly improved Ti resistance to Reduced Nitric Aqua Regia (3.3 HCl : 0.1 HNO_3)



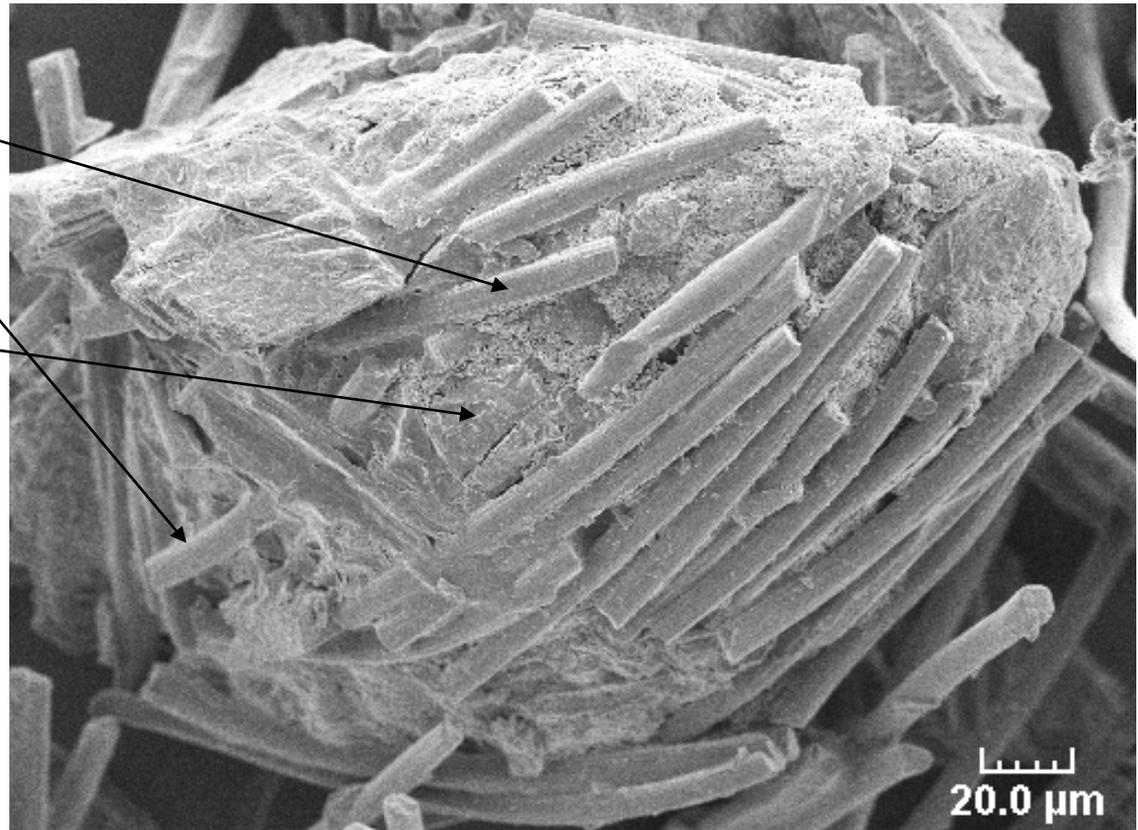
- Simplified the process so that leaching can be performed in one step in one vessel
 - Non-optimized lab results demonstrate near quantitative Pt recovery from MEA powder
 - $T < 100^{\circ}\text{C}$
 - Atmospheric pressure, no oxidant containment
 - Minimal agitation
 - **Based on this data, the Rosenmund filter dryer should be able to achieve process objectives in a single vessel**
 - **Low-speed paddle mixer**
 - **Filtration and rinsing in place**

- Identified alternatives to milling with liquid nitrogen cooling
 - Commercial, 5-layer MEA's (including aged CCM's) processed at room temperature using a HPS press side granulator
 - Process almost dust-free
 - Lost-cost operation
 - Leaching experiments show that the milling product is fully accessible to reagents
 - Downside is that the product is very heterogenous and sampling must be performed carefully

Cost of liquid nitrogen and embrittling mechanism are avoided.

Photomicrograph of Agglomerated MEA's (Pre-embrittled/LN₂ Milled GDE)

- Carbon fibers
- Agglomerated carbon particles



Technical Accomplishments

- Reduced the nitric acid required for Pt leaching
 - HNO_3 added to leach vessel at ~10% of aqua regia stoichiometry
 - Roughly \$0.12 per kg of MEA powder
 - Using less acid reduces NO_x scrubbing requirements, including NaOH for neutralization
 - Using less acid increases HCl available for recycle (~90%)
 - Azeotrope breaker needed to convert HCl /water distillate to concentrated HCl

- Surfactant usage reduced significantly
 - Surfactant requirement minimized by:
 - Granulation of MEA's
 - Use of sonication for rapid particle wetting and dispersion

Surfactant usage impacted by GDL material

- » For woven fiber*, use 1% wt/wt of MEA
- » For carbon paper, use 0.2% wt/wt of MEA

This usage corresponds to roughly \$0.30 of surfactant per kg of MEA material.

* Granulated woven fiber material is very bulky.

Progression of MEA Milling Studies

Methodology with Characteristics

Option A

Granulate MEA at Room Temp using a Cutting mill

Low cost solution, with high yield in milling. Coarse, heterogenous mixture requires sampling, wetting with surfactant.

2009

Methodology with Characteristics

Cryo-mill MEA with hammer mill/LN₂

LN₂ off-gas can carry away fines. Fine, homogenous powder requires wetting with surfactant.

2007

Pre-embrittle MEA in LN₂, then hammer-mill with LN₂

Milling rate is increased. Very fine, homogenous powder requires wetting with surfactant.

2007

Option B

Agglomerate pre-embrittled, milled MEA

Hot melt agglomeration simplifies wetting of milled MEA powder. Very high Pt yields.

2008

Reduced Nitric Acid used @ 2 surfactant levels shows adding HCl first is good leaching milled carbon-cloth GDE's

Treatment	Acid Priority	Surfactant	% Pt yield
Milled and wetted	Aqua Regia ¹	2g of 5% wt/wt	86.3 (90.6*)
	HNO ₃ ² , then HCl	1g of 1% wt/wt	86.8
	HNO ₃ ² , then HCl	0.5g of 5% wt/wt	97.2
	HCl, then HNO ₃ ²	1g of 1% wt/wt.	96.6
	HCl, then HNO ₃ ²	0.5g of 5% wt/wt	98.5
Milled and Agglomerated	HCl, then HNO ₃ ² or HNO ₃ ² , then HCl	Melt agglomerated @ 22% of MEA	99.1

1 - 5 mL of HNO₃, 2 - 1g or 0.65 mL of HNO₃

* Value obtained at Ceralink using pressurized microwave method.

Pt Yields for Cryo-milled and Agglomerated GDE Powders (Process 1)- One-step extraction + rinse

- 99.1 % average yield when concentrated HCl added first
- High yield (98.8 average) when HNO₃ added first if g sample/g HNO₃ > 0.5 and concentrated HCl is then added

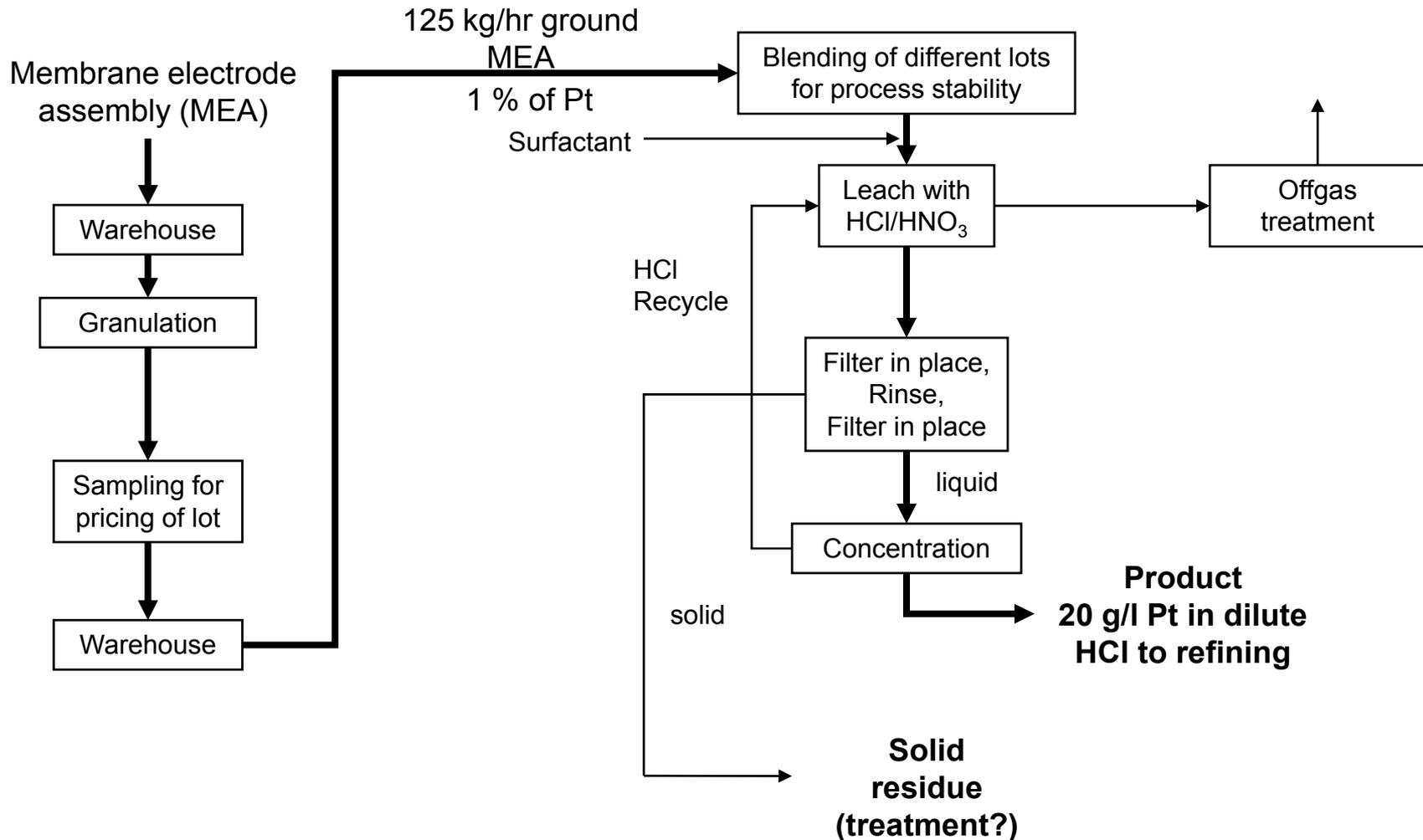
Acid Priority	% HCl	g HNO ₃	g sample		% Pt yield
HNO₃	37	0.96	0.514	0.54	97.9
HNO ₃	37	2.98	0.537	0.18	91.7
HCl	37	1.04	0.518	0.50	98.9
HCl	37	3.06	0.534	0.17	98.3
HNO₃	37	1.02	1.022	1.00	98.9
HNO₃	37	1.08	1.532	1.42	98.9
HCl	37	1.14	1.043	0.91	99.2
HCl	37	1.12	1.546	1.38	99.1
HNO ₃	21	1.08	1.005	0.93	95.4
HNO ₃	21	1.07	1.547	1.45	94.6
HCl	21	1.07	1.012	0.95	97.3
HCl	21	1.30	1.530	1.18	96.5

Pt Yields for Cryo-milled and Agglomerated GDE Powders (Process 2)- One-step extraction + rinse

- 98.9 % average yield when concentrated HCl added first
- High yield (98.5 average) when HNO₃ added first if g sample/g HNO₃ > 0.5 and concentrated HCl is then added

Acid Priority	% HCl	g HNO ₃	g sample		% Pt yield
HNO₃	37	0.96	0.514	0.54	97.9
HNO ₃	37	2.98	0.537	0.18	91.7
HCl	37	1.04	0.518	0.50	98.9
HCl	37	3.06	0.534	0.17	98.3
HNO₃	37	1.02	1.022	1.00	98.9
HNO₃	37	1.08	1.532	1.42	98.9
HCl	37	1.14	1.043	0.91	99.2
HCl	37	1.12	1.546	1.38	99.1
HNO ₃	21	1.08	1.005	0.93	95.4
HNO ₃	21	1.07	1.547	1.45	94.6
HCl	21	1.07	1.012	0.95	97.3
HCl	21	1.30	1.530	1.18	96.5

Pt Recovery Modified to Achieve 98% Pt Recovery in One Leach (Option A shown)



Comparison of Pt Yields for Granulated MEA's - >97% yield for GDE's and >98% for Aged CCM's (Single Leach Step)

GDE MEA's

1g Sonicated with trace surfactant

0.5g of granulated and milled MEA wet manually

Run	Surfactant usage, wt/wt	% Pt yield	Surfactant usage, wt/wt	% Pt yield
A	0.0058	97.3	0.05	97.6
B	0.0109	97.5	0.05	97.8
C	0.0157	97.5	0.02	97.1
D			0.02	97.2

Aged CCM MEA's

1g Sonicated with trace surfactant

0.5g of granulated and milled MEA wet manually

Run	Surfactant usage, wt/wt	% Pt yield	Surfactant usage, wt/wt	% Pt yield
A	0.0062	98.4	0.05	98.5
B	0.0022	98.1	0.05	98.6
C	0.0009	98.4	0.02	98.4
D			0.02	98.5

Comparison of Est. Variable Costs per kg MEA - Granulation vs. Cryo-milling with Agglomeration (Pt value ~ \$320/kg MEA)

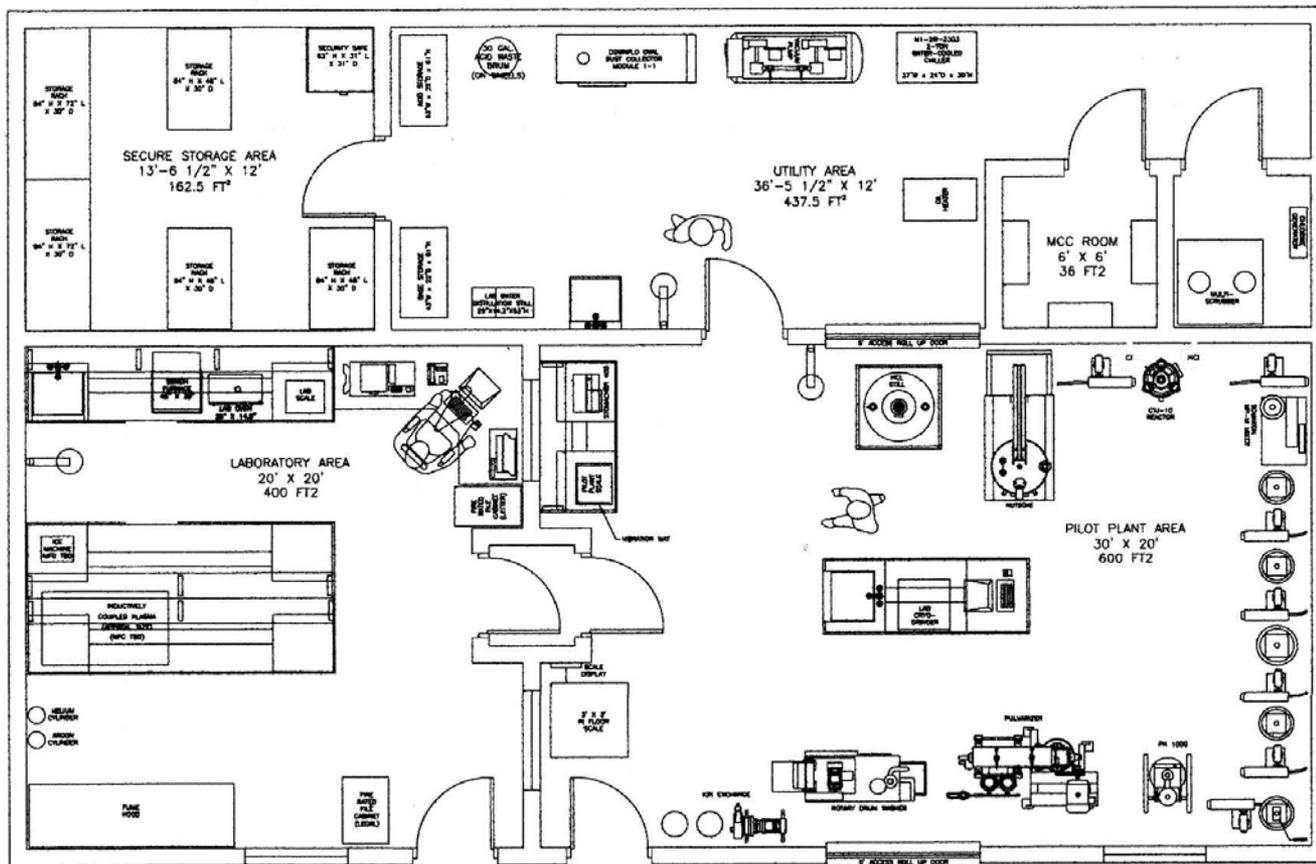
- **Granulation – 98% yield**
- Raw materials - \$0.60/kg
- Energy - \$0.35/kg
- Waste disposal- \$0.06/kg (dry)
- Labor - \$1.20/kg
- **Total variable - \$2.21**
- **Cryo-milling and agglomeration- 99% yield**
- Raw materials - \$1.05/kg
- Energy - \$0.35/kg
- Waste disposal- \$0.08/kg (dry)
- Labor - \$1.20/kg
- **Total variable - \$2.68**
- **Differential (variable + depreciation) <\$0.60/kg**

1% increase in Pt yield is equivalent to \$3.20/kg MEA based on 1% Pt content in MEA and \$1000 per troy ounce of Pt.

Potential Improved Pt Yield from Leached Granulated MEA Using Sonicated Rinse

Rinse method	Reagent	% Pt yield
Manual rinse	Hot water	97.4
Sonicated rinse	Warm water	98.2
Sonicated rinse	1:9 HCl/water solution	98.0
Sonicated rinse	1% NaOH solution	98.6

Proposed Pilot Plant Layout- 1600 sf (Pilot plant, Lab Area, Utility and Storage) Estimated cost of \$1.5MM



G-1 GENERAL ARRANGEMENT - PLAN VIEW
SCALE: 3/8" = 1'-0"

Collaborations

- Hammerhead Engineering, Flemington, NJ (Consultant, industry)
 - Completed cost estimate and floor plan for a pilot plant
- Ceralink, Troy, NY (Consultant, industry)
 - Corrosion studies of titanium
 - Comparative MEA leaching in a sealed environment
 - Scale-up studies using a stirred Parr reactor
- B.F. Enterprizes, Pittsburgh, PA (Supplier, industry)
 - Contributed a leaching solution for phosphoric acid from 'PBI' MEA's combining hardware from Omegasonics and chemicals from MEC Chemicals

Collaborations (continued)

- Hosokawa Polymer Systems, Berlin, CT (Supplier, industry)
 - Demonstrated capability to granulate as-received MEA's using a knife-edge cutting mill
- Thermo Fisher, Chicago, IL (Supplier, Industry)
 - Determined carbon interference factors for ICP-MS
- DeDietrich/Rosenmund (Supplier, industry)
 - Helped design an all-in-one reactor

Summary

- Pt recovery of >98% has been achieved from MEA's (milled and granulated) using a oxidative leaching process
- A simplified leaching process can be practiced in a single vessel
- Reduction of reagent usage has decreased process cost while increasing Pt yield
- Operated commercially, the process requires little manual labor and generates minimal waste (solid residue of the leached MEA's)
- Direct analysis of leached MEA slurry can be practiced for process quality control

- Quantify Pt yield improvement using a sonicated rinse
- Use titanium-lined Parr reactor to test scale-up using HCl-rich leaching conditions
 - Optimize temperature, pressure and agitation
 - Preliminary results @ 100°C
 - LN₂ milled GDE 98.5% yield
 - Pre-embrittled/milled/agglomerated GDE 99.5% yield
- Compile final project report

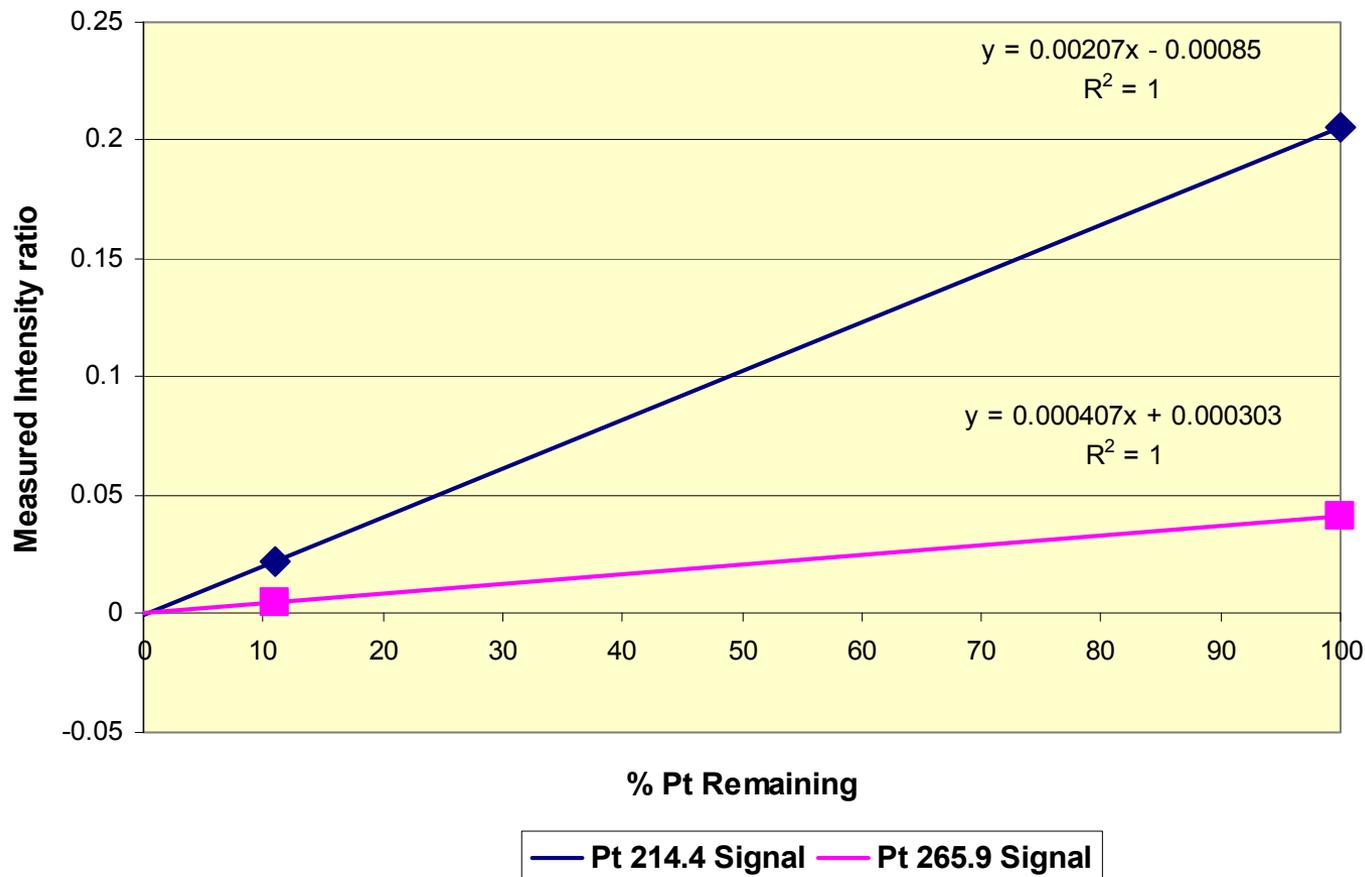
Supplemental Slides

Technical Accomplishments – At-line QC test based on residual Pt measurement and Mg Silicate as internal standard

- Calibrated the laser ablation-ICP method as an at-line QC test for leach efficiency
 - Calibration performed using MEA powder with 2.5% Pt and leached powder with ~0.25% Pt
 - Linearity achieved between 0 and 2.5% Pt
 - Good precision achieved using in-line addition of an internal standard powder (10% by weight of MEA)
 - Relative standard deviation of mean <6% (based on statistics for sets of 5 second integrations) at 0.25% Pt level
 - Sensitivity of measurement can be increased using ICP-MS in place of ICP-OES

Calibration of Pt Signal from Milled CCM Sample (W.L. Gore)- Laser Ablation-ICP with Mg Silicate Internal Standard

Relationship between Intensity Ratio and Residual Pt for Leached CCM Powder- Pt 214.4 nm and Pt 265.9 nm Lines



Technical Accomplishments – Use of Mass Spec using Laser Ablation and ICP

- Mg is difficult to use as an internal standard for ICP-OES because of excessive sensitivity
- Using ICP-MS, Mg_{24} can be used as the internal standard
- Molecular interferences from carbon may exist
 - Potential for C_{12} dimer interference on Mg_{24} was investigated at Thermo Fisher and found to be negligible
 - When using a collision reaction cell, insignificant bias measured at 10^7 carbon/magnesium ratio
 - Using a standard configuration, a 50% bias was measured at a 10^7 carbon/magnesium ratio

Technical Accomplishments

- Validated a process for pre-leaching of PBI membranes to remove H_3PO_4
 - Leaching performed in an ultrasonic bath using 1/2" wide strips of PBI-based MEA's
 - 75% of acid leached using cold water, independent of contact time
 - >99% of the acid removed using a two-step treatment of proprietary cleaning aids
 - Virgin MEA's delaminated, used MEA's stayed intact
 - Residual H_3PO_4 determined by leaching in a sealed vessel using HCl
 - Accuracy of leaching in HCl validated by milling, then re-leaching of sample

Ultrasonic Extraction of Used MEAs with Additives Greatly Improves H_3PO_4 Extraction. Residual acid reduced from ~25% to <0.2% (or 99+% removal.)

Effect of Treatment and time on H_3PO_4 Residue for Used PBI MEA's
(Samples not delaminated, contain moisture)

