Platinum Group Metal Recycling Technology Development

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Overview

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

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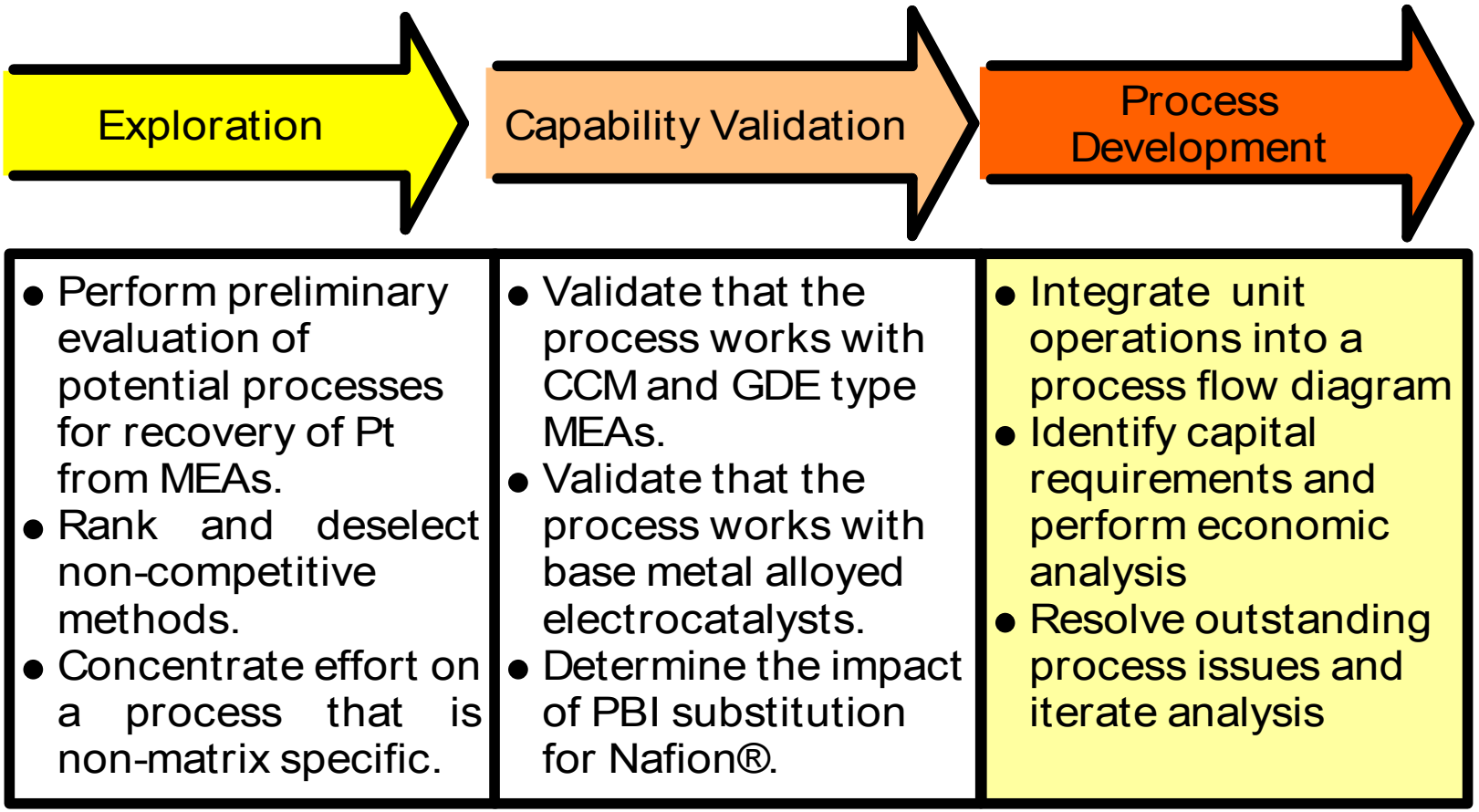
Date	Milestone
Oct-08	✓Evaluate hot-melt agglomeration as a substitute for MEA surfactant wetting
Oct-08	✓Demonstrate feasibility of pre-embrittlement with LN_2
Oct-08	✓Complete evaluation of Laser ablation-ICP for QC testing
Dec-08	✓Determine preferred order of reagent addition in leaching
Mar-09	✓Reduce reagent consumption
Mar-09	✓Re-examine reactor materials of construction
Mar-09	✓Recalculate process economics

Approach - Overview



Technical Accomplishments (Summary)

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- 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

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- Achieved the objective of 98% Pt recovery
  - Determined that a limiting factor is low HCl concentration
    - Minimizing HNO_3 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 HNO_3
      - This information impacts the selection of reactor materials of construction

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

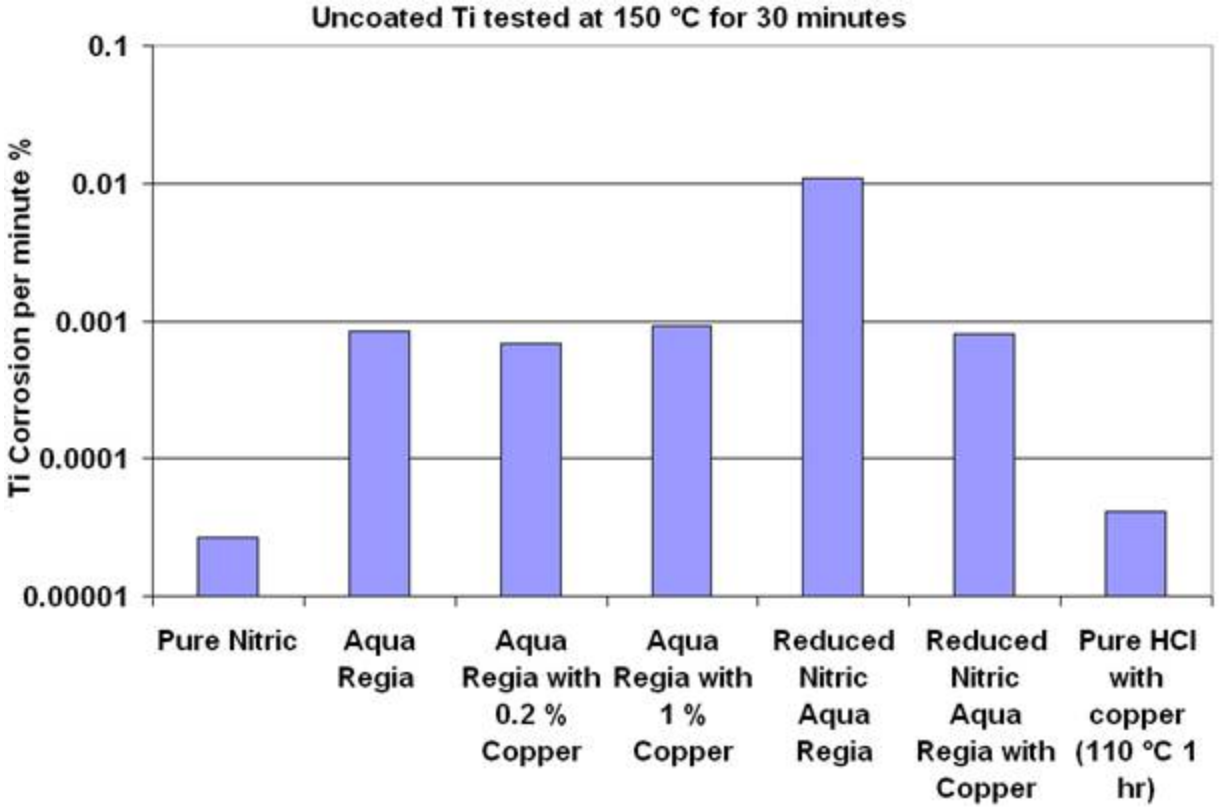
- Ti attacked by reducing acids – HCl, HF

- 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
    - HCl:H_2O_2 → Ti has good resistance at low temperature < 0.01 % at 100 – 125 °C
    - HCl:H_2O_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)



Technical Accomplishments

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- 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°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**

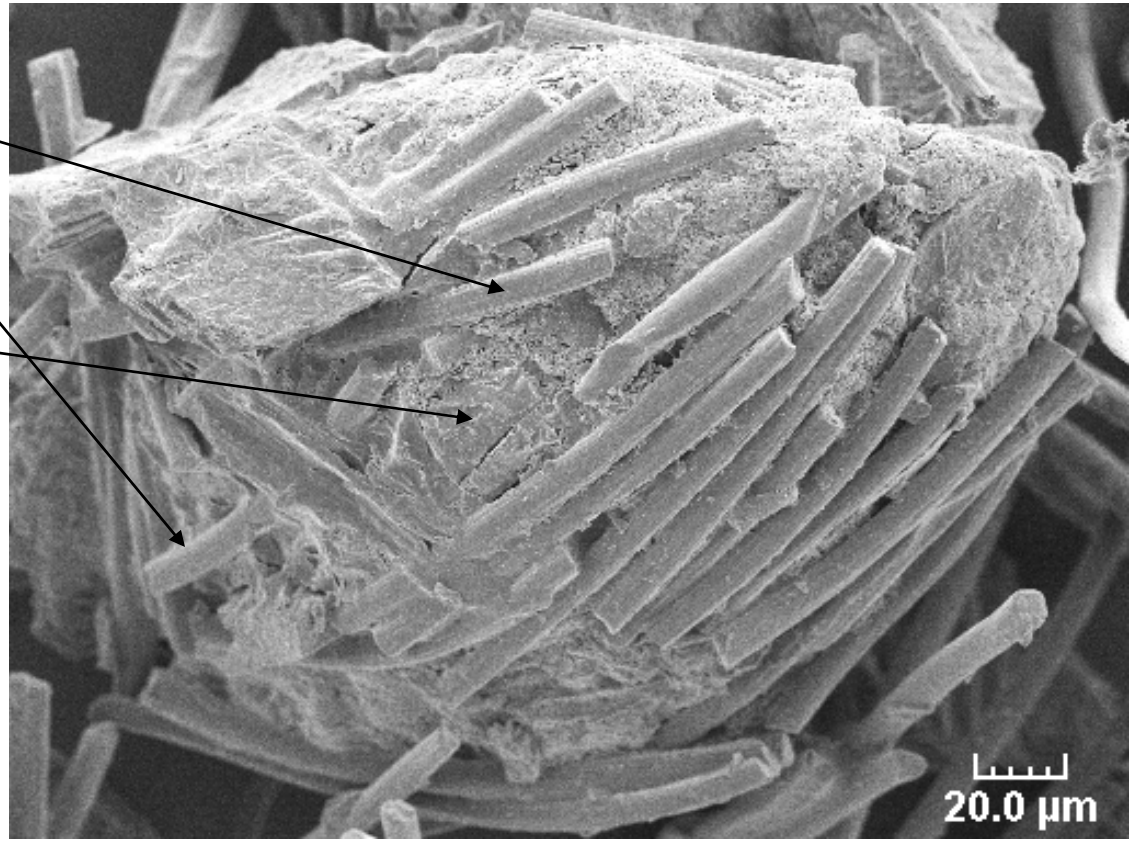
Technical Accomplishments

- 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/LN_2 Milled GDE)

- Carbon fibers
- Agglomerated carbon particles



Technical Accomplishments

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- 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 NOx 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

Technical Accomplishments

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- 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

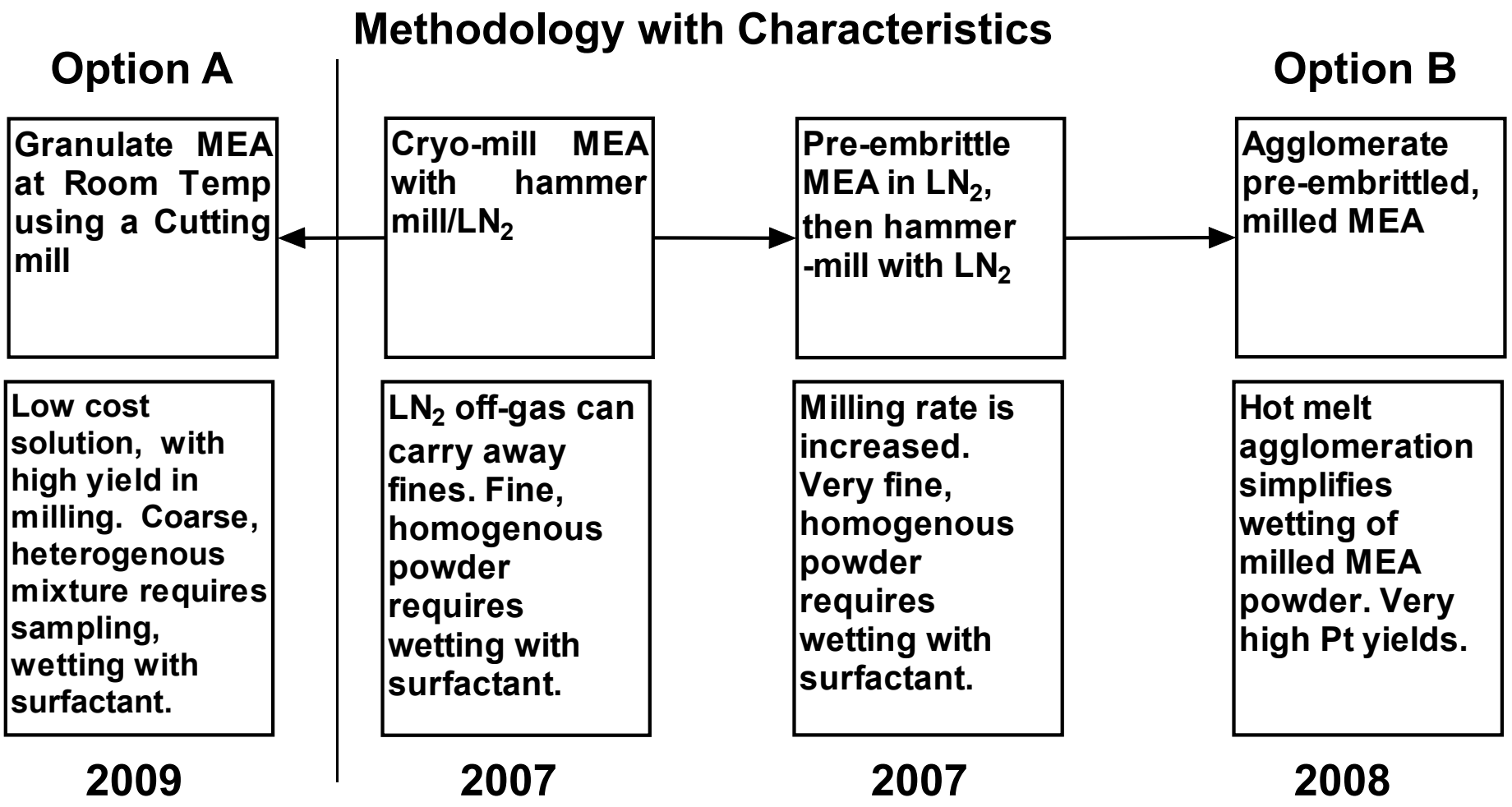
    » For woven fiber*, use 1% wt/wt of MEA

    » 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



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

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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

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- 99.1 % average yield when concentrated HCl added first
- High yield (98.8 average) when HNO_3 added first if g sample/g HNO_3 > 0.5 and concentrated HCl is then added

Acid Priority	% HCl	g HNO3	g sample		% Pt yield
HNO3	**37**	**0.96**	**0.514**	**0.54**	**97.9**
HNO3	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**
HNO3	21	1.08	1.005	0.93	95.4
HNO3	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

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- 98.9 % average yield when concentrated HCl added first
- High yield (98.5 average) when HNO_3 added first if g sample/g HNO_3 > 0.5 and concentrated HCl is then added

Acid Priority	% HCl	g HNO3	g sample		% Pt yield
HNO3	**37**	**0.96**	**0.514**	**0.54**	**97.9**
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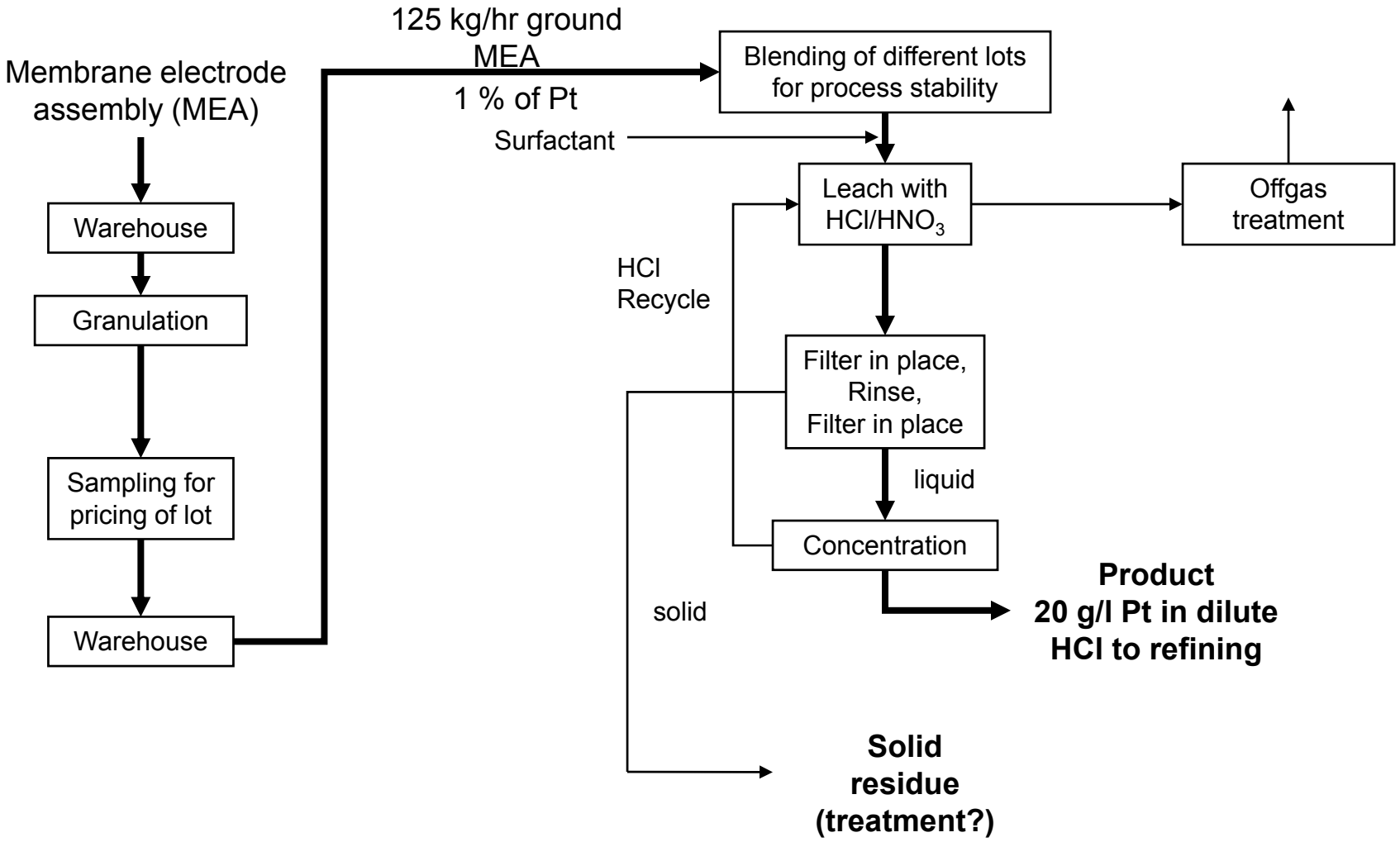
Pt Recovery Modified to Achieve 98% Pt Recovery in One Leach (Option A shown)



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

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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)

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- **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

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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

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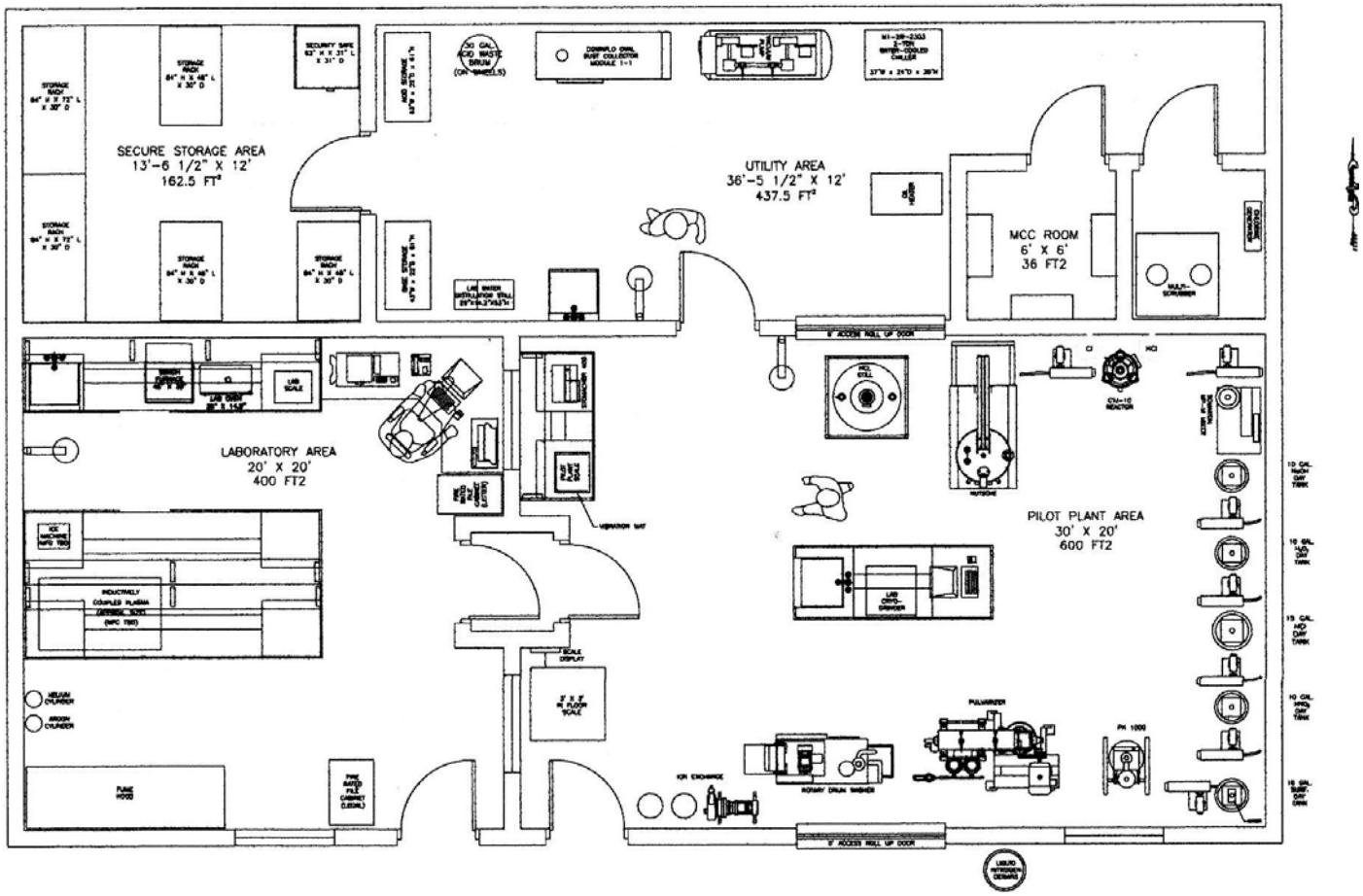

Collaborations

- 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

Future Work

- 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
    - LN_2 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

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- 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

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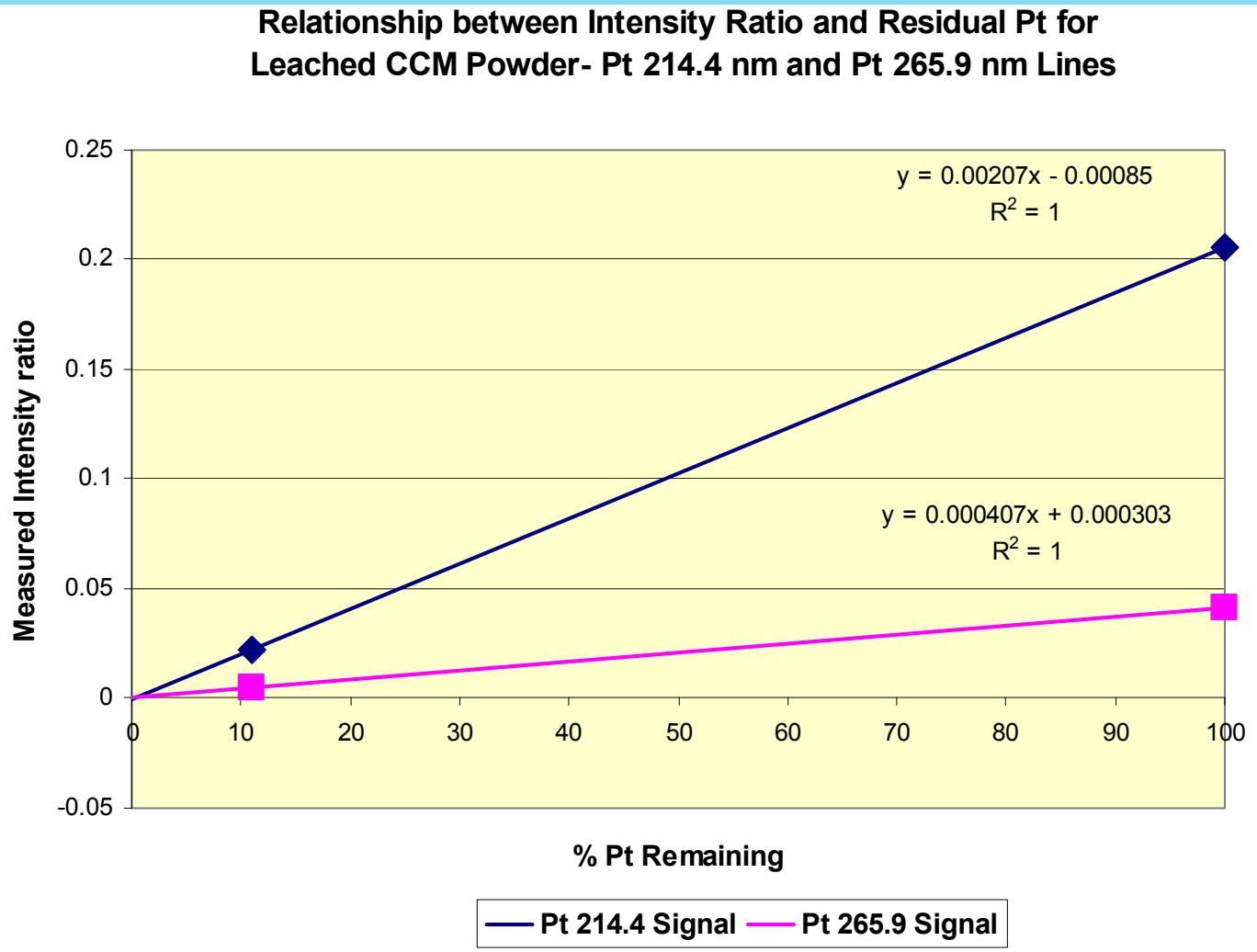

Technical Accomplishments – Use of Mass Spec using Laser Ablation and ICP

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- 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

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- Validated a process for pre-leaching of PBI membranes to remove H_3PO_4
  - Leaching performed in an ultrasonic bath using ½" 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.)

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