Platinum Group Metal Recycling Technology Development

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FCP2

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Overview

Timeline

- Start - 11/2003
- Finish – extended to 3/2009
- 90% Complete

Budget

- Total project funding
  - DOE share = \$4.25MM
  - Engelhard share = \$1.07MM
- \$579k received in FY07
- \$993k budgeted for FY08

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 (reactor design)
- Hosakawa Micron (milling)
- New Wave, Cetac (Laser ablation)

Objectives for 2007-2008

- Determine
  - commercial practicality of cryo-grinding of MEAs
  - utility of the process for varied MEA architecture and materials
- Define unit operations for Pt recovery from MEAs , integrate them into a Process Flow Diagram and estimate process economics
- Identify apparatus/materials of construction for:
  - pilot plant (1 kg/day)
  - full-size (1000 MT/year) operation
- Develop a rapid process control method to determine Pt remaining in leached MEA residues

Milestones

Date	Milestone
May-07	✓Validated cryo-grinding with pre-embrittlement as best practice
Dec-07	✓Completed ruggedness test with next-generation (alloyed) electrocatalysts and MEAs with PBI membranes
Oct-07	✓Completed draft of Process Design
Nov-07	✓Generated Process Cost estimate
Feb-08	✓Identified Ti and Ta as possible corrosion-resistant reactor liners
Oct-08	Complete evaluation of Laser ablation-ICP for QC testing
Dec-08	Determine effect of mass transfer, T and P on Pt yield

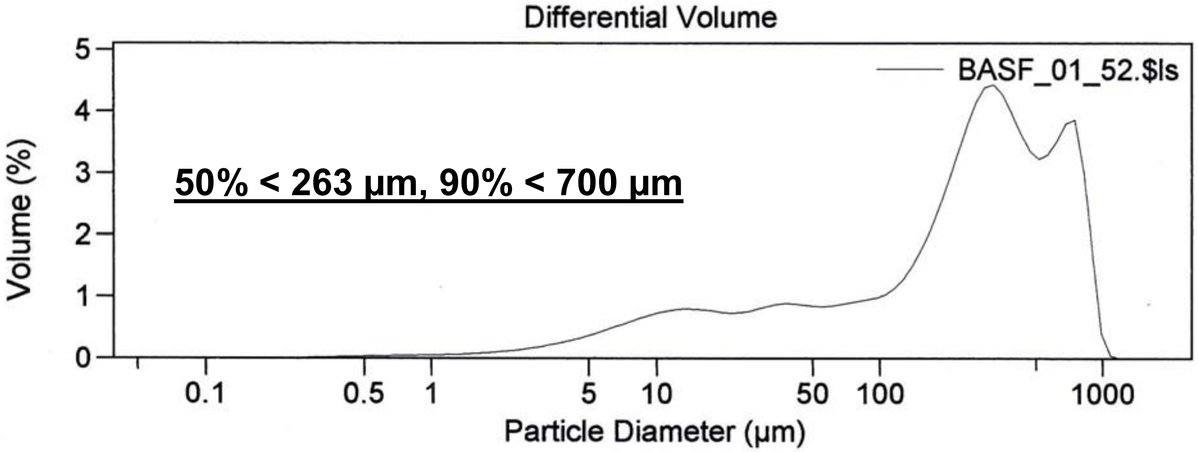
Approach - Overview

Exploration	Capability Validation	Process Development
● Perform preliminary evaluation of potential processes for recovery of Pt from MEAs. ● Rank and deselect non-competitive methods. ● Concentrate effort on a process that is non-matrix specific.	● Validate that the process works with CCM and GDE type MEAs. ● Validate that the process works with base metal alloyed electrocatalysts. ● Determine the impact of PBI substitution for Nafion®.	● Integrate unit operations into a process flow diagram ● Identify capital requirements and perform economic analysis ● Resolve outstanding process issues and iterate analysis

Technical Accomplishments (Summary)

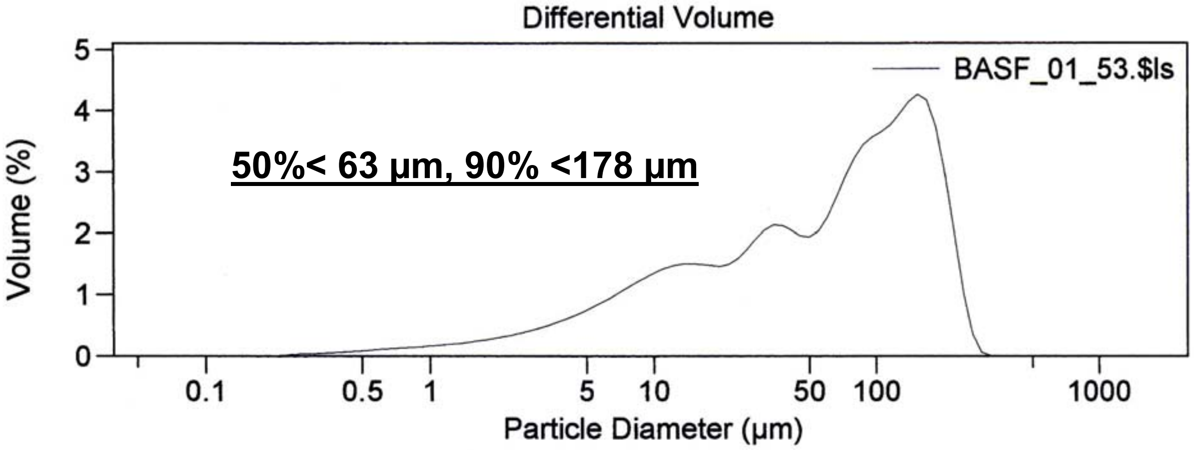
- Using a hammer mill, LN_2 pre-embrittlement is shown to improve MEA cryo-grinding.
- Mass transfer limitation of current apparatus may limit Pt leachability
  - Heat and pressure help liberate Pt from ‘difficult’ samples
- Corrosion studies have identified passivated-titanium and tantalum as suitable for construction of high-pressure leaching reactors
- The proposed process incorporates an ‘azeotrope breaker’ that facilitates recovery of HCl above the concentration of the HCl/water azeotrope while concentrating Pt in the distillation bottom.

Pre-embrittlement with LN_2 reduces particle size distribution



50% < 263 µm, 90% < 700 µm

A. CCM w/ gasket milled with LN_2.



50%< 63 µm, 90% <178 µm

B. CCM w/ gasket chilled in LN_2 bath, then milled with liquid nitrogen.

Excellent MEA Sampling Statistics Achievable Using Cryo-milling Procedure

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MEA batch contained rigid gasket material, which made milling difficult.

Run 7 had external embittlement; run 6 performed with only cryo cooling of the mill.

Run	Portion	wt.	mg F	mg R	mg T	% Pt	% yield
6	1	0.543	8.5	0.64	9.14	1.683	93.00
	2	0.594	9.47	0.59	10.06	1.694	94.14
7	1	0.52	8.49	0.52	9.01	1.733	94.23
	2	0.518	8.21	0.63	8.84	1.707	92.87

7% higher Pt leach yield achieved using GDE pre-embrittled with LN_2

(Material balance, expressed as % Pt, unchanged)

Milling Condition			Open Vessel		Sealed Vessel	
			% Pt	% yield	% Pt	% yield
Cryo-cool mill only			3.08	81.1	2.93	72.5
			3.2	77.2	2.89	92.1
					3.25	84.3
					3.25	80.4
	avg.		3.14	79.15	3.08	82.325
Pre-embrittle, then cryo-cool mill			3.15	86.6	3.27	90.6
			3.1	86.2	3.04	90.6
	avg.		3.125	86.4	3.155	90.6

Comparison of Experimental conditions

Condition	BASF - Open Vessel	Ceralink – Sealed Vessel
Reagents	Acid “A” only	Acid “A” or “B”
Temperature	Hot plate at 125-150°C setting	Variable to 200°C using microwave heating
	Bulk temperature of 60-70°C	Measured in vessel
Pressure	Ambient	10-40 bar

Leaching Conditions (T and P) have Major Impact on Ability to Recover Pt from MEA Scrap Material

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Run	Condition	Open Beaker		Sealed Vessel		avg	SD	RSD
		% Pt	% yield	% Pt	% yield			
1	ambient	0.605	23.2	0.624	90.4	0.609	0.011	1.86
		0.608	24.6	0.597	88.4			
2	Cool mill	0.584	9.9	0.609	88.1	0.596	0.015	2.57
		0.582	14.9	0.61	84.2			
3	ambient	0.725	23.8	0.753	85.5	0.739	0.030	4.11
		0.705	23.9	0.774	86.8			
4	ambient	0.608	45.0	0.622	87.7	0.623	0.023	3.64
		0.606	44.5	0.655	91.5			
5	Cool mill	0.655	28.5	0.693	93.1	0.690	0.037	5.41
		0.74	24.3	0.697	85.6			
		0.639	28.3	0.714	88.0			
	Avg.	0.642	**26.445**	0.668	**88.118**			
	SD	0.057	**10.569**	0.062	**2.684**			
	RSD	8.90		9.25				

Leaching efficiency not time-dependent- 0.25g CCM sample in sealed vessel

Minutes held @ 200°C	1st leach yield
10	**94.40**
20	**93.47**
30	**93.60**
40	**94.15**

>99% Pt Recovery achieved with two leaches
30 minute @ 200^{o}C with 0.5g MEA powder-

Data collected at Ceralink using sealed vessels

CCM with either
Acid “A” or “B”

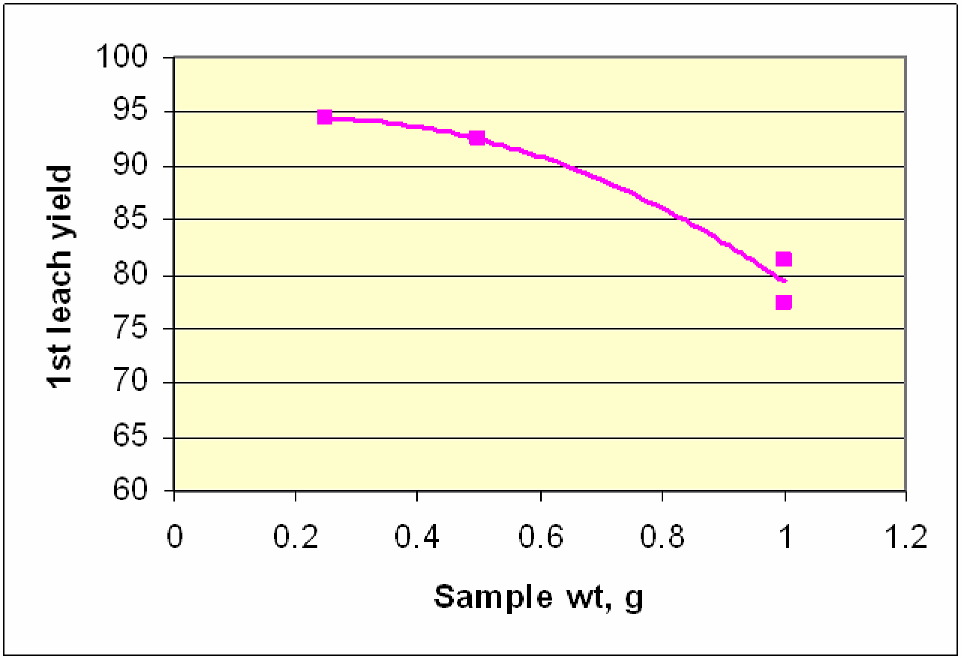
Leach #	Cumulative %Yield	Leach #	Cumulative %Yield
Acid “A”	1g surfactant	Acid “B”	0.5g surfactant
1	96.9	1	90.3
2	99.8	2	99.4

Leach #	Cumulative %Yield	Leach #	Cumulative %Yield	Leach #	Cumulative %Yield
1	96.9	1	86.9	1	95.6
2	100	2	99.7	2	99.5

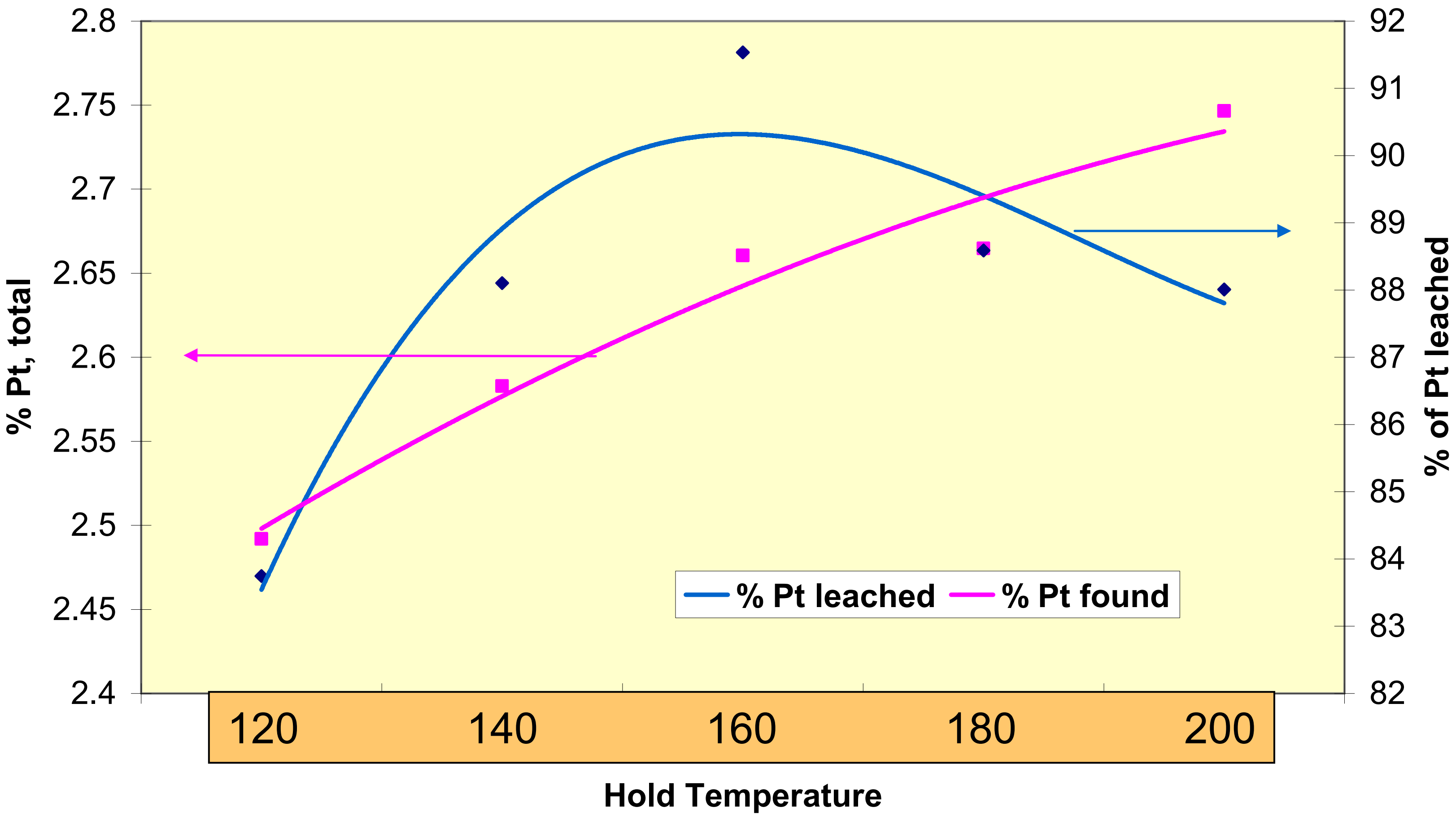
GDE with
Acid “B”

1st leach yield decreases as sample size is increased – Acid “B” runs

Sample/ surfactant	Run time	% Pt yield
0.25g/1g	36 min	94.4
0.5g/2g	36 min	92.5
1g/2g	16 min	81.2
1g/2g	36 min	77.4



Leaching Temperature influences Pt leachability – Kinetics vs. Cl_2 solubility?

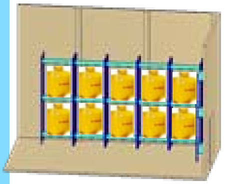


Process Challenges

- Collect a powder sample suitable for determination of lot value
- Design for corrosive nature of leaching reagents
  - HCl, chlorine, trace HF
- Simplify process design
  - Eliminate transfers
- Close HCl loop
- Develop rapid QC method for process control
- Update business model based on new process

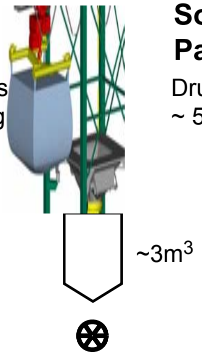
Precious Metal recovery from Membrane Electrode Assemblies, Source: Fuel Cells for automotive applications Part I MEA-Grinding

Delivery of Membrane Electrode Assemblies (MEA) in drums or Big Bags



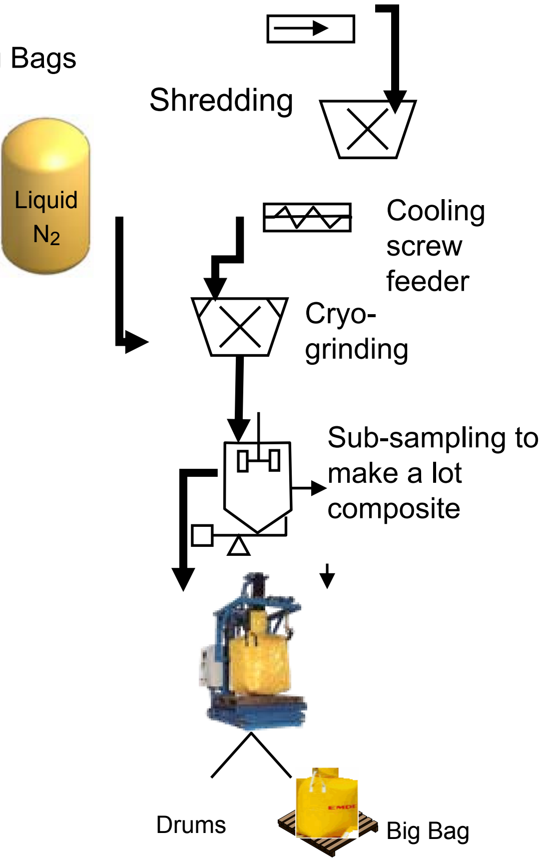
Storage in drums or Big Bags

Big Bags ~ 500 kg



Drums ~ 50 kg

~3m^3



Shredding

Liquid N_2

Cooling screw feeder

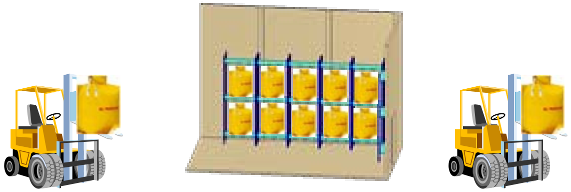
Cryo-grinding

Sub-sampling to make a lot composite

Drums

Big Bag

Analyze lot sample to determine value of the lot



Store ground MEAs pending settlement

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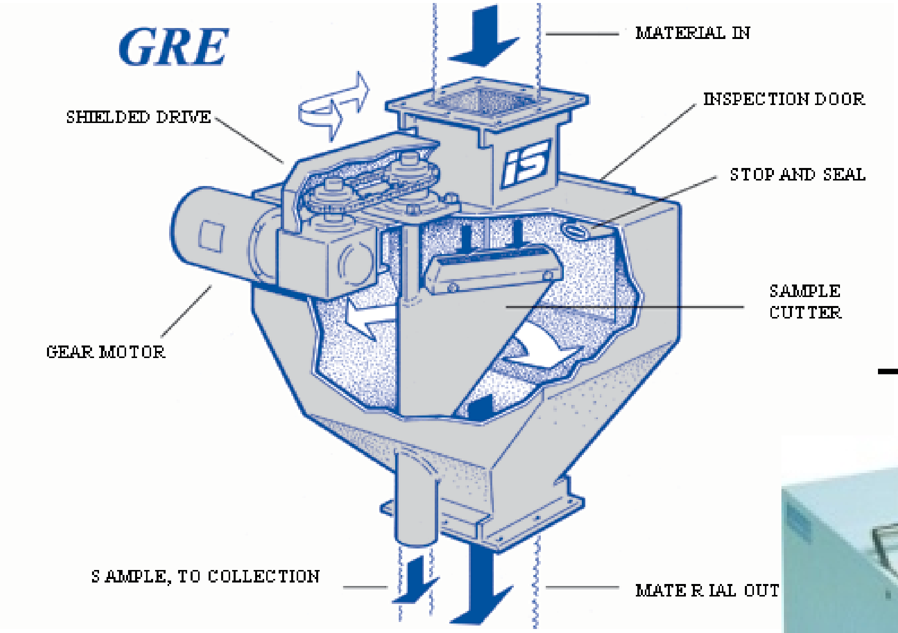
Obtaining a ‘Lot” Sample

- Current – Combust lot, then recover and blend ashes. Assay sub-sample (method must be free of interference from base metals).
  - Pros – gravimetric analysis of Pt-rich
  - Cons – loss of fine ash during blending; commercial settlement delayed by process steps.
- Proposed – Shred and grind a lot, then sub-sample and blend. Assay the final sample.
  - Pros – Settlement possible almost immediately
  - Cons – Instrumental analysis required; sample more likely to have a non-negligible moisture content

Representative Sampling Technologies



Master sample
Intersystems in-line cross-cut ('pelican') sampler (US)
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Sub-sample
Retsch spinning riffler w/vibrating feeder (DE).
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Sample Homogenizer
Stomacher blender (UK)
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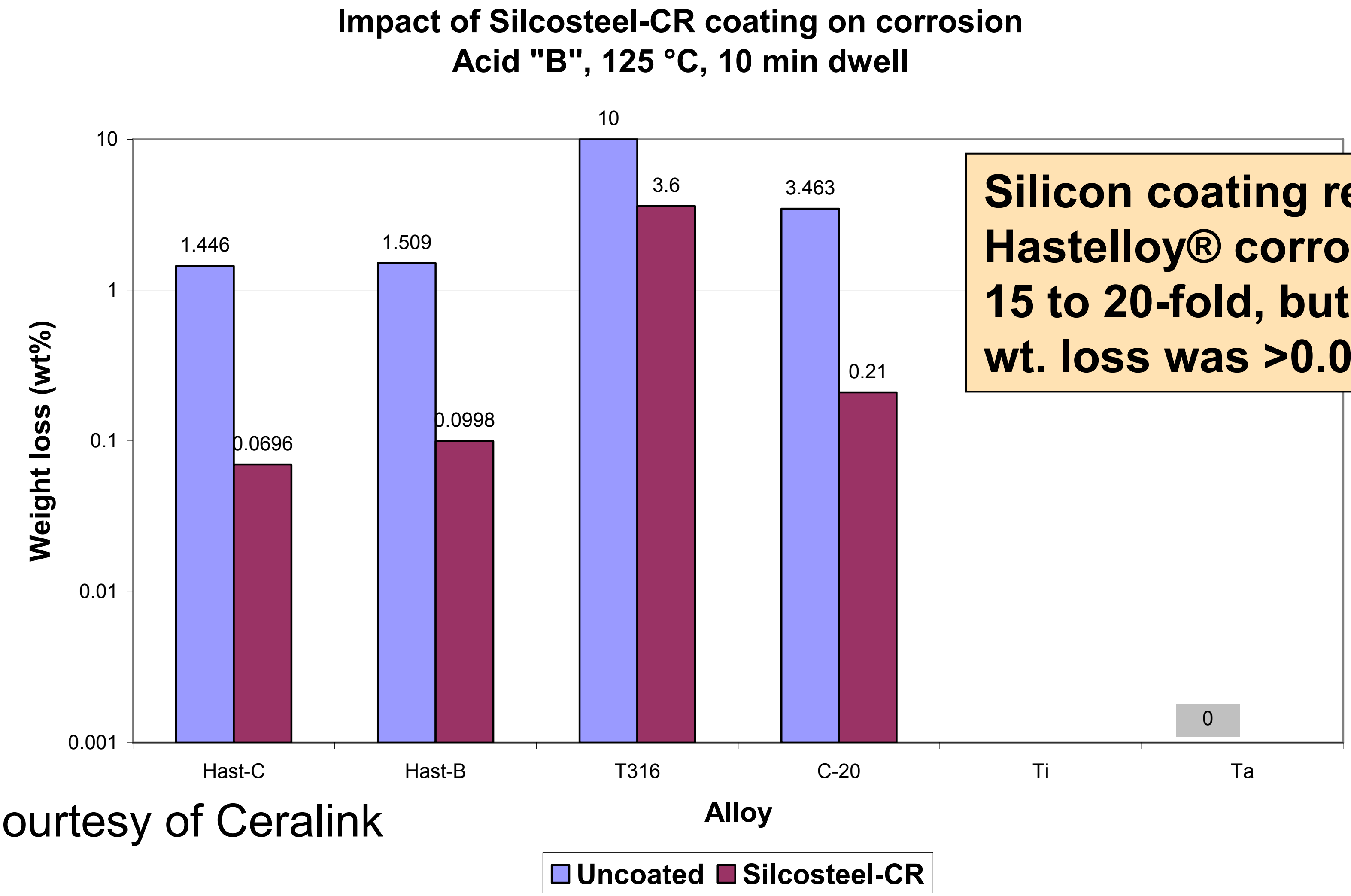
Even with silicon coating, ‘normal’ corrosion-resistant alloys like Hastelloy® do not survive exposure to chlorine.


Impact of Silcosteel-CR coating on corrosion
Acid "B", 125 °C, 10 min dwell

Silicon coating reduced Hastelloy® corrosion 15 to 20-fold, but wt. loss was >0.05%.

Courtesy of Ceralink

Titanium Corrosion Resistance study – Silicon coating is an effective barrier*

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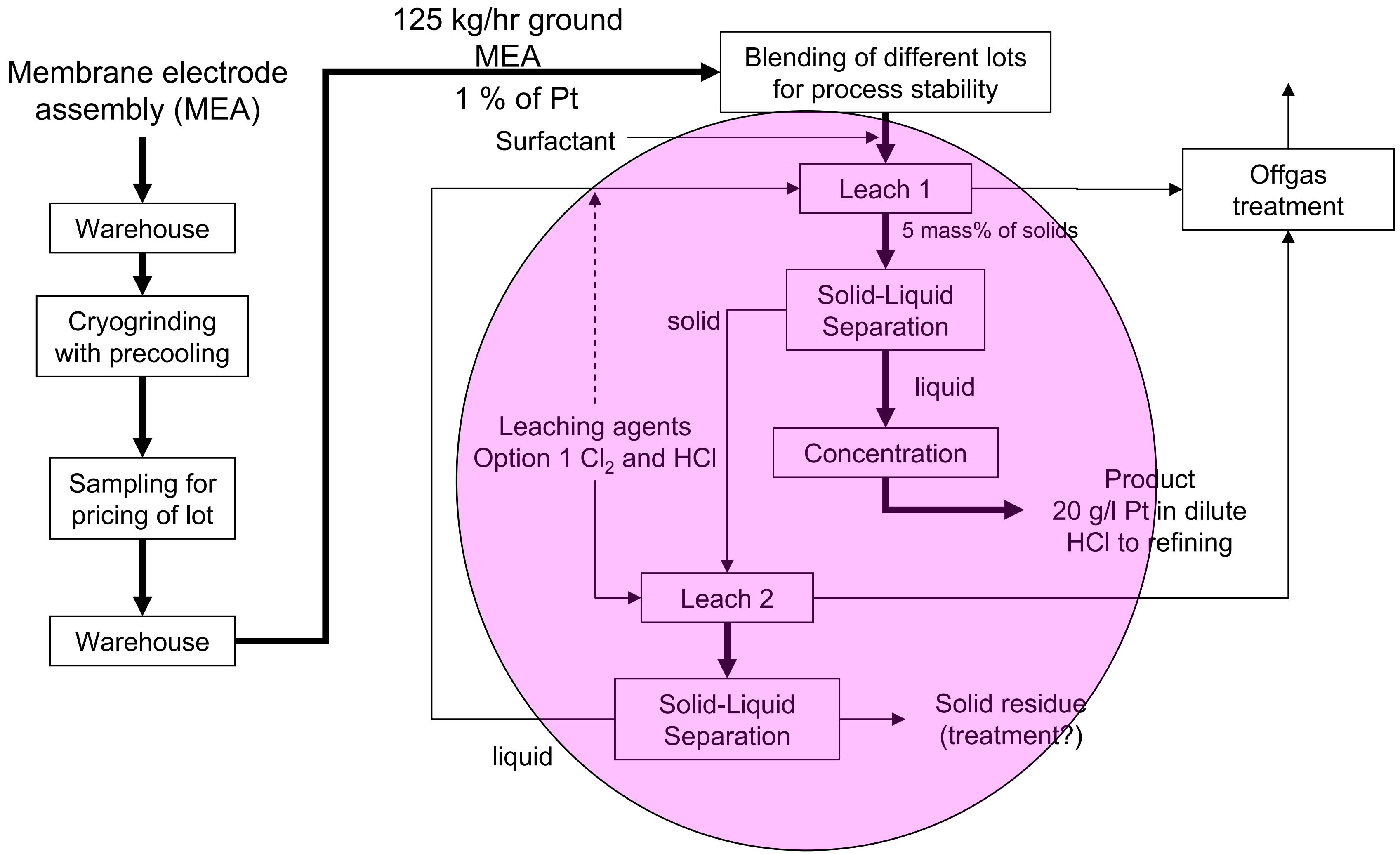
Experimental Conditions	**mg Ti leached****	**% wt loss**
1. Uncoated Ti – Acid “B”, 10 minutes @ 125^{o}C	0.61	**0.0074**
2. Silicon-coated Ti –Acid “B”, 10 minutes @ 125^{o}C	0.022	**0.0003**
3. Silicon-coated Ti –Acid “B”, 30 minutes @ 150^{o}C	0.32	**0.0039**
4. Silicon-coated Ti –Acid “A”, 10 minutes @ 125^{o}C	0.038	**0.0005**

Trials 2 through 4 run in order using the same Ti sample.

* Silicon coating commercially applied by Restek

** Leachable Ti determined by ICP determination of Ti in leachate.

Pt Recovery Anticipated to Require 2 Leaches and 2 Filtrations w/pumps, transfer lines, valves, etc.



Membrane electrode assembly (MEA)

Warehouse

Cryogrinding with precooling

Sampling for pricing of lot

Warehouse

125 kg/hr ground MEA

1 % of Pt

Blending of different lots for process stability

Surfactant

Leach 1

Offgas treatment

5 mass% of solids

Solid-Liquid Separation

solid

liquid

Leaching agents Option 1 Cl_2 and HCl

Concentration

Product 20 g/l Pt in dilute HCl to refining

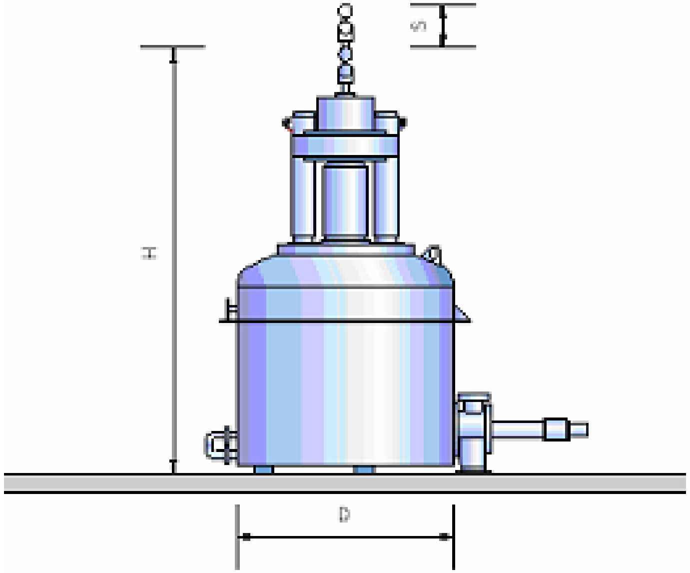
Leach 2

Solid-Liquid Separation

Solid residue (treatment?)

liquid

Single Apparatus for Leaching, Filtering, Washing, Neutralization and Solids Drying Simplifies Process



Rosenmund
Filter/Dryer

Paddle Assembly

Is low rpm agitator design sufficient for replenishment of oxidant (e.g. chlorine) in liquid phase?

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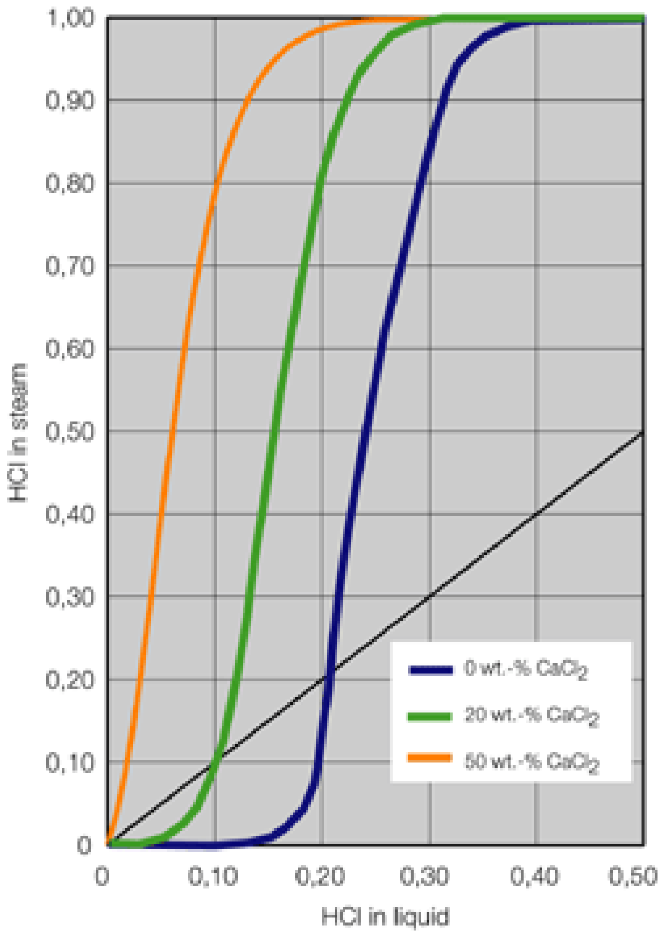
HCl Recycling Enhanced Using an Azeotrope Breaker

- HCl content decreases as HCl is converted to Cl_2 by reaction with added oxidants.
- HCL/water azeotrope has a BP of 109^{o}C and a composition of 20% HCl vapor. By comparison, concentrated acid is 37% HCl.
- HCl in vapor phase can be enriched using an ‘azeotrope breaker’
- In this example, a hydroscopic alkaline earth chloride reduces water in the vapor phase
- After saturation with water, the salt is thermally regenerated and re-used



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Halving added HCl has a small effect (~3%) on Leaching Efficiency

Hot Plate Setting	% HCL Dosage	% Oxidant "A" Dosage	% Yield
125^{o}C	**100**	**100**	**93.7**
	50	100	90.1
	50	**50**	**89.6**
150^{o}C	**100**	**100**	**95.8**
	50	100	93.5
	50	**50**	**92.5**

Water added in place of HCl to maintain volume.

Process Control Methodology- Laser Ablation – Inductively Coupled Plasma Emission

- Example of track of 213 nm laser through a layer of MEA powder deposited on a filter paper

- Note non-uniformity of sample layer

Laser Power has major impact on ICP signal derived from ablated sample

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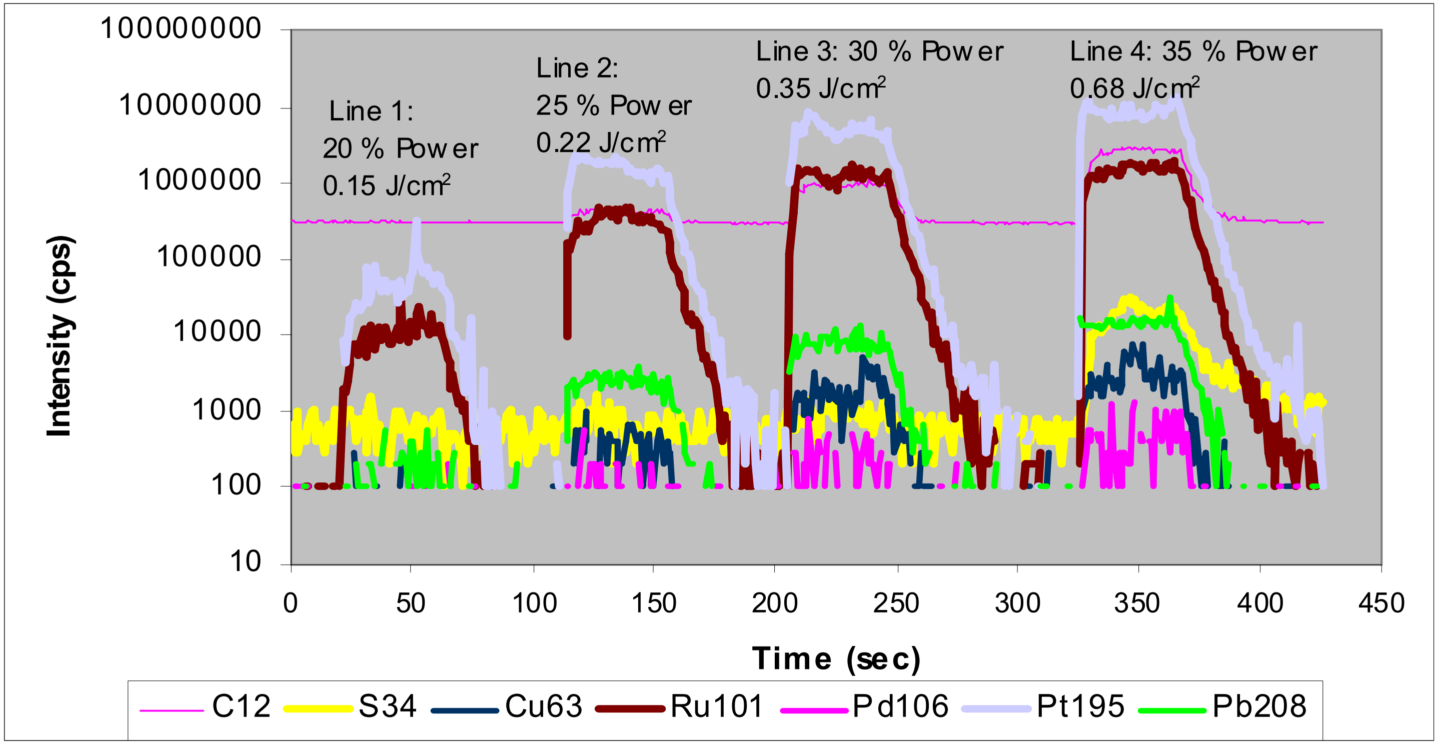
- Dramatic increase in Pt and Ru signal when laser power raised from 20 to 25% (minimum power required)
- Minimal change going from 30 to 35% (Layer completely ablated)



Internal Standardization Method Proposed for Improved Powder Analysis

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- Laser ablation transfers MEA powder as an aerosol to the ICP torch, where the particles are vaporized
- The ICP emission/MS signal will depend on the aerosol loading in the carrier gas
- The expected non-spatially uniform deposition of MEA powder on a filter substrate will result in poor precision
- Blending an internal standard powder with the MEA is shown to improve reproducibility of data

internal standard method improves LA-ICP precision (CCM MEA powder w/Mg silicate)

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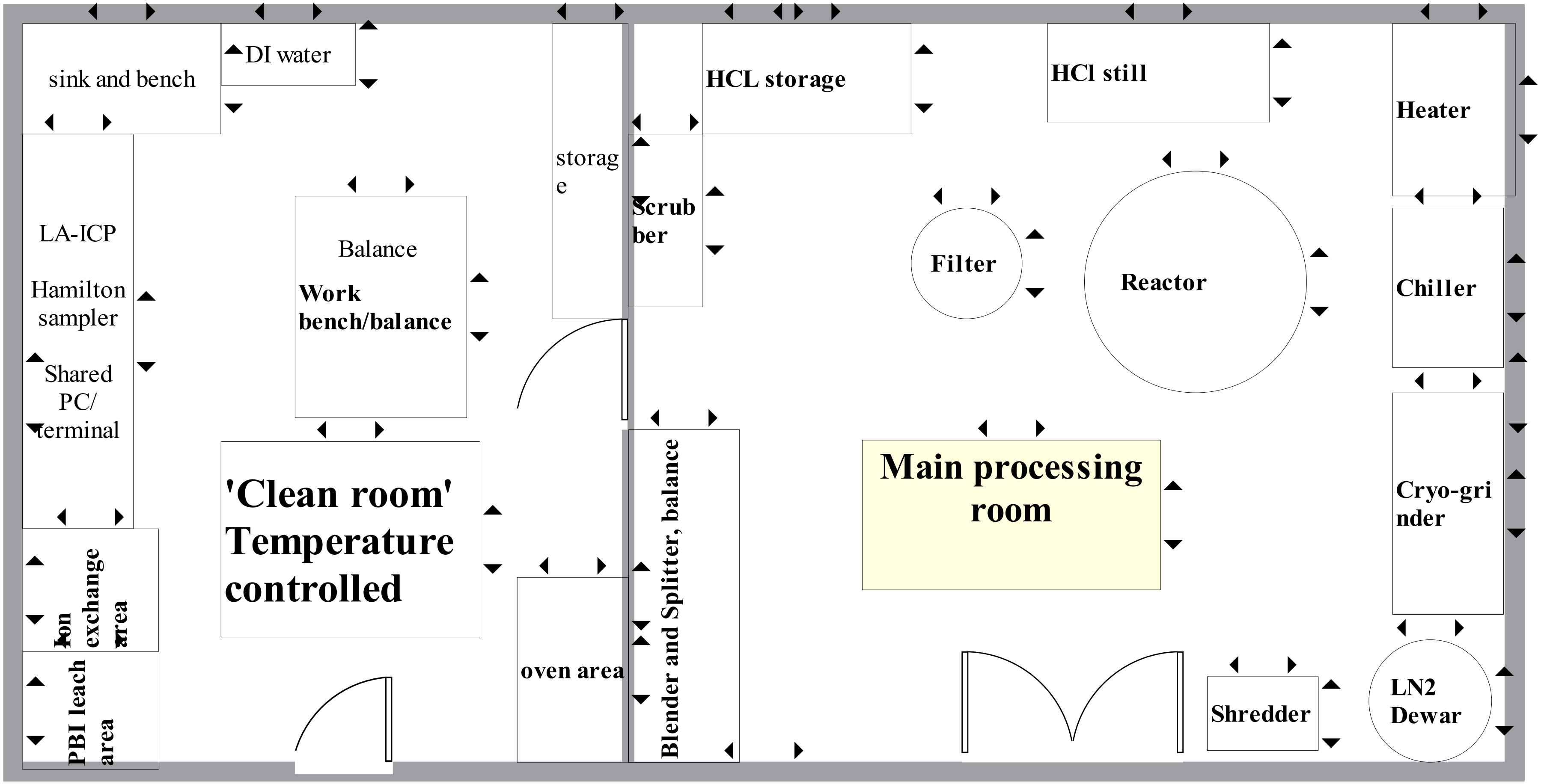
	Pt 1/ Si 1 Count Ratio	**Pt 2/ Si 2 Count Ratio**	**Pt 1 Counts**	**Pt 2 Counts**
Run 1	0.209	0.0438	4383 (raw)	4485 (raw)
Run 2	0.205	0.0414	3330 (raw)	3316 (raw)
$\frac{\textbf{Run 1}}{\textbf{Run 2}}$	**1.02**	**1.06**	**1.32**	**1.35**

ICP Emission Wavelengths
Pt 1 = 214.4 nm, Si 1 = 212.4 nm
Pt 2 = 265.9 nm, Si 2 = 251.6 nm
8 sets of five-second integrations per run

Proposed Pilot Plant Layout
20’ x 40’ (Roughly $1MM cost)



Future Work

- Install an agitated glass reactor and determine Pt yield at atmospheric pressure and T ~ 100°C (BASF) -9/08

- Install an agitated titanium-lined reactor and determine Pt yield at elevated pressure and variable temperature > 100°C (Ceralink) - 12/08.

- Improve economic model for process based on reactor design- 12/08.

Summary

- Pt recovery of >98% is achievable from milled MEAs using a oxidative leaching process
- The process has been shown to work with all types of MEAs and electro-catalyst compositions
- Operated commercially, the process requires little manual labor and generates minimal waste (solid residue of the leaching)
- Integration of unit operations will better define actual process costs
- New, rapid technology has been invented to accurately analyze slurry solids composition