Platinum Group Metal Recycling Technology Development

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FCP2

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The Chemical Company

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Overview

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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

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- 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

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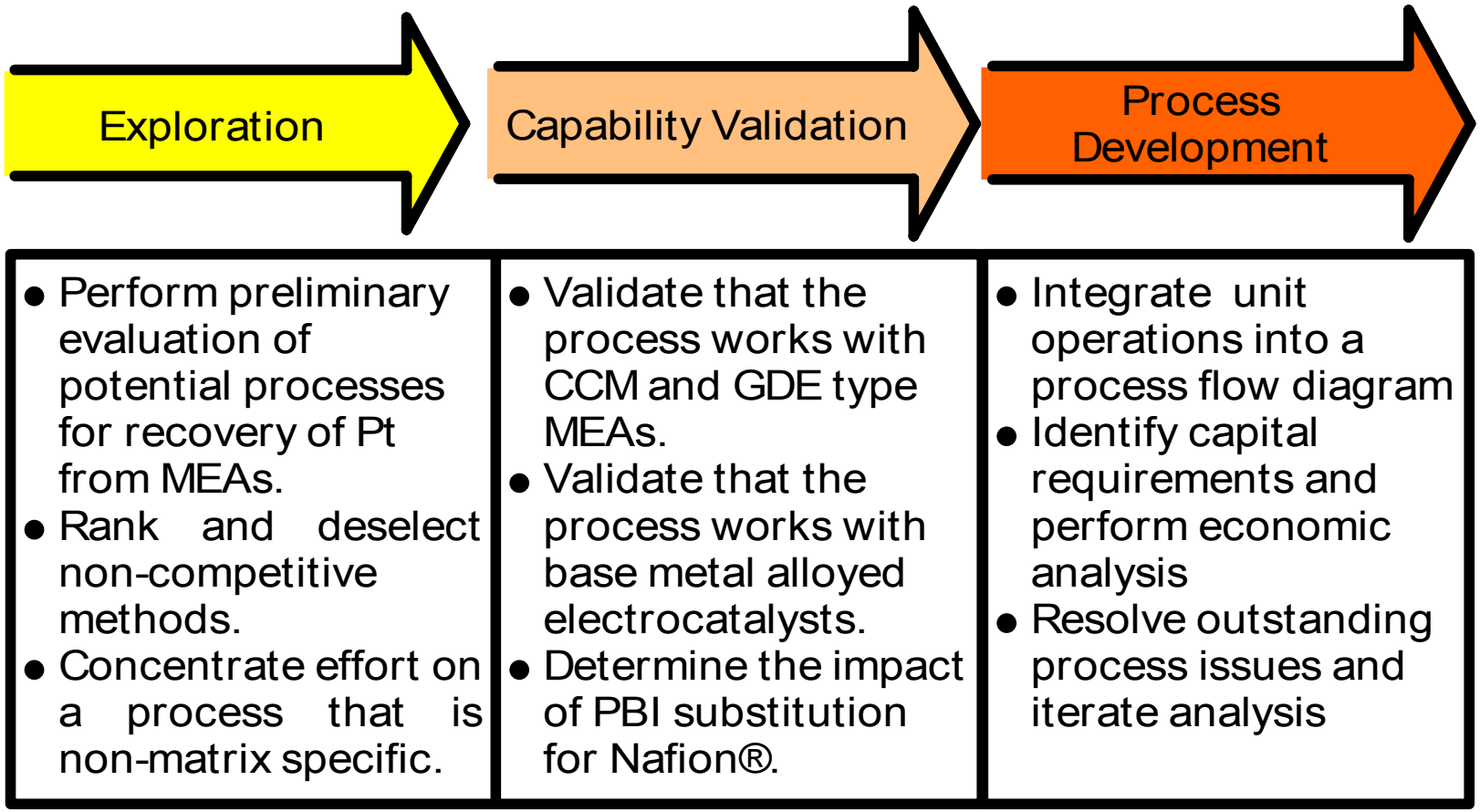
Date	Milestone
May-07	✓Validated cryo-grinding with pre-embrittlement as best practice
Dec-07	✓Completed ruggedness test with next-generation (alloyed) electrocatalysts and MEAs with PBI membranes
Oct-07	✓Completed draft of Process Design
Nov-07	✓Generated Process Cost estimate
Feb-08	✓Identified Ti 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

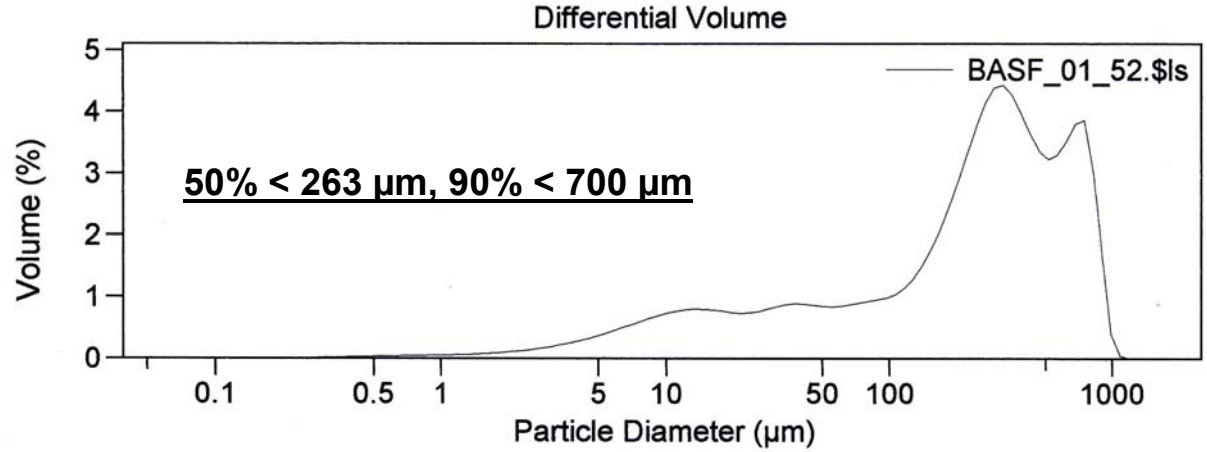
Approach - Overview



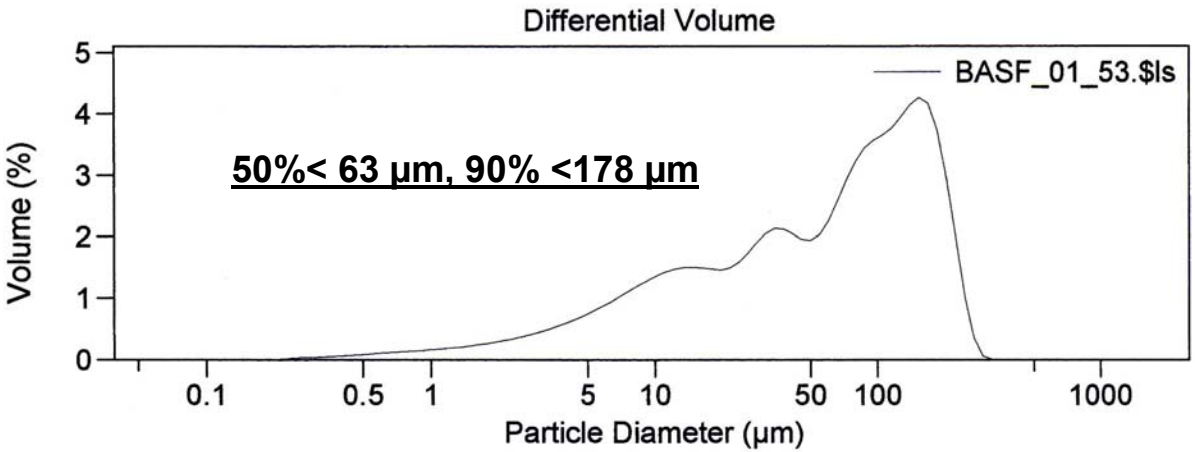
Technical Accomplishments (Summary)

- 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



A. CCM w/ gasket milled with LN_2.



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)

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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

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Condition	BASF - Open Vessel	Ceralink – Sealed Vessel
Reagents	Acid “A” only	Acid “A” or “B”
Temperature	Hot plate at 125-150^{o}C setting	Variable to 200^{o}C using microwave heating
	Bulk temperature of 60-70^{o}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

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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°C with 0.5g MEA powder-

Data collected at Ceralink using sealed vessels

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CCM with either Acid "A" or "B"

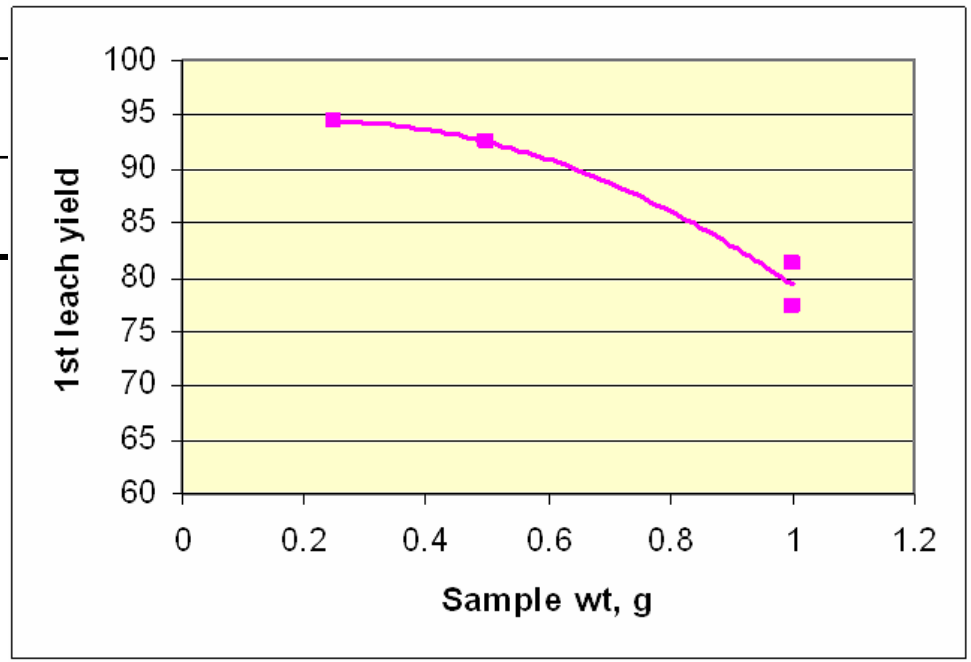
Leach #	Cumulative %Yield	Leach #	Cumulative %Yield
Acid "A"	1g surfactant	Acid "B"	0.5g surfactant
1	96.9	1	90.3
2	99.8	2	99.4

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

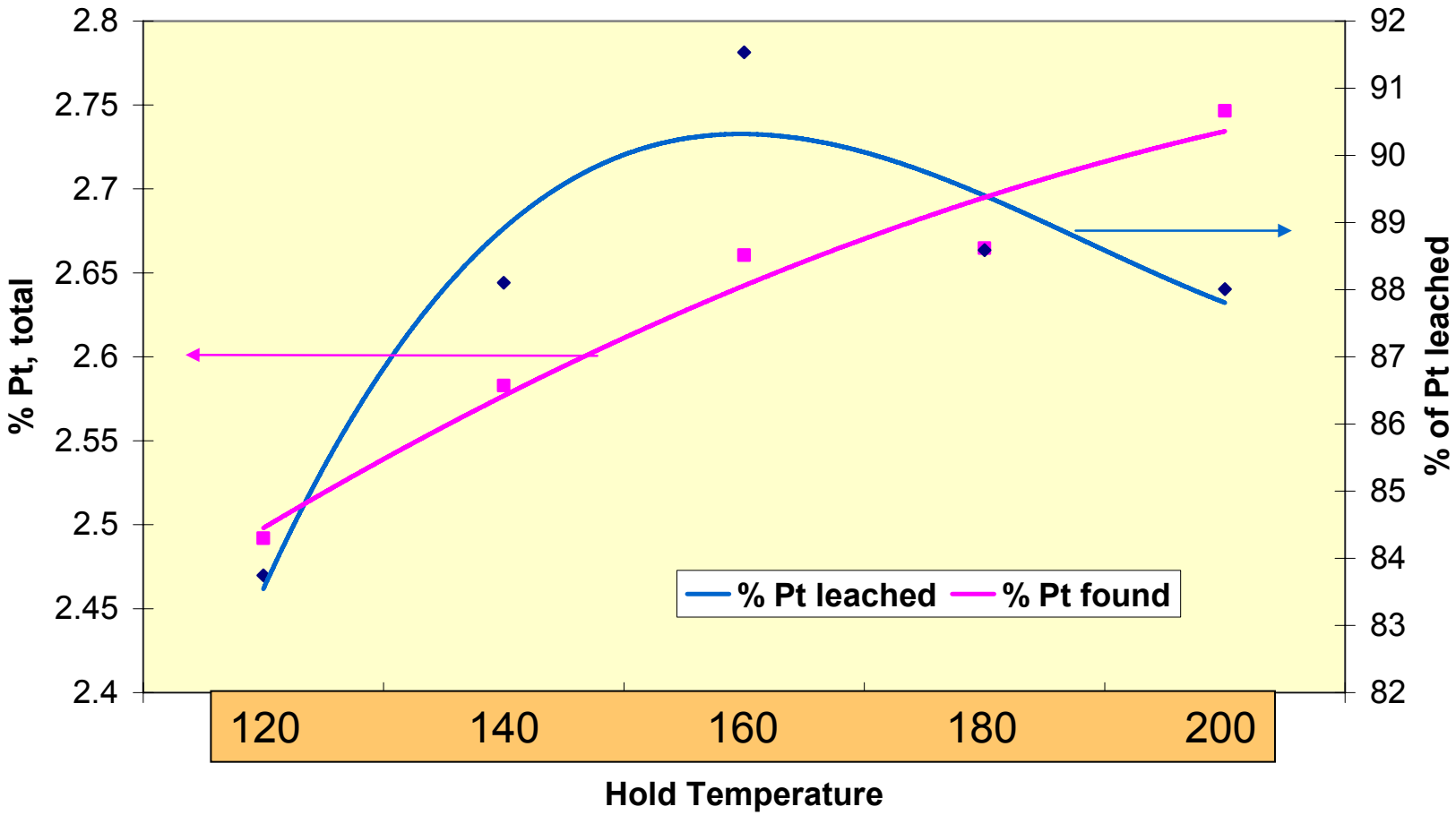
GDE with Acid "B"

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?

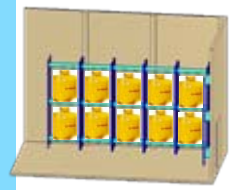


Process Challenges

- 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

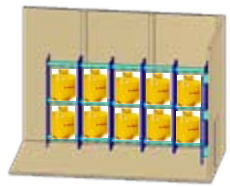
Precious Metal recovery from Membrane Electrode Assemblies,
Source: Fuel Cells for automotive applications
Part I MEA-Grinding

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



Storage in drums or Big Bags

Analyze lot sample to determine value of the lot



Store ground MEAs pending settlement

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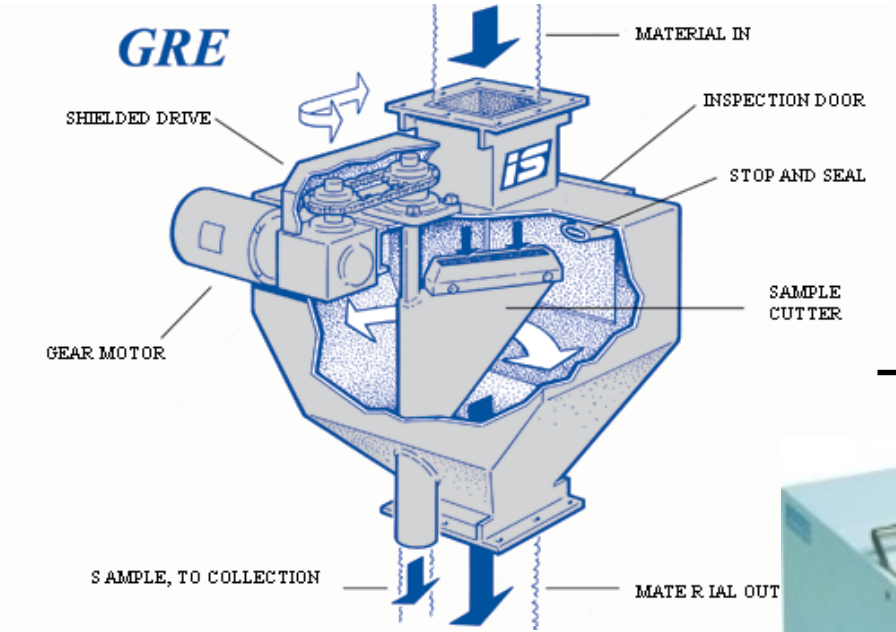
Obtaining a ‘Lot” Sample

- 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



Sub-sample
Retsch spinning riffler w/vibrating feeder (DE).
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Master sample
Intersystems in-line cross-cut ('pelican') sampler (US)
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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.

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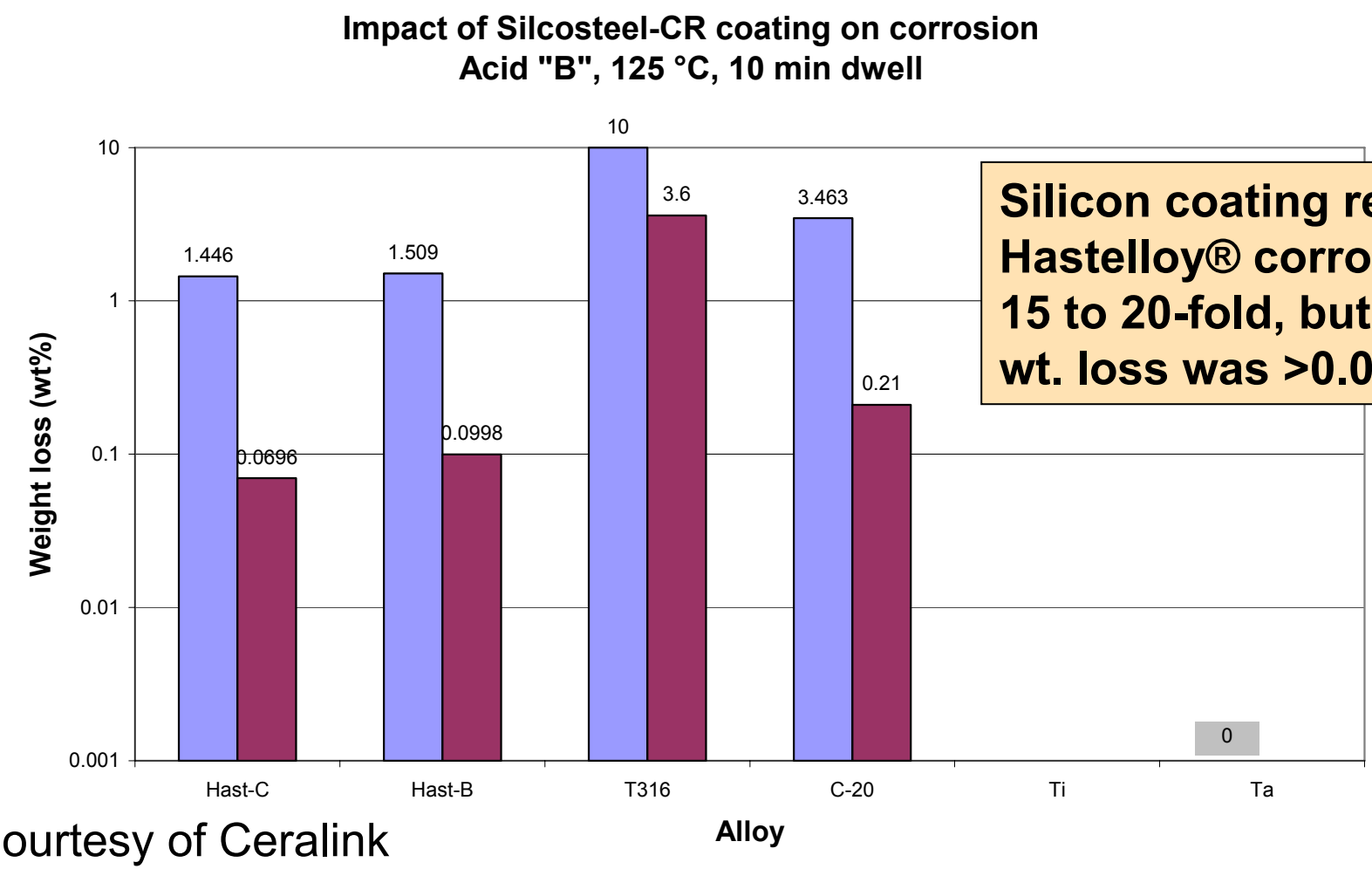

Silicon coating reduced Hastelloy® corrosion 15 to 20-fold, but wt. loss was >0.05%.

Courtesy of Ceralink

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

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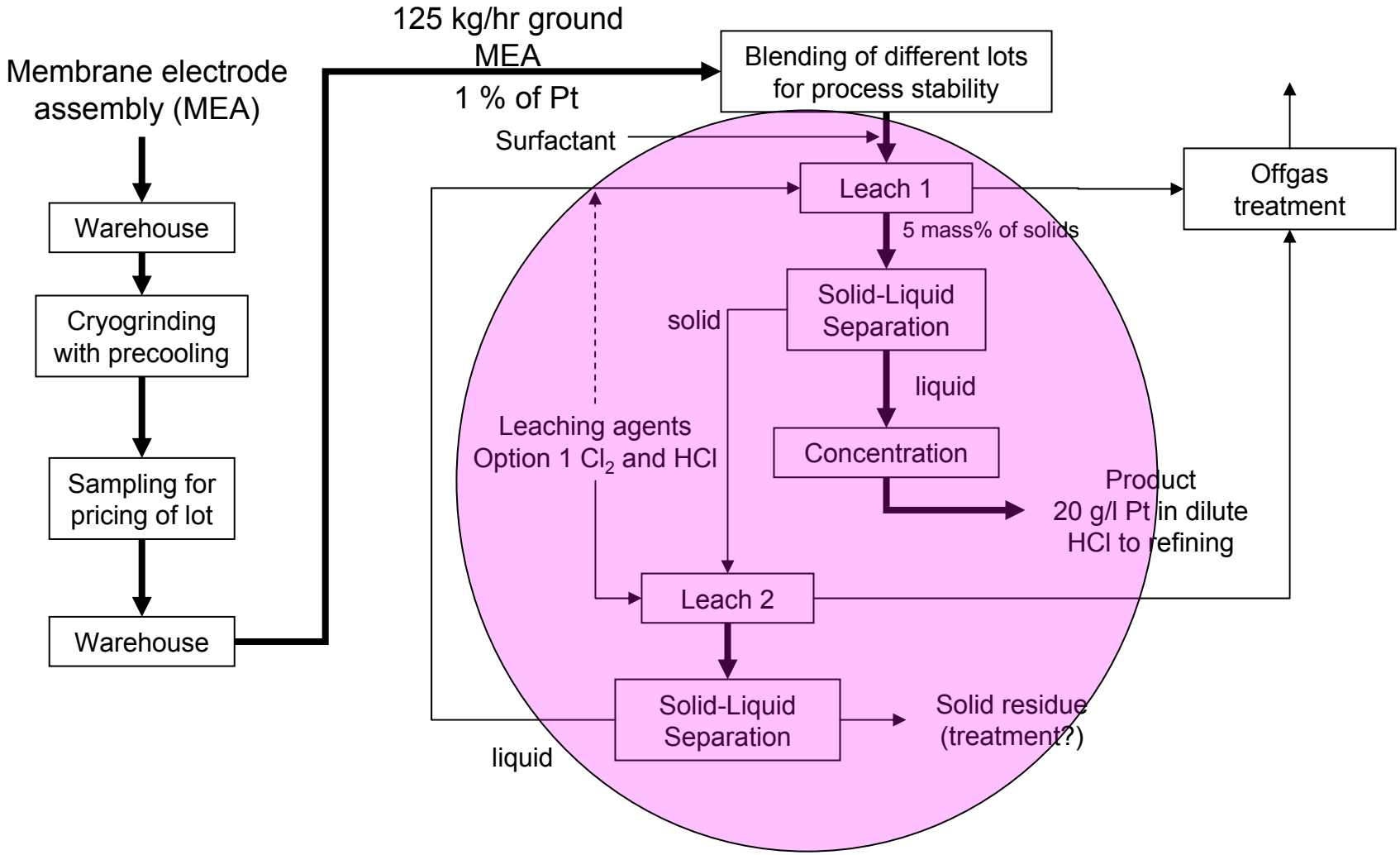
Experimental Conditions	mg Ti leached**	% wt loss
1. Uncoated Ti – Acid "B", 10 minutes @ 125°C	0.61	**0.0074**
2. Silicon-coated Ti –Acid "B", 10 minutes @ 125°C	0.022	**0.0003**
3. Silicon-coated Ti –Acid "B", 30 minutes @ 150°C	0.32	**0.0039**
4. Silicon-coated Ti –Acid "A", 10 minutes @ 125°C	0.038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

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

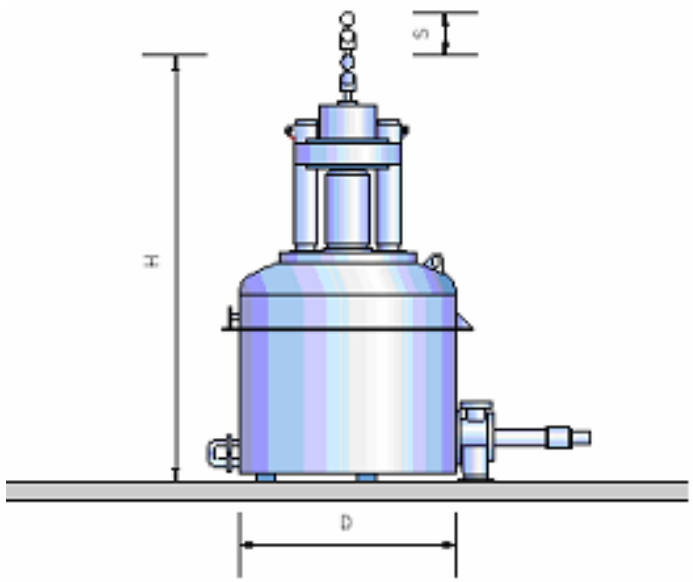
* Silicon coating commercially applied by Restek

** 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.



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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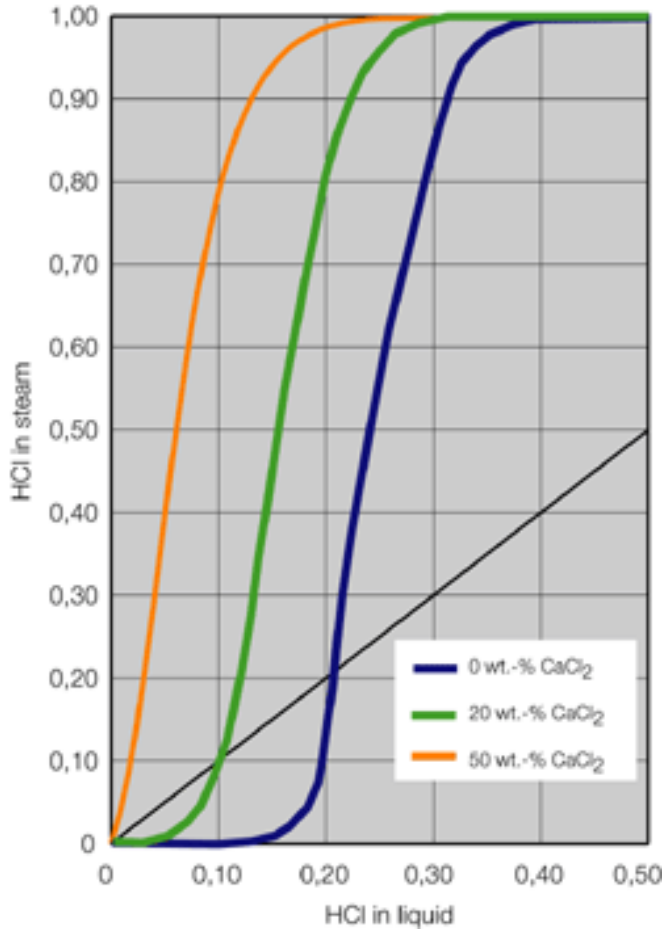
HCl Recycling Enhanced Using an Azeotrope Breaker

- HCl content decreases as HCl is converted to Cl_2 by reaction with added oxidants.
- HCL/water azeotrope has a BP of 109°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°C	**100**	**100**	**93.7**
	50	100	90.1
	50	**50**	**89.6**
150°C	**100**	**100**	**95.8**
	50	100	93.5
	50	**50**	**92.5**

Water added in place of HCl to maintain volume.

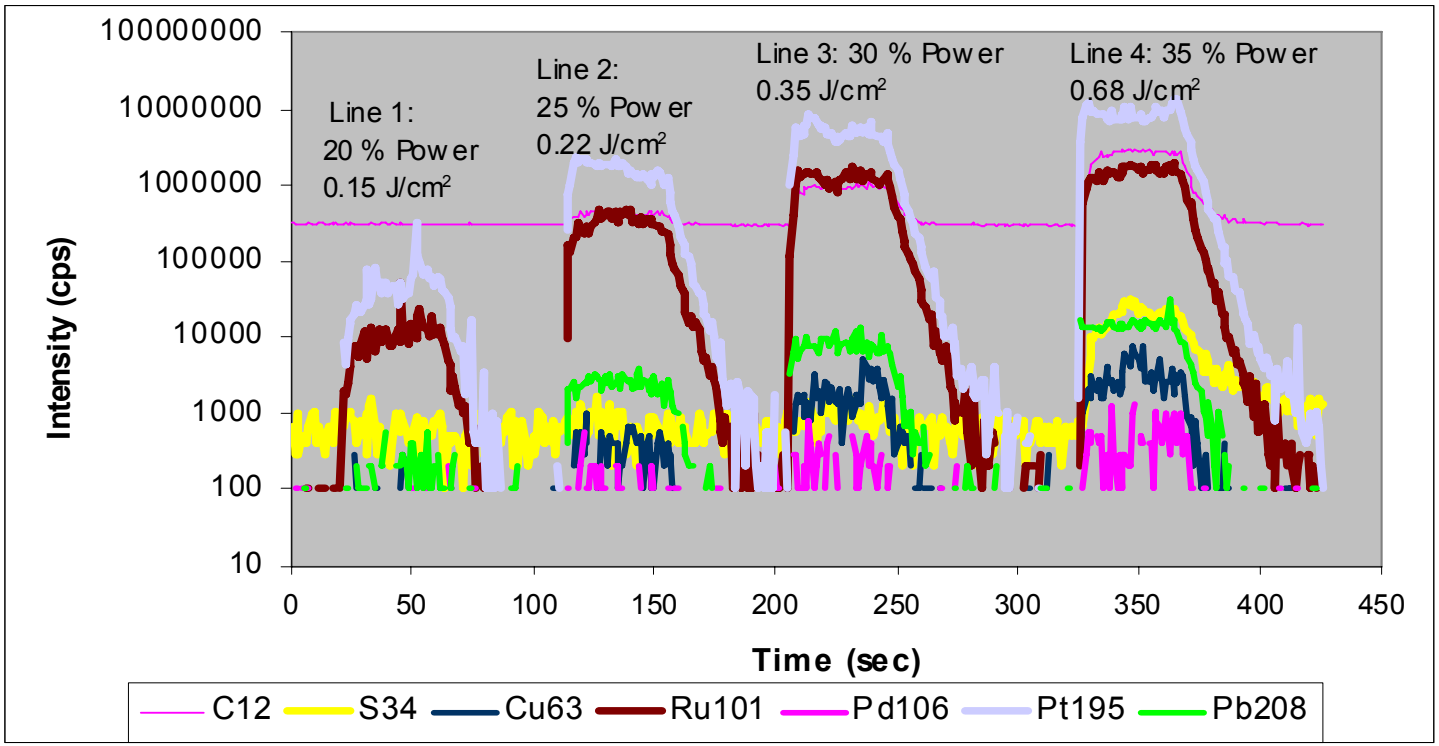
Process Control Methodology- Laser Ablation – Inductively Coupled Plasma Emission

- 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

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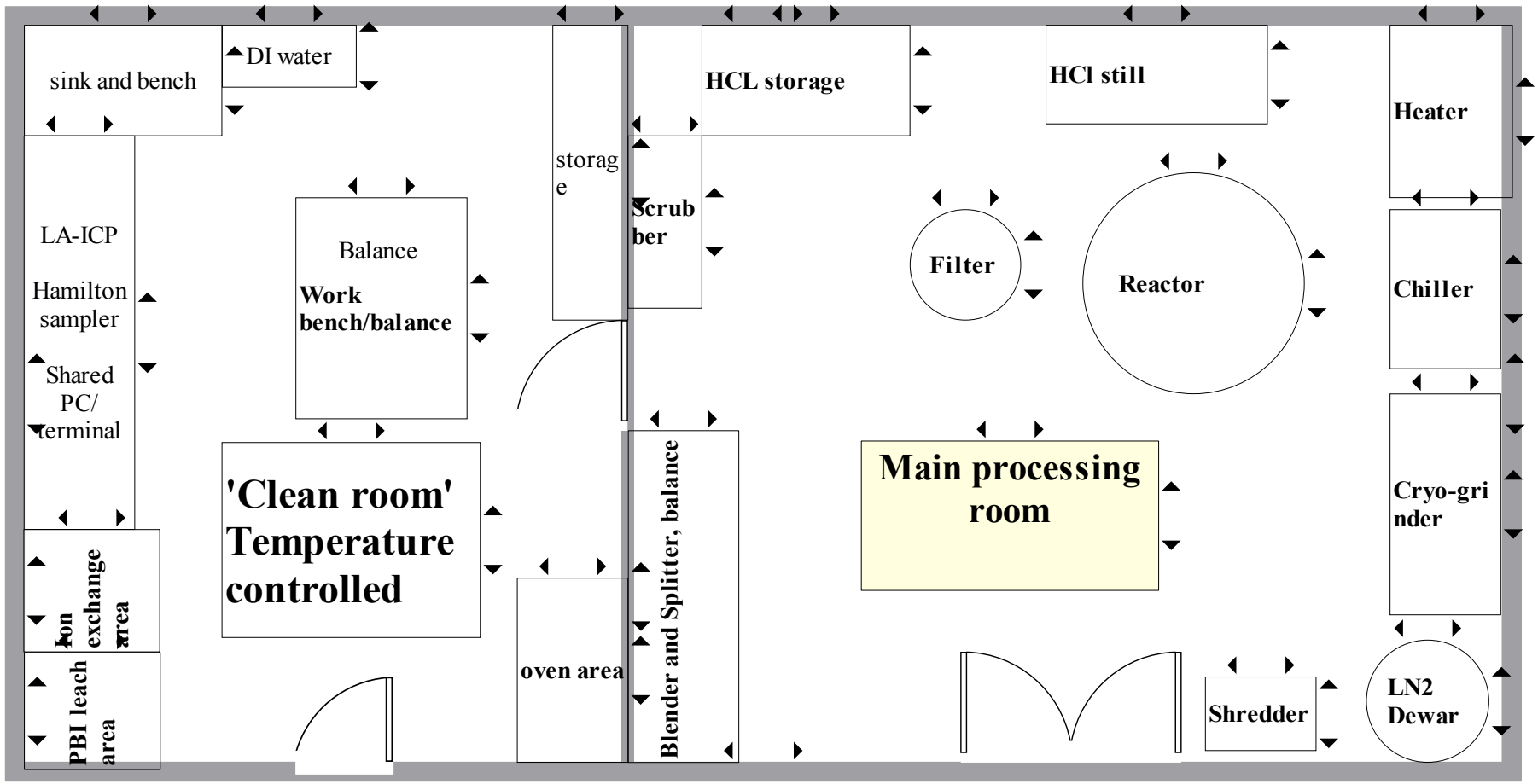
- Laser ablation transfers MEA powder as an aerosol to the ICP torch, where the particles are vaporized
- The ICP emission/MS signal will depend on the aerosol loading in the carrier gas
- The expected non-spatially uniform deposition of MEA powder on a filter substrate will result in poor precision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

	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)
Run 1 / 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^{o}C (BASF) -9/08

- Install an agitated titanium-lined reactor and determine Pt yield at elevated pressure and variable temperature > 100^{o}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