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Platinum Group Metal Recycling Technology Development

This presentation does not contain any proprietary or confidential information

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Fuel Fuel Recycling - Project Recapitulation

- In aggregate, fuel cells will represent a large inventory of platinum
  - This Pt inventory will have to be recycled to meet ongoing demand for new fuel cells
- Recycling of Pt via MEA combustion is counter-productive
  - The high fluorine content is converted to HF, a hazardous and corrosive vapor
  - The potential value for recovered perfluoropolymer is lost
- Engelhard was awarded a DOE funding for a five-year project to circumvent environmental issues, while developing a commercially-viable Pt recycling process.

Overview

Timeline

- Start - 11/2003
- Finish - 10/2008
- 70% Complete

Budget

- Total project funding
  - DOE share = $4.8MM
  - Engelhard share = $1.2MM
- $875,000 received in FY05
- $1.3M Funding for FY06
  - FY06 funding reduced 20% from budget

Barriers

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

Partners

Virginia Tech, Ceralink

Collaborators

- W.L. Gore, Etek
- MMT and Autoclave Engineers
- Milestone Scientific
- Pall Corporation
- Wyatt Technology, Malvern

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Objectives

Overall	Develop and demonstrate a process for recycling of PEM fuel cell MEA's without HF emission
2003-2006	Determine the processing steps necessary to optimize Pt recovery from aged fuel cell MEA's
2005-2006	Develop a solid-state adsorbent that will capture HF and COF_2 vapors
2005-2006	Evaluate the practicality of recovery of Nafion® polymer as part of a fuel cell recycling process
2006-2007	Determine process economics and build a prototype

Plan and Approach

- **Task 1: Pt recovery** — 50% Complete
  - Compare acids used to dissolve Pt
  - Compare conventional vs. microwave heating
- **Task 2: Sample preparation** — 50% Complete
  - Balance MEA handling requirements with Pt yield
- **Task 3: HF remediation** — 50% Complete
  - Develop solid-state adsorber
  - Modify process to minimize amount of adsorber required
- **Task 4: Process integration** — 80% Complete
  - Integrate unit operations based on results of Tasks 1-3
- **Task 5: Process Economics** — 25% Complete
  - Estimate scale of pilot-sized plant
  - Identify capital costs using process identified in Task 4
- **Task 6: Process demonstration** — 10% Complete
  - Build recycling prototype

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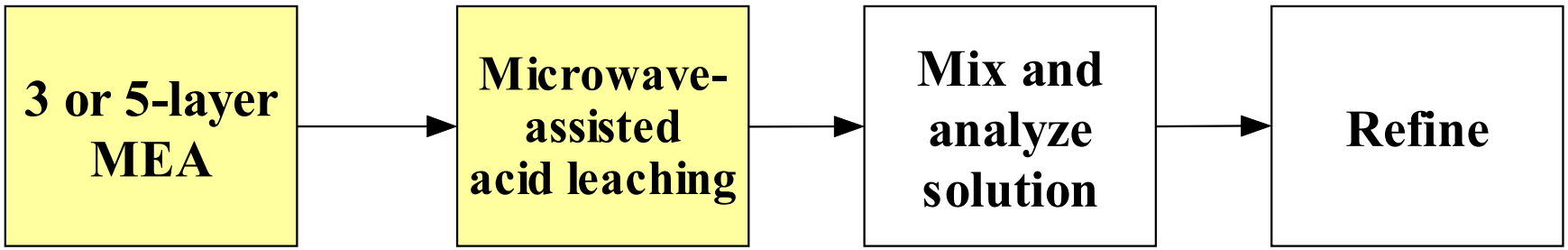
Approach - Preliminary PM Recycling Process (No HF evolved)



Engelhard's preliminary work focused on Pt recovery from MEA's by leaching Pt from the carbon layers on the membrane; the membrane was left intact.

Nafion® recycling was not included in the process.

Technical Accomplishments

- Task 1 and 2 (Pt recovery and Sample Preparation)
  - Conflicting conditions for near quantitative Pt recovery determined

Results of Microwave-Assisted Acid Leaching			
Sample	**GDL present?**	**Temperature / Pressure**	**% Pt removal (based on residue)**
3-layer MEA	no	200 / 10 bar	100, 100
5-layer MEA	yes	200 /10 bar	**82, 65**

- Removal of the GDL increases Pt leachability from the membrane.

- However, 1.5 to 10% of Pt left on GDL 'dry' stripped from aged MEA

Conclusion - A process that reconciles this contradiction is needed.

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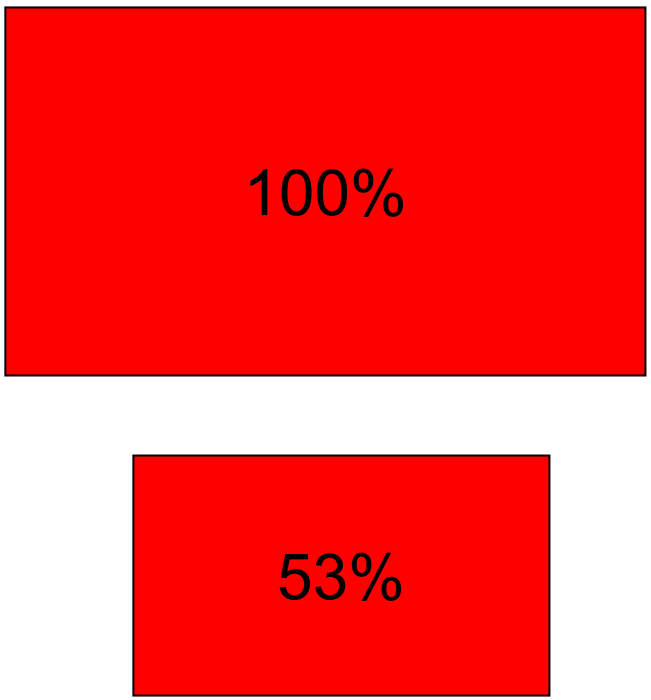
Approach – Alternate Process with Combustion



1 kg of 5-layer MEA has
~360g of F

335g of 3-layer MEA has
~190g of F

100g of electrode catalyst has
17g of F

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Why Consider the 'Combustion' Option

Commercial settlement depends on a homogenous sample, an accurate assay of Pt content and a known lot weight.

- Commercial settlement is facilitated using a metal or metal oxide with a low moisture content.
- Commercial settlement using a 'wet' carbon sample or a solution is not preferred.
- Representative sampling of a shredded 5-layer MEA is difficult to achieve.

While adding complexity to the process, igniting the filtered electrode catalyst is in line with current refinery protocol for handling carbon catalysts.

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Critical Evaluation of Microwave Combustion of 'GDL' MEA's

Engelhard has experience in purifying Pt obtained from carbonaceous material.

- Feasibility of combustion
  - Only 3-layer MEA's combust with microwave heating
    - GDL on 5-layer MEA's dissipate microwave energy
  - Preliminary stripping of the GDL from the membrane may result in Pt loss
- Capacity of Fluorine Adsorbent is limited
  - 3-layer MEA contains about 70% Nafion
  - Filtered electrode catalyst contains a small fraction of the total fluorine
    - Overall 90% reduction in fluorine emissions compared to 3-layer MEA

Conclusion – Combustion of filtered electrode catalyst is preferred

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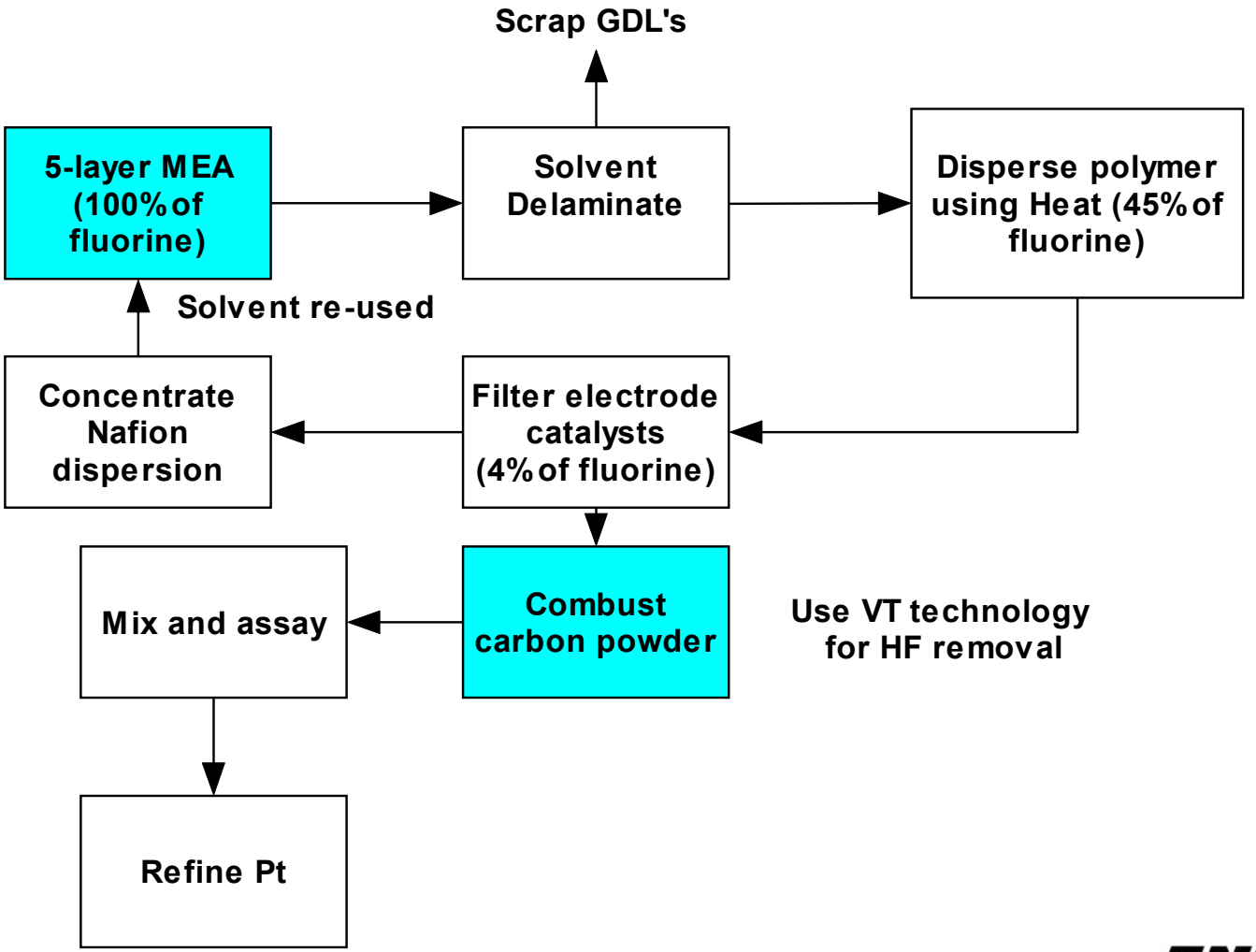
Approach – Alternate Process with Combustion



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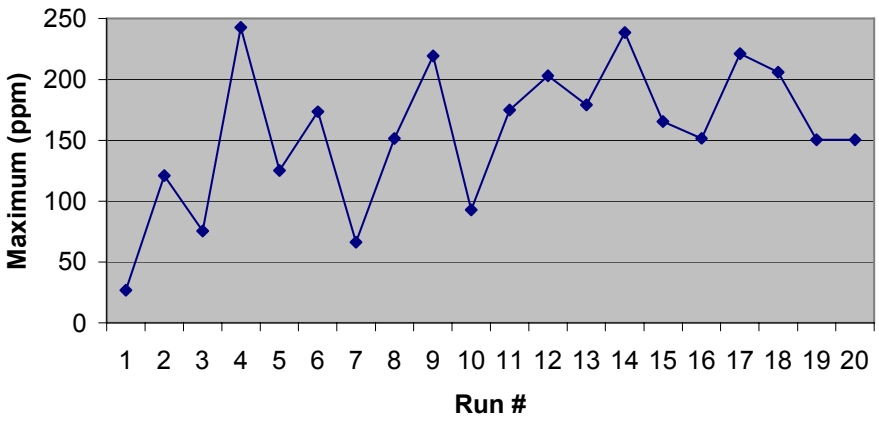
Technical Accomplishments –cont.

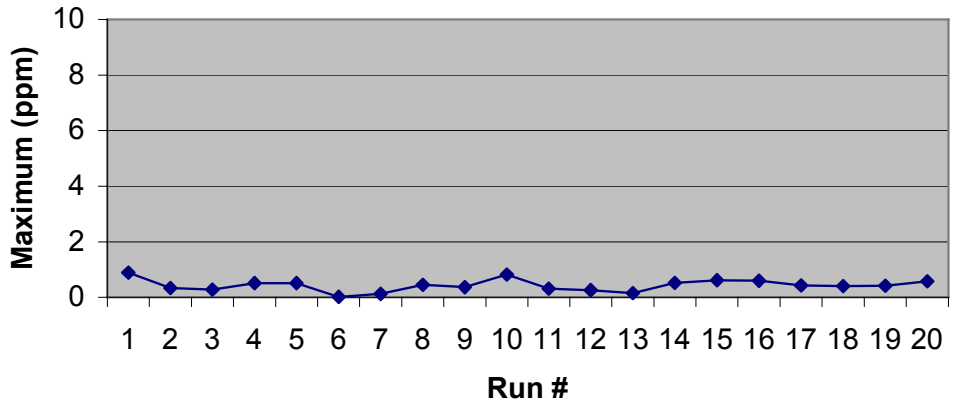
Task 3 – HF Remediation – 99.5% HF removal achieved

Maximum HF Emission, Empty Adsorbent Tube



No adsorbent, 0-250 ppm scale

Maximum HF Emission, Half Tube, 50% filled with adsorbent, 500°C



Adsorbent present, 0-10 ppm scale

Conclusion: Conditions have been identified to chemically remove fluorine-containing gases after Nafion combustion

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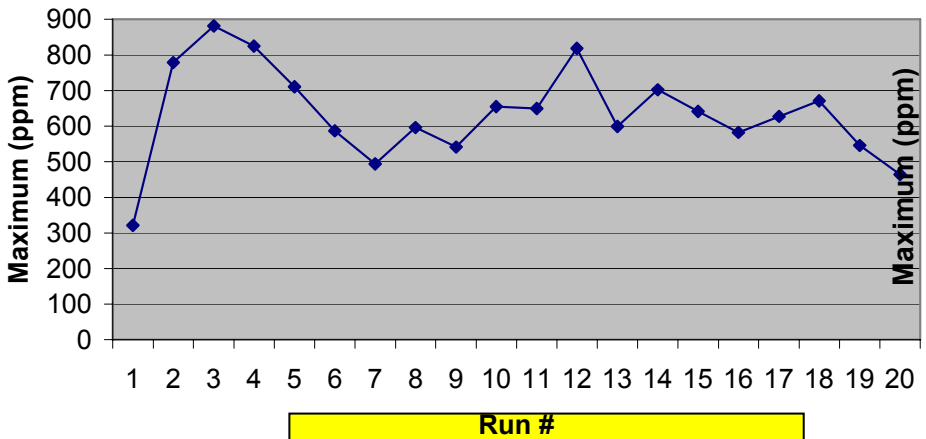
Technical Accomplishments –cont.

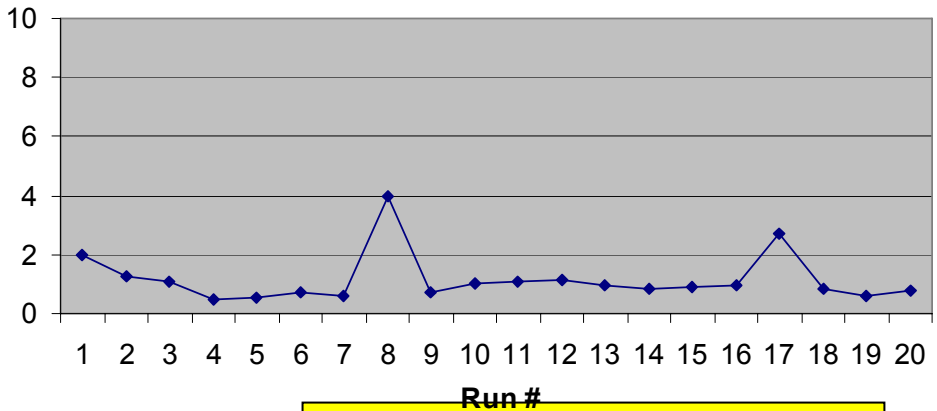
Task 3 – COF_2 Remediation – 99.8% HF removal achieved

Maximum COF2 Emission, Empty Adsorbent Tube



No adsorbent, 0-900 ppm scale

Maximum COF_2 Emission, Half Tube, 50% filled with adsorbent, 500°C



Adsorbent present, 0-10 ppm scale

Conclusion: Conditions have been identified to chemically remove fluorine-containing gases after Nafion combustion

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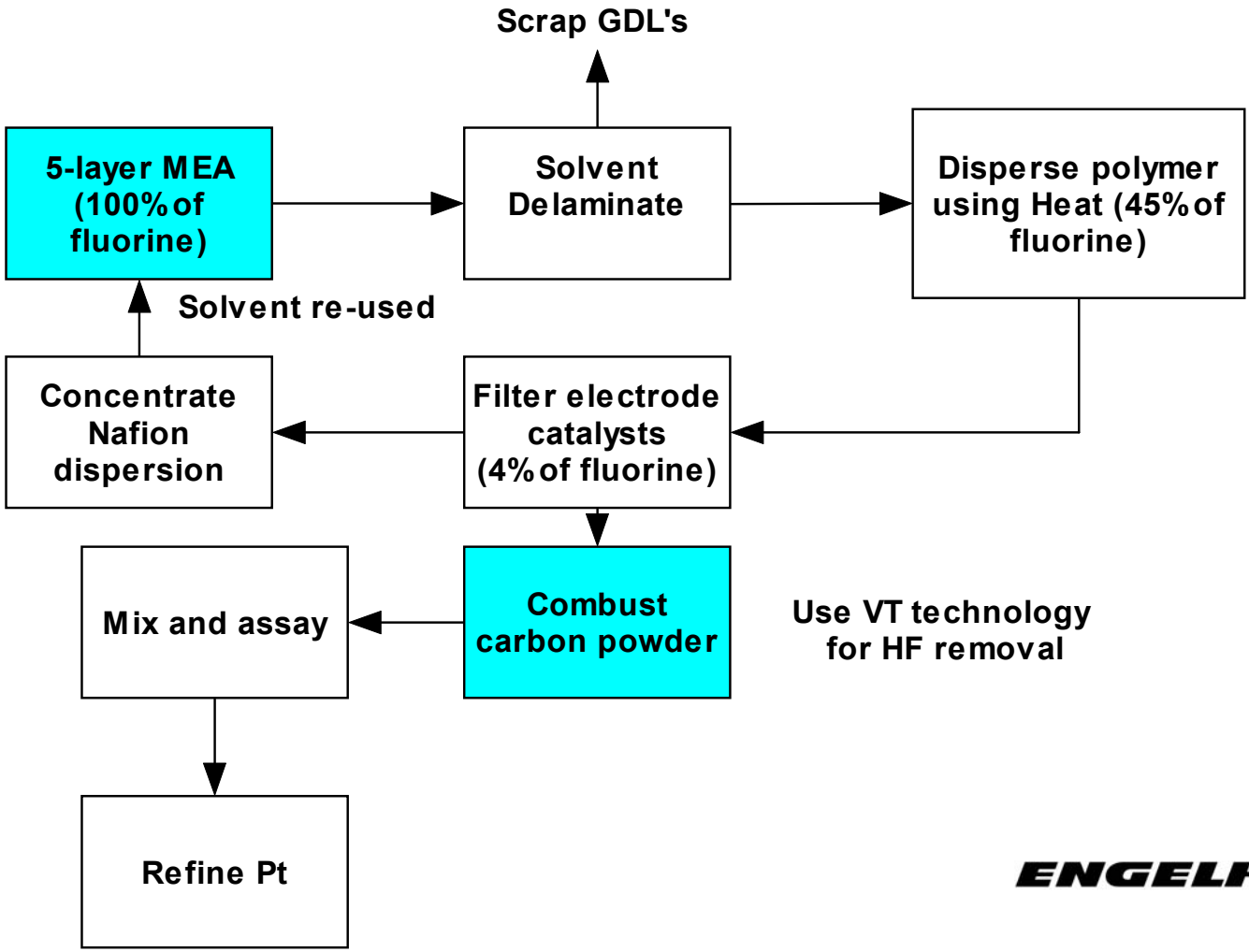
Technical Accomplishments –cont.

Task 4: **Engelhard Preferred MEA Recycling Process**



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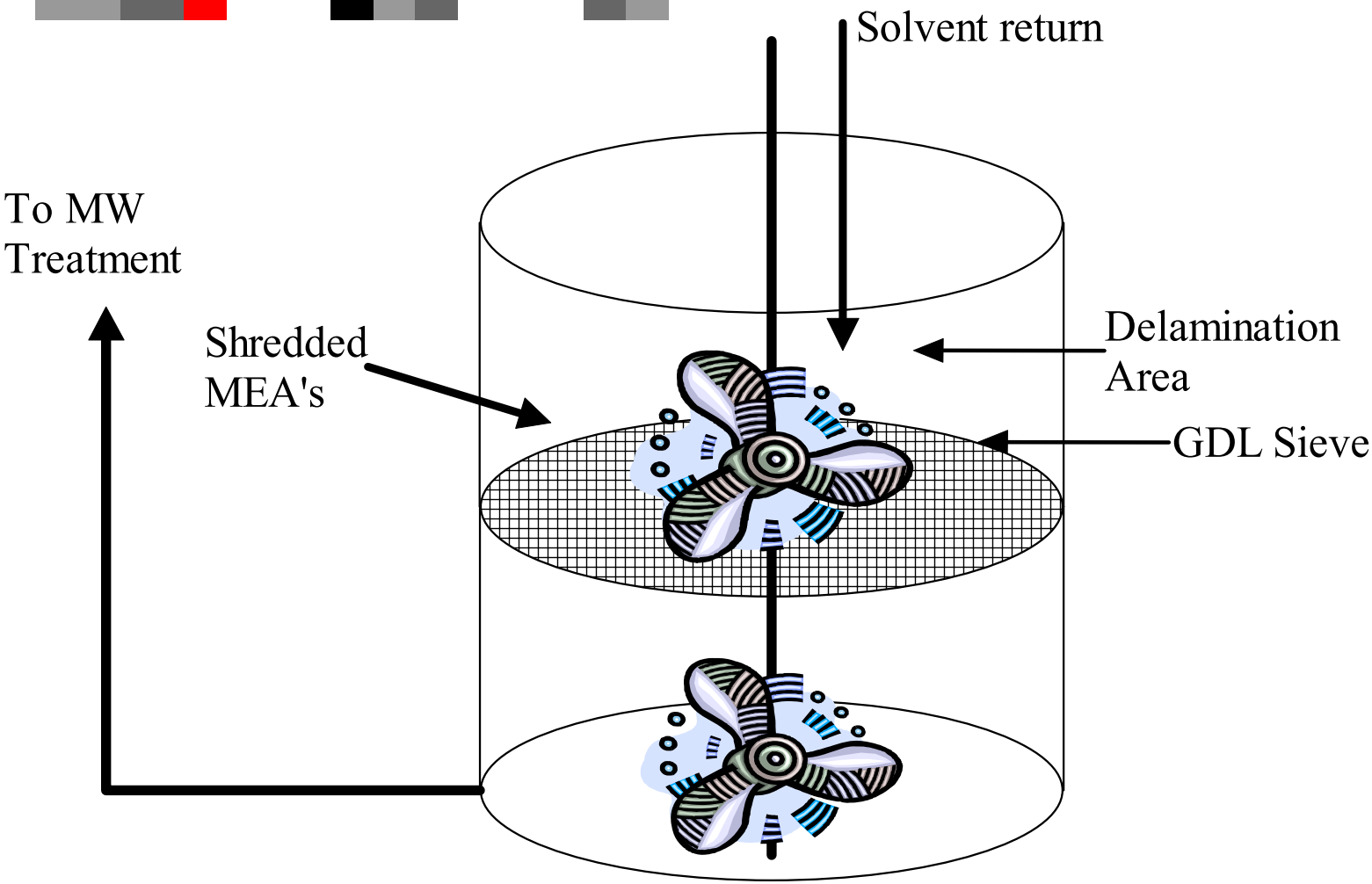
Process Explanation

- Used GDL-style MEA's have been shown to rapidly delaminate in alcohol/water mixtures, with partial membrane disintegration
- The membrane emulsion, with electrode catalyst, flows through a reactor and is heated with microwave energy to form a dispersion
- The carbon electrode particles are separated from the polymer dispersion for metal recovery
- The carbon is combusted, and the minimal HF emission is captured
- The polymer dispersion is then concentrated and the purified solvent reused
  - Engelhard is evaluating commercial outlets for recovered polymer
    - Applications will all be cost-driven
- The GDL's can be checked for residual Pt, then discarded

Visualization of Delamination Tank Using Alcohol/Water Mixtures



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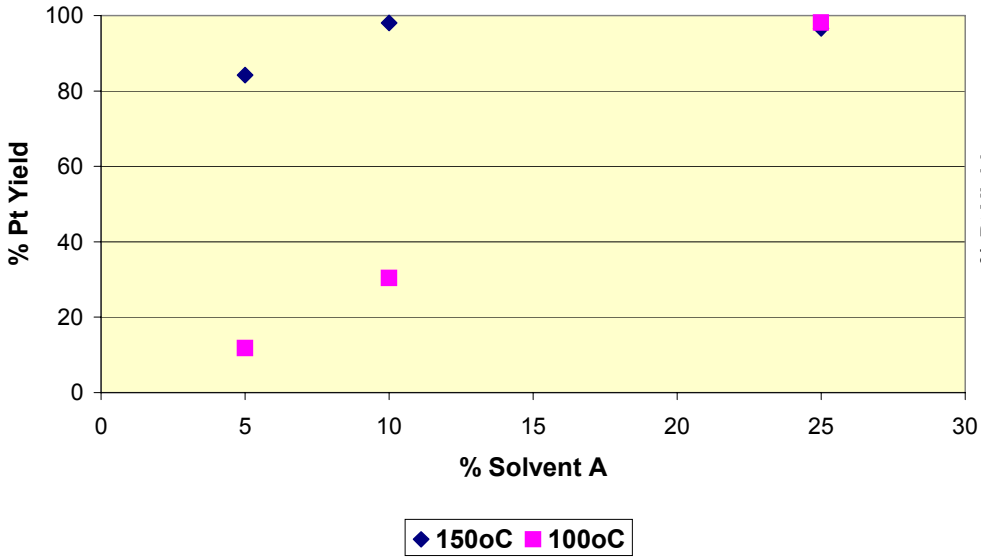
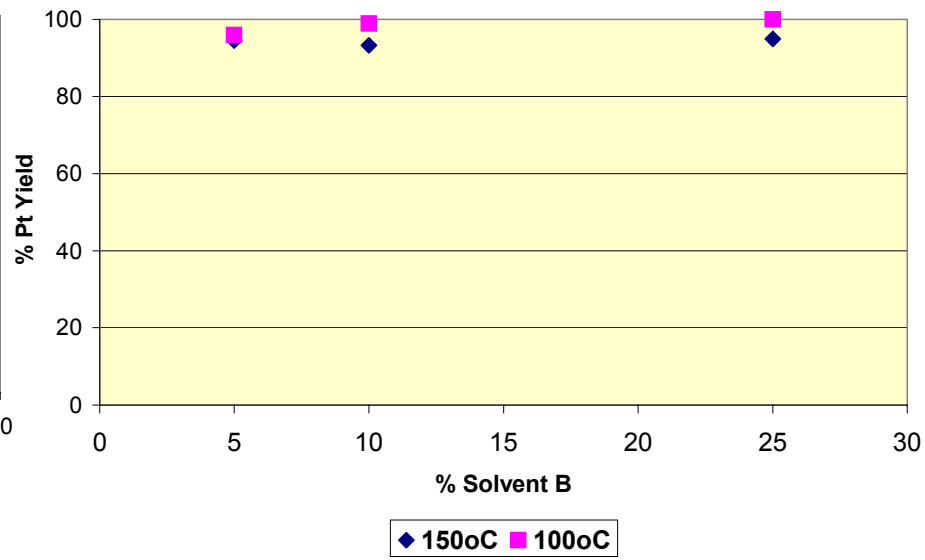
Technical Accomplishments- Effect of % Solvent and Temperature on Pt Recovery from Aged PEM MEA's is Solvent dependent -





Influence of temperature important for Pt recovery using Solvent A Mixtures

Temperature has little effect on Pt recovery with Solvent B Mixtures

* Results obtained from batch experiments

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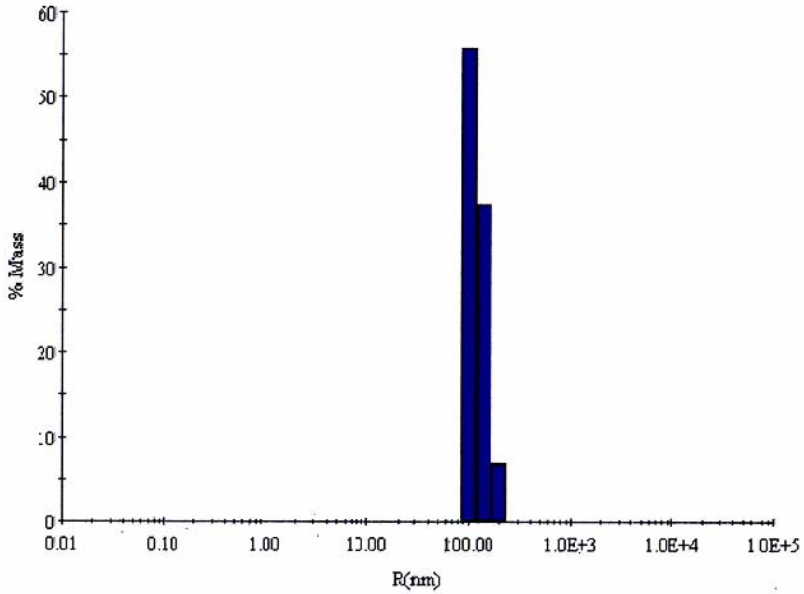
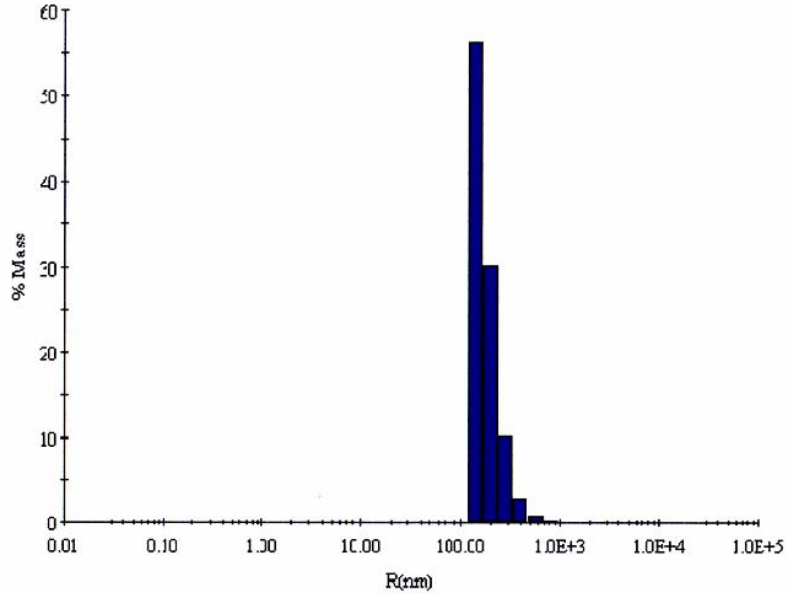
Technical Accomplishments – Dynamic Light Scattering Can be Used for Process Development and Quality Control

Nafion® Dispersed in 25% Solvent B @ 100°C (Batch)



Item	D (cm²/s)	R (nm)	%Pd	%Int	%Mass
Peak 1	1.97E-08	124.7	23.4	100	100

Nafion® Dispersed in 20% Solvent B, 5% Solvent A using a Continuous Method, 150°C



Item	D (cm²/s)	R (nm)	%Pd	%Int	%Mass
Peak 1	1.30E-08	188.4	42.1	100	100

(Results courtesy of Wyatt Technology)
Data obtained using DynaPRO

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Future Work - Milestones

- Complete demonstration of scaled-up microwave digestion unit – 6/06
- Determine capacity of the VT adsorbent for fluorine gases – 9/06
  - Acid leaching of electrode catalyst will be substituted for combustion if fluorine gas removal is not scalable
- Validate the two-step filtration process for recovery of fuel cell catalyst and perfluoroploymer emulsion- 9/06
- Certify the process
  - Estimate economics, including combustion of electrode catalyst, based on daily rate of 100 kg of 5-layer MEA – 9/06
  - Purchase continuous reactor – 10/06
  - Integrate delamination, dispersion and filtration – 4/07

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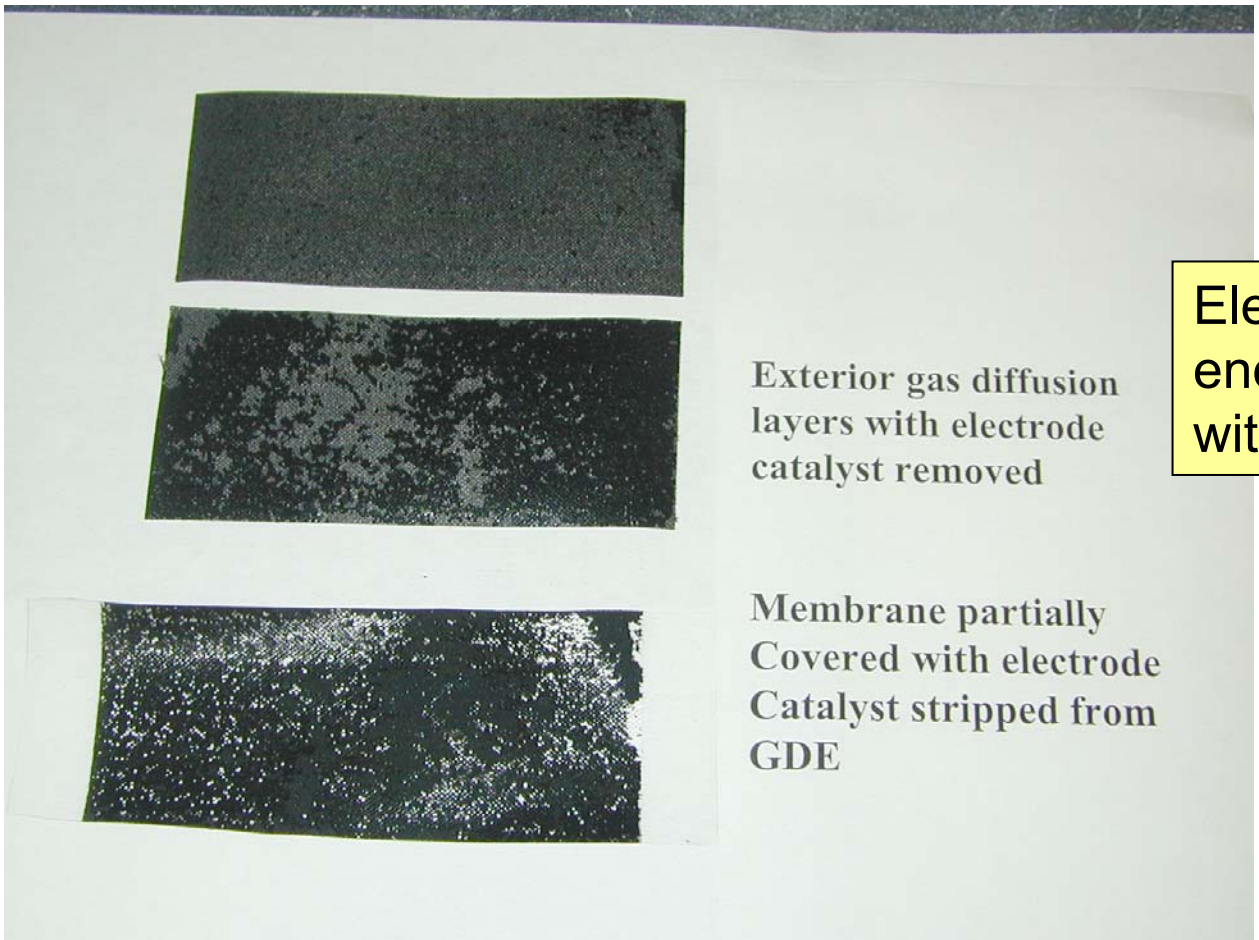
Critical Reviewer Comments From 2005

- Increase technical collaboration
- Continue with Nafion® recycling efforts (Value driven research)
- Why age MEA's? (500 vs. 2000 hours)
- What about GDE's? (This was a major concern of USCAR)

Recycling of GDE- style MEA's

- GDE's have electrode catalyst on the gas diffusion layer instead of on the membrane
- Layers of a fresh MEA do not split apart after exposure to hot water, steam or solvents
- The GDE has to be manually separated from the membrane to facilitate Pt recovery
  - **The electrode catalyst is partially left on the membrane during this process**
- After heating in boiling water, pulling apart the layers keeps all the electrode catalyst on the GDE
- High yields of Pt are achieved with microwave assisted acid-digestion of the GDE layers

Electrode catalyst is stripped from the GDE when the membrane is ripped from the outer (GDE) layers – No pre-treatment



Electrode catalyst ends up on all surfaces with dry dismemberment

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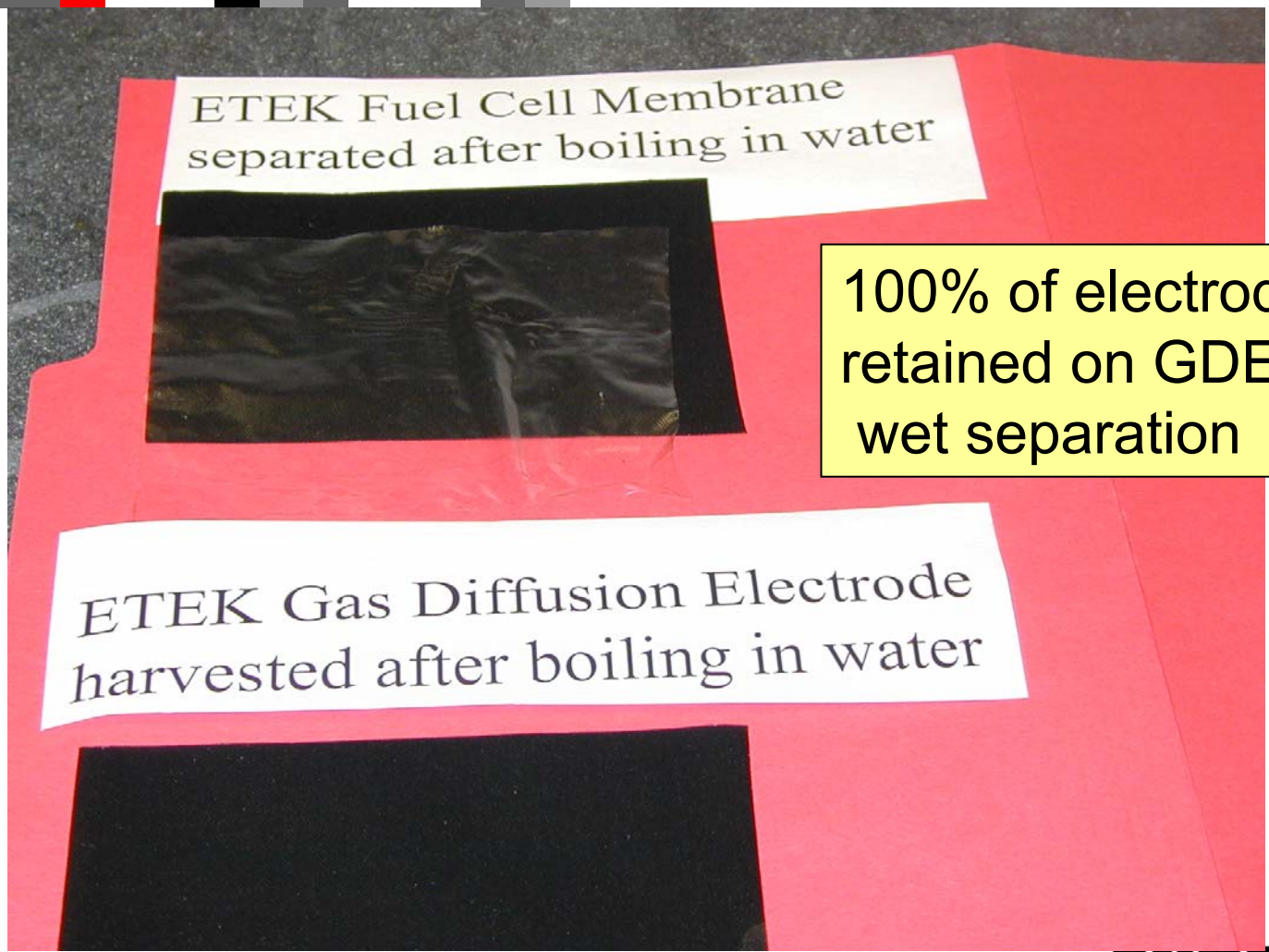
Value of preliminary membrane separation in retaining electrode catalyst on the (outer) gas diffusion layer – Boil, then Strip



100% of electrode catalyst retained on GDE with wet separation

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Recovery of Electrode Catalysts from new GDE MEA's (Etek) after membrane removal (except for Ignition Method)

- **U of K High T/P Autoclave process or Solvent Delamination**
  - **Not viable- Most of the Pt/Carbon stays on the GDE**
- **Ignition (no pre-treatment)**
  - **High HF release**
  - **Estimated >95% Pt recovery**
- Atmospheric acid leach (hot plate)
  - Nafion ® membrane recycling possible
  - **91% Pt recovered**
- Microwave assisted (under pressure) acid leach
  - **Nafion ® membrane recycling possible**
  - **96% Pt recovered**

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Back-up slides

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Highlights of Milestone Flowsynth Continuous Reactor (Courtesy of Milestone Scientific, Shelton, CT)

Pump

Reactor mixer

Reactor inside
Microwave oven

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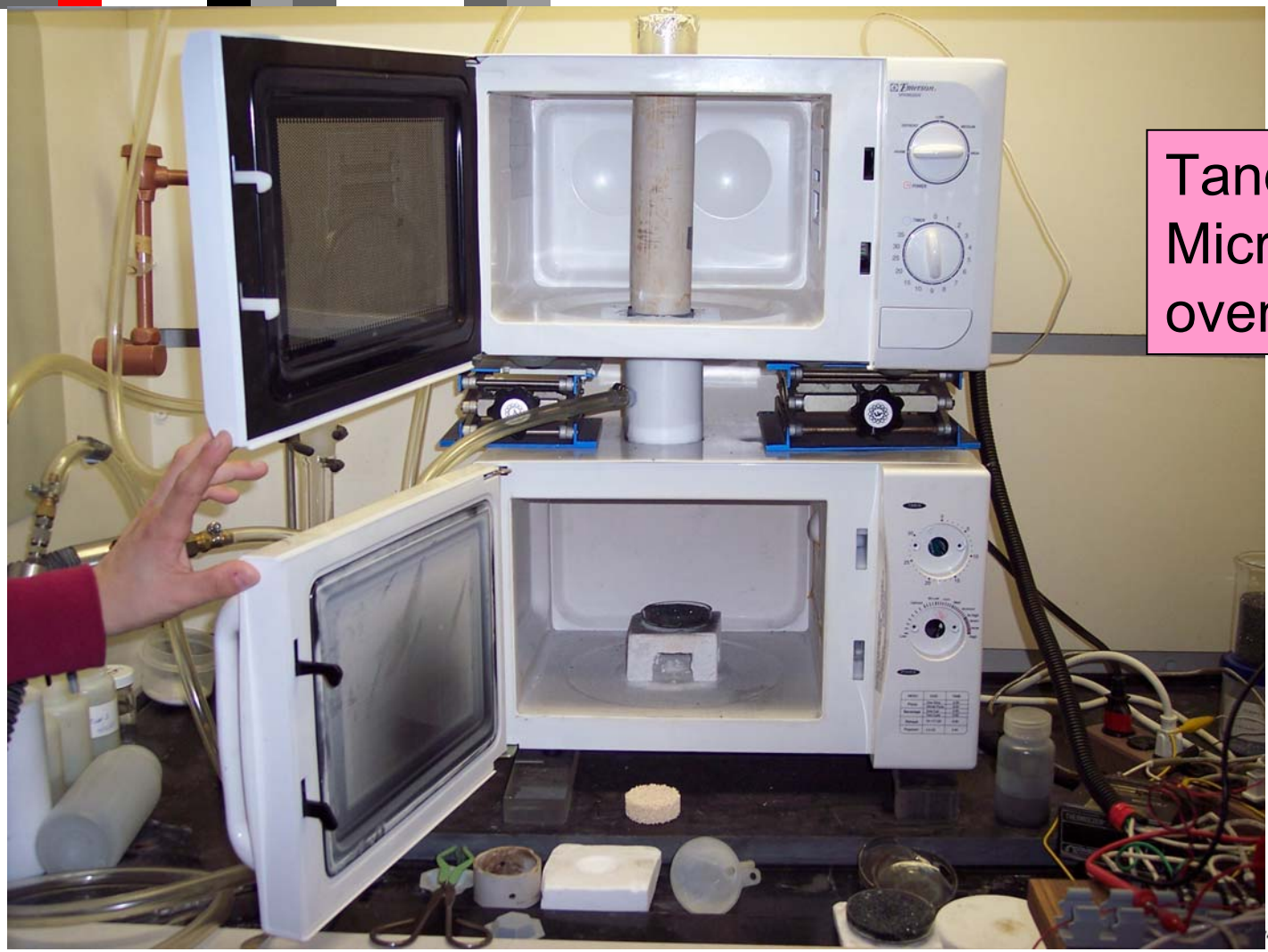

Tandem Microwave ovens