

Coal Syngas Testing at NETL



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Goal

Identify the effects of trace coal syngas species on SOFC anodes, and identify the trace material exposure levels that will be acceptable to fuel cell operation.

At present, no data exist to guide developers on how to design coal syngas cleanup systems suitable for SOFC operation

Trace elements: <1000ppm (Ref. Speight)



Effect of Trace Species on SOFC Anode

- **Affect the ability of Ni to promote the electrochemical reactions**
 - Trace species on Ni surface inhibit the adsorption of H_2 , CO, or dissociation of H_2
- **Affect the ability of YSZ to transport oxygen ion**
 - Formation of secondary zirconia phases
- **Affect the electrical conductivity**
 - Formation of secondary nickel phases such as nickel-phosphide

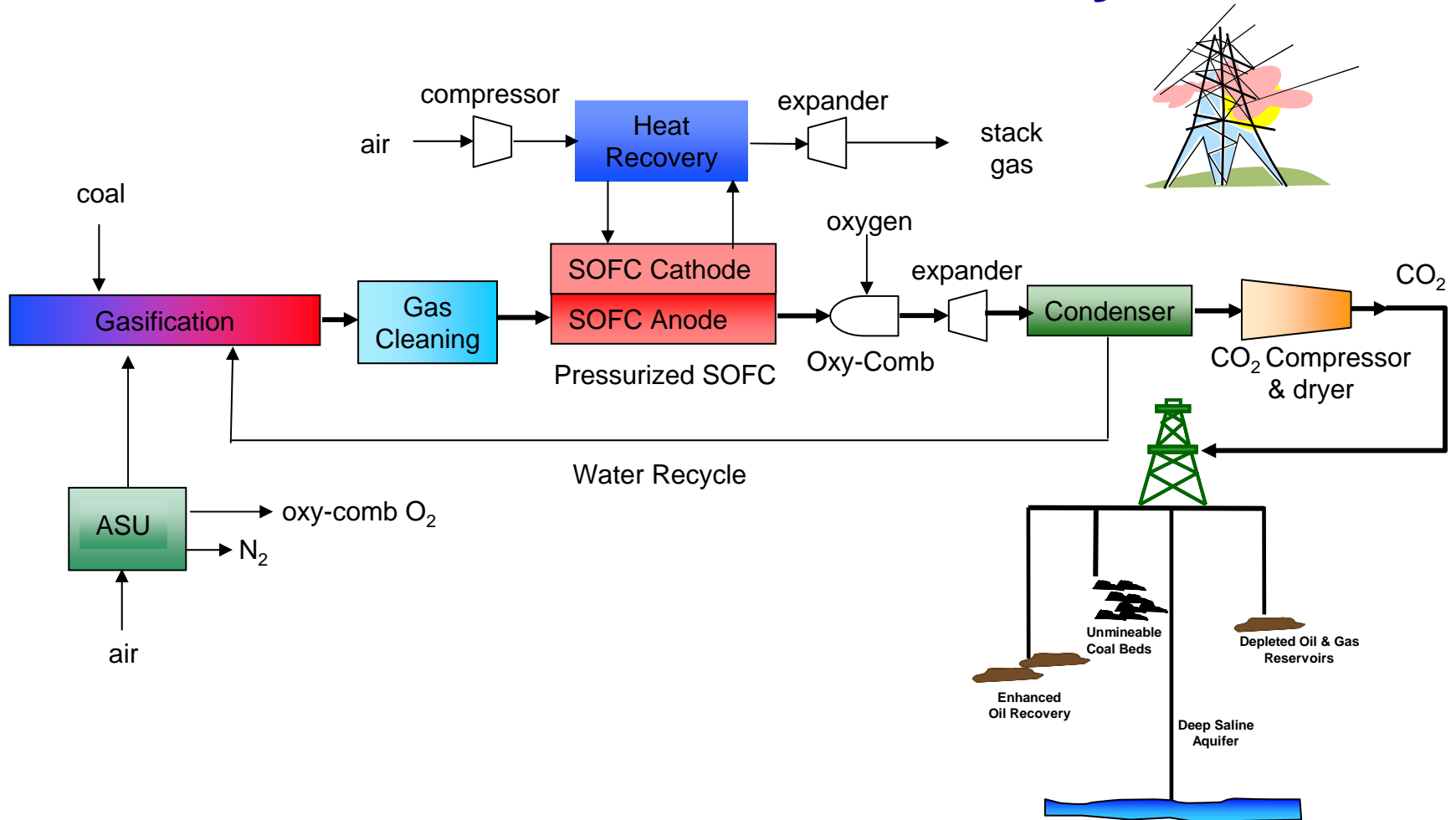
Questions

- **What is the variability of trace elements in coal?**
- **What is the effect of different gasification technology on the potential for anode attack?**
- **Aside from trace metal species, are other 'contaminants' (e.g., tars) important to consider?**
- **Is individual contaminant testing representative of actual coal syngas operation?**

Outline

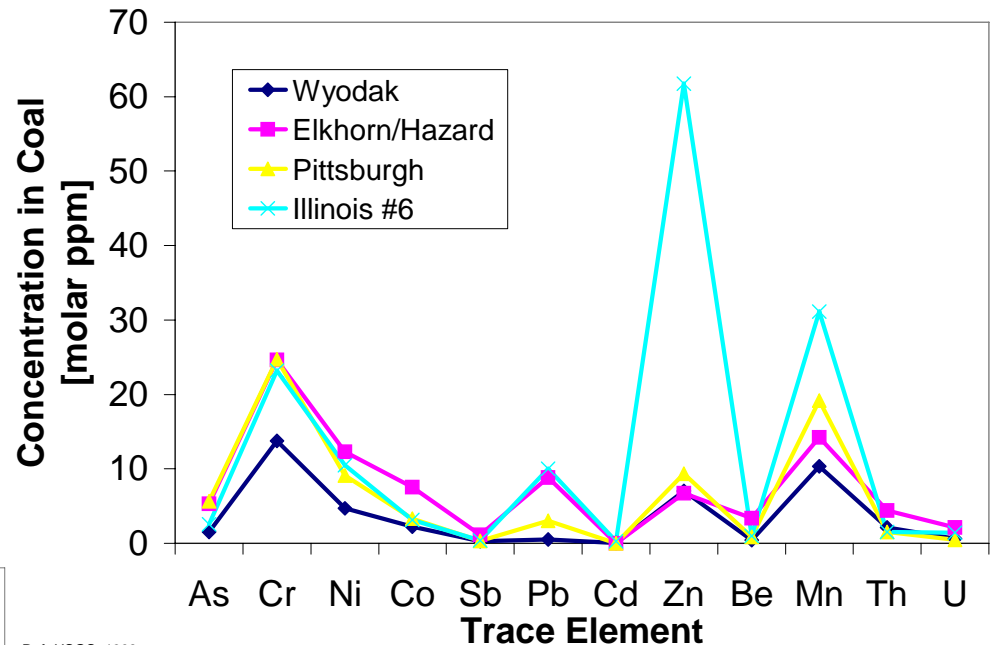
- **Analysis**
 - Assess the contaminants in variety of coals
 - Identify potential sensitivities of gasification design on trace species attack
- **Experimental**
 - Individual trace specie evaluations
 - Direct coal syngas testing

Advanced Coal Based IGFC System

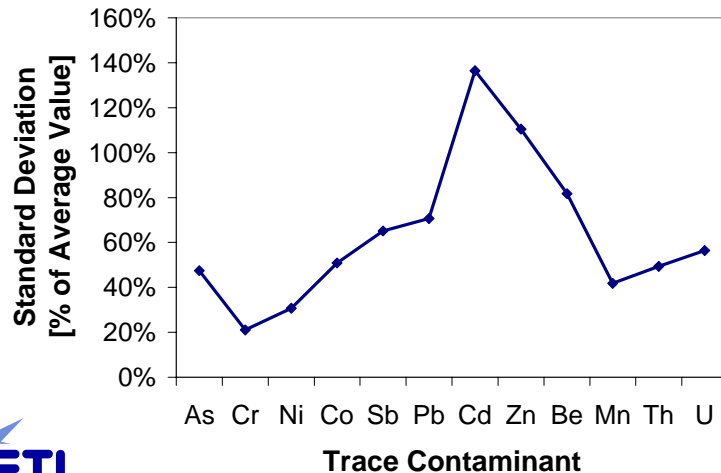


Trace Metal Contaminants (Coal-Type Dependency)

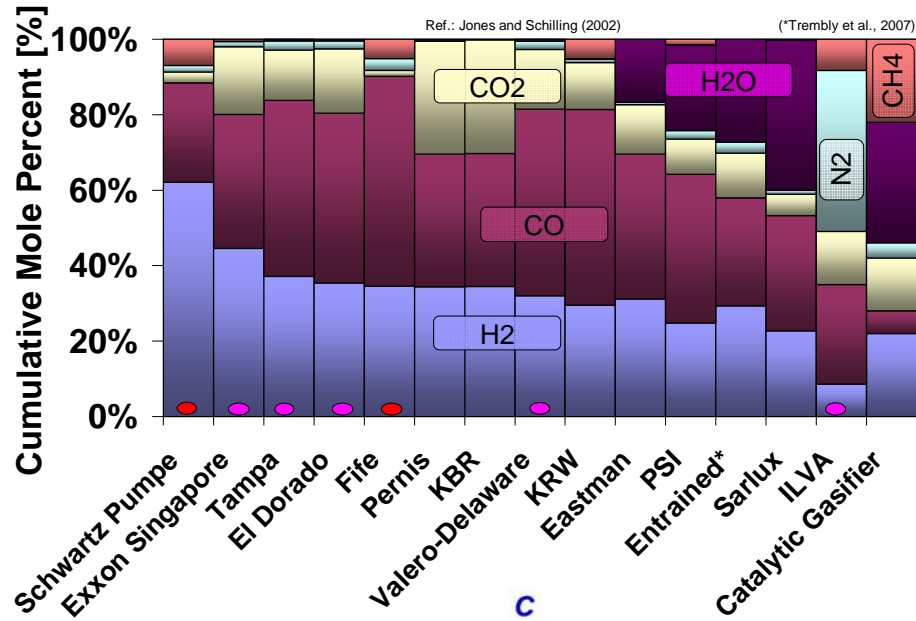
- USGS analysis of trace elements in coals.
- Different coals have different levels of given a given contaminant.
- Data given here shows deviations (from average) approach 140%.



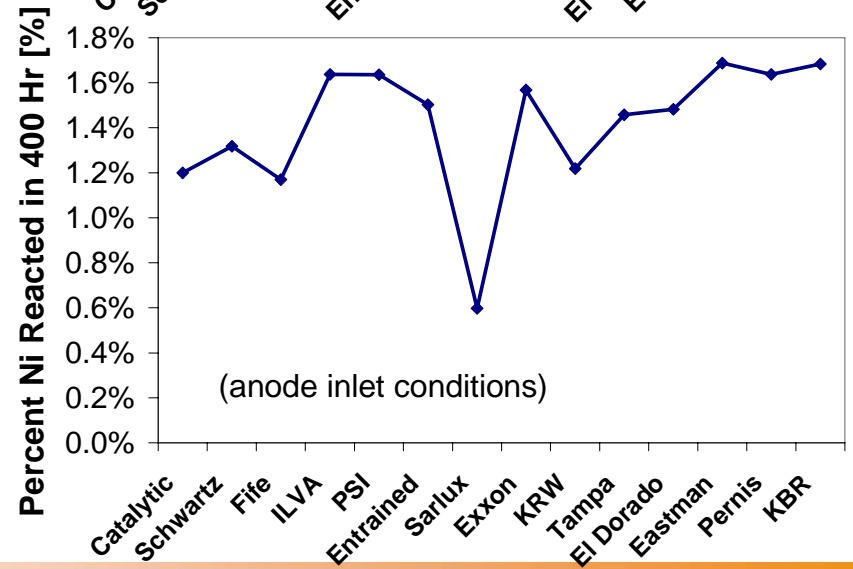
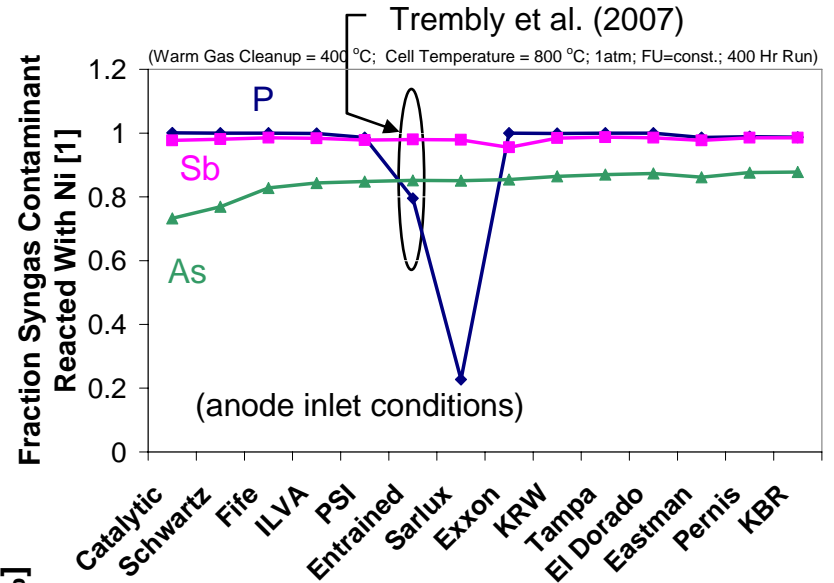
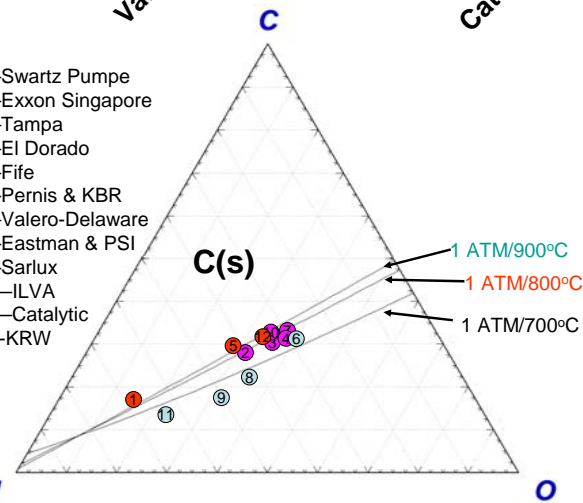
Ref. USGS, 1998



Gasification Dependencies



- 1—Swartz Pumpe
- 2—Exxon Singapore
- 3—Tampa
- 4—El Dorado
- 5—Fife
- 6—Pernis & KBR
- 7—Valero-Delaware
- 8—Eastman & PSI
- 9—Sarlux
- 10—ILVA
- 11—Catalytic
- 12—KRW

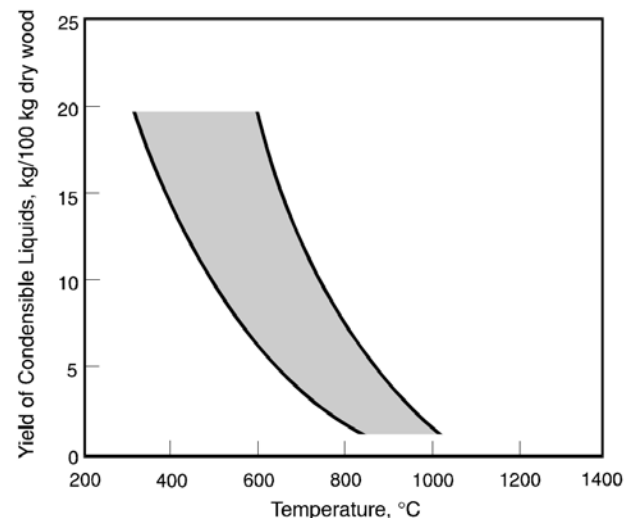


Contaminant Loading from Tremby et al. (2007)



Gasification Tars

- Gasifier syngas consists of tars in addition to H_2 , CO , CO_2 , H_2O , char, and volatile trace material.
- A typical tar yield is about 3–4%, by weight, of the coal charged (Menéndez and others, 2000).
- Coal tar elemental analysis: 80% C, 6% H, 1% N, 3% S, 10% O.
- Benzene soluble tar components by volume:
 - Benzenes (3%), Naphthalenes (15%), Aromatics (12%), Acenaphthenes (12%), Fluorenes (9%), Indenes (5%), Dibenzofurans (6%), Phenyl naphthalenes (7%), Others (31) (Bureau of Mines (1974))
- Tars = All organic components having molecular weight higher than benzene. (Bergman et al. 2002).
- Major factors affecting tar composition are the temperature profile, gasifying agent, partial pressure of hydrogen, the residence time of the coal in the gasifier, and coal structure (Miller et al. 1980).
- Syngas treatment:
 - Filters and scrubbers
 - Cool syngas to below 100 to 260 °C to remove tars. (e.g., U.S. Patent 4198212)
 - Catalytic reaction beds
- Short term exposures (ca. 20 hrs) of Ni/GDC anode to tar from bio-fuel gasifier result in no carbon or fuel cell performance changes. (Hofmann et al. 2008)



Outline

- **Analysis**
 - Assess the contaminants in variety of coals
 - Identify potential interactions between trace species and anode across a variety of gasification systems
- **Experimental**
 - Perform individual trace specie evaluations
 - H₂Se and Benzene
 - Perform direct coal syngas testing

Methodology to Identify Cleanup Target Levels

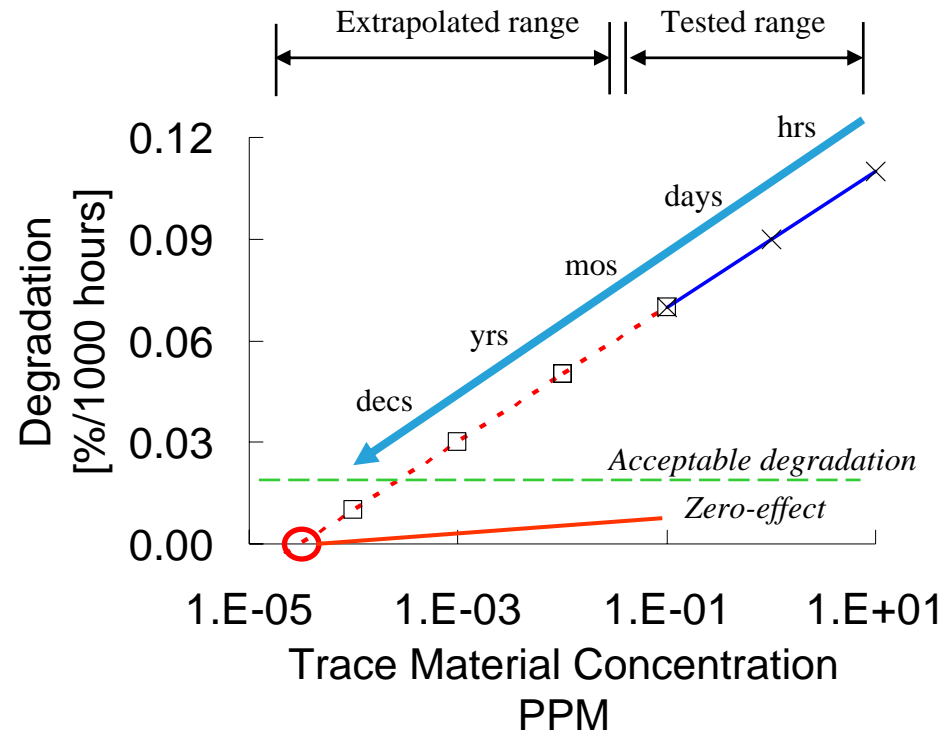


- **Single trace material testing is used to assess impact of specific species**
 - Attack on active sites at the electrochemical TPB (relatively short time constant)
 - Attack on SOFC material to generate resistive secondary phase (relatively large time constant)
 - Other ... ?

- **Method of attack characterized by $V(t)$ and post test analysis (XRD, SEM, EDS) from test data:**

- 0.1 ppm, 1 ppm, 10 ppm

- **Rates extrapolated to ‘zero-effect’ level (continually refined as more data is available!)**
- **Avoid time and expense required to experimentally show “zero-effect”**



Experimental Methodology

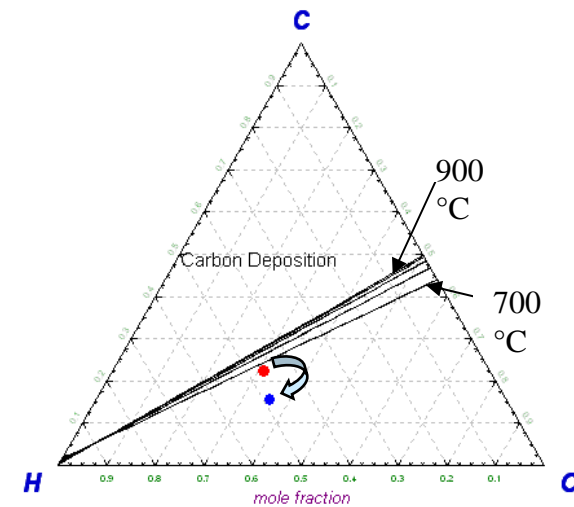
- Anode supported SOFCs with Ni/YSZ anodes operated between 750-800°C
- Cells operated with simulated coal syngas containing single trace species of interest
- VI scans and EIS methods used during testing
- Post trial SEM, EDS, and XRD used



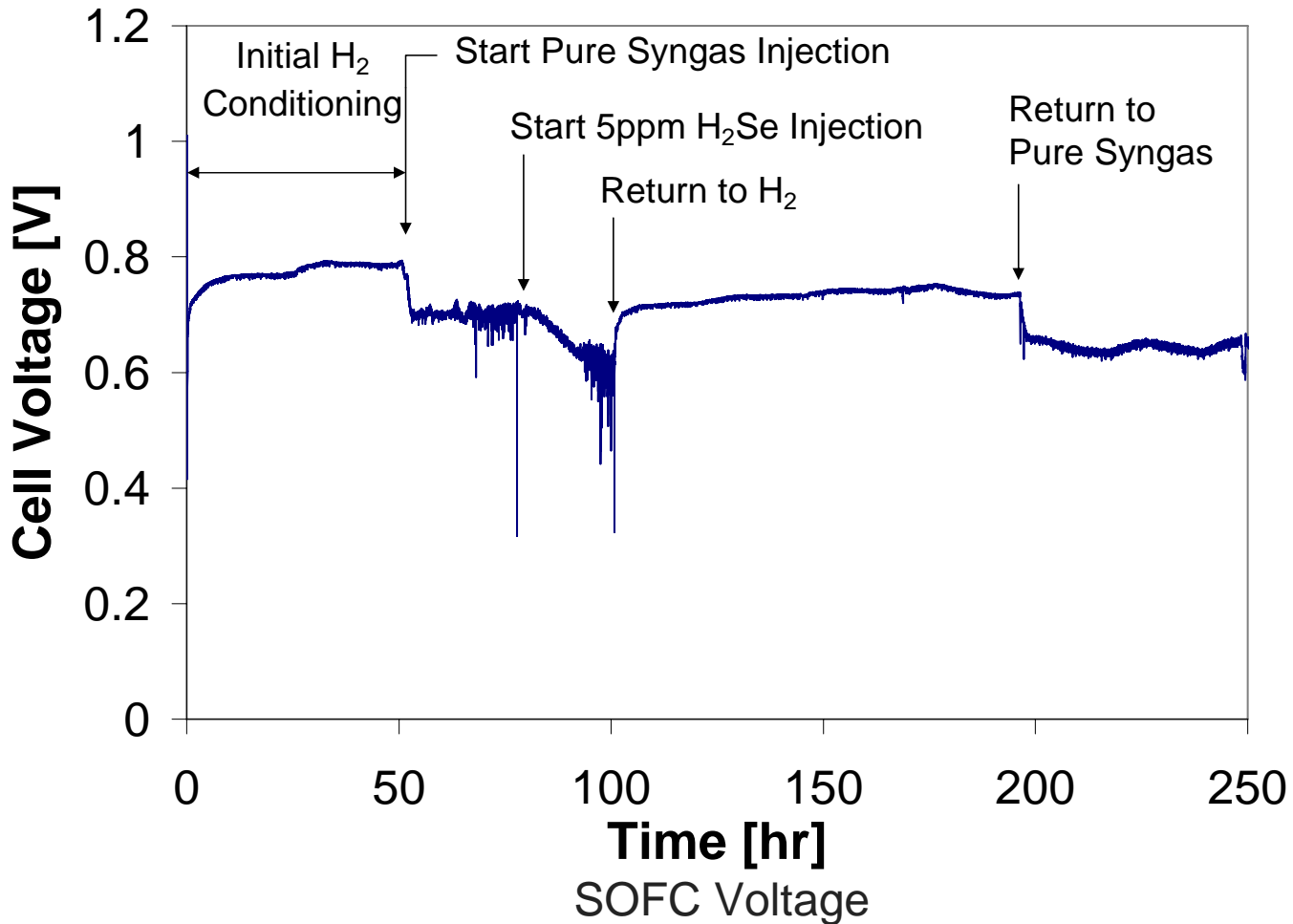
Permeation Tube



Ca—Pt Mesh/Paste;
An—Ni Mesh/Paste

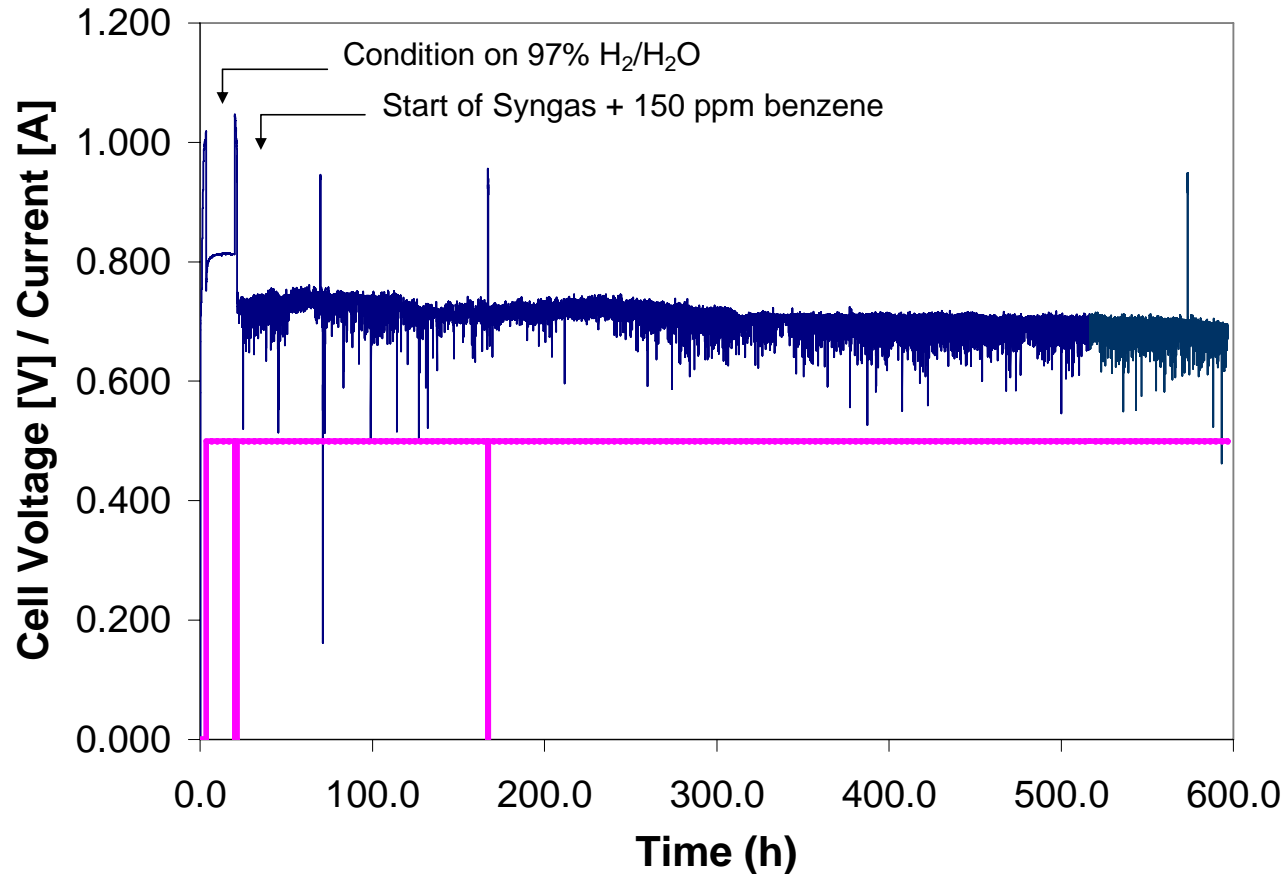


Results: H₂Se Testing



Operating at 800 °C at 0.25 Acm⁻² Over Time with 5 ppm H₂Se

“Light Tar” Test

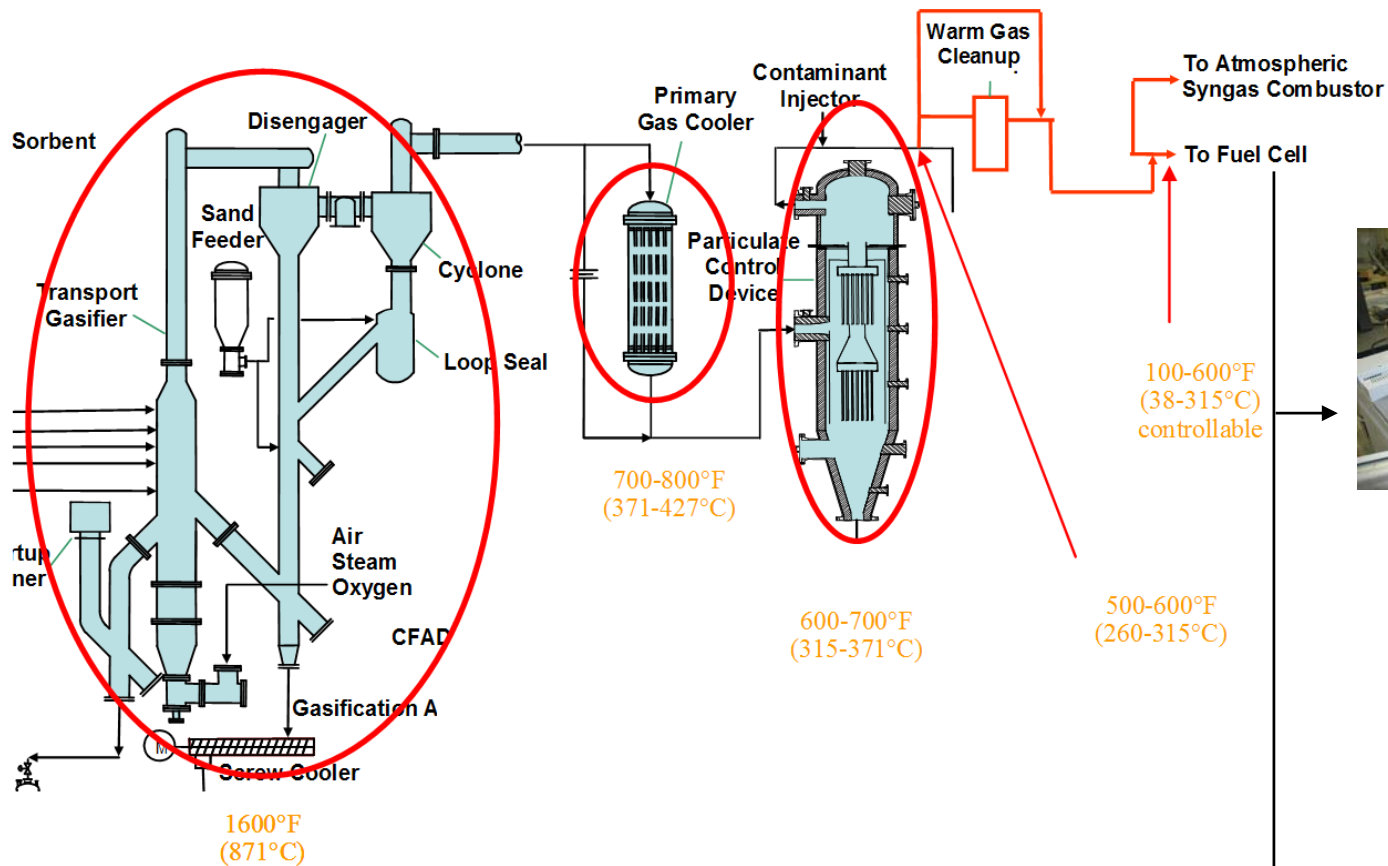


No visual carbon was observed on cell after test.
No significant carbon was measured via XPS.

SOFC Operation on Direct Syngas



PSDF Process Flow Diagram



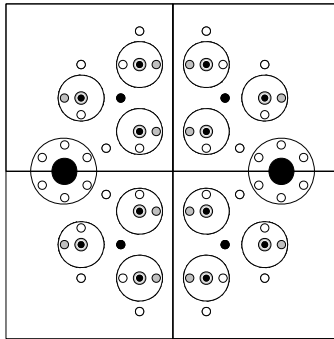
Gas Analysis



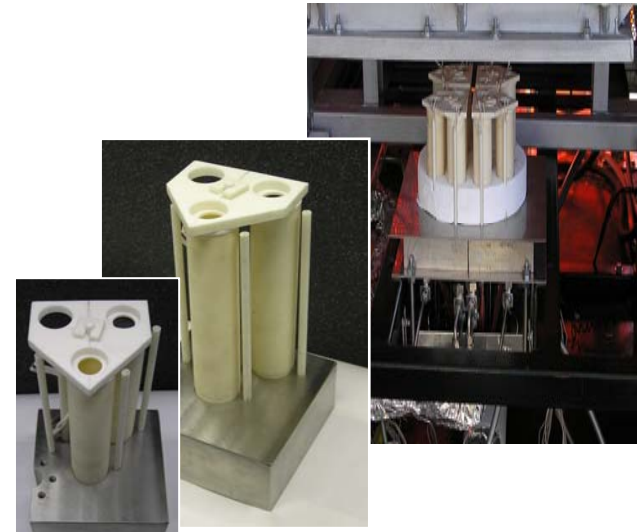
MCA Test Rig

Test Rig

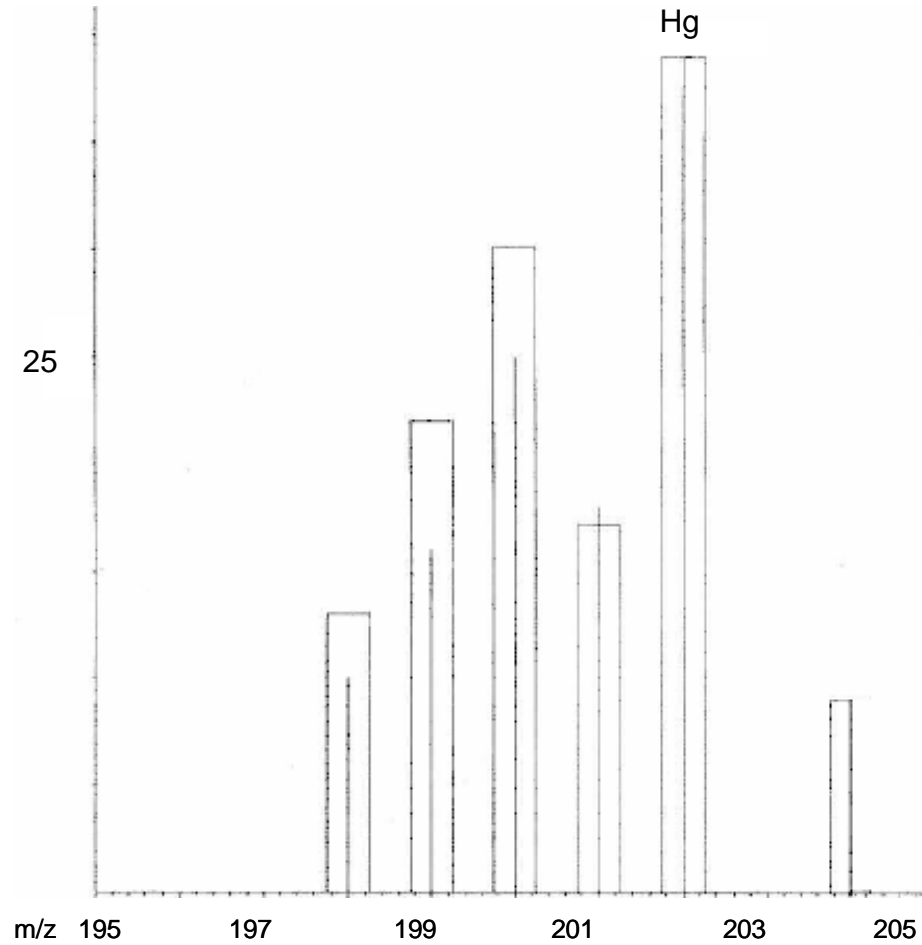
Multi-cell Array



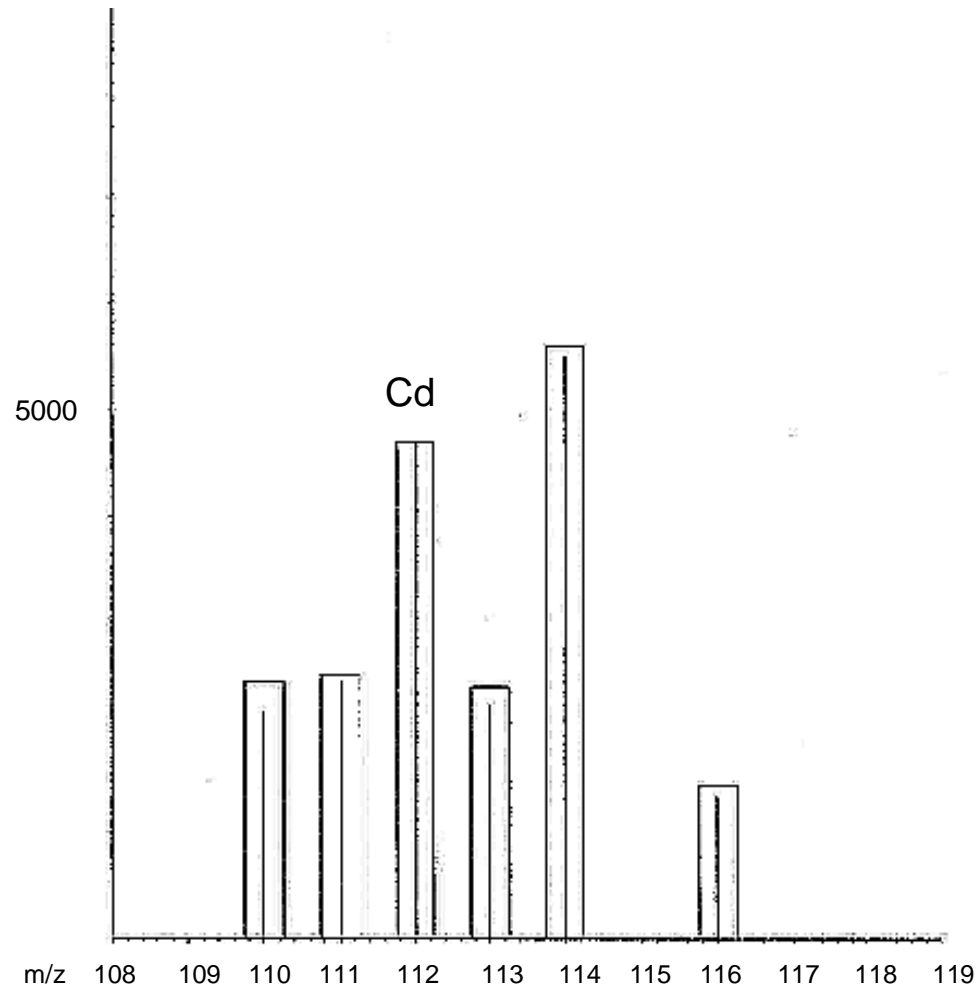
- **Permits parallel operation of 12 button cells**
- **Divided into 4 channels of 3 cells each**
- **Improves testing method**
 - Rapid collection of repeat data
 - Reduces systematic experimental error
- **Reduces sources of contamination**
 - Seals
 - Materials
- **Status**
 - Field test started on Mississippi lignite coal.



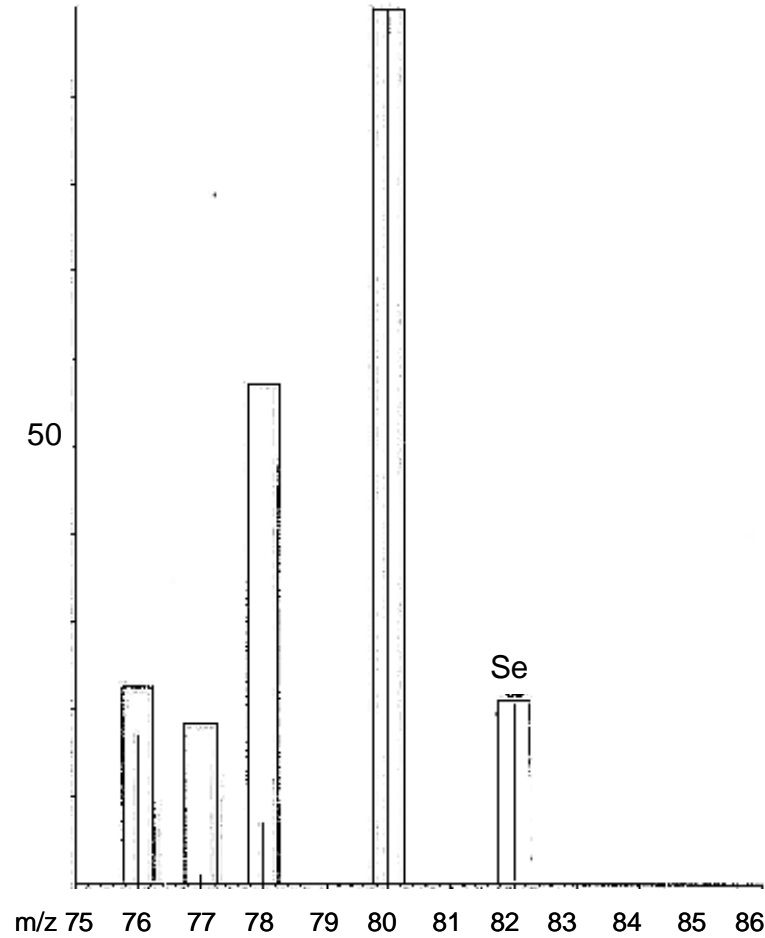
Gas Analysis—Mercury



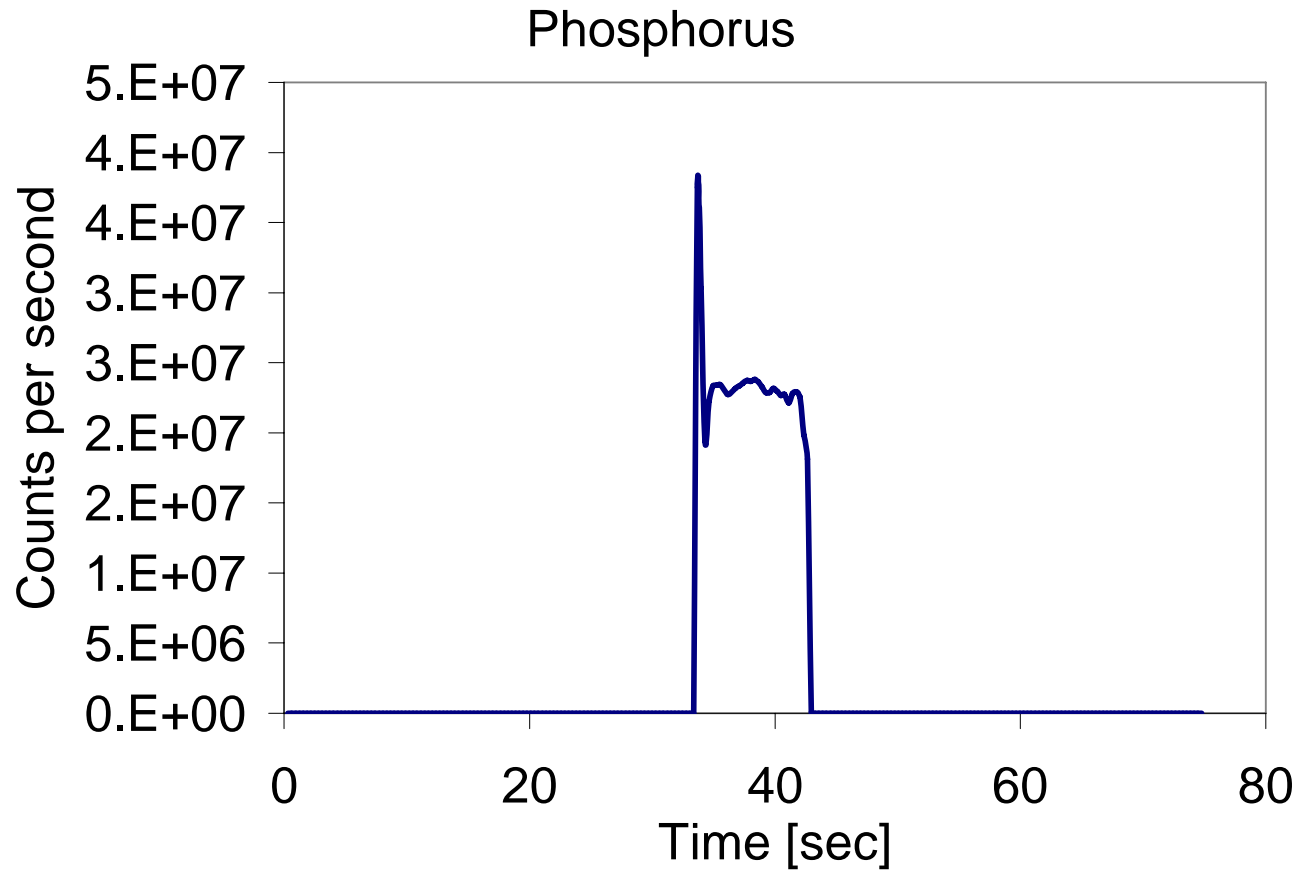
Gas Analysis—Cadmium



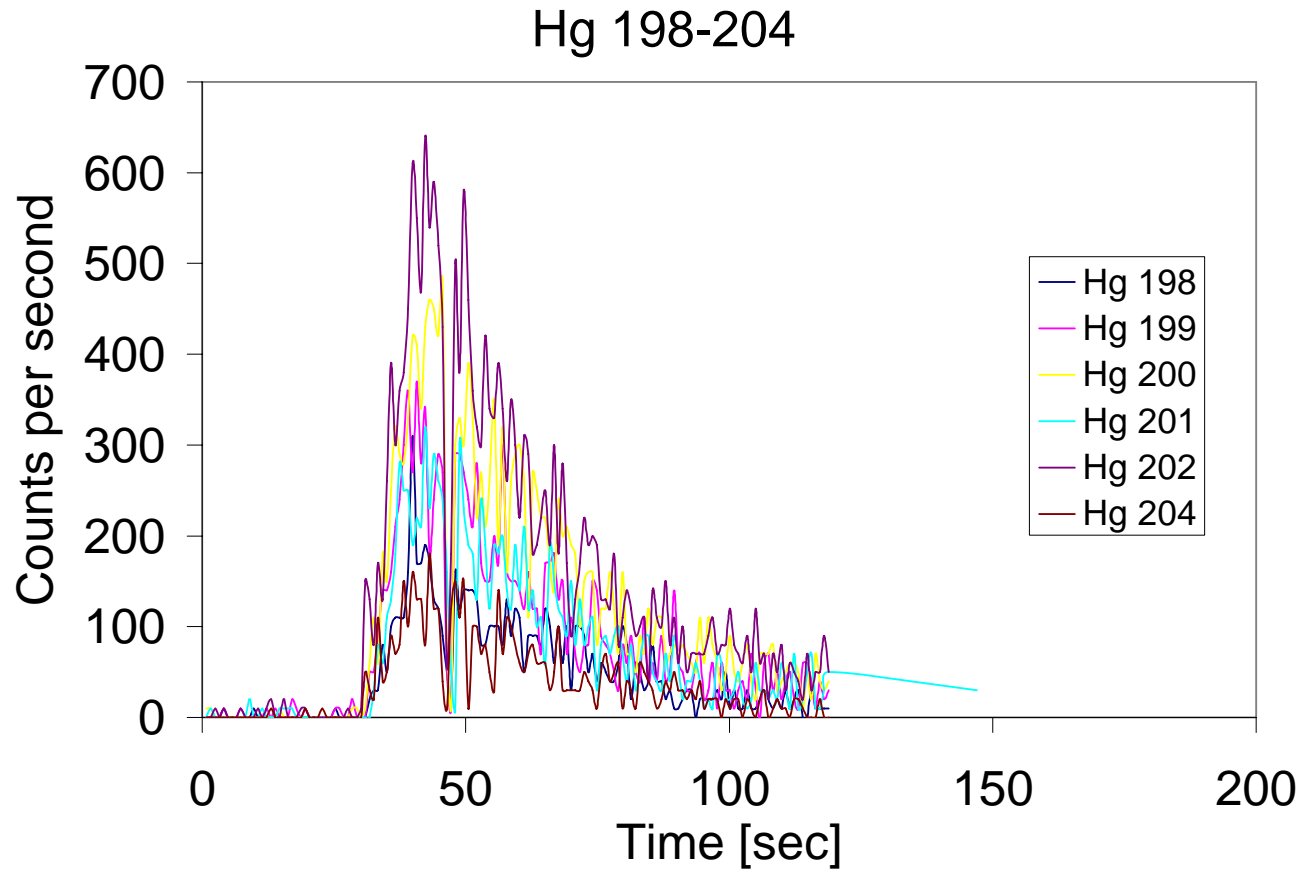
Gas Analysis—Selenium



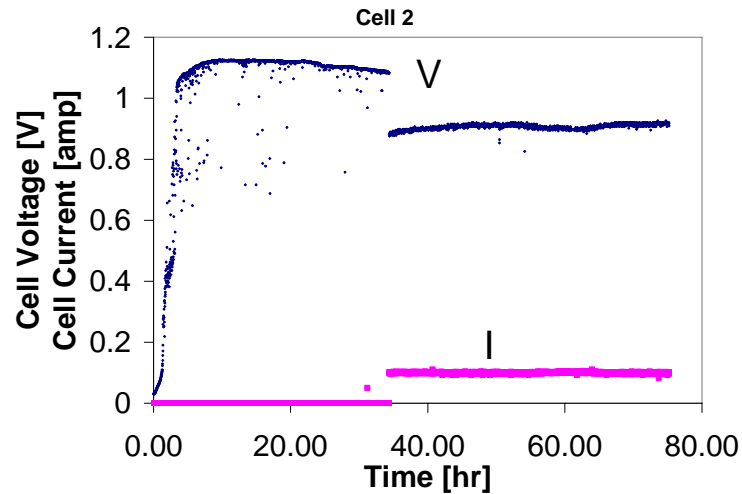
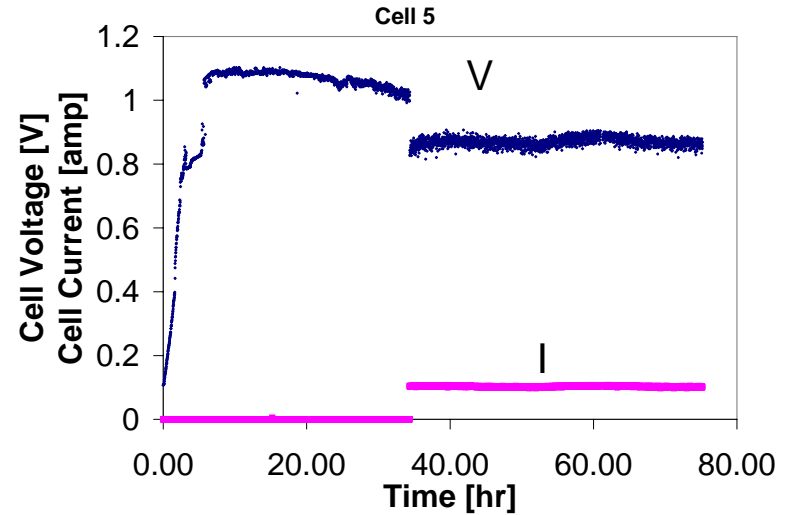
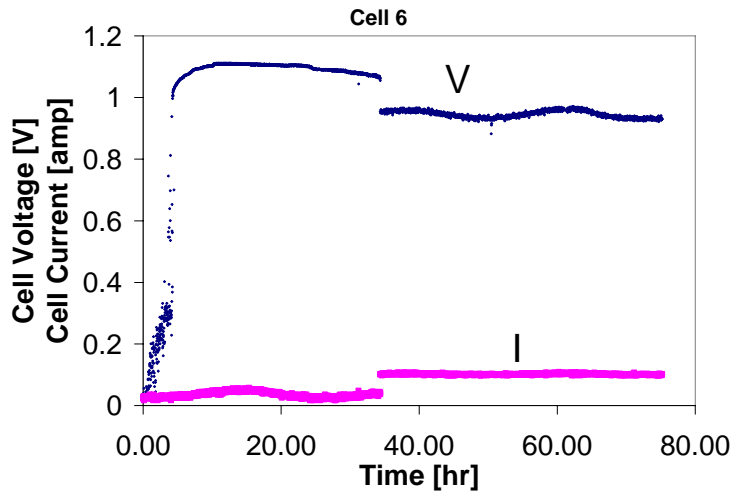
Gas Analysis—Phosphorus



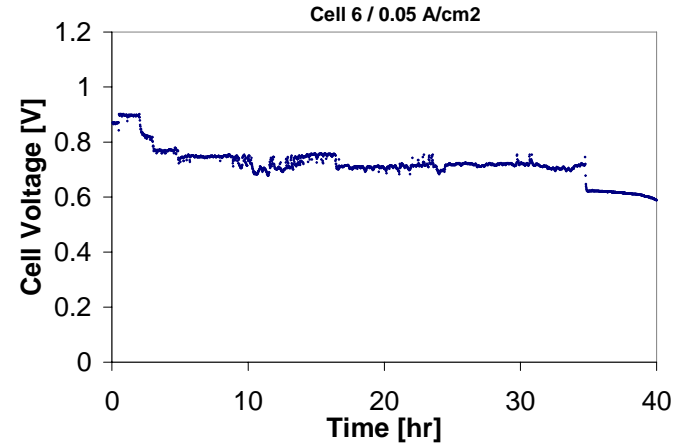
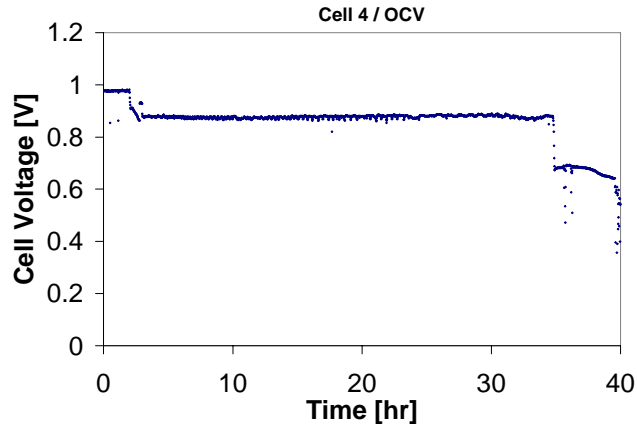
Gas Analysis—Mercury



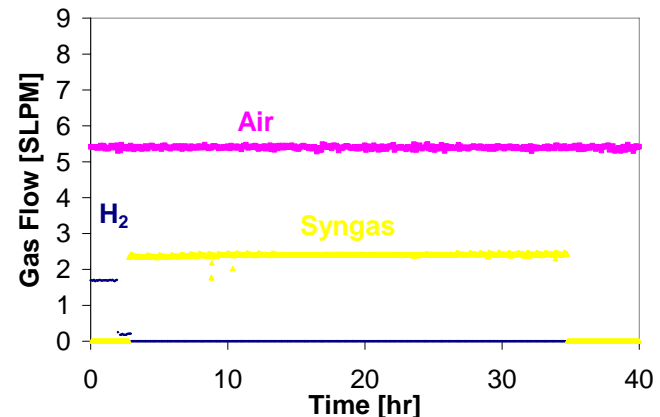
Cell Conditioning on Hydrogen (92% H₂/H₂O)



Syngas Started



- Planned end date for syngas run is mid August.
- Post test analysis--Cells will be examined using a variety of micro analytical techniques to assess possible trace material effects.



Trace Coal Species Summary

Programmatic driver:

*Quantification of cleanup target levels for trace materials
in coal syngas delivered to SOFC*

- Some variability of trace metals due to coal types—this will need to be accounted for in cleanup design.
- Tars may be present for low temperature gasifiers, but no negative impact has been shown yet—suggest further studies on higher MW compounds.
- Continuing individual coal trace species studies to determine impact on fuel cell performance
- Awaiting completion of SOFC operation on direct syngas to assess actual effect of operating on coal syngas
- Our work and work of other labs will be brought together in the future to give clear cleanup target levels

