Trace Elements in Coal – A Magical Journey Across the Periodic Table

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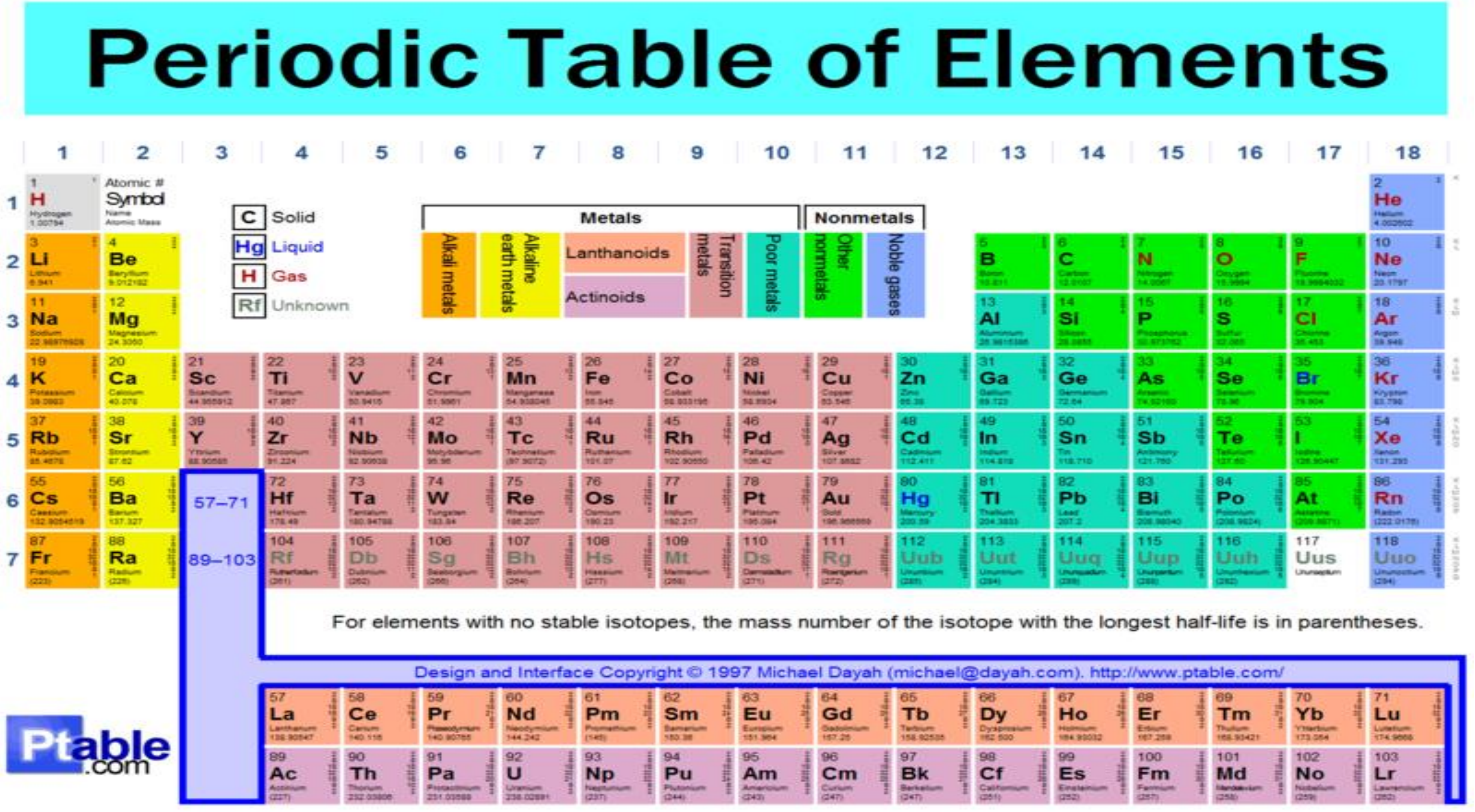
Why is this Important?

Natural Gas, Petroleum and Coal =

Health, Wealth & Prosperity of Humanity (Granite Equation)

- **Heating**
- **Cooking**
- **Electricity**
- **Transportation Fuels**
- **Chemicals**
- **Plastics and Materials**
- **Clothing, Shelter, Vehicles**
- **Everything We Need to Survive/*Thrive*!**

The Trace/Minor Elements – Hg, As, Se, P, Cd, REE, Sc, Y



Periodic Table of Elements

Atomic #
Symbol
Name
Atomic Mass

C Solid
Hg Liquid
H Gas
Rf Unknown

Metals: Alkali metals, Alkaline earth metals, Lanthanoids, Actinoids, Transition metals, Poor metals

Nonmetals: Other nonmetals, Noble gases

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57–71	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89–103	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Uub	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo

For elements with no stable isotopes, the mass number of the isotope with the longest half-life is in parentheses.

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57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Ptable.com

Brief History Trace/Minor Elements at NETL

- **Papers in Science, Mercury from Coal (1971-1972)**
- **Measurements of Mercury in Flue Gas (1972-1975)**
- **SO_x, NO_x (1970 – 2005)**
- **DOE Mercury Program (1992-2008), HAPs**
- **DOE Gasification Program (Hg, As, Se, P, Cd, S, N, Cl)**
- **Lanthanides, Y, Sc in Coals and Ash (2013) - Tim Skone**
- **“Fossil Fuels as a Source of Mercury Pollution”, Oiva Joensuu, Science, vol. 172, no. 3987, pp. 1027-1028, June 4, 1971.**
- **“Mercury Emissions from Coal Combustion, Charles Billings and Wayne Matson, Science, vol.176, no. 4040, pp.1232-1233, June 16, 1972.**
- **“Fate of Trace Mercury During Combustion of Coal”, Rod Diehl, E.A. Hattman, Hy Schultz, R. Haren, Bureau Mines Tech Prog. Report, 54, May 1972.**
- **“The Fate of Some Trace Elements During Coal Pretreatment and Combustion”, Hy Schultz et al, Advances in Chemistry Series, No. 141, Chapter 11, pp. 139-153, ACS Publisher, 1975.**
- **“DOE’s Mercury Control Technology Research, Development, and Demonstration Program”, Tom Feeley, Andy Jones, Jim Murphy, Ron Munson, Jared Ciferno, Chapter 10 in “Mercury Control for Coal-Derived Gas Streams”, Evan Granite, Henry Pennline, Connie Senior, editors, Wiley VCH, pp. 165-190, January 2015.**

From Concept (1992) to Commercial Reality (2008)

Transitioning Hg Control Technology

FULL-SCALE DEMOS

- *Field testing of Hg sorbents (e.g., ACI) and oxidation systems on operating power plants*

PROCESS & ENGINEERING DEVELOPMENT

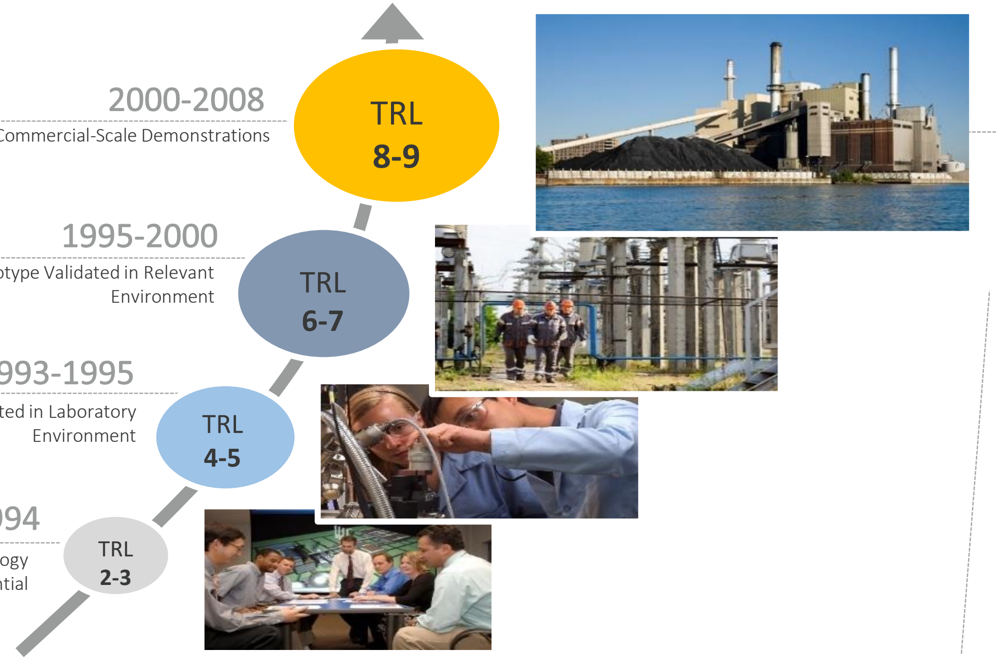
- *Pilot-scale & additive testing*
- *Hg measurements and methods development & testing*

APPLIED RESEARCH

- *Sorbent & Hg oxidation system development*
- *Hg emissions characterization*

BASIC RESEARCH

- *Flue gas characterization*
- *Hg speciation*



COMMERCIAL DEPLOYMENT

- *~150 GW ACI commercially installed*

2000-2008
First-of-a-kind Commercial-Scale Demonstrations

TRL
8-9

1995-2000
Pre-Commercial Prototype Validated in Relevant Environment

TRL
6-7

1993-1995
Component/Subsystem Validated in Laboratory Environment

TRL
4-5

1992-1994
- Analytical Studies Predict Technology Potential

TRL
2-3

Keys to Success:

- GOGO Lab model allowed direct collaboration with EPA on Hg regulatory developments
- GOGO model protected IP and encouraged strong industry participation and cost sharing
- Inhouse R&D expertise strengthened extramural partnerships

Abundant US Coal

- 30% Electricity Generated by Burning Coal

- USA - 250 Year Supply of Coal

- Typically Burn ~ 1 Billion Tons Coal/Yr Make Electricity (1990-2014)
- 739 Million Tons for 2016

- Problem/Opportunity – Coal Can Be a Dirty Fuel
- Contains: S, N, Al, Si, Cl, Hg, As, Se, Cd,……

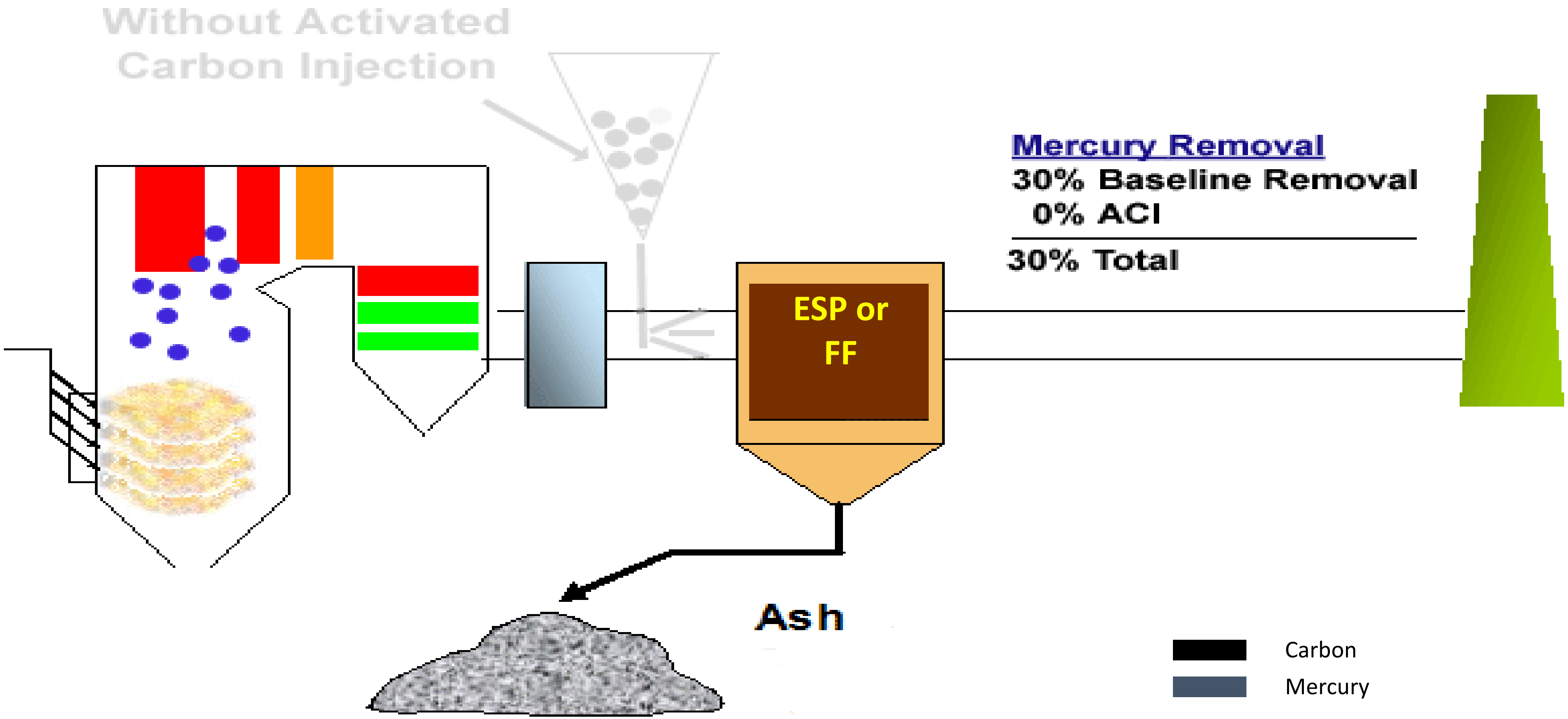
On-Going Research For Mercury Capture: Flue Gas

- Continuous Measurement of Mercury
- Sorbent-Flue Gas Contact
- Poison-Resistant Sorbents & Catalysts
- Scrubber Additives
- Novel Promoters
- Concrete-Friendly Activated Carbons
- Byproducts Research
- Sorbent Index Test
- Impacts on Utility Operation
- Capture in Other Industries and Countries

Unmet Needs For Mercury Capture: Fuel Gas

- **High Temperature Capture of Mercury**
- **Coal-Derived Syngas**
- **400^{o}F – 700^{o}F**
- **Preserve Thermal Efficiency IGCC System**

Activated Carbon Injection



Without Activated Carbon Injection

Mercury Removal

30% Baseline Removal
0% ACI

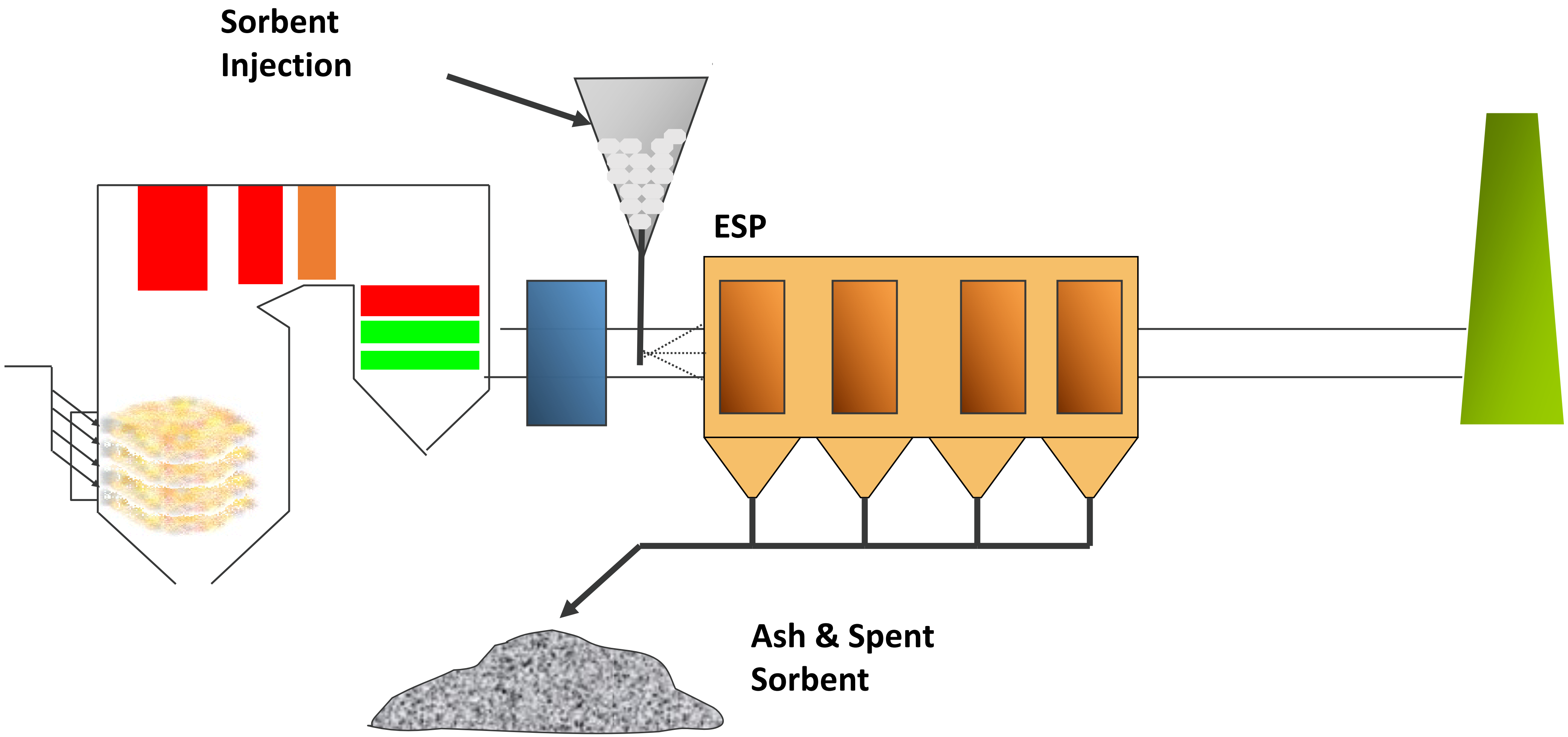
30% Total

■ Carbon

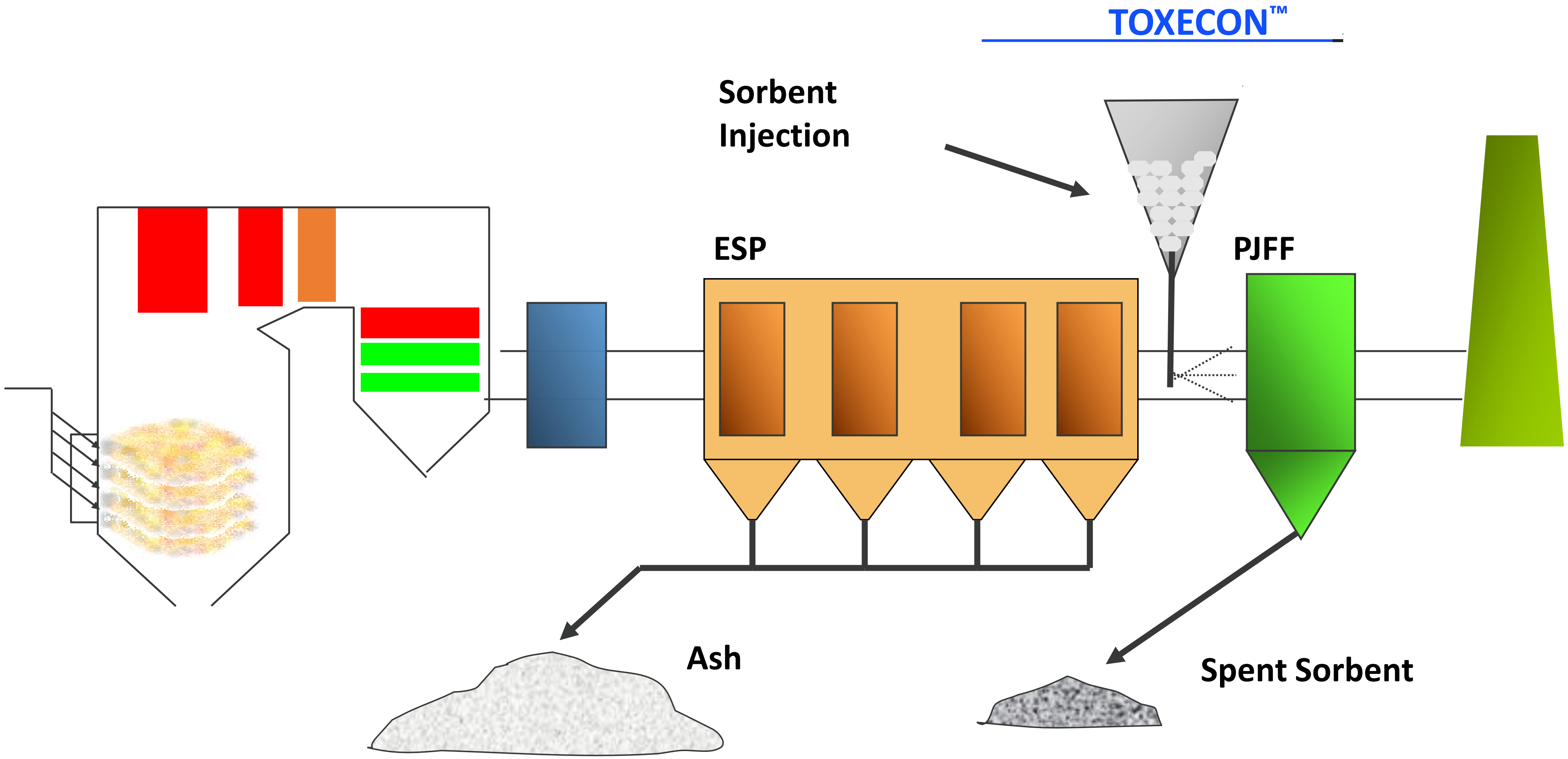
■ Mercury

This configuration applies to conventional (*i.e.,* untreated) and chemically-treated ACI

Sorbent Injection Configuration



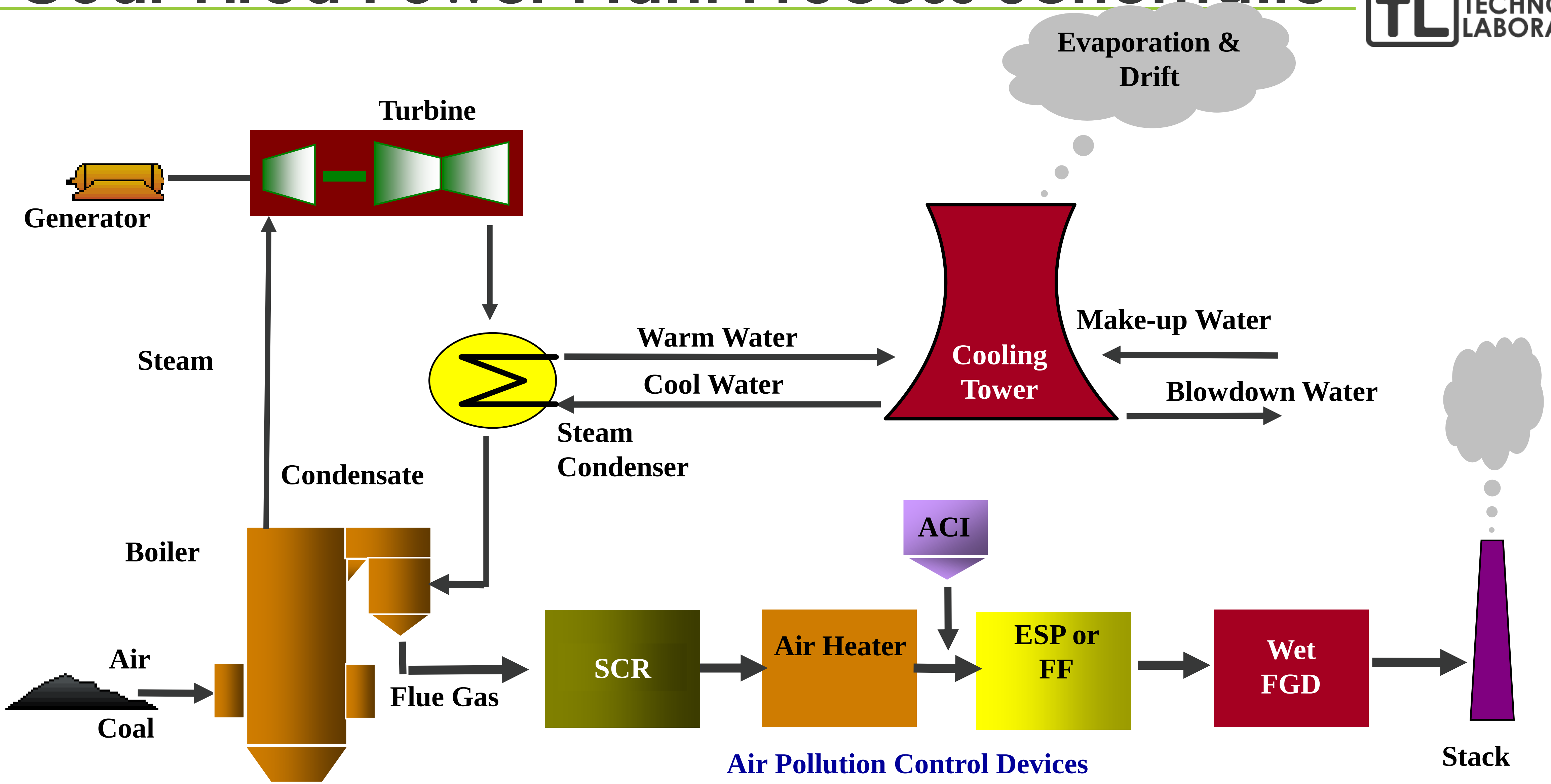
TOXECON™ Configuration



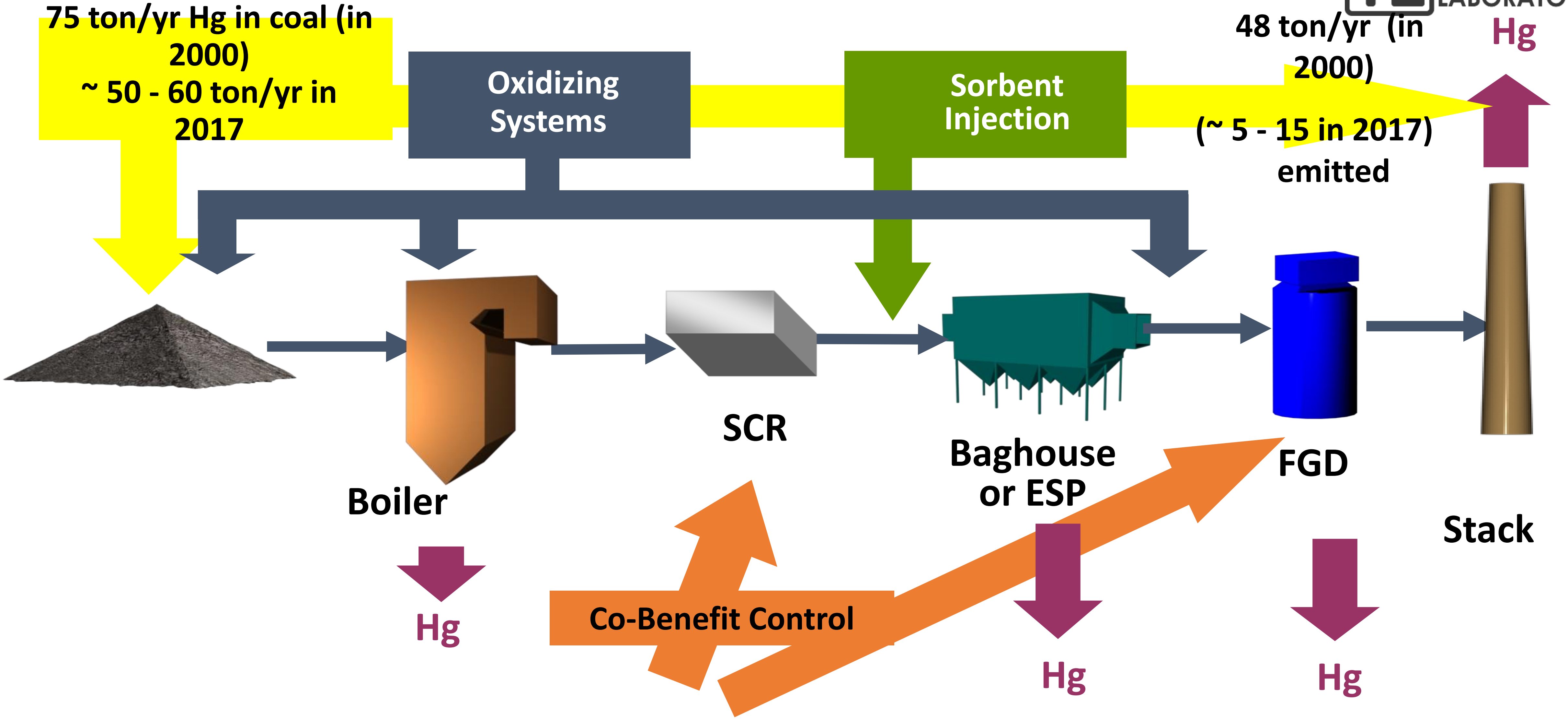
Alternatives to Activated Carbon

- Sorbents – Oxides, Sulfides, Thief
- Catalysts – Pd, SCR, Carbons
- Scrubbers – $HgCl_2$ Soluble
- Combustion Modification – Carbon in Fly Ash
- Flue Gas Cooling – Carbon in Fly Ash
- Additives: Flue Gas, Fuel, or Scrubber
- Barrier Discharges
- Flue Gas Irradiation – GP-254

Coal-Fired Power Plant Process Schematic



Mercury Control Technology Options



75 ton/yr Hg in coal (in 2000)
~ 50 - 60 ton/yr in 2017

Oxidizing Systems

Sorbent Injection

48 ton/yr (in 2000)

(~ 5 - 15 in 2017)

emitted

Hg

Boiler

SCR

Baghouse or ESP

FGD

Stack

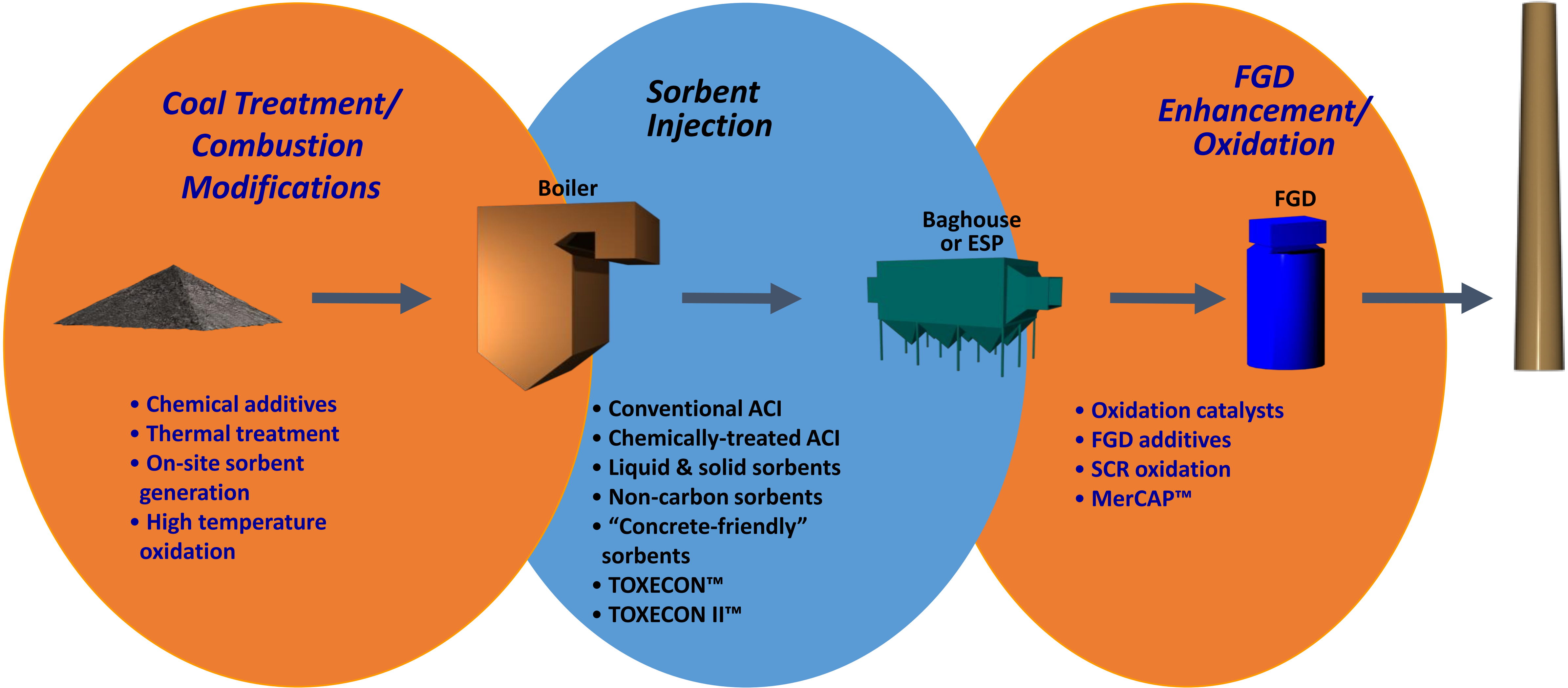
Hg

Co-Benefit Control

Hg

Hg

DOE/NETL Funded Approaches for Controlling Mercury



Coal Treatment/ Combustion Modifications

- Chemical additives
- Thermal treatment
- On-site sorbent generation
- High temperature oxidation

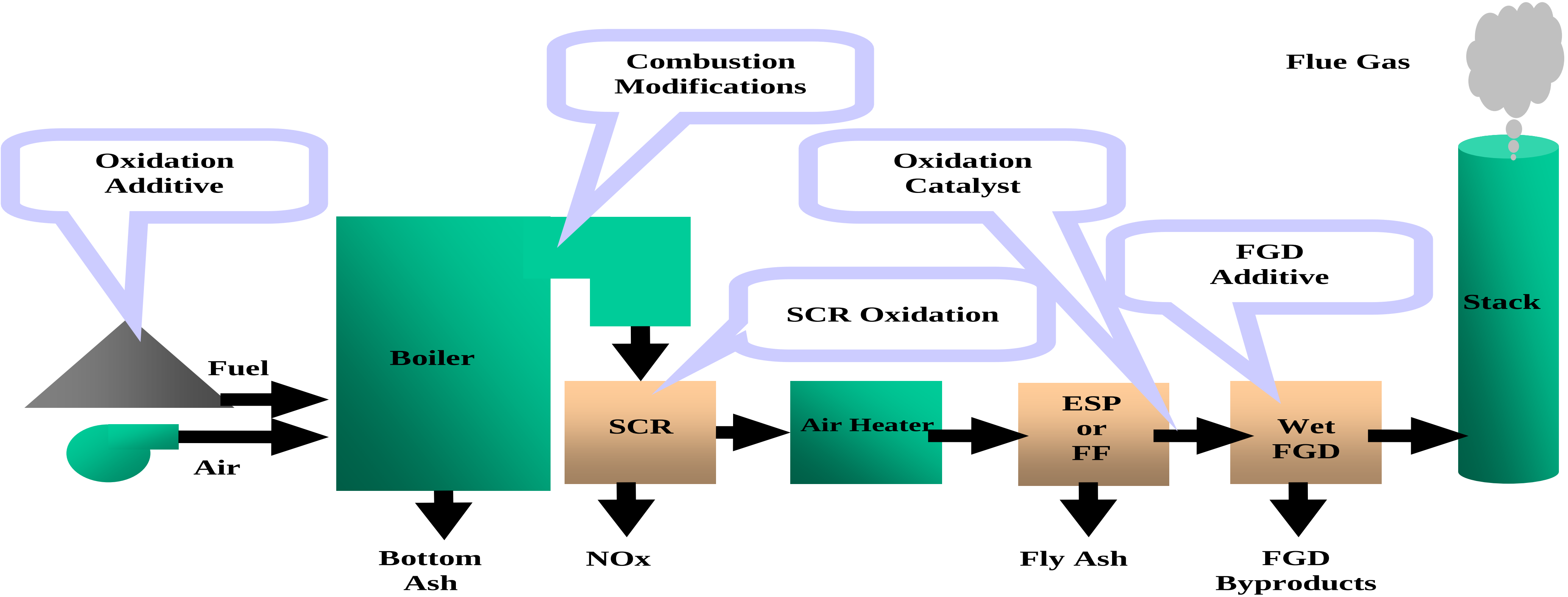
Sorbent Injection

- Conventional ACI
- Chemically-treated ACI
- Liquid & solid sorbents
- Non-carbon sorbents
- “Concrete-friendly” sorbents
- TOXECON™
- TOXECON II™

FGD Enhancement/ Oxidation

- Oxidation catalysts
- FGD additives
- SCR oxidation
- MerCAP™

Enhancing Mercury Removal with FGD



- ***Oxidized mercury is removed across FGD systems***
- ***Evaluate technologies that facilitate mercury oxidation***
- ***Ensure that captured mercury is not re-emitted from FGD***

What is Coal-Derived Flue Gas?

Composition Untreated Flue Gas

CO_2	13 – 16%
O_2	3 – 4%
H_2O	5 - 7%
N_2	balance – approximately 73%
HCl	10 – 100 ppm
SO_2	100 – 2000 ppm
SO_3	1 – 40 ppm
NO_x	100 – 500 ppm
CO	20 ppm
HC	10 ppm
Hg	1 ppb
Fly ash	entrained particulates

What is Fuel Gas?

- Carbon-Steam Reaction
- Pyrolysis
- Combustion
- Elevated Pressure

Major Products

- CO, H_2, CO_2, H_2O, Tars & HCs

Minor Products

- NH_3 , HCl, Cl_2 and particulates
- H_2S, COS, CS_2
- Trace Contaminants: Hg, AsH_3, H_2Se, and PH_3

Introduction

In-House Research at NETL on Mercury

- Trace Metal Control and Measurement
- Mercury, Arsenic, Selenium & Phosphorus
- Carbon Dioxide Capture from Flue Gas
- Seven Technologies Developed
- Eight Patents/Patents-Pending
- Three Commercial Licenses
- One CRADA
- Encourage Collaboration on Many Topics

Mercury and Air Toxics Standards (MATS)

- EPA Announcement: March 16, 2011
- EPA National Rule: 12/21/11, 2/16/12
- 91% Removal Required – Existing Plants
- Higher Removal Levels – New Plants
- 4/16/15 Deadline for Compliance
- 5/15 Supreme Court Review
- 4/16 – Final Rule

Mercury and Air Toxics Standards (MATS)

Supreme Court Review

- 5/15 – EPA Must Consider Cost for Compliance
- 4/16 - EPA confirmed that it is appropriate and necessary to regulate air toxics, including mercury, from power plants after including a consideration of costs.
- EPA determined the annual cost of MATS is a small fraction of overall sales in the power sector.
- https://www.epa.gov/mats/regulatory-actions-final-mercury-and-air-toxics-standards-mats-power-plants

Past Fossil Energy Program Goals

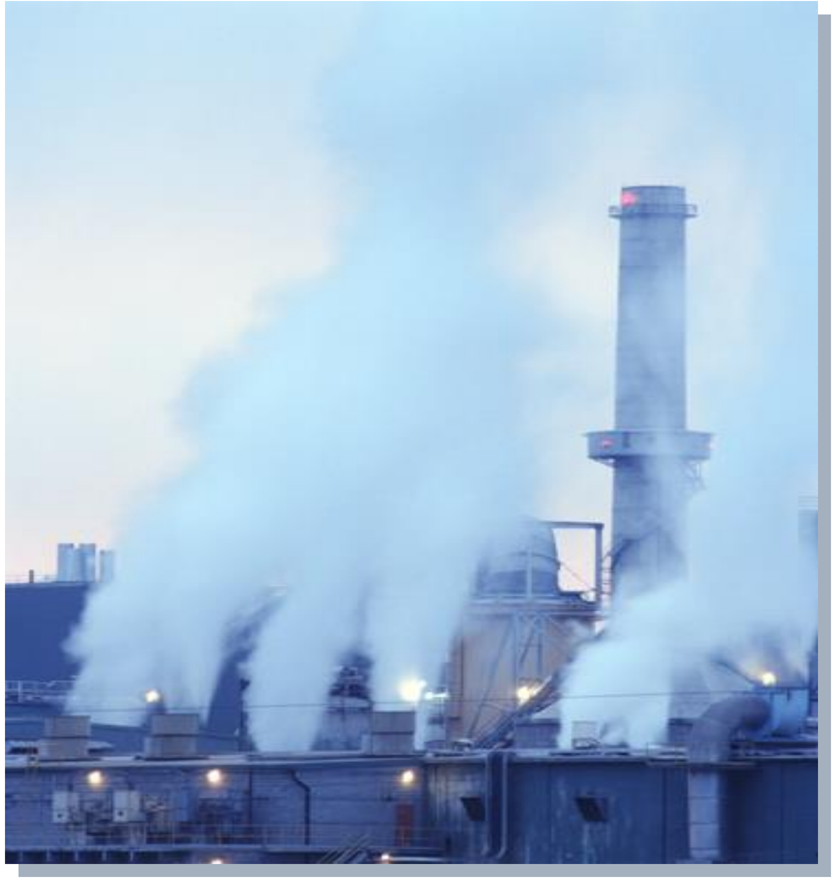
Develop more effective mercury control options

- **Cost-effective and high level of mercury removal**
- Meet long-term IEP program goal of 90% mercury reduction at cost reduction of 25 - 50%
- Must be better than ACI

Technical Challenges

Mercury is Difficult to Capture

- Low concentration
- Can exist as Hg^0
- Harsh conditions of coal-derived flue gas
- Competitive adsorption / poisoning
- Low sorbent reactivity
- Hg is semi-noble metal



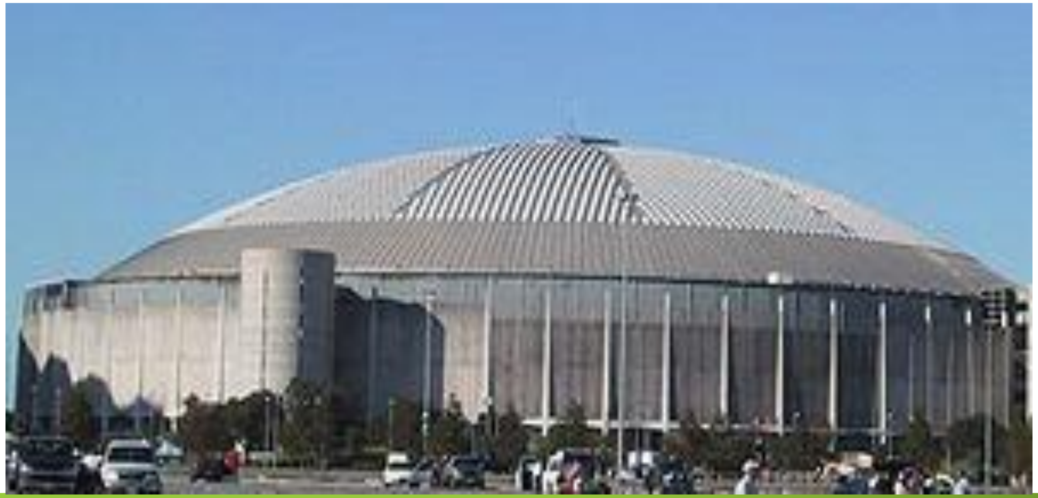
ACI for Mercury Removal

- Benchmark technology but has drawbacks for flue gas application
- General adsorbent
- Limited temperature range
- Sequestration
- High sorbent to Hg ratio (3,000:1 to 100,000:1)
- Contacting methods
- Expensive: $1,500 - 5,000/ton
- 500 MW_e power plant: $1-10 MM/yr
- Potential US market of $1-10 billion/year

Mercury Capture Challenge

The Infinitesimally Small Concentrations in Flue Gas

- Imagine the Houston Astrodome
- Holding 30 Billion Ping Pong Balls Representing Flue Gas (1 ppb Hg)
- Remove 27 - 30 of the 30 Different Colored Mercury Ping Pong Balls
- Can We Do This?
- Yes



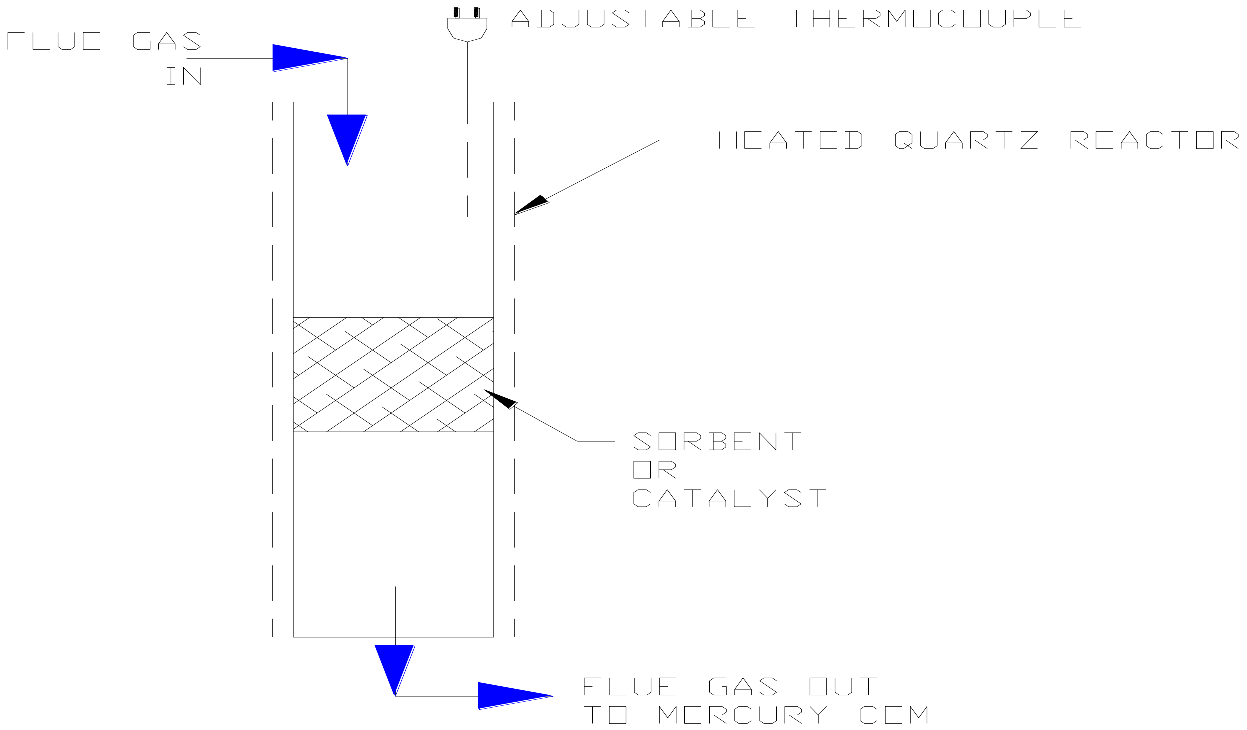
NETL R&IC In-House Technologies

- Thief Process – Carbon Extracted from Furnace
- GP-254 Process – Application of UV
- PG Sorbents – High Temperature Sorbents for Hg, As, Se and P
- Catalysts – For Oxidation of Mercury
- Mercury Detection – sub ppb Levels Flue Gas
- Electrochemical Separation of CO_2 and O_2

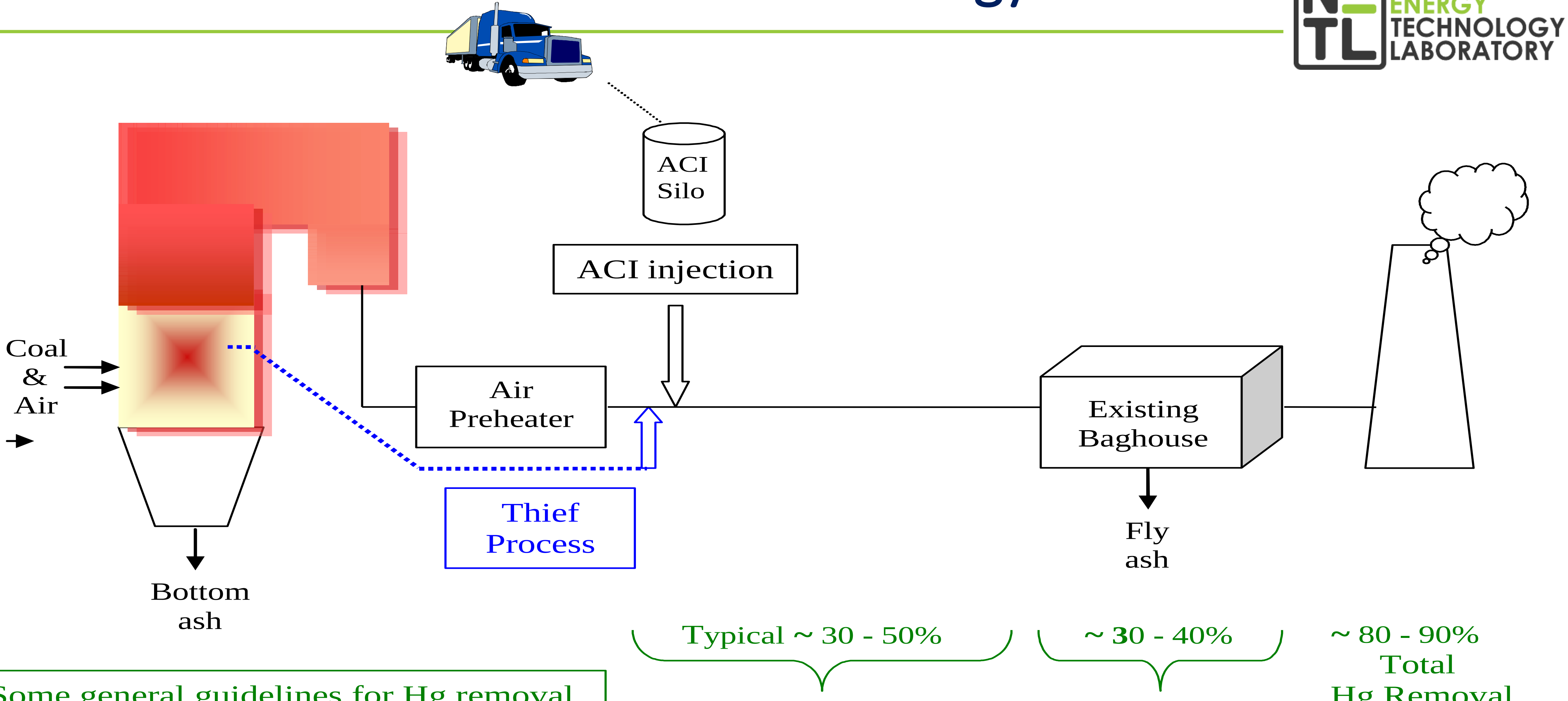
1. Thief Process

- Alternative to activated carbon injection (ACI)
- Extraction of partially combusted coal from furnace & re-injection downstream of preheater
- Recent results show similar removals to ACI
- Recent Large-Pilot Tests
- FLC Tech Transfer Award May 2009
- R&D 100 Award November 2009
- Previously Licensed to Mobotech and Nalco

NETL BENCH-SCALE PACKED BED REACTOR



Thief Process and ACI Technology



ACI Silo

ACI injection

Coal & Air

Air Preheater

Thief Process

Existing Baghouse

Bottom ash

Fly ash

Typical ~ 30 - 50%

In-Duct Hg Removal

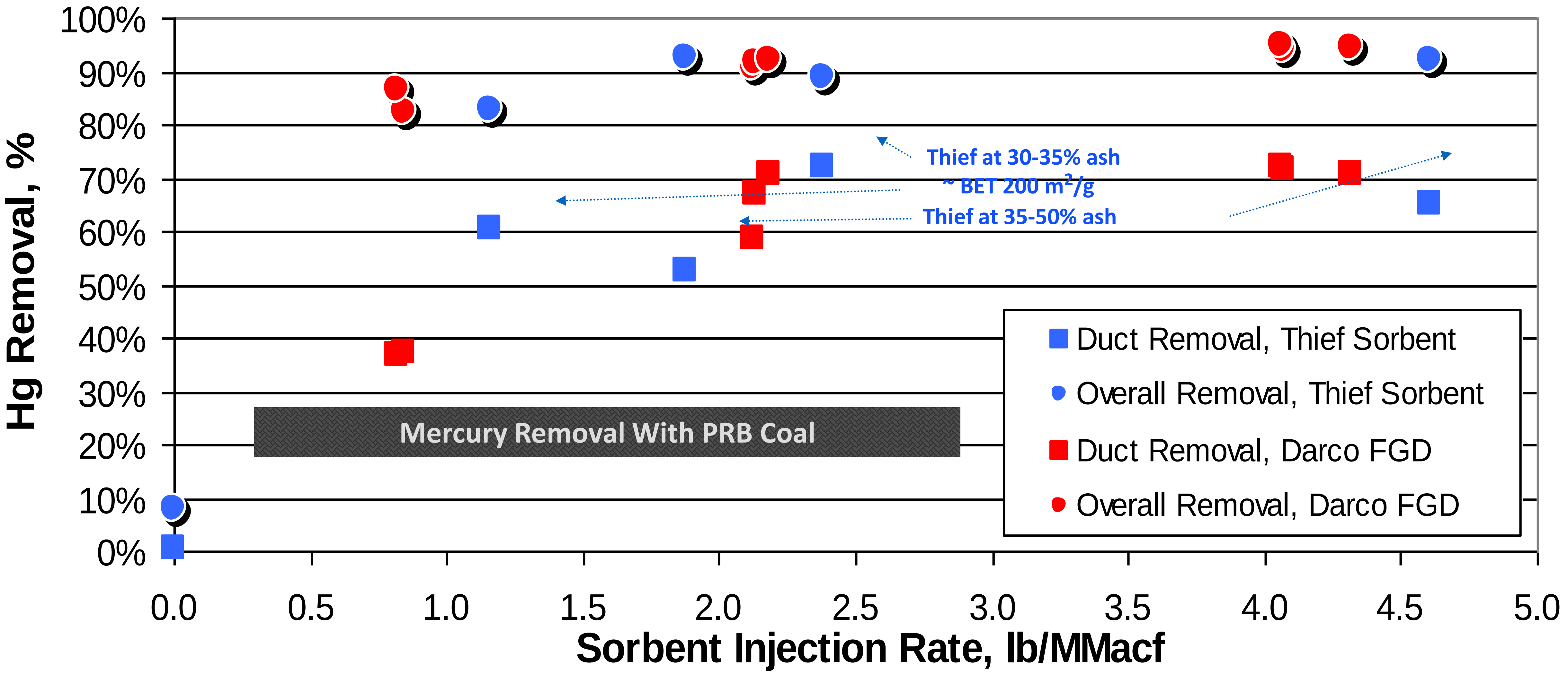
~ 30 - 40%

Hg Removal Across BH

~ 80 - 90% Total Hg Removal Goal

Some general guidelines for Hg removal performance for lower levels of sorbent injection at ~ 2 - 4 lb/MMacf

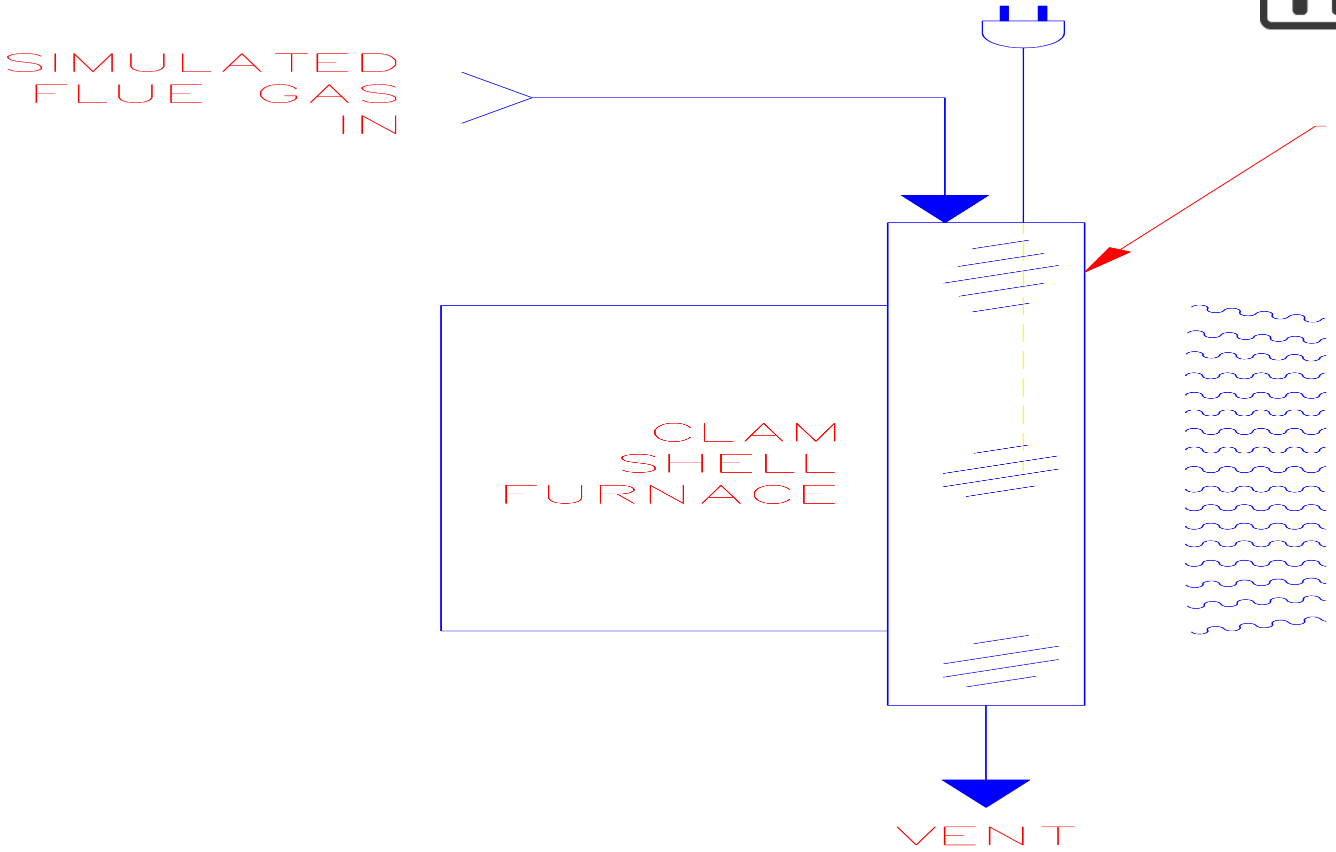
Mercury Removal Results - Darco FGD versus Thief Sorbent



2. GP-254 Process

- Alternative to ACI Developed
- Oxidation of Mercury
- Irradiation of Flue Gas with 254-nm Light
- 99% Oxidation Achieved at Lab-Scale
- 91% Oxidation Attained at Bench-Scale
- FLC Tech Transfer Award 2005
- Tests: DOE, Powerspan, Canmet, University of Florida
- Low Parasitic Power (less than 0.35%)
- Potential Pilot Tests

Lab-Scale Photoreactor



Photochemical Oxidations

- First described in 1926 by Dickinson & Sherrill (O_2)
- Gunning discovered others in 1950s (HCl, H_2O, CO_2)

<u>**Relevant Overall Reactions**</u>

$Hg + 2\ O_2 + 253.7\text{ nm light} \rightarrow HgO + O_3$

$Hg + HCl + 253.7\text{ nm light} \rightarrow HgCl + 1/2\ H_2$

$Hg + H_2O + 253.7\text{ nm light} \rightarrow HgO + H_2$

$Hg + NO_2 + 253.7\text{ nm light} \rightarrow HgO + NO$

$Hg + CO_2 + 253.7\text{ nm light} \rightarrow HgO + CO$

$Hg + SO_3 + 253.7\text{ nm light} \rightarrow HgO + SO_2$

- Interferes with UV-based CEMs
- Removal method

Previously Licensed - Powerspan

- Flue Gas Clean-up
- Coal-Burning Power Plants – Polishing Step, High SO_3
- Ensure Near 100% Removal of Mercury

Incinerators

- Municipal
- Medical
- Weapons
- Sewage Sludge

Other Industries

- Metal Refining
- Concrete Industry
- Chloralkali

3. PG Sorbents for Mercury Capture

Palladium-Based Sorbents

- High Temperature Removal of Hg, As, Se, P, Cd
- Application to IGCC Systems
- Preserve High Thermal Efficiency

Technology Transfer

- Patent Issued April 2006
- CRADA with Johnson Matthey September 2005
- License with Johnson Matthey March 2007
- R&D 100 Award October 2008

Past DOE Program Goals

- **Develop Advanced Techniques For Near-Zero Emissions**
- **Create Novel Concepts to Meet Rigid Syngas Quality Specifications**
- **Advance Gas Cleanup Technologies to Support Vision 21 Goals**
- **< 1 lb Hg/trillion BTU   (90% removal)**

Source: NETL Gasification Technologies Web Site

Technical Benefits of High Temperature Mercury Removal

- **Maintain Thermal Efficiency of IGCC**
- **Remove Inlet Coal Mercury in Single Step**
- **Less Volumetric Processing of Gas Versus Flue Gas**

  Current Pilot Testing – session on Thursday
- **100% Removal of Hg, As and Se in Eleven Pilot Tests at 500°F; Each over Several Weeks; Regenerable**

4. Catalysts for Oxidation of Mercury

Simple Strategy

- $HgCl_2$ Water Soluble; Hg Insoluble
- Enhance Capture in Scrubbers
- Improve Capture in Particulate Control Device
- ESP or Baghouse
- Inexpensive Carbons – Disposable Catalyst
- Regenerable Metal Catalysts
- Patents Issued August 2010, December 2011

Catalytic Oxidation of Mercury

- Chlorine Present in Coal
- HCl and Cl_2 in Flue Gas
- Can Adsorb on Metals and Carbons
- React with Hg
- Eley-Rideal, Langmuir-Hinshelwood, or Mars-Maessen Mechanisms
- Form Water-Soluble $HgCl_2$
- Removed in Wet Scrubber

5. CEM for Mercury in Coal-Derived Gases

- **Determination of Mercury in Flue or Fuel Gases (ppb levels)**
- **Measurement of Mercury in Air (ppt levels)**
- **Through Photo-deposition Using UV**
- **Spin-Off of GP-254 Process**
- **Patent Issued December 2011**

Conclusions

- Highly Successful DOE Program
- Power Plants Are Removing Mercury
- Activated Carbon Most Well-Developed

- Many Technologies for Mercury Control

- Reflect Numerous Coals & APCDs

Opportunities

Stringent Removal Requirements

New or Improved Capture Techniques

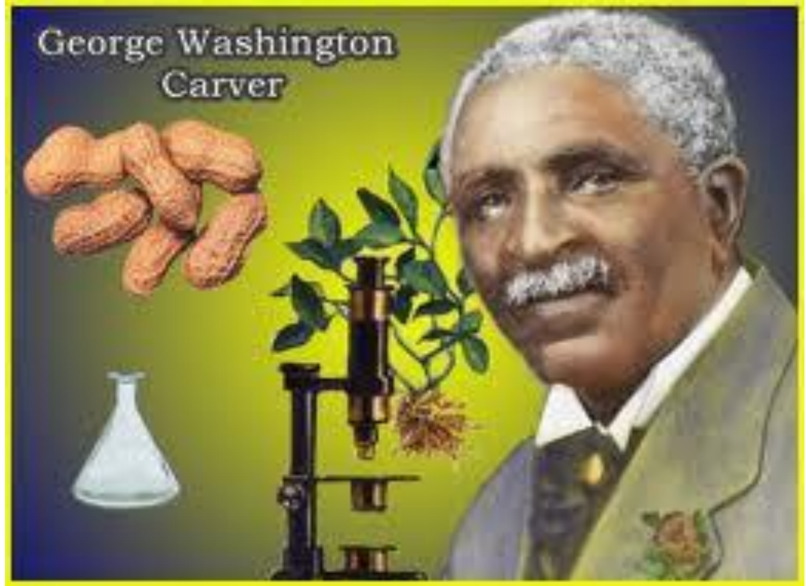
- Measurement of Mercury: CEM Development
- Sorbent/Catalyst –Flue Gas Contact
- Poison Tolerant Carbons
- Novel Promoters
- Concrete-Friendly Activated Carbons
- Scrubber Additives
- Sorbent Index Test
- Hg Capture: Other Industries (IGCC), Countries
- Carbon Dioxide Capture (and Clean-Up?)

Additional Opportunities

- **Rare Earth Recovery**

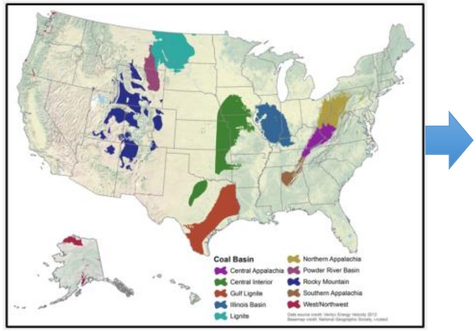
Coal – A Precious Domestic Resource

- Typically Mine One Billion Tons/Year (739 MM tons in 2016)
- 275 Year Supply
- 90% Burned in United States to Make Electricity (Power, Mining, Rail)
- Rest – Steel, Activated Carbon, Chemicals
- We Can Do So Much More With Coal & By-Products
- Inspiration



Integrated Field Sampling, Characterization, Separations, & Modeling

U.S. Coal Basins



1. Coal Production Samples
2. Coal Processing Samples
3. Coal Utilization Samples

Screen Field Samples

Portable XRF
Sensitized Fluorescence – sensor development
Portable LIBS
Well Logs
Gamma Detection
Magnetic Detection
Database Interpretation (USGS CoalQual), EDX
Literature Review
Geochemistry interpretation

Collect Field Samples
>300ppm REE+Y

Collectors and Agreements
LTI, DOE, NETL, EPRI, USGS, and Individual Coal Industry Companies

Characterization

Elemental Concentrations
ICP-MS, ICP-OES, CHNS, TGA

Mineralogy and Mineral Size
SEM/EDS, XRD, Advanced Microscopy, etc

REE Associations (Minerals and Elements)
Sequential Extraction
Laser Ablation ICP-MS
SEM/EDS, XRD, Advanced Microscopy
ICP-MS, ICP-OES, CHNS, TGA

Techno Economic Analysis (TEA)

Separations: Chemical/Thermal

2Wt% REE+Y Solid

Sorbents

Polymer fibers/sorbents
Amines on organic and inorganic supports

Clays intercalated with organics
Ionic Exchange Resins

Inorganic Clays

Thermal Energy
Melt, Precipitation, Roasting

Photophoretic Separation

REE+Y Solution (Chemical Separations or Field Samples)

Sequential Extraction

Ion Exchangeability Tests (Ammonium Sulfate/Chloride)

Novel Solvents (Deep Eutectic and Ionic Liquids, etc)

Alkaline/Acid Leaching, Reactive Ball Milling, Microwave, Ultrasound

Solid Product REE 4,000 – 20,000ppm

Integrate Modeling Techniques with Separation Projects

Separations: Physical Beneficiation

Ultrasiever

Flotation Column

Organic/Coal Flotation

Size Separation/Sieving (wet or dry)

Density Separation (Heavy Liquid, Cross-flow Separator, etc)

Electrostatic

Magnetic Separation

REE Froth Flotation

Mini Lab Crusher

Hammermill

Crushing/Coarse Grinding

Fine Grinding

Lab Attrition Mill
Union Processing Mill

Sample Divider

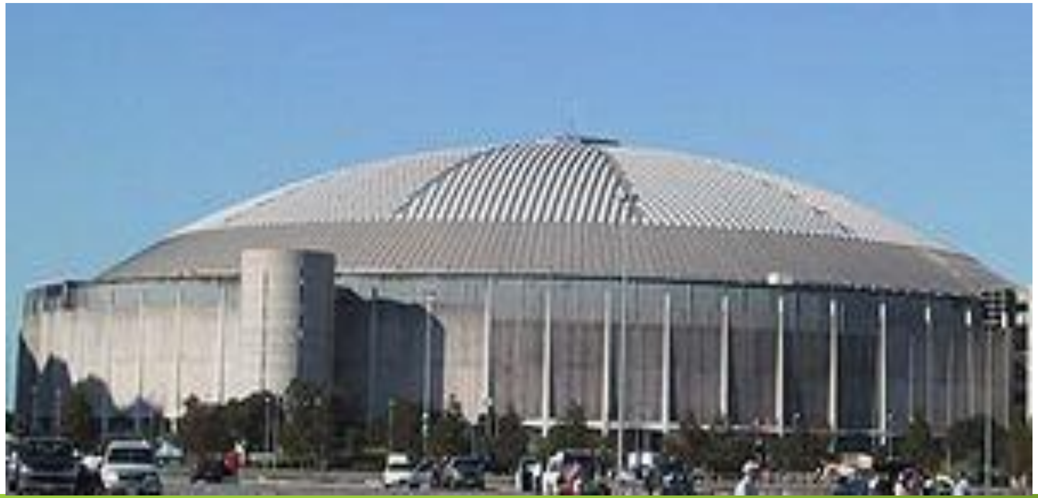
Rare Earth Element Challenges

- **Approximately 90% of REEs come from China**
- **Potential national security and supply risk for critical rare earths for defense and clean energy**
    - Y, Nd, Eu, Dy, Tb
- **Not typically found in concentrated ores**
- **Modest Concentrations in Coal and By-Products**
- **Difficult to extract and separate**
- **REs are not distributed evenly**
    - Causes excess supply for some REs and shortages for other REs
    - Price significantly different for individual REs

Rare Earth Element Challenges

The Modest Concentrations in By-Products

- Imagine the Houston Astrodome
- Holding 30 Billion Ping Pong Balls Representing Fly Ash (470 ppm RE+Y)
- Remove Many of 14 Million Different Colored Rare Earth Ping Pong Balls
- Can We Do This?
- Yes



Coal – Precious Domestic Resource

Opportunity

- 275 billion tons – Resource
- Typical REE Concentration of 62 ppm
- $275*10^9$ tons coal * ($62*10^{-6}$ parts REE/coal) = 17 million tons REE in US coal
- US consumes around 16 – 17 thousand tons REE annually
- Over 1,000 year supply of REEs in US Coal at Current Rate of Consumption

Coal By-Products - Opportunities

- Everything in the earth's crust, good and bad, is found to some extent in coal and coal by-products

- The US typically produces 1 billion tons of coal a year (1990-2014)
  - 100-150 million tons of coal ash/year with concentration of ~470 ppm REE+Y
  - Coal ash produced yearly based on average concentrations contains ~47,000-70,500 tons of REE+Y or 2.8 - 4 times the US consumption
  - Coal mining and coal prep by-products provide additional opportunities
  - Other critical or valuable elements could also be extracted
  - Provide a stable source of REEs and other critical metals
  - Extraction of REEs can be environmentally friendly by utilizing already mined materials and potentially treating and utilizing by-product materials

Field Sampling

- Identification of Promising By-Products for Rare Earths
- Rare Earth Archive houses over 1,000 samples
- 867 samples collected since June 30, 2015 (nearly all solids, a few aqueous)
- 258 sample analyses uploaded onto EDX website
- Promising Materials identified with over 500 ppm RE+Y on dry whole basis (more than 27)
- Geochemistry – origins and mobilization mechanisms
- Marker Elements (such as Th) and Element Associations

Characterization

- Over 1,000 assays – bulk elemental analyses
- More than 100 SEM-EDX, 200 XRD analyses
- ICP-MS – best in class - digestion, uncertainty, publications
- ICP-OES – bulk multi-elemental analysis (supplementary)
- C, H, N, S, Ash, and Moisture
- SEM-EDX – identified phosphates in by-products, possible Ca-association in ash
- XRD – determine minerology of the sample
- LA-ICP-MS – Spot and Depth Analyses; State-of-the-Art Mass Spectrometer to Resolve Overlapping Peaks; No Digestion
- Ion Exchange Capacities and pH – novel technique developed
- Stanford Synchrotron – several awards of beam time – identified sulfates, oxides, phosphates in ash – now examining mine by-products
- Sequential Extractions – current – form of RE in coal and by-products
- LIBS: Laser Induced Breakdown Spectroscopy
- Sensitized Fluorescence, Portable XRF, Gamma Detection, SHRIMP-RG

Separations

- **Mineral Processing and Physical Beneficiation**
- **Density Float-Sink**
- **Magnetic**
- **Size**
- **Froth Flotation – Shakedown and Commercial Interest**
- **Bench/Pilot Scale Process Design**
- **Ammonium Sulfate**
- **Deep Eutectic Solvents/Ionic Liquids**
- **Acid Dissolution – Over 90% recovery**
- **High Temperature Phase Separations - 100% Recoveries as Monazite**
- **REE Selective Sorbents – 100% Capture**
- **Photophoresis – Novel Particle Separation**
- **Reactive Grinding**

Modeling

Extraction of REEs from clays and other coal and coal by-products

- **CFD Modeling**
- **Mass/Heat Transfer**
- **Kinetic/Reaction Modeling**
- **REE Extraction Simulations**

Techno-Economic Modeling

- **Various Separation and Sampling Techniques**

Recent Highlights: Sampling

- Identification of promising coal by-products for rare earths
- Unique rare earth archive houses over 1,000 samples
- ~ 867 samples collected since June 30, 2015 (nearly all solids, a few aqueous)
- Samples analyzed (ICP-MS) for rare earths and many other elements
- 258 sample analyses uploaded onto EDX website
- Promising materials (≥ 27) identified with over 500 ppm RE+Y on dry whole basis

Geochemistry

- Marker elements (Th, Y) identified using portable x-ray fluorescence (XRF)
- Element Associations; Geological Origins; & Geomobilizations Identified
- 2 Memorandums of Agreement (MOAs) for sampling (United States Geological Survey (USGS), Electric Power Research Institute (EPRI), others pending) and many collaborations

EPRI Research Collaboration

Unique Opportunity

- Mass Balance Within Power Plant
- Differences Between Bottom and Fly Ash
- Extractability of Various Byproducts
- Percent Critical Rare Earths
- Other Critical Elements

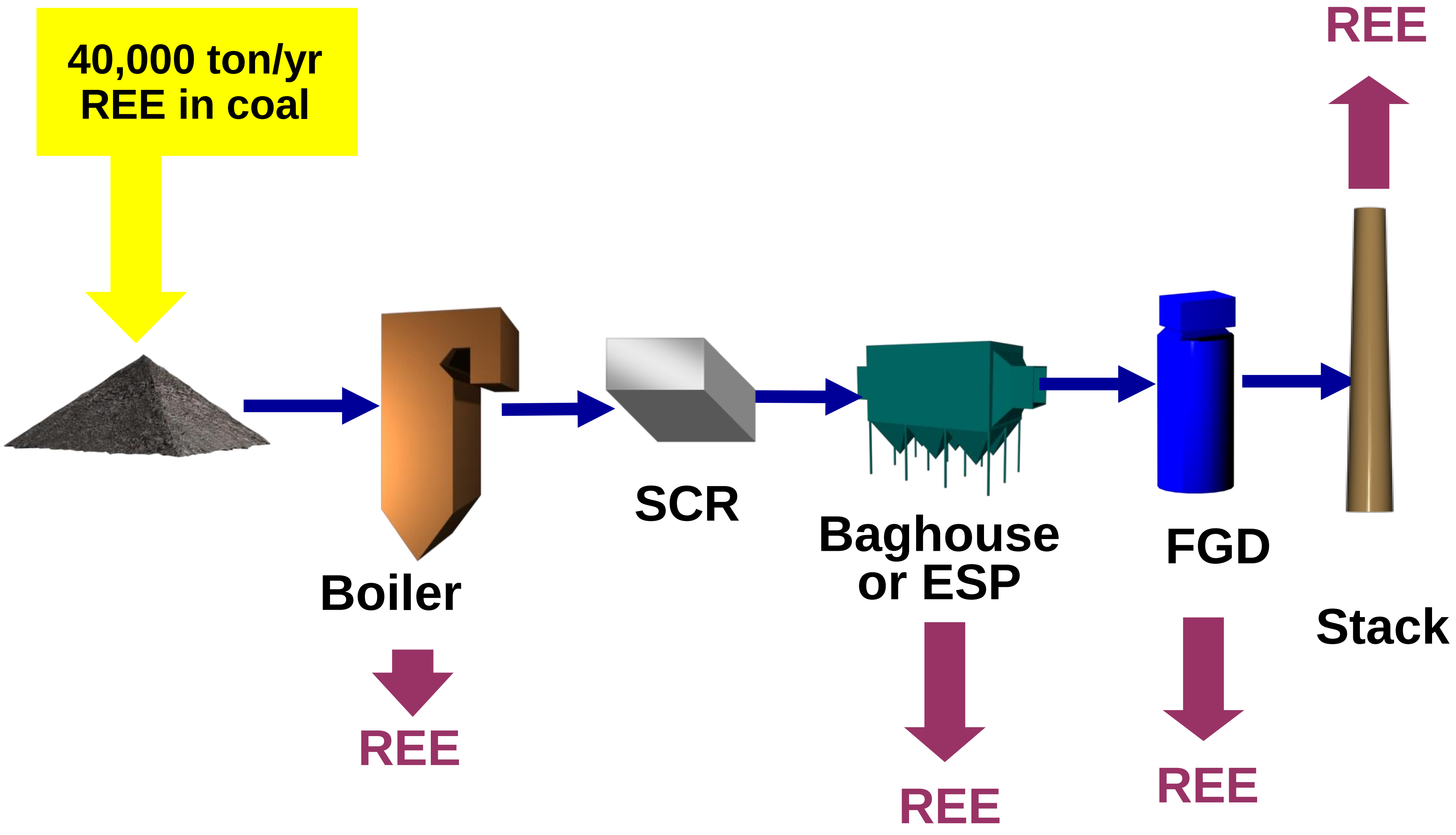
EPRI Samples: Coal-Burning Power Plants

- **Over 90% Coal Produced in US is Burned to Make Electricity**
- **728 Million Tons Coal Mined in 2016**

Coal-Burning Power Plant – A Treasure Chest for the Trace Elements

- **Victor Goldschmidt (1933) – Recover Valuable Elements from Ash**
- **EPRI (1979) – Sponsored Research on Recovery of Metals from Ash**
- **Hower, Dai, Seredin (2000's) – Recover Elements from Ash**

Trace Elements in Coal-Fired Power Plants: Lanthanides



40,000 ton/yr
REE in coal

Boiler

SCR

Baghouse
or ESP

FGD

Stack

REE

REE

REE

REE

Recent Highlights: Characterizations

- Development of digestion methods for accurate determination of trace REE contents by inductively coupled plasma mass spectrometry (ICP-MS) – minimize uncertainty in trace RE determinations.
- Use of geologic interpretation and elemental characterization results to identify geochemical markers that may assist in identifying high REE zones.
- Distribution and speciation of Ce in coal combustion by-products, rock materials, and clays was determined using synchrotron-based techniques.
- REE-containing minerals were identified in various coal-related materials using advanced microscopic methods. The distribution of those minerals was examined, including their 3-D volume images.
- Feasibility of using high-temperature confocal microscopy for studying the reaction of dispersed REEs and phosphate to produce distinct monazite phases for later separation was demonstrated.
- Advances were made in the development of techniques that would lead to field probes for REEs in solid and liquid matrices. Progress was made in overcoming interferences with qualitative detection of REEs in solids by laser induced breakdown spectroscopy (LIBS), while the concept of using a fluorescence-based fiber-optic coupled probe integrated with sensitizers was demonstrated for detection of REEs at low-ppm and high-part-per-billion (ppb) in aqueous liquids under ideal conditions.

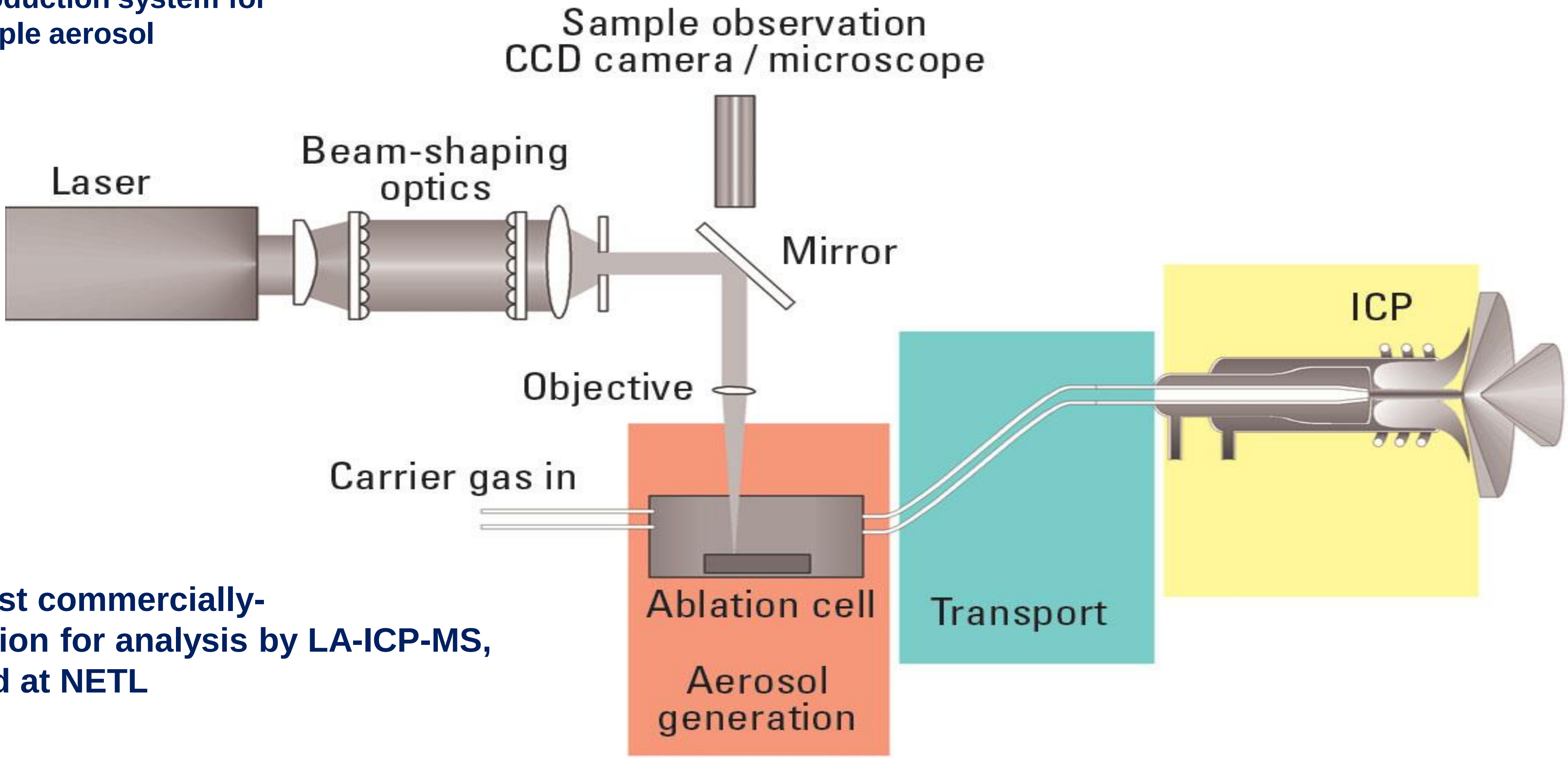
Characterization of Rare Earths in Coal and By-Products

Sampling and Characterization Techniques

- Identify Abundant By-Products Containing Highest Concentration of Extractable Rare Earths
- Improve Rapid & Accurate Characterization Techniques for Concentration & Species
- *Obtain Predictive Capabilities for Geological Location of High RE Content*
- Accomplishments for Sampling
- 867 samples collected since June 30, 2015 (nearly all solids, a few aqueous)
- Promising materials (≥ 27) identified with over 500 ppm RE+Y on dry whole basis
- 2 Memorandums of Agreement (MOAs) for sampling (United States Geological Survey (USGS), Electric Power Research Institute (EPRI), others pending) and collaborations
- Development of digestion methods for accurate determination of trace REE contents by inductively coupled plasma mass spectrometry (ICP-MS) – minimize uncertainty in trace RE determinations
- Identified Rare Earth Phosphate in Coals& Ashes; Rare Earth Phosphate, Sulfate and Oxides in Fly Ashes – Important for Developing Extraction Processes

LA-ICP-MS Analysis: Instrumentation

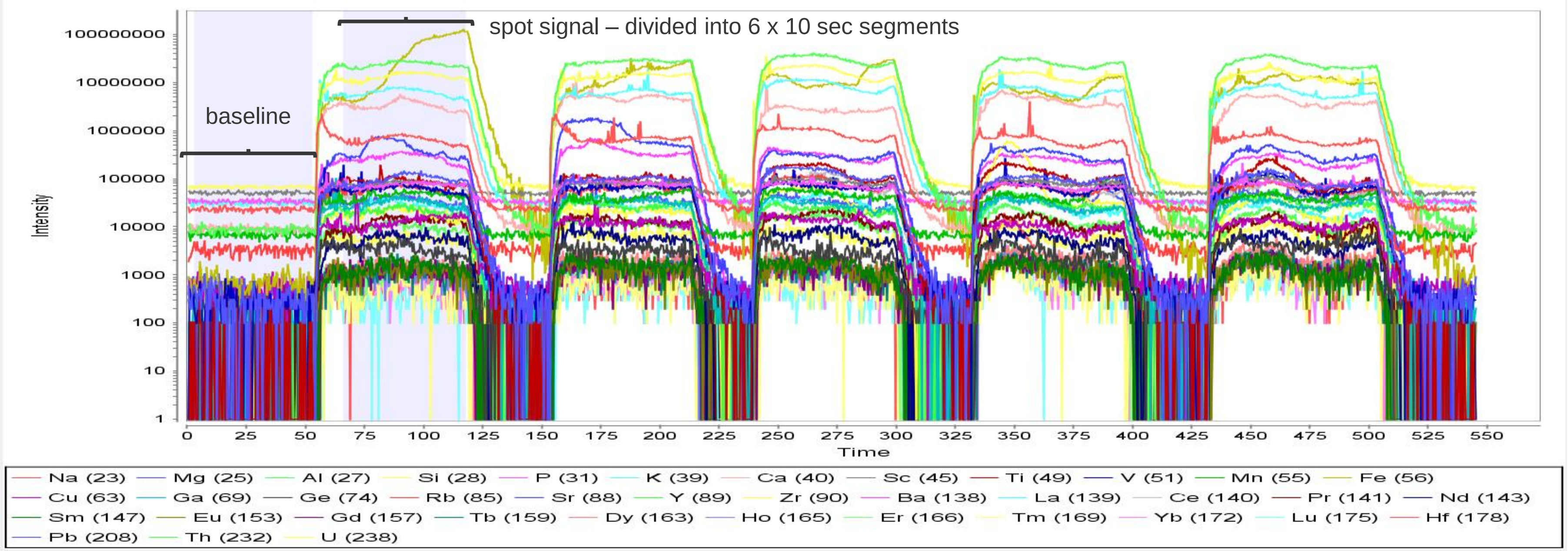
laser acts as sample introduction system for ICP-MS by providing sample aerosol



principal setup for most commercially-available instrumentation for analysis by LA-ICP-MS, including the one used at NETL

Typical Laser Sequence

SRM 1633b epoxy mounted – all 60 μm spots



- Each sample was analyzed in multiple spots for approximately 1 min per spot
- Each spot was then segmented into 6 x 10 sec slices to see if trends could be observed
- Different spot sizes from 32 μm to 60 μm were used
- Elemental content of 10 sec. segments were compared to 1 min spot
- 3 mounted samples were measured, with a total of 46 spots sampled
- Pearson’s correlation matrices were calculated for each set of 6 spot segments

Recent Highlights: Separations

- Physical Separations – Size, Density, Magnetic, Flotation
- Sorbents – 100% Removal of REs from lab aqueous solutions
- Acid Digestion – Over 90% Recovery of Rare Earths from Fly Ashes
- Thermal – 100% Recovery as Monazite from Synthetic Lab Slags
- Chemical – High Conversion of RE Phosphates to More Amenable Species
- Novel – Photophoresis shows great early promise

Physical Separation Methods

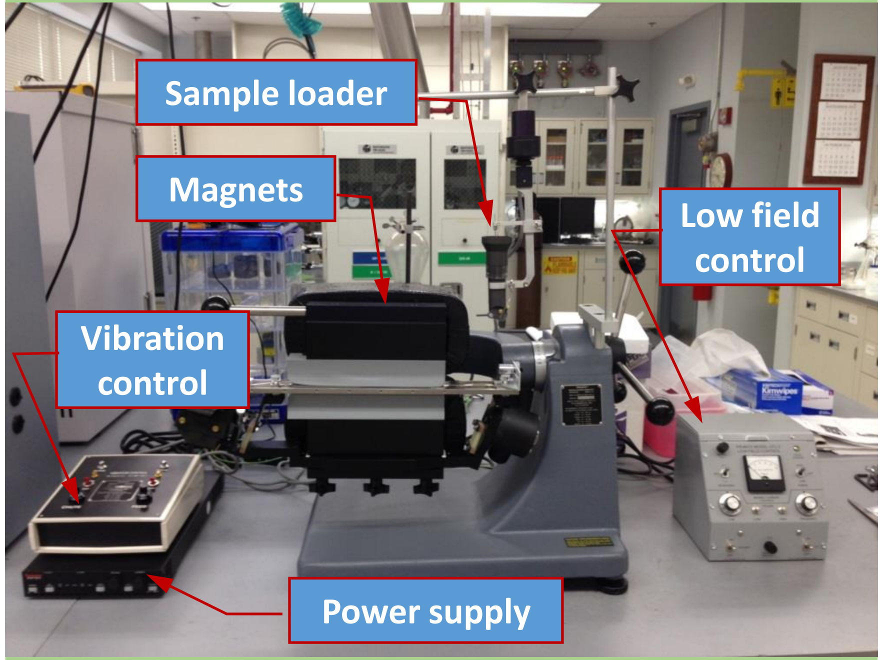
Density Separation

Float-sink separation
Bottom dense fraction

Size Separation

Ultrasound Shaker
Sieve size down to 5 micron

Magnetic Separation

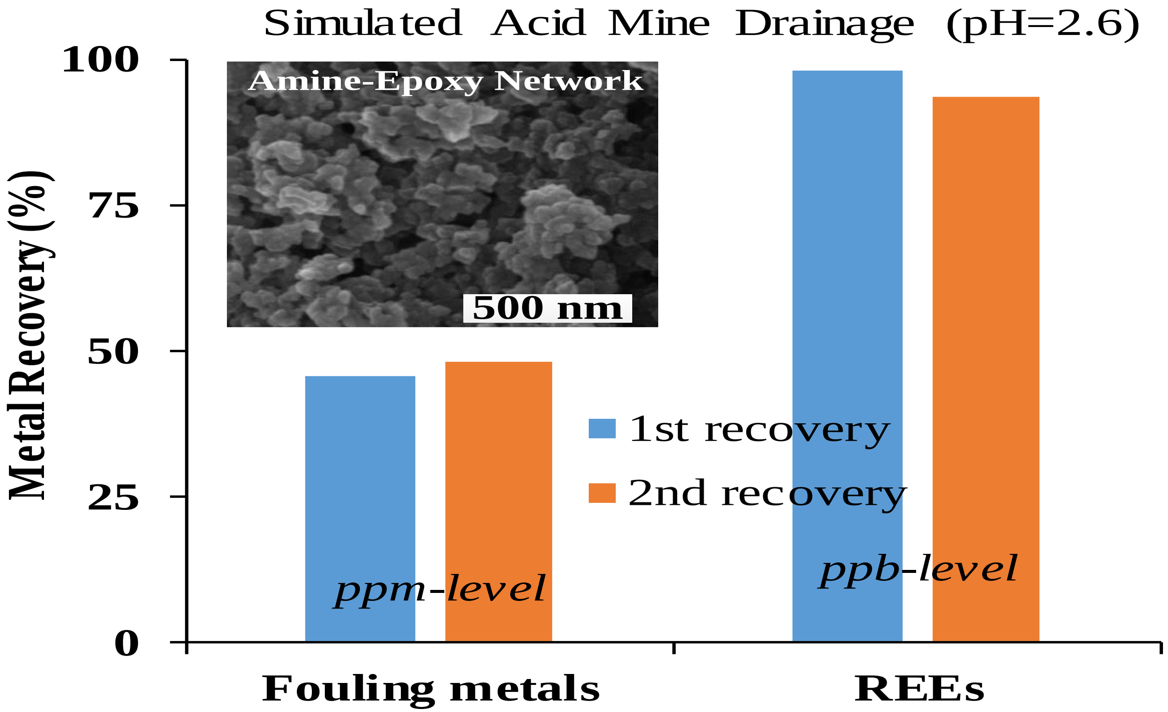


The Frantz Magnetic Barrier
Laboratory Separator

Recent Highlights: Sorbents

Porous Amine Epoxy Particles

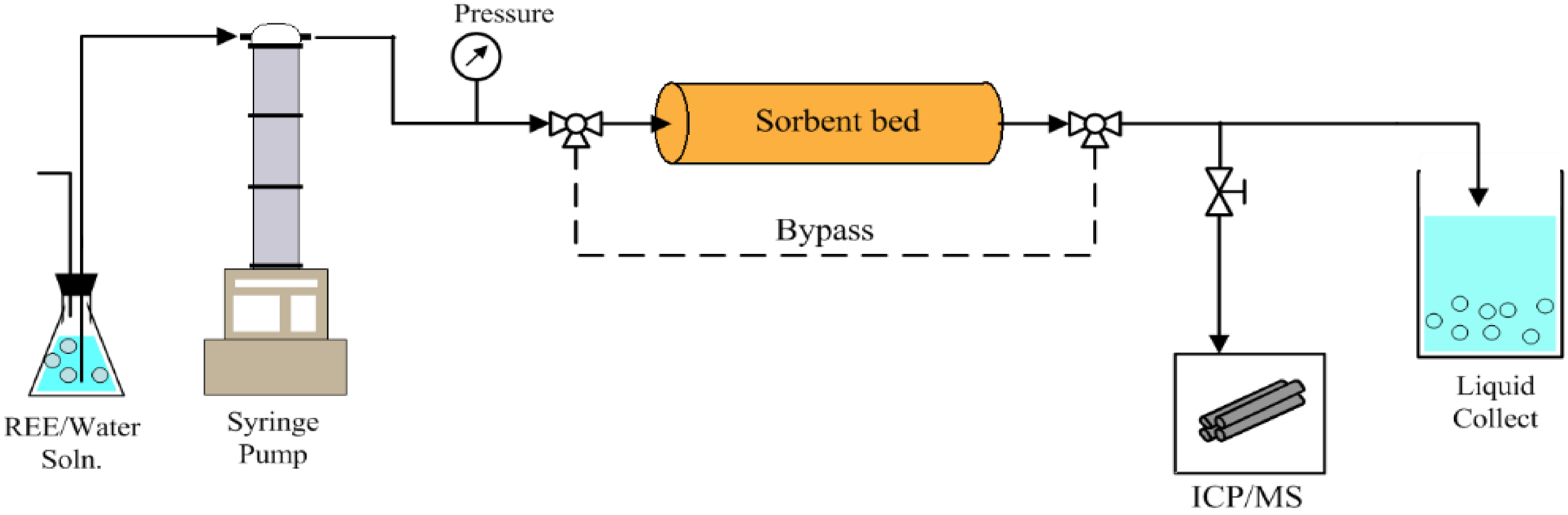
- Near 100% Removal of Rare Earths from Simulated Acid Mine Drainage
- Some Capture of Heavy Metals



Recent Highlights: Sorbents

Organoclay Particles

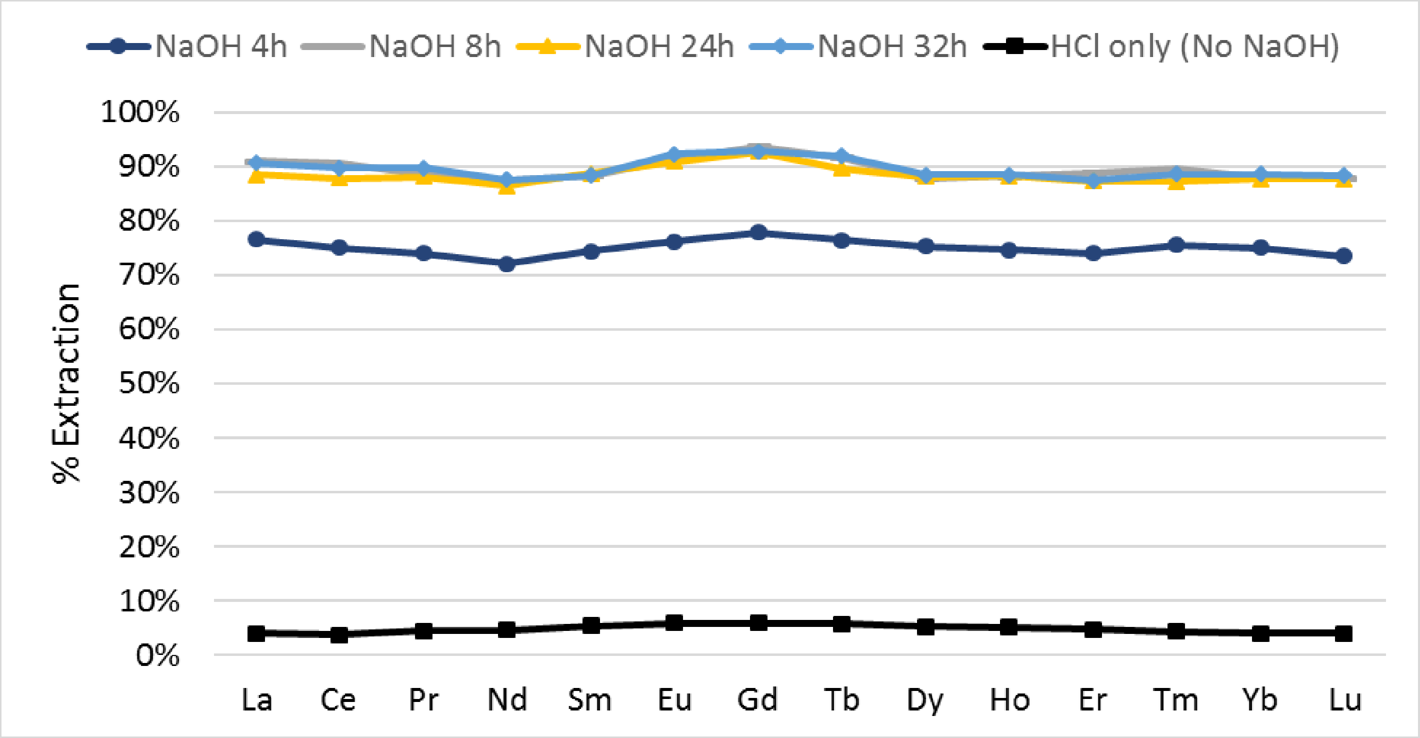
- **Near 100% Removal of Rare Earths from Lab Solutions**



Recent Highlights: Acid Digestions

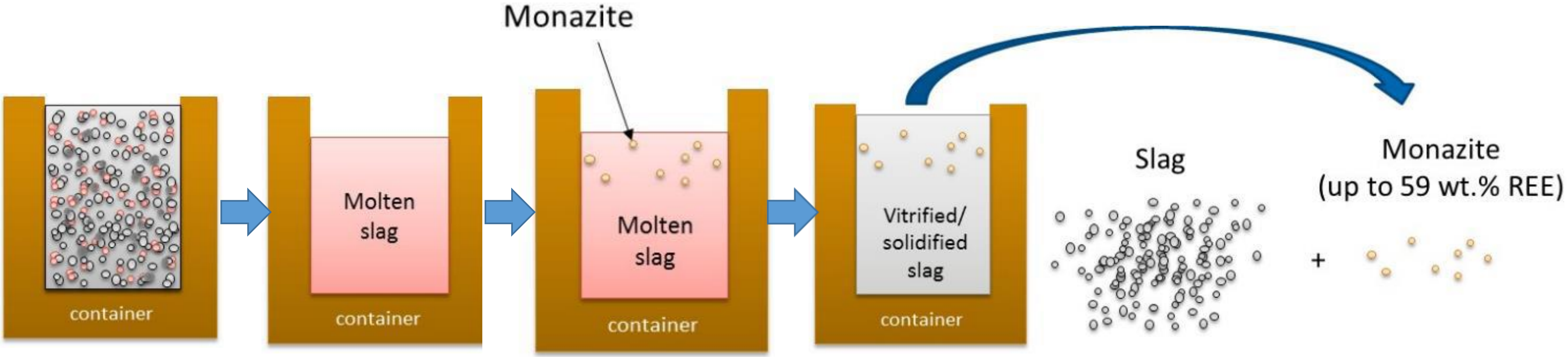
Extraction of Rare Earths from Fly Ash

- Often Difficult Due to Glassy Matrix
- NaOH Pretreatment Greatly Enhances Recovery of Rare Earths



Recent Highlights: Thermal Separations

Capture of Rare Earths from Slag



- Additive to Slag
- Forms Monazite
- 100% Rare Earth Recovery in Lab as Monazite

Recent Highlights: Technology Transfer

Inventions, Patent Applications, and Licenses

- Bennett, J., Nakano, J., and Nakano, A., "Thermal Separation of Rare Earths," Report of Invention filed, June 2016.
- Gray, M., Wilfong, C., and Kail, B., "Regenerable Immobilized Amine Sorbents for REE and Heavy Metals Recovery from Liquid Sources," approved for filing US Patent Application, June 2016.
- Ohodnicki, P., Baltrus, J., Ahern, J., and Poole, Z., "A Luminescense Based Fiber Optic Probe for the Detection of Rare Earth Elements," Provisional Patent Application, filed July 21, 2016.
- Siriwardane, R., "Organo Clays for Recovery of Rare Earth Metals," approved for filing Patent Application, September 21, 2016.

Other Products

- 46 Presentations at National Conferences; 14 Publications; 1 book chapter; 2 MOAs; and 6 Sessions Organized at International Conferences
- The information developed by NETL R&IC is made available to the public through the EDX website, updated regularly with all NETL R&IC publications, presentations, sessions, and field data listed.
- Many Visitors to Web Site
- Rare Earth EDX website: https://edx.netl.doe.gov/ree/.

The NETL Rare Earth EDX Database

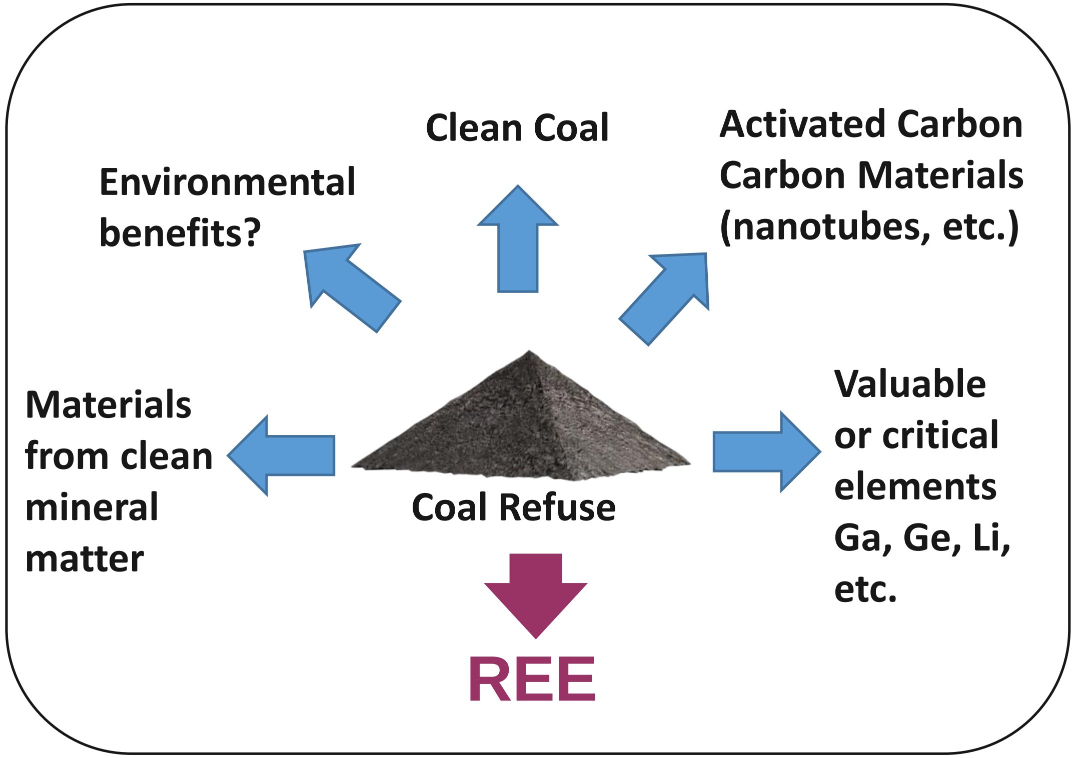
A Great Resource for Rare Earth Information

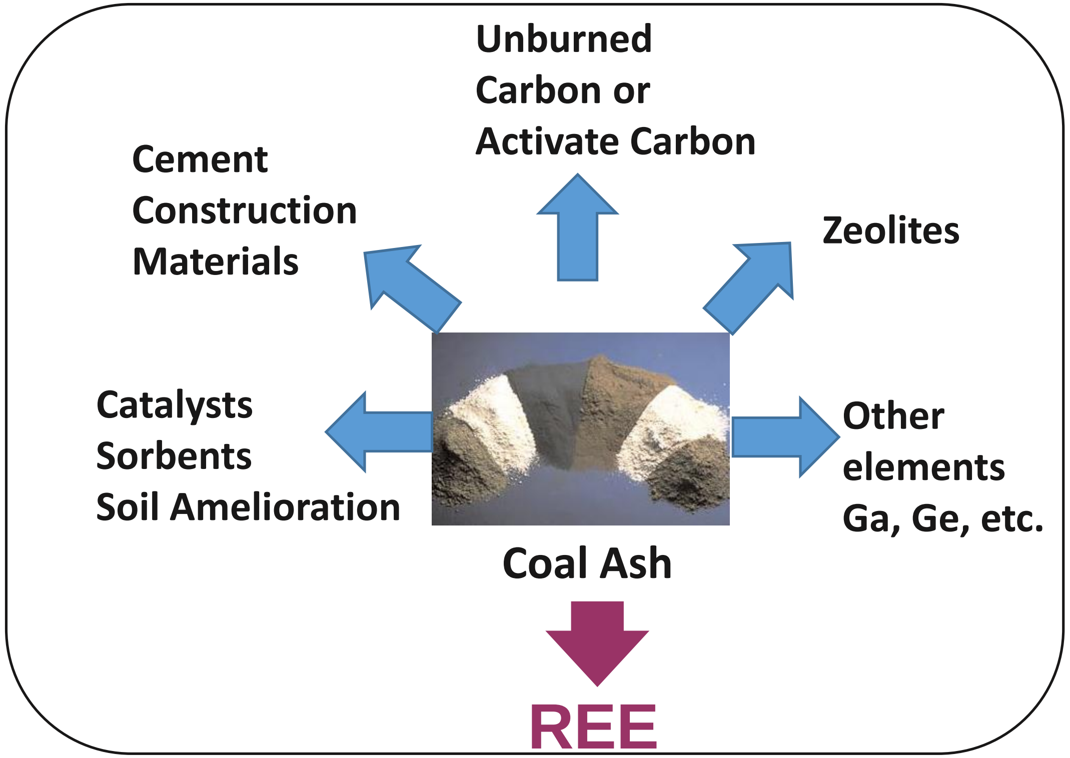
- Coal Materials
- Rare Earth Content - DOE's Coal-Based Rare Earth Element (REE) Data Bank
- Reports
- Publications and Presentations
- Upcoming Meetings
- Latest News
- Solicitations/Funding Opportunity Announcements
- Receive E-Mail Updates
- Submit Questions to NETL Experts
- https://edx.netl.doe.gov/ree/

Future Work

Identify Most Promising Co-Products

- Clean Coal
- Unburned Carbons, Activated Carbons
- Clean Ash
- Zeolites
- V
- Y
- Zr
- Co
- Li
- Ga
- Ge





Conclusions and Future Research

- Much of the recent research on coal utilization in the United States has focused upon the capture of pollutants such as acid gases, particulates, and mercury, and the greenhouse gas carbon dioxide.
- The possible recovery of rare earth elements from abundant coal and byproducts is an exciting new research area, representing a dramatic paradigm shift for coal.
- Additional data is needed on the rare earth contents of coals and byproducts in order to determine the most promising potential feed materials for extraction processes.
- Future work will focus on the characterization of coals and byproducts, and separation methods for rare earth recovery.
- Co-recovery/Co-production of other products may be needed.

Questions

- Visit Our Labs

Additional Information

- Trace Elements in Coal
- Separations
- Characterizations
- Contact: evan.granite@netl.doe.gov

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