Studies of Mercury Speciation and Emissions

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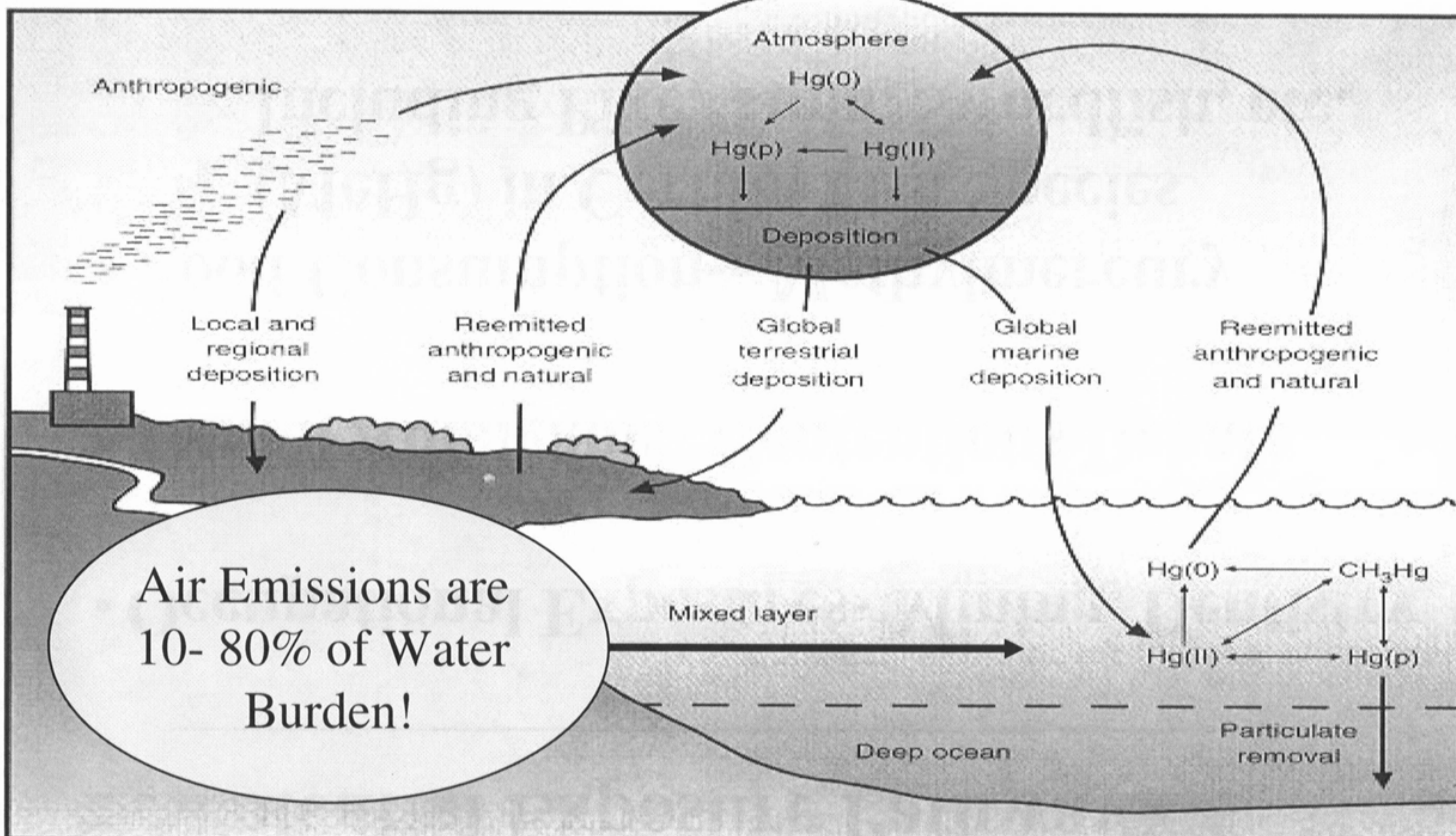
Geochemical Cycle of Mercury



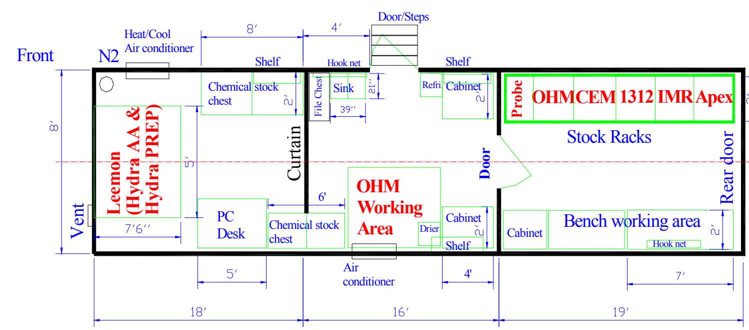
Clear Skies Initiative for Electric Generating Units

	Actual Emissions in 2000	Clear Skies Inititative	Initiative			
			2005	2010	2015	2020
SO_2	11.2 million tons	Final 3.0 million ton cap in 2018	7.8 million tons	6.6 million tons	5.2 million tons	3.9 million tons
NO_x	5.1 million tons	Final 1.7 million to cap in 2018	4.1 million tons	2.1 million tons	2.1 million tons	1.7 million tons
Mercury	48 tons	Final 15 ton cap in 2018	37 tons	26 tons	23 tons	18 tons

Mercury Sampling Methods

- Ontario Hydro Method
  - Wet chemistry
  - Snapshot
  - Limited data on mercury emission and its speciation
- Continuous Mercury Monitor
  - Near real-time data collected under changing conditions as well as in normal ranges of operating conditions
  - A statistical approach (huge data sampling required) is scientifically defensible in accounting for plant operational variability
  - Evaluation of data over longer-term tests shows the range of mercury emissions due to the variability of mercury in the coal and of the normal operational range.

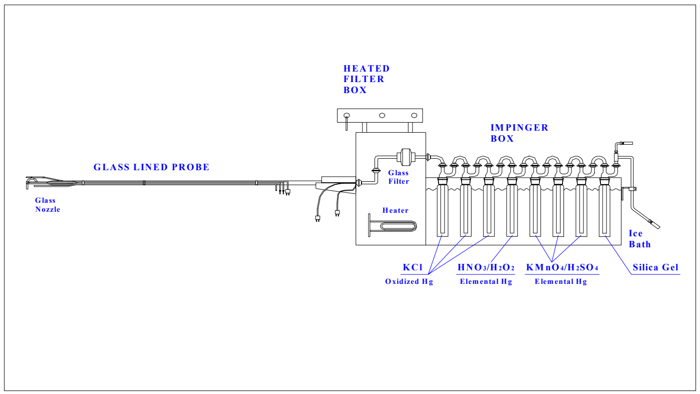
Mobile Laboratory at WKU



Top View of the Inside 53' Trailer

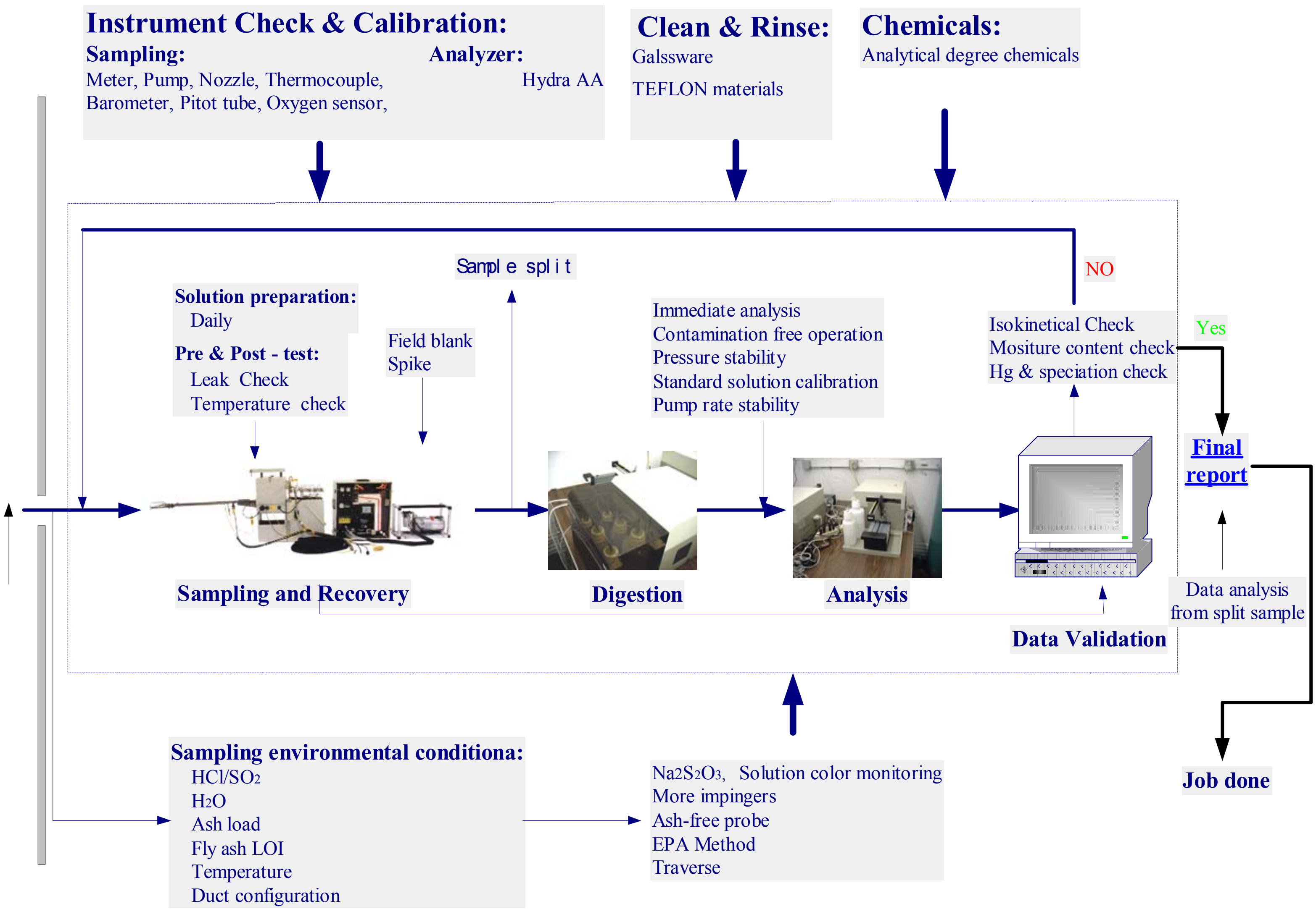
Room 1 : Analytical Room (front)
Room 2 : Preconditioning Room (middle)
Room 3 : Stock Room (back)

EPA Ontario Hydro Method for Mercury

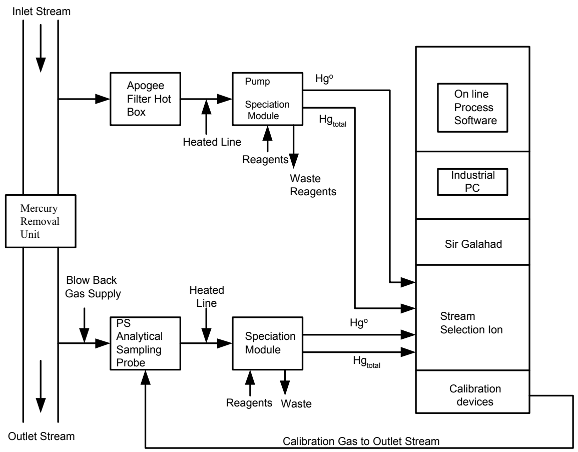


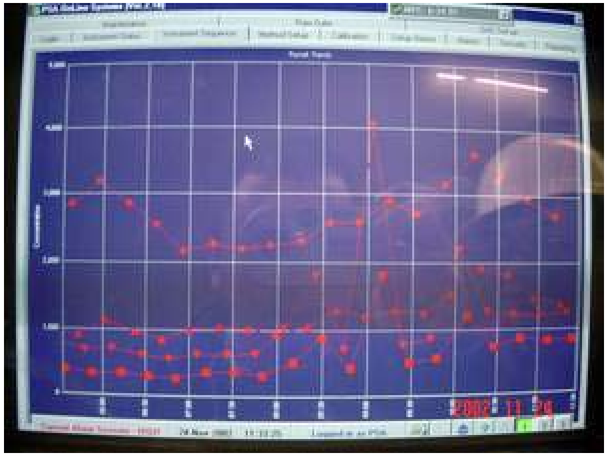
- **Preparation of Mercury Absorbing Solutions**
  - 1mol/L KCl
  - 5%v/v HNO_3, 10%v/v H_2O_2
  - 4% w/v $KMnO_4$, 10%v/v H_2SO_4
- ↓ **Flue Gas Sampling**
- ↓ **Chemical Pretreatment**
  - 5% w/v $KMnO_4$
  - 10%w/v Hydroxylamine Sulfate
- ↓ **HYDRA PREP Digestion**
  - Concentrated H_2SO_4
  - Concentrated HNO_3
  - 5% w/v $KMnO_4$
  - 5% w/v $K_2S_2O_8$
  - 12%:12% NaCl:Hydroxylamine Sulfate
- ↓ **HYDRA AA Mercury Measurement**
  - 10% v/v HCl
  - 10%w/v $SnCl_2$, 0.5N H_2SO_4

QA/QC for OHM

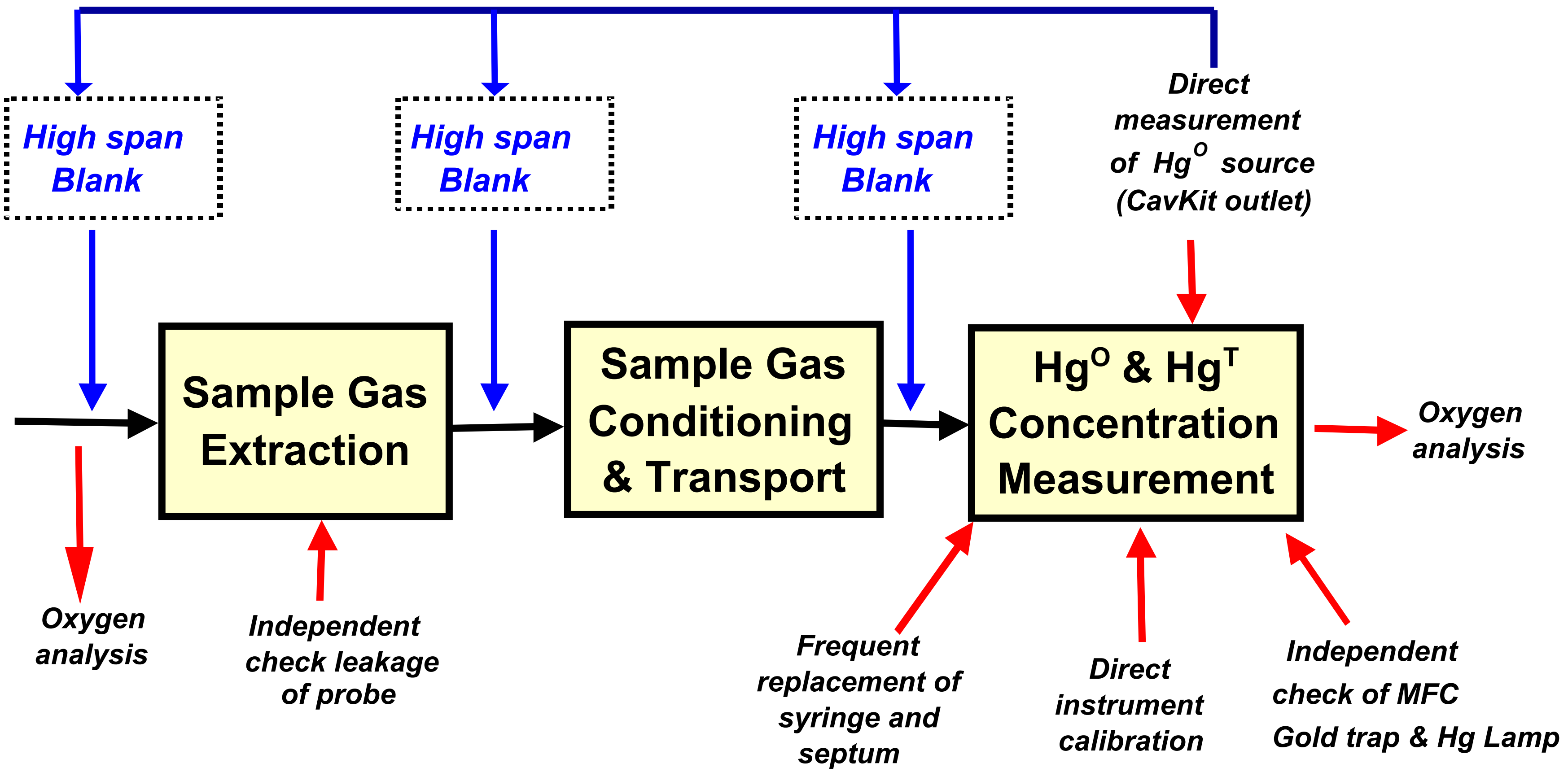

Instrument Check & Calibration:
Sampling:
Meter, Pump, Nozzle, Thermocouple,
Barometer, Pitot tube, Oxygen sensor,
Analyzer:
Hydra AA
Clean & Rinse:
Galssware
TEFLON materials
Chemicals:
Analytical degree chemicals
Sampl e spl i t
NO
Solution preparation:
Daily
Pre & Post - test:
Leak Check
Temperature check
Field blank
Spike
Immediate analysis
Contamination free operation
Pressure stability
Standard solution calibration
Pump rate stability
Isokinetical Check
Mositure content check
Hg & speciation check
Yes
Final report
Sampling and Recovery
Digestion
Analysis
Data analysis from split sample
Data Validation
Sampling environmental conditiona:
HCl/SO_2
H_2O
Ash load
Fly ash LOI
Temperature
Duct configuration
$Na_2S_2O_3$, Solution color monitoring
More impingers
Ash-free probe
EPA Method
Traverse
Job done

Semi-Continuous Mercury Monitor

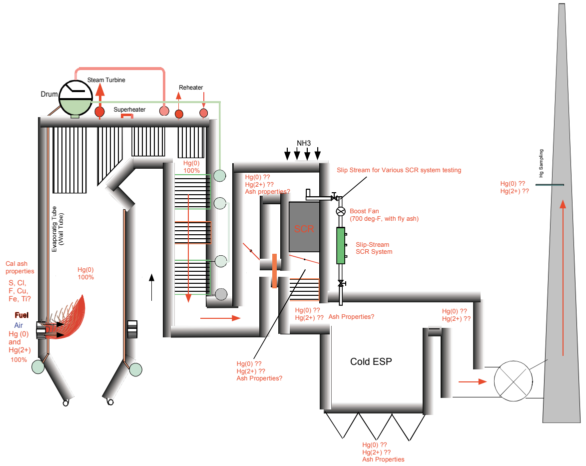


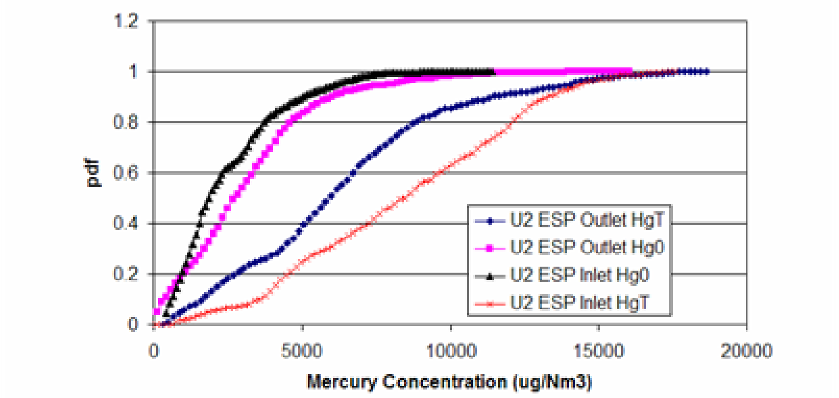


Hg SCEMs QA/QC Techniques



Mercury Determinations





List of Research Projects

- **Fundamental Investigation:**
  - Mercury Behavior in An FBC System, ICCI, 2000.
  - Field Testing Combining High Chlorine Coal with Control Technology to Minimize Hg Emissions In A Utility Boiler with Low-NOx Burner, EPRI, 2001
  - Investigation of the Reliability of a Mercury SCEM, EPRI, 2001
  - Partitioning and Mechanism Studies for Mercury in SCR Control Systems, EPRI, 2003
  - Prediction of Mercury Emissions from Utility Boilers, DOE and Cinergy, 2003.
  - Sorbent Development and Integrated Control of Contaminations in Hot Gas Produced from An Advanced Fossil Fuel-Fired System, 2003.

Field/Contract Service

- Investigation of Mercury Emission from a Full Size Utility Boiler at EKPC. East Kentucky Power Cooperative, 2002-2003.
- Investigation of Mercury Emission from a Full Size Utility Boiler at Cinergy. Cinergy Corp., 2002-2003.
- The Effect of SCR and FGD on Mercury Emission at TVA's Paradise Fossil Station. EPRI/DOE, 2002.
- Advanced Utility Mercury-Sorbent Field Testing, US Sorbent Technology Corp., 2003.
- The Effect of SCR and SD FGD on Mercury Emission at Mirant's Birchwood Station, EPRI, 2003.
- Mercury Emissions from A Multi-Pollution Control Device, Airborne Pollution Control, 2003.
- The Effect of SCR and FGD on Mercury Emission at TVA's Paradise Fossil Station, TVA, 2003.

A List of Various Boiler/Unit Configurations Tested by WKU

- Configuration 1 -- Wall fired boiler with cold ESP (a 90 MWe boiler with low-NOx front wall burner; a 100 MW PC boiler with low-NOx front wall burner; a 150 MWe PC boiler with low-NOx front wall burner; and a 650 MWe PC boiler with opposite wall burners)
- Configuration 2 -- Wall fired boiler with SCR, WFGD and cold ESP (a 650 MWe PC boiler with opposite wall burners and counter current WFGD)
- Configuration 3 -- Wall fired boiler with SCR, WFGD and hot ESP (a 600 MWe PC boiler with opposite wall burners)
- Configuration 4 -- Wall fired boiler with WFGD and cold ESP (a 650 MWe PC boiler with opposite wall burners and cross current flow WFGD
- Configuration 5 – Cyclone boiler with SCR and WFGD (a 700 MW unit)
- Configuration 6 -- Wall fired boiler with SCR and cold ESP (a 525 MWe PC boiler with opposite wall burners and a 650 MWe PC boiler with opposite wall burners)
- Configuration 7 – Four corners fired boiler with cold ESP (165 MWe PC boiler, a 175 MWe PC boiler; a 342 MWe PC boiler, a 450 MWe PC boiler; and a 500 MW PC boiler)
- Configuration 8 – Four corners fired boiler with SCR and cold ESP (a 300 MW PC boiler)
- Configuration 9 – Four corners fired boiler with SCR and hot ESP (a 500 MW PC boiler)
- Configuration 10 – Four corners fired boiler with SCR; spray dryer FGD and cold baghouse; and a 260 MW PC boiler)

Inventory of Instrumentation Related to Mercury Study

- EPA Ontario Hydro Methods (Gaseous and Particulate Mercury) – 5 sets
- PS Analytical Semi-Continuous Mercury Monitors (Vapor Mercury) – Two sets
- PS Analytical Mercury Analyzer (Mercury in Solution)
- PS Analytical Arsenic Analyzer (Arsenic in Solution)
- Leeman Hydra Prep and Hydra AA Mercury Analyzer (Mercury in Solution)
- LECO AMA-254 Mercury Analyzer (Mercury in Solids and Solution)
- Flue Gas Analyzer (INNOVA 1312, IMR-7000, Tempest 100)
- THERMOAPL XRD
- RIGAKU XRF
- LECO Optical Microscope and Renaissance ICP-MS
- SEM-EDX
- LECO C, H, N, S Analyzer, and Calorimeter
- DIONEX IC for Cl
- LECO Pegesus II ThemalEx GC/MS-TOF

Analyzers Related to Mercury Measurement

XRD

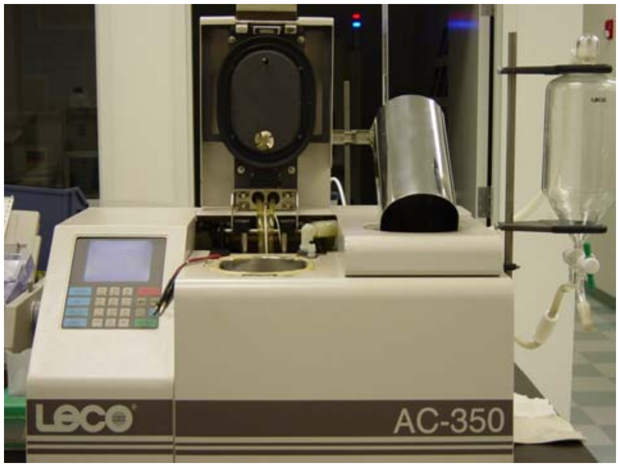
XRF

ICP/TOF-MS

AMA-254

Analyzers Related to Mercury Measurement

Calorimeter

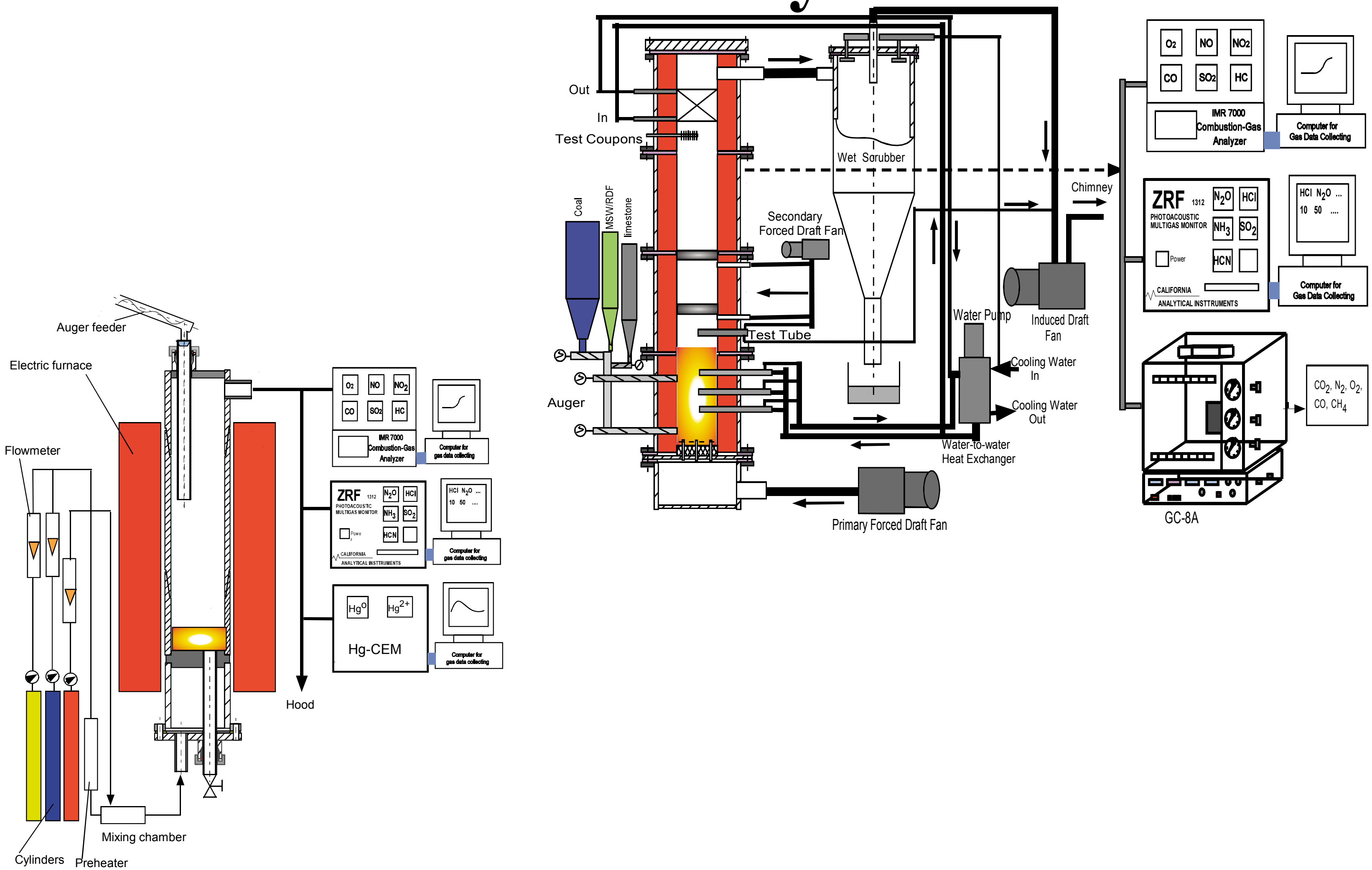


IC

C, H, N

S

The Schematic diagram of WKU Combustion system



Main Parameters

- **Combustor Size:**
  - 12” I.D. and 24” O.D. with 15 ft height
- **Capacity:**
  - 20-30lb/h coal, 4 lb/min air
- **Sample Location:**
  - Alloy specimen -- 10 ft above distributor
  - A210-C -- 5.3 ft above distributor
- **Identified Component in Flue Gas:**
  - SO_2, HCl, O_2, CO_2, H_2O and CO

Identified Component in Flue Gas

- Inorganic:
  - SO_2, HCl, Nitrogen compounds (NO, NO_2, N_2O, HCN, NH_3)
- Organic:
  - PAHs (polycyclic aromatic hydrocarbons)
  - PCDD/Fs (polychlorinated dibenzo-p-dioxins/ dibenzofurans)

Analytical Values[A] for the Coals Procured for the Study

	Phase 0 (1995-1997)		Phase I (1998-1999)			Phase II (1999)	
	95011	95031	97025	98011	98111	99426	99626
Proximate Analysis							
% Moisture	10.07	8.32	4.56	10.63	10.25	2.33	6.96
% Ash	9.37	10.78	10.97	10.10	9.67	8.70	13.81
% Volatile Matter	43.34	37.21	36.25	34.03	34.84	36.98	34.14
% Fixed Carbon	47.29	52.02	52.78	55.87	55.49	54.32	52.05
Ultimate Analysis							
% Ash	**9.37**	**10.78**	**10.79**	**10.10**	**9.67**	**8.70**	**13.81**
% Carbon	74.08	72.16	74.69	75.59	74.18	76.25	69.53
% Hydrogen	5.08	4.82	4.95	4.52	4.73	4.89	4.49
% Nitrogen	1.54	1.54	1.63	1.51	1.59	1.79	1.55
% Sulfur	**3.2**	**2.38**	**3.06**	**1.09**	**1.68**	**0.97**	**4.48**
% Oxygen	6.72	7.57	4.50	6.73	7.72	7.37	5.73
Miscellaneous Analysis							
Chlorine (%)	**0.012**	**0.31**	**0.21**	**0.47**	**0.42**	**0.026**	**0.41**
BTU/pound	13203	12842	13152	13017	13226	13655	12406

[A] Moisture is as-received, all other values are reported on a dry basis

The Final Metal Loss after 1,000 Hours Exposed to 0.1MWth WKU-FBC System

	Phase 0 (1995-1997)		Phase I (1998-1999)			Phase II (1999)	
	95011	95031	97025	98011	98111	99426	99626
Ultimate Analysis							
% Ash	**9.37**	**10.78**	**10.79**	**10.10**	**9.67**	**8.70**	**13.81**
% Sulfur	**3.2**	**2.38**	**3.06**	**1.09**	**1.68**	**0.97**	**4.48**
% Chlorine	**0.012**	**0.31**	**0.21**	**0.47**	**0.42**	**0.026**	**0.41**
% Alkali	**4.72**	**6.93**	**1.89**	**4.51**	**4.00**	**2.30**	**2.73**
Thickness of coupon (mils)							
Alloy **304**: *Initial*	91.535	103.150	106.142	107.283	108.464	114.370	113.228
After 1,000 hours	90.945	102.480	105.512	106.929	107.874	114.213	112.638
Loss per year* (mils)	**2.586**	**2.931**	**2.759**	**1.552**	**2.586**	**0.689**	**2.587**
Alloy **309**: *Initial*	103.346	134.291	128.150	127.165	101.614	128.583	130.118
After 1,000 hours	103.150	134.095	127.992	127.047	101.457	128.504	129.646
Loss per year(mils)	**0.862**	**0.862**	**0.670**	**0.517**	**0.670**	**0.345**	**2.069**
Alloy **347**: *Initial*	92.244	123.661	115.196	114.213	114.213	119.724	122.441
After 1,000 hours	91.772	123.032	114.606	114.016	114.016	119.606	121.811
Loss per year(mils)	**2.069**	**2.759**	**2.586**	**0.862**	**1.207**	**0.517**	**2.759**

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*Based on full time run (8760 hours/year)

Advantages of Co-firing MSW/RDF or Biomass with High Sulfur Coals

- Energy recovery
- Sulfur dioxide in combustion gases minimizes production of molecular chlorine to control the formation of polychlorinated organics. through co-firing high sulfur coals
- Convert elemental mercury to oxidized mercury in the presence of HCl and fly ash acting as catalysts in the upper combustion area of a utility boiler
- Reduce CO_2 emission.

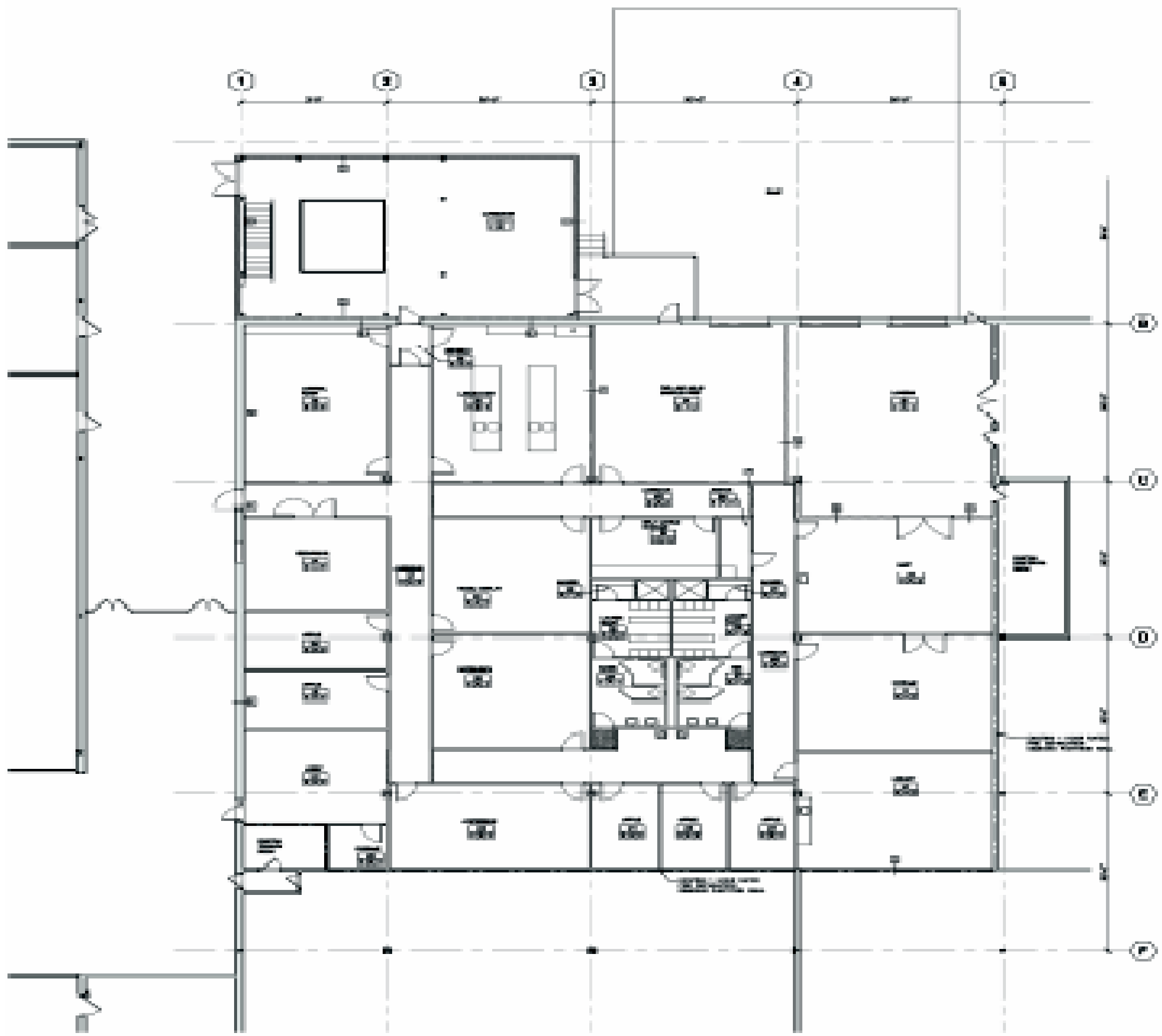
Benefits

- Reduction in landfill costs, in carbon dioxide, chlorinated organic and PAH compounds, heavy metal and other greenhouse gases emissions

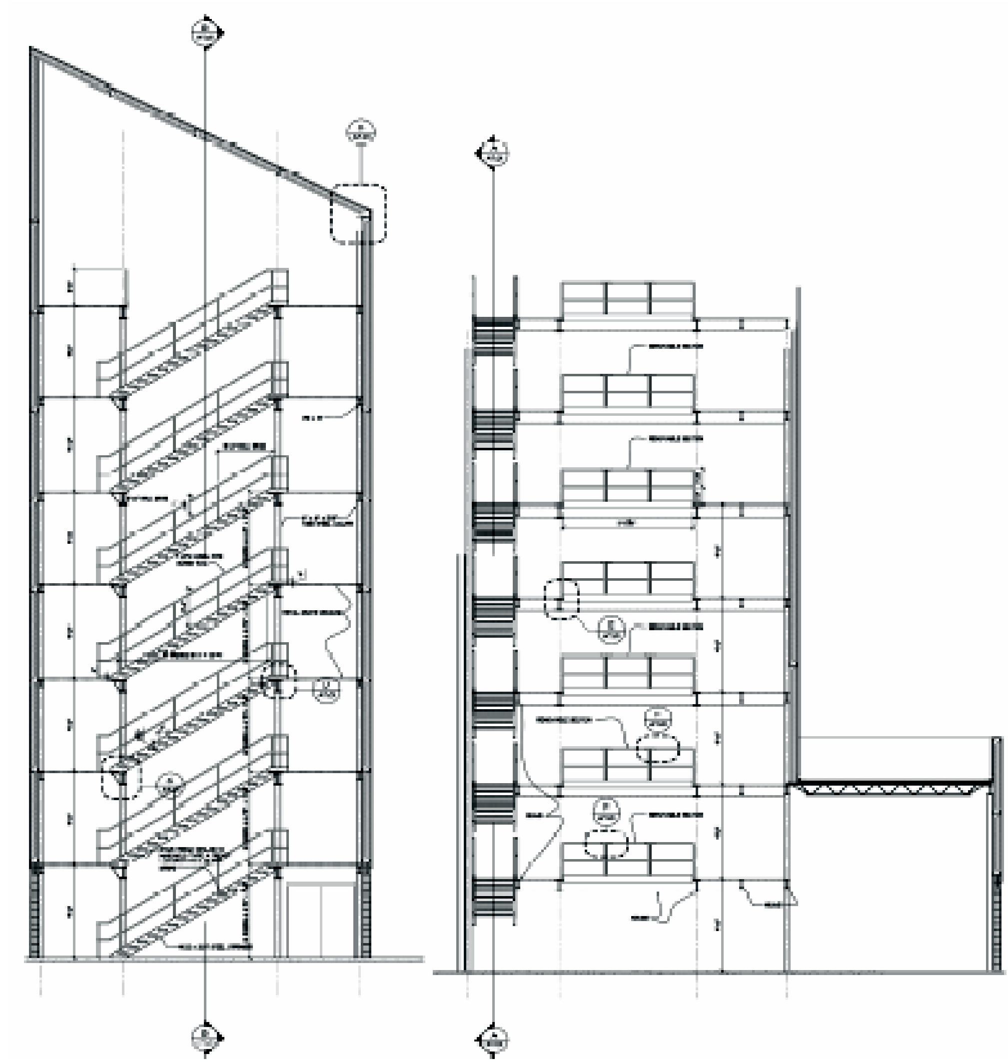
- Energy recovery from waste

- Open new markets for processed MSW/RDF, biomass and Western Kentucky, Illinois, and Ohio high sulfur coals.

Combustion Laboratory and CFBC Facility



Building for CFBC



3D views of CFBC Layout

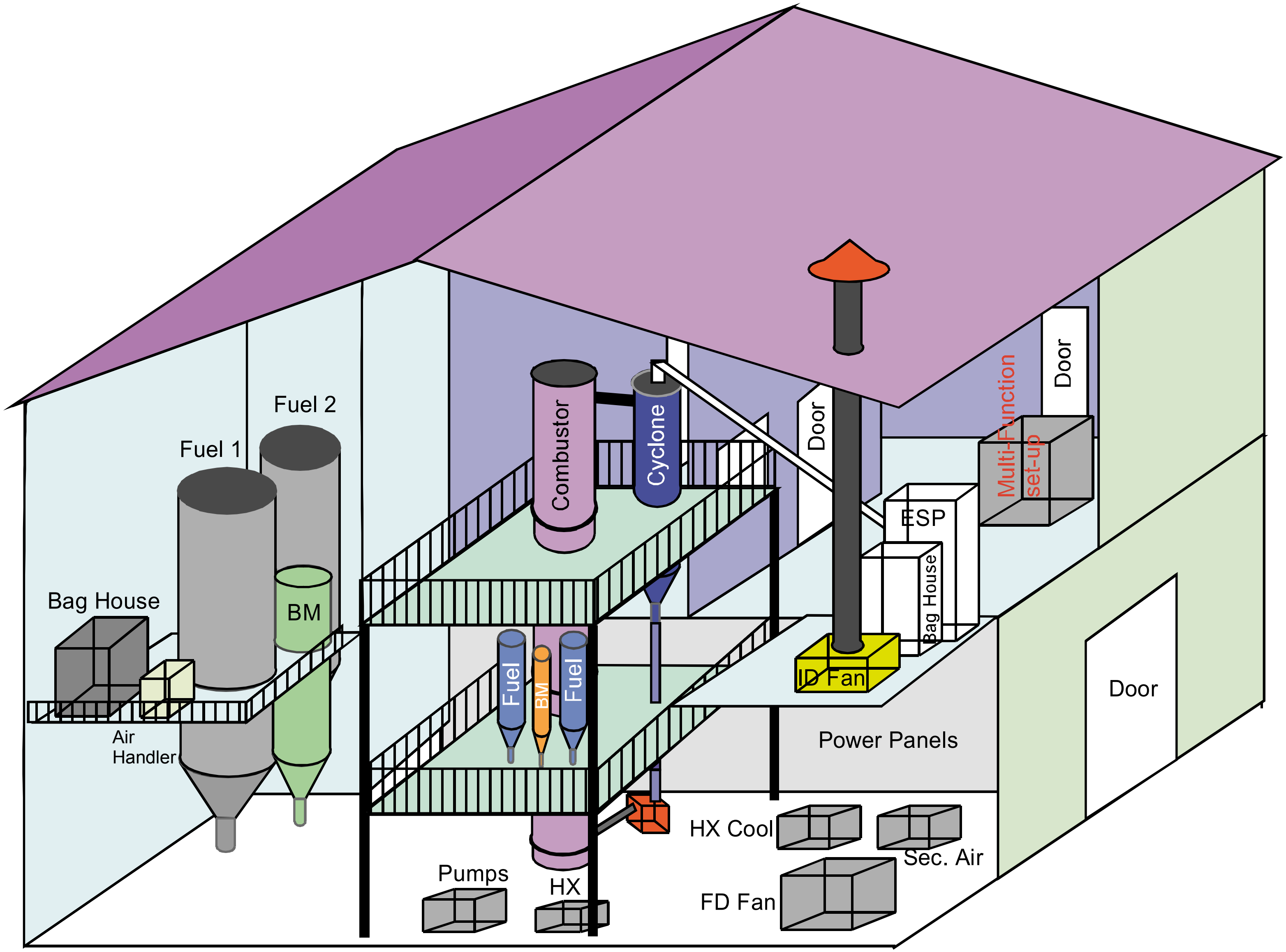
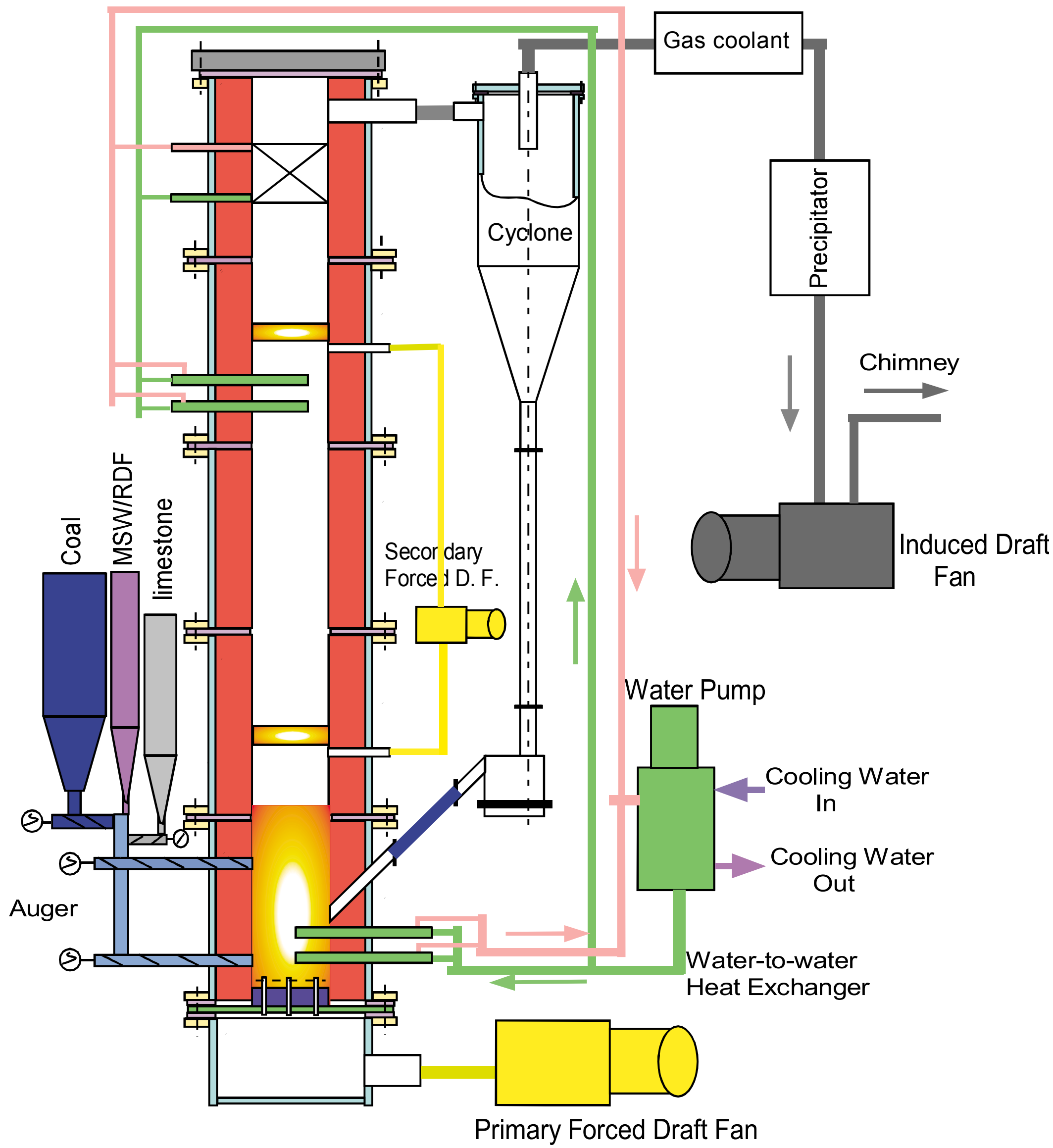
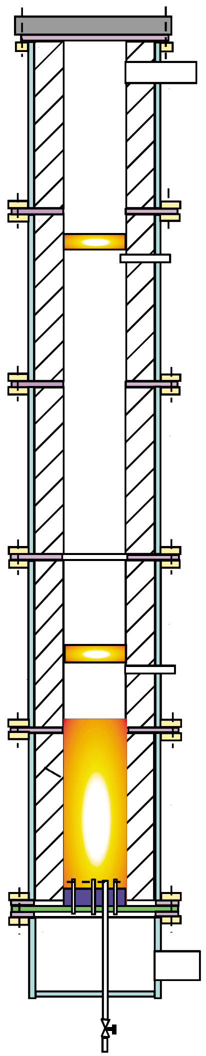


Diagram of 0.6 MWth CFBC System



Brief Design Parameters of 0.6 MWth CFBC System



The major parameters:

If inside diameter is chosen as 0.3 meter, 16-20 meters effective height
and fluidizing velocity: 5 m/s (maximum)
and combustion temperature: 850 ^{o}C

and coal feeding rate: 45-55 kg/h (~0.6 MWe)

Then, the capacity of F.D.F:
Flow rate: 20 lb/min (minimum) (15 lb/min request)
Pressure: 2500 mmH_2O (99 inch WC) (max.)

the capacity of I.D.F.:
If we choose water exchange tube for flue gas cooling
Flowrate: 25 lb/min (minimum)
Pressure: 500 mmH_2O (20 inch WC) (max.)

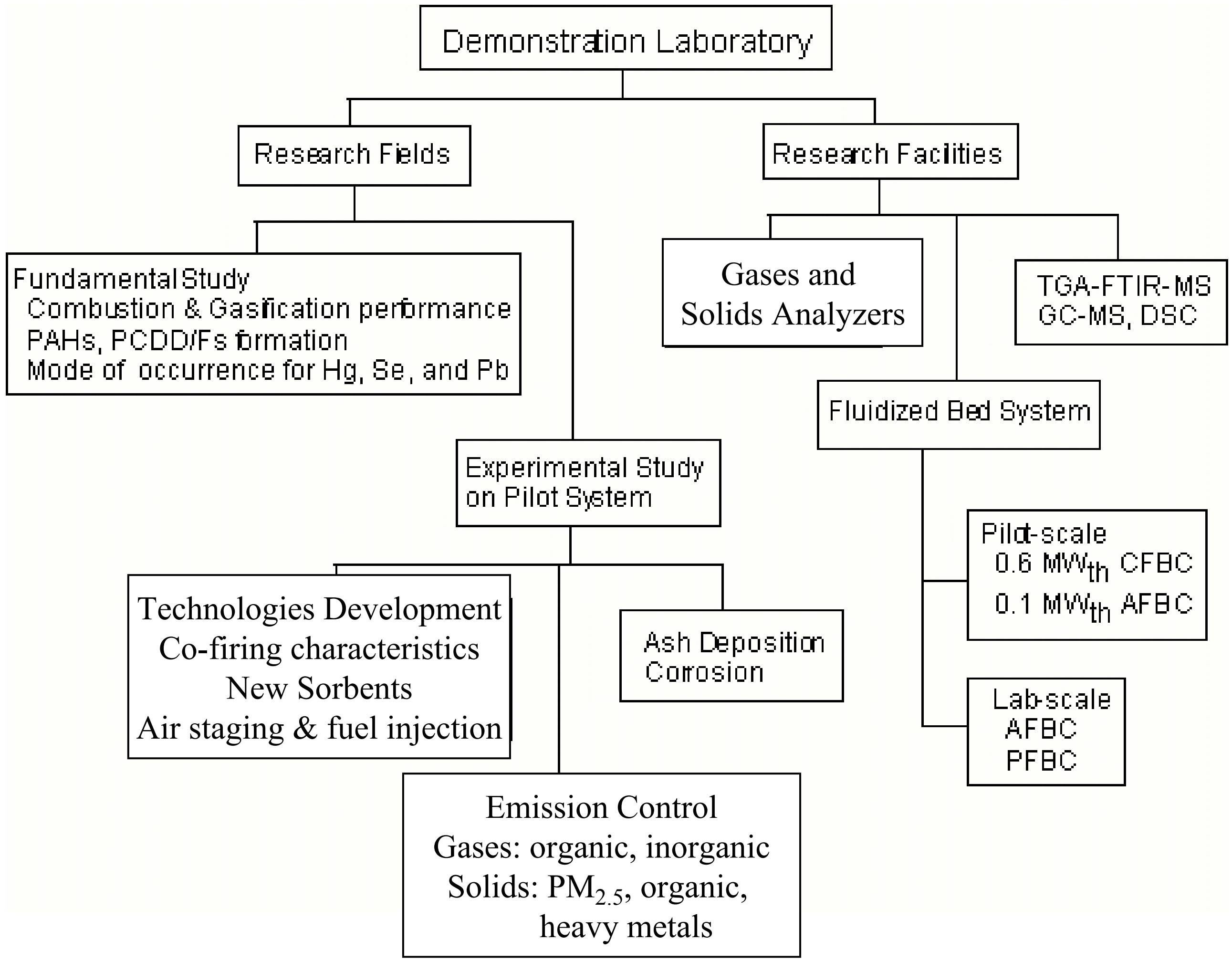
If we use cold air to mix with hot gas for flue gas cooling
Flowrate and Pressure will depend on the temperature at outlet of cyclone and the maximum temperature of baghouse.

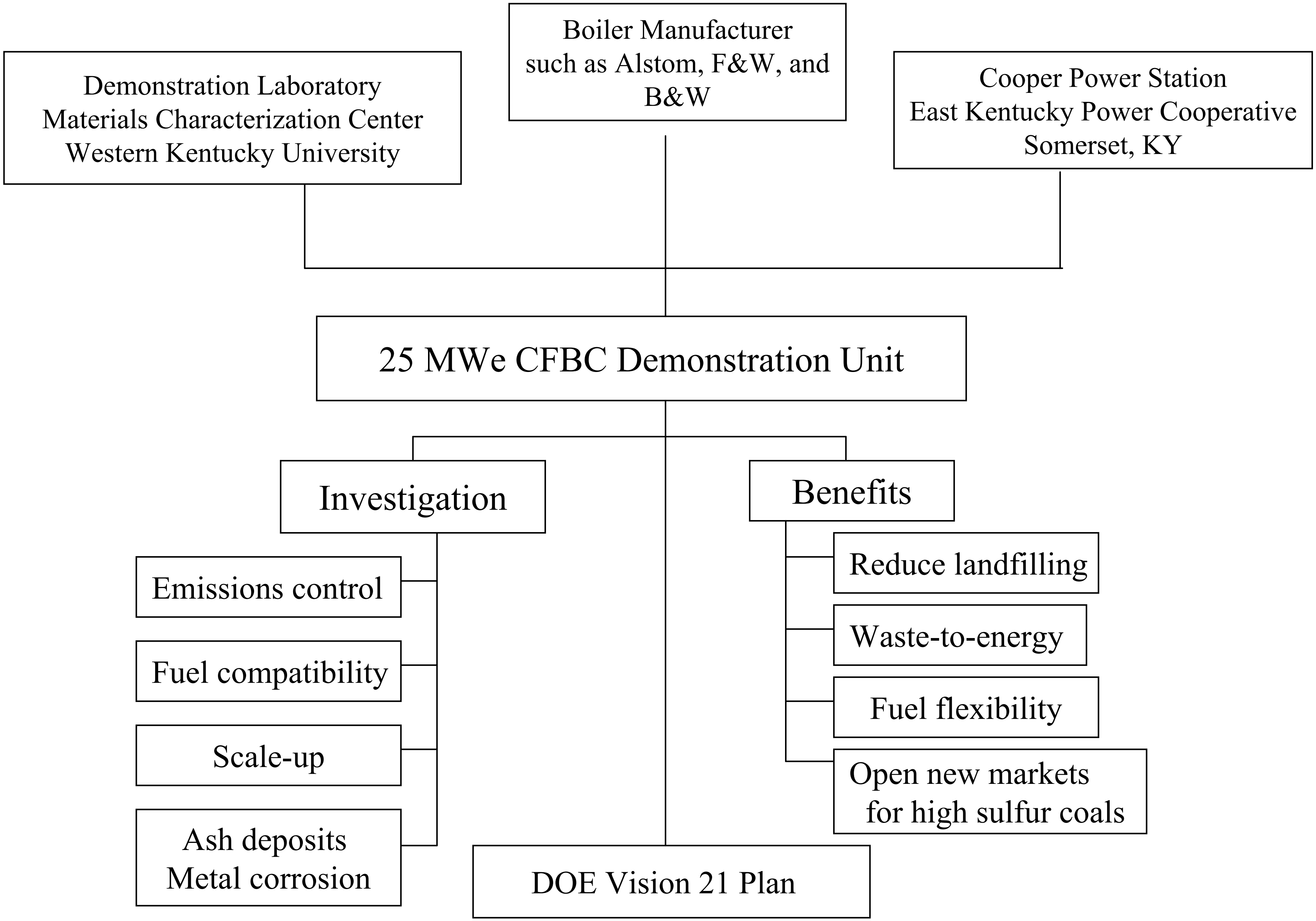
the capacity of secondary F.D.F.:
Flowrate: 9 lb/min
Pressure: 1000 mmH_2O (40 inch WC) (max.)

the set-plate:
Pressure drop: 150--250 mmH_2O (6--10 inch WC)

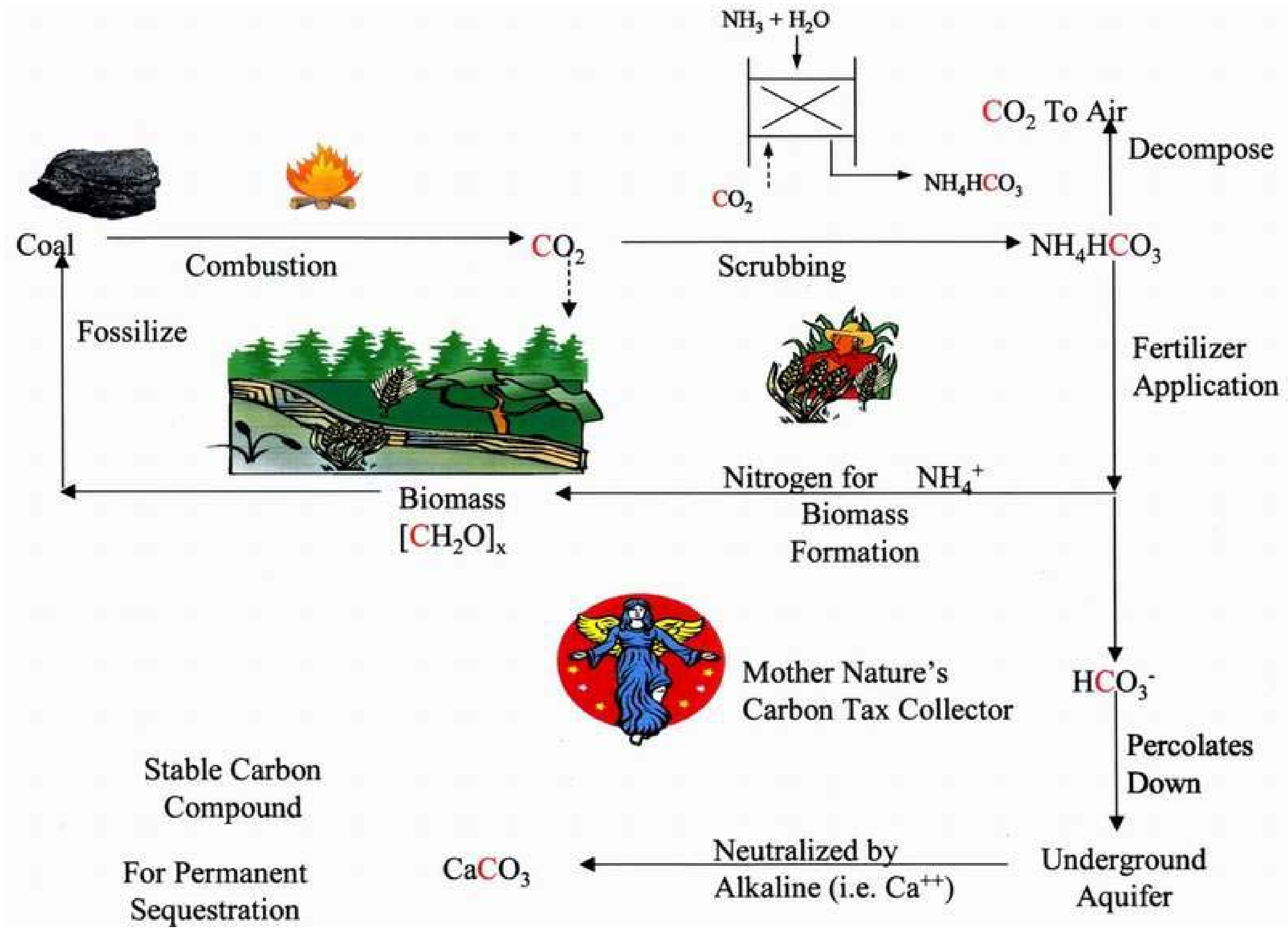
Estimated weight:
Combustor: 12,000 lbs
Cyclone: 2,000 lbs
Coal and limestone system: 2,000 lbs
Heat exchange tubes: 1,000 lbs
Platform: 2,000 lbs
Another accessories: 3,000 lbs

Establishment of a Demonstration Laboratory for Co-firing Refuse Derived Fuels with High Sulfur Coals

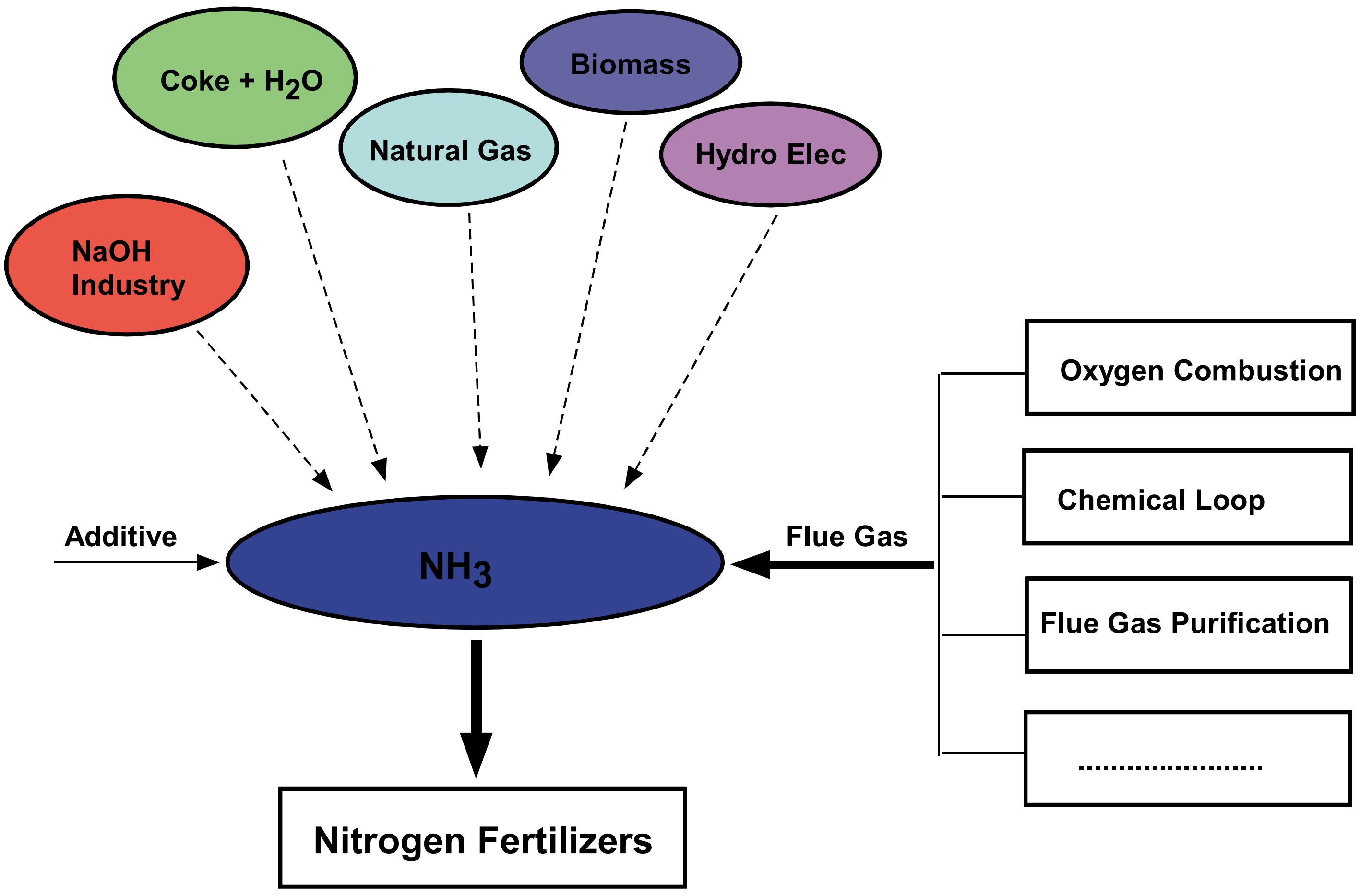



Demonstration Laboratory
Materials Characterization Center
Western Kentucky University
Boiler Manufacturer
such as Alstom, F&W, and B&W
Cooper Power Station
East Kentucky Power Cooperative
Somerset, KY
25 MWe CFBC Demonstration Unit
Investigation
Emissions control
Fuel compatibility
Scale-up
Ash deposits
Metal corrosion
Benefits
Reduce landfilling
Waste-to-energy
Fuel flexibility
Open new markets
for high sulfur coals
DOE Vision 21 Plan

Studies of Carbon Dioxide Sequestration



Processes for Fertilizers



Processes for De-Carbonation