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Experimental validation of coal gasification with neutron imaging

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Oak Ridge National Laboratory

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  - David Lyons, Diane Madden, Lynn Brickett, Jonathan Leske, James Bennett, Bill Rogers
- Jacob LaManna (NIST Center for Neutron Research, Gaitherburg MD)
- Coal samples
  - A: Joe Sheets (3J Enterprises, Newburg WV)
  - B: Jim Mullins, Shelby Howard (Covol Fuels No. 3, Beverly KY)
  - C: Cosmin Dumitrescu (West Virginia University, Morgantown WV)
  - D: Jeff Barron (WWC Engineering, Sheridan WY)
  - E: Mike Heger (BNI Inc., Center ND)
- Other ORNL contributors
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Motivation

- Coal gasification is a complex process
- Simulations are critical to designing next-generation advanced reactors
- Models such as MFiX rely on validation data for tuning and accuracy
- Measurement observations from inside operating gasifiers are difficult to obtain
- **Approach:** Use neutrons which interact strongly with H and weakly with metals, giving the ability to view coal pyrolysis and gasification *in situ*

Project Objective

- Obtain nonintrusive validation data from an operating gasifier, acquiring internal information and product-gas measurements to enable accurate simulations of coal gasification.

An updraft, moving bed gasifier is a candidate design

See presentation "Advanced Reaction Systems (MFiX)" by Mehrdad Shahnam, NETL (Tuesday)

4×coal inlets, uniformly fed

syngas outlet

air+steam in,
ash+UC out

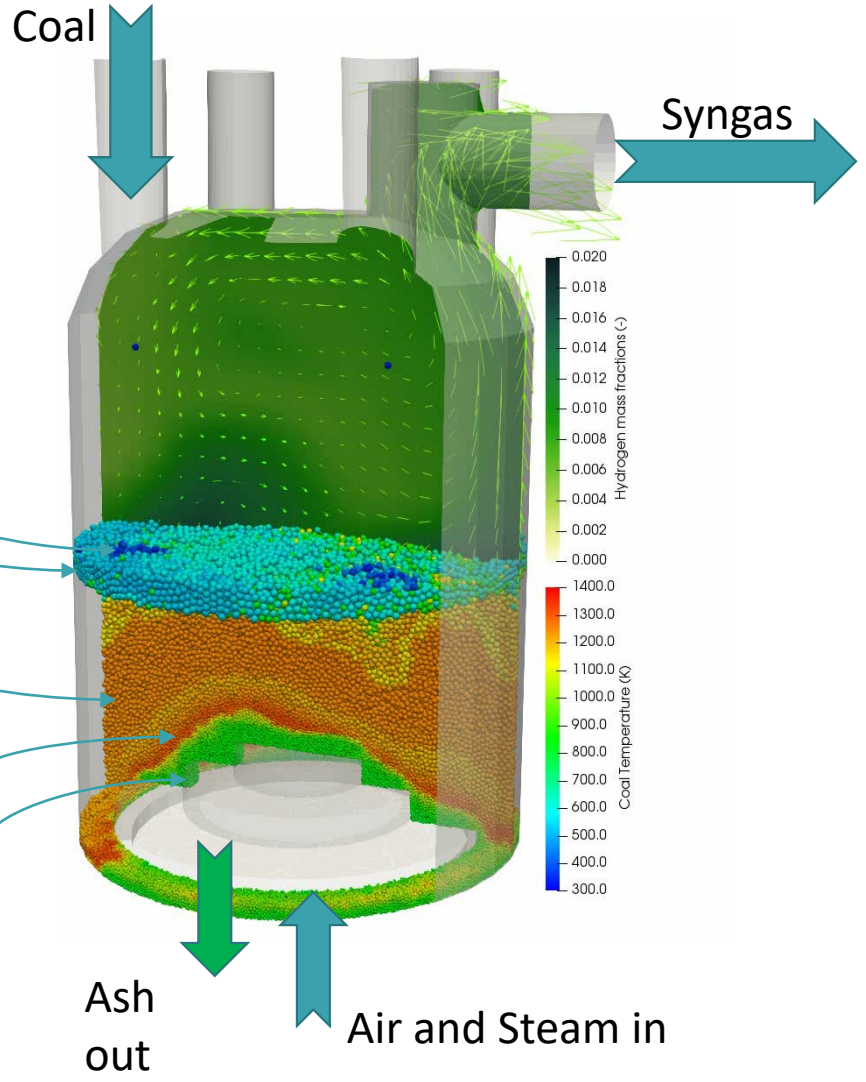
Cold coal falling in

Drying, devolatilization zone

Char gasification zone

Char combustion zone

Ash and unburned carbon-cooled by inlet flow

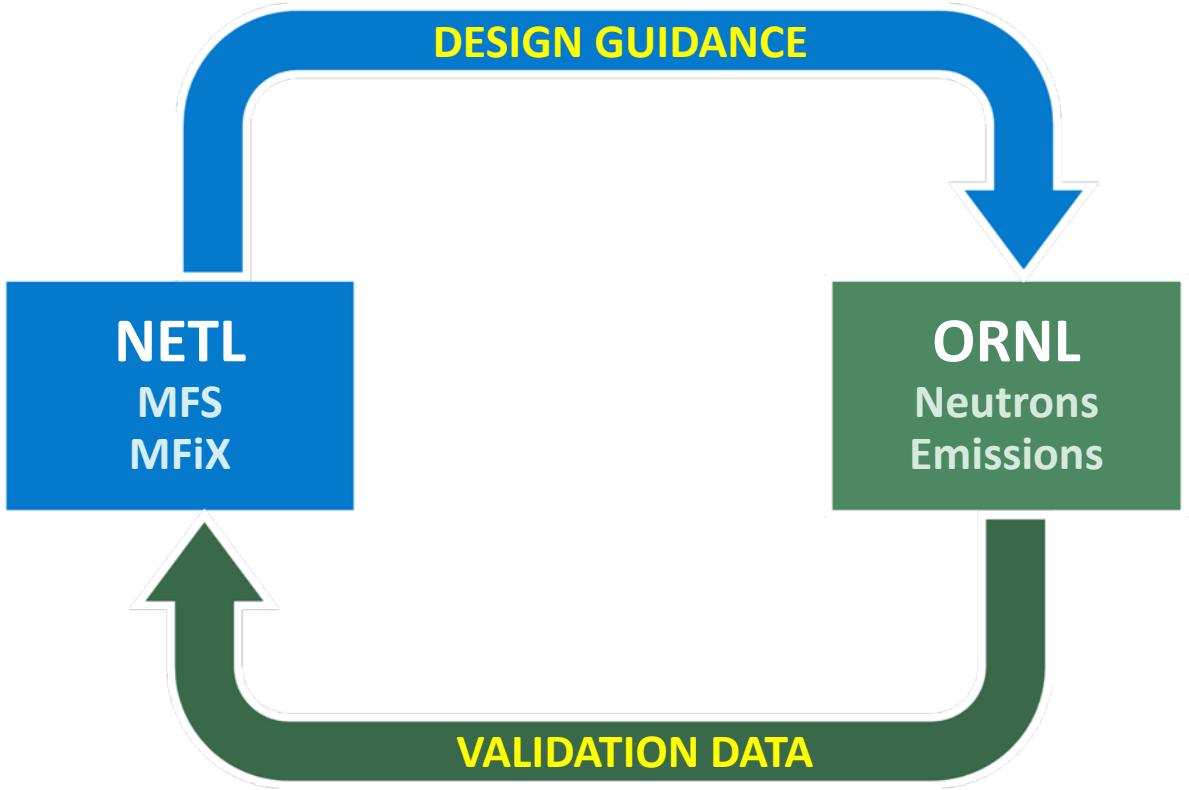


We aim to peer inside a similar reactor using neutrons to map the degree of gasification in space and time.

Graphics courtesy of W.A. Rogers (NETL)

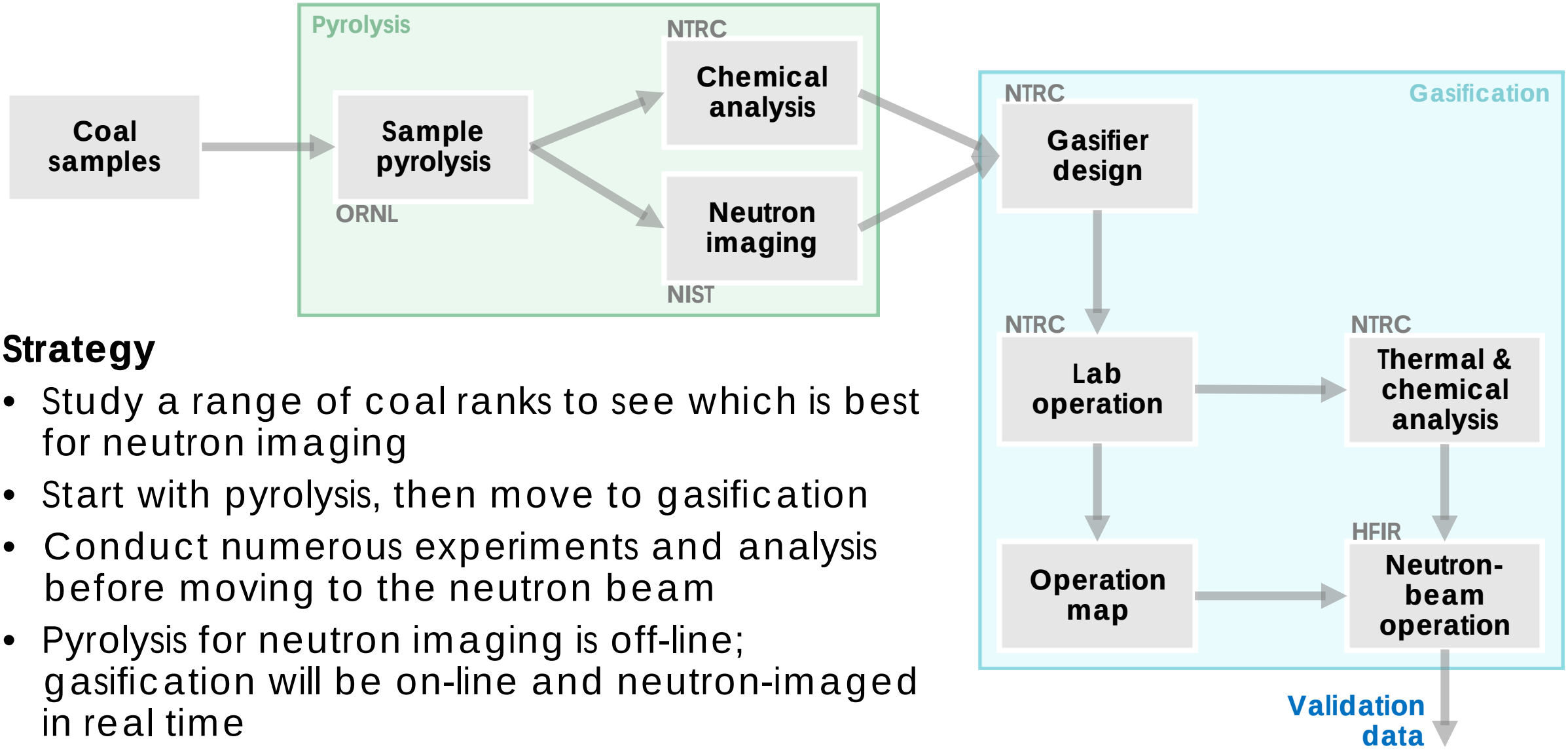
ORNL research to support NETL in this project

- Coal gasification expertise
- Multiphase flow experimental & computational expertise
- MFiX – Multiphase Flow with Interphase eXchange – CFD suite



- Neutron-scattering science facilities and expertise (High Flux Isotope Reactor)
- Gaseous emissions facilities and expertise (National Transportation Research Center)

This project employs an incremental approach



Strategy

- Study a range of coal ranks to see which is best for neutron imaging
- Start with pyrolysis, then move to gasification
- Conduct numerous experiments and analysis before moving to the neutron beam
- Pyrolysis for neutron imaging is off-line; gasification will be on-line and neutron-imaged in real time

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Coal characterization

- Pyrolysis mass loss
- Micropyrolyzer GC-MS

Coal samples

Various samples of coal were acquired to determine suitability for neutron studies and for design of the experimental apparatus.

Sample	Rank	Source	Carbon [1] [wt %]	Moisture [2] [%]	Mass loss [3] [%]
A	Anthracite	Reading Coal Company (PA)	87–98	3	5
B	Bituminous	Blue Gem (Pineville KY)	77–87	1	42
C	Bituminous	**Pittsburgh #8** †	77–87	1	42
D	Sub-bituminous	Monarch PRB (Sheridan WY)	71–77	19	45
E	Lignite	Center Coal Mine (Center ND)	60–70	29	52

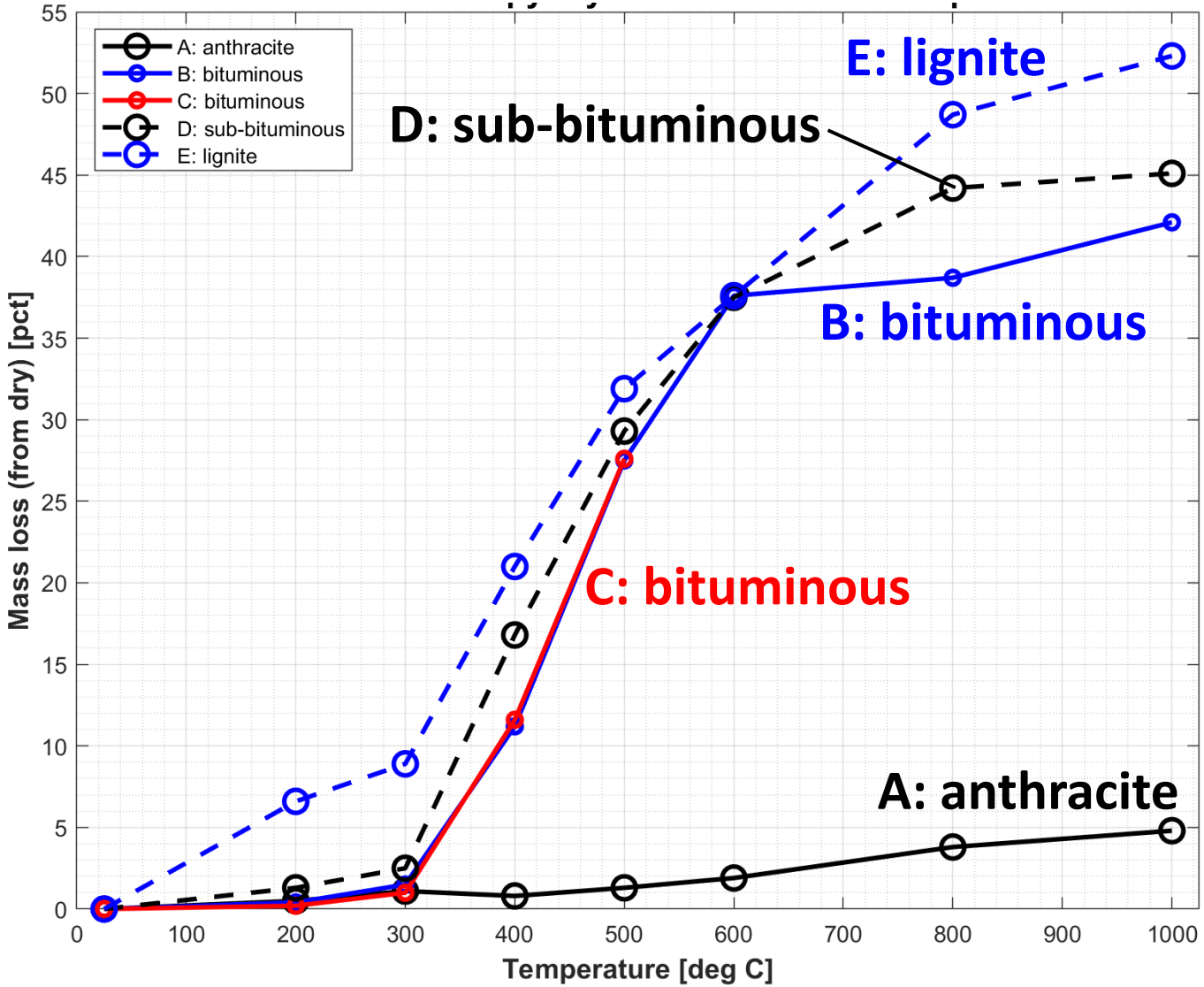
[1] From USGS dry, mineral-content-free basis. Specific coal ranks and ultimate analysis in progress.
[2] Based on weights as-received and after desiccation.
[3] Based on weights after desiccation and pyrolysis in argon at 1000 °C.
† Also used by NETL and WVU in FE projects

Mass loss should correlate with neutron attenuation, which will vary with degree of pyrolysis.

Mass loss under pyrolysis varies by coal rank

- Coal cylinders (D,L = 1 cm) pyrolyzed in a tube furnace in argon to estimate total mass loss versus temperature
- Bituminous problematic because of volatility
- Pyrolyzed sub-bituminous and lignite somewhat brittle/friable

Tube furnace used to pyrolyze samples



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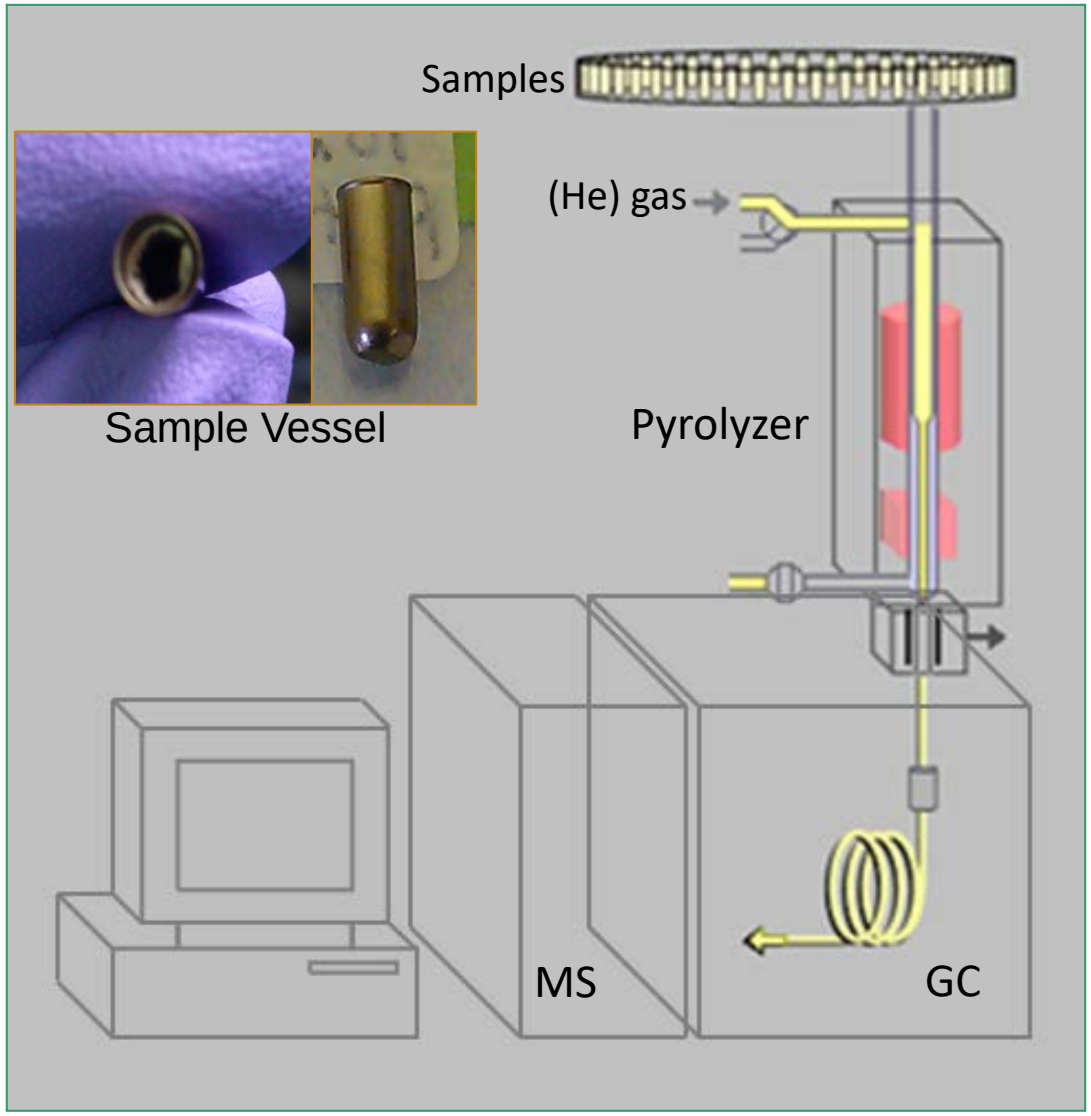
Thermal desorption / pyrolysis GC-MS

2-step sample intake method:
1) temperature programmed thermal desorption (TD)
2) isothermal pyrolysis (Py)

Directly sample, rapidly characterize myriad materials, with surface vs. bulk differentiation…soot, sludge, bio-oil, catalyst, etc.

Procedure:

- ~1 mg sample He-purged (30s) then thermally pyrolyzed (300°C) using a Frontier Laboratories LTD multi-shot pyrolyzer
- Desorbed compounds then transferred to the GC/MS by He to Restex Rxi-5ms column for separation
- GC Temperature Program: (1) Initial temperature 40°C for 3 min, (2) ramped from 40-T °C at 6°C/min, and (3) held at T °C for 5 min
- Mass Spectrometry Analysis: Analytes scanned from 35 to 550 daltons at a 1 sec scan rate



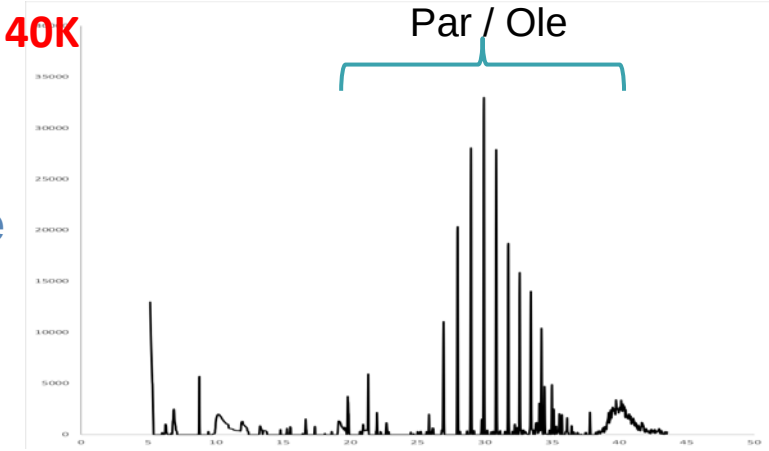
Thermal GC-MS 100–300 °C

- Chemical profiles between coal ranks much different
- Differences in scale consistent with relative mass loss measurements

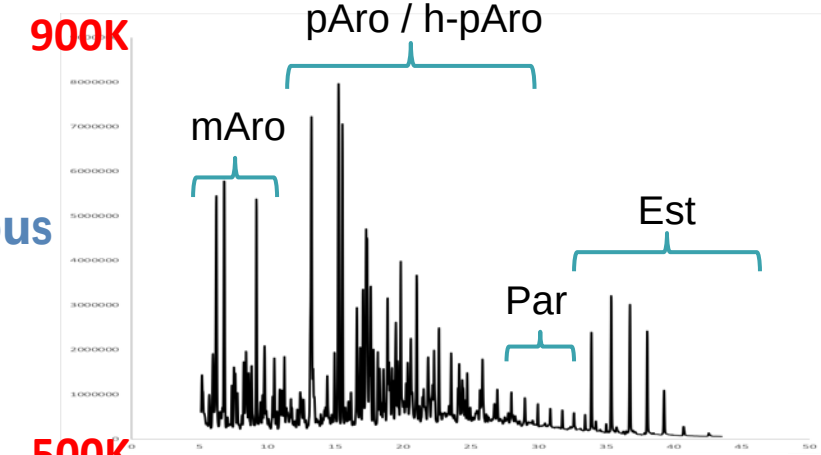
Key:

Ac	acetic acid
Est	esters
h-pAro	hydrogenated polyaromatics
mAro	monoaromatics
Ole	olefins
Par	paraffins
pAro	polyaromatics

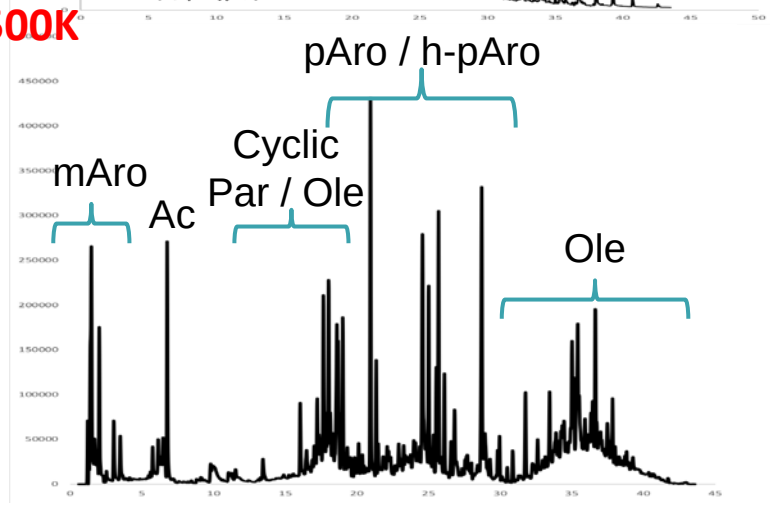
A: anthracite



C: bituminous



E: lignite



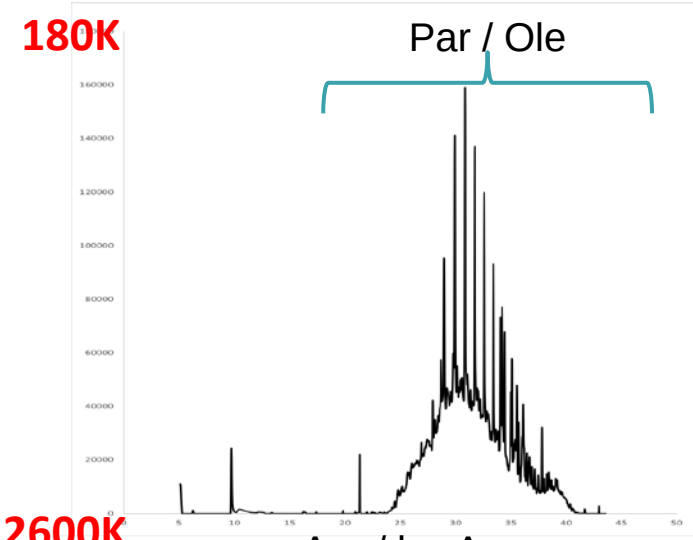
Pyrolytic GC-MS 550 °C

- Anthracite still comparatively stable compared with other ranks
- Count activity ~10× of thermal (100–300 °C) program, which matches trends seen with mass loss

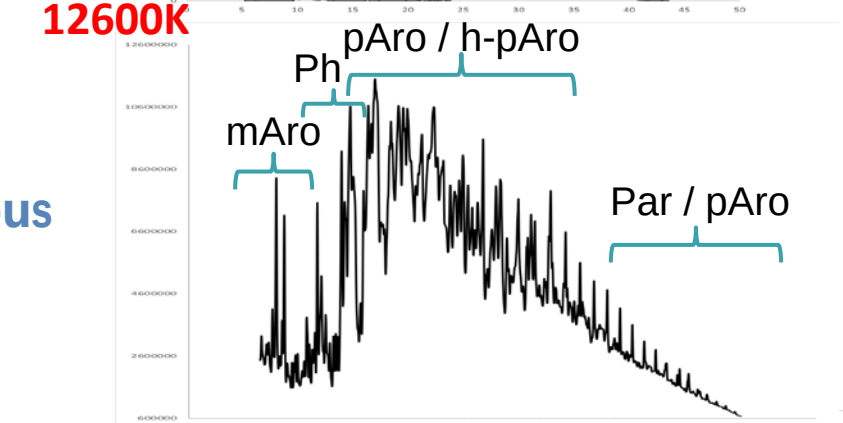
Key:

mAro	monoaromatics
h-pAro	hydrogenated polyaromatics
Ole	olefins
ox-pAro	oxygenated polyaromatics
Par	paraffins
Ph	phenols
pAro	polyaromatics

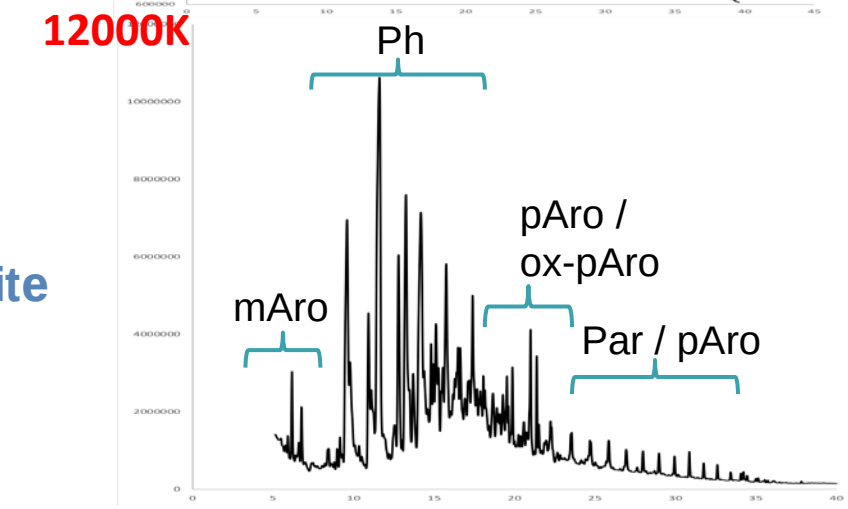
A: anthracite



C: bituminous



E: lignite



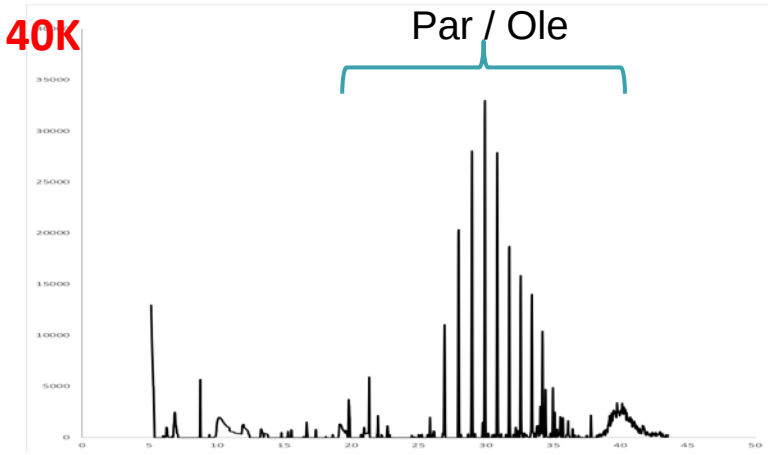
GC-MS temperature comparison

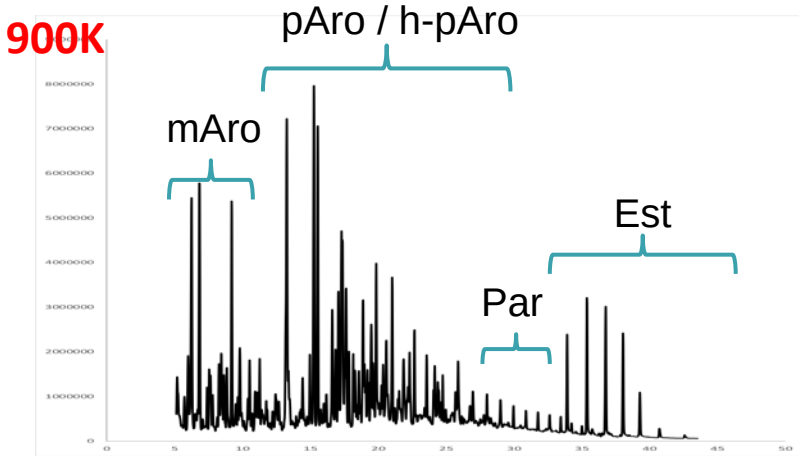
A: anthracite

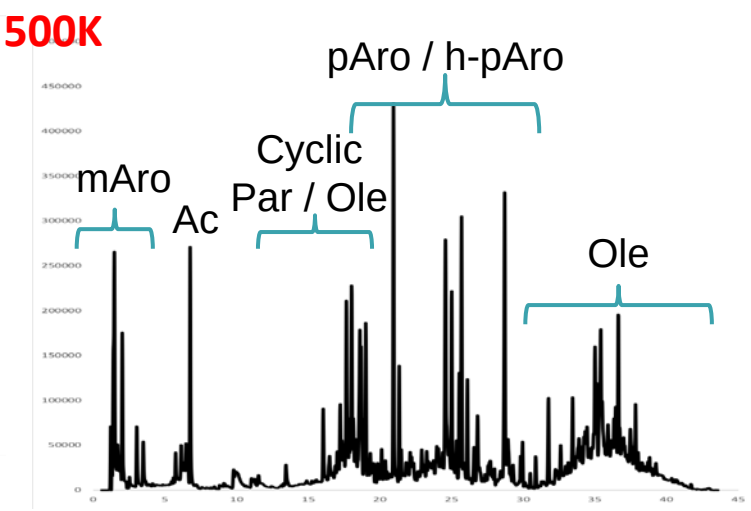
C: bituminous

E: lignite

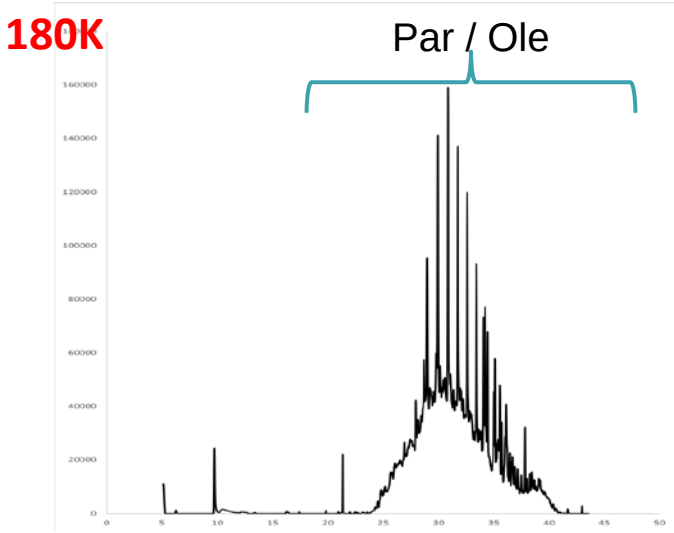
100–300 °C

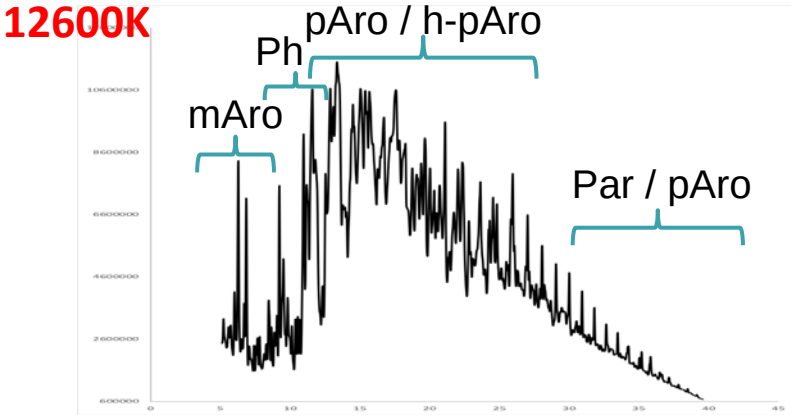


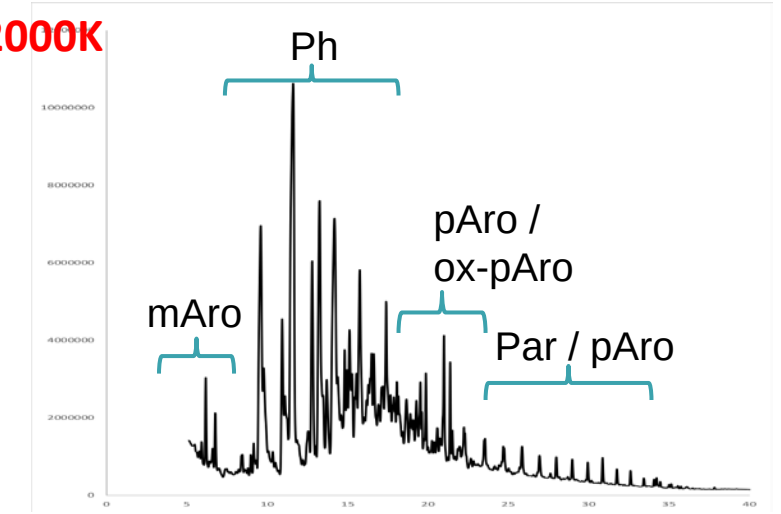




550 °C







Characterization continues to aid neutron analysis

- Purpose: relate changes seen in neutron images with chemical and structural changes in the coal under pyrolysis and gasification

- Methods
  - Proximate and ultimate analysis etc
  - Prompt Gamma-Ray Activation Analysis (PGAA)
  - GC-MS – over a large range of temperatures

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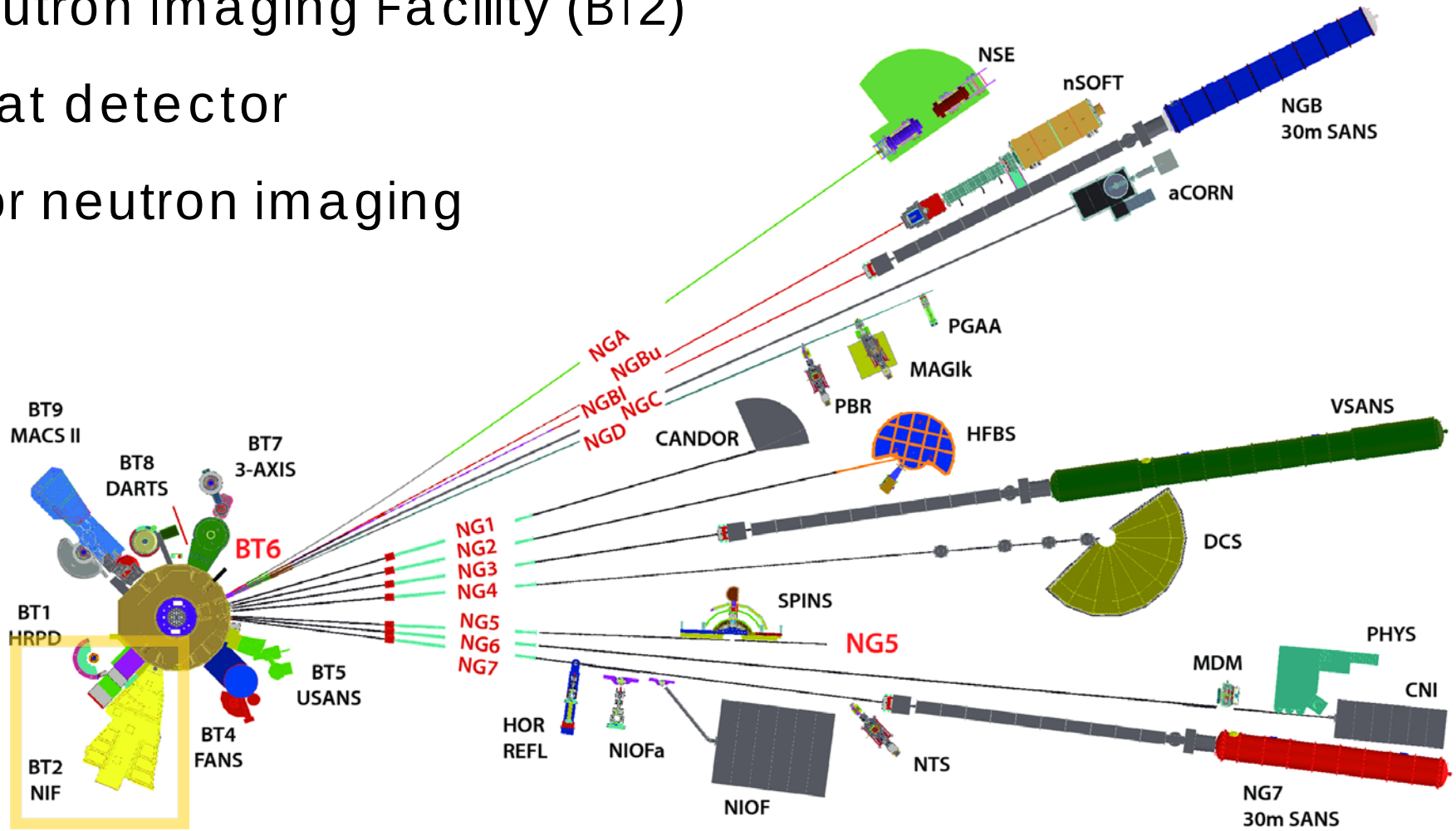
Neutron imaging

- Center for Neutron Research at the National Institute of Standards and Technology
- High Flux Isotope Reactor at Oak Ridge National Laboratory
- Spallation Neutron Source at Oak Ridge National Laboratory

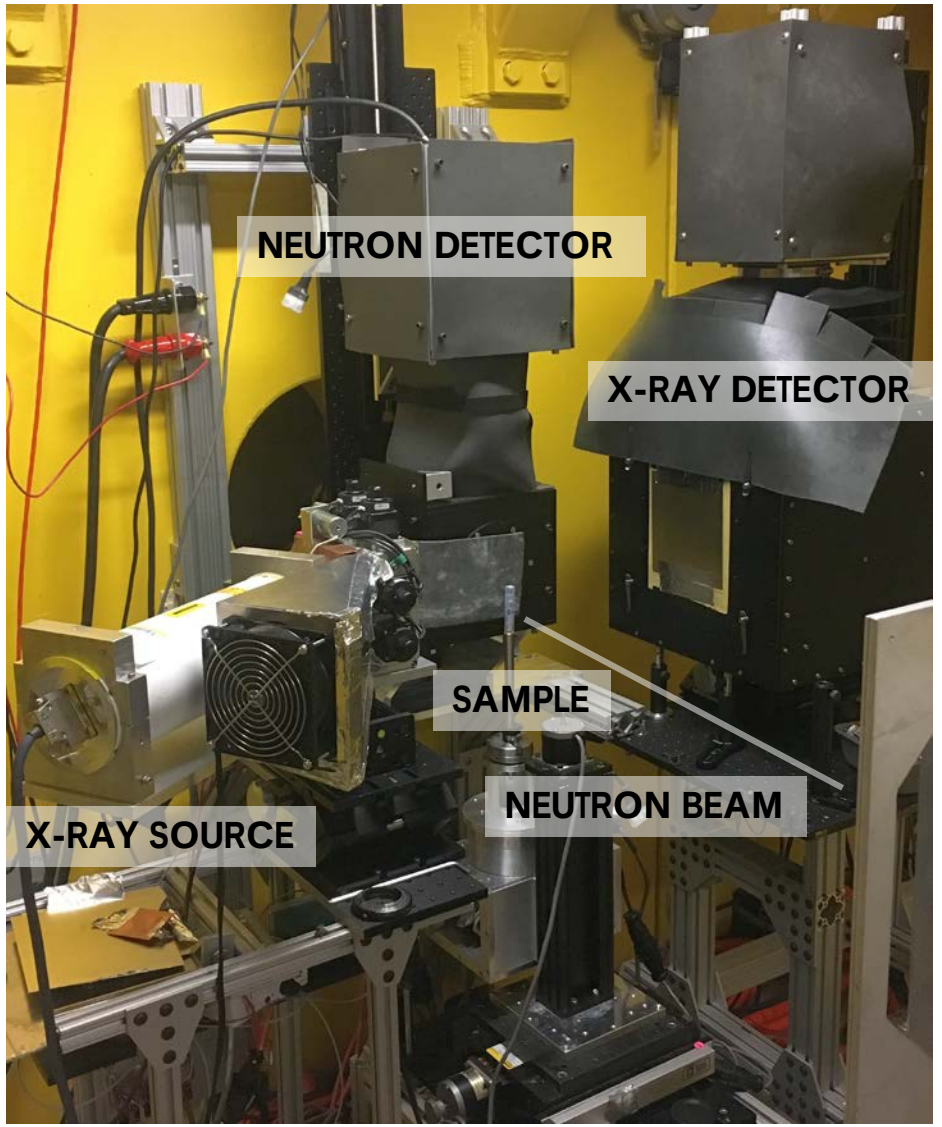
NIST Center for Neutron Research (Gaithersburg MD)

- NeXT – simultaneous neutron and X-ray tomography available at the Neutron Imaging Facility (BT2)
- ~ 10^6–10^7 n cm^{-1} s^{-1} at detector
- Gd-Ox scintillator for neutron imaging

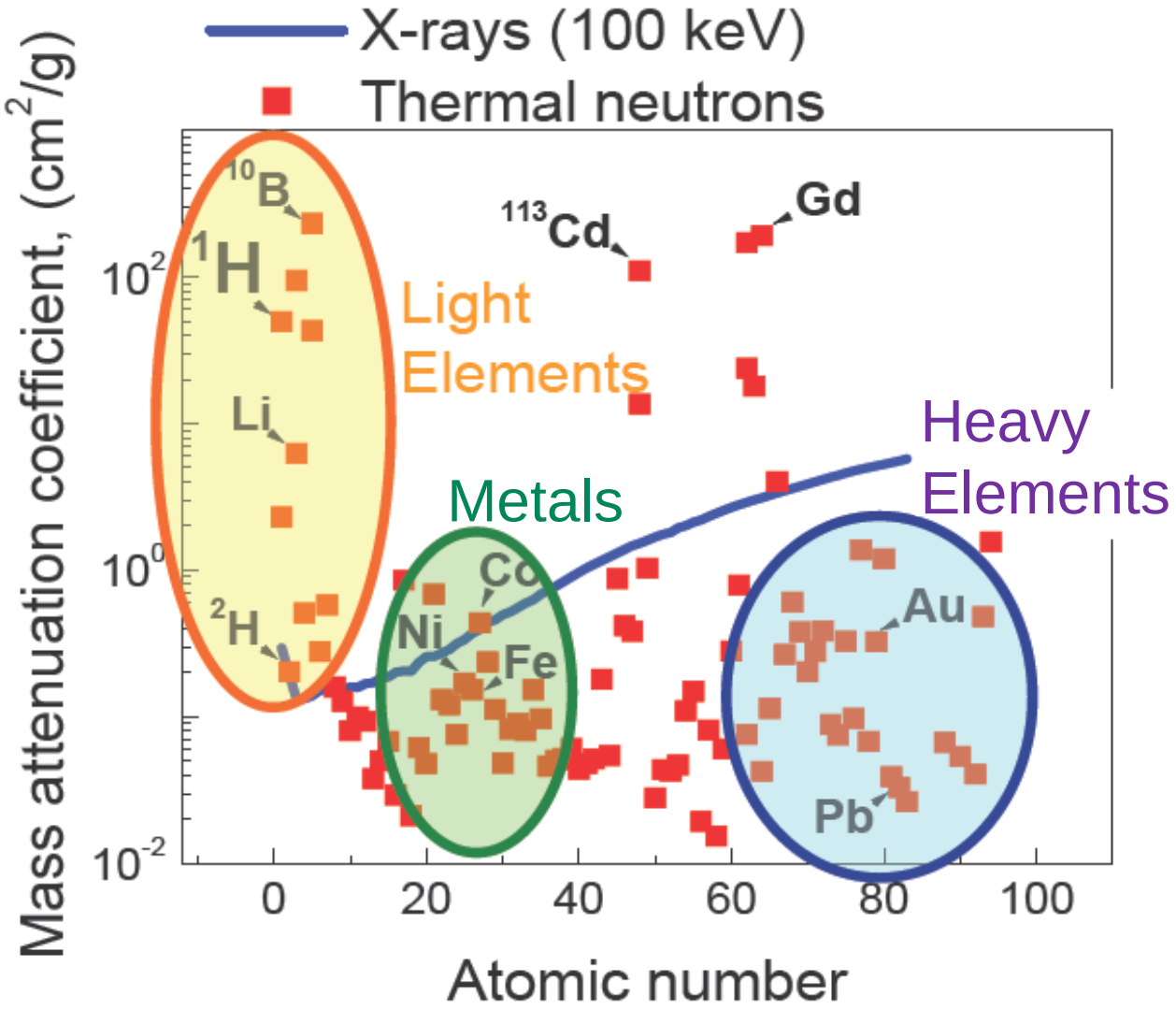


Overview of NCNR experiments

- Samples A–E
  - Unpyrolyzed (desiccated) (2)
  - Pyrolyzed at 200, 300, 400, 500, 600, 800, 1000 °C
  - Graphite (desiccated), as a standard
- Imaging
  - Radiography – 2D maps of transmission through samples
  - Tomography – neutron and X-ray CT for 3D maps of sample sets B and D



Neutron attenuation follows a complex relationship



Neutron interaction with light elements suggest that neutron imaging will be a suitable diagnostic to view pyrolysis and gasification *in situ*. This project will develop that capability.

Neutron attenuation for H >> attenuation for C

N. Kardjilov's presentation at IAN2006
http://neutrons.ornl.gov/workshops/ian2006/MO1/IAN2006oct_Kardjilov_02.pdf

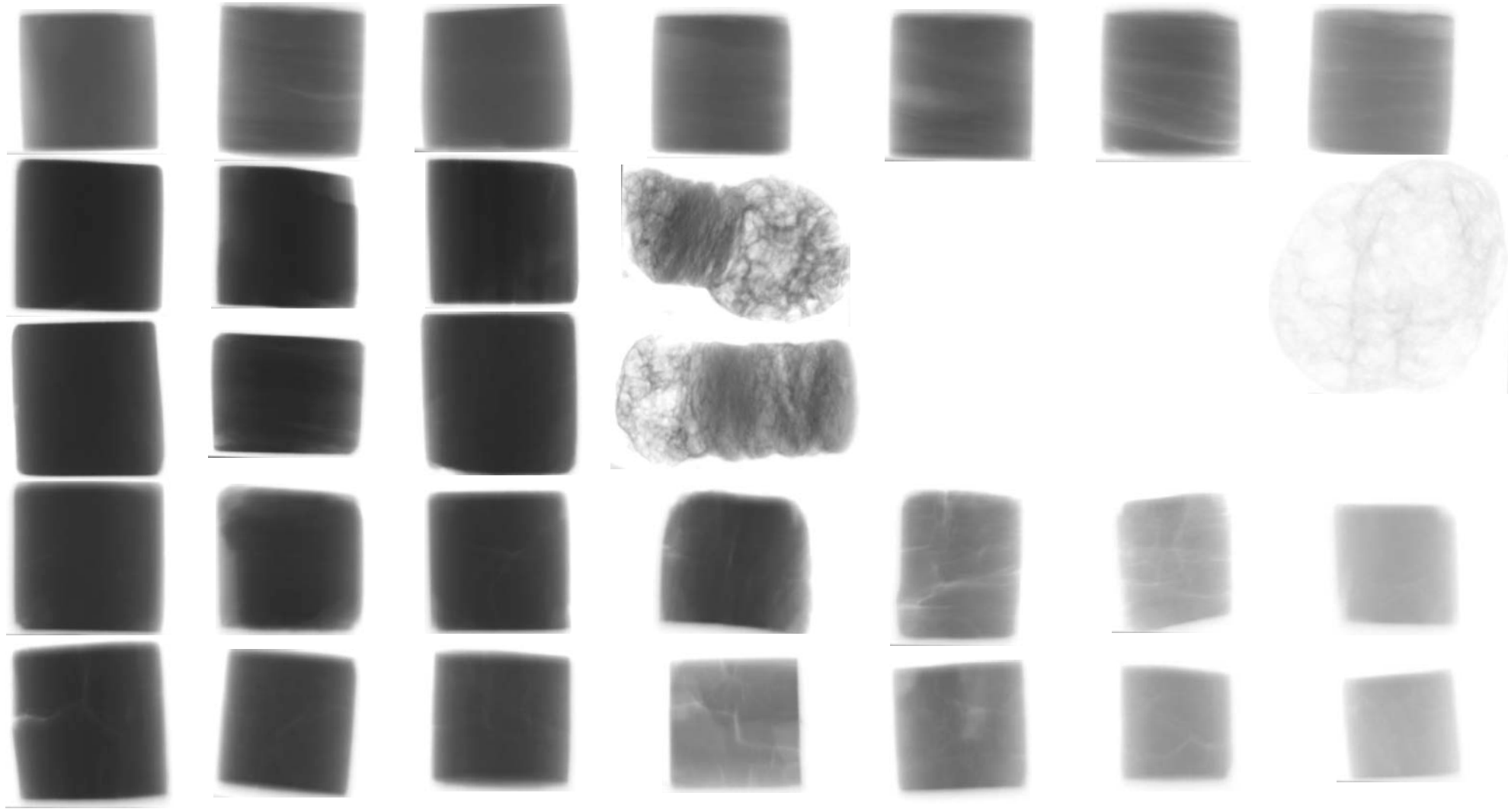
Samples were imaged in groups based on pyrolysis level

Photograph of samples in aluminum frame

Neutron radiograph of samples pyrolyzed at 200 °C

Samples wrapped in aluminum foil for containment.

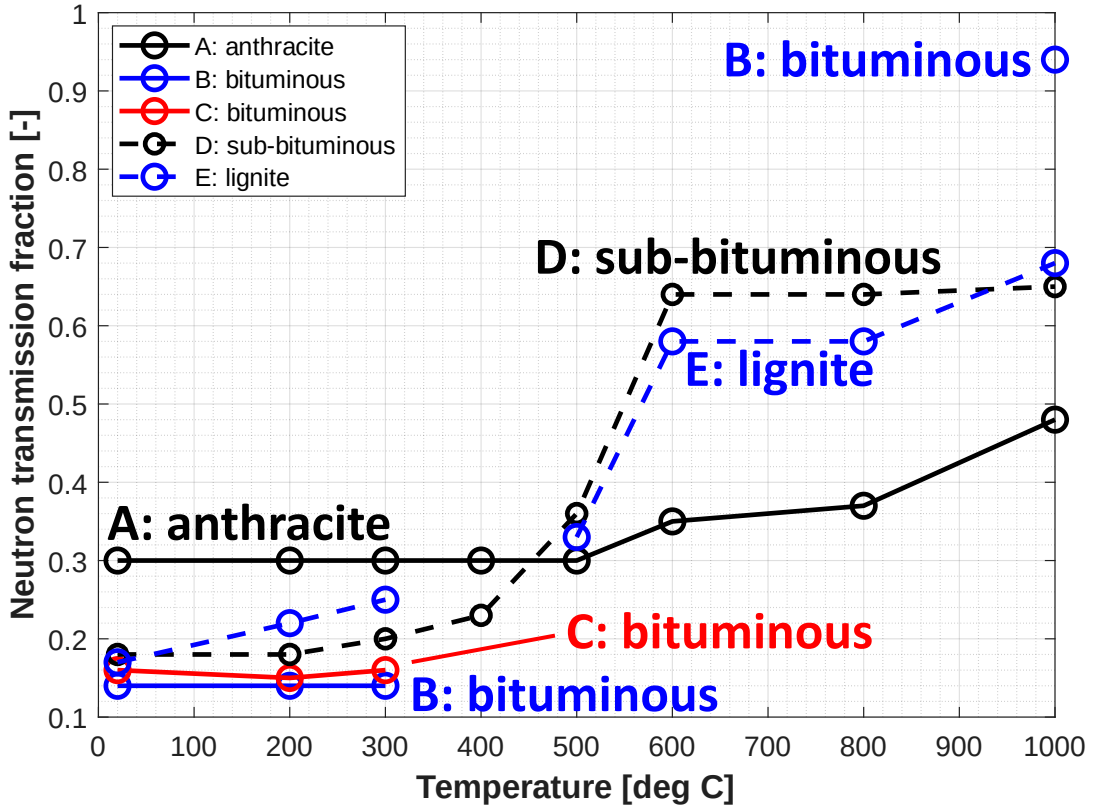
Radiographs show coal degradation with temperature



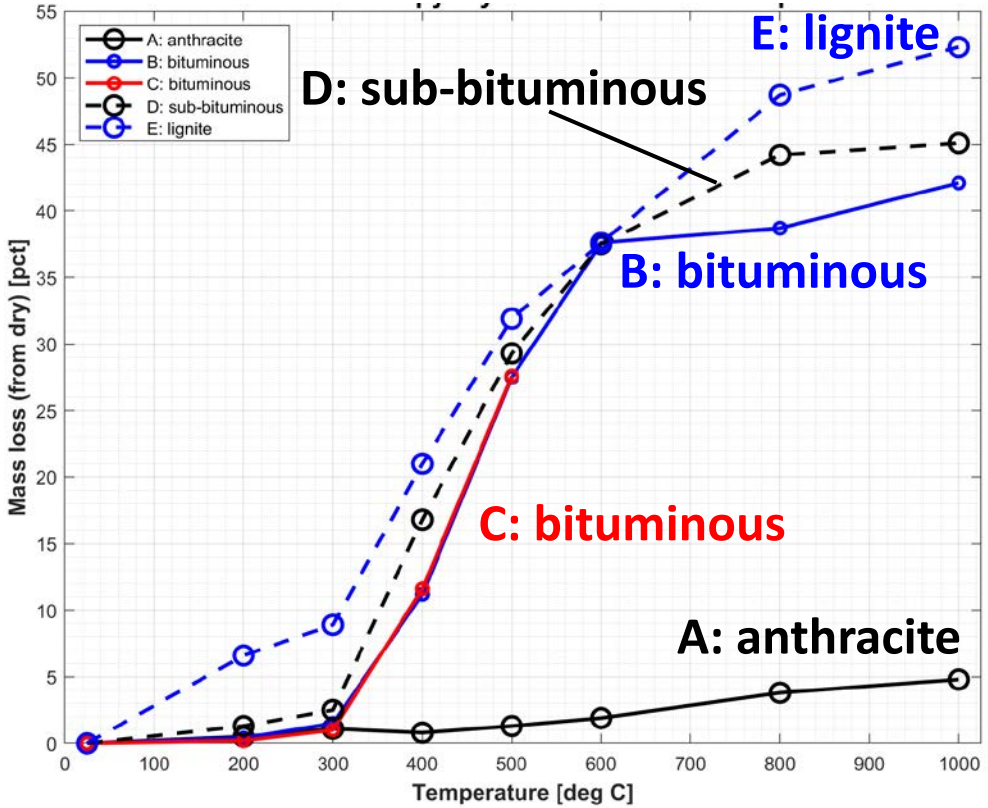
Relative image sizes approximate.

Neutron transmission increases with degree of pyrolysis

Neutron transmission / cm



Mass loss



Neutron interactions follow rough trends with mass loss, but there is a complex relation dependent on the pyrolysis chemistry.

Analytical chemistry characterization enables correlation of chemistry and neutron attenuation data

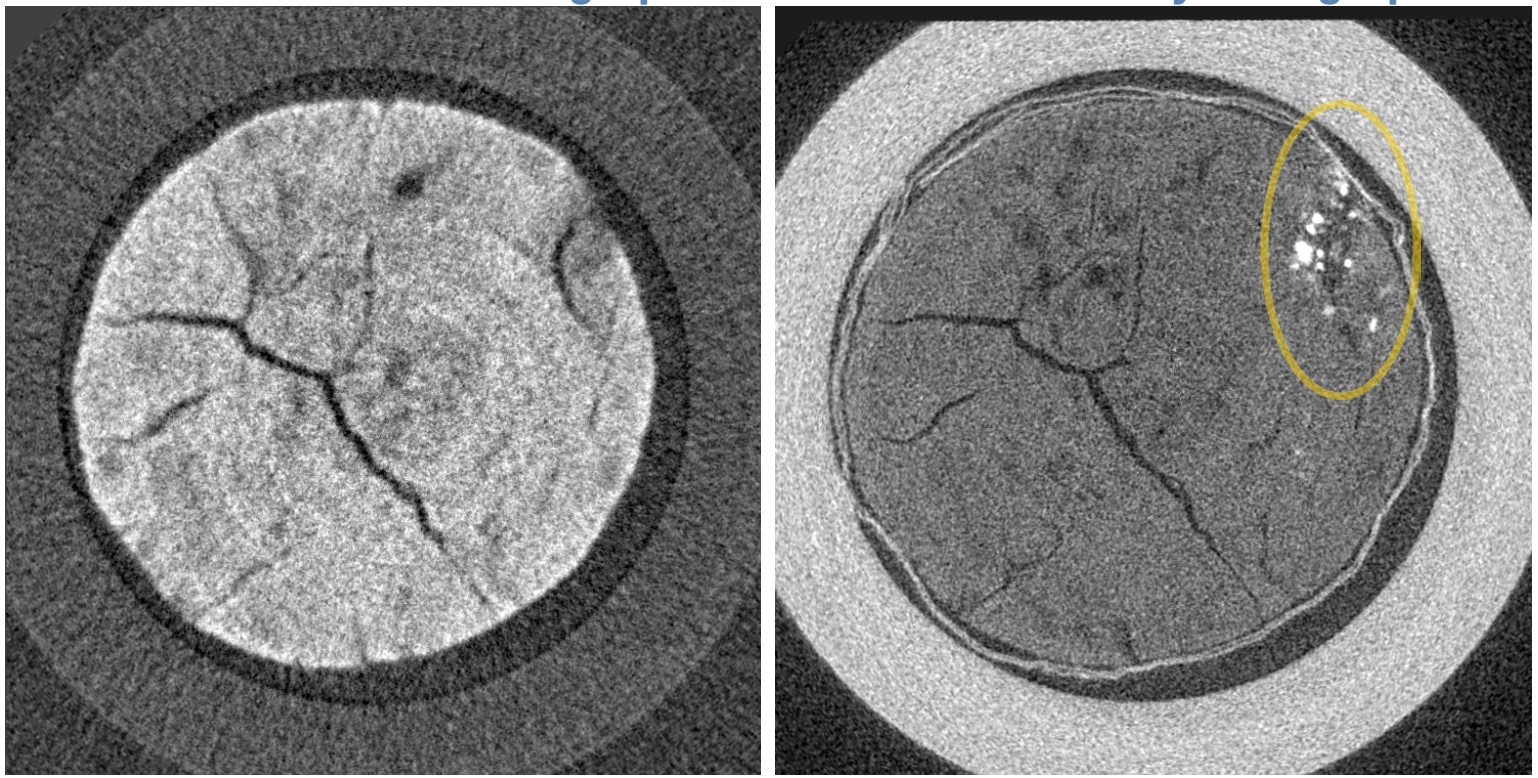
These data provide guidance for gasifier design and experiments in the neutron beam.

Neutrons and X-rays provide complementary information

- Simultaneous neutron CT and X-ray CT, volume-registered, allows direct comparison
- X-rays see features not seen by neutrons, and vice versa
- X-ray highlighted area probably mineral inclusions
- Al foil essentially transparent to neutrons

Slice from neutron tomograph

Slice from X-ray tomograph



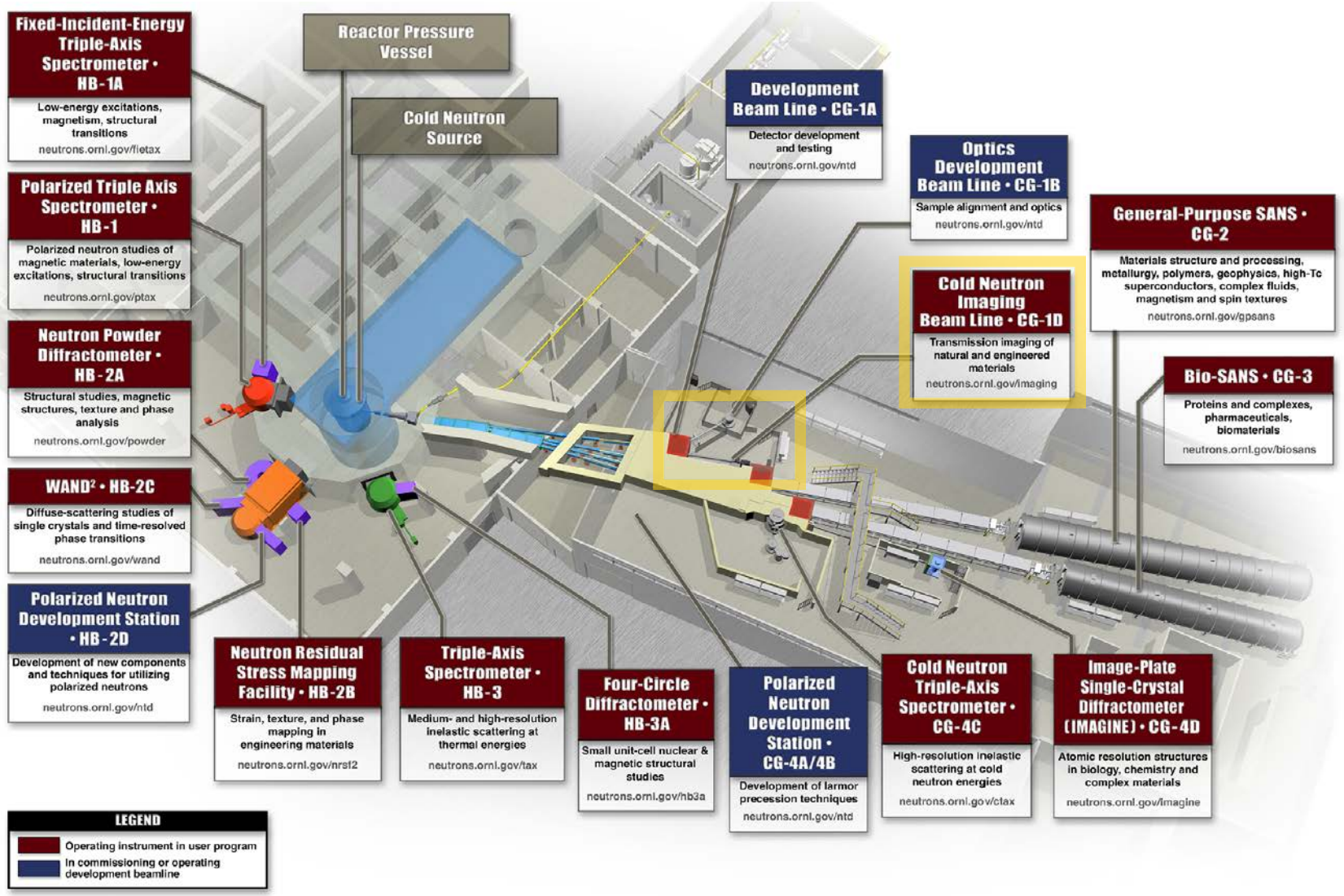
D: sub-bituminous

Both images contrast-enhanced here for display visibility

Details of particle morphology are important for understanding particle consumption and/or fracture during gasification

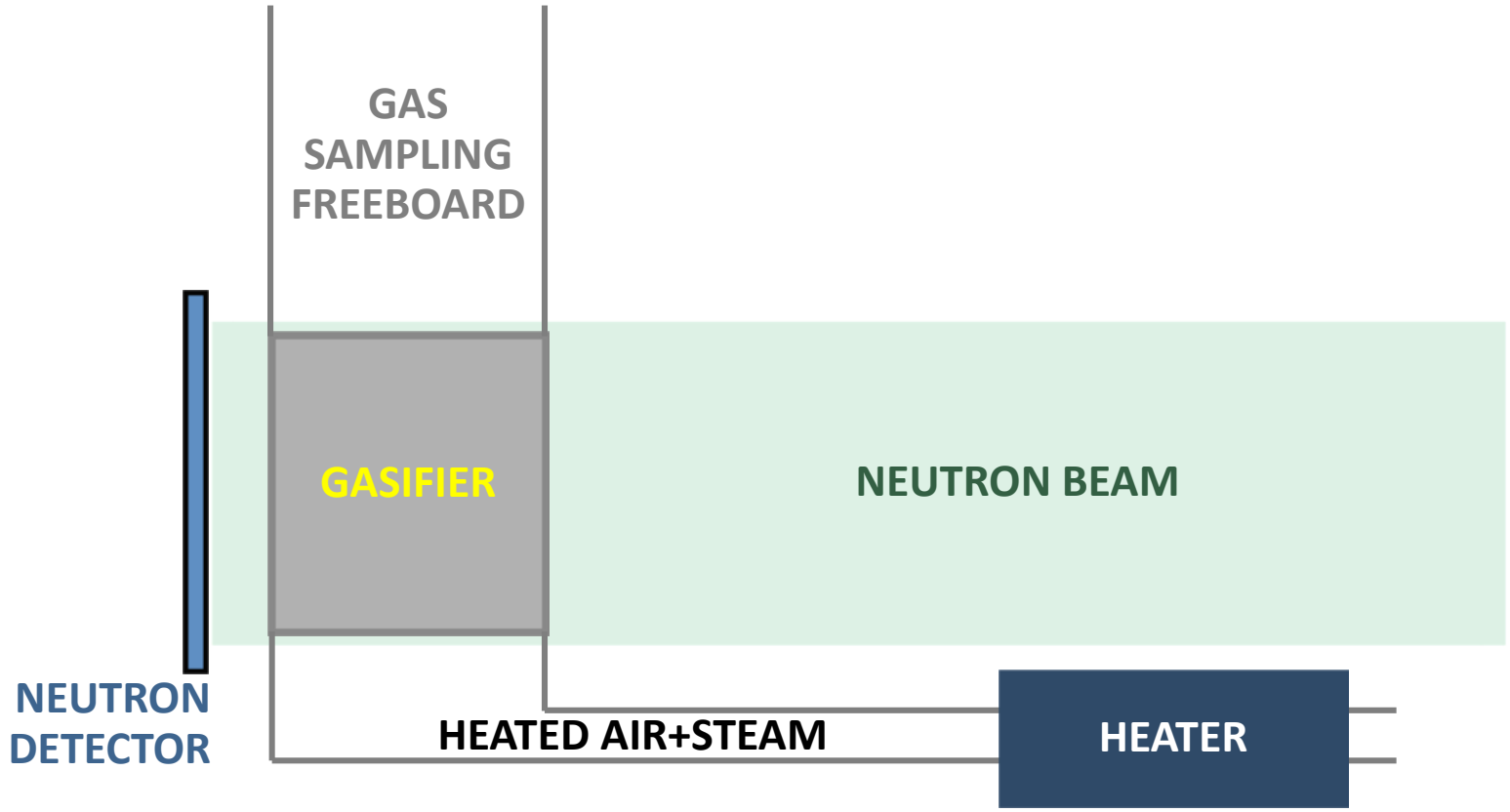
High Flux Isotope Reactor (Oak Ridge National Laboratory)

- Highest flux reactor-based source of neutrons for research in the US
- Imaging Beamline (CG-1D)
- Flux ~ 10^6–10^7 n cm^{-1} s^{-1} at detector
- ^{6}LiF scintillator or Micro Channel Plate detector for neutron imaging



Future Work: Overview of HFIR experiments

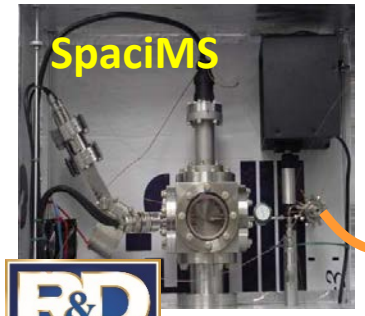
- Simultaneous neutron and gas emissions measurements during gasification
- Nonintrusive measurements for model validation
  - 2D map of gasification progress
  - Correlated product stream composition

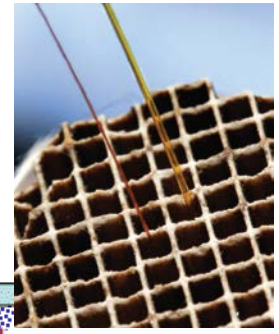


Future Work: Spatio-temporal Gas Emission Measurements

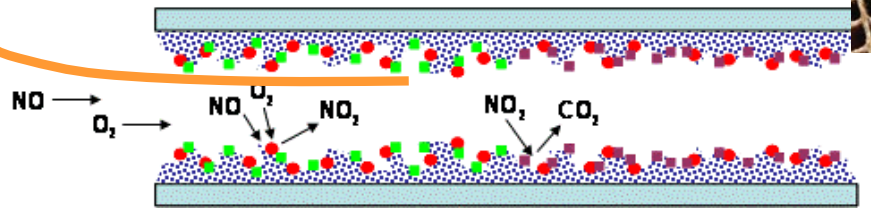
- As research moves from pyrolysis focus to gasification focus, will shift gas species experimental focus from detailed hydrocarbon chemistry to light gas products (CO, H_2, etc.)
- Will utilized SpaciMS technique to give both spatial and temporal data on emissions

SpaciMS technique developed at ORNL provides unique insight into gas chemistry in reactors



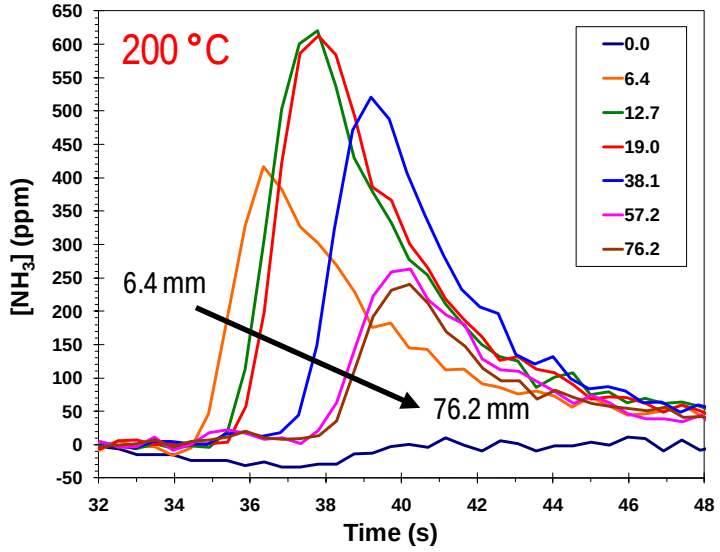


Lean NOx Trap emission control catalyst



Insights from emission control catalyst experiments have strengthened models through better understanding of

- Intermediate roles of NH_3
- Spatial distribution of NO_x



Conclusions

- Neutrons offer ability to see into reactor and observe gasification process *in situ*
- Complex relationship of neutron attenuation and mass loss
  - Dedicated experiments using multiple analytical chemistry techniques under controlled conditions enable mapping neutron attenuation data to chemical changes in the coal
- Coal of different ranks gave widely varying results as expected with additional complexity due to morphological changes in bituminous coal during the pyrolysis process
- Work is progressing from pyrolysis to gasification

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Backup slides

Determining elemental composition of pyrolyzed coal using Prompt Gamma-Ray Activation Analysis (PGAA)

- PGAA is a nondestructive technique for quantifying elemental composition of samples
  - Samples irradiated by cold (≤ 25 meV) or thermal (25 meV) neutrons
  - Nuclei in sample capture neutrons and emit characteristic prompt gamma rays upon de-excitation
  - Energy spectra of emitted gamma rays enables identification of neutron-capturing elements in sample
  - Peak intensities in spectra provide method for quantifying elemental concentrations; quantity determined from ratio of count rate of characteristic peak in sample to count rate in known mass of elemental standard when irradiated under identical conditions

Detection limits (minimum concentrations) for elements of interest in samples of coal (24-h measurement interval)

Elements	Approximate Detection Limits [ppm]
H, Cl	0.1 – 1
Na, S, K, Ti	1 – 10
Mg, Al, Si, P, Ca, Fe	1 – 100
C, N	100 – 1000

PGAA identifies elements remaining in coal sample during pyrolysis, which comprise the particles to be imaged with neutrons