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Elucidating Arsenic and Selenium Speciation in Coal Fly Ashes

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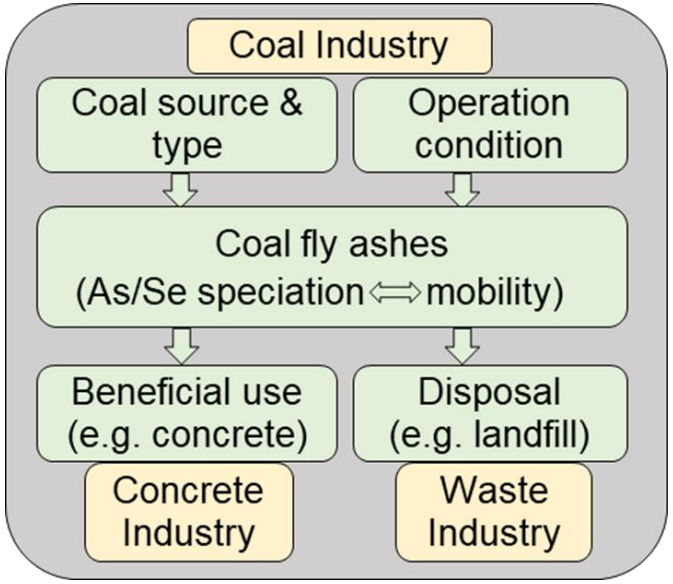
Background

Recent EPA CCR and ELG regulations – First federal boundaries on the amount of toxic metals (e.g. Hg, As, Se, Cr) and other pollutants that steam electric power plants are allowed to discharge to their waste streams (e.g. bottom ash, fly ash, FGD purge).

Addressing compliance with these regulations can present a significant financial and environmental burden to the coal industry.

Challenges and project objectives

- To systematically characterize As and Se speciation within a representative matrix of coal fly ashes.
- To develop a comprehensive correlation and database for coal source/type, generation condition, As/Se speciation, and As/Se mobility.



- What is the speciation of As and Se in coal fly ashes? **Characterization**
- How do coal source/type and utility operation conditions affect As/Se speciation? **Survey**
- How do As/Se speciation affect their subsequent mobility? **Mobility**

Survey study

- A survey of fossil power generating units as a function of coal source/type, operating conditions, environmental control systems, additive use, and fly ash handling methods
- Representative subset of candidate units to collect fly ash samples from existing particulate control devices, such as electrostatic precipitator (ESP) and fabric filter (FF).
- A matrix of coal feedstock sources/types, boiler designs, upstream environmental control systems/operation modes, as well as the use of additives and sorbent injection for the removal of acid gases and specific trace metals (e.g. Hg, As)

Characterization: Multi-scale approach

Elemental composition
Surface area, particle size, and porosity
Particle morphology
Mineralogical composition

Oxidation state, structure, elemental association: Synchrotron X-ray microscopy and spectroscopy

Mobility: EPA Toxicity Characteristic Leaching Procedure

Mobility and phase: Sequential chemical extraction

Project Update – Survey study and sample collection

Scope of Work:

- Survey of latest U.S. Electrical Generating Units (EGUs) in operation
- Identification of Samples for Analysis
- Sample collection from selected sites

Survey of Current Operating Plants

- Objective: Determine the current outlook of Coal-Fired EGUs generating fly ash across the U.S. according to:
  - Capacity
  - Coal rank(s) burned
  - Installed emission controls: NOx, SOx, PM, Hg
- Compilation and cross-check of various databases
- Focus on EGUs >90MWg nameplate capacity

U.S. Coal Fields from USGS to identify major coal regions

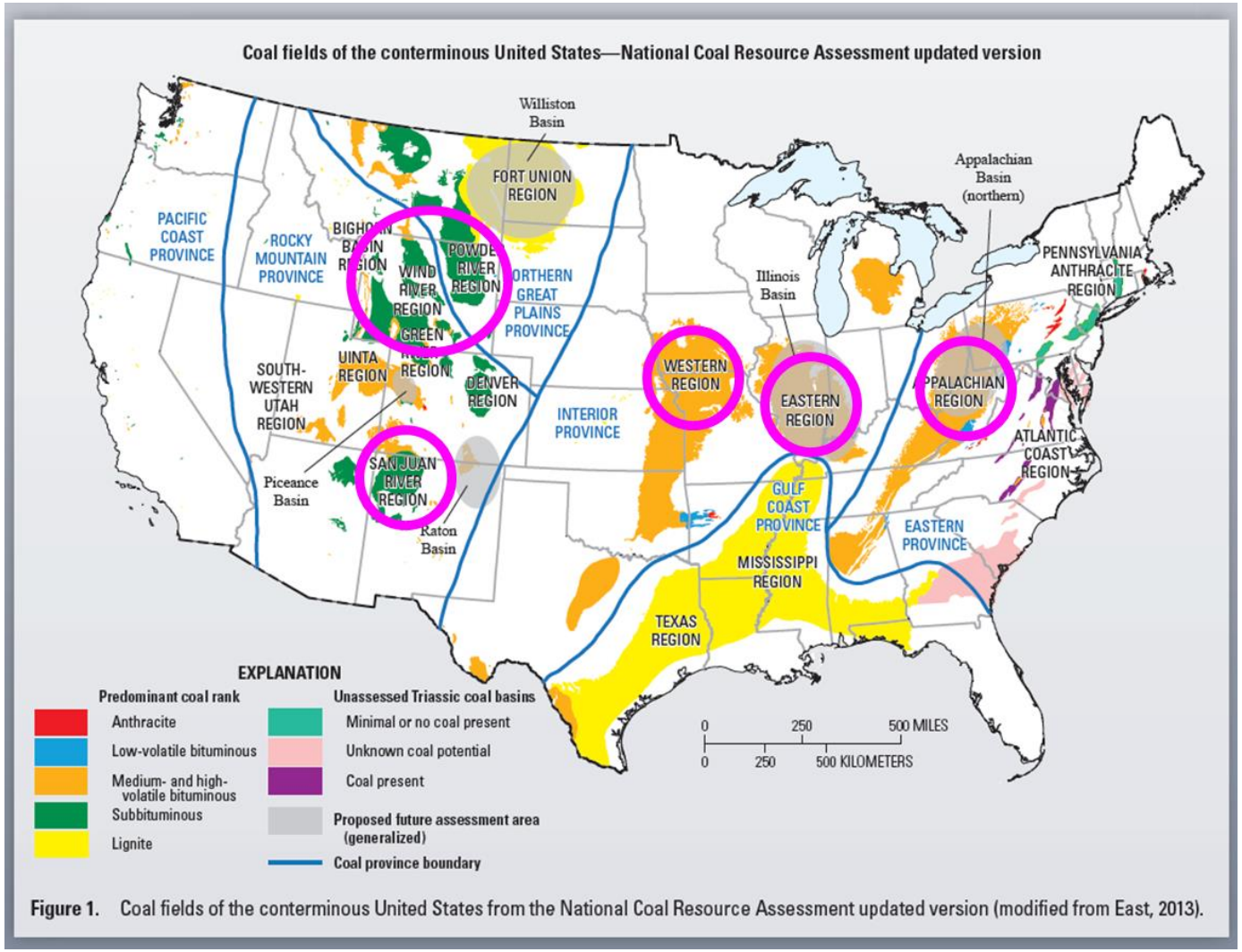
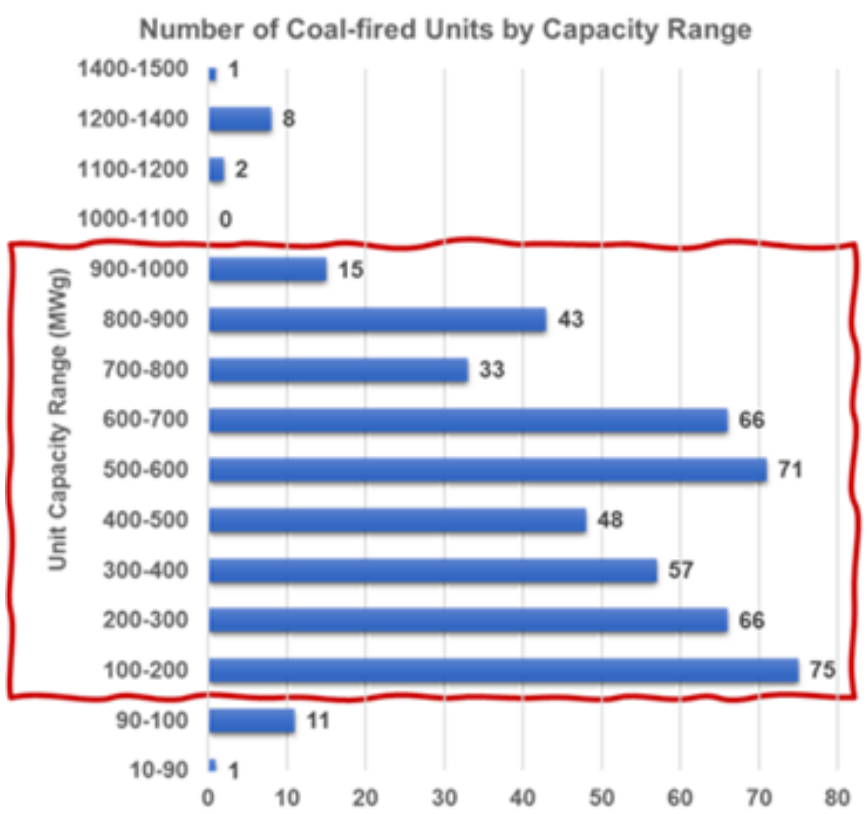
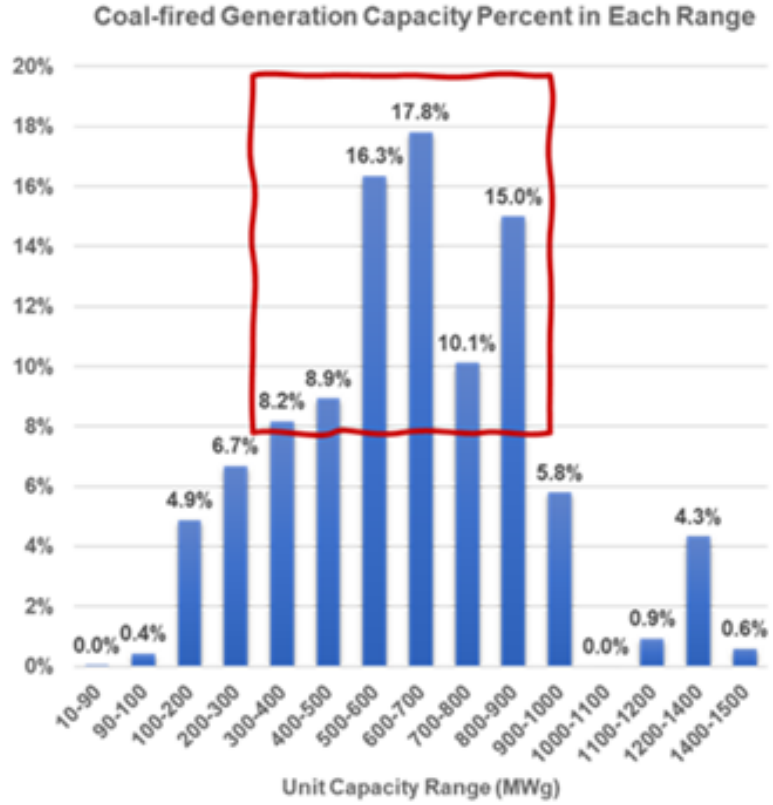


Figure 1. Coal fields of the conterminous United States from the National Coal Resource Assessment updated version (modified from East, 2013).

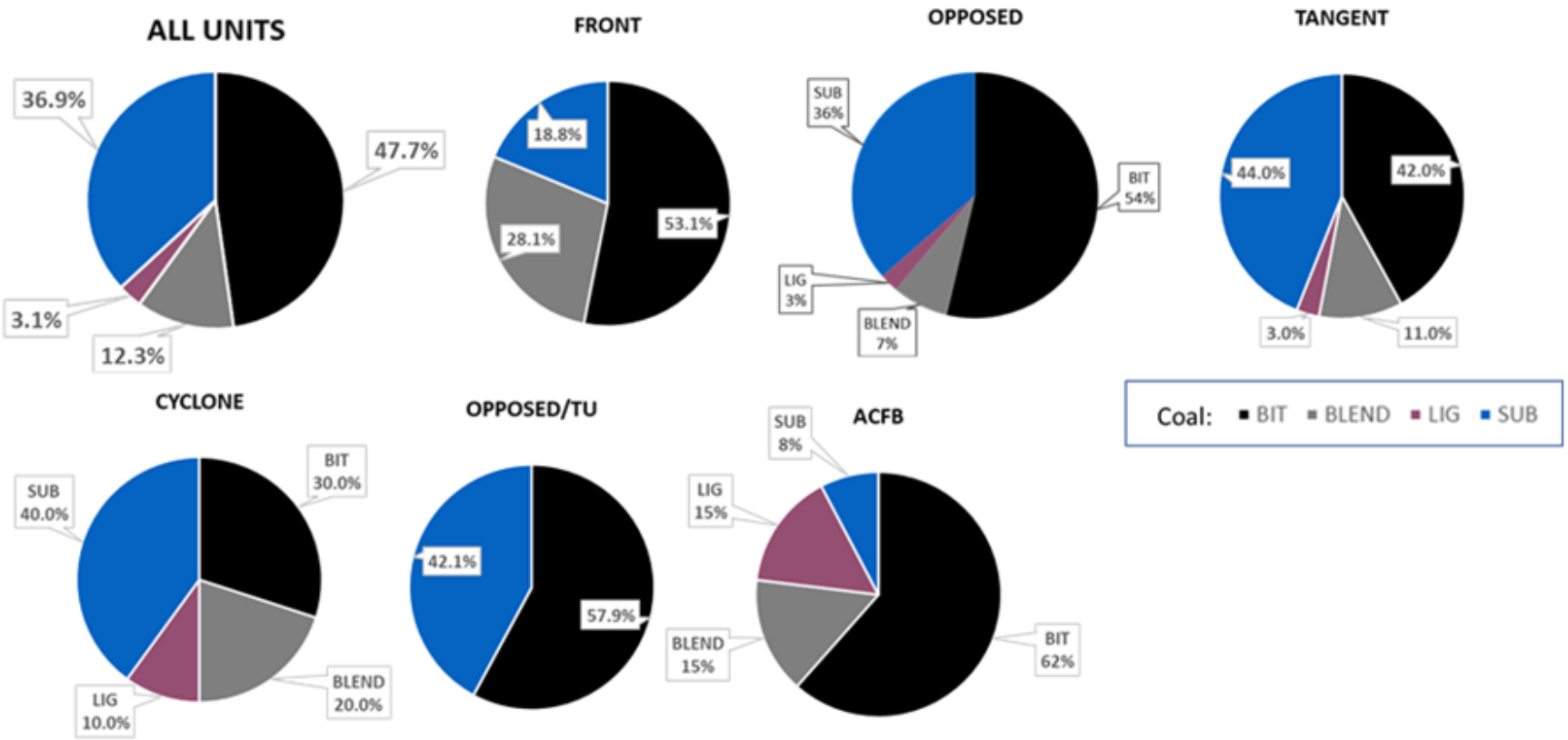
Source: USGS Fact Sheet 2017-3067

Overview of Coal Fired EGUs by Capacity





Overview of EGUs by Furnace Burner Design



Preliminary Samples for Consideration

Grab samples collected at PM Control Collection Hoppers

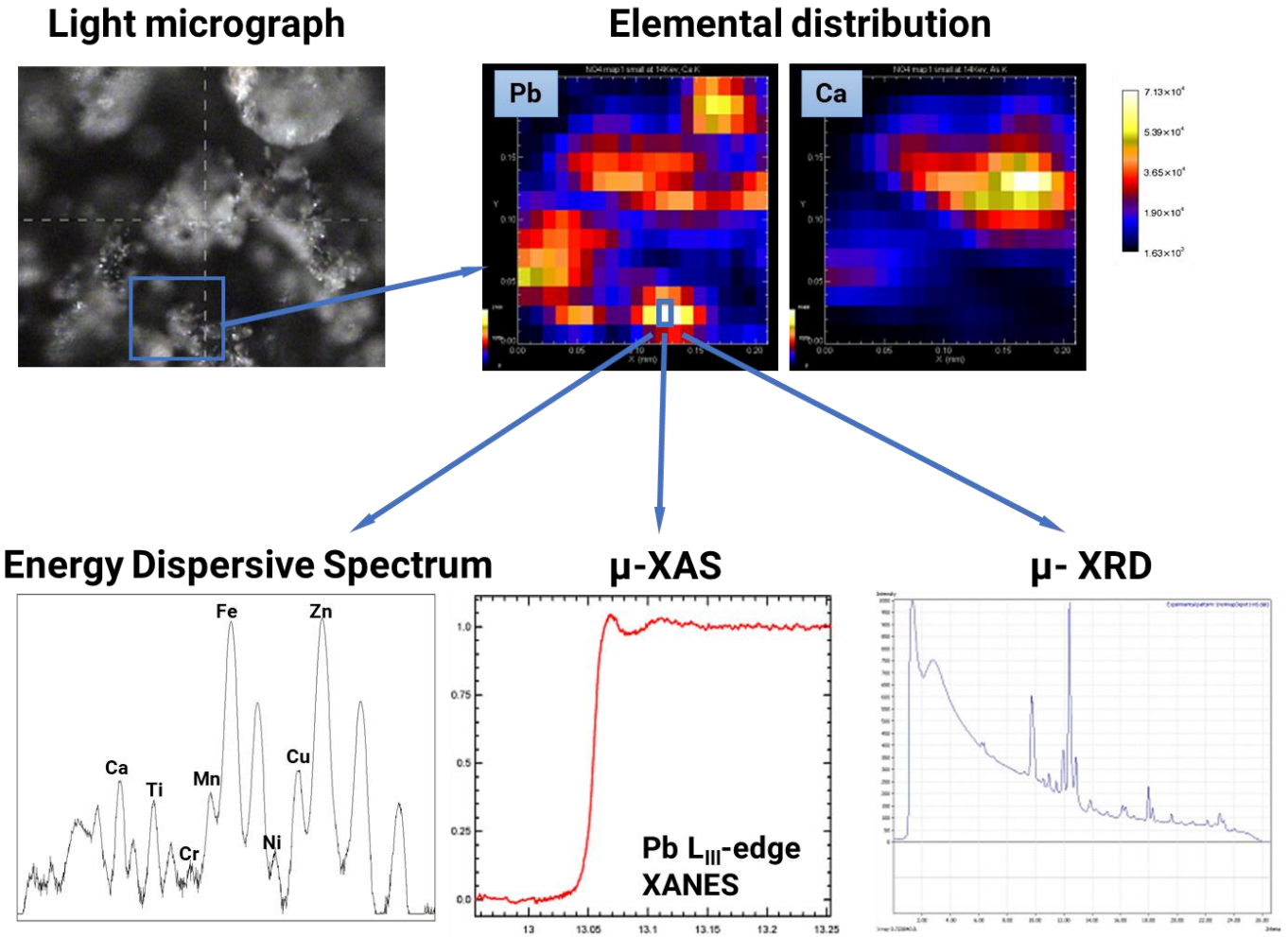
Summary of survey work and sample collection

- Database compilation and summary completed
- Database analysis and reporting is ongoing
- Initial samples collected given opportunity to do so which is limited by COVID restrictions

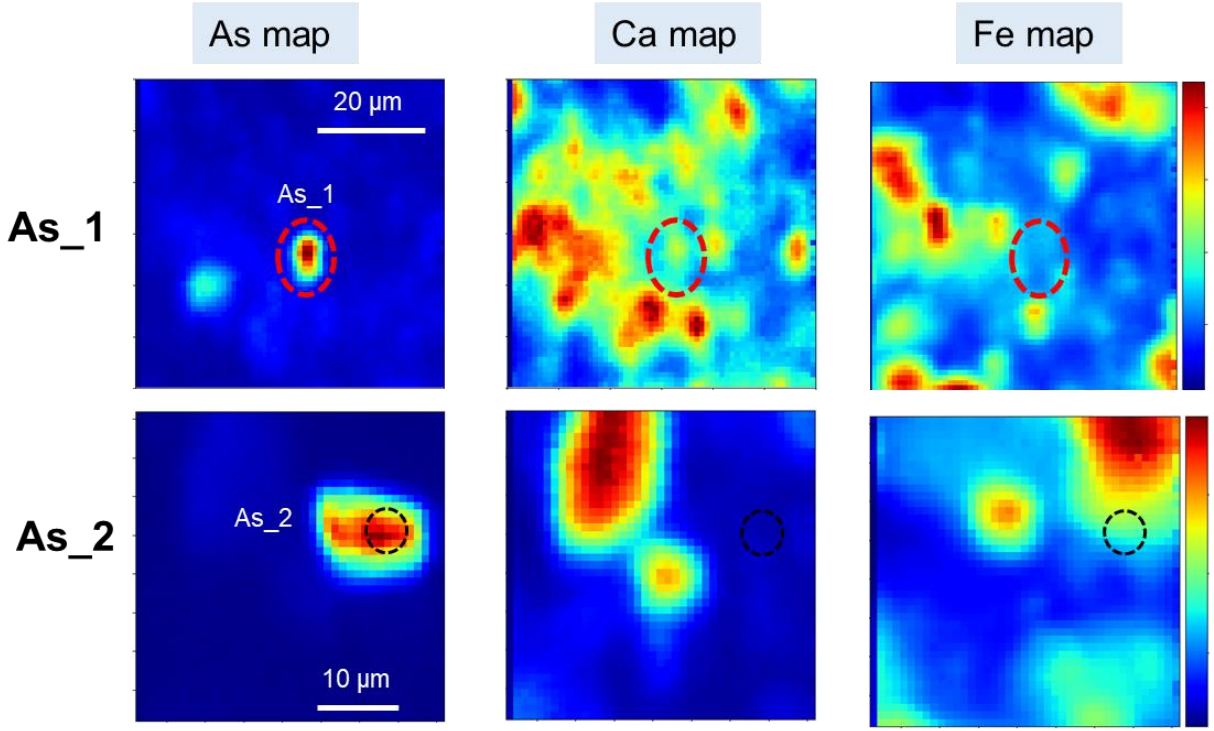
- Further sample identification and collection is ongoing

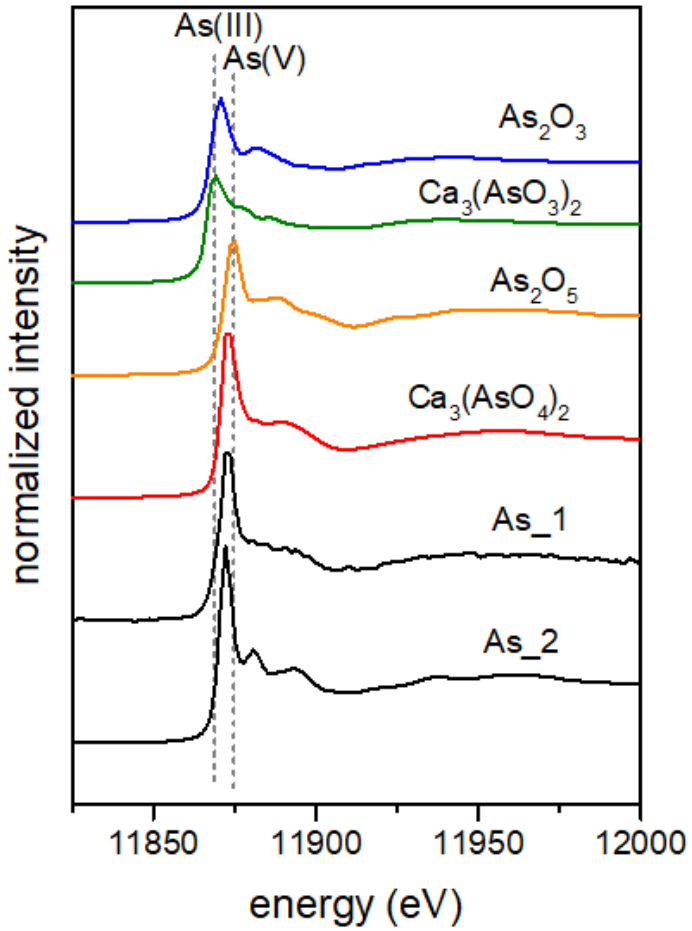
Project update – Synchrotron analysis

- As and Se X-ray absorption near edge structure (XANES) spectroscopy: bulk scale oxidation state, local structure, and phase
- Micro-X-ray fluorescence Imaging (μ-XRF): element distribution and correlation
- μ-XANES: micro-scale oxidation state, phase, and structure information



As XRF map and μ-XANES





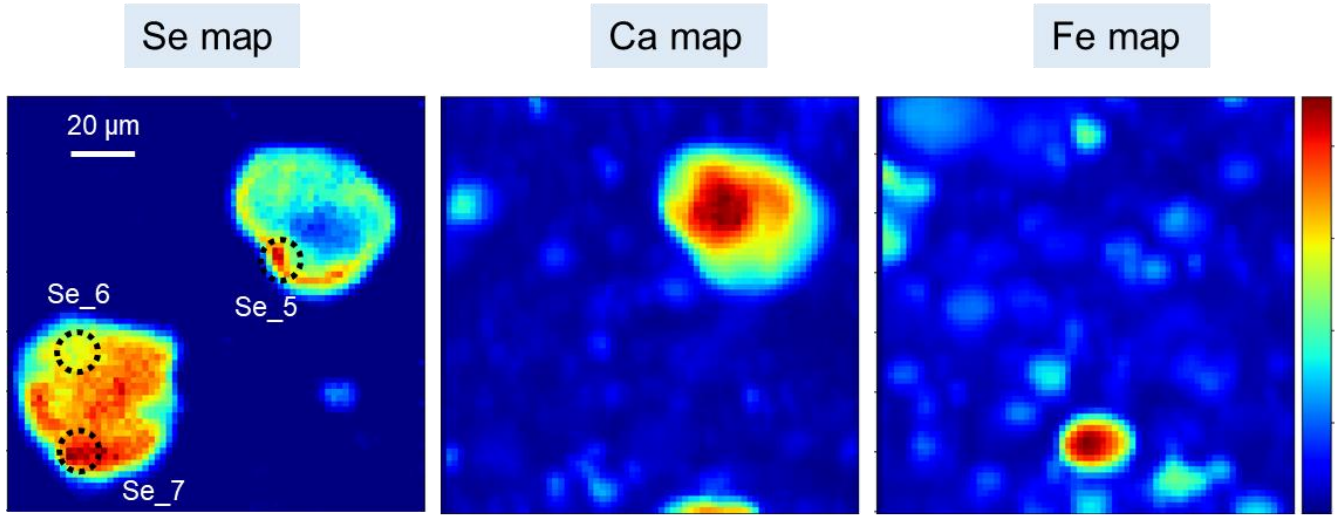
As_1:

- 10 μm x 5 μm particle
- As co-localized with Ca
- 20% As(III) and 80% As(V)

As_2:

- 10 μm x 10 μm particle
- As co-localized with Fe
- 25% As(III) and 75% As(V)

Se XRF map and μ-XANES



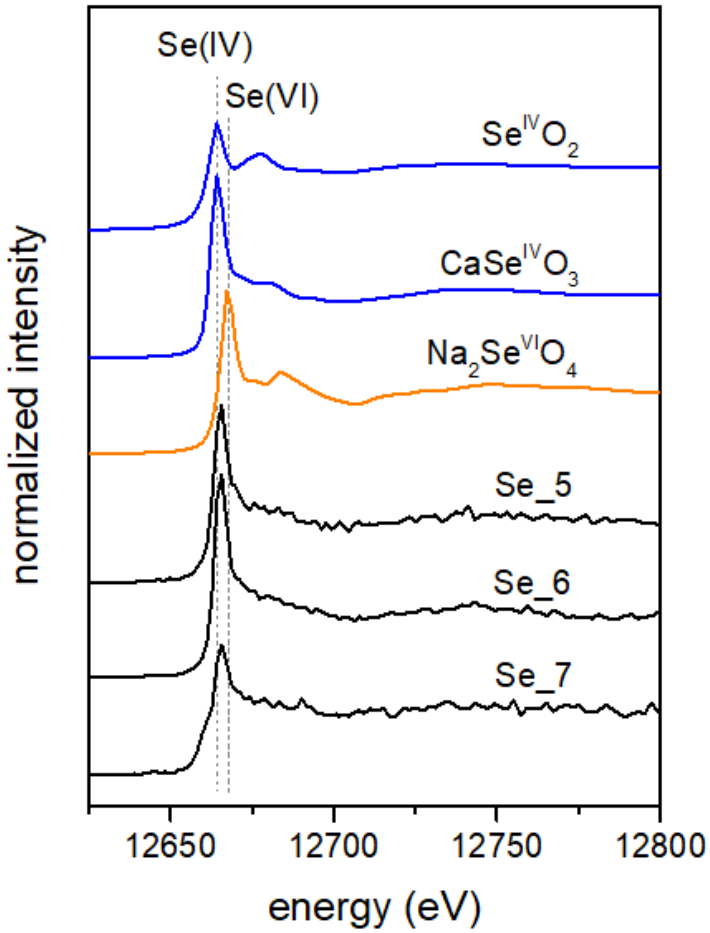
Particle size: two 40 μm x 40 μm particles

Se distribution:

- Se enriched on the surface of a Ca-rich particle
- Discrete Se-bearing particle with no other elements detected

Se oxidation:

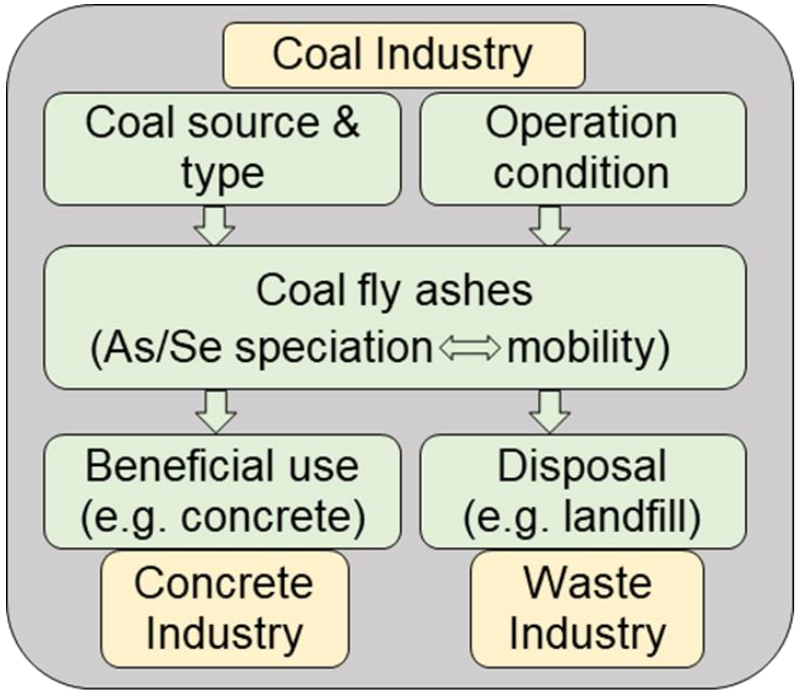
- Se_5: ~70% Se(IV) and ~30% Se(VI)
- Se_6: ~40% Se(IV) and ~60% Se(VI)
- Se_7: ~65% Se(IV) and ~35% Se(VI)



Next Steps

- Survey and sample collection: continue sample identification and collection
- Sample characterization: Composition, surface area, particle size, morphology, mineralogy
- As/Se speciation: synchrotron analyses
- As/Se mobility: leaching tests

Concluding Remarks



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