Project # DE-FE0031739

Elucidating Arsenic and Selenium Speciation in Coal Fly Ashes

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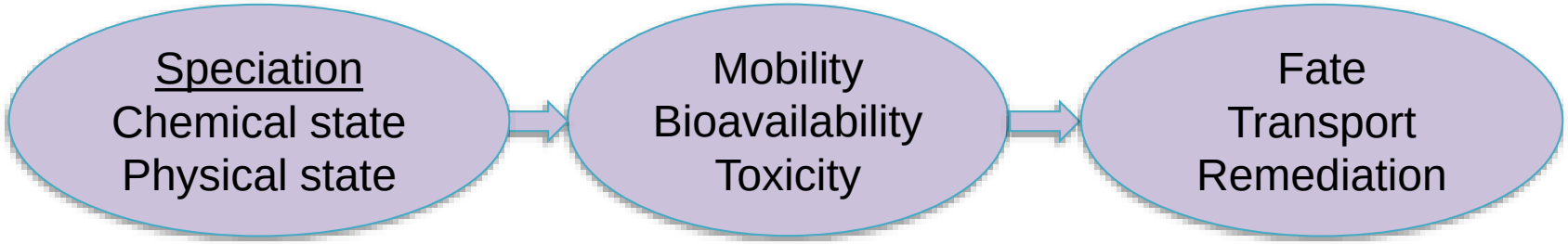
Research background

- 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.

- Toxic metals: total content vs. speciation



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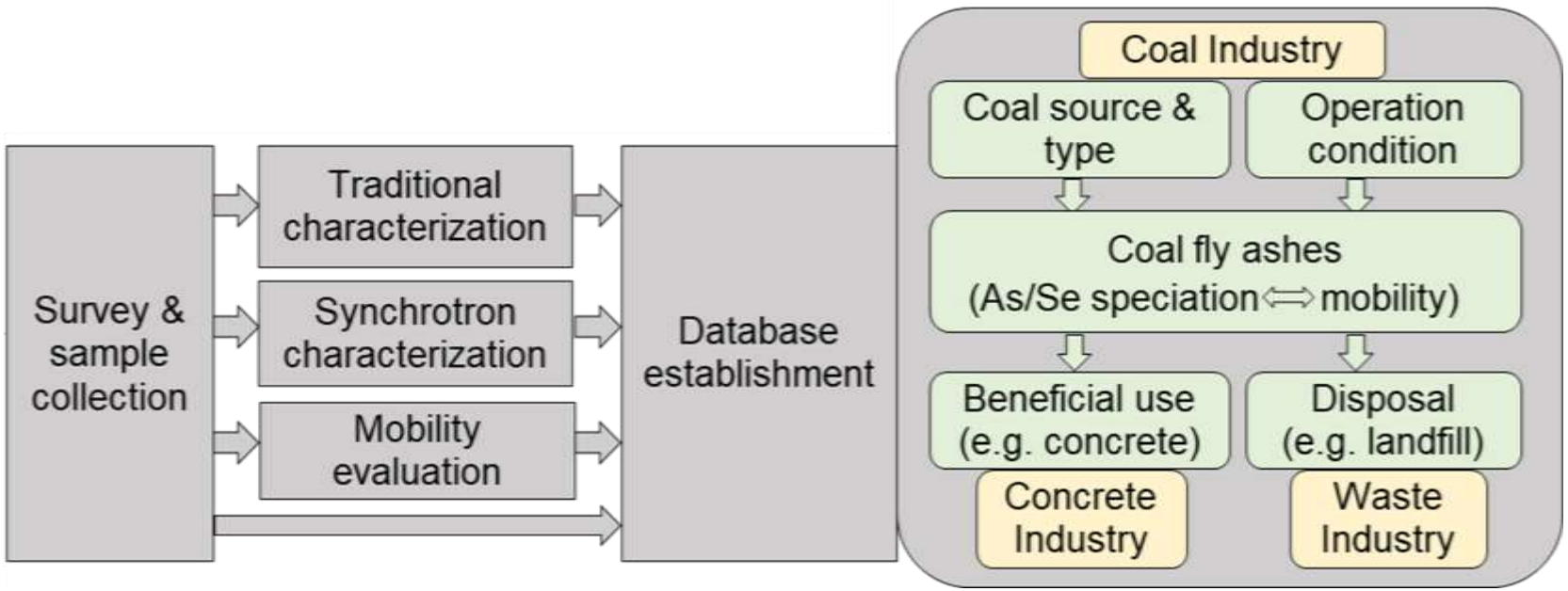
Project goals

- To systematically characterize As and Se speciation within a representative matrix of coal fly ashes.

- To develop correlations for coal source/type, generation condition, As/Se speciation, and As/Se mobility.



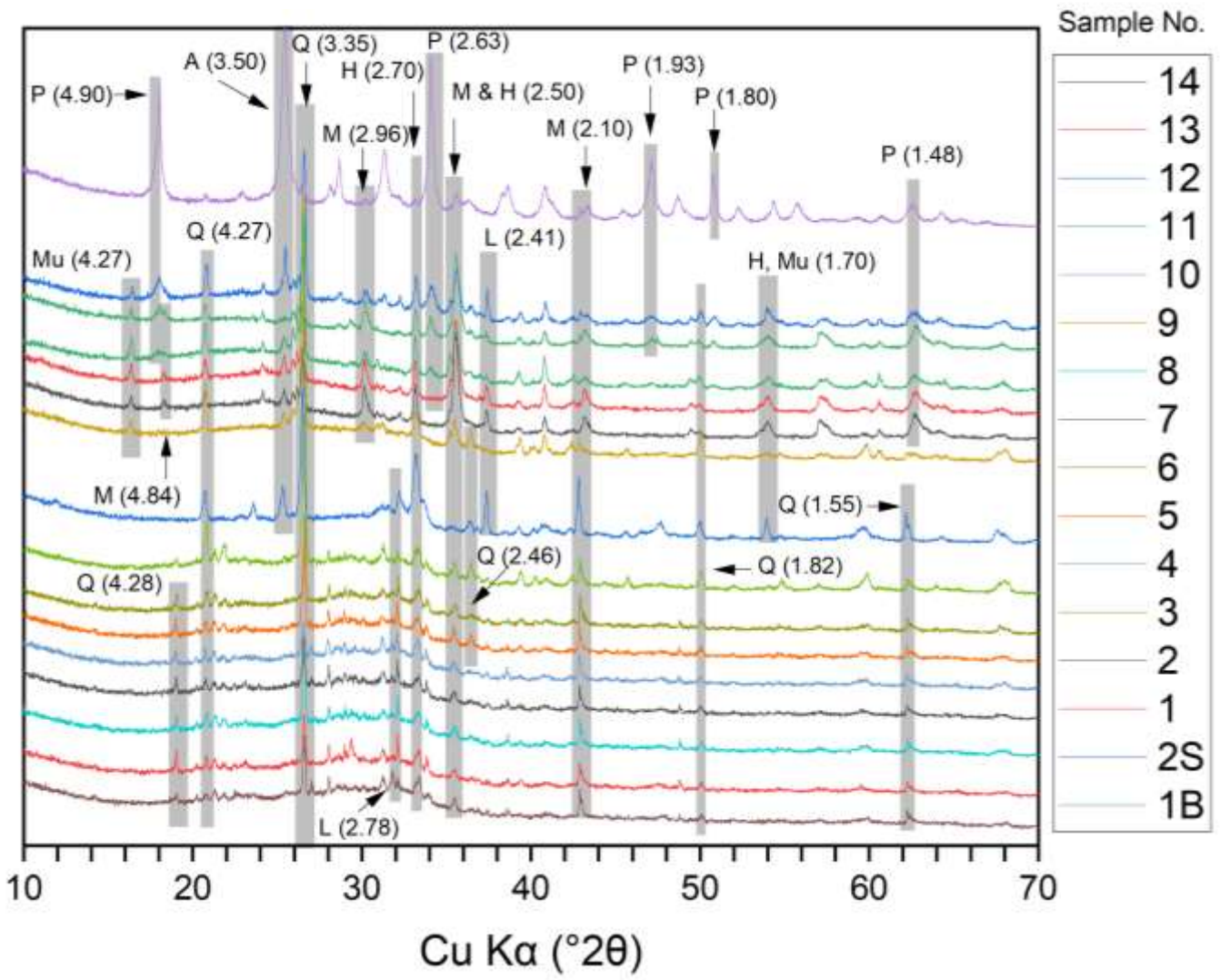
Survey of current operating plants

- Determined the current outlook of coal-fired EGUs generating fly ash across the US

- Collected total 20 samples representing:
  - Coal basin/rank
  - Capacity
  - Furnace burner design
  - NOx control
  - SOx control
  - Particulate matter control

Unit A	Bit - ILB	Tang. + SCR + ESPc or BH + WFGD
Unit B	Sub - PRB	Tang. + SCR + BH + WFGD
Units C & D	Sub - PRB	OPP + ESPc
Unit E	Sub-PRB 85% + Bit-MSW 15%	Tang. + ESPc
Unit F	Bit-ILB	Tang. + ESPc + BH + WFGD
Unit G	Bit-ILB	OPP + ESPc + BH + WFGD

Mineralogical analysis by XRD



P: Portlandite $Ca(OH)_2$
A: Anhydrite
Mu: Mullite
M: Magnetite
H: Hematite
Q: Quartz
L: Lime

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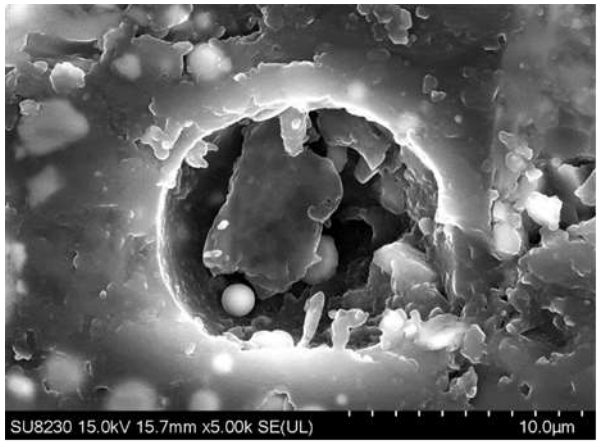
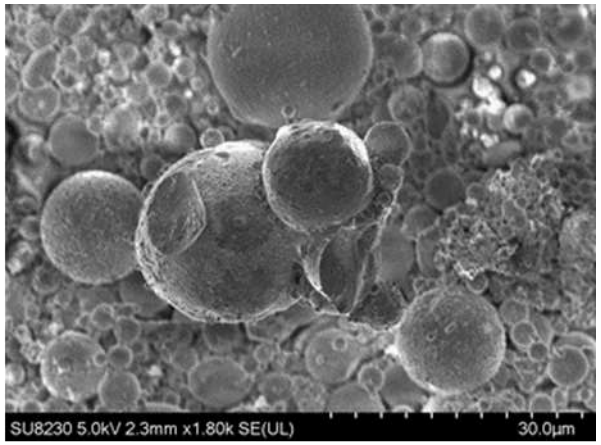
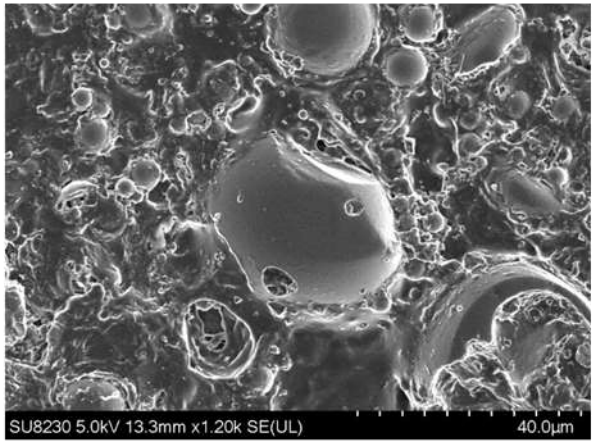
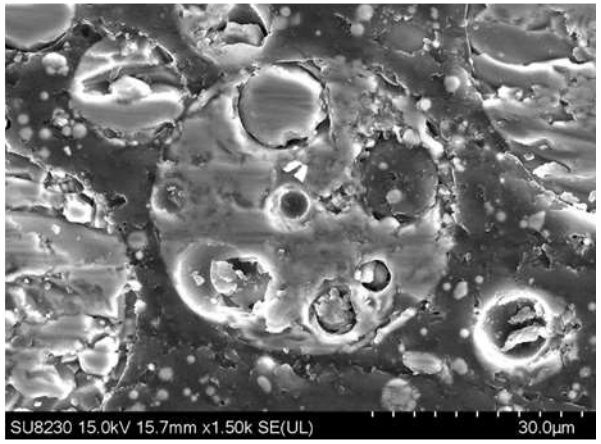
Morphological analysis by SEM-EDS





Spherical morphology





Irregular morphology and plerosphere

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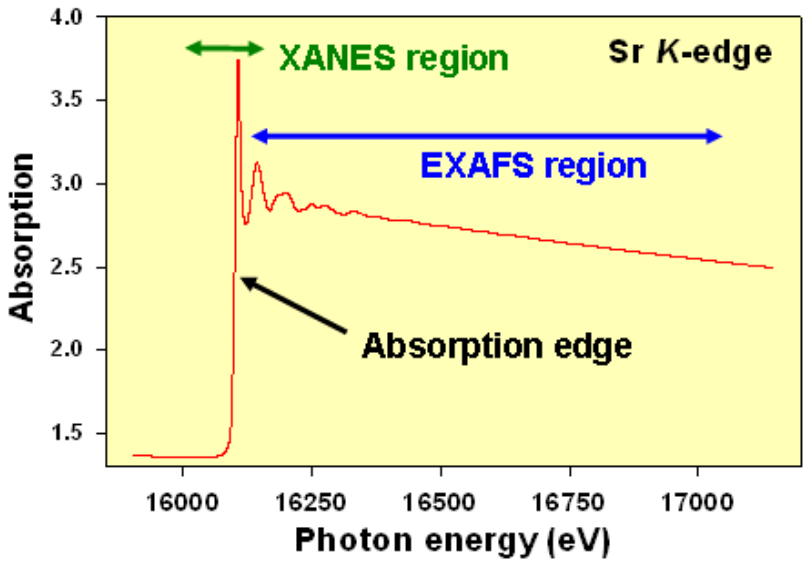
Bulk X-ray absorption spectroscopy (XAS)

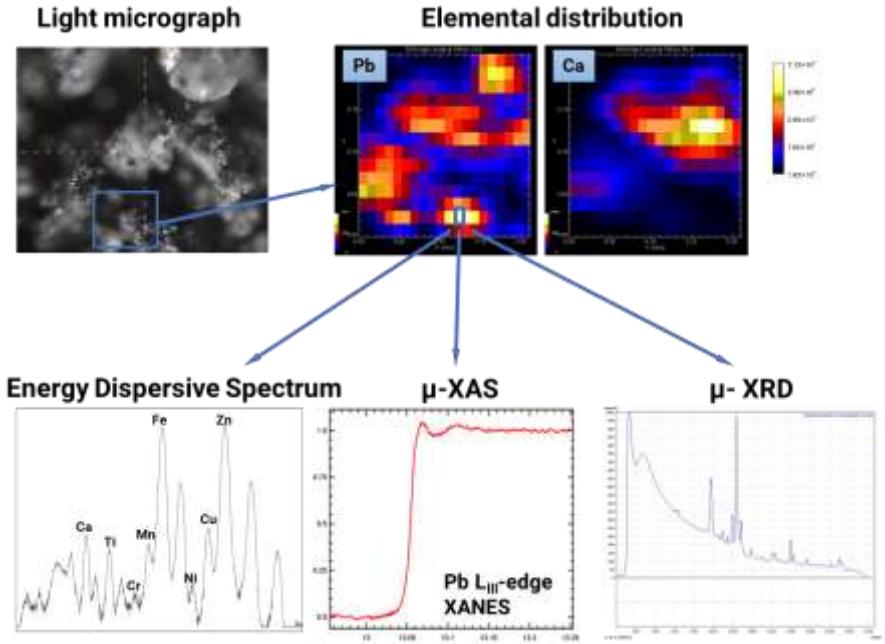
- Element specific
- In situ, non-destructive
- High resolution (ppm)
- Highly desired for complex heterogeneous samples

- XANES (X-ray absorption near edge structure)
- EXAFS (Extended X-ray absorption fine structure)



Micro-X-ray fluorescence microscopy (μ-XRF) and μ-XAS

- μ-XRF: element distribution and correlation
- μ-XANES: micro-scale oxidation state, phase, and structure information
- X-ray beam size: μm to nm
- Suitable for samples with low bulk concentration and heterogeneous distribution



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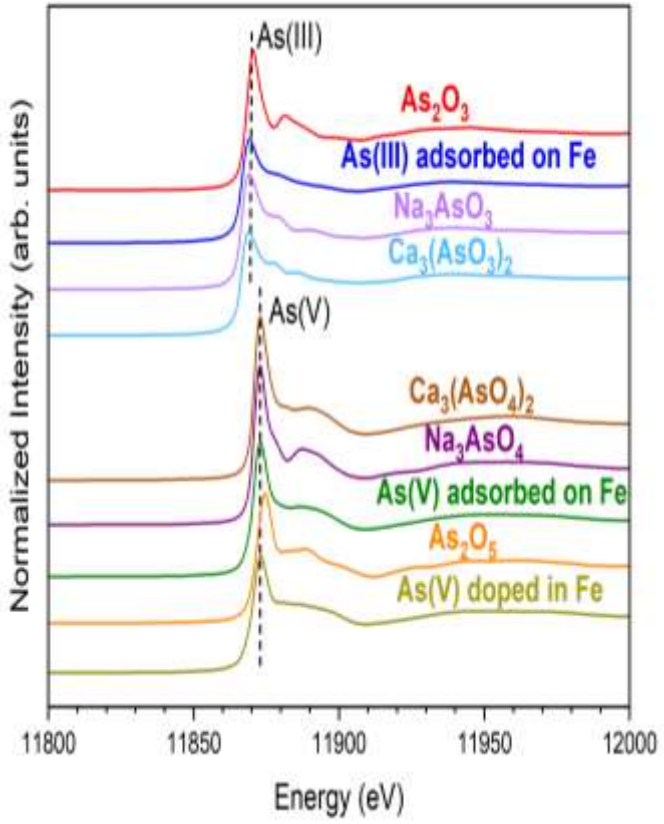
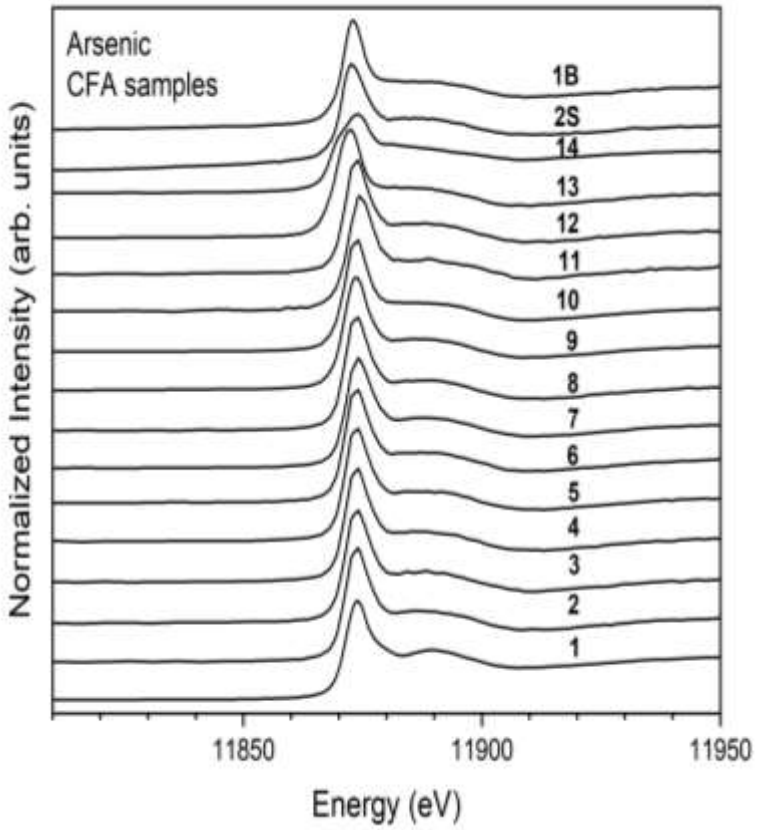
As K-edge bulk XANES analysis

- Bulk XAS data for 9 model compounds and 20 fly ash samples
- Principal component analysis, target transformation, and linear combination fitting (LCF) to identify the dominant As species and their relative contribution

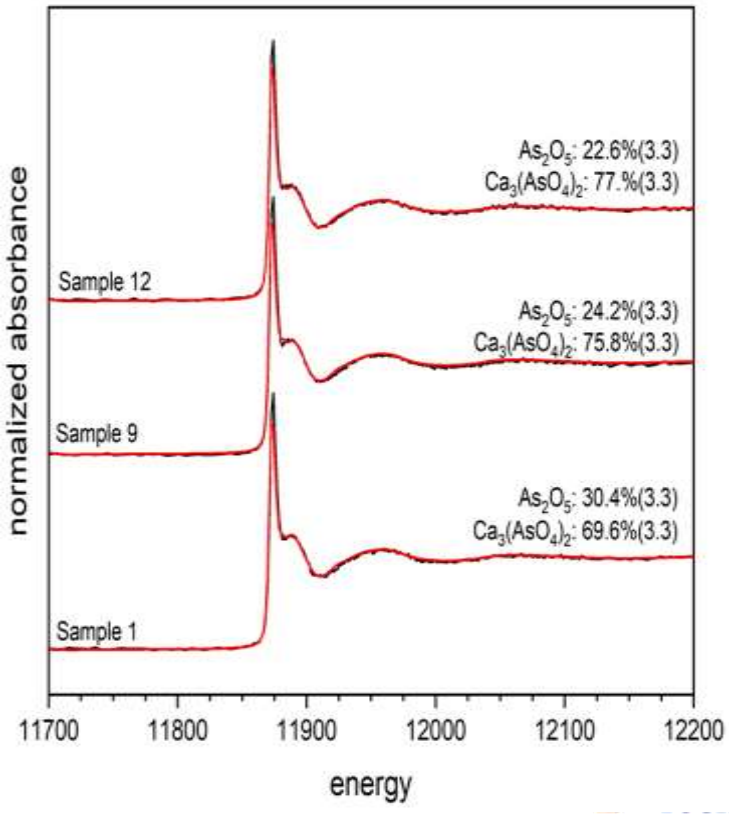
Model compounds



CFA samples



Example LCF analysis



As speciation obtained from LCF of As bulk XANES

Sample ID	As(III) species (%)				As(V) species (%)				
	As_2O_3	As(III) adsorbed Fe oxide	Na_3AsO_3	$Ca_3(AsO_3)_2$	As_2O_5	$Na3AsO_4$	As(V) adsorbed Fe oxide	As(V) doped Fe oxide	$Ca_3(AsO_4)_2$
2691					19.3(2.6)	46.0(5.8)	27.6(7.2)		
2690								31.7(3.5)	59.1(3.0)
C	14.3(3.4)								88.1(3.1)
F					13.4(1.3)	14.8(1.5)		70.0(2.1)	
CFA-2			19(1.1)						81.6(1.0)
CFA-1				11.5(0.7)					85.9(0.7)
14	44.3(0.8)				37.3(1.4)				17.2(1.4)
13	56.4(1.8)				52.0(1.6)				
12					24.8(3.4)				76.1(3.3)
11					28.9(5.7)				75.3(5.9)
10					22(2.7)				77.7(2.6)
9					30.1(2.9)				75.5(2.5)
8					22.6(3.5)				78.1(3.4)
7					49.6(4.2)				51.3(4.1)
6					24.9(3.4)				76.1(3.4)
5					25.5(3.5)				75.4(3.4)
4					27.4(3.6)				73.5(3.5)
3					29.6(3.7)				72(3.6)
2					27.8(3.6)				73.3(3.5)
1					58.2(2.4)				40.3(2.1)

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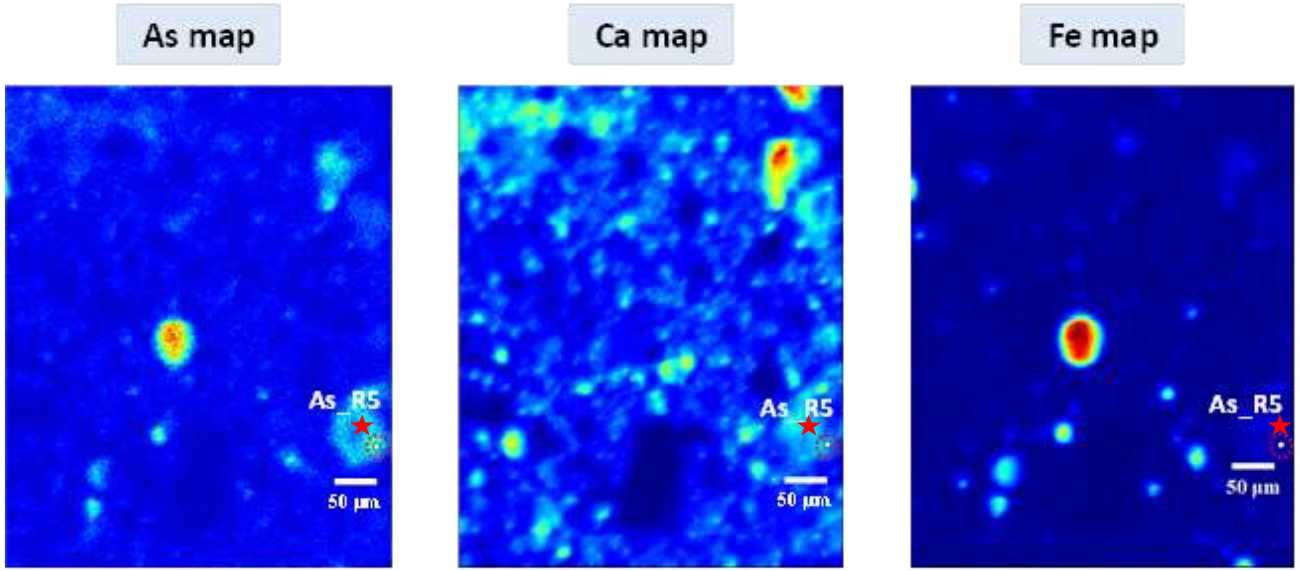
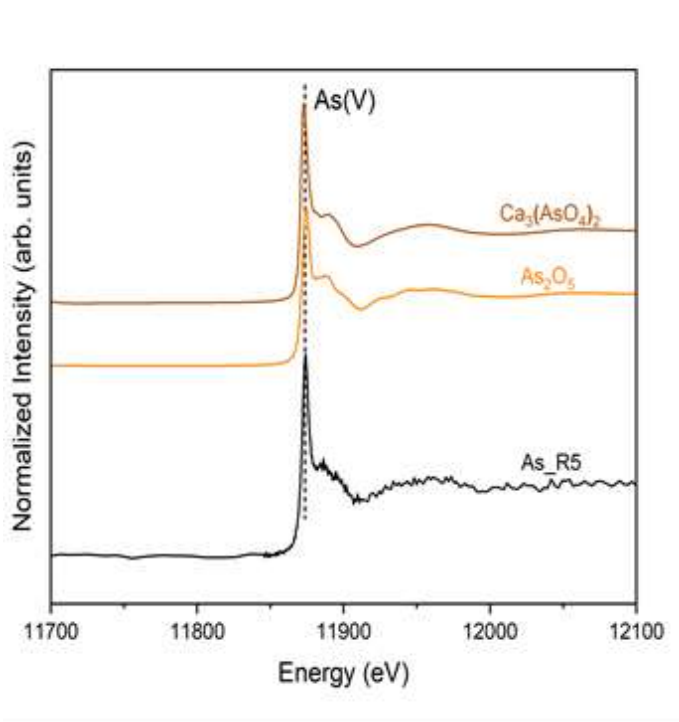
Microscopic distribution of As





Linear Combination Fitting Results

- $CaAsO_4$ 49.2% and As_2O_5 50.8%

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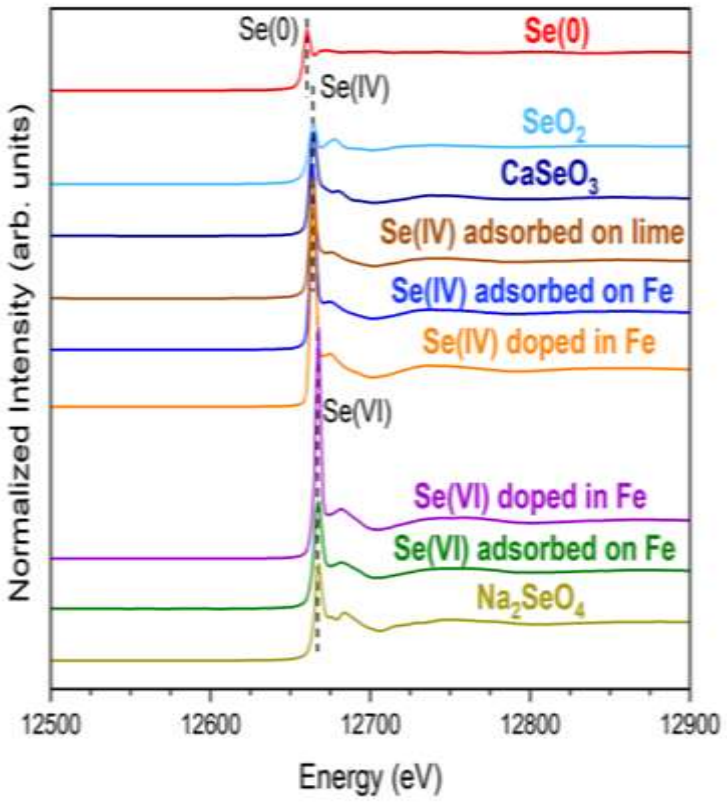
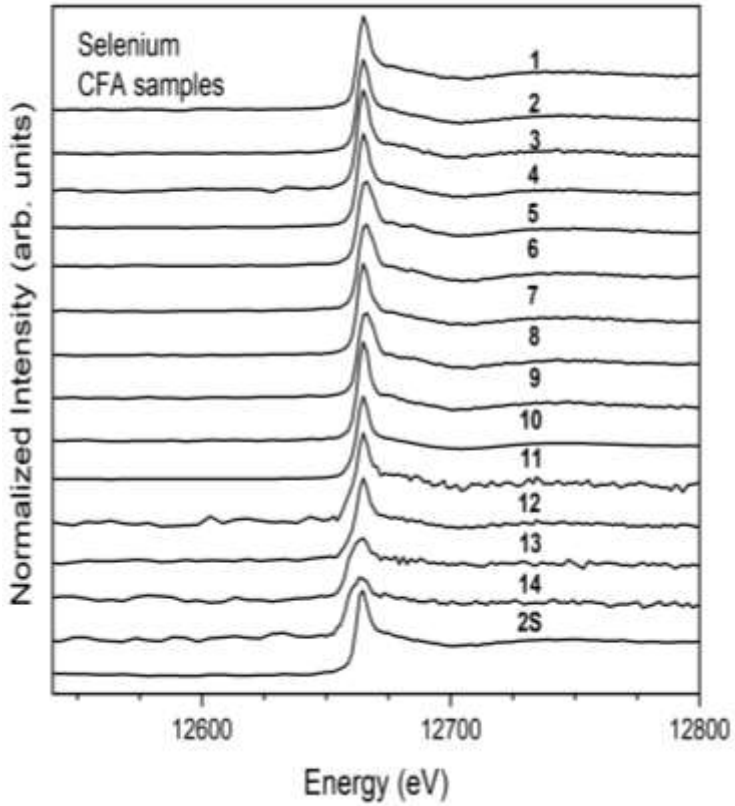
Se K-edge bulk XANES analysis

- Bulk XAS data for 9 model compounds and 20 fly ash samples
- Principal component analysis, target transformation, and linear combination fitting (LCF) to identify the dominant Se species and their relative contribution

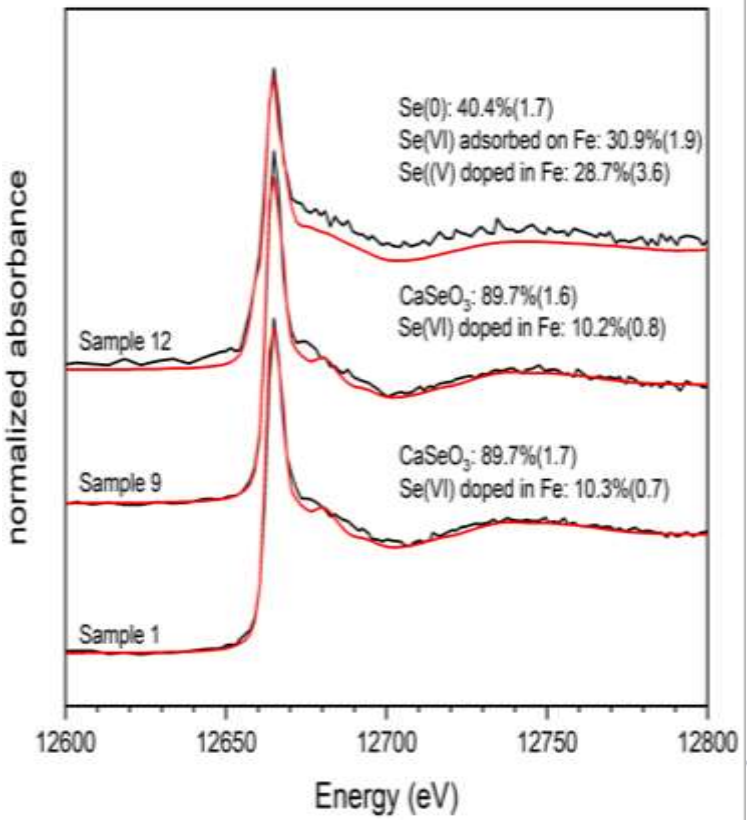
Model compounds



CFA samples



Example LCF analysis

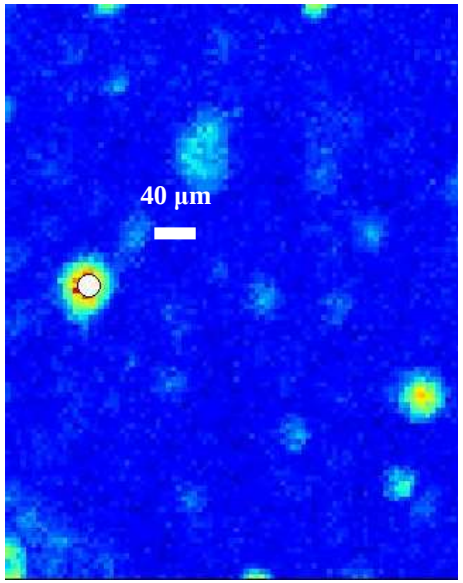


Se speciation obtained from LCF of Se bulk XANES

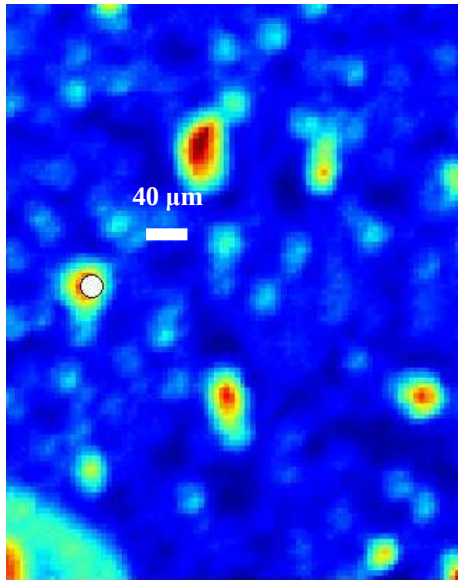
Sample ID	Se(0) (%)	Se(IV) species (%)					Se(VI) species (%)		
		Se(IV) adsorbed Fe oxide	Se(IV) doped Fe oxide	Se(IV) adsorbed lime	SeO_2	$CaSeO_3$	Se(VI) adsorbed Fe oxide	Se(VI) doped Fe oxide	Na_2SeO_4
2691		28.6(4.3)				41.5(8.6)	34.8(4.0)		
C				97.8(1.1)			14.0(1.2)		
F				19.4(1.5)	55.6(2.4)		28.5(1.1)		
CFA-1									
CFA-2	11.5(0.7)			64.5(0.6)			23.2(0.6)		
14	87.9(1.2)		19.2(0.8)						
13	76.6(1.4)		17.1(0.7)				10.2(1.4)		
12	45.4(1.3)		27.8(0.7)				31.5(1.4)		
11	46.9(2.6)		29.8(1.5)				34.0(2.7)		
10	12.9(0.5)					72.2(0.7)	13.6(0.6)		
9						93.2(0.8)		9.6(0.7)	
8	13.8(0.9)		22.3(0.5)				65.7(0.9)		
7						78.1(1.1)	24(1.1)		
6	13.7(1.0)		23.2(0.6)				65.8(1.0)		
5	15.1(0.8)		22.9(0.5)				63.9(0.9)		
4						80.7(1.2)	22.2(1.2)		
3						96.4(1.1)		9.8(0.9)	
2			28.4(0.6)		33.3(1.3)		41.2(1.1)		
1						78.5(1.2)	24.2(1.2)		

Microscopic distribution of Se

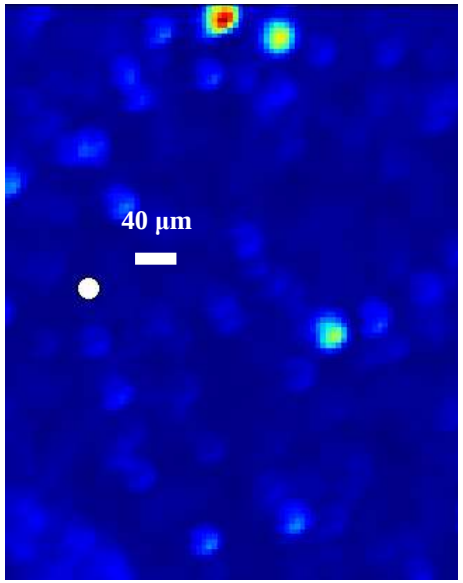
Se map

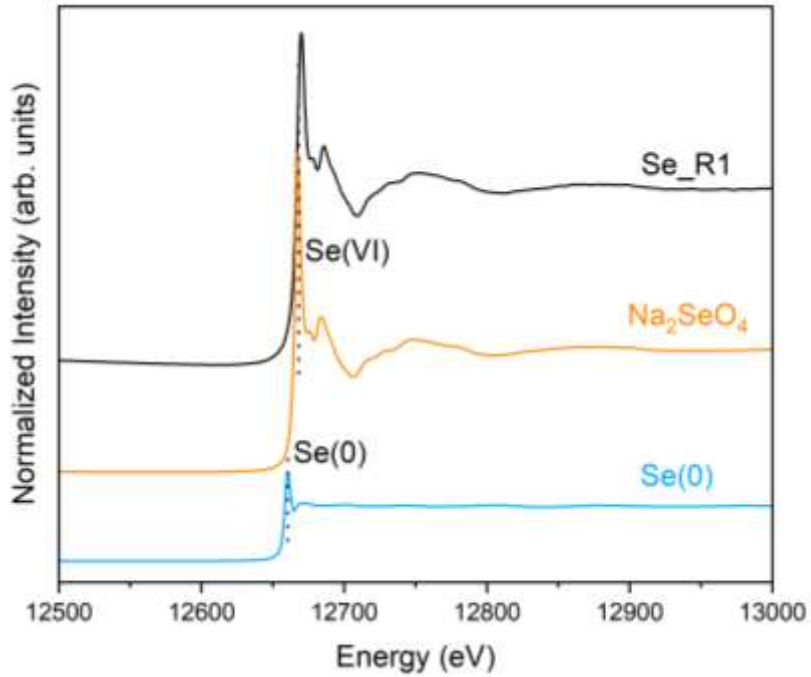


Ca map



Fe map





Linear Combination Fitting Results

- Se(0) 30.9% and Na_2SeO_4 69.1%

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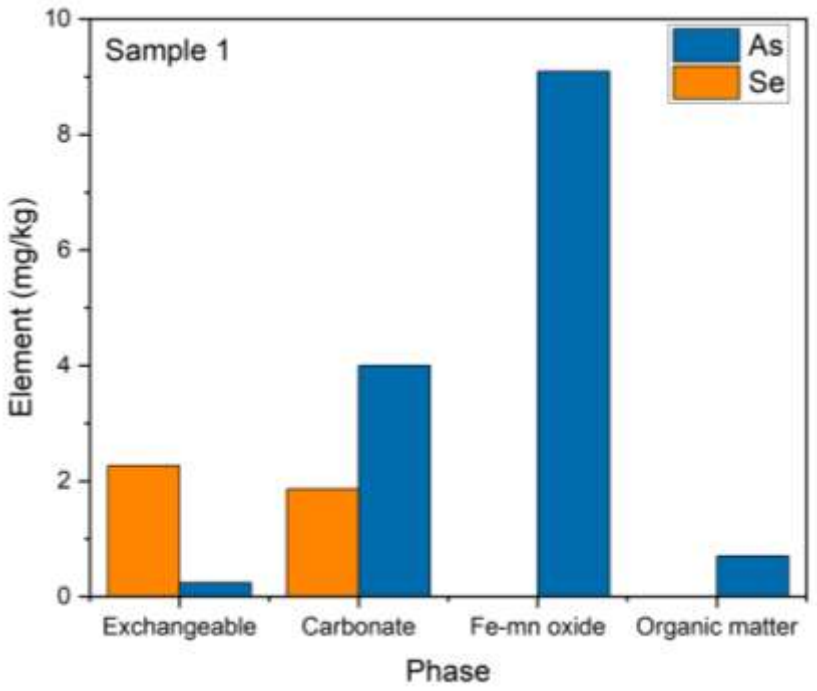
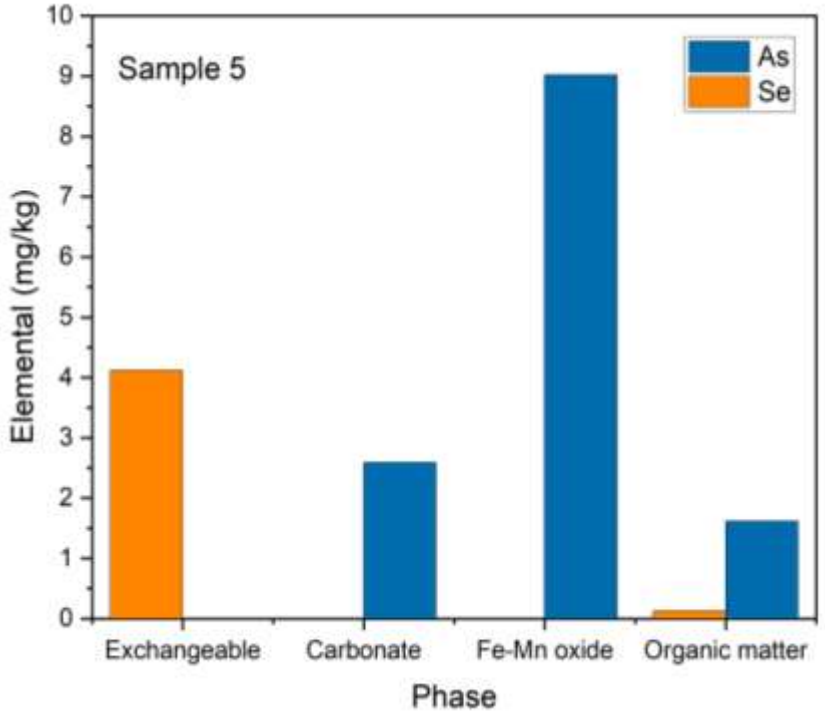
Mobility Analysis





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Acknowledgements

This material is based upon work supported by the Department of Energy Award Number DE-FE0031739.

Synchrotron X-ray analyses were conducted at Stanford Synchrotron Radiation Lightsource (SSRL) and Advanced Photon Source (APS).