Supporting Information

Systematic Characterization of Selenium Speciation in Coal Fly Ash

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Text S1. Statistical Analysis

R-studio was used for principal component analysis (PCA). Principal component analysis was also performed in R-studio for samples 1-14, 1B, and 2S with respect to Al_2O_3, SiO_2, FeO, CaO, LOI, average particle size, Se concentration, Se(0)%, Se(IV)%, and Se(VI)%.[1] To determine which principal components (PCs) held a majority of the variance within this data set, scree plot and eigen values were used. The scree plot in Fig. S5 shows PCs above the blue dashed line hold a majority of the variability, in this case PCs 1 and 2. Additionally eigen values for each PC are shown in Table S5, by squaring their standard deviations. The Kaiser criterion was used to determine the significance of each component, where eigen values >1 are significant. Based on this, PCs 1 and 2 are significant in capturing the variance, with eigen values of 3.91 and 3.56. A summary of PCA results is shown in Table S6, with a complete list of loadings for each PC in Table S7. The significance of each variable to each PC may be assessed by the loadings value (ranging from ±1, a value closer to ±1 indicates a strong relationship), to determine the significance of a loading the following formula was used:

$$\sqrt{\frac{1}{ncol(mypcadata}}.$$ ref 2

This produced a value of 0.30, therefore loadings ± 0.30 were considered significant for that particular PC. Lastly, to better interpret the significance of each variable to each component, a varimax rotation was applied. From Table S10, loadings for PC1-2 were < ± 0.4683, after varimax rotation values were ±1.

Table S1. Sample information on coal source, type, and combustion conditions.[3]

Sample ID	Coal source[a]	Coal type	Class	Furnace type	SOx control	NOx control	Particulate matter control
1	PRB	Sub.	C	Opposed			ESPc
2	PRB	Sub.	C	Opposed			ESPc
3	PRB	Sub.	F	Opposed			ESPc
4	PRB	Sub.	C	Opposed			ESPc
5	PRB	Sub.	C	Opposed			ESPc
6	PRB	Sub.	C	Opposed			ESPc
7	PRB	Sub.	C	Opposed			ESPc
8	PRB	Sub.	C	Opposed			ESPc
9	PRB+MSW	85% Sub. + 15% Bit.	F	Tangent			ESPc
10	ILB	Bit.	F	Tangent	WFGD		ESPc + BH
11	ILB	Bit.	F	Opposed	WFGD		ESPc + BH
12	ILB	Bit.	F	Opposed	WFGD		ESPc + BH
13	N. App.	Bit.	F	Opposed		SCR	ESP
14	N. App.	Bit.	F	Opposed		SCR	ESP
1B	ILB	Bit.	F	Tangent	WFGD	SCR	ESPc/BH
2S	PRB	Sub.	C	Tangent	WFGD	SCR	BH
90	Surface mine in Co.	Sub.	F				
91	PRB	Sub.	C				
F	ILB	Bit.	F				

[a] PRB: Powder River Basin, MSW: Municipal solid waste, ILB: Illinois basin, N. App.: North Appalachia, Sub.: subbituminous, Bit.: bituminous, WFGD: wet flue gas desulfurization, SCR: selective catalytic reduction, ESP(c): electrostatic precipitator (cold side), and BH: baghouse.

Table S2. Information on model compounds and sources.

Oxidation State	Model Compounds	Source
Se(0)	Se foil	APS, beamline 12-BM
Se(IV)	$CaSeO_3$	Pfaltz & Bauer
	SeO_2	Sigma Aldrich
	Se(IV) doped in FeOx	0.1 M Na_2SeO_3 and 0.2 M $FeCl_3$ were mixed into 15 mL of MQ water. This mixture was titrated with NaOH until a pH of 7 was reached. The product was rinsed and centrifuged.
	Se(IV) adsorbed on lime ($CaCO_3$)	5 mM Na_2SeO_3 and 100 mg calcite was dissolved to a total volume of 20 mL. 10 mM of NaCl was added until pH 6.0 was reached. The mixture reacted for 24 hours and was syringed filtered with a 0.45 µm filter.
	Se(IV) adsorbed on FeOx	5 mM Na_2SeO_3 and 100 mg ferrihydrite was dissolved to a total volume of 20 mL. 10 mM of NaCl was added until pH 6.0 was reached. The mixture reacted for 24 hours and was syringed filtered with a 0.45 µm filter.
Se(VI)	Se(VI) adsorbed on FeOx	5 mM Na_2SeO_4 and 100 mg ferrihydrite was dissolved to a total volume of 20 mL. 10 mM of NaCl was added until pH 6.0 was reached. The mixture reacted for 24 hours and was syringed filtered with a 0.45 µm filter.
	Se(VI) doped in FeOx	0.1 M Na_2SeO_4 and 0.2 M $FeCl_3$ were mixed into 15 mL of MQ water. This mixture was titrated with NaOH until a pH of 7 was reached. The product was rinsed and centrifuged.
	Na_2SeO_4	Alfa Aesar

Table S3. Summary of characterization techniques for each sample.[3]

Sample ID	XRD	SEM/EDX	ICP-MS	XRF	XANES	μ-XRF and μ-XANES	Particle Size analysis	Density analysis
1	X		X	X	X		X	X
2	X		X	X	X	X	X	X
3	X	X	X	X	X		X	X
4	X	X	X	X	X		X	X
5	X	X	X	X	X		X	X
6	X		X	X	X		X	X
7	X		X	X	X		X	X
8	X	X	X	X	X	X	X	X
9	X	X	X	X	X	X	X	X
10	X		X	X	X	X	X	X
11	X		X	X	X		X	X
12	X	X	X	X	X	X	X	X
13	X	X	X	X	X		X	X
14	X		X	X	X		X	X
1B	X	X	X	X	X	X	X	X
2S	X	X	X	X	X	X	X	X
90	X		X	X	X		X	X
91	X		X	X	X		X	X
F	X	X	X	X	X		X	X

Table S4. Composition and physical properties of all CFA samples.[3] Normalized major elements for XRF. Samples 90 and 91 are Standard Reference Materials 2690 and 2691 from the National Institute of Standards and Technology. Major element composition for sample F is from Renew et al.[4] Residual standard deviation used for ICP. NM – not measured.

Sample ID	Major element (wt%)				Class	Se (ppm)	Average particle size (μm)	Surface Area (cm^2/cm^3)	Bulk density (mg/cc)	LOI
	Fe_2O_3	Al_2O_3	SiO_2	CaO						
1	5.27	20.49	38.95	19.72	C	11.8 ± 0.68	13.2	9724.7	2.63	1.75
2	5.26	20.06	40.92	18.65	C	9.4± 2.07	12.7	8917.9	2.56	0.91
3	6.73	16.88	49.12	15.6	F	5.2 ± 2.31	51.4	4271.7	2.53	0.86
4	5.44	19.99	40.2	19.19	C	9.9 ± 2.27	11.5	9735.4	2.59	1.05
5	5.69	20.95	41.18	17.56	C	10.3 ± 0.95	14.0	9972.8	2.59	0.76
6	5.66	21.07	40.82	17.73	C	10.3 ± 0.29	13.5	9780.5	2.57	0.71
7	5.28	20.46	38.91	19.79	C	10.2 ± 0.22	10.1	10022	2.61	0.95
8	5.68	20.9	41.17	17.52	C	10.2 ± 0.83	13.7	9867.3	2.56	0.66
9	9.84	21.84	44.45	17.07	F	10.1 ± 0.51	21.2	9233.7	2.56	3.41
10	9.95	11.24	24.13	51.61	-	260.6 ± 0.58	8.3	16478	2.53	9.72
11	30.26	17.42	42.12	8.49	F	4.4 ± 3.2	107.5	892.15	2.41	1.66
12	15.87	19.15	46.36	13.31	F	8.8 ± 0.93	17.4	7314.3	2.48	2.43
13	24.13	22.89	42.9	7.47	F	5.9 ± 0.71	41.3	3623.2	2.56	8.86
14	28.36	21.48	40.92	7.49	F	5.6 ± 3.1	42.6	3514.8	2.69	3.96
1B	17.48	22.56	51.04	4.94	F	9.4 ± 1.93	30.2	4996.1	2.37	0.42
2S	6.22	17.14	37.78	28.68	C	13.5 ± 0.34	23.9	7017.8	2.69	3.07
90	5.11 ± 0.06	23.30 ± 0.28	55.29 ± 0.17	8.00 ± 0.13	F	0.8	NM	NM	NM	0.53
91	6.32 ± 0.03	18.53 ± 0.39	36.00 ± 0.12	25.81 ± 0.32	C	17	NM	NM	NM	0.23
F	11.90	25.20	54.30	1.60	F	NM	NM	NM	NM	NM

Table S5. Linear combination fitting results of Se bulk XANES.

Sample ID	Se(0)%	Se(IV)%					Se(VI)%	Sum	R-factor
		$CaSeO_3$	SeO_2	Se(IV) doped FeOx	Se(IV) adsorbed on lime	Se(IV) adsorbed on FeOx	Se(VI) adsorbed on FeOx		
1		79.0 ± 1.2					24.4 ± 1.2	103.4	0.0074
2			34.7 ± 1.4	28.0 ± 0.6			40.8 ± 1.1	103.6	0.0067
3		88.5 ± 1.9					20.5 ± 1.9	109.0	0.0160
4		81.4 ± 1.2					22.4 ± 1.2	103.8	0.0070
5	15.9 ± 0.9			22.5 ± 0.5			63.8 ± 0.9	102.3	0.0058
6			20.8± 1.5	19.9± 0.7			63.3± 1.2	104.0	0.0072
7		78.5 ± 1.1					24.1 ± 1.1	102.6	0.0058
8	14.7 ± 1.0			22.0 ± 0.5			65.6 ± 1.0	102.3	0.0061
9		65.2 ± 3.6		10.1 ± 1.7			28.4 ± 2.0	103.7	0.0100
10	13.1 ± 0.7	72.1 ± 0.8					13.9 ± 0.7	99.1	0.0030
11	46.0 ± 2.4			27.7 ± 1.3			33.3 ± 2.4	107.1	0.0415
12	47.3 ± 1.4			26.8 ± 0.8			31.5 ± 1.4	105.7	0.0160
13	90.7 ± 1.3			18.3 ± 0.9				108.9	0.0538
14	89.9 ± 1.3			16.9 ± 0.8				106.8	0.0554
2S	11.9 ± 0.7				64.0 ± 0.6		23.2 ± 0.6	99.1	0.0041
91		42.3 ± 8.8				28.2 ± 4.4	34.5 ± 4.1	105.1	0.0227
F			56.7 ± 2.4		18.9 ± 1.5		28.3 ± 1.1	103.9	0.0073

Commented [TY1]: Move to SI and update text

Table S6. LCF results for Se K-edge μ-XANES. The first number of the hot spot label corresponds to CFA sample number.

Hot spot	Se(IV) %			Se(VI) %		Sum	R-Factor
	$CaSeO_3$	Se(IV) adsorbed on lime	Se(IV) adsorbed on FeOx	Se(VI) adsorbed on FeOx	Na_2SeO_4		
2_R5_003				16.0 ± 5.9	99.2 ± 6.3	115.2	0.0186
9_001	19.6 ± 0.9			77.7 ± 0.9		97.3	0.0080
10_R1_001	43.0 ± 2.0				53.0 ± 2.1	96.0	0.0641
10_R1_002	46.5 ± 4.4				47.7 ± 4.6	94.2	0.3138
10_R1_003	52.5 ± 3.1				36.0 ± 3.3	88.5	0.1932
10_R1_004	43.7 ± 1.7			54.9 ± 1.7		98.6	0.0297
10_R2_001	56.9 ± 4.0				31.4 ± 4.3	88.3	0.3123
10_R2_002	50.3 ± 1.5				50.6 ± 1.5	100.9	0.0284
10_R2_003	36.4 ± 1.9			71.6 ± 1.9		108.0	0.0274
10_R3_001	37.3 ± 1.8			61.8 ± 1.8		99.4	0.0293
10_R3_02	27.1 ± 1.7				67.3 ± 1.8	94.4	0.0432
10_R3_003	33.4 ± 1.9					98.9	0.0337
12_R2		53.9 ± 0.9			46.5 ±1.0	100.4	0.0149
12_001	39.2 ± 0.8			17.3 ± 3.3	42.4 ± 3.3	98.9	0.0064
12_002		55.6 ± 1.3			43.2 ± 1.4	98.8	0.0358
12_003		56.6 ± 1.3			42.4 ± 1.4	99.0	0.0346
1B_Se5	58.7 ± 3.3				40.7 ± 3.4	99.4	0.0683
1B_Se6			38.4 ± 1.8	64.6 ± 2.0		103.0	0.0380
1B_Se7	65.3 ± 2.6			33.3 ± 2.6		98.6	0.0280
2S_Se4	48.5 ± 2.2				52.0 ± 2.2	100.6	0.0242
2S_Se3	43.0 ± 2.1				57.8 ± 2.2	100.8	0.0255
2S_Se2	53.5 ± 2.8				44.4 ± 2.9	97.9	0.0466
2S_Se1	60.4 ± 2.0				39.2 ± 2.0	99.5	0.0201

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Table S7. Eigen values for each component in PCA, by squaring the standard deviation. PCs with values >1 are considered significant.

PC	Eigen Value
PC1	3.91
PC2	3.56
PC3	0.94
PC4	0.85
PC5	0.43
PC6	0.13
PC7	0.09
PC8	0.05
PC9	0.04
PC10	0.00

Table S8. Summary of PCA with standard deviation, proportion of variance, and cumulative proportion of variance for each principal component (PCs).

Principal Component	Standard Deviation	Proportion of Variance	Cumulative Proportion
PC1	1.977	0.391	0.391
PC2	1.8864	0.3559	0.7469
PC3	0.96763	0.09363	0.84052
PC4	0.92214	0.08503	0.92555
PC5	0.65291	0.04263	0.96818
PC6	0.36402	0.01325	0.98143
PC7	0.30478	0.00929	0.99072
PC8	0.22831	0.00521	0.99593
PC9	0.20165	0.00407	1
PC10	2.16E-08	0.00E+00	1.00E+00

Table S9. Loadings for each PC and variable.

PC	FeO	CaO	Al_2O_3	SiO_2	Average particle size	Se concentration	Se(0)	Se(IV)	Se(VI)	LOI
PC1	0.46	-0.27	-0.28	-0.27	0.29	0.14	0.42	-0.24	-0.32	0.35
PC2	-0.19	0.43	-0.37	-0.41	-0.21	0.47	-0.13	0.30	-0.02	0.31
PC3	0.03	-0.06	-0.09	0.20	0.32	-0.13	-0.23	0.62	-0.62	-0.08
PC4	-0.06	-0.10	0.40	0.07	-0.67	-0.02	0.13	-0.03	-0.50	0.31
PC5	0.20	-0.20	-0.12	0.15	-0.12	0.49	-0.60	-0.40	-0.21	-0.25
PC6	-0.07	-0.13	0.38	0.22	0.35	0.19	-0.31	0.03	0.23	0.69
PC7	0.15	-0.10	0.55	-0.74	0.12	0.02	-0.19	0.11	-0.02	-0.23
PC8	-0.49	0.41	0.20	0.00	0.40	0.14	0.17	-0.42	-0.39	-0.10
PC9	0.01	-0.16	0.24	0.23	0.03	0.67	0.46	0.32	0.12	-0.28
PC10	0.66	0.68	0.23	0.21	0.00	0.00	0.00	0.00	0.00	0.00

Table S10. FeO content for CFA samples.

Sample ID	FeO (wt%)
1	4.720954
2	4.70542
3	6.023256
4	4.870642
5	5.089477
6	5.068768
7	4.723226
8	5.083602
9	8.805308
10	8.91
11	27.08938
12	14.20713
13	21.59544
14	25.3878
1B	15.65
2S	5.57

Table S11. Loading values after varimax rotation.

PC	PC1	PC2	PC3	PC4	PC5	PC6	PC7	PC8	PC9	PC10
FeO	1	-	-	-	-	-	-	-	-	-
CaO	-	-	-	-	-	-	-	-	-	1
Al_2O_3	-	-1	-	-	-	-	-	-	-	-
SiO_2	-	-	-	-	-	-	-1	-	-	-
Average particle size	-	-	-	-1	-	-	-	-	-	-
Se concentration	-	-	-	-	-	-	-	-	1	-
Se(0)	-	-	-	-	-1	-	-	-	-	-
Se(IV)	-	-	1	-	-	-	-	-	-	-
Se(VI)	-	-	-	-	-	-	-	-1	-	-
LOI	-	-	-	-	-	1	-	-	-	-

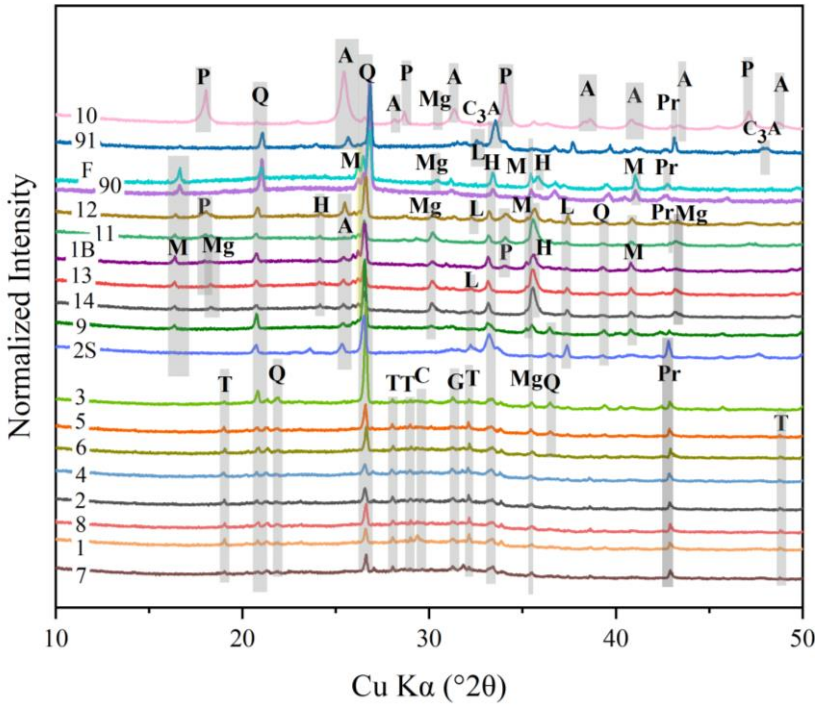

Figure S1. XRD spectra of all samples, normalized by quartz (101) peak. Mineral phases are shown as vertical gray bars. Thenardite (T), Mullite (M), Quartz (Q), Hematite (H), Anhydrite (A), Magnetite (Mg), Calcite (C), Periclase (Pr), Gehlenite (G), Lime (L), Portlandite (P), and tricalcium aluminate (C_3A).[3]

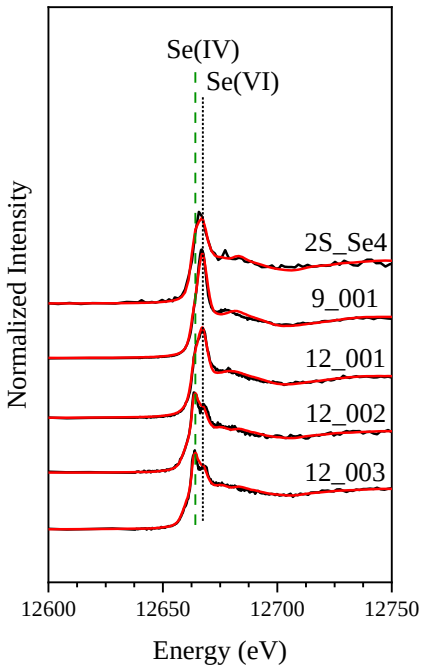

Figure S2. Se K-edge μ-XANES spectra (black lines) and LCF fitted spectra (red lines) for hot spots from samples 2S, 9, and 12. Vertical dashed lines represent the edge peak positions for Se(IV) and Se(VI) adsorbed on FeOx in green and gray.

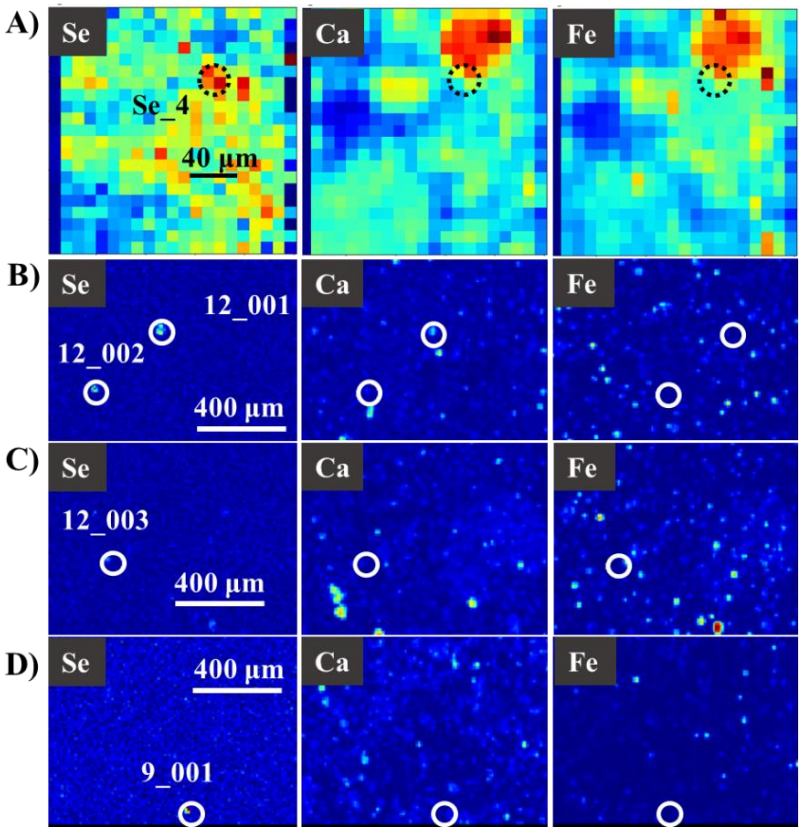

Figure S3. µ-XRF heat maps for Se, Ca, and Fe distribution. Hot spots where µ-XANES data was collected are shown as circles. A) Hotspot Se_4 from sample 2S. B) Hotspots 12_001 and 12_002 for sample 12. C) Hotspot 12_003 for sample 12. D) Hotspot 9_001 from sample 9.

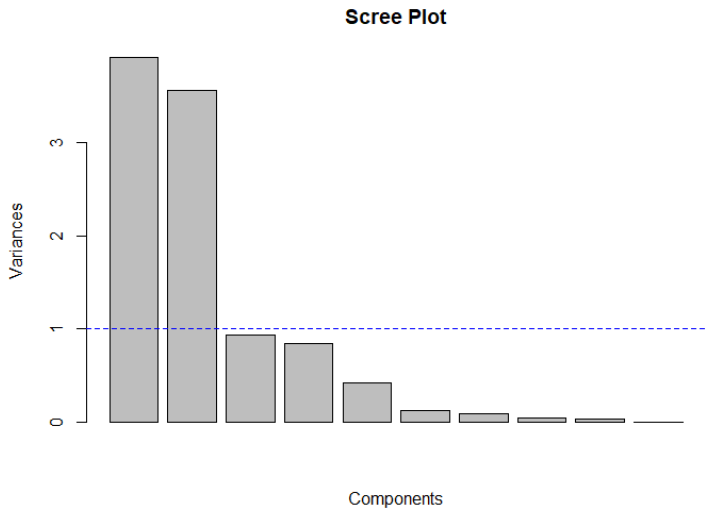

Figure S4. Scree plot of principal components, with components above the blue line representing significant components capturing a majority of the variability of the data.

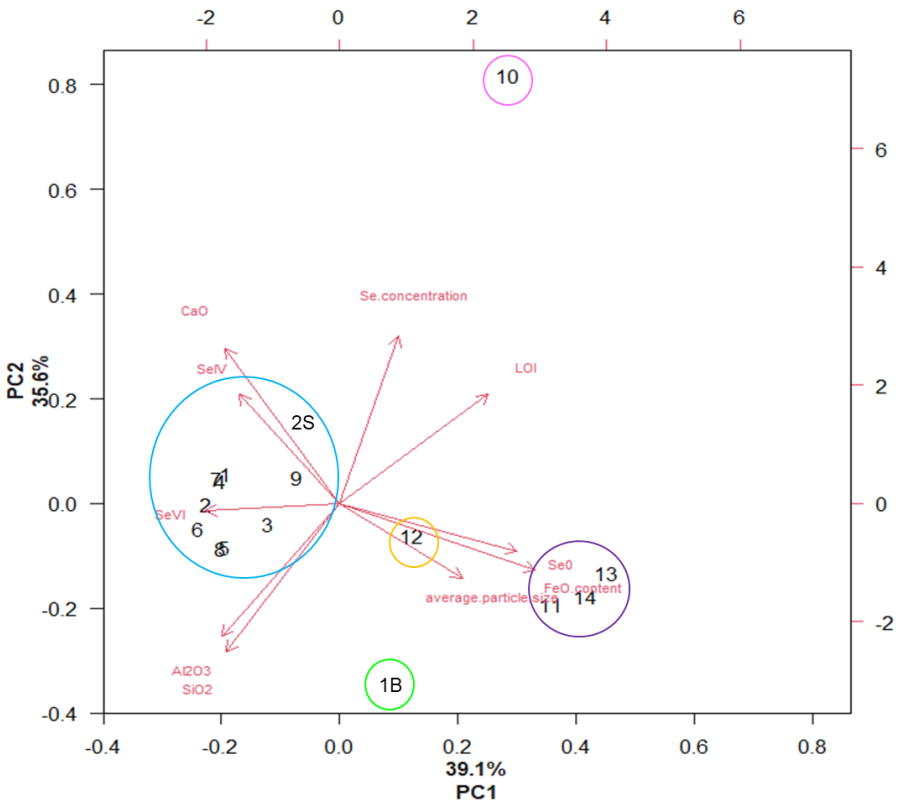

Figure S5. Biplot of PCs 1 and 2 with 39.1% and 35.6% of the variance. Scores are presented in the right and top axes while loadings are presented in the left and bottom axes. Samples are black numbers, and variables are shown in red with corresponding vectors.

References

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(3) Garcia, E.; Liu, P.; Sanchez, J.; Lee, S.; Wang, Q.; Wen, Y.; Shivaprakash, S.; Burns, S.; Tang, Y. A survey study on arsenic speciation in coal fly ash and insights into the role of coal combustion conditions. *Applied Geochemistry* **2024**, *170*, 106095. DOI: https://doi.org/10.1016/j.apgeochem.2024.106095.
(4) Renew, J. E.; Huang, C.-H.; Burns, S. E.; Carrasquillo, M.; Sun, W.; Ellison, K. M. Immobilization of Heavy Metals by Solidification/Stabilization of Co-Disposed Flue Gas Desulfurization Brine and Coal Fly Ash. *Energy & Fuels* **2016**, *30* (6), 5042-5051. DOI: 10.1021/acs.energyfuels.6b00321.