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Speciation, Distribution, and Mobility of Hazardous Trace Elements in Coal Fly Ash: Insights from Cr, Ni, and Cu

Pan Liu, Qian Wang, Haesung Jung, and Yuanzhi Tang*

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ABSTRACT: Coal fly ash (CFA) has gained increasing societal concerns as hazardous trace elements (HTEs) in CFA might pose environmental and public health risks. To develop better management and remediation strategies, it is highly important to obtain an in-depth understanding of the occurrence and mobility of HTEs in CFA. This study systematically characterized the speciation, distribution, and mobility of Cr, Ni, and Cu in class F and class C CFA samples using scanning electron microscopy with energydispersive X-ray spectroscopy (SEM–EDX), X-ray absorption near-edge spectroscopy (XANES), and sequential chemical extraction. SEM–EDX results show that Cr, Ni, and Cu are present in a range of $2-15 \ \mu$ m sized particles either as discrete particles or encapsulated in the glass phase. XANES results suggest that Cr is mainly present in Fe oxides or silicates and spinel minerals; Ni mainly in Fe oxides and as NiO; and Cu mainly as Cu₂O/CuO or in Fe oxides. Cr(III) and Cu(I) are the dominant oxidation states for Cr and Cu, respectively. Sequential extraction generally shows higher mobility of trace elements (Cr, Mn, Co, Ni, Cu, Zn, Cd, and Pb) in class C CFA, as compared to the mobility of those in class F CFA, implying potentially higher environmental risks for class C CFA.

1. INTRODUCTION

A great portion of electricity generation in the United States relies on coal combustion, which generates an average of 110 M tons of coal ash or coal combustion residuals (CCR) annually, being the second largest industrial waste stream in the United States.¹ Coal contains relatively high content of hazardous trace elements (HTEs), as compared to other geological materials² and, after coal combustion, some HTEs might even be enriched by 4–10 times in CCR.³ Over the last century, CCR were either dumped in landfills or, more frequently, pumped into surface impoundments commonly in proximity to lakes and rivers,¹ posing prolonged risks to the environment and public health. CCR have drawn the national attention after several catastrophic coal ash spills, such as at Kingston, Tennessee,⁴ combined with the findings of elevated contaminant levels in ground water via leaking of CCR ponds.⁵ Since 2015, the U.S. Environmental Protection Agency (EPA) has issued the Final Rule to establish national minimum criteria for the disposal of CCR.⁶ As the ultimate environmental fate and health impact of HTEs are heavily dependent on their chemical forms, oxidation states, and physical distribution in CCR, there are urgent needs to systematically characterize the occurrence (i.e., both the speciation and distribution) and mobility of HTEs to provide better management strategies and risk predictions.

Coal fly ash (CFA), a major constituent of CCR, has been the focus in recent years because of its high annual production, enrichment in HTEs, and potential for beneficial reuse.^{7–12} American Society for Testing and Materials (ASTM) C 618 defines main CFA types as class F (bituminous) and class C (sub-bituminous):¹³ class F CFA is characterized by SiO₂ + $Al_2O_3 + Fe_2O_3 \ge 70$ wt % and generally originates from the combustion of bituminous and anthracite coal; class C CFA has 50 wt % \leq SiO₂ + Al₂O₃ + Fe₂O₃ < 70 wt % and a higher CaO content and generally originates from the combustion of sub-bituminous coal and lignite. Among all HTEs in CFA, much attention was traditionally paid to As and Se (e.g., refs^{14,16}) and previous findings suggested the fundamental influence of CFA chemical composition on the properties of As and Se.^{17–20} For example, more As was found to occur as Ca₃(AsO₄)₂ in CaO-rich class C CFA in comparison to CaO-poor class F CFA.²⁰ Additionally, class C CFA leaches significantly less As than class F CFA under neutral to alkaline pH probably due to Ca–As precipitation.¹⁹

In contrast to the highly volatile As and Se that can gasify in boilers and condense on particle surfaces,^{10,15,21} other HTEs such as Cr, Ni, and Cu are considered to be relatively low in volatility.^{22–25} A few studies have explored the speciation of the abovementioned HTEs (e.g., Cr) in CFA (e.g., refs 15 and 26–29), yet very few studies have compared the similarity/ difference of these elements in different types of CFA in terms of speciation, distribution, and mobility. Intriguingly, in an extensive study on trace element speciation in coal,² HTEs such as Cr have generally similar occurrence among different coal types (bituminous vs sub-bituminous coal) and coal sources (the United States vs other countries), and other HTEs including Co, Ni, Cu, Zn, Cd, and Pb also display such

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Tab	le 1.	Summary	r of	CFA	Samples	s in	This	Study	
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	F-1	F-2	C-1	C-2
coal source	Illinois Basin	surface mine in Craig, Colorado	Powder River Basin	Powder River Basin
coal type	bituminous	sub-bituminous	sub-bituminous	sub-bituminous
coal ash type	F	F	С	С
$SiO_2 (wt \%)^a$	54.3	55.3	36.6	36.0
Al ₂ O ₃ (wt %)	25.2	23.3	18.2	18.5
Fe ₂ O ₃ (wt %)	11.9	5.1	6.4	6.3
CaO (wt %)	1.6	8.0	28.1	25.8
MgO (wt %)	0.8	2.5	0.8	5.2
K ₂ O (wt %)	2.6	1.2	0.4	0.4
P_2O_5 (wt %)	1.0	1.2	0.9	1.2
TiO_2 (wt %)	1.6	0.9	1.6	1.5
Cr (ppm)	174.6 ± 3.0	59.2 ± 1.7	85.9 ± 9.9	67.9 ± 0.4
Mn (ppm)	104.1 ± 2.5	155.4 ± 5.5	207.4 ± 2.8	153.3 ± 0.7
Co (ppm)	45.1 ± 7.8	14.9 ± 0.0	23.1 ± 0.0	28.4 ± 6.0
Ni (ppm)	116.8 ± 6.2	42.2 ± 1.2	57.0 ± 3.5	59.4 ± 5.4
Cu (ppm)	128.3 ± 5.1	66.8 ± 0.8	183.5 ± 8.0	180.7 ± 0.2
Zn (ppm)	169.9 ± 12.6	92.2 ± 1.6	109.4 ± 4.5	120.2 ± 12.8
Cd (ppm)	48.1 ± 4.2	39.0 ± 3.3	43.1 ± 1.2	54.1 ± 3.4
Pb (ppm)	84.4 ± 7.5	33.6 ± 0.1	40.5 ± 0.1	35.5 ± 0.5
plerospheres (%) ^b	36.5	37.3	20.5	25.9

^aMajor element information is from ref 62 (for samples F-1 and C-1) and NIST certificates (for samples F-2 and C-2). Standard deviation of HTEs was calculated based on duplicates. ^bFraction of plerospheres in CFA, which was manually counted using SEM images, with f(%) = number of plerospheres/total number of observed particles.

characteristics. A follow-up question is whether the occurrence and mobility of HTEs with low volatility (e.g., Cr, Ni, and Cu) would be similar or distinct in different types of CFA after combustion. The potential difference in HTEs in different CFA matrices might provide an insight into developing tailored waste management strategies for CFA.

From the methodology perspective, a range of complementary techniques have been employed to investigate trace elements in CFA, such as total digestion, sequential extraction, scanning/transmission electron microscopy (SEM/TEM),³⁰ laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS),³¹ and X-ray absorption spectroscopy (XAS).³² However, most previous studies relied on one or two technique(s), which might be biased and failed to provide a full picture of HTEs in complex matrices such as CFA. Developing a more robust methodology framework is essential for gaining an in-depth understanding of the speciation, distribution, and mobility of HTEs in CFA. Our previous work has developed a methodology framework to characterize the properties of rare earth elements (REEs) in CFA using complementary methods including total digestion, SEM and energy-dispersive X-ray spectroscopy (SEM-EDX), XAS, and sequential chemical extraction.⁷ In this study, its effectiveness for investigating other trace elements in complex matrices is further tested.

The goal of this study is to obtain a comprehensive understanding of the speciation, distribution, and mobility of HTEs in different types of CFA. Two class F CFA samples and two class C CFA samples were selected to examine the similarity/difference of embedded HTEs. Cr, Ni, and Cu were selected as representative low-volatility HTEs because of their relatively high abundance in CFA and potential carcinogenic effects. Complementary techniques including total digestion, SEM–EDX, XAS, and sequential extraction are employed in this study. The combined results of these complementary techniques provide a quantitative understanding of the occurrence and mobility of HTEs in different types of CFA. Our results are further compared with previous studies and show a general trend regarding the mobility of HTEs in different types of CFA.

2. MATERIALS AND METHODS

2.1. CFA Samples and Reference Compounds. Four representative CFA samples were collected by considering their chemical composition and important coal sources in the United States (Table 1). Briefly, samples F-1 and C-1 were collected from coal-fired power plants located in the Southeastern United States, and samples F-2 (SRM-2690) and C-2 (SRM-2691) were from the National Institute of Standards and Technology (NIST). Samples F-1 and F-2 are class F CFA, and their feed coals are bituminous coal from the Illinois Basin and sub-bituminous coal from a surface mine in Craig, Colorado, respectively. Samples C-1 and C-2 are class C CFA, with the feed coal being sub-bituminous coal from the Powder River Basin.

Unless otherwise specified, chemicals used in the study were all of ACS grade or higher. A set of reference compounds containing Cr, Ni, or Cu for XAS analysis was obtained or synthesized (details are given in the Supporting Information, Table S1) based on previous studies on the speciation of trace elements in CFA and SEM–EDX results in this study. Chromium reference compounds include CaCrO₄, FeCr₂O₄, Cr₂O₃, Ca₃Cr₂(SiO₄)₃,³³ Cr(III)-doped Fe₂O₃, and Cr-(III)-doped glass. Nickel reference compounds include NiO, Ni₃(PO₄)₂, NiFe₂O₄,³⁴ Ni(II)-doped Fe₂O₃, and Ni(II)-doped glass. Copper reference compounds include Cu₂O, CuO,³⁵ Cu(II)-doped Fe₂O₃, and Cu(II)-doped glass.

2.2. Chemical Composition Analysis. 2.2.1. Total Digestion. The concentrations of HTEs including Cr, Mn, Co, Ni, Cu, Zn, Cd, and Pb in CFA samples were determined after total digestion following our previous method.⁷ Briefly, 1 g of CFA samples was ashed at 600 °C in a muffle furnace for 3 h to remove unburned carbon before total digestion. Then, ~50 mg of CFA samples was reacted with 3 mL of HF and dried at 120 °C to partially remove Si. The mixtures were then mixed with 2 mL HF and 1 mL HNO₃ and heated at 190 °C for 24 h, after which the mixtures were evaporated to near dryness. This step was repeated until no residue was left. Finally, the samples were redissolved in 10 mL 2% (v/v) HNO₃.

Cr	Component 1	Component 2	Component 3	Sum	R-factor
F-1	Cr(III)-doped Fe ₂ O ₃ , 78.6±5.3%	FeCr ₂ O ₄ , 25.2±5.9%		100.0%	0.01190
C-2	Ca ₃ Cr ₂ (SiO ₄) ₃ , 51.6±15.2%	FeCr ₂ O ₄ , 40.6±15.5%	CaCrO ₄ , 14.0±4.1%	106.2%	0.03866
Ni	Component 1	Component 2		Sum	R-factor
F-1	Ni(II)-doped Fe ₂ O ₃ , 65.2±6.6%	NiO, 36.9±6.7%		102.1%	0.01217
F-2	Ni(II)-doped Fe ₂ O ₃ , 65.9±8.4%	NiO, 34.8±8.7%		100.7%	0.01922
C-1	Ni(II)-doped Fe ₂ O ₃ , 57.4±9.2%	NiO, 42.7±9.5%		100.1%	0.02846
C-2	Ni(II)-doped Fe ₂ O ₃ , 71.1±8.0%	NiO, 29.0±8.2%		100.1%	0.01682
Cu	Component 1	Component 2		Sum	R-factor
F-1	Cu ₂ O, 99.0±4.5%			99.0%	0.02590
F-2	Cu ₂ O, 79.8±2.8%	Cu(II)-doped Fe ₂ O ₃ , 19.6±2.8%		99.4%	0.01038
C-1	Cu ₂ O, 81.6±2.4%	CuO, 18.4±2.3%		99.9%	0.00798
C-2	Cu ₂ O, 73.0±2.3%	CuO, 27.5±2.2%		100.5%	0.00706

Table 2. Summar	y of Cr, Ni	, and Cu Spec	ciation in CFA Sa	amples Quantified	l by LCF of XANES

Samples after total digestion were further diluted to a proper concentration level using HNO₃, and multielement internal standards (SPEX CertiPrep Inc) were added to samples with a final concentration of 20 ppb. Prepared samples were finally analyzed by ICP-MS (Table 1).

2.2.2. Sequential Chemical Extraction. Sequential extraction was conducted to evaluate the mobility of HTEs in CFA samples. A modified three-step European Community Bureau of Reference (BCR) method³⁶ was used. Four fractions are defined: (1) water-/ acid-soluble and exchangeable (step 1, e.g., carbonates), (2) reducible (step 2, e.g., Fe-Mn oxides), (3) oxidizable (step 3, e.g., organic matter and sulfides), and (4) residue (e.g., glass phase). step 1 was conducted by reacting 0.5 g of CFA samples at room temperature with 16 mL of 1 M CH₃COONa at pH 5.0 for 6 h. For step 2, the residue from step 1 was reacted with 20 mL of 0.04 M NH₂OH·HCl in 25% (v/v) CH₃COOH for 6 h at 96 °C. In step 3, the residue from step 2 was reacted with 6 mL of 0.02 M HNO3 and 10 mL of 30% H₂O₂ at 85 °C and pH 2.0 for 6 h. After cooling, 5 mL of 3.2 M CH₃COONH₄ in 20% (v/v) HNO₃ was added. At the end of each step, the solution was separated from the residue by centrifugation at 10,000 rpm for 10 min. The solution was filtered and acidified for the measurement of HTEs by ICP-MS. The fraction in the residue was calculated as residue = total - (step 1 + step 2 + step 3), where total, step 1, step 2, and step 3 are fractions of elements determined by total digestion and from steps 1-3 of sequential extraction, respectively.

2.2.3. Concentration Measurement by ICP-MS. Concentration measurement after total digestion and sequential chemical extraction was conducted at the Georgia Institute of Technology. The mass spectrometer (Agilent 7500a) was carefully tuned for high sensitivity before measurement. A series of calibration standards (SPEX CertiPrep Inc) with known metal concentrations (0, 1, 5, 10, 20, 50, 80, 100, 150, and 200 ppb) were prepared, and each standard was spiked using multielement internal standards at a final concentration of 20 ppb. Calibration standards were measured for every 20 samples to ensure accuracy.

2.3. Solid-Phase Analysis. 2.3.1. Scanning Electron Microscopy and Energy-Dispersive X-ray Spectroscopy. Petrographic thin sections of epoxy-bound CFA samples were prepared by the National Petrology Services, Inc. and coated with carbon for SEM–EDX analysis. SEM images were obtained at 5 kV and 10 μ A with a working distance of 5 mm using a Hitachi SU8230. EDX spectra for particles of interest were collected at 30 kV and 30 μ A with a working distance of 15 mm using an Oxford X-Max^N EDX detector. Elemental maps were collected on selected areas at 30 kV and 30 μ A with a 200 ms dwell time. A total of ~100 h was spent on SEM–EDX analysis, and 4000+ particles in CFA samples were examined.

2.3.2. X-ray Absorption Near-Edge Structure Spectroscopy. Cr, Ni, and Cu K-edge X-ray absorption near-edge structure (XANES) spectra of CFA samples and reference compounds were collected at Beamlines 5-BM-D and 12-BM-B at Advanced Photon Source (APS, Lemont, IL) and Beamline 4-1 at the Stanford Synchrotron Radiation Lightsource (SSRL; Menlo Park, CA). Linear combination fitting (LCF) analysis was conducted on the sample spectra using corresponding reference compounds to identify and quantify the speciation of contributing phases. Samples were finely ground and brushed onto Kapton tapes. Energy was calibrated by measuring the corresponding metal foils (Cr at 5989 eV, Ni at 8333 eV, and Cu at 8979 eV) simultaneously in the reference channel during sample scans. XANES data for samples were collected in the fluorescence mode at room temperature using a Vortex detector (APS 5-BM-D) or a 13-element Ge solid-state detector (APS 12-BM-B and SSRL 4-1). Typically, 2–6 scans were collected for each sample. XANES analysis was conducted using the software Ifeffit.³⁷ Spectra were merged and normalized for LCF analysis as detailed below.

In order to identify and quantify the speciation of Cr, Ni, and Cu in CFA, LCF was conducted using corresponding reference compounds in the energy range from -30 to +150 eV relative to the edge position of individual elements. Fits were selected to minimize the *R*-factor and the number of reference compounds involved. It was found that each sample spectrum could be fitted by a combination of two or three reference compounds. Fits with the smallest *R*-factors are listed in Table 2.

3. RESULTS AND DISCUSSION

3.1. Chemical Composition and Mineralogy of CFA. The chemical composition of CFA samples is listed in Table 1. The examined HTEs in all CFA samples are generally at 20-200 ppm. The concentrations of Cr (174.6 ppm), Co (45.1 ppm), Ni (116.8 ppm), Zn (169.9 ppm), and Pb (84.4 ppm) in sample F-1 are almost twice those of other CFA samples, except for Mn (104.3 ppm), Cu (128.3 ppm), and Cd (48.1 ppm) that are slightly less than or similar to other samples (Table 1). The X-ray diffraction (XRD) patterns of the CFA samples (Figure S1)⁷ showed the presence of quartz (SiO₂), mullite (Al₆Si₂O₁₃), hematite (Fe₂O₃), and magnetite (Fe₃O₄) in F-1 and F-2. Quartz, mullite, tricalcium aluminate (Ca₃Al₂O₆), anhydrite (CaSO₄), periclase (MgO), and lime (CaO) were identified in C-1 and C-2. The mineralogical composition of F-2 and C-2 was previously quantified using the Rietveld method (Table S2),³⁸ and aluminosilicate glass (>60%) is the most abundant phase in both F-2 and C-2, followed by quartz (\sim 10%) and mullite (\sim 8%) in F-2, with other phases at <5%.

CFA particles are mainly spheres, cenospheres (particles with an empty hollow core), or plerospheres (particles with a hollow core that is filled with other particles), with an average particle size of 1–100 μ m (Figure S2). Our previous study suggested that the occurrence of plerospheres (i.e., particle encapsulation) might significantly influence the mobility of REEs.⁷ In order to quantitatively compare the potential difference of particle encapsulation in class F versus class C CFA samples, the fraction of plerospheres in CFA was manually counted using SEM images, with f (%) = number of plerospheres/total number of observed particles. These values are found to be 36.5 and 37.3% for class F CFA samples

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Cr₂O₃: 45.6% Cr Fe₂O₃: 27.5% Cr Al₂O₃: 16.1% MgO: 10.9% Fe Si Mg Ca 2 4 keV 6 8 10 Fe Fe₂O₃: 80.9% SiO₂: 6.4% Cr Al₂O₃: 3.8% CaO: 1.4% Cr₂O₃: 0.9% AISi Са Cr 2 4 keV 6 8 10 SiO₂: 67.2% Si CaO: 14.5% Fe₂O₃: 13.0% Ca Cr₂O₃: 2.7% NiO: 0.7% 7e Ni 0 2 4 keV 6 8 10

Figure 1. SEM images (left panels), EDX maps (middle small panels), and EDX spectra (right panels) showing Cr-bearing phases in CFA samples: (a) F-2, (b) C-1, and (c) C-2. Yellow arrows in SEM images indicate the particles for EDX measurements.



Figure 2. SEM images (left panels), EDX maps (middle small panels), and EDX spectra (right panels) showing Ni-bearing phases in CFA samples: (a) F-2, (b) C-2, and (c) C-2. Yellow arrows indicate the particles for EDX measurements.

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Figure 3. SEM images (left panels), EDX maps (middle small panels), and EDX spectra (right panels) showing Cu-bearing phases in CFA samples: (a) F-1 and (b) F-2. Yellow arrows indicate the particles for EDX measurements.

F-1 and F-2, respectively, as compared to 20.5 and 25.9% for the class C CFA samples C-1 and C-2, respectively (Table 1).

3.2. Speciation and Distribution of Cr, Ni, and Cu by SEM-EDX. SEM-EDX analyses were conducted to reveal the speciation and distribution of HTEs in CFA samples. Particles containing Cr, Ni, and/or Cu are summarized in Table S3. Chromium was usually found to coexist with Fe in particles. The particles in Figures 1a, S3a (sample F-2), and S3b (sample F-1) mainly contain Cr and Fe and display a compositional change from Cr-dominated (Cr₂O₃, 45.6%) to Fe-dominated $(Fe_2O_3 > 66\%)$. Based on the chemical composition, they might be metal oxides belonging to the spinel group (AB_2O_4) where $A = Fe^{2+}$, Mg^{2+} , or Ni^{2+} ; $B = Fe^{3+}$, Cr^{3+} , or Al^{3+}).³⁹ The particle in Figure 1a might be chromite spinel [(Fe,Mg)- $(Cr,Al)_2O_4$ with partial substitutions of Mg²⁺ for Fe²⁺ at site A and Al³⁺ for Cr³⁺ at site B. The particles in Figure S3a,b might be magnetite spinel $[(Fe,Ni)(Fe,Cr)_2O_4]$ with minor sub-stitutions of Ni²⁺ for Fe²⁺ at site A and Cr³⁺ for Fe³⁺ at site B. Cr-bearing spinel minerals were previously observed in coal from Kentucky³⁰ and in coal ash based on XAS data²⁶ and thermodynamic calculations.⁴⁰ The Fe-dominated particles in Figures 1b (sample C-1) and S3c (sample F-2), probably Fe oxides (e.g., hematite $[Fe_2O_3]$), contain only a minor amount of Cr_2O_3 (~1%). The Cr-bearing particles in Figures 1 and S3 have a particle size of around $2-15 \ \mu m$ and are either discrete particles without association with other phases (particles in Figures 1a and S3a) or embedded in the glass phase (particles in Figures 1b and S3b,c).

Chromium was also detected in Si-enriched particles. Figure 1c (sample C-2) shows that low-concentration Cr (Cr₂O₃, 2.7%) is colocalized with Si, Ca, Fe, and Ni on the edge of a >75 μ m Si-enriched particle. The larger Si-enriched particle might be quartz based on its irregular shape and absence of other elements, while the Cr-bearing phase on the edge might be a glass phase derived from partial melting of Cr-bearing silicate minerals (e.g., illite).¹⁵ Another Si-enriched particle that contains a minor amount of Cr (Cr₂O₃, 0.7%) is shown in Figure S4a (sample F-1). It has a particle size of 5 μ m and is encapsulated in a ~75 μ m porous glass phase. Finally, Cr with colocalization of Fe and Zn was detected in a ~5 μ m Ca-enriched particle (CaO, 69.5%), probably Ca oxides (e.g., lime

[CaO]). This particle is encapsulated along with other fine particles in a \sim 75 μ m glass phase (Figure S4b, sample C-2).

As for Ni, three types of Ni-bearing phases were observed. First, Ni was detected in magnetite spinel $[(Fe,Ni)(Fe,Cr)_2O_4]$ with NiO content at <8.5%, as shown in Figures S3a (sample F-2) and S3b (sample F-1). In an investigation of Ni speciation in pulverized coal and petroleum coke cocombustion ash, Nibearing Fe oxides were identified using TEM-EDX.41 Second, some Si-enriched particles might contain Ni. One example is the Si-enriched particle in Figure 1c (sample C-2), as described previously, which contains a minor amount of Ni (NiO, 0.7%). More frequently, Ni was found to be present in Ni-enriched phases with the NiO content generally >70% and colocalize or not with P (P₂O₅, <15%). Figure 2a (sample F-2) and 2b (sample C-2) are two examples of Ni likely deposited on unburnt carbon particles, both of which are colocalized with P and encapsulated in the glass phase. The Ni-enriched particle (~15 μ m) in Figure 2c (sample C-2), on the other hand, is encapsulated in a glass phase as well, but without unburnt carbon detected. Figure S5a (sample C-2) displays a discrete particle (~10 μ m) containing Ni and P without association with the glass phase. While in Figure S5b (sample C-2) and S5c (sample F-2), Ni is present in two particles with a particle size of $<5 \ \mu m$ and both particles are encapsulated in the glass phase. It is intriguing to observe that Ni and P are colocalized in CFA. Its mineralogy remains unknown but is unlikely $Ni_2(PO_4)_3$ which has 50.1% NiO and 49.9% P_2O_5 .

As for Cu, only two Cu-bearing particles were observed using SEM–EDX and both are encapsulated in the glass phase. Figure 3a (sample F-1) shows a ~8 μ m particle containing moderate amounts of Cu (CuO, 31.7%) and Zn (ZnO, 18.4%). Because of its relatively high Cu–Zn content, this particle might be Cu–Zn oxides, probably a product of Znbearing Cu sulfide (e.g., covelline, CuS) after coal combustion.³⁰ An Fe-enriched particle (~5 μ m) containing minor amounts of Cu (CuO, 0.6%) and Cr (Cr₂O₃, 0.9%) is presented in Figure 3b (sample F-2). This particle might be Fe oxides as well, similar to the Cr-bearing Fe oxides, as previously discussed (Figure 1b), but contains both Cu and Cr.

3.3. Speciation of Cr, Ni, and Cu by XANES. The Cr, Ni, and Cu XANES spectra of reference compounds and CFA

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Figure 4. (a) Cr, (b) Ni, and (c) Cu K-edge XANES spectra of the reference compounds and CFA samples (black lines) with LCF results (red lines). The peak at 5991 eV (labeled with *) of F-2 and C-1 samples in (a) likely arise from the L_1 -edge absorption of Ba (thousands of ppm in CFA). Results of the LCF are listed in Table 2.

samples are present in Figure 4. The Cr XANES spectra of Cr(III)- and Cr(VI)-bearing reference compounds display distinctively different features (Figure 4a): CaCrO₄ shows a prominent pre-edge peak at 5992.6 eV, arising from the 1s to 3d electronic transition,³³ while the pre-edge peak is absent and the main edge position is at a lower energy for Cr(III)bearing reference compounds. On the other hand, Cr XANES spectra of the Cr(III)-bearing reference compounds can be differentiated by the features of the main peak. For example, the spectrum of $Ca_3Cr_2(SiO_4)_3$ (uvarovite) has a split main peak at 6008 eV and a shoulder at 6018 eV. The spectra of $FeCr_2O_4$ (chromite), Cr(III)-doped Fe_2O_3 , and glass are similar but different in the relative intensity between the main peak at 6010 eV and the shoulder at 6022 eV. The Cr XANES spectra of samples F-1 and C-2 are similar to that of Cr(III)doped Fe₂O₃, while the spectra of F-2 and C-1 are noisy and likely influenced by the L₁-edge absorption (peak at 5990.9 eV) of Ba (~5800 ppm in F-2). LCF was conducted on samples F-1 and C-2 to quantify Cr species in CFA samples (Table 2), while XANES spectra of F-2 and C-1 were not fitted because of the interference. Sample F-1 is best fitted by 78.6% Cr(III)-doped Fe₂O₃ and 25.2% FeCr₂O₄, and sample C-2 is composed of 51.6% Ca₃Cr₂(SiO₄)₃, 40.6% Cr(III)-doped Fe₂O₃, and 14.0% CaCrO₄. Both fits suggest the dominant presence of Cr(III) (>86%) in CFA, which is consistent with previous studies showing that typically >80% of Cr occur as Cr(III) in CFA.^{26,27,29} Additionally, the presence of $FeCr_2O_4$ and Cr(III)-doped Fe₂O₃ in CFA samples based on LCF is in line with the identification of Cr-bearing spinel minerals (Figures 1a and S3a,b) and Fe oxides (Figures 1b and S3c) by SEM-EDX, respectively. At last, the presence of $Ca_3Cr_2(SiO_4)_3$ in sample C-2 agrees well with the previous observation of significant occurrence of Cr in silicates.^{15,26,40}

For Ni-bearing reference compounds, the Ni XANES spectra are generally similar in appearance, characterized by a prominent peak at 8350 eV and a shoulder at 8366 eV, while the relative intensity between the peak and the shoulder is slightly different (Figure 4b). For example, NiO has a more evident shoulder and Ni(II)-doped Fe₂O₃ shows a featureless shoulder. The Ni XANES spectra of the CFA samples are similar and characterized by a main peak at 8350 eV but has a featureless shoulder at 8366 eV, suggesting a slightly disordered local environment of Ni in CFA. LCF finds that 60-70% Ni occurs as Ni(II)-doped Fe₂O₃ in CFA samples, with the remaining fraction (30-40%) as NiO (Table 2). Although the reference compound $NiFe_2O_4$ (trevorite spinel) was included, it is not an important Ni species in all CFA samples based on LCF. Indeed, Ni was observed in magnetite spinel [(Fe,Ni)(Fe,Cr)₂O₄], as shown by SEM–EDX in Figure S3a,b. It is possible that the local structure of Ni in magnetite spinel is more similar to Ni(II)-doped Fe₂O₃, and thus, LCF suggests the dominant presence of Ni as Ni(II)-doped Fe₂O₃ in CFA samples. In addition, Ni-enriched particles (NiO wt % >70%) with colocalization with P and Si (generally P_2O_5 wt % <15% and SiO₂ wt % <10%, Figures 2 and S5) were observed using SEM-EDX. It is likely that the local coordination environment of Ni in those Ni-enriched particles, on the other hand, resembles that of pure NiO, and the significant presence of Ni as NiO in CFA is obtained by LCF. The LCF results of Ni as NiO and Ni(II)-doped Fe₂O₃ in this study agree well with previous studies,^{15,42} suggesting that Ni predominantly coordinated with oxygen in the local structure for both bituminous and sub-bituminous coal-derived ashes. The presence of NiO in CFA is expected, as Ni sulfides, which have been identified in coal,^{30,43} might decompose and form NiO after coal combustion.

The Cu XANES spectra of Cu-bearing reference compounds and CFA samples are plotted in Figure 4c. The Cu XANES spectrum of Cu₂O, a Cu(I) reference compound, is distinct from that of Cu(II) reference compounds, in that Cu₂O has a strong pre-edge peak at 8982.5 eV. The spectra of Cu(II) reference compounds are different in the energy positions of



Figure 5. Percentages of trace elements in CFA samples (a) F-1, (b) F-2, (c) C-1, and (d) C-2 that are associated with sequential extraction steps for (1) water-/acid-soluble and exchangeable (e.g., carbonates), (2) reducible (e.g., Fe–Mn oxides), (3) oxidizable (e.g., organic matter and sulfides), and (4) residual (e.g., silicates) fractions. Standard deviation was based on triplicate.

the main peak and the shoulder. For example, the main peak and the shoulder of CuO are located at 8998 and 9013 eV, respectively; in contrast, they left-shifted to 8996.6 and 9011 eV, respectively, for Cu(II)-doped glass. The XANES spectra of CFA samples are similar to each other and characterized by a strong pre-edge peak at 8983 eV, especially for sample F-1, implying the significant presence of Cu(I) in CFA samples. LCF results support this conclusion as XANES spectra of CFA samples were best fitted by >70% Cu_2O with the remaining fraction as CuO or Cu(II)-doped Fe₂O₃ (Table 2). The fits are not optimal in the energy range 9000-9025 eV, where the spectral shoulder is located. This might be due to the distortion or reduced ordering of Cu local coordination environments in CFA after combustion, which can lead to the presence of a featureless spectra shoulder, as compared to the reference compounds with a better ordered structure. Such changes in spectral features for the same compound due to combustion-induced structure distortion were observed for the combustion of REE-containing minerals in our recent study.⁴⁴ The observed dominant presence of Cu(I)/(II) oxides and/or Cu(II)-doped Fe₂O₃ by LCF is consistent with the SEM-EDX observation of Cu-enriched particles (Figure 3a) and Cubearing Fe oxides (Figure 3b).

3.4. Trace Element Association and Mobility by Sequential Extraction. Sequential chemical extraction was conducted to investigate the HTE mobility under different conditions (Figure 5 and Table S4). HTEs in class F versus class C CFA samples are characterized by distinct chemical associations and mobility. In general, >65% of Cr, Mn, Co, Ni, Cu, and Zn in samples F-1 and F-2 are associated with the residue fraction, with <10% trace elements in the water-/acidsoluble and exchangeable fraction (step 1), \sim 10–20% in the reducible fraction (step 2), and <5% in the oxidizable fraction (step 3). In marked contrast, only <20% of these elements in samples C-1 and C-2 are in residue, while \sim 30–40% are in the water-/acid-soluble and exchangeable fraction, \sim 30–40% in the reducible fraction, and <10% in the oxidizable fraction. The chemical associations of Cd/Pb are not distinct between class F and class C CFA samples, but again, more Cd/Pb are associated with the residue in class F CFA samples (>90%) than in class C CFA samples (~60%).

Generally, the water-/acid-soluble and exchangeable, reducible, and oxidizable fractions are considered to be more mobile, which might be leached into environments and become bioavailable under different conditions. In this regard, mobile fractions of HTEs in class C CFA samples (40-90%) are 2-7 times higher than those in class F CFA samples (10-50%). Considering that the contents of each HTE in class F versus class C CFA samples are different, it is more straightforward to compare the amount of mobile fraction of each HTE (mg/kg CFA or ppm) (Table S4). With this approach, the calculated mobile fraction amount of each HTE in class C CFA is still 2-5 times higher than that of class F CFA. The risk assessment code is another criterion commonly used to evaluate the risk level of HTEs.⁴⁵⁻⁴⁷ Based on the water-/acid-soluble and exchangeable fractions (%), there are five risk levels: no risk for <1%, low risk for 1-10%, medium risk for 10-30%, high risk for 30-50%, and very high risk for >50%. As such, all the HTEs examined in class F CFA samples show low to medium risk. On the other hand, HTEs in class C CFA samples should be categorized as medium to high risk (Table S4). Overall, based on the results of sequential extraction, HTEs in class C CFA samples are characterized by higher mobile fractions (e.g., water-/acid-soluble) and mobility than class F CFA samples, implying relatively higher environmental risks.

3.5. HTEs in Class F versus Class C CFA. In this study, a range of complementary techniques were employed to obtain a full image of the speciation, distribution, and mobility of HTEs in different types of CFA. The speciation of Cr, Ni, and Cu in class F and class C CFA is found to be broadly similar (Figures 1-4 and Table 2). Chromium is mainly present in Fe oxides/ silicates and spinel minerals, while Ni and Cu mainly occur as corresponding oxides or impurities in Fe oxides. Cr. Ni, and Cu in Fe oxides could result from pyrite (FeS₂) decomposition during coal combustion. Pyrite is an important host phase of a variety of HTEs, such as As, Se, Mo, Sb, Tl, Hg, Ni, Cu, Zn, and Pb.48,49 On the other hand, the presence of Ni and Cu oxides in CFA might arise from the decomposition of their sulfides or organically associated forms in coal.² Additionally, although Cr and Cu have multiple oxidation states, the majority of them (>70%) stays in the lower oxidation states Cr(III) and Cu(I), respectively (Table 2). Limited oxidation of Cr and Cu might be due to rapid coal combustion (~ 2 s) and cooling (\sim 30 s) processes³² or strong reducing microenviron-ments within the matrix,²⁶ which restrict the extent of the oxidation reaction.

The mobility of HTEs (including Cr, Ni, and Cu) is distinct between class F and class C CFA based on sequential extraction (Figure 5). Recent studies on CFA from the United States also show a general trend that the mobility of trace elements (Cr, Mn, Cu, Zn, Pb, and REEs) in class C CFA is 2-5 times higher than the mobility of those in class F CFA^{7,50-54} (Table S5). For example, Taggart et al.⁵⁰ investigated the leachability of REEs in a range of CFA samples in the United States and found that class C CFA showed a notably higher extractability of REEs and other trace elements than class F CFA. A compilation of literature data on CFA around the world is listed in Table S5. Because of the lack of sample details and the use of different leaching/extraction methods, directly comparable studies are limited. Nevertheless, available data on class F CFA from China,^{29,55-57} Brazil,⁵⁸ Poland and Slovakia,⁵⁹ and Japan and Indonesia²⁹ show similarly low mobile fraction of trace elements (generally <30%) as those from the United States (Table S5).

Possible explanations for the distinct mobility of class F versus class C CFA include different chemical speciation (e.g., oxides vs silicates) and distribution (discrete vs encapsulated particles) of HTEs. Considering the similar occurrence of each HTE (Cr, Co, Ni, Cu, Zn, Cd, and Pb) among different coal types (bituminous vs sub-bituminous coal) and coal sources (the United States vs other countries)² and the broadly similar speciation of Cr, Ni, and Cu in different types of CFA after coal combustion based on SEM and XANES results (this study), the difference in the chemical speciation of HTEs in CFA, if present, may not completely result in the distinct mobility of class F versus class C CFA.

Upon careful examination of our results, the difference is more likely due to different physical distributions of HTEs in class F versus class C CFA. As demonstrated in Section 3.2, particles containing Cr, Ni, and/or Cu are found to be discrete particles or encapsulated in the glass phase (plerospheres) (Figures 1–3). The fractions of encapsulated particles in all HTE-bearing particles observed by SEM are not distinct between class F versus class C CFA (Table S3). However, on counting the abundance of plerospheres in CFA, around 37% particles in class F CFA samples are found to be plerospheres, which is approximately twice the amount found in class C CFA samples (20–26%), suggesting the higher possibility of HTE- bearing particles being encapsulated in plerospheres in class F CFA. Additionally, XRD analysis of the residual solids after each sequential extraction step (Figure S1) revealed that lime, periclase, anhydrite, and tricalcium aluminate in class C CFA samples dissolved after step 1 (water-/acid-soluble and exchangeable fraction) and step 2 (reducible fraction). In marked contrast, there were no obvious mineralogical changes associated with class F CFA samples, and most of the Fe oxides (e.g., hematite and magnetite) which might contain plenty of HTEs retained in the residue after all extraction steps (Figure S1). This supports the fact that even though HTEs might occur in similar chemical forms in class F versus class C CFA. the particles bearing them (e.g., oxides) in class F CFA are more likely to be encapsulated in the glass phase than those in class C CFA, which might prevent the dissolution and release of HTEs during sequential extraction. Recent studies on REE extraction from class F versus class C CFA also concluded that more REE encapsulation in the glass phase might be the reason for low REE extractability of class F CFA.7,52,60,61 Nevertheless, such an explanation of particle encapsulation may be more applicable to HTEs with low volatility (Cr, Ni, Cu, and REEs), as the retention of low-volatility HTEs in solid and/or melt phases during coal combustion increases the chance of them being captured by glass phases; while particle encapsulation has less influence on highly volatile elements (As, Se, and Hg), which tend to become a gaseous phase and condense on the particle surfaces.

The observation on the distinctively different mobility of HTEs in class F versus class C CFA suggests that specific strategies might be implemented for better management or beneficial reuse of different types of CFA. For instance, the EPA Final Rule⁶ requires monitoring groundwater quality near the CCR disposal sites, and more careful and frequent monitoring approaches might be required for ash landfills and surface impoundment with class C CFA. As for the beneficial utilization of CFA in construction or soil amelioration, one might need to consider the type and amount of CFA used in order to minimize the amount of trace elements leached by rain or ground water. Future studies are warranted to further investigate the mobility of trace elements in class F and class C CFA worldwide, which would set a baseline for investigating and implementing better CFA management strategies.

4. CONCLUSIONS

The occurrence and mobility of HTEs (with an emphasis on Cr, Ni, and Cu) in different types of CFA samples (class F vs class C) were systematically characterized using a series of complementary techniques. The concentration of trace elements in all CFA samples is generally within 20–200 ppm. High-quality SEM–EDX results show a range of particles bearing Cr, Ni, and/or Cu. Specifically, Cr was found in spinel minerals, Fe oxides, glass phase, and Ca oxide; Ni was observed in spinel minerals and probably as Ni oxide; and Cu was present in Fe oxides and probably as Cu–Zn oxide.

Those particles generally have a particle size of $2-20 \ \mu m$ and might be either discrete particles or encapsulated in the glass phase. Using the LCF of XANES, quantitative results on trace element speciation were obtained. It is found that for a specific HTE (e.g., Cr), its speciation in class C versus class F CFA samples is broadly similar. Specifically, Cr is mainly present in Fe oxides or silicates (>50%) and spinel minerals (20-40%); Ni mainly occurs in Fe oxides (60-70%) and as pubs.acs.org/EF

NiO (30–40%); and Cu mainly occurs as Cu_2O (>70%) and CuO or in Fe oxides (20–30%).

Although Cr and Cu have multiple oxidation states, the majority of Cr and Cu (>70%) stays in the lower oxidation states. Based on sequential extraction, trace elements (including Cr, Co, Ni, Cu, Zn, Cd, and Pb) in class C CFA are much more mobile than those in class F CFA, implying more environmental risks for class C CFA. Low-mobility fractions of trace elements in class F CFA might be a result of particle encapsulation by the glass phase in class F CFA.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.energyfuels.0c02164.

Preparation of reference compounds, CFA mineralogy quantified using the Rietveld method, sequential extraction results; and XRD patterns and SEM images of CFA samples (PDF)

AUTHOR INFORMATION

Corresponding Author

Yuanzhi Tang – School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, Georgia 30332-0340, United States; orcid.org/0000-0002-7741-8646; Phone: 404-894-3814; Email: yuanzhi.tang@eas.gatech.edu

Authors

- Pan Liu School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, Georgia 30332-0340, United States
- Qian Wang School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, Georgia 30332-0340, United States
- Haesung Jung School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, Georgia 30332-0340, United States; o orcid.org/0000-0002-8795-248X

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.energyfuels.0c02164

Notes

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