# Formation and Speciation of Arsenic-, Chromium-, and Nickel-Bearing $PM_{2.5}$ Produced in a 7-kW Coal Combustion System

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## Summary

Mode of occurrence analyses indicate that As, Cr, and Ni in the Illinois No. 6 (Herrin) coal are generally associated with relatively large discrete mineral grains, whereas these elements are much more strongly associated with macerals and fine-grained minerals in Absaloka (McKay or Rosebud seam) coal. The coals were burned using conventional and low-$NO_x$ conditions in an ~7-kW combustion system to evaluate the importance of elemental modes of occurrence, coal properties, and combustion conditions on As, Cr, and Ni volatility and speciation.

Chemical analyses of size-classified (~0.4–7.7-µm) fly ash samples indicated that Cr in fly ash was characterized by relatively uniform particle-size distributions and relative enrichment/depletion (RED) factors for all four fly ashes, which is indicative of nonvolatility. In Absaloka fly ashes, As exhibited similar nonvolatile partitioning characteristics. Consistent with an elemental vaporization–particle surface deposition process, As and Ni concentrations and RED factors for the Illinois No. 6 fly ashes generally increased with decreasing particle size. Conventional and low-$NO_x$ combustion of Illinois No. 6 coal did not significantly affect trace element volatility; however, low-$NO_x$ Absaloka combustion promoted Ni volatilization.

The inorganic phase compositions of fly ash particle matter ~2.5 µm in aerodynamic diameter ($PM_{2.5}$) were determined using x-ray diffraction. Illinois No. 6 and Absaloka $PM_{2.5}$ contain aluminosilicate glass, quartz ($SiO_2$), ferrite spinel ($AB_2O_4$; *e.g.*, where $A^{2+}$ = Fe, Mg, Ni, and $B^{3+}$ = Al, Fe, Cr), and mullite ($Al_6Si_2O_{13}$). These phases may be useful tracers for investigating the influence of coal-burning power plant emissions on ambient $PM_{2.5}$ composition. Absaloka $PM_{2.5}$ is distinguished from Illinois No. 6 $PM_{2.5}$ by the presence of lime (CaO) and periclase (MgO) and lack of anhydrite ($CaSO_4$).

The As, Cr, and Ni speciation of $PM_{2.5}$ samples was determined using x-ray absorption fine structure spectroscopy. Differences in Illinois No. 6 and Absaloka coal combustion conditions did not significantly affect As, Cr, or Ni speciation. $As^{5+}O_4$-containing phases occur in Illinois No. 6 and Absaloka $PM_{2.5}$. Presumably, carboxyl-bound $As^{3+}$ and Ca in Absaloka coal promoted the formation of $Ca_3(AsO_4)_2$. $Cr^{3+}/Cr^{6+}$ is much greater in Illinois No. 6 $PM_{2.5}$ relative to Absaloka $PM_{2.5}$. The predominance of maceral-bound $Cr^{3+}$ and oxygen functional groups in Absaloka coal may have promoted $Cr^{6+}$ formation. Illinois No. 6 and Absaloka $PM_{2.5}$ contain similar NiO-containing phases, possibly ferrite spinel.