TRANSITION METAL SPECIATION OF FOSSIL FUEL COMBUSTION FLUE GASES

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Project Description

Chromium in its highest valence state, Cr^{6+}, is more toxic than Cr^{2+} and Cr^{3+} forms and is a carcinogen. X-ray absorption fine structure spectroscopy (XAFS) analyses indicate that Cr^{3+} is the dominant (Cr^{3+} >95% of the total Cr) species in bituminous coal and oil fly ashes [1–3]. However, Cr XAFS measurements of Powder River Basin (PRB) subbituminous coal fly ashes are lacking. Limited Cr XAFS measurements of a PRB Wyodak coal and ash (ashed at 500°C in air for 24 hr) and Absaloka coal and fly ashes (produced in a 7-kW combustion system) indicate that maceral-bound Cr^{3+} occured in these coals and that, on average, 52% ±5% and 57%, respectively, of the total ash Cr occurs as Cr^{6+} [1, 4]. These Cr^{6+} proportions are much larger than those observed in previous XAFS measurements on bituminous coal fly ashes (Cr^{6+} <5% of the total Cr) produced under typical coal combustion conditions. As part of an ongoing investigation, five PRB coal fly ashes are being analyzed using XAFS to determine whether PRB subbituminous coal fly ashes do indeed contain greater proportions of Cr^{6+} relative to bituminous coal fly ashes. Thermodynamic modeling is also being used to investigate whether differences in bituminous and PRB subbituminous coal compositions and/or combustion conditions control the formation of Cr^{6+}. Differences in coal Cr modes of occurrence will also be examined to explain potential variations in Cr^{6+} concentrations.

XAFS and x-ray diffraction analyses of residual (No. 6 fuel) oil combustion fly ash indicate that $NiSO_4 \cdot xH_2O$ and Ni-bearing spinel ($NiFe_2O_4$) are the dominant species [3, 5–7]. Evidence presented by Galbreath et al. [6] suggests that the addition of magnesium hydroxide ($Mg[OH]_2$) to residual (No. 6 fuel) oil, added to suppress sulfuric acid mist formation and coke formation and promote the formation of friable deposits, impedes nickel sulfation and promotes $NiFe_2O_4$ formation during the combustion and/or ash formation process. The presence of $NiFe_2O_4$ may increase future inhalation health risk estimates because it is generally considered a carcinogen, whereas $NiSO_4 \cdot xH_2O$ is not [8, 9]. Thermodynamic modeling is being used to evaluate the potential effects of $Mg(OH)_2$ injection on the Ni speciation of residual oil combustion flue gas and fly ash.

Goal

Project goals are threefold:

- Determine whether PRB subbituminous coal fly ashes contain greater proportions of Cr^{6+} relative to bituminous coal fly ashes.
- Evaluate the roles of coal Cr modes of occurrence and flue gas compositions on Cr oxidation.
- Evaluate the effects of $Mg(OH)_2$ injection on the Ni speciation of residual oil combustion flue gas and fly ash.

Rationale

Two hypotheses are being evaluated:

- The predominance of maceral-bound Cr^{3+} and oxygen-functional groups in PRB subbituminous coals promotes Cr^{6+} formation during combustion and/or fly ash formation.
- The addition of $Mg(OH)_2$ to residual oil impedes Ni sulfation and promotes the formation of $NiFe_2O_4$ during combustion and/or fly ash formation.

Approach

Five representative PRB fly ash samples from power plants equipped with different pollution control devices (e.g., baghouse, electrostatic precipitator, scrubber) were obtained from the EERC Coal Ash Resources Research Consortium℠. Cr contents of the fly ash samples were determined using microwave-assisted acid digestion (U.S. Environmental Protection Agency [EPA] Method 3050 and American Society for Testing and Materials Standard Practice D 5513) followed by inductively coupled plasma–mass spectrometry. Coal fly ash Cr^{3+} and Cr^{6+} are being determined using XAFS. Cr^{3+} and Cr^{6+} results for the PRB subbituminous coal fly ashes will be compared to published Cr^{3+} and Cr^{6+} values for bituminous and lignite coals.

A thermodynamic model, the Facility for Analysis of Chemical Thermodynamics (FACT), is being used to investigate potential differences in the Cr^{3+}/Cr^{6+} of bituminous and PRB subbituminous coal fly ashes. Comprehensive equilibrium gas-phase calculations similar to those of Kashireninov and Fontijn [10] are being performed, with emphasis on Cr^{6+} behavior. Representative bituminous and PRB subbituminous flue gas and fly ash compositions are being used to investigate whether compositional differences alone can explain potential variations in Cr^{3+}/Cr^{6+}. Differences in coal Cr modes of occurrence will also be considered in explaining potential differences in the Cr speciation of bituminous and subbituminous coal fly ashes.

Although chemical equilibrium is probably not attained in such a dynamic system as a utility-scale combustion flue gas, an equilibrium analysis can provide useful information on speciation and mass distributions toward which chemical reactions proceed under given conditions of temperature, pressure, and composition. Given that actual coal combustion conditions will be subject to kinetic control, the results of this proposed equilibrium investigation will be used for future development of a reaction scheme for a kinetic model using CHEMKIN-III.

FACT is also being used to model the apparent effect of a $Mg(OH)_2$ oil additive on Ni sulfation reactions. $Mg(OH)_2$ concentrations are being varied to evaluate the sensitivity of Ni sulfation reactions to the alkaline-earth content of residual oil. The $Mg(OH)_2$ injection rate into an oil-fired unit may be optimized to promote Ni sulfation and suppress the formation of $NiFe_2O_4$, a suspected carcinogen.

Progress

Five PRB coal fly ash samples, containing 45 to 80 ppm Cr, were analyzed using XAFS in July 2002. The XAFS data are being reduced and interpreted. A report from the University of Kentucky on the XAFS analysis results is expected before January 1, 2003.

The chemical compositions of a PRB subbituminous Absaloka coal and a bituminous Illinois No. 6 coal were used as input into FACT. A pressure of 1 atm, temperature range of 100° to 1500°C, and an excess air concentration of 20 mol% were considered in the equilibrium calculations. Equilibria among approximately 25 solid (s) and gaseous (g) Cr species were calculated assuming ideal gas mixtures and pure condensed species. A given species was considered only within the temperature range for which thermochemical data exist; i.e., data extrapolation was not performed. Predicted Cr species equilibria for the Absaloka and Illinois No. 6 coal combustion flue gases are presented in Figures 1 and 2, respectively. Above 1100°C, Cr^{4+} and Cr^{6+} oxide species, CrO_2 and CrO_3, respectively, are the dominant gas species in both flue gases. CrO_3(g) is predicted to be stable only at very high temperatures and not at stack temperatures. Spinel phases, $FeCr_2O_4$ and/or $MgCr_2O_4$, containing Cr^{3+} are the first solid phases to form in both flue gases. The Cr^{3+}-bearing Cr_2O_3(s) phase is predicted to form in both flue gases at lower temperatures, but in the Illinois No. 6 fly ash, Cr_2O_3(s) becomes sulfated at $\leq$ 500°C because of the much higher sulfur content of this bituminous coal relative to the PRB coal. Theoretically, Cr^{6+} phases are not expected to occur in PRB subbituminous Absaloka or bituminous Illinois No. 6 coal fly ashes.

Status

Ongoing Ni speciation modeling, data reduction, and interpretation activities will continue until the spring of 2003. Reporting aspects of the project are anticipated to be completed during June 2003.

Potential Users/Technology Transfer

Knowledge of the Cr and Ni species being released by coal- and oil-burning power systems will ultimately result in a more realistic inhalation-based risk assessment. Such an assessment is necessary for EPA to properly address public health risks and regulatory decisions for fossil fuel-burning boilers.

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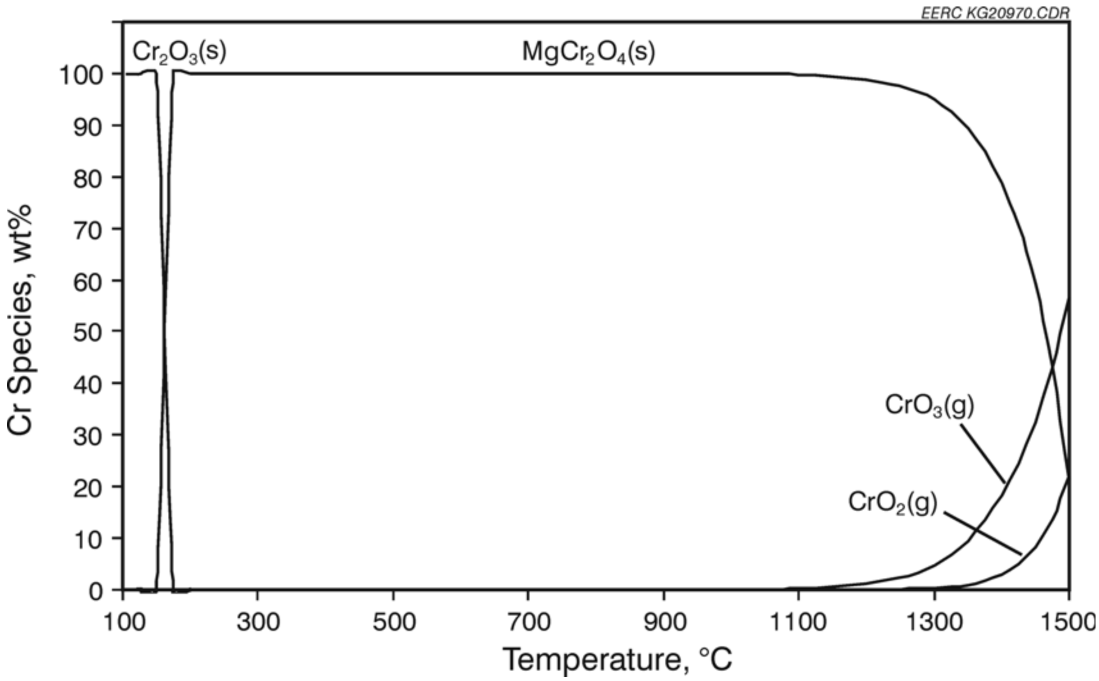

Figure 1. Predicted Cr Speciation Distribution of Absaloka Coal Combustion Flue Gas

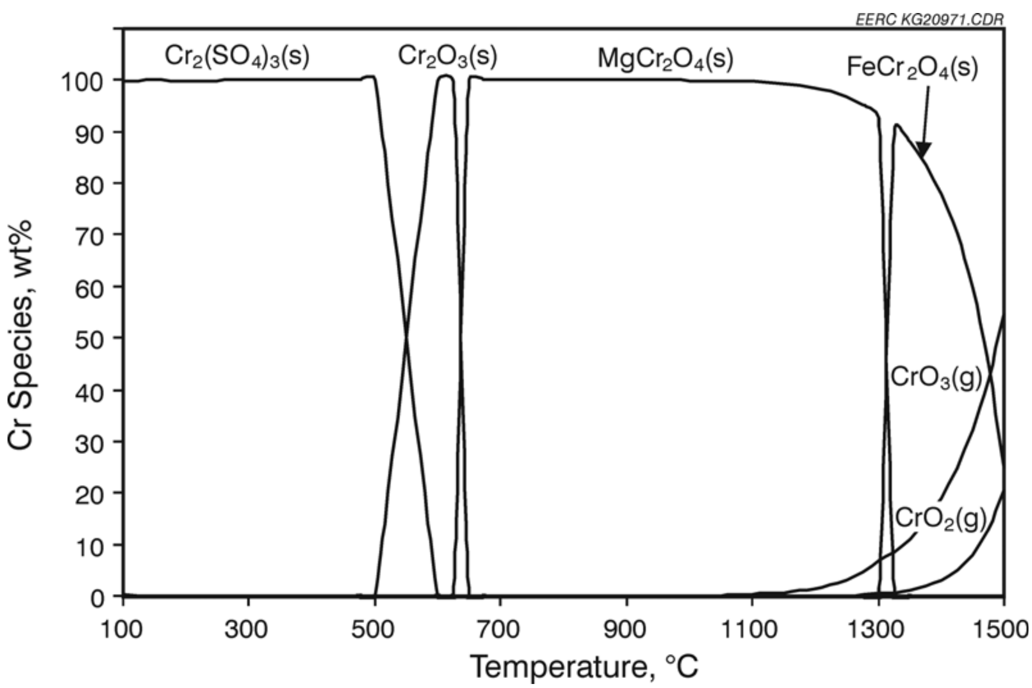

Figure 2. Predicted Cr Speciation Distribution of Illinois No. 6 Coal Combustion Flue Gas

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