

Theoretical Investigations of Mercury Interaction with the Hematite (1-102) Surface

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Theoretical investigations using density functional theory (DFT) were carried out in conjunction with experimental studies to investigate the interaction between oxidized Hg and hematite ($\alpha\text{-Fe}_2\text{O}_3$), an important mineral component of fly ash. The experimental study designed to simulate Hg sorption in a coal-fired power plant flue gas system, involved the exposure of the fine fraction of bituminous coal fly ash ($\leq 0.1 \mu\text{m}$) to methane combustion flue gas, supplemented with SO_2 , NO_x , HCl, and Hg in a packed-bed reactor. Sorption reaction products were characterized by synchrotron-based x-ray fluorescence mapping (s-XRF) and x-ray diffraction (XRD). Preliminary s-XRF results showed that Hg in the sample is correlated with Fe, S, Cl, Br, and to a lesser extent with Se and As. From the XRD analysis, the dominant mineral phases detected were quartz, hematite, and various sulfate-bearing cements.

Based on the experimental results, DFT studies were carried out to investigate the adsorption of oxidized Hg on the $\alpha\text{-Fe}_2\text{O}_3(1-102)$ surface, which shows high stability in the temperature range of flue gases from *ab initio* thermodynamics. All DFT calculations were carried out with the VASP (Vienna *Ab initio* Simulation Package) code. The two $\alpha\text{-Fe}_2\text{O}_3(1-102)$ surface terminations are: (1) M2-clean, which corresponds to the oxygen-terminated r-cut surface with the first layer of cations removed and with no surface hydroxyl groups and (2) M2-OH₂-OH, which has bi-hydroxylated top oxygen atoms and a second layer of hydroxylated oxygen atoms. The most probable adsorption sites of Hg, Cl, HgCl and HgCl₂ on the two $\alpha\text{-Fe}_2\text{O}_3$ surface terminations were suggested based on calculated adsorption energies. Additionally, Bader charge and projected density of states (PDOS) analyses were conducted to characterize the oxidation state of adsorbates and their bonding interactions with the surfaces. Preliminary results indicate that oxidized Hg physically adsorbs on the M2-clean surface with a binding energy of -0.103 eV. Chlorine added to the Hg-adsorbed surface enhances Hg adsorption, which is evidenced by a shorter Hg-surface interaction distance compared to a surface with singly bound Hg. Bader charge and PDOS analyses suggest that a slight charge transfer and bonding interaction occurs during adsorption in spite of the weak binding energy.