Chemisorption of Cu(II) and Co(II) on Allophane and Imogolite

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Abstract: Adsorption of Cu^{2+} and Co^{2+} by synthetic imogolite, synthetic allophanes with a range of SiO_2/Al_2O_3 ratios, and allophanic clay fractions from volcanic ash soils was measured in an ionic medium of 0.05 M $Ca(NO_3)_2$. The effect of pH (and metal concentration) on adsorption was qualitatively similar for the synthetic and natural allophanes with relatively minor changes in behavior caused by variable SiO_2/Al_2O_3 ratios. Cu and Co were chemisorbed by allophane at pH 5.0 – 5.5 and 6.9 – 7.2 (pH values for 50% adsorption level), respectively, with concomitant release of 1.6 – 1.9 protons/metal ion adsorbed. Quantitatively, adsorption by imogolite was less than that by the allophanes, presumably because of fewer sites available for chemisorption on the tubular structure of imogolite. Electron spin resonance studies of the imogolite and allophanes revealed that Cu^{2+} was adsorbed as a monomer on two types of surface sites. The preferred sites were likely adjacent AlOH groups binding Cu^{2+} by a binuclear mechanism; weaker bonding occurred at isolated AlOH or SiOH groups. These chemisorbed forms of Cu^{2+} were readily extracted by EDTA, CH_3COOH, and metals capable of specific adsorption, but were not exchangeable. In addition, the H_2O and/or OH^- ligands of chemisorbed Cu^{2+} were readily displaced by NH_3, with the formation of ternary Cu-ammonia-surface complexes.

Key Words: Allophane • Chemisorption • Cobalt • Copper • Electron spin resonance • Imogolite • SiO_2/Al_2O_3

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