2.1.P13

Modeling the thermodynamics at the transition state of monochlorophenol -pyrite interactions

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Pyrite is the most abundant metal sulfide in nature. It is present in many geochemical settings and is associated with mineral and coal deposits. Pyrite showed promise for removing organic pollutants both in the presence and absence of light. Pyrite defect sites are capable of splitting H_2O to form reactive OH radicals in the absence of light. Hence, pyrite can be used as a substitute for Fe^{2+}/H_2O_2 in the design of Fenton's process which is commonly used for organic pollutants. The motivation for this project is to propose an *in situ* degradation mechanism for the chemical oxidation of monochlorophenols (MCP) in pyrite-mediated systems. The pyrite-mediated catalytic process is believed to occur via an adsorptive step preceding the degradation of organic pollutants on the pyrite surface. Thus, the aim was to evaluate the thermodynamics of MCP adsorption. MCP was chosen because these compounds are mutagenic and carcinogenic industrial chemicals and are listed as priority pollutants.

Thermodynamic parameters of the activation state for phenol and three monochlorophenol (MCP) isomer-pyrite complexes were derived from temperature dependent kinetic data. We used 2-chlorophenol (2-CP), 3-chlorophenol (3-CP) and 4-chlorophenol (4-CP). Both the initial rate and adsorption density increased in the order phenol < 2-CP < 3-CP < 4-CP, suggesting that the increasing number of chlorine on the aromatic ring results in enhanced CP adsorption. The activation energy (E_a), Gibbs free energy (ΔG^o), entropy (ΔS^o) and enthalpy (ΔH^o) of the activation stage for MCP adsorption onto pyrite were calculated by the Arrhenius and Eyring models. The ΔS^o values were always approximately zero and $-T\Delta S^o$ values were positive indicating that the activation state of MCP adsorption process was entropy-controlled. The observed linear dependence of ΔH^o with $-T\Delta S$ signals an entropy-enthalpy compensation effect of MCP adsorption. The Γ_{MCP} data were fit well by a 1-pK diffused double layer model (1-pK DLM) considering the following reaction stoichiometries.

Reaction stoichiometry	Log K
$>SS^{-1/3} + HL = >SSHL^{-1/3}$	-3.2
$>FeSS^{-1/3} + HL => FeSSHL^{-1/3}$	3.2
$>SSFe^{+1/3} + HL => SS$	-2.7

Molecular configurations of MCP-pyrite surface complexes were determined by infrared spectroscopy and *ab initio* molecular modeling methods. The results will provide firm theoretical basis for the development of a pyrite-induced unit process to remediate aquatic systems polluted with chlorinated organic compounds.

2.1.P14

Spectacular silver segregation on the surface of sulfides

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The study of mineral surfaces is critical to understanding the behaviour of minerals during processes used in metal extraction, espically froth flotation (and leaching). Of particular interest to sulfide mineral flotation is their behaviour in alkaline solutions. The major aim of this study is to examine the effect of solutions containing $Ca(OH)_2$ on the surface chemistry of the complex sulfide minerals of the tetrahedrite $Cu_{12}Sb_4S_{13}$ –tennantite $Cu_{12}As_4S_{13}$ group. Of specific interest are the changes in the amount and speciation of silver at the mineral surface following treatment with $Ca(OH)_2$. Natural samples of tennantite ($Cu_{10}Zn_2As_4S_{13}$) from Casapalca, Peru where analysed using X-ray photoelectron spectroscopy (XPS). Analysis of the fresh surface of tennantite sample showed that copper, silver, zinc, arsenic, antimony and sulfur are all present at the surface as sulfide species. Following treatment in a saturated $Ca(OH)_2$ solution the surface chemistry of the tennantite changed dramatically. The most notable change was the decrease in concentrations of all elements except carbon, oxygen and silver, the latter being increased to at least 4 monolayer coverage. It is clear from XPS analysis that silver at the surface of tennantite is not a metallic species but is consistent with a cuprous proustite species.

The mechanisms for the migration of silver from the bulk to the surface, and the environment of the silver at the surface of the minerals are critical to understanding the process of silver enrichment at the surface of tetrahedrites-tennantites following alkaline leaching. A potential driving force for the mechanism of migration of silver through the bulk to the surface is the leaching of copper resulting in a metal-depleted surface; copper concentrations were observed in the $Ca(OH)_2$ solution. This could act as an 'effective' geochemical gradient causing the movment of silver cations through the bulk to stabilise the surface. The enormous enrichment of silver at the surface subsequent to migration results in the formation of a layer of a new phase on the surface of the mineral. Diffusion through sulfides is known to occur through a variety of pathways, for example via microfractures, structural planes and vacancies, and all these mechanisms are likely to have contributed to the migration of silver from the bulk of the tennantite to the surface.