

Organic-Inorganic interactions and the earth's resources and environment

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Introduction : Although organic-inorganic interactions are often considered to play significant roles not only in the evolution of the earth and life but also in the earth's resource and environment, concrete mechanistic and quantitative views on these interactions are still lacking. I will first review geohistorical backgrounds for organic-inorganic interactions with special reference to heavy metal deposits such as U and Fe and also to hydrocarbons. I will then introduce new approaches for investigating reaction mechanisms and rates of some typical interactions in order to provide predictive methods for the earth's resource and environment. Mechanisms of U deposition associated with coals, thermal decomposition of dissolved humic substances, possible transformations of organic pollutants in soils will be given as examples of such predictive approaches.

Mechanisms and time scales of U deposition in coals : Our previous experimental studies on uranium reduction by lignite under diagenetic or hydrothermal conditions (100-200 °C) suggested that the dehydrogenation of hydroxyl groups and aliphatic hydrocarbonaceous moieties are responsible for the U reduction (Nakashima et al., 1984, 1987; Nakashima, 1992a). These reactions have been further verified by the simulation experiments by simple alcohols and aliphatic hydrocarbons (1-octadecanol, 2-propanol and n-octacosane). The apparent rate constants and the activation energies have been measured and compared with the same type of experiments with natural lignite samples (Nakashima, 1992b). These results support the proposed reaction mechanisms from a kinetic point of view. The equilibria of the system lignite - aqueous uranyl solution at 150-200°C have been studied to calculate standard free energy changes of the reactions (Nakashima, 1992b). These data are consistent with the experimental results that the lignite - aqueous uranyl solution system reaches the equilibrium after the dehydrogenation of hydroxyl groups and aliphatic hydrocarbonaceous moieties. All these kinetic and thermodynamic data on simple organic molecules confirm our U reduction mechanisms by lignite based on simple organic functional groups.

These experimentally determined kinetic parameters were applied to evaluate time scales of U deposition (Nakashima et al., 1999). The half-life of U precipitation is estimated to be 3 hours - 1 year under modest thermal conditions (200 - 100°C), 340 years for radioactive waste repositories (50°C) and 10^4 - 10^5 years at the earth's surface (25 - 4°C).

Thermal decomposition of dissolved humic compounds : In natural aquatic environments, humic substances are the most abundant organic compounds dissolved in near-surface waters. They have many functional groups capable of complexing toxic heavy metals and they can be a stable carrier of pollutants.

However, their thermal stability has not been known to date. We have conducted heating experiments of humic acid in aqueous solution. By tracing the decrease of dissolved humic acids at different temperatures, the reaction rates and activation energies were determined. By extrapolating these to lower temperatures, the half lives of the humic acid in water were about 8 years at 40 °C and 70 years at 20°C. These results indicate that dissolved humic substances are not stable at the earth's and some pollutants might not be carried by these compounds. These results are particularly important in the long-term assessment of organic-hosted pollutants in the environment.

Transformation of organic pollutants on minerals : The organic pollutants such as chlorinated hydrocarbons are actually important environmental issues. The data are accumulated on their contents and distribution in soils and groundwaters. However, their chemical forms in soils/groundwaters and their fate in the future are not yet known. They have a possibility to interact with minerals to be transformed in different chemical compounds which can be either more or less toxic. We are now developing a new method to study mechanisms and rates of the interaction of organics on minerals based on the attenuated total reflectance infrared (ATR-IR) spectroscopy. This method will be employed to evaluate the possible transformations of organic pollutants in soils.

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