

論文の内容の要旨

論文題目 **Reactive transport and adsorption-desorption processes of fluoride in a granitic soil**

(花崗岩質土壤中のフッ化物の反応性輸送および吸脱着プロセス)

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Fluoride contamination of groundwater is a serious environmental concern due to its possible effect on drinking water resources and natural ecosystems. Excessive fluoride intake (exceeding the WHO guideline value of 1.5 mg/l in drinking water) results in serious health hazards. The source of fluoride in groundwater can be due to natural or anthropogenic. While interaction of groundwater with the fluoride bearing minerals is ascribed to be the major controlling factor for fluoride contamination of groundwater, leachable fluoride from soil can be a potential source of fluoride to the shallow groundwater under suitable conditions. Hence, it is necessary to decipher the mechanism of fluoride transport processes in soil in order to understand the possible contribution of soil leachable fluoride to groundwater. The overall objectives of this study were (1) to identify the mechanism of fluoride sorption/desorption in a granitic soil under wide range of pH and solid/solution ratio and validating the results with spectroscopic studies, (2) to develop a fluoride reactive transport model describing the physical and chemical non-equilibrium processes observed in laboratory scale, and (3) to discuss the impact of leachable soil fluoride on the geo-environment.

First, areas with fluoride contamination of groundwater in India (e.g. Rangareddy, Telengana) and Japan (Nishinomiya, Japan) were selected and investigated to understand the behavior of fluoride in groundwater and soil system. Granitic soils from Nakatsugawa (Japan) and Tsukuba (Japan) were also investigated to understand the geochemical factors responsible for fluoride mobilization in the soil system, although fluoride concentrations in groundwater in the respective areas are negligible. The results of field observation and analysis show that the leachable fluoride in Rangareddy, India is comparatively high (1.2-30 mg/kg) and corresponds to the occurrence of dissolved fluoride in groundwater in the respective area (2.0-2.3 mg/l). Fluoride in groundwater and soil leachate is negligible in Nakatsugawa (Japan) and Tsukuba (Japan). In Nishinomiya (Japan), soil leachable fluoride is in lower range although shallow groundwater is contaminated with fluoride. Further analysis of geochemical parameters that are related to occurrence of fluoride in soil and of climatological conditions revealed that soil pH, mineral constituents and infiltrating solutions were responsible for the amount of soil leachable fluoride. From the field observations, it can also be inferred that in areas with heavy rainfall, the leachable fluoride is negligible whereas in arid/semi-arid areas, the leachable fluoride

is rather high, which may suggest secondary enrichment of fluoride in soil.

Second, the processes of fluoride removal by calcite were investigated by conducting laboratory batch experiments for kinetic and equilibrium studies. The pH dependent fluoride sorption isotherm data were then studied with surface complexation modeling.

The results showed that adsorption of fluoride decreases as pH increases. Ionic strength also influences fluoride adsorption. In this study, fluoride removal by calcite was modeled with a constant capacitance model with and without precipitation, and the intrinsic surface complexation constants for fluoride sorption were obtained by considering the weighted average minimum error between the observed and modeled sorbed fluoride concentrations. Fluoride adsorption was described by the formation of two surface complexes, >CaF^0 and $\text{>CO}_3\text{FCa}^0$. The formation of >CaF^0 complex was evidenced from thermodynamic approach, whereas inclusion of $\text{>CO}_3\text{FCa}^0$ was necessary to explain fluoride sorption to calcite surface. The existing surface complexation database does not include calcite as a sorbing mineral. Hence, the database for fluoride sorption by calcite was created in this study, which can be used in other applications involving fluoride sorption to calcite considering the experimental conditions. The mechanism of fluoride sorption was found to be adsorption at low fluoride concentrations whereas precipitation plays a role at higher fluoride concentration and lower pH.

Next, the mechanism of fluoride sorption on a granitic soil from Tsukuba was studied through a series of batch kinetic and equilibrium experiments, surface complexation modeling and FTIR spectroscopy.

Fluoride sorption was pH dependent, increase in sorption with decreasing pH. Sorption was found to be influenced by mass loading and surface area. Fluoride sorption on soil was also found to be influenced by increase in electrolyte concentration. Aluminum release was observed during fluoride sorption. Experiment with different ionic strength concentrations suggest that Aluminum release is enhanced by increase in ionic strength.

The observed temporal behavior was best explained by second order kinetic model, suggesting chemisorption processes, whereas the low reaction rate constant ($K_2 = 0.098 \text{ g mg}^{-1}\text{min}^{-1}$) suggests that the sorption processes are fast. The pH dependent isotherm was fit to the non-linear equilibrium isotherm models (Langmuir model, Freundlich model and Dubinin-Raduschkvick model). The maximum sorption density, as calculated from the Langmuir model (at pH 4, because maximum sorption occurs at pH 4) was found to be 0.93 mg/g and the mean free energy of sorption as calculated from the Dubinin-Raduschkvick model was found to be 9.27 kJ/mol, which suggests that ion-exchange is occurring during the sorption processes.

In order to better explain the mechanism of fluoride sorption by soil, the sorption data were explained with a constant capacitance model. The model considers fluoride sorption to a generic surface site (>SOH) and the sorption processes were represented via inner sphere surface complexation. Fluoride sorption was considered by the formation of >SF , >SOHF and >SF_2^- complexes. Speciation of the experimental solutions shows presence of Al-F complexes (AlF_2^+ and AlF_3) in solution although F^- is the major fluoride species. Hence, sorption of AlF_2^+ was included in the model in addition to the F sorption reactions. The intrinsic surface complexation constants for

fluoride sorption reactions and site protonation reaction along with surface site density were optimized in this study. The mechanism of fluoride sorption in a complex soil assemblage was explained to be ion exchange, surface adsorption and Al-F complex sorption. The results reveal that fluoride may be released into the environment under alkaline conditions because of the weak binding and no precipitation.

Finally, fluoride transport processes in a granitic soil were investigated by laboratory column experiment and numerical modeling during fluoride sorption and desorption. Sorption of fluoride in the soil column during transport showed that sorption is high with breakthrough occurring after 17 pore volumes of fluoride injection. Fluoride desorption was comparatively fast, and desorption was slow after 10 pore volumes of flushing. Both fluoride sorption and desorption are found to be kinetically controlled, as evidenced from concentration change in the effluent after stop flow events.

A geochemical model considering fluoride sorption in soil by surface complexation was developed and used to explain fluoride transport during sorption in the column. The transport parameters were optimized from the tracer data (stable isotope of water, δO^{18} and δD). Fluoride sorption was described by sorption to a generic surface site, and the intrinsic surface complexation constants for fluoride sorption reactions and surface site protonation and deprotonation reactions were similar to the optimized values for the soil from batch experiment results.

The results of this study show that fluoride desorption is highly affected by pH and the interfering ions, and fluoride desorption from soil should be considered in evaluation of shallow groundwater fluoride contamination in the areas where soil is contaminated with fluoride.