Extended Summary

Modelling Sorption of Radionuclides on Sorbent Containing Surface Sites With Variable Charges: Ni-Sr-Goethite System**M. GOPALA RAO**

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Results presented in this paper are a part of on-going research at Howard University on retardation of radionuclides by sorption processes during host rock-ground water interactions. Several scientists from various government laboratories and also from private companies are currently involved in studies that will determine if Yucca Mountain in south-western Nevada is a suitable site for a high-level nuclear waste repository. The mountain is composed of tuff, a volcanic rock rich in minerals with relatively high sorption capacity for radionuclides. Several types of zeolite minerals, clay minerals such as montmorillonite, and ferric oxyhydroxides such as goethite are known to occur in the host rock. Traditional ion-exchange theory (Helfferich, 1962) is generally used to describe adsorption of metal ions on fixed-charge exchange sites which is the case for zeolites and clay minerals. Till now, triple-layer surface complexation model (Kent, et al., 1986) is used to describe sorption of nuclides on minerals such as goethite which has pH-dependent charges on its surface. In the present investigation, ion-exchange phase equilibrium theory is used for the first time to describe sorption of mixtures of nickel and strontium ions in aqueous phase on goethite at a constant pH.

Radionuclides used in the study, Ni and Sr are of interest in high-level nuclear waste management. Nickel is present in reactor and fuel rod components; Strontium is an important fission product in high-level nuclear waste. Also, sorption studies of Ni-Sr binary mixtures on 'Nonscents', a zeolitized tuff material, and Beidellite, a clay mineral have been conducted earlier by our research group. A comparison of sorption

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characteristics of this binary pair on three different minerals will be of considerable interest.

Geochemists have traditionally been using mathematical models such as Linear, Langmuir, Freundlich and modified Langmuir to describe sorption isotherms. Parameters of these models K_D and β are not fundamental constants, but are functions of experimental variables such as solid-liquid ratio and the initial concentration of the competing solutes in the liquid and sorbent phases (W.L. Polzer, et al., 1992). Triple-layer surface-complexation model has not been tried to correlate sorption data of mixtures of radionuclides over a wider range of compositions.

Even though goethite contains surface sites with variable charges, the sorption process can still be modelled with ion-exchange phase equilibrium theory provided the pH of the aqueous phase is kept constant. Relevant theoretical considerations and model derivations have been presented earlier (Rao, 1993; Rao, et al., 1992).

Samples of goethite mineral from Biwabik, Minnesota have been supplied by Ward's Natural Science Establishment, Inc. of Rochester, New York. The sorbent samples were crushed, and ground to -80 +150 Tyler mesh size, and the material was first washed with 1M NH_4Cl solution in a columnar mode, and then washed free of the electrolyte with deionized water. 95g of the air dried pretreated goethite samples were equilibrated in a columnar mode with an electrolyte solution containing known mixtures of Ni and Sr, keeping total anion (Cl^-) concentration of 0.3 N constant for all sorption runs. Sorption measurements were made at a constant solution pH of around 7, and a temperature of $27 \pm 1^\circ\text{C}$. A detailed experimental procedure was given earlier (4, 5). Equilibrium condition between the sorbent and solution phases was assured by using small flow rates of solution phase (20-25 ml/hr), concentrated solution phase (0.3 N Cl^-) and a long period of equilibration (5 weeks).

Ni-Sr isotherm shows a very strong preference for Ni ion in the sorbent phase over Sr ion. This result is in stark contrast to the isotherm data of Ni-Sr-'Nonscents' (a zeolitized tuff). In the case of Nonscents, Sr ion is strongly favored on the sorbent phase over Ni ion. In the case of Ni-Sr Beidellite system, there is no preference of Ni or Sr on the sorbent phase.

This selectivity variation from mineral to mineral is of utmost significance in the performance assessment calculations of a nuclear repository. Rational equilibrium constant and sorbent phase activity coefficients of Ni and Sr as functions of sorbent phase solute composition are calculated. Thermodynamic equilibrium constant for Ni-Sr-Goethite system was calculated.

The research strategy used in the present investigation can be summarized as the following: Study sorption characteristics of binary pairs of solutes on single minerals. Ensure equilibrium sorption by using long periods of equilibration, columnar flow system and concentrated electrolyte solutions. Model the sorption process with the more fundamental phase-equilibrium theory. Using fundamental thermodynamic parameters of binary pairs, predict ternary and multi-component solute systems, and validate the theory with experimental data. Finally, predict sorption characteristics of multi-component solute mixtures on mixtures of minerals from the single mineral studies.

Results of the present investigation will be useful in understanding sorption processes, and in the prediction of contaminant mobility in ground water over a range of contaminants and soils.

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References:

1. Helfferich, F., 1962 "Ion Exchange", McGraw-Hill, New York.
2. Kent, D.B., V.S. Tripathi, N.B. Ball, J.O. Leckie, and M.D. Siegel, 1988 "Surface Complexation Modelling of Radionuclide Adsorption in Subsurface Environments", Albuquerque, New Mexico, Sandia National Laboratories, SAND86-7175.

3. Polzer, W.L., M. Gopala Rao, H.R. Fuentes and R.J. Beckman, 1992 "Thermodynamically Derived Relationships Between Modified Langmuir Isotherm and Experimental Parameters", Environmental Science & Technology, Vol. 26, No. 9, pp. 1780-1786.
4. Rao, M. Gopala, 1993, "Modelling Adsorption of Mixtures of Radionuclides by Zeolitized Tuff", High-Level Radioactive Waste Management, Proceedings of the Fourth Annual International Conference, Las Vegas, Nevada, Vol.2, pp. 1496-1503.
5. Rao, M Gopala, P.C. Das, E.U. Honga and A.E. Helou, 1992, "Effect of Solid-Phase Selectivity On Sorption of Cobalt and Strontium by Zeolitized Tuff", High-Level Radioactive Waste Management, Proceedings of the Third Annual Conference, Las Vegas, Nevada, Vol. 2, pp. 1587-1592.

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