AN APPROACH FOR ESTIMATING KINETIC MASS TRANSFER RATE PARAMETERS IN MODELING GROUNDWATER TRANSPORT AT FERNALD, OHIO

H. N. Lee

Environmental Measurements Laboratory, U.S. Department of Energy
201 Varick St., 5th Floor, New York, NY 10014-4811, USA
Tel: (212) 620-6607, Fax: (212) 620-3600, E-mail: hnlee@eml.doe.gov

Abstract

We present an alternative approach for improving the estimation of mass transfer rates among the phases used in groundwater models. The objectives of this study are to understand in detail the sorption processes occurring at Fernald, Ohio, and to refine Fernald's groundwater model. The distribution coefficients with and without considering chemisorption will be determined by laboratory experiments using sediment samples. Once the distribution coefficients are determined, the rates of adsorption, desorption and chemisorption will be calculated by the proposed approach that includes analytical methods and the laboratory experiments.

Introduction

The injection/extraction of groundwater can cause the mass transfer processes among the phases to be in a nonequilibrium state. The importance of nonequilibrium sorption processes involving adsorption, desorption, chemisorption, dissolution and precipitation among the phases has been recognized (Harmon et al., 1992; Brogan and Gailey 1995; Lee et al., 1998). The rate for each process that needs to be determined can greatly affect the model calculations of the underground distribution of a contaminated plume. The accurate determination of rates, particularly for the chemisorption, in which the sorbed contaminant is in the chemically bonded state, is essential for modeling groundwater transport studies. At present, there are no specific formulations that can be used for determining the rate for each process. The values of the adsorption and desorption rates were studied and reported from laboratory studies (for example, Harmon et al., 1992) and from field studies (for example, Goltz and Roberts, 1986). The present study will emphasize the determination of the chemisorption rate that has been shown to have a profound impact on the calculations of underground uranium plumes at the Fernald Environmental Management Project (FEMP), Fernald, Ohio (Lee et al., 1998). In addition, we will also determine the adsorption and desorption rates.

Analytical Method

The governing equations for kinetic mass transfer among phases (Nkedi-Kizza et al., 1984) are:

$$\left[1 + \frac{F \rho \ K_d}{\theta}\right] \frac{\partial C}{\partial t} + \frac{\rho}{\theta} \frac{\partial S_2}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \tag{1}$$

$$\frac{\partial S_2}{\partial t} = (1 - F) k_f \ C - k_r \ S_2 \tag{2}$$

$$= \ k_r \ [(1 - F) K_d \ C - S_2] \tag{3}$$

where C and S_2 represent the concentrations associated with the aqueous and sorbed species, respectively; θ is porosity; ρ is bulk density; K_d is the distribution coefficient; v is the pore-water velocity; D is the diffusion coefficient of aqueous species; k_f and k_r denote the coefficients of adsorption and desorption rate, respectively; and F is the fraction of adsorption in equilibrium with solution concentration for sorbed species, S_1. Total adsorption at equilibrium is simply:

$$S = S_1 + S_2 \tag{4}$$

where

$$S_1 = F K_d C \tag{5}$$

$$S_2 = (1 - F) K_d C \tag{6}$$

To consider the chemisorption process for the sorbed species, S_2, we can rewrite Eq. (2) as following

$$\frac{\partial S_2}{\partial t} = (1-F)k_f\,C - k_r\,S_2 - k_c\,S_2 \tag{7}$$

$$= (k_r + k_c)[(1-F)K_d^*\,C - S_2] \tag{8}$$

where k_c denotes the coefficient of chemisorption rate. The following expressions for K_d^* in Eq. (8) and K_d in Eq. (3) are the distribution coefficients with and without considering chemisorption, respectively,

$$K_d^* = \frac{k_f}{k_r + k_c} \tag{9}$$

$$K_d = \frac{k_f}{k_r} \tag{10}$$

Estimating site specific k_c values is the primary focus of this paper. Hence, by substituting Eq. (10) into Eq. (9), we obtain the following equations

$$k_c = k_f\left[\frac{K_d - K_d^*}{K_d K_d^*}\right] \tag{11}$$

$$= k_f\left[\frac{K_d^c}{K_d K_d^*}\right] \tag{12}$$

where K_d^c is a measure of the ratio of the chemically bound solid phase to the aqueous phase.

Eqs. (11) and (12) can also be derived by applying the time moment analysis (Fahim and Wakao 1982) to the above Eqs. (1), (3) and (8). Hence, the expression for k_r can be obtained by equating the second moment of the above Eqs. (1) and (3) to the diffusion physical nonequilibrium model (Valocchi 1985) because Eqs. (1) and (3) are mathematically equivalent to the first-order physical nonequilibrium model (Nkedi-Kizza et al., 1984), which is a simplified version of the diffusion physical nonequilibrium model. The expression then becomes:

$$k_r = \frac{15\,D_e\,\theta}{a^2 \rho\, K_d (1 - F)} \qquad (13)$$

where D_e is an effective molecular diffusion coefficient within the aggregates and a is the aggregate radius. From Eqs. (10) and (13), we then obtain

$$k_f = \frac{15\,D_e\,\theta}{a^2 \rho\, (1 - F)} \qquad (14)$$

Once the adsorption rate, k_f, is calculated from above Eq. (14), the value of the chemisorption rate, k_c can be calculated by Eq. (11) which requires the values of K_d and K_d^* that can be determined from the following laboratory experiments.

Laboratory Experiments
   To understand the distributions and the site characterization of underground contaminants, sample analyses including sequential leaching, microscopic analyses and sorption experiments are necessary to provide detailed information about sorption processes occurring in groundwater. In this study, we will perform sorption experiments in the laboratory to determine the values of K_d and K_d^*. We will use the sediment samples taken from FEMP where the groundwater has been contaminated by uranium. The detailed description of experiments and the results will be presented in the near future.

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