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Standard Test Method for Distribution Ratios by the Short-Term Batch Method[1]

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INTRODUCTION

As an aqueous fluid migrates through geologic media, certain reactions occur that are dependent upon the chemistry of the fluid itself and upon the chemistry and geochemistry of other fluids and solid phases with which it comes in contact. These geochemical interactions determine the relative rates at which chemical species in the migrating fluid (such as ions) travel with respect to the advancing front of water. Processes of potential importance in retarding the flow of chemical species in the migrating fluid (movement of species at velocities less than the ground-water velocity) include ion exchange, adsorption, complex formation, precipitation (or coprecipitation, for example Ba^{++} and Ra^{++} co-precipitating as the sulfate), oxidation-reduction reactions, and precipitate filtration. This test method applies to situations in which only sorptive processes (adsorption and ion exchange) are operable for the species of interest, however, and is restricted to granular porous media.

It is difficult to derive generalized equations to depict ion exchange-adsorption reactions in the geological environment. Instead, a parameter known as the *distribution coefficient* (K_d) has been used to quantify certain of these sorption reactions for the purpose of modeling (usually, but not solely, applied to ionic species). The distribution coefficient is used to assess the degree to which a chemical species will be removed from solution as the fluid migrates through the geologic media; that is, the distribution coefficient provides an indication of how rapidly an ion can move relative to the rate of ground-water movement under the geochemical conditions tested.

This test method is for the laboratory determination of the *distribution ratio* (R_d), which may be used by qualified experts for estimating the value of the distribution coefficient for given underground geochemical conditions based on a knowledge and understanding of important site-specific factors. It is beyond the scope of this test method to define the expert qualifications required, or to justify the application of laboratory data for modeling or predictive purposes. Rather, this test method is considered as simply a measurement technique for determining the distribution ratio or degree of partitioning between liquid and solid, under a certain set of laboratory conditions, for the species of interest.

Justification for the distribution coefficient concept is generally acknowledged to be based on expediency in modeling-averaging the effects of attenuation reactions. In reference to partitioning in soils, equilibrium is assumed although it is known that this may not be a valid assumption in many cases. Equilibrium implies that (*1*) a reaction can be described by an equation and the free energy change of the reaction, within a specific system, is zero, and (*2*) any change in the equilibrium conditions (T, P, concentration, etc.) will result in immediate reaction toward equilibrium (the concept is based upon reversibility of reactions). Measured partitioning factors may include adsorption, coprecipitation, and filtration processes that cannot be described easily by equations and, furthermore, these solute removal mechanisms may not instantaneously respond to changes in prevailing conditions. Validity of the distribution coefficient concept for a given set of geochemical conditions should not be assumed initially, but rather should be determined for each situation.

This is a short-term test and the attainment of equilibrium in this laboratory test is not presumed, although this may be so for certain systems (for example, strictly interlayer ion exchange reactions of clays). Consistent with general usage, the result of this test could be referred to as "distribution coefficient" or as "distribution ratio;" in the strictest sense, however, the term "distribution ratio" is preferable in that the attainment of equilibrium is not implied.

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The distribution ratio (R_d) for a specific chemical species may be defined as the ratio of the mass sorbed onto a solid phase to the mass remaining in solution, which can be expressed as:

$$R_d = \frac{\text{(mass of solute on the solid phase per unit mass of solid phase)}}{\text{(mass of solute in solution per unit volume of the liquid phase)}} \quad (1)$$

The usual units of R_d are mL/g (obtained by dividing g solute/g solid by g solute/mL solution, using concentrations obtained in accordance with this test method).

Major difficulties exist in the interpretation, application, and meaning of laboratory-determined distribution ratio values relative to a real system of aqueous fluid migrating through geologic media.[2] Typically, only reactions between migrating solutions and solid phases are quantified. In general, geochemical reactions that can result from interaction of the migrating fluid with another aqueous phase of a differing chemistry have not been adequately considered (interactions with other liquids can profoundly change the solution chemistry). Additionally, as noted above, the distribution coefficient or K_d concept implies an equilibrium condition for given reactions, which may not realistically apply in the natural situation because of the time-dependence or kinetics of specific reactions involved. Also, migrating solutions always follow the more permeable paths of least resistance, such as joints and fractures, and larger sediment grain zones. This tends to allow less time for reactions to occur and less sediment surface exposure to the migrating solution, and may preclude the attainment of local chemical equilibrium. Thus, the distribution coefficient or K_d concept is only directly applicable to problems involving contaminant migration in granular porous material.

Sorption phenomena are also strongly dependent upon the thermodynamic activity of the species of interest in solution (chemical potential). Therefore, experiments performed using only one activity or concentration of a particular chemical species may not be representative of actual in situ conditions or of other conditions of primary interest. Similarly, unless experimental techniques consider all ionic species anticipated to be present in a migrating solution, adequate attention is not directed to competing ion and ion complexation effects, which may strongly influence the R_d for a particular species.

Many "sorption" ion complexation effects are strongly influenced, if not controlled, by conditions of pH and Eh. Therefore, in situ conditions of pH and redox potential should be considered in determinations of R_d. To the extent possible, these pH and Eh conditions should be determined for field locations and must be approximated (for transition elements) in the laboratory procedure.

Other in situ conditions (for example, ionic strength, anoxic conditions, or temperature) could likewise have considerable effect on the R_d and need to be considered for each situation. Additionally, site-specific materials must be used in the measurement of R_d. This is because the determined R_d values are dependent upon rock and soil properties such as the mineralogy (surface charge and energy), particle size distribution (surface area), and biological conditions (for example, bacterial growth and organic matter). Special precautions may be necessary to assure that the site-specific materials are not significantly changed prior to laboratory testing.

The choice of fluid composition for the test may be difficult for certain contaminant transport studies. In field situations, the contaminant solution moves from the source through the porous medium. As it moves, it displaces the original ground water, with some mixing caused by dispersion. If the contaminant of interest has an R_d of any significant magnitude, the front of the zone containing this containment will be considerably retarded. This means that the porous medium encountered by the contaminant has had many pore volumes of the contaminant source water pass through it. The exchange sites achieve a different population status and this new population status can control the partitioning that occurs when the retarded contaminant reaches the point of interest. It is recommended that ground water representative of the test zone be used as contact liquid in this test; concentrations of potential contaminants of interest used in the contact liquid should be judiciously chosen. For studies of interactions with intrusion waters, the site-specific ground water may be substituted by liquids of other compositions.

The distribution ratio for a given chemical species generally assumes a different value when any of the above conditions are altered. Clearly, a very thorough understanding of distribution coefficients and the site-specific conditions that determine their values is required if one is to confidently apply the

[1] This test method is under the jurisdiction of ASTM Committee D18 on Soil and Rock and is the direct responsibility of Subcommittee D18.06 on Physical-Chemical Interactions of Soil and Rock.

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[2] Coles, D. G., and Ramspott, L. D., "Migration of Ruthenium-106 in a Nevada Test Site Aquifer: Discrepancy Between Field and Laboratory Results," *Science*, Vol. 215, pp. 1235–1237, March 5, 1982.

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K_d concept (and the measured R_d values) to migration evaluation and prediction.

The adoption of a standard method for determining distribution ratios, R_d, especially applicable for ionic species, is important in that it will provide a common basis for comparison of experimental results (particularly for near-similar conditions).

The most convenient method of determining R_d is probably the *batch method* (this test method), in which concentrations of the chemical species in solid and liquid phases, which are in contact with one another, are measured with time. Other methods include the dynamic test or column flow-through method using (*1*) continuous input and (*2*) pulsed input, the in situ dual tracer test, and the thin-layer chromatography (TLC) test.

In summary, this distribution ratio, R_d, is affected by many variables, all of which may not be adequately controlled or measured by the batch method determination. The application of experimentally determined R_d values for predictive purposes (assuming a functional relationship such as $R_d = K_d$) must be done judiciously by qualified experts with a knowledge and understanding of the important site-specific factors. However, when properly combined with knowledge of the behavior of chemical species under varying physicochemical conditions of the geomedia and the migrating fluid, distribution coefficients (ratios) can be used for assessing the rate of migration of chemical species through a saturated geomedium.

1. Scope

1.1 This test method covers the determination of distribution ratios of chemical species for site-specific geological media by a batch sorption technique. It is a short-term laboratory method primarily intended for ionic species subject to migration in granular porous material, and the application of the results to long-term field behavior is not known. Distribution ratios for radionuclides in selected geomedia are commonly determined for the purpose of assessing potential migratory behavior at waste repositories. This test method is also applicable to studies of intrusion waters and for parametric studies of the effects of variables and of mechanisms which determine the measured distribution ratios.

1.2 The values stated in acceptable metric units are to be regarded as the standard.

1.3 *This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 422 Test Method for Particle-Size Analysis of Soils[3]

D 2217 Practice for Wet Preparation of Soil Samples for Particle-Size Analysis and Determination of Soil Constants[3]

D 2488 Practice for Description and Identification of Soils (Visual-Manual Procedure)[3]

D 3370 Practices for Sampling Water[4]

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *distribution coefficient,* K_d—is identically defined as R_d for equilibrium conditions and for ion exchange-adsorption reactions only. To apply R_d values to field situations, an assumption such that $R_d = K_d$ is necessary. The validity of such an assumption can only be determined by informed experts making a judgment (albeit uncertain) based on a detailed study of the specific site.

3.1.2 *distribution ratio,* R_d—the ratio of the concentration of the species sorbed on the soil or other geomedia, divided by its concentration in solution under steady-state conditions, as follows:

$$R_d = \frac{\text{(mass of solute on the solid phase per unit mass of solid phase)}}{\text{(mass of solute in solution per unit volume of the liquid phase)}} \quad (2)$$

by steady-state conditions it is meant that the R_d values obtained for three different samples exposed to the contact liquid for periods ranging from 3 to at least 14 days, other conditions remaining constant, shall differ by not more than the expected precision for this test method.

The dimensions of the expression for R_d reduce to cubic length per mass (L^3/M). It is convenient to express R_d in units of millilitres (or cubic centimetres) of solution per gram of geomedia.

3.1.3 *species*—a distinct chemical entity (such as an ion) in which the constituent atoms are in specified oxidation states.

4. Significance and Use

4.1 The distribution ratio, R_d, is an experimentally determined parameter representing the distribution of a chemical species between a given fluid and a geomedium sample under certain conditions, including the attainment of a steady state. Based on a knowledge and understanding of the important site-specific factors, R_d values may be used by qualified experts for estimating the value of the distribution coefficient, K_d, for a given set of underground geochemical conditions. The K_d concept is used in mass transport modeling, for example, to assess the degree to which an ionic species will be removed from solution as the solution migrates through the geosphere. For applications other than transport modeling, batch R_d measurements also may be used, for example, for parametric studies of the effects of variables and of mechanisms related to the interactions of fluids with geomedia.

[3] *Annual Book of ASTM Standards,* Vol. 04.08.

[4] *Annual Book of ASTM Standards,* Vol. 11.01.

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