



Designation: **C1733–20** C1733 – 21

Standard Test Method for Distribution Coefficients of Inorganic Species by Batch Method¹

This standard is issued under the fixed designation C1733; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reappraisal. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reappraisal.

INTRODUCTION

As an aqueous fluid migrates through geologic media or contacts an engineered material, 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 chemical and geochemical interactions affect 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 transport 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^{2+} and Ra^{2+} co-precipitating as a sulfate), redox reactions, and precipitate filtration. Partitioning may be caused by processes that include adsorption, precipitation, and coprecipitation that cannot be described easily by equations and, furthermore, these solute removal mechanisms may not instantaneously respond to changes in prevailing conditions and may not be entirely reversible.

An empirical ratio known as the *distribution coefficient* (K_d) is defined as the mass of the solute on the solid phase per unit mass of solid phase divided by the mass of solute in solution per unit volume of the liquid phase (Eq 1). This ratio has been used to quantify the collective effects of these processes for the purpose of modeling (usually, but not solely, applied to ionic species). K_d is used to assess the degree to which a chemical species will be removed from solution (permanently or temporarily) as the fluid migrates through the geologic medium or contacts a solid material; that is, K_d is used to calculate the retardation factor that quantifies how rapidly an ion can move relative to the rate of ground-water movement.

This test method is for the laboratory determination of the K_d , which may be used by qualified experts for estimating the retardation of contaminants 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 degree of partitioning between liquid and solid, under a certain set of conditions, for the species of interest.

Justification for the K_d 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.

The K_d for a specific chemical species may be defined as the ratio of the mass sorbed per unit of solid phase to the mass remaining per unit of solution, as expressed in the above equation. The usual units of K_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).

¹ This test method is under the jurisdiction of ASTM Committee C26 on Nuclear Fuel Cycle and is the direct responsibility of Subcommittee C26.13 on Spent Fuel and High Level Waste.

Current edition approved Feb. 1, 2020/Jan. 1, 2021. Published April 2020/March 2021. Originally approved in 2010. Last previous edition approved in 2017 as C1733 – 17a. DOI: 10.1520/C1733-20; 10.1520/C1733-21.

Major difficulties exist in the interpretation, application, and meaning of laboratory-determined K_d values relative to a real system of aqueous fluid migrating through geologic media **(1)**.² The K_d concept is based on an equilibrium condition for given reactions, which may not be attained 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.

Sorption phenomena also can be strongly dependent upon the concentration of the species of interest in solution. Therefore, experiments performed using only one concentration of a particular chemical species may not be representative of actual in situ conditions or of other conditions of primary interest. Similarly, experimental techniques should consider all ionic species anticipated to be present in a migrating solution, in order to address competing ion and ion complexation effects, which may strongly influence the sorption of a particular species.

Sorption can be strongly controlled by pH. Therefore, in situ pH, especially of groundwater, should be considered in determinations of K_d . Values of pH must be determined, preferably in the field when materials are sampled and must be carefully determined in the laboratory procedure. Other in situ conditions (for example, ionic strength, anoxic conditions, or temperature) could likewise have considerable effect on the K_d and need to be considered for each situation.

Site-specific materials must be used in the measurement of K_d . This is because the determined K_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. This may require refrigeration or freezing of both soil and water samples. Chemical means of preservation (such as addition of acid to groundwater) will cause changes in sample chemistry and must be avoided.

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 a K_d of any significant magnitude, the front of the zone containing this contaminant will be considerably retarded. This means that the granular 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 (but containing added tracers) be used as contact liquid in this test, or a carefully prepared simulated (site-specific) groundwater; 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 K_d for a given chemical species generally assumes a different value when conditions are altered. Clearly, a very thorough understanding of the site-specific conditions that determine their values is required if one is to confidently apply the K_d concept to migration evaluation and prediction.

The most convenient method of determining K_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. Other methods include dynamic column flow-through methods using continuous input of tracer or pulsed input. In the field, a dual tracer test can be conducted using a conservative (non-sorbing) tracer and one that does sorb; from the difference in travel times of the two tracers, K_d can be calculated.

In summary, the distribution coefficient, K_d , is affected by many variables, some of which may not be adequately controlled or measured by the batch method determination. The application of experimentally determined K_d values for predictive purposes 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 solid surface (or geomedium) and the migrating fluid, K_d can be used for assessing the rate of migration of chemical species through a saturated geomedium.

² The boldface numbers in parentheses refer to the list of references at the end of this standard.

1. Scope

1.1 This test method covers the determination of distribution coefficients, K_d , of chemical species to quantify uptake onto solid materials by a batch sorption technique. It is a laboratory method primarily intended to assess sorption of dissolved ionic species subject to migration through pores and interstices of site specific geomeia, or other solid material. It may also be applied to other materials such as manufactured adsorption media and construction materials. Application of the results to long-term field behavior is not addressed in this method. K_d for radionuclides in selected geomeia or other solid materials are commonly determined for the purpose of assessing potential migratory behavior of contaminants in the subsurface of contaminated sites and out of a waste form and in the surface of waste disposal facilities. This test method is also applicable to studies for parametric studies of the variables and mechanisms which contribute to the measured K_d .

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 ASTM Standards:³

[C859 Terminology Relating to Nuclear Materials](#)

[D422 Test Method for Particle-Size Analysis of Soils](#) (Withdrawn 2016)⁴

[D1293 Test Methods for pH of Water](#)

[D2217 Practice for Wet Preparation of Soil Samples for Particle-Size Analysis and Determination of Soil Constants](#)

[D2488 Practice for Description and Identification of Soils \(Visual-Manual Procedures\)](#)

[D3370 Practices for Sampling Water from Flowing Process Streams](#)

[D4448 Guide for Sampling Ground-Water Monitoring Wells](#)

[D5730 Guide for Site Characterization for Environmental Purposes With Emphasis on Soil, Rock, the Vadose Zone and Groundwater](#) (Withdrawn 2013)⁴

[E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods](#)

[E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method](#)

3. Terminology

3.1 Definitions:

3.1.1 Please refer to Terminology [C859](#) for additional terminology which may not be listed below.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *distribution coefficient, K_d , n* —the concentration of a species sorbed on a solid material, divided by its concentration in solution in contact with the solid material, under constant concentration conditions, as follows:

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

3.2.1.1 Discussion—

By constant concentration conditions, it is meant that the K_d values obtained for samples exposed to the contact liquid for two different time periods (at least one day apart), other conditions remaining constant, shall differ by not more than the expected precision for this test method. It is convenient to express K_d in units of mL (or cm^3) of solution per gram of solid material.

3.2.2 *species, n* —specific form of an element defined as to isotopic composition, electronic or oxidation state, complex or molecular structure, or combinations thereof (2).

³ For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

⁴ The last approved version of this historical standard is referenced on www.astm.org.

3.2.3 *tracer, n*—an identifiable substance, such as a dye or radioactive isotope, that can be followed through the course of a mechanical, chemical, or biological process.

4. Significance and Use

4.1 The distribution coefficient, K_d , is an experimentally determined ratio quantifying the distribution of a chemical species between a given fluid and solid material sample under certain conditions, including the attainment of constant aqueous concentrations of the species of interest. The K_d concept is used in mass transport modeling, for example, to assess the degree to which the movement of a species will be delayed by interactions with the local geomedium as the solution migrates through the geosphere under a given set of underground geochemical conditions (pH, temperature, ionic strength, etc.). The retardation factor (R_f) is the ratio of the velocity of the groundwater divided by the velocity of the contaminant, which can be expressed as:

$$R_f = 1 + (\rho_b / \eta_e) K_d \quad (2)$$

where:

ρ_b = bulk density of the porous medium (mass/length³), and
 η_e = effective porosity of the medium (unitless) expressed as a decimal.

4.2 Because of the sensitivity of K_d to site specific conditions and materials, the use of literature derived K_d values is strongly discouraged. For applications other than transport modeling, batch K_d measurements also may be used, for example, for parametric studies of the effects of changing chemical conditions and of mechanisms related to the interactions of fluids with solid material.

5. Apparatus

5.1 *Laboratory Ware* (plastic bottles, centrifuge tubes, open dishes, pipettes), cleaned in a manner consistent with the analyses to be performed and the required precision. Where plateout may have significant effect on the measurement, certain porous plastics should be avoided and the use of fluorinated ethylene propylene (FEP) or tetrafluoroethylene (TFE) containers is recommended.

5.2 *Centrifuge*, capable of attaining 1400 g, or filtering apparatus.

5.3 *Filters*, filtration apparatus, including syringe filters, capable of removing particles of $\geq 0.45 \mu\text{m}$. Filter media should be selected to not sorb species of interest under the experiment conditions. Sorption has been observed on filter media composed of certain materials (3).

5.4 *Laboratory Shaker/Rotator*, ultrasonic cleaner (optional).

5.5 *Environmental Monitoring Instruments*, a pH meter, conductance meter, and thermometer.

5.6 *Analytical Balance* capable of measuring to 0.01 g.

5.7 *Appropriate Equipment*, necessary to replicate in situ conditions within the laboratory apparatus.

5.8 *Analytical Instrumentation*, appropriate for determination of the concentration of major constituents (cations and anions) and of the species of interest (for which K_d is being determined) in the contact solutions (and, optionally, in the solid material samples).

6. Sampling

6.1 The solid samples of soil, rock, sediment, or other materials shall be considered to be representative of the stratum from which it was obtained by an appropriately accepted or standard procedure (for example, methods outlined in Guide D5730) and based on expert judgment.

6.2 The sample shall be carefully identified as to origin in accordance with Practice D2488.

6.3 When using site specific materials, a geological description shall be given of the core material used for the K_d measurement. This may include particle-size analysis (Test Method D422) for unconsolidated material, depth of sample, and boring location.

6.4 Field collected solid phase geomedium samples should not be dried. Freezing is recommended for storage of solid samples.

6.5 Sampling of representative ground water in the test zone for use as the contact liquid in this test method shall be accomplished in accordance with Practices D4448 and D3370, using sampling devices that will not change the quality or environmental conditions of the waters to be tested. Proper precautions should be taken to preserve the integrity of in situ conditions of the sampled water, and in particular to protect against oxidation-reduction, exposure to light for extended periods, and temperature variations. Chemical methods of preservation, such as acidification, shall not be used.

NOTE 1—It is recognized that sampling is likely to be a major problem. Materials (or fractures) that the contaminants pass through are likely to be the most difficult part of the geologic section to sample. In addition, proper sampling entails determining the path of groundwater flow so that the critical materials can be sampled. This determination is seldom accomplished in sufficient detail in normal geologic site exploration programs, and, if it is attempted in some cases, the exploration program may become unacceptably expensive. Specific guidelines are beyond the scope of this test method, however, it is recommended that geologic and water sampling procedures be carefully considered by the personnel involved in the site examination.

7. Procedure

7.1 This test method can be applied directly to unconsolidated material samples or to disaggregated portions of samples. If necessary, ultrasonic methods may be used, although it should be noted that the effect of ultrasonics on the microstructure of the material may lead to higher sorption values in certain cases. Chemical dispersants shall not be used.

NOTE 2—A significant source of error with regard to how well the experimental environment represents natural conditions may be introduced by disaggregating the sample in a batch test in that (a) disaggregation can mask a preferred flow path (either horizontal or vertical), (b) disaggregation can destroy the effect of preferred flow paths caused by fractures or perhaps thin sand stringers, and (c) disaggregation will tend to increase the available surface area of the geologic materials. It is for the purpose of achieving uniformity of application, however, that disaggregation is recommended for this test method. It should be realized by persons applying results from this method that inclusion of the disaggregating operations may for these reasons tend to maximize the values of the K_d obtained from this test method. It may be useful to do replicate tests using as-received and disaggregated samples.

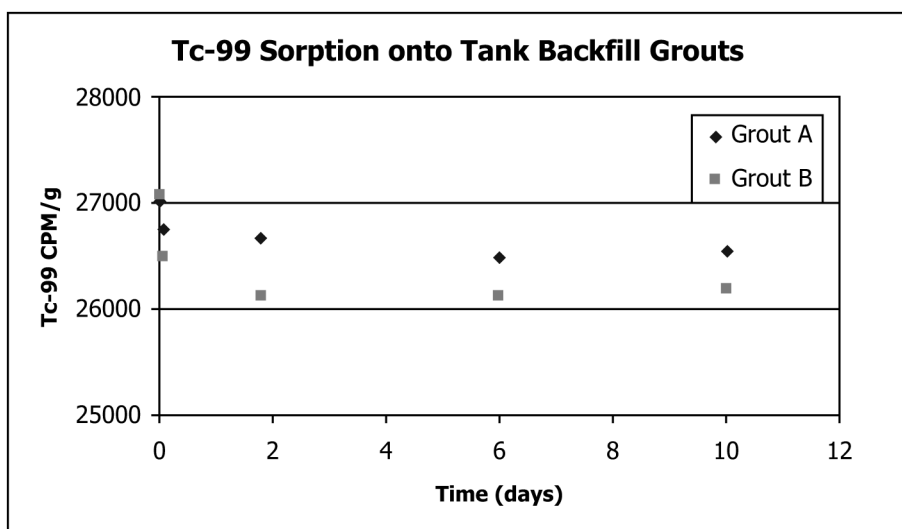
7.2 Using standard analytical procedures, characterize the solid specimen as considered appropriate (for geologic samples see Guide D5730).

7.2.1 Analysis of the solid may include percent elemental composition, mineralogy, carbonate content, specific surface area (m^2/g), total organic carbon, and cation and anion exchange capacity (at specified pHs).

7.2.2 Similarly, characterize the contact liquid obtained from the test zone as appropriate for interpreting the results. Chemical analysis of the liquid should include macro constituents, pH of the contact liquid (Test Method D1293), as well as the concentration (if present) of the chemical species of interest. If the species of interest may exist in the contact liquid in a variety of valence or chemical states (for example, with studies of actinides), care with maintaining chemical conditions to preserve speciation is especially important.

7.3 Before completing the actual K_d determinations, ascertain the time required for the tracer/solid system to achieve constant solution concentrations for each species of interest. This is best done by doing a preliminary K_d batch experiment that is sampled over several time intervals to determine the time required to attain constant solution concentrations of the various species of interest in the liquid. Run these tests as described below, preferably with the highest tracer concentration used in the K_d experiments. These should be conducted with the 25:1 liquid (mass) to solid mass ratio (see 7.7) and only small aliquots of liquid removed for analysis. If larger volumes are needed for analysis, then a larger total volume of experiment (keeping the 25:1 mass ratio) should be used. Sampling intervals at least 1 day apart should be used. If the variation of K_d determined in the last two intervals is greater than the precision expected for the experiment then the test should be continued to longer times until constant concentrations are attained (see Fig. 1). The preliminary tests and the actual tests may be started at the same time but the preliminary samples must be evaluated first to assess the minimum contact time needed.

7.4 For dry materials, pass each sample through a “nonbias” riffle splitter and place 1 to 5 g portions (record weight to nearest 0.01 g) in pre-weighed centrifuge tubes or bottles. The mass of the sediment used may be varied depending on grain size (for example, very fine-grained samples may only require 1 g while greater masses should be used for coarser materials). For wet cohesive samples (for example, fine-grained marine sediment), subsample numerous small portions from a well mixed mass of sediment and combine to obtain 1 to 5 g portions. Record the weight of the sample, to nearest 0.01 g, that was added to preweighed



The two independent starting concentrations were 27 021 and 27 077 CPM/g. Experiments were conducted at room temperature under oxic conditions, pH 12.5.

FIG. 1 Sorption Kinetics of Tc-99 on Two Grouts

centrifuge tubes or bottles. Also record the combined weight of the sample plus the tube. The water content of the sample material should be determined on subsamples separate from those used for the K_d determinations.

NOTE 3—Unless it is decided that the samples may be allowed to dry by exposure to the open air, record a wet weight. Some soils never dry in nature, and characteristics may be greatly altered when dried. This is especially true for originally anoxic sediments. If the samples are not to be allowed to dry before testing, follow Practice D2217 (Procedure B) for maintaining a moisture content equal to or greater than the natural moisture content. In all cases, the contact liquid used in this test is the sampled ground water from the site test zone spiked with the appropriate contaminant of interest.

7.5 If radioactive or stable tracers are used, pretreat the solid samples with the exact solution (contact liquid) used in the determination but without the tracer present. This solution will be a site-specific ground water, a carefully prepared simulated (site-specific) groundwater, or a selected intrusion water. Wash the samples three times with the pretreatment solution. For the first two washes, stir the mixtures of solid and pretreatment solution several times over a 15 min period, centrifuge at ≥ 1400 g for 20 min, and decant off the wash. Apply the third wash for at least 24 h with occasional stirring, and again separate the wash from the sample by centrifugation and decantation as before. After the last wash record the combined weight of the sample and tube. It may be advisable to pre-equilibrate the treatment solution (contact liquid) with the sample prior to the start of this test method. Proceed as in 7.6, using the solution recovered during the third wash after centrifugation and decantation as the treatment solution.

7.6 Prior to the K_d test, the contact solution (either the liquid prepared in 7.5, or some other liquid as needed) should be spiked with the species of interest at a known concentration prepared by the addition of chemically pure reagents. If the contaminant is expected to be present in the aqueous phase at a variety of concentrations, then the tracer used should span the range of interest and the use of isotherms (see 7.15) should be considered. If tracers are used, first equilibrate the tracer with the ground-water (or treatment solution) sample by allowing it to stand for ≥ 12 h (or overnight) and then filter it using a ≤ 0.45 μm pore size membrane filter. Following this step, analyze the contact solution. Care must be taken that the tracer does not alter the contact solution, especially with regard to pH. It may be advisable to dry tracers and then redissolve them into the contact solution (4).

7.7 Add a defined quantity of tracer-bearing solution to the pre-weighed solid sample; the mass of liquid being 25 times that of the calculated dry mass of solid sample. If the solid is moist, then the water content of the solid sample should be subtracted from the liquid phase added to the experiment so that the total mass of water is that needed to provide the proper ratio. Shake occasionally during the course of the test to suspend the solids. The time of contact between the solid and liquid will be maintained as determined in the preliminary test (see 7.3). It is recommended that the liquid be measured in terms of mass and, if necessary, its bulk density should be determined to correct to volume.

NOTE 4—Experiments have shown that K_d will vary depending on the solution-to-solid ratio used in the test. If ratios other than the 25:1 mass ratio are used (for example, to more closely approximate normal field conditions), duplicate runs should be made using the ratio prescribed here as the reference case.

7.8 Measure the pH of the liquid (Test Method D1293); if the pH has changed or if other than the natural pH is desired, adjust

by addition of NaOH solution or HCl, or by an appropriate buffer. Be careful that the buffer does not contain any complexing agents. The in situ redox potential (E_h) should be maintained, if necessary, under an inert atmosphere.

7.9 When taking a sample for analysis, shake the mixture and allow it to settle for several minutes. Remove an appropriate volume of liquid, filter it, and preserve it for analysis. An effective technique is to draw a quantity of solution into a disposable plastic syringe, connect an appropriate syringe filter to the syringe and dispense filtered liquid into a small disposable plastic cup. This liquid may be preserved for analysis. If necessary (for example, for radionuclide analysis) use a plastic tipped calibrated pipette to withdraw a defined volume of filtered solution from the cup to be placed into analysis tubes.

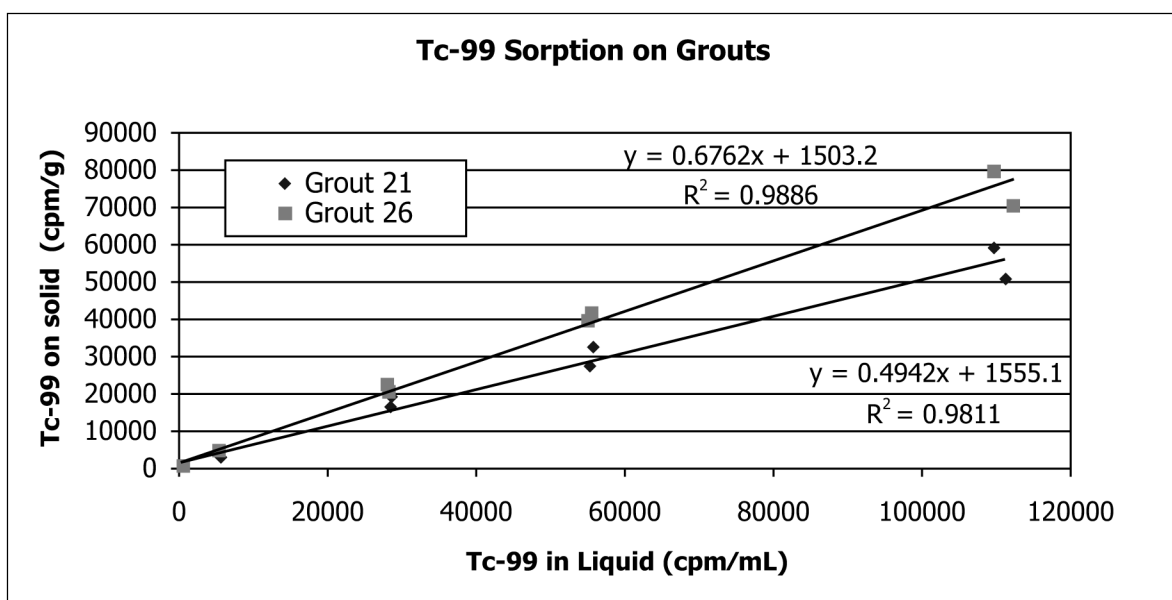
7.10 Measure and report the pH of all mixtures. It is recommended that pH be measured on filtered subsamples that are separate from those to be analyzed for the species of interest to avoid contamination.

7.11 Check the possibility of sorption of tracers onto the bottle, filter and other materials. This may be done by setting up two test solutions. One is a blank containing tracer and contact solution (no solid phase added, but make sure that pH is similar to the actual experiments). The other solution, a reference solution, is composed of distilled water, the tracer and preservative (for example, acid or base) to assure that the tracer remains in solution. Both solutions contain the same quantity of tracer and liquid such that the tracer concentrations should be identical. Sample the two solutions (the blank and the reference) as described in 7.9, at several times as discussed above. If no sorption has occurred, measured concentrations of tracer should be identical within the error of the procedure.

7.12 As an alternative to filtration, centrifuge each mixture for 20 min at a setting of ≥ 1400 g. Controlled temperature centrifugation may be advised, particularly in the case of experiments run below ambient temperature. Carefully separate the phases. For the supernatant, the concentration of the species of interest can be directly determined using an appropriate standard analytical method.

7.13 After analysis of the liquid, the K_d may be calculated by difference between the tracer concentrations in the reference solution and the tracer concentrations in the contact solution after reacting with the solid phase. The concentration of the reference solution (see 7.11) may be used as the starting solution concentration when calculating the quantity of tracer sorbed on the solid by difference.

7.14 If necessary or if desired for comparative purposes or for a mass-balance determination, determine the concentration of the species of interest associated with the solid phase; accounting for material remaining in the experimental tube (and if necessary, on the filter). In this case, note the necessity of removing the residual solution from the solid phase, or correcting for it, particularly



Here data are expressed as counts per minute (CPM) per unit mass and volume (5).

FIG. 2 Isotherm for Sorption of Tc, as Pertechnetate ($Tc(VII)O_4^-$), onto Grout Materials at pH of 12.5 after 43 Days Contact Time