CONSTITUTIVE MODEL DEVELOPMENTS FOR BENTONITE BUFFER BEHAVIOR

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The thermohydrologic behavior of swelling materials used for buffers and seals in geologic disposal of radioactive waste strongly influences the barrier capability of the disposal system. Techniques, such as Mercury Intrusion Porosimetry, reveal pores at one to three distinct scales in swelling materials commonly proposed for buffers, in addition to the inter-layer pores within clay tactoids that are too small to be detected. These distinct pore scales range from the nanometer to the millimeter scale. Some thermohydrologic processes are strongly affected by the pore size. Electrostatic forces drive swelling at the nanometer scale between mineral layers in clay particles; electrostatic forces respond to bulk changes in capillary pressure, electrolyte composition, and applied stresses. Changes in clay particle geometry and orientation due to inter-layer expansion and contraction within the clay particles induce a cascade of changes at the larger pore scales. Laboratory and field tests suggest that rewetting of some media proposed for buffers, including MX–80 and FEBEX bentonite, induces irreversible pore structure rearrangement as the clay particles rearrange. For example, the macropore space between dried bentonite granules irreversibly closes during rewetting and measured initial wetting and drying retention curves often differ in clayey materials. The current generation of numerical models tends to rely on either single-porosity models or empirical models fit to laboratory data, which makes it difficult to account for the full range of reversible and irreversible conditions that might occur in a swelling medium in a repository setting. Recent constitutive models for swelling media in the literature are beginning to (i) link bulk thermohydrologic properties to characteristic pore scales and (ii) link changes in pore structure across scales. Such models show promise, but are typically limited to two characteristic pore scales. We discuss progress using the same general approach to develop bulk constitutive relationships suitable for numerical simulators in order to represent thermohydrologic processes in granular bentonite. The proposed approach focuses on thermal conductivity and moisture retention relationships accounting for several factors, such as changing saturation, swelling, and temperature-dependence.

I. INTRODUCTION

Concepts for geologic disposal of high-level radioactive waste canisters often rely on buffers that incorporate swelling smectite clays such as sodium montmorillonite, one of several forms of bentonite. Swelling smectite consists of platy minerals that increase in size upon hydration. A buffer that includes partially dehydrated swelling bentonite during emplacement expands during buffer rehydration, (i) filling pre-existing gaps that might allow unrestricted fluid movement to and from the waste packages and (ii) isolating the waste packages from external ground movement. Buffer recipes must balance the benefits of swelling with (i) the potential for restricted venting of gases produced by the waste form, (ii) the potential for elevated temperatures due to the relatively low thermal conductivity of bentonite, (iii) the potential for bentonite degradation under elevated temperatures, (iv) the potential for excessive swelling that could over-pressurize the canisters, and (v) the potential for bentonite degradation due to the chemical composition of the formation fluids. Current concepts use solid blocks or disks, pelletized bentonite, or bentonite blended with less expensive granular materials, like silica sand.

Evaluating the long-term response of different buffer designs to environmental and waste characteristics necessitates numerical modeling supported by appropriate experiments. These areas have seen a great deal of activity over the past decade or two. Our recent numerical modeling work has used standard constitutive relationships to describe the thermohydrologic response of fluids in extensively characterized bentonite buffer materials

with some success[1]. However, it is useful to be able to develop appropriate constitutive relationships that can account for the swelling behavior at several pore scales without needing to perform expensive and difficult laboratory characterization studies. This paper documents intermediate steps in synthesizing the approaches described in the open literature into a family of constitutive relationships useful for numerical modeling of the thermohydrologic processes encountered during buffer rewetting and heating.

II. BENTONITE CHARACTERISTICS AND IMPLICATIONS

Bentonite is used as a component in buffer design concepts because of its swelling and self-healing properties. These properties result from forces at small scales that are less important in other granular media. A bentonite tactoid consists of several mineral layers, each layer just a few molecules thick. A tactoid is akin to a very small granular particle, but may vary in size as individual mineral layers are added or removed, or as the separation between mineral layers responds to environmental conditions. Bentonite tactoids are much smaller than other granular constituents, such as sand. Tactoids can assemble into quasicrystalline structures called aggregates. Depending on the mass fractions of other mineral constituents and degree of reworking, individual aggregates may range over many orders of magnitude in dimension. The following describes a conceptual model for how the tactoid properties influence composite medium constitutive properties.

II.A. Forces at Small Scales

Numerical simulators considering unsaturated porous media typically characterize water retention and water fluxes in terms of water potential. However, there are additional forces that become active at the extremely small scale of typical clay tactoids. These forces are likely to play a strong role in determining intertactoid orientations; therefore, affecting constitutive relationships. In particular, electrostatic forces and surface forces (which decay with separation by the inverse powers of 2 and 6, respectively) are likely to become important when tactoids are close or touching (discussed in detail in subsequent paragraphs).

Bentonite is a platy mineral that typically forms by weathering of volcanic ash. A single layer in a montmorillonite tactoid, for example, is approximately 1 nm thick and may extend 2 to 3 orders of magnitude times the thickness

perpendicular to the plate thickness. For comparison, a single mineral layer is approximately as thick as four water molecules.

Swelling bentonite differs from most granular materials because of its swelling characteristic. The swelling behavior stems from diffuse double layers of electrical charges in the water immediately adjacent to the mineral surfaces. These charges provide a repulsive force between the mineral layers, which is counterbalanced by (i) short-range attractive surface forces, (ii) opposing ionic charges in the interlayer water, and (iii) the bulk water potential. Under unsaturated conditions, water potential acts like a negative surface pressure that pulls the mineral layers together. Changes in the bulk water potential change the degree to which surface charges are counteracted, allowing water to move in and out of the interlayer zone between the mineral layers, as the water potential becomes less or more negative. This process may be shut down if the interlayer zone is completely dehydrated, allowing short-range surface forces to dominate, which is one reason that buffer designs attempt to limit the bentonite temperature after emplacement.

Tuller and Or[2] summarize experimentally determined separation data for Na-montmorillonite tactoids in aqueous solutions[3,4] and provide theoretical relationships for disjoining pressure components caused by charges in the diffuse double layer adjacent to the charged mineral surface. The data are well fit using the Langmuir formula for the electrostatic component of the disjoining pressure in the form

$$\Pi_e = 2\epsilon\epsilon_0 \left(\frac{\pi kT}{zeh}\right)^2 \qquad (1)$$

where Π_e is electrostatic disjoining pressure [Pa], ϵ is the relative permittivity of the medium, ϵ_0 is free space permittivity [$8.8541878176 \times 10^{-12}$ C^2 J^{-1} m^{-1}], k is the Boltzmann constant [$1.3806488 \times 10^{-23}$ J K^{-1}], T is absolute temperature [K], z is the ion valence, e is the elementary charge [$1.60217657 \times 10^{-19}$ C], and h is layer spacing (interlayer thickness) [m]. The Langmuir formula implies that Π_e goes to infinity as h goes to zero; however, when the discrete charges on opposing faces are offset as the faces are being brought together, the disjoining pressure plateaus as h approaches the charge separation distance.

The Langmuir formula suggests that h is 1 nm (~4 water layers) and 10 nm when Π_e is

approximately 10 and 0.1 MPa, respectively, implying that the inter-layer pore space is half of the clay tactoid volume at 10 MPa and 91 percent of the tactoid volume at 0.1 MPa .

An attractive force between similar materials arises from van der Waals interactions[5]. The van der Waals interaction free energy U, for two parallel infinitely extended slabs of fixed thickness a and variable separation h, is

$$U = -\frac{A_{\text{Ham}}}{12\pi}\left[\frac{1}{h^2} - \frac{2}{(h+a)^2} + \frac{1}{(h+2a)^2}\right] \qquad (2)$$

where A_{Ham} is the Hamaker coefficient (typically in the range of 1 to 100 zJ, where 1 zJ is 10^{-21} J). The van der Waals force per unit area is the derivative of U with respect to h. It is proportional to h^{-3} when $h \ll a$ and is proportional to h^{-5} when $h \gg a$. A_{Ham} is in the range of 3 to 13 zJ for a mica/water/mica system. In this range, the van der Waals force overcomes the electrostatic repulsion only when the final water molecule layer is removed from between two mineral layers. The final water layer might be spontaneously squeezed out if A_{Ham} is >40 zJ.

Not all surface charges in diffuse double layers are located within the interlayer zones between mineral layers; there also are surface charges on the exterior of the clay tactoids. The same forces active between mineral layers also are active between tactoids, implying that interactions between clay tactoids are likely to be constrained in ways that are not important for other granular materials. In particular, clay tactoids in close proximity are likely to be preferentially aligned face-to-face rather than randomly oriented and will tend to maintain uniform separation rather than contacting tactoid to tactoid.

Electrostatic forces act to separate mineral layers and clay tactoids, balanced by the van der Waals forces, bulk water potential, and bulk confining pressure. When the medium is unsaturated, suction pressure from the bulk water potential and bulk confining pressure are the primary balances to the electrostatic disjoining pressure. Under saturated conditions, van der Waals forces and bulk confining pressure are the primary balances. Electrostatic forces between tactoids can be negated by ions in solution, causing the electrostatic disjoining pressure to drop more rapidly with separation than implied by the Langmuir equation; thus, in solutions the weak van der Waals forces may be the dominant force acting between clay tactoids separated by significant distances.

II.B. Clumping and Aggregation

When bentonite is initially formed by *in situ* weathering, the original ash-fall structure is transformed into sheets of mineral layers. Once disturbed or eroded from the initial formation, the tactoids are influenced by the small-scale forces during aggregation or deposition. The electrostatic interactions between platy tactoids imply that tactoids aggregating from solution would tend to form a relatively homogeneous layered system with relatively uniform separations.

Charges in the diffuse double layer or interlayer spaces are restrained from lateral movement as layer faces approach, transmitting the normal forces to the mineral faces. These charges are able to displace along the mineral faces while exerting minimal lateral force on the faces as tactoid ends move together. Accordingly, repulsive electrostatic charges influence interactions between layer faces more than layer edges. As a result, the attractive van der Waals forces more readily draw tactoid ends together, resulting in a flexible link or connection between tactoids due to van der Waals forces, as the edges touch. Scanning Electron Microscope (SEM) images[6] suggest that such links often join three and even four tactoids. As tactoids assemble, edge joining results in a flexible quasicrystal structure (called an aggregate) that can expand and contract. When aggregates assemble in an existing porous medium, it appears from SEM images that the first tactoids assemble perpendicular to a mineral tactoid and subsequent tactoids expand edge-to-edge outwards from the tactoid. Such assembly would likely occur within the host medium, as bentonite erodes from the buffer.

The shape of the micropore space between joined tactoids responds strongly to changes in bulk water potential in Na^+ montmorillonite, causing the tactoid structure to expand from flattened sheets to a honeycomb structure as the bulk potential changes from −1 MPa (nearly unsaturated) to less than −0.01 MPa[6] (nearly saturated). The micropore space between the tactoids may be orders of magnitude larger than the interlayer pore space. For example, the honeycomb structure has dimensions on the order of one or more tactoid face lengths (1,000 to 4,000 nm) rather than the interlayer separation distance (1 to 10 nm)[2]. The micropore space remains filled with water, even under large bulk suction pressures, because the flexibly joined tactoid structure draws together to close the micropore space rather than admit gas.

II.C Aggregates and Composites

Buffers are not usually constructed from pure undisturbed montmorillonite due to concerns about cost, excessive swelling pressures, and relief of gas generated at the canister and waste form. Instead, most programs are considering reworked bentonite in the buffer. Some concepts consider sand and bentonite mixtures; others consider dried bentonite pellets. These concepts result in the emplaced buffer forming a composite medium.

In the sand and bentonite concept, the sand and bentonite are worked into a relatively homogeneous mixture prior to emplacement. Various ratios of sand to bentonite are being considered, ranging from sand dominance to bentonite dominance. Sand dominance occurs when the bentonite fraction is small relative to the pore space between sand grains. Bentonite dominance occurs when the bentonite fraction is large relative to the pore space between sand grains.

In sand-dominant media, individual bentonite aggregates are akin to a microporous grain. In this case, the pore space has three scales: (i) interlayer, (ii) micropore, and (iii) residual intergrain pore space (i.e., mesopores). The mesopore space is the remnant pore space between the sand grains and the aggregates. Mesopores are typically several orders of magnitude larger than micropores under unsaturated conditions; thus they are the primary pathway for fluid movement. As the aggregates swell during rewetting, mesopores close off if there is sufficient bentonite content.

In bentonite-dominant media, the bentonite aggregates form the dominant matrix with sand grains mixed in. In principle, the initial properties of the composite medium should be like a bentonite aggregate. However, the mechanical process of mixing may result in voids between aggregates and sand grains, sand grains locally clump into sand-dominant zones, and the structure of individual aggregates may be damaged.

Dried bentonite pellets also form a composite medium prior to rewetting, consisting of the pore space outside the pellets (analogous to the pore space in a granular porous medium) and the micropore space within the pellets. The process of reworking bentonite into pellets may form auxiliary pore space around aggregates within the pellets or damage the aggregate structure.

III. CONSTITUTIVE MODEL APPROACHES

From the standpoint of predicting the performance of a bentonite-based buffer in a repository setting, three phases are important: (i) initial performance prior to rewetting, including any heat-induced drying; (ii) rewetting; and (iii) long-term performance after rewetting. In other applications, such as liners and other near-surface environments, cyclic behavior to wetting and drying may be more important. Thermal conduction and diffusion of gaseous species (water vapor and hydrogen) are important during the initial period. Water redistribution, bentonite swelling, and thermal conduction are important during the rewetting period. Migration of dissolved species is important during the performance period after rewetting, especially as it relates to corrosion, buffer degradation, and release. In the following, the focus is on constitutive behavior through the end of the unsaturated period (i.e., up to completion of rewetting).

III.A Composite Behavior With Respect to Water

The quasicrystal structure of bentonite aggregates strongly influences where water is located for buffers formed from both sand/bentonite mixtures and dried bentonite pellets. In our conceptual model for water and air partitioning among the available pore spaces, we expect that water is preferentially sequestered into the micropores and air is preferentially sequestered into the mesopores. Both the interlayer pores and the aggregate micropores are very small relative to other pore spaces within the composite, and can shrink in response to greater suction pressures, so that these pore spaces remain water-saturated regardless of the state of the remaining pore space within the composite.

After emplacement and prior to rewetting, the mesopores are predominantly air-filled, with the water content limited to a water film covering exposed granular surfaces (if present). As the water content increases during rewetting, the water preferentially partitions to the micropores and aggregate swelling closes off the mesopores. The mesopores remain essentially air-filled until the suction pressures decrease enough to allow pendular water to form around grains unless water is supplied more rapidly than can absorb into the aggregates.

III.B. Thermal Conductivity

Thermal conductivity in granular media is often represented using the form

$$k_t(S_w) = k_{tdry} + S_w^p(k_{twet} - k_{tdry}) \qquad (3)$$

where k_t is thermal conductivity, S_w is effective water saturation, k_{tdry} and k_{twet} are the thermal conductivity values at dry and wet extremes, and p is an interpolation parameter[7,8]. In this approach, dry and wet thermal conductivities are approximately estimated using

$$k_{twet} = k_{ts}^{1-\varepsilon} k_{tw}^{\varepsilon} \qquad (4)$$

$$k_{tdry} = k_{ts}^{1-\varepsilon} k_{ta}^{\varepsilon} \qquad (5)$$

where k_{ts}, k_{tw} and k_{ta} are the solid mineral, water, and air thermal conductivities and ε is porosity. Note that k_{ts} is approximately proportional to T^{-1} for many minerals, where T is absolute temperature, whereas k_{ta} is proportional to T and k_{tw} is approximately proportional to T below 100 °C and transitions to inversely proportional to T at elevated temperatures.

The square-root dependence of the Somerton et al. model[8] ($p = 1/2$) approximately captures the strongly enhanced bulk thermal conductivity stemming from pendular rings around grain-to-grain contacts in coarse granular porous media (e.g., sand). With water-saturated aggregates and air-saturated mesopores, pendular water may be unimportant in fine-grained media and a mixture model may be more appropriate for describing bentonite-based composites, in the form[9]

$$k_t = \sum_{\alpha=1}^{N} k_{t\alpha}^{\epsilon_\alpha} \qquad (6)$$

where $k_{t\alpha}$ is thermal conductivity of phase α, ϵ_α is the volume fraction of phase α, and N phases are present, including water, air, and the different minerals. Quartz sand $k_{t\alpha}$ is typically several times larger than $k_{t\alpha}$ for other minerals, thus quartz content should be explicitly included when modeling sand/bentonite buffer mixtures. Equation (6) automatically accounts for changing volume fractions, which is useful for swelling media. Equation (3) fits this model reasonably well by replacing $S_w^{1/2}$ with S_w^p, where $p \approx 0.9 + 1.5\varepsilon$ and ε is porosity.

Figure 1 compares thermal conductivities measured for Na^{+} bentonite granules[10] and Ca^{2+} bentonite and sand/bentonite mixtures mixed from bentonite powder[9] with Equation (6) estimates. The mineral component parameters are included in the figure. The trends with respect to changing saturation and
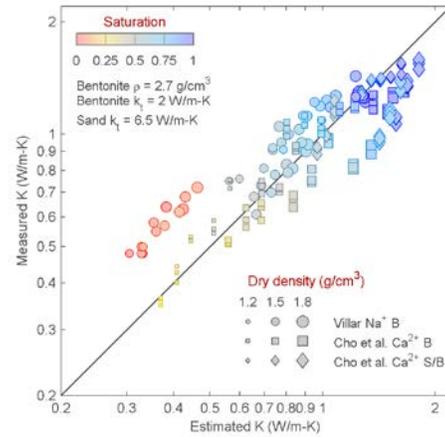

Fig 1. Measured Thermal Conductivity for Two Types of Bentonite and a Bentonite/Sand Mixture, at Different Water Contents and Packing Densities, Compared to a Geometric Mixing Model

changing mineral content are captured, although the relationship may overestimate k_t for densely packed media. Component k_t for Na^{+} bentonite may be larger than component k_t for Ca^{2+} bentonite, based on this figure. Villar[10] proposed a sigmoidal relationship to fit her data and Cho et al.[9] proposed a form of Equation (6) with adjustable exponents. It is notable that measured k_t values may vary by up to a factor of two for nominally identical media and water content, which might represent residual uncertainty in bulk buffer k_t for different waste packages in a repository setting.

III.C Multicontinuum Retention and Conductivity

Simultaneously representing water retention, bulk hydraulic conductivity, and bulk pneumatic conductivity over a range of dry densities, water contents, and temperatures when the porous medium contains significant fractions of swelling bentonite is challenging. Water preferentially partitions to the smallest pore scales, which remain saturated, but the size and shape of the pores respond to the bulk potential. The pore scales vary by orders of magnitude, thus it is useful to consider the various pore scales as overlapping continua. Each continuum represents the pores in a particular size range within an averaging volume. The continua overlap because each averaging volume contains pores in more than one size range.

Mercury Intrusion Porosimetry investigations (e.g., Dieudonné et al.[11]; Romero[12]; Hoffmann et al.[13]) of pore size density (PSD) functions suggest

that several characteristic pore sizes exist in media with clay fractions. PSD functions describeModes of the pore density functions correspond to micropores, mesopores, and macropores associated with granular inclusions in the clay fabric or interpellet voids. Particular modes respond to changing water content; as water content increases, the micropore mode moves toward larger pore sizes and modes for larger pore scales move toward smaller pore sizes. The PSD for each characteristic pore size is approximately lognormal, but may be skewed.

Dieudonné et al.[14] extend the classic van Genuchten water retention curve to consider water retention in bimodal media (micro and macro pores in their terminology). Micro and macro pores appear to correspond to intra- and inter-aggregate pores (micropores and mesopores in our terminology). This general approach is likely to provide a useful framework for a l arger range of pore scales. Extended to multiple continua, the relationship can be expressed by

$$e_w(P_c) = \sum_i e_i \theta_{wi}(P_c) = \sum_i e_i \left[1 + \left(\frac{P_c}{P_{0i}}\right)^{n_i}\right]^{-m_i} \quad (7)$$

where e_w is total water ratio (defined as volume of water per unit volume of solid), e is void ratio, θ_w is water saturation, P_c is capillary pressure, P_o is a reference capillary pressure, n and m are van Genuchten exponents, and subscript i indexes a particular continuum. The different continua should remain in local equilibrium (unless a rapid transient is occurring) because of the small spatial scales in bentonite, thus same value of P_c applies in each continuum. Dieudonné et al.[14] link the parameters for each medium to its respective PSD mode: (i) the maximum value of the PSD links to P_o, (ii) the width of the PSD links to n, and (iii) the shape of the PSD links to m.

Dieudonné et al.[11] considered experimental data from seven different media, including MX-80 bentonite and sand/bentonite mixtures, to fit a bimodal distribution of pore sizes with various structural changes. Dieudonné et al.[14] suggest that the e_i and P_{0i} values tend to vary with water content but the other parameters are almost constant. The n and m van Genuchten exponents are not related with the usual assumptions of $m = 1 - 1/n$ for these data sets.

Dieudonné et al.[14] describe the evolution of P_{0i} with void ratio using exponential relationships

$$P_{0m}(e_m) = P_{1m} \exp(-\alpha_m e_m) \quad (8)$$

$$P_{0M}(e_M) = P_{1M} \exp\left(-\alpha_M \frac{e - e_m}{e}\right) \quad (9)$$

where the m and M subscripts represent the micro and macro structures and the α values are fitting parameters, and provide parameter values for Boom and London clays. These clays have much smaller specific surface than MX-80 and FEBEX bentonite. Dieudonné et al.[14] and Romero[12] provide several relationships linking e_m, e, and saturation for different media. Romero[12] shows the specific surface area strongly influences these relationships.

Romero et al.[15] provide several sets of data describing the response of FEBEX bentonite, Barcelona clayey silt, and Boom Clay to changes in water content at various bulk dry densities. Independently applying the two-scale retention model approach reveals that multiple degrees of freedom exist to fit individual datasets, even with constraints on parameter ranges from the literature. T esting revealed the fit between retention models and data is not seriously degraded if the n and m van Genuchten exponents are related with the assumption that $k = m - 1 + 1/n$, where k is an integer, needed for a closed-form relative permeability function using the van Genuchten approach. Typically it i s assumed that $k = 0$, as recommended by van Genuchten[16].

The van Genuchten retention function is essentially a PSD, where capillary pressure $P_c = 2\sigma/r$, σ is air-water surface tension, and r is the pore radius. The assumption of $k = 1$ gives a nearly symmetric PSD, like measured modes, while $k = 0$ leads to a long tail of small pores. A typical measured PSD mode representing micropores or mesopores in bentonite might have r varying over one to two orders of magnitude, implying that $n > 2$.

Explicit links among retention, permeability, and the PSD might use simple relationships between pore radius r and (i) capillary pressure (inversely proportional to r) and (ii) permeability (proportional to r^2). A given capillary pressure corresponds to a particular value of r. Assuming that all pores with a smaller r are filled with water implies the cumulative PSD corresponds to saturation. T he water permeability is the integral of permeability weighted by the PSD for all water-filled pores, and the air permeability is the integral of permeability weighted by the PSD for all air-filled pores. The largest wetted and dry pores dominate the water and air permeability relationships, respectively. The retention relationships are insensitive to the largest

pores except near saturation conditions, which is problematic in characterizing swelling bentonite because the largest pores shrink dramatically from dry to wet conditions.

In extending the bimodal approach to consider air and water permeability in swelling buffer media, it may be reasonable to consider one or two additional modes in order to explicitly account for the permeability from the largest pores, which is not necessarily well captured with a bimodal model.

IV. SUMMARY AND CONCLUSIONS

Concepts for geologic disposal of high-level waste canisters often rely on buffers that incorporate bentonite. M odeling of experiments with coupled heating and water injection for buffer media has led to a d esire to better represent the constitutive properties implemented in the model. The physics of individual bentonite platelets, aggregated into tactoids, suggest that tactoids preferentially connect end to end, with each connection able to bend like a hinge. As a result, an assemblage of tactoids forms flexible quasicrystalline aggregate structures with intra-aggregate pores that expand in response to changes in bulk water potential. Additional pore structures in a b uffer exist between aggregates, and even larger structures may exist around sand included in the buffer or around dry granular pellets used for emplacement.

The thermal conductivity of buffer media appears to be usefully described with a s imple geometric model to combine the thermal conductivity for each of the constituent components. For coarse media, it is necessary to account for pendular water at low water contents, but this does not appear important for buffer media. The mixing model accounts for changing saturation, swelling, and temperature-dependent thermal conductivities for each of the components. L aboratory measurements exhibit residual variability for nominally similar media, which may arise from slightly different packings in different samples, and this variability may be appropriate for representing packing and material variability for buffers in a repository setting.

Retention relationships are currently being developed in the literature based on bimodal pore-size distributions that scale with changing water content. T he approach appears to be useful for describing retention, further refinement appears to be necessary to describe air and water permeability in buffers after emplacement. The van Genuchten relationships used to describe relative permeability require that two of the fitting parameters for each mode are related in a particular way, which is not yet incorporated in the available models. Further, buffer media are likely to have at least three pore scales separated by orders of magnitude, at least during the period after emplacement and before rewetting; the largest pore scale is important for air permeability but not for retention.

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