Pore-scale measurements of solute breakthrough using microfocus X-ray computed tomography

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Abstract. X-ray computed tomography (CT) offers distinct advantages to study fundamental physical processes of water movement and contaminant transport in porous media. Tomography provides nondestructive and noninvasive cross-sectional or three-dimensional representations of porous media and has the potential to measure phase distribution and species concentration at the pore scale. Sources of error are discussed for the application of industrial microfocus CT to quantitative studies of flow and transport. Specifically, effective resolution and measurement uncertainties due to photon randomness are considered for a miscible displacement experiment. A calibration method for the measurement of solute concentration is proposed that accounts for the effect of beam hardening, which is characteristic for polychromatic industrial X-ray sources. The results of an X-ray microfocus CT experiment are presented, emphasizing the need to correct for beam hardening and describing the inherent spatial variability of solute breakthrough through a glass-bead porous medium with an effective spatial resolution of approximately 85 μm.

1. Introduction

X-ray computed tomography (CT) provides nondestructive cross-sectional or three-dimensional object representations from the attenuation of electromagnetic radiation. Attenuation depends on the density and the atomic constituents of the material that is scanned. Since it has the potential to noninvasively measure phase distribution and species concentration, X-ray CT offers significant advantages to study fundamental physical processes of water movement and contaminant transport in porous media.

Following the introduction of CT in the medical sciences [Hounsfield, 1973], the technique was adopted by Earth science research beginning in the early 1980s. Linear relationships were established between attenuation and soil bulk density [Petrovic et al., 1982; Anderson et al., 1990] and between attenuation and volumetric water content [Anderson et al., 1988; Brown et al., 1987; Crestana et al., 1985; Hainsworth and Aylmore, 1983; Hopmans et al., 1992]. Tomography has also been used to measure two- or three-dimensional heterogeneity of soil bulk density and water content [e.g., Hopmans et al., 1994] and to monitor the transport and breakthrough of solutes in porous media [Stieude et al., 1990; Vinegar and Wellington, 1987]. These investigations were performed using medical scanners, which provide a spatial resolution of about 0.1–1.0 mm.

The application of industrial scanners, in contrast to medical devices, is not subject to biological dose restrictions and allows spatial resolutions of 1 μm or less [Haddad et al., 1994] if combined with a synchrotron X-ray source providing parallel and monochromatized radiation. Industrial scanners have also produced effective results when equipped with X-ray sources that emit polychromatic radiation, such as produced by conventional tube sources. The introduction of microfocus X-ray sources and cone-beam reconstruction methods [Jasti et al., 1993; Martz et al., 1993] has provided the capability to obtain high-resolution (∼10 μm) three-dimensional data sets from a single object rotation thereby drastically reducing the total acquisition time needed [e.g., Klobes et al., 1997].

On the basis of the same principles of X-ray CT the radiation of γ rays consists of high-energy photons emitted from transitions of atomic nuclei. Using radioactively decaying sources, monochromatic γ-ray beams can be obtained at the expense of longer acquisition times because of small photon fluxes. Brown et al. [1993] present a quantitative analysis of such a system for porous-media applications.

As an alternative to radiation-based CT, magnetic field gradients are applied in nuclear magnetic resonance (NMR) imaging to measure nuclear spin density within an object. Using NMR, spatial information about porous medium properties can be obtained. NMR imaging can provide a spatial resolution of 10–100 μm and superior time resolution. As an example, the technique has been successfully applied recently to study dispersion in porous media [e.g., Greiner et al., 1997]. The major limitation, however, is its inability to study samples containing ferromagnetic or paramagnetic materials [Gladden and Alexander, 1996] thereby excluding many soils.

Given the successful history of application of CT in general and the increasing availability of industrial microfocus X-ray scanners in particular, this paper is intended as a contribution to define the realm of applicability of microfocus X-ray CT regarding quantitative studies of flow and transport in porous media. Specifically, effective resolution and measurement uncertainty due to photon randomness is considered in miscible displacement experiments.

2. Theory

2.1. Physical Background

X rays, like visible light, are a form of electromagnetic (EM) radiation with a wavelength of 0.3 pm–3.0 nm. The correspond-
ing high energies of X rays enable their penetration of objects impermeable to light, allowing physical characterization from attenuation measurements. For a detailed treatment of the principles of EM radiation the reader is referred to Knoll [1979].

2.1.1. Emission. Industrial and medical X-ray sources generate X rays by bombarding a specific target material (e.g., tungsten) with electrons in an electron-ray tube. X-ray photons are emitted from the target by two main mechanisms. First, deflection of incident electrons after collision with atomic electron clouds in the target results in conversion of kinetic energy into electromagnetic radiation; that is, radiation is emitted as the electrons are decelerated. The resulting continuous bremsstrahlung X-ray energy spectrum has an upper bound at the X-ray photon energy corresponding to complete conversion of the kinetic energy of an electron. For example, the maximum X-ray energy is 125 keV for a tube with a source potential of 125 kV (Figure 1). Second, target atoms become excited as orbital electrons are transferred to a higher energy level by the incident radiation. As an excited atom returns to its ground state, characteristic X-ray photons are emitted with a total energy equal to the difference between the excited and ground energy levels. The characteristic photon-energy values depend on the atomic constituents of the target material. In the resulting X-ray source spectrum the contributions by excitation appear as distinct peaks superimposed on the continuous bremsstrahlung spectrum. As an example the theoretical energy spectrum for a tungsten target using a source potential of 125 kV is shown in Figure 1 by the bold curve.

2.1.2. X-ray interactions. Along the path through the object the photons of the X-ray beam interact with the atoms of the object material. Within the energy range of typical industrial sources (<1 MeV), photons are removed from the beam by two mechanisms. First, photons can be scattered out of the beam path following the collision with object electrons. Second, they can disappear because of photoelectric absorption by an object atom whereby the atom ejects a photoelectron from a shell whose binding energy is less than the absorbed photon’s energy, with the excess energy converted to kinetic energy of the photoelectron. As a result of both removal mechanisms, the X-ray beam is attenuated by losing a certain fraction of its intensity $I$ [photons/s] per increment $ds$ [$L$] of straight path length:

$$dI/ds = -\mu I,$$  

(1)

where the linear attenuation coefficient $\mu$ [$L^{-1}$] is the probability per unit path length that a given photon is removed from the beam. For a stationary heterogeneous porous medium, $\mu$ is spatially distributed, whereas in transient flow and transport experiments, $\mu$ can also be a function of time owing to miscible or immiscible fluid displacement. Integration of (1) along the beam path yields

$$I/I_0 = \exp \left(-\int L \mu \, ds \right),$$  

(2)

where $I_0$ and $I$ are the X-ray beam intensities entering and exiting the object, respectively, and $L$ is the length of the path through the object.

Owing to the physical nature of the attenuation process, $\mu$ is related to the electron density encountered by the beam. Consequently, $\mu$ depends on the mass fractions of the object material’s atomic constituents and total mass density. As a result, $\mu$ is linearly related to concentration $c$ of a specific solute in liquid solution. In addition, attenuation is a function of the X-ray radiation frequency or photon energy level $E$. The contributions to attenuation by scattering and photoelectric absorption for many elements have been tabulated as a function of photon energy [e.g., Hubbell, 1969], which allows computation of theoretical linear attenuation coefficient values for composite materials. Figure 2 presents such theoretical relationships of $\mu$ as a function of $E$ for the materials used in the experimental study to be discussed in section 3.2. Although $\mu$ generally decreases with increasing $E$, distinct peak values appear at the characteristic energy levels for photoelectric absorption. For example, the specific increase at 33.3 keV in the two $\mu(E)$ curves for NaI solutions of 50 and 100 mg/mL is caused by photoelectric absorption, involving the atomic K shell of iodine. Since such relationships between $\mu$ and photon energy for different materials are so distinct, theoretical $\mu(E)$
2.1.3. Detection. Beam intensity values are determined by integrating a measure of either the photon incidence rate or the energy deposition rate over a defined time interval $\Delta t$. In contrast to traditional devices that generate and count electrical impulses for each incident photon, scintillating detectors emit visible light when exposed to radiation. Planar X-ray-sensitive scintillators, which are made of glass or inorganic crystals, provide an instantaneous, two-dimensional radiographic projection of the object. The increase in dimension reduces the required scanning time for a given object position dramatically as beam energy is measured simultaneously for all beams, without the need for vertical and/or horizontal object translations that are required by line or point detectors. The radiographic image can be recorded by any camera for a selected exposure interval $\Delta t$. The image is usually mirrored at an angle sufficient to place the camera away from the X-ray beam path.

2.2. CT Principles

In contrast to radiology, which projects cumulative X-ray attenuation of an object on a two-dimensional radiograph, computed tomography (CT) provides cross-sectional or three-dimensional representations of the scanned object. The technological and mathematical principles of CT are covered in detail by McCullough [1975], Brooks and DiChiro [1975, 1976], McCullough and Payne [1977], Panton [1981], and Kak and Slaney [1988].

Briefly, the common principle of CT scanners is to measure the spatial distribution of attenuation from $I$ values obtained from the scanning of the object using many different beam directions. The term “beam” is used here to include all possible straight lines from the X-ray origin at the source to points on the face of an individual detector cell. Following (2) and assuming $I_0$ is fixed and known, each $I$ measurement can be converted into a value for the integrated attenuation along the corresponding beam path. To calculate an approximate solution of the spatial attenuation distribution, the scanned portion is considered to consist of a set of nonoverlapping volume elements or voxels. Each voxel is assumed to be homogeneous in composition and represented by a single $\mu$ value. After a sufficient number of independent integrated-attenuation measurements have been obtained, the discrete approximation of the $\mu$ distribution within the three-dimensional object is reconstructed. Various mathematical approaches to solve the reconstruction problem for a given scanner geometry are available and have been compared in the literature [e.g., Kak and Slaney, 1988; Brooks and Di Chiro, 1975].

Main differences between available industrial scanners include the number of beams/detectors simultaneously active, beam geometry, and whether the object is moved relative to the radiation source and detector assemblage or vice versa. A fan (two-dimensional) or cone (three-dimensional) geometry inherently magnifies the object by casting an enlarged radiographic projection of the object onto the detector line or plane, as shown in Figure 3 for the cone-beam scanners used in this study. Consequently, the spatial resolution obtainable from these beam types is larger, while the object size must be reduced correspondingly. Note that the spatial resolution refers to the minimum distance over which phases can be discriminated and is not necessarily equal to the voxel size. Moreover, voxel size is not necessarily equal to the detector size but is a user-defined parameter in the reconstruction. As resolution increases, voxels can be made smaller.

2.3. X-Ray CT Equipment

The reported experiments were performed at Scientific Measurement Systems (SMS), Inc., Austin, Texas. Two different cone-beam systems were used, both equipped with industrial microfocuss X-ray tubes of 10-$\mu$m source spot size and planar detector arrays. Each scan took approximately 30 min to complete.

2.3.1. System A. Source current and potential settings were 0.1 mA and 125 kV, respectively. Individual $58.6 \times 58.6 \mu m^2$ detector cells were combined in groups of four, resulting in an effective detector-cell size of $117.2 \times 117.2 \mu m^2$. A total of 360 radiographic projections per scan were taken with a 6.37-fold magnification using $1^\circ$ increments and 1-s exposure time. The three-dimensional reconstruction by cone-beam backprojection was performed with the RECON code [Martz et al., 1990] resulting in cubic voxels of 23 $\mu$m side length.

2.3.2. System B. Source current and potential were set to 0.08 mA and 124.7 kV, respectively. Individual detector cells measured $20 \times 20 \mu m^2$. A total of 720 exposures per scan were taken in $0.5^\circ$ increments at 1-s exposure time each. The magnification factor was 1.375. Reconstruction was performed by SMS using proprietary software. As the algorithm used assumes parallel horizontal beam planes, reconstruction was limited to 30 circular cross sections. Final voxel size was $17.1 \times 17.1 \times 14.5 \mu m^3$.

2.4. Error Sources

2.4.1. Instrument. Local defects in the scintillator or in the charge-coupled device chips of the digital camera may cause erroneous and unlikely low or high beam intensities resulting in ring artifacts after reconstruction. We used a simple algorithm to identify those extreme readings and to replace their respective value by the average reading of all adjacent detector units at the expense of a small loss in spatial resolution for the affected voxels.

Errors can also be introduced by temporal variations of the position of the X-ray source or object, for example, by temperature changes caused by the stepper motors that rotate the object between scans. This error is particularly significant in
transient experiments, where several scans of the same object are taken. To eliminate such errors, radiographs for the same object angle are compared for all scans to exclude or to correct for any shift in the projection of the object.

Also, the correction for variations in the X-ray beam source intensity is critical in the quantitative analysis of scan sequences. Biased changes (drift) in \( I_0 \) may occur because of target heating, even under conditions of constant source potential and current. Drift can also be caused by an unstable focus of the electron beam on the target, resulting in fluctuations in size and/or position of the “beam spot.” Drift is best corrected before the reconstruction algorithm is applied to the radiographic projections. A change in \( I_0 \) by a factor \( \alpha \) for a given photon-energy level will result in a difference of \( \ln \alpha \) in \( \ln (I) \), independent of the attenuation encountered by the respective beam. Assuming that drift affects all photon-energy levels similarly, temporal changes in \( \ln \alpha \) for each detector line can be detected by measurements of \( I_0 \) as a function of time for beams that pass only through air. Changes in the \( \ln \alpha \) value can then be used to correct for \( \ln (I) \) for the other beams in the detector line.

The effectiveness of this simple approach is demonstrated in Figure 4. The rapidly oscillating values represent measured microfocus source intensity as a function of time during a sequence of scans lasting approximately 30 min each. Using system A, intensity values were obtained at the center horizontal detector line by averaging \( I \) readings from 100 beams through air. All values were divided by a fixed reference average obtained in advance. The drift in \( I_0 \) due to heating is evident for nearly all scans of the sequence depicted in Figure 4, most strongly for the initial scans (the large gap between the first and second one reflects the time needed for initial object positioning). The source voltage was turned off during repositioning of the object between subsequent scans, which most likely caused the jumps in \( I_0 \) at the beginning of each scan. Continuous application of the source voltage, rather than turning the voltage off and on between scans, can eliminate this short-term drift. The long-term trend in \( I_0 \), however, is dominating and causes most of the variation of the reconstructed \( \mu \) values (solid line and diamonds in Figure 4) that were not corrected for drift. Each attenuation value in Figure 4 represents the mean of \( 3 \times 10^6 \) voxels of the 0.8-mm-thick Plexiglas wall. For comparison, mean \( \mu \) values for the same voxel set are also shown after the described drift correction method was applied to the radiographs, indicating that correction of the drift-induced error largely eliminated temporal variations.

2.4.2. Systematic errors. Systematic errors lead to apparent attenuation variations of the X-ray beam that are not caused by differences in the electron density of the scanned medium.

2.4.2.1. Partial-volume effect. The reconstructed linear attenuation coefficient for voxels containing a phase interface will, in general, be underestimated. The theoretical average \( \mu \) value based on the volume fractions for the phases present within the voxel is a maximum value that represents the effective linear attenuation coefficient only if beam and interface are normal to each other. For all other alignments the effective value of \( \mu \) is smaller and has a minimum value if the beam direction is parallel to the interface (e.g., compare with electrical analog of serial versus parallel resistors). For radiation-based CT the partial-volume effect is trivial if the voxel size is much smaller than \( \mu^{-1} \) [Hsieh et al., 1998]. Since this criterion is overly satisfied for the microfocus systems and porous media used in this study, errors caused by the partial-volume effect are insignificant.

2.4.2.2. Aliasing and blurring. So-called aliasing artifacts (streaks forming symmetric patterns) arise during image reconstruction because of undersampling of each projected radiograph (finite number of detector cells) and the finite number of projections. Theoretically, the spatial sampling frequency for each radiograph should be at least twice the maximum frequency determined by the spatial pattern within the image (the “Nyquist rate”) to avoid aliasing [e.g., Kak and Slaney, 1988, p. 180]. Thus, even for optimum scanning systems with infinitely small X-ray emission spot and detector cells, some aliasing will occur for objects with sharp interfaces. However, several sources of blurring or unsharpness combine to inevitably smooth each projection thereby filtering out the highest radiograph frequencies and reducing the potential for aliasing. First, a certain amount of blurring is introduced by the finite size of the detector cells (i.e., final beam width). Indeed, this effect alone may be sufficient to prevent aliasing from horizontal projection sampling if rotation increments are smaller than one half a detector-cell width [Kak and Slaney, 1988, p. 188]. Second, in scanners with a spot X-ray source, that is, with a fan or cone geometry, the spot has a finite size (often \( \sim 10 \mu m \)). Denoting the ratio of source-detector to source-object distance as magnification \( K \), it follows from simple geometric arguments that the projection of an object point onto the detector plane will be blurred over a distance equal to the spot size multiplied with \( (K - 1) \). Third, additional blurring is caused by the varying penetration depth of the X-ray photons within the thickness \( \sim 2 \) mm of the scintillating detection layer, since a perfect camera focus can be obtained only for a single penetration depth.

The combined effect of unsharpness contributions is best measured by obtaining a CT image of a well-defined interface within the object. For example, Figure 5 shows reconstructed \( \mu \) values for the vertical glass-liquid interface (represented by vertical dashed line) at the inside of a water-filled capillary tube that was scanned using system A. To (nearly) exclude the influence of noise, attenuation values in Figure 5 represent averages over vertical columns of 60 voxels each. Horizontal bars indicate \( \pm 1 \) standard error (SE). After reconstruction the figure 4
well-defined interface is blurred over at least three voxel lengths as indicated by the rectangle outlined by shading. Thus attenuation values for voxels adjacent to phase interfaces will be in error, if interpreted as a concentration measurement. Hence blurred voxel values may be inadvertently interpreted as a different phase. In heterogeneous systems with large interfacial areas the fraction of blurred voxels may be potentially larger than each of the individual phases [Clausnitzer and Hopmans, 1999]. If one half of the blurred phase-interface length is considered as a measure of the effective spatial resolution, a resolution value of 35–45 μm is obtained, which is approximately equal to the resolution value of 40 μm measured independently from radiographs of test-pattern objects.

2.4.3. Polychromatic beam. Even though specific attenuation is a function of beam energy, the reconstruction computations implicitly assume a single effective beam energy. Because X-ray sources are typically polychromatic, “beam-hardening” artifacts result; that is, voxels near the circumference of a homogeneous cross section of a scanning object appear to be of higher attenuation. In reality, photons of strongly attenuated energy levels (those with relatively low energy) are eliminated from the beam at a faster rate than photons of weakly attenuated energy levels (those with relatively high energy). Consequently, beams that pass near the center of the scanned object, and whose path through the object is longer, become relatively more penetrating as their energy spectrum becomes increasingly skewed toward higher photon-energy values. This change in the energy spectrum is demonstrated in Figure 1, where the complete beam spectrum as emitted by a tungsten source is compared to beam spectra resulting from attenuation by materials that were used in our flow study (Plexiglas, water, and glass). It is evident that the beam spectrum changes noticeably even after relatively small penetration depths and that the lower-energy part of the spectrum is increasingly eliminated as penetration depth increases.

In Figure 1 the unattenuated (i.e., source) spectrum was computed using the program TUBDET, developed at the Nondestructive Evaluation Division at Lawrence Livermore National Laboratory as an extension of the original work by Tao et al. [1985]. Attenuated spectra were subsequently derived from the elemental composition and density of each phase using available attenuation properties. The scattering and photoelectric-absorption values for each energy level and element were obtained from tables published by the National Institute of Standards and Technology (NIST) [1995], based on the work by Chantler [1995]. Values for energies up to 100 GeV are given by Hubbell [1969]. Hence, if the atomic composition of the object is known, the systematic error associated with polychromatic radiation can be estimated by simulation based on the known atomic attenuation properties using the following analysis.

The generalization of the definition of the linear attenuation coefficient, \( \mu = I^{-1} dI/ds \), for polychromatic radiation depends on whether beam intensity is measured as photon or energy flux. When using photon flux, the total beam intensity \( I \) is the specific photon intensity \( i(E) \) [photons/eV] integrated over the photon energy range \( R \), produced by the respective source. From

\[
\mu = \frac{d}{ds} \int_{R} i(E) \, dE \tag{3}
\]

it follows that

\[
\mu = \frac{\int_{R} dI(E) \, dE}{\int_{R} i(E) \, dE} \tag{4}
\]

because \( E \) is independent of \( s \). Since at each specific energy level \( (E) \, di(E)/ds \) is identical to \( \mu(E) \, i(E) \), the effective linear attenuation coefficient for polychromatic radiation can be expressed as

\[
\mu = \frac{\int_{R} \mu(E) \, i(E) \, dE}{\int_{R} i(E) \, dE} \tag{5}
\]

that is, it represents an \( i(E) \) weighted average of all \( \mu(E) \) over the photon energy range. Note that \( i(E) \) decreases with \( s \) (Figure 1). If the detector measures energy flux (as, e.g., scintillators do), \( i \) in (5) should be replaced by \( Ei \) [McCullough, 1975], where \( E \) denotes the photon energy. As an example of the latter case, Figure 6 shows the effective linear attenuation coefficient \( \mu \) encountered by an unfiltered beam from the tungsten source of Figure 1 as it penetrates a theoretical homogeneous glass-water mixture (50% each by volume), together with the energy value for a hypothetical monochromatic beam with equivalent attenuation (effective monochromatic beam energy) at the given penetration depth. For monochromatic radiation the linear attenuation coefficient would be constant with penetration depth, depending only on the singular beam energy. However, for polychromatic radiation the effective attenuation decreases with penetration depth, because of the selective removal of photons of the more strongly attenuated energy levels.

2.4.4. Photon randomness. All radiographic and radiation-tomographic measurements are subject to noise because of the random nature of both photon emission at the source
and photon interaction with the electrons of the object material. Let the subscript \(j\) refer to the photon beam arriving at detector \(j\). Provided the X-ray source is drift-free, the average photon-emission rate for the \(j\)th beam \(\lambda_j\) is fixed for a chosen combination of source potential and current. It can then be assumed that \((I_0)\), the number of photons emitted into the \(j\)th beam over a period \(\Delta t\), follows a Poisson distribution with a mean and a variance of \(\lambda_j \Delta t\).

Along its path each photon contributing to \((I_0)_j\) will either be removed from that beam by interaction with electrons (scattering and/or photoelectric absorption), or it will pass through the object and contribute to the intensity value measured by the \(j\)th detector cell \((I_j)\). However, scattered photons whose scattering angle is sufficiently small may, instead, arrive at some other detector cell. As this applies to all beams, a given detector reading \(I_j\) will generally be an overestimate. Since the intensity of scattered photons is nearly independent of rotation phase at energy level \(E\) and the atomic composition of the solute. The intercept \((c)\), for the reported polychromatic radiation of the used CT systems, six capillary tubes of 0.82-mm inner diameter were filled with sodium iodide (NaI) solution with concentrations of 0, 20, 40, 60, 80, and 100 mg/mL. The tubes were sealed and placed vertically inside a Plexiglas tube of 4.76-mm inner and 7.94-mm outer diameter. To minimize beam-hardening effects on the final calibration, the radial distances from the vertical axis of the Plexiglas tube to the center of each capillary tube were approximately identical (1.5 mm). The capillary tubes were scanned using system A, yielding 60 horizontal slices from a single complete rotation. Average attenuation values were obtained for each NaI concentration using all voxels from the 60 slices combined (23,397) with a standard error of \(5 \times 10^{-4} \text{ cm}^{-1}\).

A linear relationship between solute concentration \(c\) and \(\mu\) is expected if radiation is monochromatic and a negligible change in liquid volume due to the iodine dissolution is assumed. The slope is determined by the photon energy \(E\) and the atomic composition of the solute. The intercept \((\mu_e\text{ }\text{at zero concentration})\) is defined by the attenuation of the pure liquid phase at energy level \(E\). Using the tabulated attenuation properties of hydrogen, oxygen, sodium, and iodine [NIST, 1995], theoretical calibration lines, \(\mu(c)\), for NaI solution were computed for energy levels at 1-keV increments in the tungsten 125-keV source spectrum. Four such curves at 50, 60, 70, and 80 keV are presented in Figure 7 and compared with the measured calibration curve (diamonds).

Also, based on the spectrum of a tungsten source beam having penetrated the plexiglas tube with capillaries near the vertical axis, the theoretical average effective beam energy \(E_{crit}\) of 64.6 keV was computed from...
where \([Ei(E)]\) represents the beam intensity as measured by a scintillating detector, using handbook values of attenuation values for glass, water, iodine, and Plexiglass. The computed \(E_{\text{eff}}\) value of 64.6 keV corresponds well with the location of the observed calibration line, suggesting that \(E_{\text{eff}}\) is a useful measure when comparing attenuation of polychromatic with monochromatic beams.

Given that the relationship \(\mu(c)\) is linear for each specific \(E\), it follows from (5) that the effective calibration curve at a fixed radial distance \(r\), \(\mu(c)\), for a polychromatic source must also be linear. The near-perfect fit of a straight line to the measured data in Figure 7 confirms this theoretical result \((R^2 = 0.9992)\). It is important to note that while the effective \(\mu\) is, indeed, a linear function of \(c\) at a given radial distance \(r\) from the vertical center axis, the slope will vary with \(r\) because the energy spectrum changes with \(r\) because of beam hardening. This will become important later in the analysis of iodide breakthrough. Hereafter the symbol \(\mu\) always denotes the effective linear attenuation coefficient.

### 3.2. Miscible Displacement Experiment

A 50-mm-long vertical flow cell was made from a Plexiglas tube with 4.76-mm inner and 7.94-mm outer diameter and was randomly filled with precision-grade glass beads of 0.5-mm diameter (Catophyte Inc., Jackson, Mississippi). Rubber septa were placed at both ends of the tube, leaving no free space between the bead pack and the septa. Liquid inflow occurred through two needles penetrating the septum at the top of the tube. Both needle openings of 0.6-mm diameter were positioned at the horizontal center of the septum. A constant flow rate of 100 mm³/h was maintained by a double syringe pump to “instantaneously” switch injection between water and 100-mg/mL NaI solution, with each liquid entering through one of the inflow needles.

As indicated in section 3.1, one cannot simply use the calibration curve in Figure 7 to determine the concentration distribution within the bead pack from liquid-phase \(\mu\) values because the effective X-ray energy changes as the beam passes through the medium. Hence a calibration method is needed that incorporates horizontal radial distance \(r\) from the object axis. Since the first scan of the glass-bead pack used pure water as the liquid phase, it provides the intercept \((c = 0)\) for the \(\mu(c)\) calibration line at any given radial position \(r\). However, to completely define the respective linear calibration line at \(r\), a second fixed point is required. Since the local iodide concentration at any \(r\) during the breakthrough experiment is unknown, the second calibration point was obtained from the observed attenuation for the glass phase, \(\mu_{\text{glass}}(r)\). Figure 8 shows values of \(\mu_{\text{glass}}\) as a function of \(r\), with each value representing the mean of 9 × 9 × 9 (729) voxel values centered within a specific glass bead. Horizontal bars represent ±1 SE based on the observed noise in the \(\mu_{\text{glass}}\) values. The shape of the observed relationship \(\mu_{\text{glass}}(r)\) was well described by a quadratic function, which was fitted through the data points. The nonlinear behavior is the result of beam hardening, causing an apparent increase in attenuation from the center \((r = 0)\) to the perimeter of the Plexiglass tube. This increase in

![Figure 7. Measured NaI calibration line (diamonds) and theoretical NaI calibration lines at energy levels of 50, 60, 70, and 80 keV.](image)

![Figure 8. Fitted curve for the attenuation of glass as a function of radial distance from the center axis.](image)
m_{\text{glass}}(r)$ corresponds to a decrease in effective photon energy $E_{\text{eff}}(r)$, that is, $E$ of the equivalent monochromatic radiation (Figure 2). For each $E_{\text{eff}}(r)$, there is a NaI concentration $c_{\text{equiv}}(r)$ whose attenuation coefficient matches the corresponding observed value of $m_{\text{glass}}(r)$. According to Figure 2 the NaI concentration value at which the attenuation coefficient matches that of glass decreases as $E_{\text{eff}}$ decreases within the applicable range of 60–70 keV. The concentration $c_{\text{equiv}}(r)$ can be computed from the NIST [1995] tables using the chemical composition of the glass beads and iodide solutions. A plot of computed $c_{\text{equiv}}$ values as a function of $r$ is shown in Figure 9 together with a straight-line fit. Standard error values in $c_{\text{equiv}}$ are based on the respective SE for $m_{\text{glass}}$ by applying standard error propagation. The values $m_{\text{glass}}(r)$ and $c_{\text{equiv}}(r)$ together provide the second point of the linear $\mu(c)$ calibration curve at radial position $r$.

The final calibration equation to compute a solute concentration at a pore location $x$ within the three-dimensional voxel set is then given by

$$c(x) = \frac{\mu(x) - \mu_{\text{H2O}}(x)}{\mu_{\text{glass}}(r) - \mu_{\text{H2O}}(x)} c_{\text{equiv}}(r),$$

(9)

where $\mu_{\text{glass}}(r)$ and $c_{\text{equiv}}(r)$ are the respective fitted functional expressions and $\mu_{\text{H2O}}(x)$ is the $\mu$ value of the voxel at location $x$ in the first data set obtained (i.e., before application of the NaI pulse). Note that the units of concentration are mass of solute per volume of liquid phase and that $c$ represents resident concentration. To reduce the standard error due to photon noise in the individual reconstructed voxel $\mu$ values, the mean $\mu$ value for a group of 5 × 5 × 5 adjacent liquid-phase voxels was considered a measurement at the center location $x$ of the voxel group. Given the voxel side length of 17.1 $\mu$m, the effective spatial resolution of the local solute breakthrough was thus approximately 86 $\mu$m, while the actual spatial resolution of the scanner had been measured at 28 $\mu$m for negligible noise. A still larger group size would result in even smaller SE values but would limit the number of applicable pore locations to a few large pore bodies because of the necessary “safety distance” from the glass-liquid interface to prevent blurring effects.

An expression for the variance of the resulting local concentration values, $\sigma^2[c(x)]$, at a given time $t$ is obtained by substituting the respective derivative expressions from (9) into the error propagation equation while assuming that $\mu$, $\mu_{\text{H2O}}$, $\mu_{\text{glass}}$, and $c_{\text{equiv}}$ are independent:

Figure 9. Fitted curve for the NaI concentration resulting in an attenuation identical to that of glass at the effective energy corresponding to the respective radial distance from the center axis.

Figure 10. Local breakthrough curves at 10 random positions (see Figure 14 for locations): (a) 1, 2, 4, and 5, (b) 6–9, and (c) 3 and 10.

Figure 11. Concentration values estimated from equation (9) for pure water and 100 mg/mL NaI. True values are indicated by horizontal lines.
The local value for the variance of the liquid-phase attenuation, $\sigma^2[\mu(x)]$, was approximated by the estimated variance of the mean $\mu$ value for the considered group of 125 liquid-phase voxels. The value of $\sigma^2[\mu_{\text{H}2\text{O}}(x)]$ is identical to the $\sigma^2[\mu(x)]$ value for the first data set of the sequence (corresponding to the water-saturated sample). The values of $\mu_{\text{glass}}(r)$ and $c_{\text{equiv}}(r)$ in (10) are those predicted from the fitted expressions given in Figures 8 and 9, respectively. Variance values,
Table 1. Mass Balance Results for Different Grid Resolutions

<table>
<thead>
<tr>
<th>Number of Segments $N$</th>
<th>Voxels/Segment</th>
<th>$\dot{M}$, mg</th>
<th>$\epsilon$, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1,794,150</td>
<td>12,456</td>
<td>16.96</td>
</tr>
<tr>
<td>2</td>
<td>448,538</td>
<td>10,732</td>
<td>28.45</td>
</tr>
<tr>
<td>4</td>
<td>142,830*</td>
<td>10,513</td>
<td>29.91</td>
</tr>
<tr>
<td>9</td>
<td>28,830*</td>
<td>16,365</td>
<td>9.10</td>
</tr>
<tr>
<td>17</td>
<td>4096*</td>
<td>15,762</td>
<td>5.08</td>
</tr>
</tbody>
</table>

$\dot{M}$, estimated total applied iodide mass; $\epsilon$, relative mass balance error.

*For segments not intersecting the circular boundary.

$\sigma^2[\mu_{\text{glass}}(r)]$ and $\sigma^2[c_{\text{equiv}}(r)]$, were computed from the covariance matrix of the respective optimized parameter set [Clausnitzer and Hopmans, 1995]:

$$
\sigma^2[\mu_{\text{glass}}(r)] = \sigma^2[A_0] + \sigma^2[A_1]r^2 + \sigma^2[A_2]r^4 + 2 (\text{Cov}[A_0, A_1]r + \text{Cov}[A_0, A_2]r^2 + \text{Cov}[A_1, A_2]r),
$$

(11a)

$$
\sigma^2[c_{\text{equiv}}(r)] = \sigma^2[B_0] + \sigma^2[B_1]r^2 + 2 \text{Cov}[B_0, B_1]r,
$$

(11b)

where $A_i$ and $B_i$ denote the fitted coefficients of $i$th order in the expressions given in Figures 8 and 9, respectively. Final uncertainty, $\sqrt{\sigma^2[c]}$, varied between 2.9 mg/mL and 3.7 mg/mL, decreasing with increasing concentration values. The variation in iodide breakthrough of both peak concentration and peak travel time is presented in Figures 10a, 10b, and 10c, which show $c(t)$ curves for 10 different pore locations $x$ within the scanned volumetric slice of 0.4-mm thickness. Breakthrough curves were obtained from 16 scans, each separated by about 20 min. The observed local breakthrough curves can be roughly classified into three groups. Breakthrough within the first group (Figure 10a) exhibits higher peak concentration values with shorter peak travel times than the second group (Figure 10b), whereas the breakthrough of the third group (Figure 10c) shows distinct multiple peaks, demonstrating possible unstable flow behavior. Observed variations are likely caused by density-driven preferential flow during the downward displacement of water by the NaI solution whose density was initially 10% higher than that of water [Liu and Dane, 1996a, b]. This interpretation was further supported by visual observation when staining dye was added to the NaI solution. Preferential flow in channels with diameters less than the effective spatial resolution of 86 $\mu$m can also explain the relatively small peak concentrations of the breakthrough curves. We note that differences in the 10 presented local breakthrough curves are noticeably reduced after 180 min of breakthrough, indicating a much more uniform flow during the subsequent displacement of the solution by the water, that is, by the liquid of lower density.

The accuracy of the predicted concentration values was supported by two independent tests. First, the calibration given by (9) was applied to liquid-phase voxels inside two capillaries attached to the outside of the flow cell, with one containing pure water and the other containing 100-mg/mL NaI solution. The two capillaries combined bracket the experimental concentration range of the breakthrough experiment. Figure 11 shows that the predicted values after calibration are approximately identical to the true values, with deviations not larger than the estimated uncertainty of 3–4 mg/mL.

Second, the measured mass of solute moving through the observed cross sectional slice, when integrated over time, must equal the total mass of applied of solute (15 mg). Voxel concentration values (milligrams of iodide per cubic centimeter of solution) for the 16 data sets representing the breakthrough were computed from

$$
c(x, t) = \frac{\mu(x, t) - \mu(x, t_0)}{(\mu_{\text{glass}} - \mu_{\text{H}_2\text{O}})(r)} c_{\text{equiv}}(r),
$$

(12)

where $\mu(x, t_0)$ denotes the voxel attenuation value for the water-saturated sample before the pulse was applied. The difference between the values of $\mu_{\text{glass}}$ and $\mu_{\text{H}_2\text{O}}$ depends on radial distance from the center because of beam hardening. If only local breakthrough is considered, the value of $\mu_{\text{H}_2\text{O}}$ is explicitly known at each considered position $x$ and can be used directly, as in (9). To compute the complete mass balance, however, a relationship is needed that predicts the difference ($\mu_{\text{glass}} - \mu_{\text{H}_2\text{O}}$) for any value of $r$. Values of the difference ($\mu_{\text{glass}} - \mu_{\text{H}_2\text{O}}$) as a function of $r$ were computed using the known $\mu_{\text{glass}}(r)$ values shown in Figure 8 and theoretical $\mu_{\text{H}_2\text{O}}$ values corresponding to the effective energy at the respective radial distance. The relationship ($\mu_{\text{glass}} - \mu_{\text{H}_2\text{O}})(r)$ was expressed as a quadratic function of $r$ whose coefficients were obtained by fitting the computed difference values ($R^2 = 0.9875$). The parametric expression for $c_{\text{equiv}}(r)$ is the same as in Figure 9. As it should, (12) predicts $c$ values of zero (subject to photon noise) for voxels located within the glass phase, assuming perfect drift correction. A sequence of the spatial distribution of iodide concentration values at selected times of 37, 58, 105, 145, 186, and 245 min is presented in Figure 12. Two rather distinct regions can be recognized in the three-dimensional representation, with relatively higher concentration values predominantly found on the left and lower values found on the right. This observation supports the likelihood of preferential flow within the bead pack.

The total mass $M$ of solute passing a horizontal cross section $A$ of the flow cell is given by

$$
M = \int_T \int_{A_{\text{liquid}}} c(x, t) N_c(x) dA dt,
$$

(13)

where $T$ denotes the duration of the experiment, $A_{\text{liquid}}$ is the fraction of $A$ within the liquid phase, and $N_c$ is the vertical component of the fluid velocity. To compute $M$, the following approximations were made:

1. The integration in time was performed numerically from the 15 scans that followed the initial scan of the water-saturated sample, using time intervals $\Delta t$, with $j = 1, \ldots, 15$.
2. The integration over $A_{\text{liquid}}$ was replaced by a summation over discrete segments of $A$. Segments were defined by overlaying the horizontal circular cross section of the flow cell with a $N \times N$ grid, with $N$ equal to 1, 2, 4, 9, and 17.
3. All 30 horizontal slices ($N \neq 17$) or the upper horizontal 15 slices only ($N = 17$) were combined into a single cross section, resulting in a vertical slice thickness of 0.436 mm (30 $\times$ 0.145 $\mu$m) or 0.218 mm (15 $\times$ 0.145 $\mu$m), respectively. The position of $A$ was defined by the vertical center of the segments.
4. An approximation to the average vertical component of the fluid velocity $N_c$ for each segment was obtained by dividing the vertical distance between inflow and $A$ (20 mm) by the time required for the center of the pulse to travel this distance for each specific segment of $A$. The center of the pulse was as-
sumed to correspond to the time at which the peak concentration is observed at the respective segment.

Replacing the integration over \( A_{\text{liquid}} \) by summation over segments of \( A \) requires that concentration values of zero are assigned to all points not within the liquid phase. This is ensured by using (12) to compute the values of \( c \) for all voxels present in each segment. Applying approximations (1) through (4), (13) is approximated by

\[
M \approx \sum_n \bar{v}_c(n) A(n) \sum_t \bar{c}(n, t) \Delta t_i,
\]

where \( \bar{M} \) denotes the approximation of \( M \), \( n \) is the summation index over all segments, \( A(n) \) is the \( n \)th segment’s area in the \( x-y \) plane, and \( \bar{c}(n, t) \) is the estimated mean \( c(t) \) value over all voxels within the \( n \)th segment during time interval \( \Delta t_i \).

The smallest segment size selected was 4096 voxels (\( N = 17 \)), so that the standard error of the mean \( c \) value, due to photon noise, was less than 1%. The value of \( \bar{v}_c \) for \( N = 1 \) was 19.7 mm h\(^{-1}\). The difference to the average pore water velocity of 13.7 mm h\(^{-1}\) previously computed from known flow rate and porosity values also supports the interpretation of preferential flow. Table 1 shows values of the estimated total iodide mass \( M \) predicted by (14) for the different selected grid sizes, as well as the magnitude of the respective mass balance error \( \varepsilon \) relative to the true total solute mass value of 15 mg. Further reducing the segment size (\( N > 17 \)) did not result in a further reduction of the computed mass balance error of approximately 5%.

To illustrate the heterogeneity in solute breakthrough within

![Figure 13. Estimated spatial distribution of cumulative solute breakthrough within the horizontal cross section at 2 cm below inflow end for (a) \( N = 2 \), (b) \( N = 4 \), (c) \( N = 9 \), and (d) \( N = 17 \).](image-url)
the flow cell, the spatial distribution of the estimated total transmitted mass of solute per area

$$\hat{M}(n) = \hat{v}_z(n) A(n) \sum_{\tau} \hat{c}(n, \tau) \Delta t_{ij}$$

is shown for decreasing segment sizes in Figure 13. The corresponding spatial distribution of \(\hat{v}_z\) values for the 17 \times 17 grid only is plotted in Figure 14 together with the x-y locations of the 10 observed local breakthrough curves of Figure 10. Again, both Figures 13 and 14 clearly show the presence of a preferential flow pattern. The local breakthrough curves in Figure 10a correspond to the region of relatively high \(\hat{v}_z\) values (>20 mm h\(^{-1}\)), those in Figure 10b correspond to the region of relatively low \(\hat{v}_z\) values (<20 mm h\(^{-1}\)), and the location of one of the curves in Figure 10c is at the approximate boundary between both regions. Given this flow pattern, it was not surprising that the overall average concentration with respect to the liquid phase and the breakthrough curve could not be predicted by the standard convection-dispersion model. For dispersivity values up to the bead size (0.5 mm) the standard model predicted a peak concentration value above 90 mg/mL, while the observed peak concentration was only about half of this value. The additional spreading of the solution pulse, relative to the standard model, can most likely be attributed to unstable flow during the displacement of water by the iodide solution.

4. Conclusions

Microfocus X-ray CT can provide local concentration measurements with acceptable uncertainty for experiments involving miscible displacement in porous media. After correction for drift, noise due to photon randomness was the dominant source of uncertainty, resulting in an effective spatial resolution of approximately 86 \(\mu\)m. As this represents a threefold loss relative to the measured scanner resolution, extended acquisition times are clearly desirable to minimize noise by maximizing the photon count. To avoid a loss in temporal resolution, the flow must be sufficiently slow. A practical limit is set by the possible duration of the experiment, that is, the maximum time of scanner access.

While the relationship between solute concentration and attenuation is linear for polychromatic as well as monochromatic radiation, the beam hardening that is typical for industrial X-ray sources requires a calibration method that takes radial distance from the vertical object axis into account. It is proposed to base the calibration on sufficiently separated attenuation values for two phases that are present in the system.
over the entire range of $r$ (water and glass).Filtering the X-ray beam before entering the object would have reduced the beam hardening effect thereby lessening the need for the additional calibration. However, beam filtering reduces photon fluxes and increases scanning times, making transient transport experiments as presented here impossible. Inferring local fluid velocity from the respective peak-concentration travel time and using concentration values predicted by the calibration resulted in an acceptable mass balance, provided a sufficiently high spatial resolution was used.

Although we maintain our enthusiasm for application of X-ray microtomography in porous media, we conclude that if higher spatial and temporal resolutions as obtained in the presented experimental study are needed, a radiation source such as a synchrotron is needed. The associated higher photon fluxes will reduce acquisition time while increasing the signal-to-noise ratio and the spatial resolution. As the X-ray spectrum produced by a synchrotron source can be controlled to produce an almost monochromatic beam, corrections for complications as caused by beam hardening become unnecessary.

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References


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