

A KINETIC MODEL OF IMBIBITION IN SOILS

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ABSTRACT

A series of imbibition tests were conducted in soil samples that were contaminated or clean. The imbibition tests were done in a counter current fashion with controlled water rates, so that instant and complete saturation was explicitly avoided. Low-field NMR was used to monitor the imbibition process as a function of time. The spectra obtained were compared to "standard" spectra obtained with unconsolidated media. A number of unexpected and seemingly counter intuitive observations were made. It was found that the NMR spectra could be resolved into peaks that correspond to different pore sizes (as expected). However, the intensities and maxima of the peaks changed as a function of time, thus allowing for the monitoring of the redistribution of water in the porous media. Water ultimately migrated towards smaller pores from larger pores. As this migration occurred, the peaks corresponding to larger pores shrunk and the peaks corresponding to smaller pores increased. It is probable that substances in or on the surfaces of smaller pores develop as colloidal components or gels. It was possible to take these peaks and perform a kinetic analysis of water uptake in the porous medium. Kinetic data for wettable soils pointed to zero order kinetics for water uptake in the small pores. It was also found that soils previously contaminated and denoted as water-repellent appeared to follow second order kinetics for the water uptake in small pores. A kinetic model of imbibition can be formulated, with constants that describe the water uptake by different pore sizes. Furthermore, NMR offered an alternative for measurements of wettability in soils. This alternative is considered to be very important because there is no quantitative tool for measuring wetting properties of soils today. Qualitative measurement tests currently used are not theoretically sound.

INTRODUCTION

Imbibition is a displacement process in which the wetting phase displaces the non-wetting phase, first in the smallest pores and then in increasingly larger pores as pressure decreases. This displacement process is controlled by pore bodies and affects parameters such as relative permeability and residual saturations¹. Soil processes can be more complex because the organic matter and hydrous oxide colloids in soil form water-swollen gels with different structures (hence, porosity) in dry and wet states. Consequently, models do not include a term to account for "displacement".

Water uptake into soils is a little-known process and recent progress suggests that water uptake into soils results directly from pore formation facilitated by the water itself². Of particular interest in wetting studies are soils that develop non-wettability, thus lose the ability to sorb water, over time³. The largest problem with attempting to explain observed non-wettability in polluted soils is that not all contaminated sites develop non-wettability. Also, development of non-wettability can take anywhere from months to years following clean-up of bulk contamination at the site⁴. In addition to this, non-wettability appears to

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develop more often in sandy soils with a relatively low organic matter content than in other types of soil⁵⁻⁷. This may be due to the fact that sandy soils have low surface area, thus less sorption sites available for water molecules to bind to. The relation between lack of organic matter in soils and development of non-wettability is well documented due to the fact that contaminant sorption is a direct function of organic matter content in soils⁸⁻¹⁰.

It appears that presence of sufficient organic matter in soil can result in one of two occurrences: labile or reversible binding to the soil organic matter and non-labile or irreversible binding to soil organic matter^{11,12}. From this it appears that in non-wettable soils, contaminants may complex to limited soil organic matter in an unfavourable fashion, resulting in water repellency³, whereas in highly organic soils, the contaminant may become part of the soil organic matter itself without inducing water repellency^{11,12}.

Water uptake can be understood when analysing the process at the pore level and nuclear magnetic resonance (NMR) is a tool capable of providing insight into the distribution of fluids within porous media¹³⁻¹⁵. The physics of NMR has been covered elsewhere¹⁶⁻¹⁸. A proton low-field NMR is used in this experimental program to analyse the interactions between water and the grain surfaces of several different porous media. One can infer the state of fluids within a porous media from looking at NMR spectra based on type-specific cutoffs of transverse relaxation (T_2) times^{15,19,20}. Water molecules near a water-wet surface will relax faster than near an oil-wet surface. This is due to restricted rotation of water molecules near a water-wet surface, a result of a polarising surface force such as that resulting from a hydrogen bond²¹. Contributions to spectra at T_2 's lower than a cutoff are considered due to bound water while contributions at higher T_2 's are considered due to water in the bulk phase^{15,19,20}.

Multiple NMR measurements obtained over time can provide insight into water migration through the porous medium. This information can be used to understand the occurrence of wettability alteration^{22,23} or the process of water uptake. In terms of understanding water uptake, NMR spectra can be used to depict imbibition if the porous medium is water-wet. This paper will show NMR spectra that depict the opposite trend at the start of imbibition, which may reflect the role of the gel components.

Kinetic treatment of data has been shown to be an effective method for monitoring water uptake into soil. Kinetics are useful because they allow for interpretation of water uptake over a long period of time, while offering insight into mechanistic possibilities of the system. The simplest approach to characterise the dynamic system is to test whether data can be fitted to one of the standard chemical rate laws²⁴. A systematic empirical data archive is created for further theoretical analysis if the fits are reasonable.

Zero order kinetics describe a process that is constant and independent of concentration over time. The general form of a zero order rate law is²⁴:

$$(1) C = k_0 t + C_0$$

where C is a concentration signal parameter, k_0 is the zero order rate constant, t is time and C_0 is initial concentration signal. In this form, kinetic data that follows zero order kinetics should result in a straight line²⁴.

First order kinetics follow a logarithmic form where the rate depends on one component. As time passes, and the concentration of this component decreases, the process will slow down. First order kinetics have the following form²⁴:

$$(2) \ln C = k_1 t + \ln C_0$$

The logarithm of the concentration signal is linear with time²⁴.

Second order kinetics that depend on only one component follow a simple inverse form of a rate law. The implication of this is that a co-operative process involving the square of the concentration signal is occurring. Like first order processes, second order processes display concentration dependence. Thus as time passes, and substrate is consumed, process rate will decrease. Second order kinetics follow the form²⁴:

$$(3) 1/C = k_2 t + 1/C_0$$

In this case, the linear form of this is a plot of $1/C$ versus time²⁴.

Kinetic treatment by this means is possible to the extent that it can be assumed that rates of successive processes are sufficiently different. This implies that peak depletion, or movement of water from larger pores, occurs at a rate equal to the observed accumulation in the smaller pores.

MATERIALS AND INSTRUMENTATION

Wettable and water-repellent soil from the Ellerslie research station, approximately 18 km south of Edmonton, Alberta, Canada were used in this experimental program. The wettable soil is deemed control-wettable and denoted as ELL CW while the water-repellent soil is denoted as ELL NW for non-wettable. The Ellerslie soil is a well-documented case of non-wettability development since contamination of this site occurred as part of a reclamation study in 1973. This soil is classified as a well-drained, Eluviated Black Chernozem of the Malmo Silty Clay Loam series that developed on fine-textured, slightly saline glaciolacustrine sediments⁴. Wettable and water-repellent soil from an agricultural field near Devon, Alberta, Canada (DEV CW and DEV NW, respectively) were also used. This soil is classified a weakly Eluviated Black Chernozem of the Ponoka Loam series developed on alluvial lacustrine, medium-textured materials. This site was contaminated as a result of a crude oil well blow-out in 1948. Much of the spilled oil was removed or burned in the subsequent fire, but substantial amounts of oil can still be found in the subsoil. The residual oil content of the non-wettable and the control-wettable soils from this site are 6.5 ± 0.3 and 1.5 ± 0.1 g oil per kg soil, respectively, on an oven-dry soil basis (determined by a 24 hour Soxhlet extraction using dichloromethane as the extractant⁴). Berea sandstone was also used for experimentation.

The NMR measurements were performed with the Corespec-1000TM relaxometer at a frequency of 1 MHz (field strength is 0.024 T). Measurements for all samples were obtained at inter-echo spacings of 0.3 ms, with a signal-to-noise ratio of at least 225, and taken every half-hour for the first four hours after water addition. Afterwards,

measurements were taken every hour for a total of eight hours or until there was no significant change in the NMR spectra. After the first day, measurements were taken once daily until there were no significant changes in the T_2 distributions. Duplicate runs were performed during each measurement in order to ensure results were genuine and not a result of experimental artifacts. The data was processed using EchoFit v. 3.02, a software package created by NUMAR Corporation, a subsidiary of Halliburton, which employed the non-negative least squares method to create the T_2 distributions.

PROCEDURE

Each unconsolidated sample was poured into a vial 3.5 cm in diameter and 5.0 cm in height. The sample was loosely packed to create a column slightly less than 1.5 cm in height. NMR measurements were taken to determine initial water content in these air-dried samples. Water was added, at a rate of approximately 1 drop per second, until the sample contained approximately 33% or 50% water by mass, so long as a thin film of water on top of the sample was visible. This film of water was used to determine whether or not the NMR spectrum would show a peak that corresponds to bulk water, which occurs at T_2 approximately equal to 3000 ms^{17} , and would help in determining the migration of water through an initially dry water-wet porous medium. The Berea sandstone was cut into slices 1.5 cm in height and 3.81 cm in diameter in order to fit into the sample holder. Sample mass was recorded prior to each measurement to determine amount of water loss. For the duration of the experiments the samples were kept in the same room with the NMR relaxometer, which has a constant ambient temperature of 25°C .

RESULTS AND DISCUSSION

NMR results can be used to determine the amount of water in a given sample. The measurements from the samples before the addition of water show the samples to have approximately 0.1 g of water, which constitutes less than 1% of the sample mass. Furthermore, the echo trains from the samples before the addition of water show only noise, which imply that there is very little or no mobile hydrogen protons (i.e., very little or no water). Figure 1 shows the NMR derived water weights and water weights determined by mass balance for most of the samples used in this experimental program after the addition of water. These numbers concur well as variability is better than 4.5%.

Ellerslie and Devon Soils

The normalised data for the two ELL soils is shown in Figures 2 and 3. Figure 2, which represents ELL CW, shows that there are no peaks at T_2 greater than 500 ms, which is much shorter than published values of approximately 3000 ms for bulk water¹⁷. This discrepancy may be due to fast exchange between surface bound water protons and water protons in the thin film of bulk water. Alternatively, the low observed value of T_2 for ELL CW may be due to either a large number of bound water molecules present or an extremely low value of T_2 for bound water in this sample. The low value of T_2 for bound water in ELL CW may be due to its organic content (61 g total carbon / kg soil, as determined from gravimetric analysis using a pressure plate apparatus⁴). Another possible explanation for the lack of a bulk water peak for ELL CW, despite the visible presence of bulk water, may be that the water has leached out paramagnetic metal ions. However, the metal ions must be leached out of the soil in order for this to occur and the only magnetic material in high enough concentrations in ELL CW to really affect the T_2 of bulk water is iron. The iron is

in the form Fe (III), which is water insoluble in the range of neutral pH. (Iron in the form of Fe (II) would have leached out long ago since it is present only in the dissolved form.) While leaching of Fe (III) is possible at a pH greater than ten or less than five, these conditions were not obtained in these experiments. Furthermore, this phenomenon occurred only in ELL CW and not in ELL NW. While there must be differences, it is unlikely that the concentration of iron in these two soils differ so drastically that there would be such a shift in the bulk water peak. Results from a similar test performed on humic acids alone also showed the absence of a bulk water peak²⁵, which suggests that the absence of a bulk water peak may be due to water bound tightly to either the humic or clay fraction in this sample.

A comparison of Figures 2 and 3 show that, although initial uptake of water is slow, wetting of the smallest pores in ELL NW is apparently a much faster process than in ELL CW. This can be observed in the complete development of the short relaxation time peaks in ELL NW soil after only eleven days, compared to the development in ELL CW, which requires twenty or more days. In addition to this, the achievement of the final peak distributions in non-wettable soil, compared to control-wettable soil, suggests that the time to end differs substantially. ELL NW has displayed cessation in spectral shift as early as eight days, where ELL CW has required as long as twenty days.

Figures 2 and 3 reveal the existence of five prevalent peaks that are separated by local minima throughout the data: between 0.1 and 2.0 ms, between 2.5 and 8.0 ms, between 10.0 and 100.0 ms, between 100.0 and 631.0 ms and between 794.0 to 10,000.0 ms. The presence of separate peaks suggests that exchange occurs between the water and the soil. For all cases separation points were adjusted, if necessary, such that peak separation fell on the local minima. Treatment of each separated peak provided insight into the mechanism by which soil wets. Figure 4 shows the kinetic analysis of the data for ELL CW and implies that this soil wets by a zero order process, which suggests that wetting occurs in a fashion similar to water entering pores under capillary forces. Zero order kinetics suggest that contribution to wetting is not a result of changing soil structure or water position. Water uptake occurs from large pores or bulk water. Figure 4 shows the same analysis for ELL NW and depicts that this soil does not wet by a zero order process because the data does not fit as well. Figure 5 shows a plot of the data from ELL NW soil that suggests this soil wets by a second order process. A second order wetting process suggests that some co-operative mechanism is occurring.

Use of acidic and basic solutions in place of water has suggested that wetting in ELL NW soil is more complex than wetting processes in ELL CW. Additional work is required to determine the mechanism of wetting in the ELL NW soil.

Figures 6 and 7 show the normalised NMR spectra for the Devon soils over time. These figures show the formation of amplitude peaks for DEV NW at T_2 's where there are peaks for DEV CW (i.e., at T_2 approximately equal to 1 and 10 ms). The fact that the non-wettable soils may eventually have similar spectra as wettable soils suggests that the time scale for water uptake may be the only difference between these two types of soils. Although time scales are longer with DEV NW soils, this soil may eventually sorb water like DEV CW. In other words, a soil that has been denoted as water-repellent is not necessarily incapable of water uptake, but may merely require more time before uptake

occurs. Figure 6 shows the development of peaks for DEV CW at 2.0 ms and 12.0 ms, which is close to the peaks for clays (i.e., T_2 approximately equal to 1 ms and 10 ms)²⁶. It is possible that the peaks for DEV CW would have moved to 1 and 10 ms if the experiments been carried out over a longer period of time. Alternatively, the differences may be due to the presence of residual petroleum hydrocarbons in DEV CW⁴. One can see from Figures 6 and 7 that peak movement is more dramatic in NW than CW. The peaks for DEV CW stay at approximately the same T_2 's as time after water addition elapses while the T_2 's for peaks changes dramatically for DEV NW. Water uptake for this non-wettable soil is initially slow, but it may begin to resemble the control-wettable soil in terms of water uptake over time.

Figures 6 and 7 also show that peaks for DEV soils lie between T_2 values of 1.3 ms and 12.5 ms, between 15.8 ms and 316.0 ms as well as between 398.0 ms and 10,000.0 ms with the different regions separated by local minima. This information was used towards kinetic analysis of the data from the Devon soils. Figure 4 shows the kinetic analysis of the DEV CW soil and suggests that this soil wets by a zero order process, like ELL CW. The kinetic analysis of the corresponding non-wettable soil (not shown) suggests that DEV NW wets by a process more complex than second order kinetics. It appears that the soil wets by a zero order process at lower T_2 's, but follows second order process at higher T_2 's. A possible explanation for this may be the fact that run times were not long enough to allow for complete water migration to occur. More research is required in this area to determine the wetting process for DEV NW.

Berea

Five millilitres of water was added to the Berea sandstone, contributing 12.5% to the total sample mass. A thin film was apparent immediately after water addition and was present throughout the duration of the test. Even after ten days, a water film 3 mm thick remained. Steps were taken to ensure that the total sample weight decreased no less than 1% as a result of water evaporation.

Figure 8 shows the total amplitude from the different sizes of pores for Berea over time, which is directly proportional to the amount of water present in the different sizes of pores. This figure shows that the total amplitude from the small pores decreases during the first seven hours after water addition, suggesting that the small pores did not receive any additional water initially. This contradicts the theory that the smallest pores fill up with the wetting phase first¹. A possible reason for the decrease in amplitude, and thus a decrease in the amount of water present in the small pores, may be that there were other surfaces in the sample more water-wet that the water preferentially bound to. Another possibility may be the design of the experiment because the counter-current fashion of imbibition in these experiments may have caused buoyancy to become a significant effect. As gas is displaced within the porous media and is pushing upwards, this phase may cause drainage in the small pores. The results may be different if water was injected in the bottom of the sample, thus allowing co-current imbibition to take place.

There is a quick increase in the total amplitude from the small size pores after seven hours and the amplitude remains constant after that point, which suggests that the small pores were filled with water. This may be the result of gas in the sample having been expelled. Figure 8 also shows that the total amplitude from the large and medium size pores remains

approximately constant for ten hours after the addition of water. After that point the total amplitude for the medium pores increases, possibly due to the introduction of water to these pores. This finding agrees with the commonly accepted theory of imbibition in that the medium pores appear to fill up with water after the small pores have been saturated¹. A similar plot for humic acids extracted using only a slight variation of procedures suggested by the International Humic Substances Society²⁷, show a similar trend for the total amplitude from small and medium pores²⁵, which suggest that the same process occurs in both consolidated and unconsolidated porous media. Some clays may remain in the humic acids, and may be responsible for the observed peaks, however an ash content test is necessary to determine this. Some question the role of diffusion in water uptake, however, this is not a question with the Berea sample. Diffusion is usually attributed to the swelling of organic matter. Since there is no organic matter present in Berea, this phenomenon does not play a significant role here.

The geometric mean for T_2 can be used as a quantitative parameter to identify water saturation in a sample²⁸. Figure 9 depicts changes in the values of geometric mean for T_2 for the samples used in this experimental program over time. This table shows that the geometric mean for T_2 decreased most dramatically for the soils deemed non-wettable. In fact, the geometric mean for T_2 is lower for both non-wettable soils than the samples deemed wettable after ninety hours. Closer inspection of Figure 9 will reveal that ELL NW has a lower geometric mean for T_2 than Berea as soon as two hours after water addition and that three hours after water addition, the geometric mean for T_2 is lower for ELL NW than it is for DEV CW. Long term monitoring of soil systems suggests that both ELL CW and ELL NW soils reach the same final point in the wetting process. This further verifies that after some time the soils deemed water-repellent takes on water uptake characteristics similar to that of the soil deemed wettable.

CONCLUSIONS

Water repellency displayed in naturally occurring soils does not necessarily imply that these soils do not possess the capacity to naturally take up water since the non-wettable soils analysed here displayed characteristics similar to those of the corresponding control-wettable soils some time after water addition. Also, the end point in saturation of the soils deemed water-repellent is very similar to the endpoint observed in control-wettable soils. The main observable difference with the ELLerslie soils, for example, is that the non-wettable soil appears to arrive at this point sooner than the control-wettable soil.

Kinetic treatment of these soils suggests that the water uptake process for the control-wettable soils is zero order, which implies that water flows into pores with no dependence on water position or soil structure. ELL NW soil follows the mathematics of a second order wetting process although the model was developed for chemical systems may not necessarily apply here. Current development of this theory is under way at this time. DEV NW soil appears to follow a second order wetting process as well, but only at longer T_2 's. The results suggest that this soil wets according to zero order kinetics at short to mid-range values of T_2 , however this may be due to the fact that the experiments were not carried out long enough for complete water migration to take place.

NMR measurements obtained over time indicates that the order of areas invaded by the wetting phase at the very start of imbibition is opposite that of commonly accepted theory.

The same measurements show that as more time passes, the path of wetting phase migration agrees with commonly accepted theory in that the medium pores do not fill up with water until the small pores are saturated.

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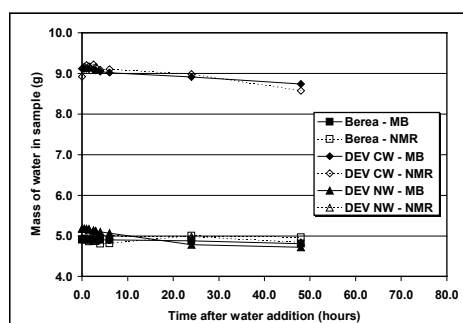


Figure 1: Mass of water calculated using mass balances and NMR spectra

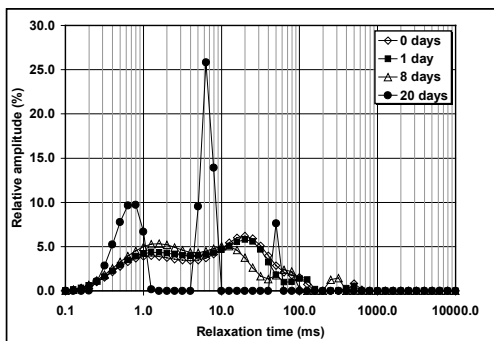


Figure 2: Normalised data for control-wettable Ellerslie soil

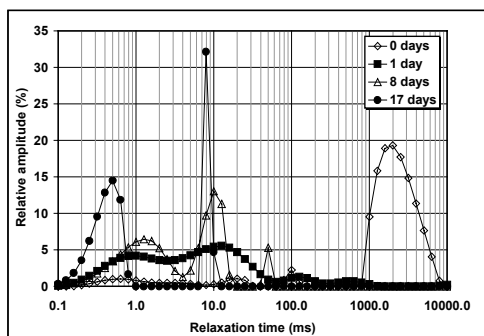


Figure 3: Normalised data for non-wettable Ellerslie soil

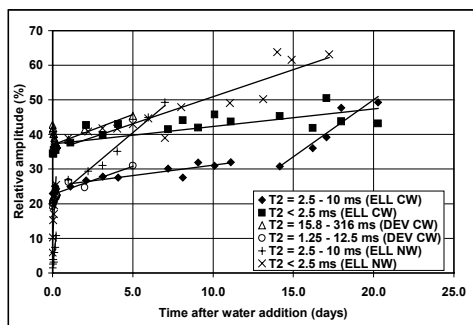


Figure 4: Kinetic treatment of data several soils (zero order)

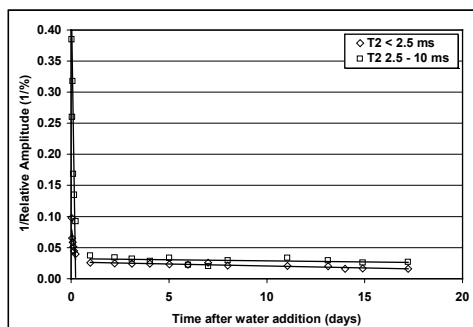


Figure 5: Kinetic treatment of data for non-wettable Ellerslie soil (2nd order)

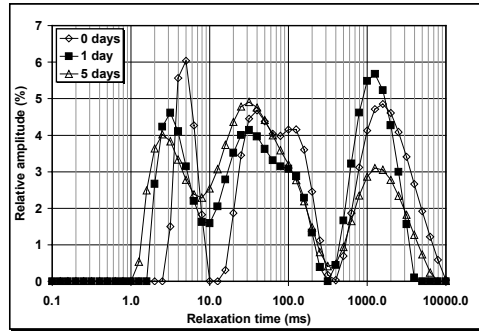


Figure 6: Normalised data for control-wettable Devon soil

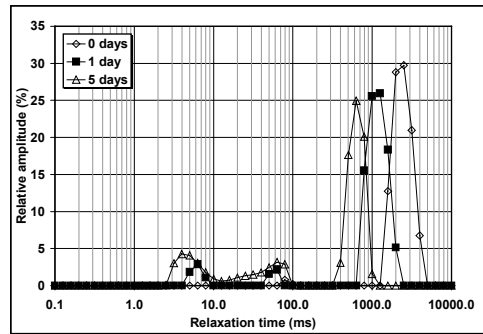


Figure 7: Normalised data for non-wettable Devon soil

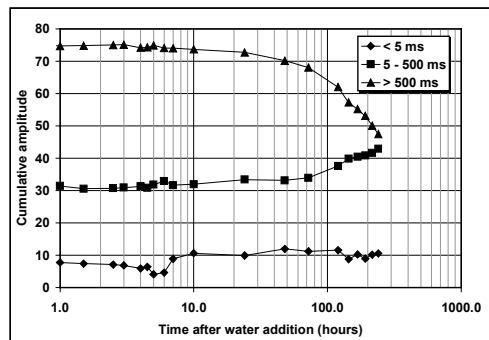


Figure 8: Contributions to total amplitude from different ranges of pore sizes for Berea

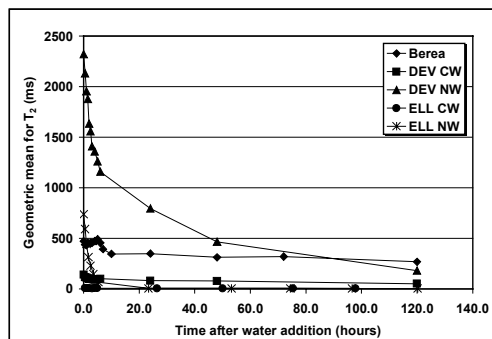


Figure 9: Changes in the geometric mean for T_2 after water addition for several samples