AN EXPERIMENTAL STUDY OF THE EFFECTS OF PARTIAL SATURATION ON ELASTIC WAVE VELOCITIES IN POROUS ROCKS

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A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE

in

THE FACULTY OF GRADUATE STUDIES
GEOPHYSICS

We accept this thesis as conforming
to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA
August 1994
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ABSTRACT

Elastic wave velocities in porous rocks containing air and water are sensitive to not only the relative levels of fluid saturation but also to the distribution of the fluids within the pore space. Three factors that have significant control over the relative distributions of fluids in multiphase saturated porous media are pore space microgeometry, saturation history and wettability. In this thesis, the effect of these factors on the form of dependence of velocities upon water saturation level in rocks is investigated experimentally.

Ultrasonic elastic wave velocity and drying rate measurements were made as a function of water saturation in a limestone, a dolomite and two sandstone samples as saturation was reduced through evaporative drying. During the later stages of drying there is a reduction in drying rate that is associated with the transition from capillary transport to diffusive transport due to a loss of hydraulic connectivity of the liquid phase. For the rocks used in this study, this suggests that velocity variations below this point can be associated with the removal of disconnected water held in surface roughness and in crack-like porosity. Using these interpretations and simplified models of the pore spaces derived from thin section analysis, fluid distribution scenarios are proposed for the drying process in these rocks. A numerical modeling routine is then used to predict the form of the velocity-saturation relationships for the rocks. The models were found to be in good agreement with the form of the experimental results.

The effect of wettability on the relationship between velocities and saturation history was investigated in the sandstone samples by conducting imbibition and drainage experiments before and after treatment with a chemical that altered their surfaces from being strongly water-wet to being oil-wet. In the water-wet sandstones, the results indicate that grain contact regions are the last to drain of water and the first to fill with water. At high
saturation levels, hysteresis is evident and is attributed to differences in the pore scale
distribution of fluids that evolves in pore bodies during the imbibition and drainage
processes. The results for the oil-wet samples during evaporative drying were found to be
similar to those for the water-wet rocks: water was replaced by air first in the pore bodies and
then in the grain contacts and cracks. In contrast, imbibition produced results that are
consistent with water entering the pore bodies first and being excluded from the cracks and
grain contacts until high saturation levels.
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ACKNOWLEDGMENTS

First and foremost I would like to express my gratitude to my supervisor Rosemary Knight, a seemingly boundless source of encouragement and enthusiasm. My thanks also go out to other members of the Rock Physics group, particularly Paullette-Tercier and Ana Abad and Ken Wilks, for their assistance at various stages of this thesis.

This research was supported by funding from Imperial Oil, Petro-Canada, Shell Canada and an Industrial Oriented Research Grant from the Natural Sciences and Engineering Research Council of Canada. The author was also supported in part by a University Graduate Fellowship.
1 INTRODUCTION

Seismic and sonic well logging surveys are two of the most widely used geophysical methods for investigating the earth's subsurface. In order for these techniques to be useful in providing information about geologic formations it is necessary to have an understanding of the seismic properties of earth materials. Laboratory experiments measuring elastic wave velocities in rocks provide important constraints in interpreting the results of such surveys. One factor that has been found, both experimentally and theoretically, to have a significant impact upon elastic wave velocities in porous rocks is nature of the fluids contained within the pore spaces. Two pore fluids that are of significant interest when considering application of seismic methods to hydrogeology as well as to the detection and monitoring of natural gas reservoirs are gas and water.

Laboratory experiments conducted at ultrasonic frequencies have shown there to be a considerable degree of variation in the form of dependence of velocities on water saturation level (Wyllie et al., 1956; Gregory, 1976; Murphy, 1982). Much of this complexity arises from ultrasonic velocities being sensitive to not only the level of water saturation but also the geometric distribution of water and air within the pore space (Endres and Knight, 1989; Knight and Nolen-Hoeksema, 1990). The distribution of fluids is in turn controlled by the complex interaction between pore space microgeometry, saturation history and the wettability of the solid surface. The focus of this thesis is to examine experimentally the influence of these three factors on the relationship between velocities and saturation level.

The thesis is divided into two main chapters. In Chapter Two, the specific nature of the distribution of fluids during evaporative drying is investigated in samples possessing three distinctly different types of pore space microgeometries. Gregory (1976) used experimental data collected during evaporative drying to infer general relationships between
porosity and the form of the velocity-saturation relationship. It appears, however, that the relationship between velocities and water saturation level is not simply related to the absolute porosity value (e.g., Cadoret, 1993). Pore geometry and saturation method are of primary importance in determining the distribution of fluids in a porous medium. Further, the nature of the pore space microgeometry also affects the extent to which rocks are sensitive to saturation state: crack-like pores are much more compressible than equidimensional pores (Walsh, 1965). The objective of this chapter is to explore how the interaction between the drying process and pore space microgeometry influences the form of the relationship between velocities and saturation level. This is accomplished by first using drying rate versus saturation level curves to resolve the transition from water being held in a funicular state to being held in a pendular state. In a funicular state, fully saturated pores will coexist with partially saturated pores and the liquid phase will be hydraulically connected. In a pendular state water will tend to be hydraulically disconnected and is held through capillary pressure in cracks, surface roughness and as an adsorbed layer. This transition has been associated with the onset of the irreducible water saturation within drying samples of porous media (e.g., Whitaker, 1985). Based on this information and simplified pore space models derived from thin section analysis, fluid distribution scenarios are proposed for the drying process. In particular, velocity variations are associated with either the drainage of funicular water in the early stages of drying or with pendular water during the later stages of drying. Numerical modeling is used to model the form of the velocity saturation relationship that would arise from these scenarios. The models are then compared with experimental results.

In Chapter Three the effect of wettability on the relationship between velocities and saturation history is investigated. Saturation history has been shown to produce hysteresis in the relationship between velocities and saturation in rocks (Knight and Nolen-Hoeksema, 1990; Cadoret et al., 1992a,b). This can be attributed to differences in the distribution of fluids in pore bodies that evolve between imbibition and drainage cycles. The distribution of
fluids during imbibition and drainage cycles in a rock is intimately related to the pore space microgeometry and the wettability of the rock surfaces. In general, capillary pressure will cause a wetting fluid to preferentially occupy smaller pores and cracks. Altering the wettability of the system can therefore influence the relative location of fluids within the pore space, which may in turn affect elastic wave velocities. To investigate these effects, imbibition and drainage experiments were first conducted on strongly water-wet sandstones. The wettability of the pore surfaces were then chemically altered to an oil-wet state and the experiments were repeated. Pore geometry and pore fluids were therefore kept constant and the effects of wettability were effectively isolated.

The issues addressed in this thesis are of significance in two main respects. The first issue is to gain a better understanding of how pore space microgeometry, saturation history and wettability interact to control the form of the relationship between velocities and saturation level. The second is the potential applicability of the results of this study to field situations. Both the transition of fluids to a disconnected state, and the wettability of the solid phase in multiphase saturated rocks have important implications to the transport properties of rocks (see Anderson, 1987a, for a review). The transport of fluids in multiphase saturated rocks is of considerable interest in hydrogeology as well as in the oil and gas industries. The ability to seismically resolve these properties in the subsurface would therefore be of significant utility. An important and necessary step towards understanding how, or if, these factors may impact the relationship between velocities and saturation is to conduct controlled laboratory experiments.
2 ELASTIC WAVE VELOCITIES DURING EVAPORATIVE DRYING

2.1 Introduction

Laboratory experiments measuring ultrasonic elastic wave velocities have shown there to be considerable variation in the form of dependence of elastic wave velocities on the level of water saturation. This variation in functional form can be attributed, in part, to differences in pore space microgeometry, saturation method, and their resulting control on the pore scale distribution of fluids. One commonly used method of varying water saturation levels in rocks during laboratory experiments is evaporative drying. Despite its widespread use, there has been little discussion in the geophysical literature about the nature of fluid distribution that is produced in rocks during the drying process. Of particular interest in this chapter is the specific nature of fluid distribution that is produced within rocks during evaporative drying and its resulting effect on the form of the relationship between elastic wave velocities and water saturation level.

In fields such as chemical engineering and soil science evaporative drying has been the subject of a considerable amount of study (see, for example, Scherer, 1990; Whitaker, 1977; Keey, 1972 for overviews of the drying process). It has been found that the way in which the drying rate of a sample of material varies with saturation level reflects the dominant mass transport processes during the drying process. In the early stages of drying a capillary porous material, the rate is constant as the liquid is in a funicular state and capillary transport is dominant. During the later stages of drying there is a decrease in rate as the connectivity of the liquid phase is reduced and there is a transition to the liquid being held in a pendular state (Ceagske and Hougen, 1937). It has also been observed that sample scale saturation heterogeneities exist during the later stages of drying. Cadoret et al. (1992a) suggested that such heterogeneities would affect the accurate measurement of velocities.
In this chapter, the application of drying rates to the interpretation of velocity data collected during evaporative drying is investigated. In particular it is proposed that, for the rocks used in this study, velocity changes during the early stages of drying are associated with the drainage of pore bodies while towards the later stages of drying they are associated with the removal of pendular water. Experiments were conducted on three types of rock, each possessing distinctly different types of pore space microgeometries. Based on the interpretation of drying rate curves, and a simplified concept of the pore spaces derived from thin section analysis, fluid distribution scenarios are proposed. A numerical modeling routine developed by Endres and Knight (1989) is used to predict the form of the velocity saturation curves that would result from such distributions, and these are compared with experimental results. Finally, velocity data collected as water saturation was increased through adsorption is used to explore the extent to which sample scale heterogeneities affect the velocities measured in the lower ranges of saturation. A better understanding of the way in which the drying process and pore space microgeometries interact is of significant importance when interpreting the form of velocity-saturation relationships produced during the drying process.

2.2 The Effects of Saturation on Velocities

Elastic wave velocities in a homogeneous, isotropic medium can be expressed in terms of the material properties of bulk modulus ($k$), shear modulus ($\mu$) and density ($\rho$) as follows:

\[ V_p = \sqrt{\frac{k + \frac{4}{3} \mu}{\rho}} \]  
\[ (2.1) \]

\[ V_s = \sqrt{\frac{\mu}{\rho}} \]  
\[ (2.2) \]

where $V_p$ is the compressional wave velocity and $V_s$ is the shear wave velocity. The bulk
modulus is a measure of the incompressibility of a solid and the shear modulus is a measure of its shear rigidity.

The influence of varying the relative saturation levels of air and water on velocities can be attributed to two primary factors. The first is a reduction in moduli that results from the addition of a small amount of water to a dry rock (Born and Owen, 1935; Wyllie et al., 1962; Pandit and King, 1979; Clarke et al., 1980; Murphy, 1982). Murphy et al. (1984) postulated that the mechanism responsible for these effects is a reduction in frame moduli that occurs when the adsorption of a fluid lowers the surface free energy of the solid phase. This occurs because the contact adhesion between grains is proportional to the interfacial free energy of the solid surface (Israelachvili, 1985). In sandstones, Knight and Dvorkin (1992) related this to the presence of three to four monolayers of adsorbed water.

Velocities are also influenced by the bulk properties of pore fluids, in particular, by the fluid densities, viscosities and compressibilities. The presence of a dense fluid in the pore space will increase the overall composite density and, as can be seen in equations 2.1 and 2.2, this will have the effect of decreasing both Vp and Vs. A more complex and generally more substantial way in which the bulk properties of pore fluids can affect velocities is through changes produced in the bulk and shear moduli of the composite system. The extent to which the bulk properties of fluids can affect the moduli depends upon the nature of the porosity and the frequency of the elastic waves.

Gassmann (1951) and low frequency Biot (1956) theory provides an expression for the bulk modulus of a fully saturated rock in terms of the porosity and the bulk moduli of the dry rock, the matrix material and the pore fluid. This formulation assumes that there is a homogeneous and isotropic pore space. It is also implicit that frequencies are low enough so that inertial effects can be neglected and that pore fluid pressures induced by the passage of an elastic waves will be equilibrated on a scale that is significantly larger than the average pore size. Dominico (1976) extended this work to account for partial saturations by assuming
the bulk modulus of the composite pore fluid could be approximated by a simple mixing law. Biot-Gassmann-Dominico (BGD) theory predicts that there will be a gradual decrease in both P and S wave velocities with increasing saturation due to density effects throughout most of the lower range of saturation. At very high saturation levels, the increase in the rigidity of the pore fluid mixture results in an increase in P wave velocity and not shear wave velocity. Murphy (1982) noted that the measured dependence of velocity on saturation could be explained reasonably well by BGD theory at frequencies less than approximately 1 kHz. Cadoret et al. (1993), however, found that there was departure from the form predicted by BGD theory during drying; this was attributed a lack of homogeneity in the saturation distribution at a pore scale, which violates a fundamental assumption of BGD theory.

Due to heterogeneities in pore shape, orientation and saturation, the passage of an elastic wave can induce pore scale pressure gradients and flow. This is referred to as local flow (O'Connell and Budiansky, 1974, 1977; Mavko and Nur, 1979) which is not explicitly taken into account in BGD theory. At low enough frequencies local flow is permitted to occur and such pore scale pressure gradients can be dissipated. At high enough frequencies, the time scale of the wave can be sufficiently small that viscous and inertial effects within the fluid will become significant enough to inhibit local fluid flow (Mavko and Jizba, 1991). The pore fluid will then become 'unrelaxed' and will in turn exert a pressure on the pore wall that will act to stiffen the frame moduli in a way that is not accounted for in BGD theory. As a consequence, ultrasonic velocities tend to be higher (Winkler, 1985) and can be sensitive to the saturation state of individual pores (Endres and Knight, 1989; Knight and Nolen-Hoeksema, 1990).

The stiffening effect of pore fluids in individual pores is dependent upon pore geometry. In equidimensional pores the induced pressure will be relatively low since the
compressional deformation due to the elastic wave will tend to be compensated for, to some extent, by extensional deformation in an orthogonal direction. In compliant regions, such as cracks, which are not equidimensional, the compressionally induced deformation in one direction will tend to not be balanced by extension in orthogonal direction (Mavko and Jizba, 1991). Consequently, moduli are more sensitive to the saturation state of thin compliant porosity than of equidimensional pores (Walsh, 1965).

The effects of pore geometry can be illustrated using a model developed by Kuster and Toksoz (1974) and expanded upon by Toksoz et al. (1976). It was proposed that the mechanical behavior of a porous rock could be modeled by considering that the pore space is composed of oblate spheriodal inclusions in a homogeneous background mineral matrix. Different types of pores are accounted for by varying the aspect ratio of the inclusions, where the aspect ratio, $\alpha$, is defined as the ratio of the lengths of the semi-minor, $a$, to semi-major, $b$, axis lengths e.g.,

$$\alpha = \frac{a}{b} \quad (2.3).$$

Crack-like pores or grain contacts are therefore described by very low aspect ratio inclusions whereas rounded pores will be represented by higher aspect ratio inclusions. For a spherical pore $\alpha = 1$.

Consider a quartz background medium containing a concentration of inclusions of a specific aspect ratio. Using the numerical approach given by Kuster and Toksoz (1974), the differences in bulk and shear moduli between when the pores were air filled, or dry, and when they are water filled, or saturated, were calculated as a function of the aspect ratio of the inclusions.
The results, shown in Figures 2.1a and b, are expressed in terms of the relative increases in moduli as defined by the following equations:

\[ \Delta K = \frac{K_{\text{sat}} - K_{\text{dry}}}{K_{\text{dry}}} \]  

\[ \Delta \mu = \frac{\mu_{\text{sat}} - \mu_{\text{dry}}}{\mu_{\text{dry}}} \]  

(2.4) 

(2.5)

where \( K_{\text{dry}} \) and \( \mu_{\text{dry}} \) are the moduli of the medium with air filled pores and \( K_{\text{sat}} \) and \( \mu_{\text{sat}} \) are the moduli of the medium when the pores are filled with water. From these figures it can be seen that the moduli of a medium containing low aspect ratio pores is very sensitive to the compressibility of the pore fluids. The moduli are also affected by the relative concentration levels of different aspect ratio pores.

It is also interesting to note that the relative increase in shear modulus is always lower than that of the bulk modulus. This is made more evident in Figure 2.1c, which shows the ratio of relative increases in bulk and shear moduli plotted as a function of aspect ratio. From this plot it can be seen that the shear modulus is not affected at all by the saturation state of spherical pores. As the aspect ratio is decreased, the ratio approaches a constant value, with the relative increase in shear modulus being about 20 percent that of the bulk modulus.

Endres and Knight (1989) adapted this model for partially saturated rocks by considering that the rigidity contribution of the pore fluids could be described with a simple mixing law. Using this model the effects of water saturation level, \( S_w \), on the moduli of a porous medium is shown in Figure 2.2. \( S_w \) is defined as the volume fraction of the pore space that is occupied by water. The gas is assumed to be distributed evenly at a pore scale and the aspect ratio is assumed to be small enough that both the bulk and shear moduli are
Figure 2.1a,b. Relative increases in bulk and shear modulus from unsaturated to saturated states as a function of aspect ratio. a) Full range of aspect ratios. b) High end of aspect ratios.
Figure 2.1c. Ratio of relative increases in bulk and shear moduli from unsaturated to saturated states as a function of aspect ratio.
Figure 2.2. Bulk and shear moduli as a function of water saturation when the water is distributed homogeneously at a pore scale.
affected. It can be seen from this figure that the introduction of even a small amount of compressible gas into the pore space will reduce the moduli sharply. The subsequent drainage of the remainder of the water has little effect on the moduli.

By approximating the pore space as being composed of a range of different aspect ratio pores, and controlling the saturation state of pores with specific aspect ratios, the model of Endres and Knight (1989) permits a wide range of velocity versus saturation relationships to be explored. This model makes two significant approximations. The first is that rock pores, which are often very geometrically complex, can be described by idealized ellipsoidal inclusions. As a first order approximation however, much of the mechanical behavior of a rock can be investigated with this type of model (Endres and Knight, 1989). It is also assumed that it is the saturation state of individual pores that will dominate the elastic behavior of the rock and that communication of fluids between pores during the passage of elastic waves can be neglected. At ultrasonic frequencies, where the time scale of the elastic wave is short enough for viscous and inertial effects to become significant, this was found to produce reasonable results in fully saturated rocks (Toksoz et al., 1976). It was also used to successfully model the velocity-saturation relationship in a partially saturated rock by Endres and Knight (1991). The numerical modeling routine of Endres and Knight (1989) will be used in this study to explore the effects of different fluid distributions on elastic wave velocities. In using this model it is recognized that the effects of fluid communication and oversimplification of the pore space microgeometry may contribute to inaccuracies in the results. However, the main purpose of using this model in this study was to examine how varying the saturation state of pores with different compliance levels can affect the form of the velocity-saturation relationship. Of particular interest are the effects of differences in the saturation states of stiff equidimensional pore bodies and very compliant crack-like porosity. It is therefore felt that the usefulness of the model in this respect outweighs any of the aforementioned limitations.
Mavko and Nolen-Hoeksema (1994) developed a model that is conceptually similar to that of Endres and Knight (1989), but avoids the use of idealized pore geometries. In this model the filling of compliant, or 'soft', porosity with water is likened to the closure of cracks under confining pressure. In this portion of the porosity, pore fluid is assumed to be unrelaxed and produces similar relative increases in bulk and shear moduli as predicted by the Kuster and Toksoz (1974) model. The remainder of the porosity is assumed to obey BGD theory.

As a final point, it should be noted that theories developed to account for variations in velocities as a function of saturation generally assume that an effective medium is being considered. When the wavelength of the propagating wave is small with respect to the scale of heterogeneities in a medium, the medium appears to be homogeneous to the wave and it is can be treated as an effective medium. If the inhomogeneities approach the scale of the wavelength then wave path dispersion may result and effective medium theory will become invalid.

2.3 Capillary Theory

In the previous section, it was made evident that velocities in partially saturated rocks are sensitive to the distribution of fluids in the pore space. The relative distributions of air and water in a partially saturated rock are controlled by capillary forces. The basic principals of capillary theory, which are discussed in detail in numerous texts (e.g., Dullien, 1979), are reviewed in the following section.

When two immiscible phases are in contact, interfacial tension will exist at their boundary. It is this interfacial tension that gives rise to capillary phenomena. In a system containing a solid phase, a liquid phase, and a gas phase there are three possible types of
interface, each with a different interfacial tension. This is illustrated in Figure 2.3a which depicts a liquid drop placed on a solid surface in the presence of another fluid. At a point of contact between the three phases, the three different interfacial tensions must balance for mechanical equilibrium to exist. The relationship between the forces, shown in Figure 2.3b, satisfies Young's equation and can written in the form

$$\sigma_{LG} \cdot \cos \theta = \sigma_{SG} - \sigma_{SL} \quad (2.6)$$

where $\theta$ is the contact angle between the liquid/gas and solid/liquid interfaces, $\sigma_{LG}$ is the liquid/gas interfacial tension, $\sigma_{SG}$ is the solid/gas interfacial tension and $\sigma_{SL}$ is the solid/liquid interfacial tension.

The contact angle is a measure of the affinity of one fluid to spread on a solid surface in the presence of another fluid. It is frequently used to define the wettability of a solid. If a fluid preferentially spreads on a solid in the presence of another fluid it is referred to as the wetting fluid. This will tend to happen if the contact angle is less than $90^\circ$. The concept of wettability and its influence on fluid distributions will be discussed in more detail in Chapter Three.

In a multiphase saturated porous medium the relative distributions of the different fluids within the pore space will be controlled by the geometry of the pore space, the wettability of the solid and the saturation history. For all but the simplest of geometries, it is not possible to obtain an analytical solution for the shapes of the interfaces between pore fluids in a porous medium. Two geometries that are well understood and illustrative to examine are the capillary tube and two adjacent spheres.
Figure 2.3  a) The contact angle of a droplet of liquid on a solid surface.
b) Surface tension force diagram.
The shape of the interface between two immiscible fluids present in a capillary tube is controlled by the radius of the tube, \( r \), the contact angle and the interfacial tension (see Figure 2.4a). The tension and curvature in the interface gives rise to a pressure difference across the boundary, the capillary pressure, \( P_C \), which is described by

\[
P_C = P_1 - P_2 = \frac{2 \sigma_{LG} \cos \theta}{r}
\]

where \( P_1 \) and \( P_2 \) are the pressures in the non-wetting and wetting fluids, respectively.

Capillary pressure is often referred to as a 'suction' potential since fluids will tend to flow from regions of low capillary pressure to regions of high capillary pressure. A pore with a smaller radius will give rise to a meniscus with a smaller radius and will therefore have a larger capillary pressure within it. In general, this will cause wetting fluids to preferentially occupy smaller pores.

A second geometry, which is of interest in studying partially saturated granular rocks, is that of a pendular ring of wetting fluid held at the region of contact between two spheres, shown in Figure 2.4b. The capillary pressure across the air/gas interface can be described by

\[
P_C = 2 \sigma_{LG} \cos \theta \left( \frac{1}{r_1} + \frac{1}{r_2} \right)
\]

where \( r_1 \) and \( r_2 \) are the two principle radii of curvature that describe the shape of the meniscus. As \( r_1 \) and \( r_2 \) decrease in magnitude, reflecting a lower saturation level, the capillary pressure will increase and the liquid will become more tightly held.

In a more realistic porous medium containing two fluid phases, capillary pressure is measured at a sample scale as a function of wetting phase saturation. The resulting pressure versus saturation plot is referred to as a capillary pressure curve. Capillary pressure curves may be either imbibition or drainage curves: drainage occurs when a wetting phase is
Figure 2.4 (a) Liquid held in a capillary tube. (b) Pendular ring of liquid held between two spheres.
displaced by a non-wetting phase; imbibition when a non-wetting phase is displaced by a wetting phase. A capillary pressure drainage curve is acquired by beginning with a sample that is fully saturated with a wetting fluid and reducing its saturation level by displacing the wetting fluid with a non-wetting fluid that is under pressure.

A typical capillary pressure curve will have the form shown in Figure 2.5. Initially, only a small amount of pressure is required to reduce the wetting-phase saturation level substantially. In this part of the curve, the wetting phase will tend to be displaced from larger pores. As saturation is lowered, higher pressure levels are required in the nonwetting phase for drainage to proceed and successively smaller pores will drain. Eventually, the pressure curve becomes vertical, and the wetting fluid can no longer be displaced through increases in hydraulic pressure. This occurs when the wetting phase loses its hydraulic connectivity. At this stage, the wetting fluid will tend to be held in pendular rings, crack-like pores, surface roughness and as an adsorbed surface layer. This is referred to as the irreducible water saturation level.

2.4 The Drying Process

In this study, water saturation levels are reduced through evaporative drying, a commonly used method of varying saturation level in rocks during laboratory experiments. Drying is a specific form of drainage by which liquid water is replaced by air in a porous medium through evaporation. The fluid distributions produced by this process are not necessarily the same as those produced by those in immiscible displacement. The two primary mechanisms responsible for mass transport in a drying porous medium are capillary transport in the liquid phase and diffusion in the vapor phase. Capillary transport results from a hydraulic pressure gradient within the sample. Diffusion, a much slower process, is driven primarily by a gradient in the concentration of water vapor.
Figure 2.5 Capillary pressure curve.
The interplay between these two mechanisms during the drying process can be illustrated using a simple model consisting of two adjacent pores connected by a pathway (Oliver and Clarke, 1971). In this model, the 'pores' are cylindrical with different radii (r_S and r_L) and fluid may flow freely between them through the pathway. It is assumed that both pores are filled with a perfectly wetting liquid (θ = 0°).

In the initial stages of drying, liquid is removed from the tubes through evaporation at the air/liquid interface and menisci, of radii r_{M1} and r_{M2}, will form (Figure 2.6a). As evaporation continues, the radii of the menisci will decrease until r_{M1} = r_L, the minimum possible radius the large pore can accommodate. When this occurs the entry pressure of the large pore will have been reached and further evaporation will cause the meniscus to recede into the larger pore (Figure 2.6b).

In the small pore the meniscus will remain at the surface and r_{M2} will continue to become smaller, thereby reducing the capillary pressure in the smaller pore below the pressure in the large pore. This will in turn result in fluid flow from the larger pore to the small pore (Figure 2.6c). Mass is therefore removed from the system by two mechanisms: firstly, the evaporation of liquid from the larger pore and its subsequent diffusion in vapor phase to the surface and, secondly, capillary transport of fluid from the large pore into the small pore and its evaporation at the surface of the sample. Since diffusion is a slow process relative to capillary transport, the dominant mass transport mechanism during this stage is capillary transport of fluid to the surface of the small pore. Eventually, r_{M2} will equal r_S in the small pore and the meniscus will recede into the small pore (Figure 2.6d). After this point, the dominant mechanism for removal of mass from the system, or the rate limiting step, will be diffusion of vapor.

In a more realistic porous medium, consisting of a large number of interconnected pores with a wide distribution of pore sizes, the drying process is considerably more complex. A commonly used method of gaining insight into the transport processes occurring
Figure 2.6 A simple drying model (a) Initial stage of drying (b) Large pore meniscus reaches minimum radius and begins to recede (c) Small pore reaches minimum radius, begins to recede (d) Both pores have receded
in such a medium during drying is to examine drying rate versus saturation level curve. A drying rate curve for a non-hygroscopic capillary porous material is shown in Figure 2.7. A non-hygroscopic capillary porous media is defined as having a rigid structure and being comprised primarily of pores greater than 1 μm in diameter (Van Brakel, 1980). The samples used in this study fall into this category.

As evaporation begins from the surface of such a medium, menisci will form in the openings of surface pores and hydrostatic tension will build up within the pores. When the entry pressure for a surface pore is reached, the meniscus will enter the pore and thereby drain it. This will tend to happen first in the larger surface pore openings due to their lower entry pressures. In the initial stages of drying a decrease in drying rate with saturation is sometimes observed. This has been attributed to a reduction in temperature of the samples surface that occurs as heat is removed from the surface water to provide the latent heat energy required for liquid water to make its transition to water vapor (Treybal, 1980).

The initial drop in rate is followed by a period of constant, or relatively constant, drying rate. During the constant rate period (CRP) capillary transport of liquid to the surface is the dominant mass transport mechanism while diffusion of vapor from within the sample to its surface is generally assumed to be negligible. At this stage the liquid within the rock is hydraulically connected and both fully saturated pores and partially drained pores will be present. This is sometimes referred to as the funicular state, shown in Figure 2.8a. Using two-dimensional micromodeling to investigate the drying process, Shaw (1987) found that fluid in the partially drained pores existed at grain contacts and in crevices. It was also found that fluid flow occurred through partially drained regions, indicating that partially drained pores remain significantly above a pendular state after their initial drainage. Saturation is reduced during the CRP as the menisci advance further into the sample by draining pores. Liquid from the pores that the menisci have passed through is transported through capillary
Figure 2.7 A typical drying rate curve. A: Initial decrease in rate; B: Constant rate period; C: Falling rate period.
During the constant rate period the sample is in a funicular state. During the falling rate period sample scale heterogeneities may exist such that the outer part of the sample is in a pendular state and the inner part is in a funicular state.
mechanisms to the sample's surface where it evaporates. Air enters the sample to replace the liquid through drained pores at the external surface. During the constant rate period the rate controlling step is the diffusion of vapor from the sample's surface into the surrounding environment.

As drying progresses, the connectivity of the liquid phase within the sample will be reduced to the point that capillary flow of liquid to the surface can no longer keep up to the rate at which water is evaporating from the surface. The wetted portion of the sample's surface is rapidly reduced and the drying rate enters the falling rate period. The beginning of this period has been associated with the onset of the irreducible water saturation level within a drying sample (e.g., Whitaker, 1985). The saturation level at which this occurs is referred to as the critical moisture content (CMC). During the early stages of the falling rate period, sometimes referred to as the first falling rate period, there is a transition within the sample from capillary dominated transport in the liquid phase to diffusive transport of water vapor. When the surface of the sample becomes completely dry the diffusion of vapor to the surface becomes the rate limiting step. This stage of drying is sometimes referred to as the receding front period, though it is not always possible to distinguish on a drying rate curve. At this point, sample scale saturation heterogeneities may exist, as shown in Figure 2.8b. Towards the outside of the sample the liquid will be hydraulically disconnected, or in a pendular state. In this region of the sample water will be in the form of adsorbed layers, pendular rings held at grain contacts, in cracks, and as adsorbed surface water (Ceagkskle and Hougen, 1937). Towards the interior of the sample the liquid phase will be more connected (i.e. above the irreducible water saturation level) and a combination of capillary transport and diffusion of vapor is possible.
2.5 Sample Descriptions and Experimental Procedures

The primary objective of this chapter is to gain insight into how the drying process and pore space microgeometries interact to produce different forms of dependence of velocities upon saturation. Pore geometry is a primary factor in influencing both the sensitivity of velocities to saturation level and also the distribution of fluids during drying. The limestone, dolomite and Berea sandstone samples were therefore selected to provide a range of different pore geometries. Also, by using two different Berea samples, the effect of varying porosity and permeability can be explored in samples with similar lithologies.

Qualitative analyses of the samples' pore space microgeometries were based on thin section analysis (Wilks and Tercier, 1993). Thin section analysis is conducted by impregnating a sample with epoxy, slicing it into a section thin enough to be optically transparent, and mounting the slice on a slide for photographing. A summary of sample permeabilities, dimensions and porosities, as measured by helium porosimetry, is shown in Table 2.1. All samples are cylindrical in shape with the ends surface ground to be parallel to within a thousandth of an inch.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Porosity</th>
<th>Permeability</th>
<th>Length</th>
<th>Diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Berea 100</td>
<td>15.0 %</td>
<td>100 mD (approx)</td>
<td>38.1 mm</td>
<td>24.7 mm</td>
</tr>
<tr>
<td>Berea 300</td>
<td>22.9 %</td>
<td>300 mD (approx)</td>
<td>38.1 mm</td>
<td>24.7 mm</td>
</tr>
<tr>
<td>Limestone</td>
<td>13.9 %</td>
<td>2.25 mD (approx)</td>
<td>22.8 mm</td>
<td>25.2 mm</td>
</tr>
<tr>
<td>Baker</td>
<td>23.4 %</td>
<td>-----</td>
<td>33.5 mm</td>
<td>24.8 mm</td>
</tr>
<tr>
<td>Dolomite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2.1 Summary of Sample Characteristics.
Figure 2.9. Limestone. Horizontal dimension of photograph is 2.1 mm. Blue areas indicate pore space.

Figure 2.10. Baker Dolomite. Horizontal dimension of photograph is 2.1 mm. Blue areas indicate pore space.
Figure 2.11. Berea 100. Horizontal dimension of photograph is 1.34 mm. Blue areas indicate pore space.

Figure 2.12. Berea 300. Horizontal dimension of photograph is 2.1 mm. Blue areas indicate pore space.
A number of methods can be used to measure the velocity of an elastic wave in a porous medium. The simplest and most direct method of determining the velocity of an elastic wave in a material is to measure the travel time of the wave through a sample of known length. This is the basis of pulse transmission techniques. The most common type of pulse transmission system is 'through transmission', in which one transducer is used as a wave source and a second is used as a receiver to detect waves that have traveled through the sample. A through transmission system was constructed and used to collect the data that will be presented in this thesis.

A block diagram of the apparatus is shown in Figure 2.13. The transducers and sample are placed in an aluminum holder, which is used to maintain alignment and to apply confining pressure to enhance the coupling. The axial pressure level, kept at 125 PSI, is monitored using an Omega-350 load cell for repeatability. Mechanical coupling was found to be enhanced significantly by interposing a layer of Saran wrap at the sample/transducer interfaces. Improved coupling increases the amplitude of the received signal and thereby sharpens the first wave arrival. Amplitudes of the first arrival were approximately 50 to 100 percent larger than without coupling. The transducers, constructed by Core Laboratories, are each capable of transmitting or receiving either compressional or shear waves. Compressional waves centered at 500 kHz are generated by pulsing a large axially oriented crystal. Similarly, 400 kHz shear waves are generated by pulsing an arrangement of eight azimuthally oriented crystals. The receiver transducer's crystals generate an electrical signal in response to elastic waves. These signals are monitored using a Tektronix 2221A digital storage oscilloscope. To reduce the effects of random background noise, the oscilloscope's averaging function is used.

Measurements are made by using a 10 volt pulse generator to simultaneously trigger the oscilloscope trace and the high voltage pulse generator. The resulting high voltage pulse stimulates the source transducer crystal(s) which in turn emit(s) an elastic wave that travels
Figure 2.13 Diagram of velocity measuring apparatus.
through the core sample into the receiver transducer. The receiver transducer signal is monitored on an oscilloscope and an arrival time is selected using 'first break' methods. The travel times through the transducer heads are then subtracted to determine the travel time through the core; velocities are calculated based on these measured travel times.

In conducting experiments measuring velocities as a function of saturation during evaporative drying, it is important to ensure that the samples are as close to being completely saturated as is possible at the beginning of the experiments. Samples were saturated by evacuating them in a pressure chamber, introducing degassed, distilled water into the sample chamber and pressurizing the chamber to 2000 PSI overnight.

Velocity measurements began immediately after the samples were removed from the chamber and Sw was reduced through evaporative drying at ambient laboratory conditions. At low levels of saturation (Sw < 0.05), Sw was reduced by placing the samples in a container that was partially filled with calcium sulphate, a commonly used laboratory desiccant. The 'dry' measurements were made on samples that had been heated to 60° C for one day and cooled in a desiccator.

Drying rates curves were acquired by placing a saturated sample on a scale at ambient laboratory conditions. The scale was interfaced with a computer and weight measurements were made at regular time intervals until the sample weight no longer decreased.

Water was adsorbed to the dry samples by placing them on a stand in a chamber that was partially filled with distilled water. The samples were thereby exposed to air with relative humidity that was close to 100 percent (Knight and Nur, 1987). In all experiments Sw was determined by weighing the sample at the time of measurement and using a void space volume determined from helium porisimetry.
2.6 Results and Discussion

A range of different velocity-saturation relationships are represented by the results for the four samples. In the first section, the drying rates are discussed and fluid distribution scenarios are proposed for the drying process. These scenarios are used in a numerical modeling routine to predict the forms of the velocity-saturation relationship which are compared with experimental results. In the final section, velocity data collected during the later stages of drying is compared to that collected during adsorption to investigate the impact of sample scale saturation heterogeneities on the velocity-saturation relationship.

2.6.1 Drying Data

The drying rate data for the samples, shown in Figures 2.14 to 2.17, are all qualitatively similar in form. An initial decrease in rate is evident and this is followed by a period of constant, or relatively constant, drying rate. Between Sw = 0.30 to 0.20 the rates begin to enter the falling rate period.

These data resemble drying rate curves that are observed for non-hygroscopic capillary porous materials (Van Brakel, 1980). The initial rate decrease at high saturations is attributed to a reduction in surface temperature (Treybal, 1980). At high saturation levels (Sw > 0.95), Cadoret et al. (1992a) noted that fluid distributions were influenced by sample geometry and that the velocity saturation relationship may therefore be distorted by wave path dispersion in this region of Sw.

During the constant rate period a capillary porous material will be in a funicular state. That is, the liquid phase is continuous and fully saturated pores will tend to be present along with partially saturated pores. In the rock samples used in this study the most relevant and concrete interpretation that can be made is that during the constant rate period continuity of
Figure 2.14. Drying rate curve for limestone sample.
Figure 2.15. Drying rate curve for dolomite sample.
Figure 2.16. Drying rate curve for Berea 100 sample.
Figure 2.17. Drying rate curve for Berea 300 sample.
the liquid phase will tend to ensure that, since water in the rock will be above a pendular state, grain contacts and cracks will tend to remain saturated. Any velocity variations can therefore be attributed to the removal of water from pore bodies. The work of Shaw (1987) indicates that saturation levels in partially drained pores are high enough to maintain fluid flow for a considerable time after the initial partial drainage occurs. Cadoret (1993) noted that partial saturation, homogeneous at a millimetric scale, was generally evident in rocks during drying by the middle ranges of saturation. As a simple model, it is therefore proposed that during the constant rate period there will be a range of saturation over which all pores will become partially drained but maintain a high degree of hydraulic connectivity. This is followed by a period over which the saturation level in the partially drained pore bodies is reduced further but the liquid remains hydraulically connected. Grain contacts and cracks are assumed to remain saturated throughout the entire constant rate period.

Another point that warrants discussion is the scale of saturation heterogeneities that may exist during this period. Cadoret et al. (1992a,b) used X-ray tomography to image the saturation distribution within limestone samples during the drying process. Between approximately \( Sw = 0.15-0.95 \), it was found that drying produced a relatively homogeneous saturation distribution, provided the scale of heterogeneity of the porous network was small with respect to the wavelength. This form of drainage appears to be present in the samples above \( Sw = 0.20 \) to 0.30. The pore scale in the Berea and dolomite samples appears to be much smaller than the wavelength (~4-5mm). In the limestone sample, millimetric scale pores are present, which may act to distort the measured velocity-saturation relationship.

During the falling rate period hydraulic connectivity is lost as the fluids make a transition to the pendular state. In a granular material, the pendular state corresponds to fluids being located at grain boundaries, cracks, in surface roughness and as adsorbed water. It is
therefore interpreted that velocity changes that are associated with the removal of water from these areas will occur below the CMC. Guillot et al. (1989) and Cadoret et al. (1992a,b) both observed that sample scale saturation heterogeneities begin to develop at low saturation levels in rocks ($Sw < 0.10-0.15$). Due to the existence of such sample scale saturation heterogeneities, it should be noted that the critical moisture content only provides an upper saturation bound for when the connectivity of the liquid phase begins to be significantly reduced. Cadoret et al. (1992a) suggested that such large scale saturation heterogeneities would distort the measured velocities through wave path dispersion. The effect of these heterogeneities in the sandstone samples was assessed using velocity data that was collected during adsorption, which will be discussed in the final section of this chapter.

Based on these interpretations of the drying rate data and simplified pore space models derived from thin section analysis, fluid distribution scenarios will now be proposed for the drying process. Numerical modeling is then used to explore the form of the velocity-saturation relationships that will result from these distributions. The main interpretation that is extracted from the drying data is that, in the rocks being considered, crack-like (compliant) porosity will tend to remain saturated until below the CMC; above the CMC, only the pore bodies, which will be stiffer, will drain of water. Since the CMC represents the onset of a reduction of connectivity of the liquid phase, it is used only to establish an upper $Sw$ bound for when the crack-like porosity will begin to drain. It should also be noted that since only the general characteristics of the pore space were considered in making up the pore space models, it is the general form of the relationships that are considered to be relevant. For the purposes of modeling the qualitative form of the velocity-saturation relationships, sample scale saturation heterogeneities will not be considered.

The pore space model for the limestone sample is composed of high aspect ratio inclusions representing pore bodies and very low aspect ratio pores representing fractures.
The proposed model for fluid distributions during drying, shown in Figure 2.18a, is divided into three main stages. In the first stage, which occurs during the early part of the constant rate period, all pore bodies will be sequentially and partially drained. A substantial amount of water is left in the partially drained pores, which is intended to indicate that the saturation level is high enough for hydraulic connectivity to be maintained. In the second stage, which lasts until just below the CMC, the saturation level in the partially saturated pore bodies is reduced. This represents the drainage of the connected water in the pore bodies until only a small amount of disconnected water remains, present as water trapped in surface roughness and as an adsorbed layer. In the final stage, lasting from just below the CMC until Sw = 0, the hydraulically disconnected surface water in pore bodies and water contained in the cracks will drain. The form of the relationship between the moduli and water saturation level that is produced by such a model is shown in Figure 2.18b. In the first stage, which lasts from Sw = 1 until the middle ranges of saturation, a gradual decrease in the bulk modulus occurs as the larger pores are drained to a partial saturation state. The shear modulus is essentially flat in this region, since it is relatively insensitive to the saturation state of high aspect ratio pores. In the second stage, both the bulk and shear moduli are constant as the saturation level of partially saturated pore bodies is reduced. The moduli are flat during this period because the moduli of a water filled pore is reduced substantially with the addition of a small amount of compressible air and the subsequent addition of more air has little effect. This principle was illustrated in Figure 2.2. In the final stage both the bulk and shear moduli exhibit sharp drops as water is removed from the cracks and surface roughness of the pore bodies. These changes in moduli are due entirely to the removal of water from the compressible cracks. In using this model it is important to note again that it is assumed that frequencies are high enough for the fluids contained in the crack-like porosity to be unrelaxed and not communicate through fluid flow with the partially drained pore bodies.
Figure 2.18a Pore saturation scenario during drainage of limestone. A to D: Sequential drainage of large and intermediate aspect ratio pores; D to E: Drainage of connected water in partially drained pores; E to F: Drainage of cracks and hydraulically disconnected surface water. Black=water, White=air.
Figure 2.18b. Moduli model for limestone sample. Upper line is bulk modulus, lower is shear modulus.
The pore space model for the dolomite sample is composed of intermediate and high aspect ratio pores. For the purposes of modeling the effects of saturation on moduli, the fluid distribution scenario during drying, shown in Figure 2.19a, can be divided into two stages. In the first stage, which corresponds to the early stages of the constant rate period, all pores will be sequentially and partially drained. A significant amount of water will be left in the drained pores, indicating that the saturation level is high enough to maintain hydraulic connectivity. In the second stage the saturation level in the partially drained pores will be then be reduced towards zero. Since no cracks are present, pendular water will consist primarily of water held in surface roughness and as an adsorbed layer, which will have no effect on the moduli. The form of the moduli-saturation relationship that is produced by this model is shown in Figure 2.19b. In the first stage, which lasts from $Sw = 1$ to the middle saturation ranges, the bulk modulus decreases steadily and the shear modulus shows a modest decrease. These decreases are due to the introduction of air into all the pore bodies. In the second stage, the subsequent and complete drainage of pore bodies produces no change in the bulk and shear moduli.

Berea sandstone porosity is represented by a range of aspect ratios. Pore bodies and throats are represented by high and intermediate aspect ratios, as in the case of Baker dolomite. The crack-like porosity evident at grain contacts is represented by very low aspect ratio pores. As with the limestones, the fluid distribution scenario during drying, shown in Figure 2.20a, is divided into three stages. In the first stage, which corresponds to the early stages of the constant rate period, pore bodies, represented by high and intermediate aspect ratio pores, sequentially and partially drain. This is then followed by a period, lasting until below the CMC, during which the saturation level of these pores is reduced to a low level. This low level is intended to represent the point at which liquid within the pores becomes disconnected and is present as water in the surface roughness and as an adsorbed layer. Finally, during the third stage, the remainder of the water contained in the pore bodies as well
Figure 2.19a  Pore saturation scenario during drainage of dolomite. A to D: Sequential drainage of large and intermediate aspect ratio pores; D to E: Drainage of connected water in partially drained pores; E to F: Drainage of disconnected surface water. Black=water, White=air.
Figure 2.19b. Moduli model for dolomite sample. Upper line is bulk modulus, lower is shear modulus.
Figure 2.20a Pore saturation scenario during drainage. A to D: Sequential drainage of large and intermediate aspect ratio pores; D to E: Drainage of connected water in partially drained pores; E to F: drainage of cracks and disconnected surface water. Black=water, White= air.
as water contained in the lowest aspect ratio pores, which represent the grain contact porosity, is drained. Figure 2.20b shows the form of the moduli-saturation relationship that is produced by this model. In the first stage the bulk modulus decreases steadily and the shear modulus decreases gradually as air is introduced into the pore bodies. The moduli then level off until below the CMC as the saturation level in the partially drained pore bodies is reduced further. Finally, in the last stages of drying, both the bulk and shear moduli decrease sharply due to the removal of water from the grain contact regions.

2.6.2 Comparison of Models With Experimental Data

The fluid distribution scenarios suggested by the drying rate data and thin section analyses represent a wide range in the form of dependence of velocities upon saturation level. These models will now be compared to the experimental results.

For the limestone sample, Vp and Vs are shown as a function of Sw in Figure 2.21; the bulk and shear moduli are shown in Figure 2.22. As Sw is reduced from the point of maximum saturation there is a gradual decrease in bulk modulus until Sw = 0.15. When Sw is decreased from this point towards zero, the bulk modulus decreases rapidly. The shear modulus remains relatively constant as Sw decreases from its maximum to approximately 0.15. After this point it drops sharply.

These data are qualitatively similar in form to the proposed relationships in Figure 2.18b. In the upper ranges of saturation it was interpreted that the larger pore bodies were draining, which produces only a small effect on the bulk modulus. The decrease in bulk and shear modulus that was associated with the drainage of cracks began at Sw = 0.15, significantly below the CMC (Sw = 0.3) indicated that hydraulic connectivity was becoming significantly reduced. That is, the data indicate that there is a distinct and pronounced region of decrease in moduli at lower saturations that is associated with the removal of water that is held in the pendular state.
Figure 2.20b. Moduli model for Berea samples. Upper line is bulk modulus, lower is shear modulus.
Figure 2.21. Velocities in limestone during evaporative drying. Top: $V_p$; Bottom: $V_s$. 
Figure 2.22. Moduli in limestone during evaporative drying. Top: Bulk modulus; Bottom: Shear modulus.
For the dolomite sample, $V_p$ and $V_s$ are plotted as a function of $S_w$ in Figure 2.23; the bulk and shear moduli are shown in Figure 2.24. The $V_s$ data above $S_w = 0.85$ was of poor quality, therefore both the bulk and shear moduli are shown only below $S_w = 0.85$. From $S_w = 0.85$ to 0.40 the bulk modulus decreases steadily. Below this point it can be seen to level off. The shear modulus is relatively flat throughout most of the saturation range. At low saturations, below approximately $S_w = 0.10$, it increases gradually as $S_w$ decreases. The increase in shear modulus at low saturations is attributed to the effects of adsorbed water though the mechanism for this increase in carbonates is not understood (Clarke et al, 1980).

Since the modeling routine can only take into account the bulk effects of fluids, only data for saturation levels above $S_w = 0.10$ will be considered. These data are distinctly different from the limestone data and are similar in form to the saturation scenario proposed in Figure 2.19b. In this case, pores are sequentially and partially drained over a range of saturation. This is then followed by the drainage of the remainder of the water from the pore bodies.

The data for both the Berea 100 and 300 samples are similar in form and will be discussed together. $V_p$ and $V_s$ for Berea 100 are shown as a function of $S_w$ in Figure 2.25; the bulk and shear moduli are shown in Figure 2.26. $V_p$ and $V_s$ for Berea 300 during drying are shown in Figure 2.27; the bulk and shear moduli are shown in Figure 2.28.

Four distinct regions can be resolved in the bulk moduli. The first region, at high saturation levels, there is a decrease in bulk modulus with $S_w$. This occurs from the point of maximum saturation until approximately $S_w = 0.35$ in Berea 100 and $S_w = 0.50$ in Berea 300. This is followed by a flattening until $S_w = 0.18$ in Berea 100 and $S_w = 0.10$ in Berea 300. In the third region there is a sharp decrease in bulk moduli. As $S_w$ is decreased towards zero, the bulk modulus levels off in Berea 100 and increases in Berea 300. The variations in shear moduli also may be divided into four regions, though the relative magnitude of changes
Figure 2.23. Velocities in dolomite during evaporative drying. Top: Vp; Bottom: Vs.
Figure 2.24. Moduli in dolomite during evaporative drying. Top: Bulk modulus; Bottom: Shear modulus.
Figure 2.25. Velocities in Berea 100 during evaporative drying. Top: Vp; Bottom: Vs.
Figure 2.26. Moduli in Berea 100 during evaporative drying. Top: Bulk modulus; Bottom: Shear modulus.
Figure 2.27. Velocities in Berea 300 during evaporative drying. Top: Vp; Bottom: Vs.
Figure 2.28. Moduli in Berea 300 during evaporative drying. Top: Bulk modulus; Bottom: Shear modulus.
are different than those in the bulk moduli. As with the bulk moduli, the shear moduli decrease with Sw in the upper ranges of saturation, and this is followed by a flattening. As Sw is reduced below 0.20 in Berea 100 and 0.10 in Berea 300 there is a small decrease followed by a sharp increase.

The increases in bulk and shear moduli at low saturation levels are attributed to the increases in surface free energy of the solid resulting in increase contact adhesion as adsorbed water is removed. The increase in velocities as Sw decreases towards zero in Berea sandstone has been previously observed by Wyllie et al. (1962), Pandit and King (1979), and DeVilbiss (1980). These effects are consistent with the interpretation that the removal of adsorbed water will occur below the CMC. For the purposes of modeling the effects of bulk fluid properties, the three regions above this saturation level will be compared to the proposed model.

The general form of the data in the upper three regions of moduli variations resembles that of Figure 2.20b. Pore bodies are partially drained at high saturations, this is then followed by a period over which they are drained more completely. Finally, disconnected surface water and water contained in cracks drains below the CMC. The decreases in moduli at lower saturations did not manifest themselves until well below the CMC. This suggests that there is a significant drop in velocities that is associated with the removal of water that is held below the irreducible water saturation level. Another point to note is the lack of decrease that is evident in the shear modulus in the third region. Core scale saturation heterogeneities may be affecting the results in this region in that the surface free energy effect may be competing with the drainage of cracks. This will be discussed in more detail in the following section when the adsorption data are presented.

Another feature in the sandstone data that is more pronounced in Berea 300 than in Berea 100, is the decrease in moduli with Sw at high saturations followed by a leveling off.
In terms of the proposed models, this could correspond to a tendency in Berea 100 for the more complete initial drainage of pore bodies. Other factors may also contribute to these differences in character of the data. Cadoret et al. (1993) observed variations in the range of saturation over which $V_p$ decreased in the upper ranges of saturation in limestone samples. It was found that samples with pore sizes that approached the acoustic wavelength tended to exhibit decreases in $V_p$ over a larger range of saturation. This was attributed to the drainage of individual large pores causing saturation heterogeneities on the order of the acoustic wavelength that in turn resulted in path dispersion. In the Berea samples the $V_p$ wavelength is approximately 5 mm and the $V_s$ wavelength is approximately 4 mm. Thin section analysis revealed that the scale of the pores is much smaller than the acoustic wavelength for both Berea 100 and Berea 300. It does not seem reasonable therefore to interpret that the observed differences could be attributed to pore scale induced saturation heterogeneities on the order of the acoustic wavelength. It is possible, however, that variations in the nature of the porosity on a scale that approaches the wavelength of the elastic waves may be present. Imaging studies of the porosity of the rock were not available to assess this possibility, though upon visual inspection the Berea samples appear to be quite homogeneous in character.

2.6.3 Adsorption Experiments

It is well established that during the falling rate period of drying sample scale saturation heterogeneities will evolve. The extent to which these effects distort the measured velocity-saturation relationship was explored in the sandstones by examining the results of experiments that measured velocities as water was adsorbed to dry rocks. Adsorption has been used as a method to increase $S_w$ in the low end of saturation in velocity experiments
(Wyllie et al., 1962; Pandit and King, 1979; Clarke et al., 1980; Knight and Nolen-Hoeksema, 1990) but it appears that the results have not been compared with those obtained during drying in the lower ranges of saturation. Adsorption is a much slower process, occurring over the course of six to eight weeks for the samples used in this study, and it is therefore interpreted that a more homogeneous distribution of moisture will evolve during this process.

The bulk and shear moduli during adsorption and drying are shown in Figure 2.29 for Berea 100 and in Figure 2.30 for Berea 300. As Sw is increased from the dry state in Berea 100, both the bulk and shear moduli decrease substantially, to 80 percent of their dry values. This is followed by an increase in bulk and shear moduli until the point of maximum adsorption at Sw = 0.16. Similarly, in Berea 300 the bulk and shear moduli decrease to 69 and 73 percent of their dry values. The moduli then increase until the point of maximum adsorption at Sw = 0.15 in Berea 100 and 0.07 in Berea 300.

As water is adsorbed to the surfaces of the dry sample there is a reduction in both bulk and shear moduli. These decreases in moduli can be attributed to a reduction in surface free energy of the quartz grain contact surfaces that occurs as water is adsorbed to the dry rock. After an initial drop, both the bulk and shear moduli increase towards the later stages of adsorption. The interpretation of the fluid distribution in the rock during the later stages of adsorption follows that by Foster (1932), which was subsequently applied to a study of the dielectric constant in partially saturated rocks by Knight and Nur (1987). As adsorption proceeds, water layers build up on the pore walls until eventually closure between the layers occurs and menisci form. In Berea, a granular sandstone, it seems reasonable to assume that menisci will form first at the grain contacts rather than in the larger pore bodies.

After menisci have been established, condensation can then occur at the menisci
Figure 2.29. Moduli in Berea 100 during adsorption and evaporative drying at low saturation levels. Top: Bulk modulus; Bottom: Shear modulus.
Figure 2.30. Moduli in Berea 300 during adsorption and evaporative drying at low saturation levels. Top: Bulk modulus; Bottom: Shear modulus.
surfaces. To gain insight into how the condensation will proceed it is illustrative to examine Kelvin's equation for the vapor pressure, \( P \), across a meniscus held in a cylindrical capillary:

\[
P = P_0 \exp \left( \frac{\sigma v}{RT} \right) \tag{2.9}
\]

where \( P_0 \) is the ambient vapor pressure, \( \sigma \) is the surface tension in the meniscus, \( v \) is the molecular volume, \( r \) is the radius of curvature of the meniscus, \( R \) is the gas constant and \( T \) is the temperature. From the above relationship it can be seen that menisci with smaller radii of curvatures will have a lower vapor pressure. Since the rate of condensation is proportional to the difference between the vapor pressure across the meniscus and the ambient vapor pressure, pores with a smaller radius will tend to fill up before those with a larger radius. Based on this argument, it is interpreted that the increase in saturation towards the later stages of adsorption is due to the filling of grain contacts, cracks and clays with water. This is supported by the observation that there is a sharp increase in both bulk and shear moduli in this range of saturation: the saturation state of compliant porosity, such as that at grain contacts, will affect both the bulk and shear moduli.

It is interesting to note that the point at which adsorption stopped corresponds to the point at which the sharp increase in both the bulk and shear moduli leveled off. In a constant humidity environment, capillary condensation will cease when the radii of the menisci become large enough so that the vapor pressure across the interface is in equilibrium with the ambient vapor pressure. In the Berea samples, it appears that adsorption stops when a substantial amount of the grain contact porosity is saturated.

In comparing the adsorption data with the data collected during the final stages of drying it is evident that there is a considerable amount of hysteresis. Experimental and theoretical evidence supports the existence of sample scale saturation heterogeneities during
the later stages of drying. In contrast, adsorption occurs very slowly, over the course of approximately eight weeks, and it is interpreted that this will tend to produce a more homogeneous saturation distribution. The following scenario, shown in Figure 2.31, is therefore proposed to explain the results during the later stages of drying. First, grain contacts towards the outside of the sample are drained of bulk water, which would result in a decrease in moduli, while towards the inside of the sample they remain saturated. As drying proceeds, adsorbed surface water begins to desorb from the contacts towards the outside of the sample while contacts towards the inside of the sample are just beginning to drain of bulk water. That is, the bulk and shear moduli will be increasing towards the outside of the sample and decreasing towards the inside of the sample. The net result appears to be that these two competing effects result in the measured velocities being significantly distorted. During adsorption, it appears that a more homogeneous saturation distribution allows these two separate effects to be resolved.

2.7 Summary

Elastic wave velocities and drying rates were measured in three different types of rock sample types as a function of saturation during evaporative drying. Drying rate curves were used to establish the transition from water being in a funicular state to water being in a pendular state, a transition that has been associated with the onset of the irreducible water saturation level within drying samples. Velocity variations below this point were thereby associated with the removal of disconnected pendular water. The implications of this
Sample scale saturation heterogeneities during the later stages of drying.
information to the form of dependence of velocities upon saturation was found to be
dependent upon the nature of the pore space microgeometry.

In the dolomite sample, there was a decrease in bulk modulus that was attributed to
the introduction of air into pore bodies. The subsequent drainage of pendular water resulted
in no further velocity variations, which was attributed to the absence of any significant
amount of crack-like porosity. In contrast, the results for the limestone and Berea sandstone
samples indicate that two distinct regions of velocity variation are present: one that is
associated with the drainage of pore bodies, and another that is associated with the drainage
of disconnected, pendular water, held in crack-like porosity. These results may be of
particular interest since this suggests that velocity variations may sometimes be specifically
associated with the removal of water that is held below the irreducible water saturation level.
The close agreement in the form of the models and data suggests that the combined use of
drying rates and even simple models of pore space microgeometries can be of considerable
use in interpreting the velocity-saturation relationship.

Finally, the differences in measured velocity data between adsorption and drying
indicate that sample scale saturation heterogeneities that exist during the final stages of
drying can significantly affect velocity measurements.
3 THE EFFECTS OF WETTABILITY ON VELOCITIES

3.1 Introduction

There have been a number of recent laboratory and theoretical studies examining the effect of pore scale fluid distributions on the elastic and electrical properties of rocks. Two of the most important parameters in determining the distribution of fluids in partially saturated rocks are saturation history and wettability. In order to characterize the relationship between a measured property and fluid distributions in a multiphase saturated porous medium, the coupled role of these two parameters needs to be understood.

Saturation history in porous rocks saturated with air and water has been shown to produce hysteresis in the relationship between saturation level and a number of geophysical parameters including elastic wave velocities (Knight and Nolen-Hoeksema, 1990; Cadoret et al., 1992a,b), elastic wave attenuation (Bourbie and Zinszner, 1984), electrical resistivity (Knight, 1992) and dielectric constant (Knight and Nur, 1987). These effects can be attributed to differences in the distribution of fluids that occur due to changes in the saturation process.

Altering the wettability of rocks has been shown in numerous studies to affect the relationship between saturation history and electrical properties in porous rocks containing oil and water (see Anderson, 1986, for a review). However, there appear to have been no published studies that examine the effects of altering wettability on the relationship between saturation history and velocities in rocks. Wyllie et al. (1958) touched upon this topic by making measurements of Vp in synthetic cores using wetting and nonwetting liquids displacing air. Velocities measured when the samples were partially saturated with nonwetting fluids were lower then for air saturated samples. It was interpreted that poor coupling
between the non-wetting fluids and the solid led to the attenuation of signals and, consequently erroneous arrival time selections. Unfortunately, measurements were only made at a single, unspecified saturation level so that density effects could not be taken into consideration, and the effects on the bulk and shear moduli could not be determined.

In the following chapter the effects of altering wettability on the relationship between elastic wave velocities and saturation level is investigated. This was accomplished by conducting imbibition and drainage experiments on samples that were initially strongly water wet and then repeating the experiments after the samples had been treated to make them oil-wet. For the purposes of this study the untreated, strongly water-wet rocks will be referred to as hydrophilic and the treated, oil-wet samples will be called hydrophobic. The proposed fluid distribution scenarios are assessed using numerical modeling.

3.2 The Effect of Saturation History On Fluid Distribution

Saturation history can affect the distribution of fluids in a porous media through two primary mechanisms: contact angle hysteresis and pore geometry effects. The principles behind these two effects can be illustrated in simple pore systems containing a wetting liquid and a non-wetting gas.

On a smooth, homogeneous surface contact angle hysteresis will tend to be negligible and the measured angle on such a surface is referred to as the intrinsic contact angle. If the surface is roughened, hysteresis will exist between the contact angle when a fluid is advancing with respect to another fluid ($\theta_A$) and the contact angle when a fluid is receding ($\theta_R$). This is illustrated in Figures 3.1a and b. In general, $\theta_A > \theta_r > \theta_R$; it has been observed that the difference between $\theta_A$ and $\theta_R$ can be as much as 60° (Johnson and Dettre, 1969).
Figure 3.1 (a) Intrinsic contact angle (b) Advancing, intrinsic and receding contact angles
Figure 3.2a illustrates how a difference in contact angles between imbibition and drainage can result in variations of capillary rise in a cylindrical tube placed in contact with a liquid reservoir. In this type of experiment, the pressure drop that exists across the interface causes a liquid column to rise up the tube. The height of the rise, \( h \), is related to the contact angle through the relationship

\[
\rho g h = \frac{2 \sigma \cos \theta}{r}
\]  

(3.1)

where \( g \) is the gravitational constant. During drainage \( \theta_r \) is small, thereby creating a meniscus with a small radius of curvature. Consequently, the resulting capillary pressure (see equation 2.5) is high, allowing the capillary tube to support a large column of liquid. In contrast, the lower contact angle present during imbibition creates a lower capillary pressure and the capillary rise is therefore reduced.

The effects of pore geometry in the absence of contact angle hysteresis can be illustrated using a tube with a large pore body in the middle (Figure 3.2b). During drainage of a wetting fluid the radius of the meniscus in the upper part of the pore is small, thereby creating a large enough capillary pressure to support the height of the water column and to retain water in the pore body. During imbibition, the water column rises until it reaches the pore body. At this point the radius of curvature in the meniscus becomes larger causing the capillary pressure to drop and the meniscus cannot rise any further.

Due to the interaction of contact angle hysteresis and the complex geometries of pore spaces that exist in rocks, characterizing the behavior of wetting and non-wetting fluids during imbibition and drainage cycles becomes difficult. At a sample scale, it has been found that these effects result in hysteresis in capillary pressure curves between imbibition and drainage cycles. A typical imbibition and drainage cycle capillary pressure curve has the
Figure 3.2 (a) The effects of receding and advancing contact angles on imbibition and drainage. Left: drainage; Right: imbibition (b) The effects of pore geometry on imbibition and drainage. Left: drainage; Right: imbibition.
form shown in Figure 3.3. During drainage, increases of pressure, relative to ambient conditions, in the non-wetting phase result in a reduction in saturation of the wetting phase. As the wetting phase saturation is reduced, higher levels of pressure are required to displace the wetting fluid until, at the irreducible water saturation level, the wetting phase becomes disconnected and the saturation cannot be reduced further. The wetting phase will tend to exist as pendular rings at grain contacts and in cracks. During imbibition, the non-wetting phase saturation level is reduced as pressure is dropped. As negative pressure is applied the non-wetting phase saturation level continues to decrease until it becomes hydraulically disconnected and the residual nonwetting phase saturation level is reached. At this point the non-wetting phase will tend to exist as isolated globules in larger pore bodies.

For intermediate wettabilities, the capillary pressure curves can become more complex. Morrow and Mungan (1971) and Morrow (1976) studied the effects of the intrinsic contact angle on imbibition and drainage capillary pressure curves. In these experiments a synthetic porous medium was saturated with air and a liquid. The liquids were selected to provide a range of intrinsic contact angles from 0° to 108°. During drainage, when the liquids were displaced by air, it was found that the form of capillary pressure curves were relatively insensitive to liquids with intrinsic contact angles below approximately 50°. During imbibition however, when liquids were displacing air, the form of the capillary pressure curve was found to be very sensitive to the intrinsic contact angle above approximately 20°. It was interpreted that these differences in the level of sensitivity of capillary pressure curves to wettability were due to the receding contact angle being sensitive to intrinsic contact angles above approximately 50° and the advancing contact angle to intrinsic contact angles above approximately 20°. These experiments indicate that, for the range of wettabilities considered in that study, the distribution of fluids is more sensitive to changes in wettability during imbibition than during drainage.
Figure 3.3 Capillary pressure curve during imbibition and drainage cycles.
3.3 Experimental Procedures

In this chapter, experiments examining the effects of wettability on the relationship between velocities and saturation were conducted on the Berea sandstone samples. Berea sandstone was selected because it is well studied and strongly water wet in the untreated state.

As in the experiments presented in Chapter Two, saturation levels were reduced using evaporative drying. Sw was increased in the samples in three stages. During the first stage water was adsorbed to the dry samples by placing them on a stand in a sealed chamber with its bottom filled with deionized water. The samples were thereby exposed to air with relative humidity that was close to 100 percent (Knight and Nur, 1987). After the samples ceased adsorbing water by this method, Sw was increased by imbibition through immersion in deionized water (Knight and Nur, 1987; Knight and Nolen-Hoeksema, 1990). In the hydrophobic samples, the saturation level was increased beyond this point by using the depressurization method. This procedure consists of first placing the samples in a chamber that is almost completely filled with water, and lowering the pressure in the chamber by pulling a vacuum on the air at the top of the container. This leads to expansion of the air in the samples, air leaves the samples and when the chamber pressure is returned to atmospheric levels the samples imbibe water. This is not, strictly speaking, a true imbibition process but has been shown to produce very uniform saturation distributions (Cadoret et al., 1992a,b).

The wettability of the samples were altered by treatment with Quilon-C, a commercially available chromium based complex that attaches to the negatively charged quartz surfaces and extends fatty acid chains into the pore space. The treatment is a monolayer thick and as such it offers the advantage of altering the wettability of the rock
surfaces without significantly affecting the microgeometry of the pore space. Porosities were altered by only 0.003 for Berea 100 and 0.002 for Berea 300. Lewis et al. (1988) found this procedure altered Berea sandstone samples from being strongly water-wet to being strongly oil-wet.

The treatment procedure was a modified version of that used by Lewis et al. (1988). A sample that had been oven dried at 60°C for one day was evacuated in a vacuum chamber for several hours. A mixture of 20 percent Quilon-C, 80 percent isopropanol (by volume) was introduced into the chamber and the sample was soaked in this solution for two days at ambient laboratory conditions. The samples were then dried at 60°C for one day and the treatment process was repeated. Following the second treatment, the samples were evacuated, saturated with distilled water, and soaked for several days. This was repeated until the conductivity of the distilled water reached an equilibrium value, which indicated that the amount of unbound Quilon-C chemical coming into solution was low and therefore that the sample was then 'clean'.

Lewis et al. (1988) used oil and water as pore fluids; in this study, air and water are the pore fluids. The wettability of a samples in this study was assessed by conducting spontaneous imbibition tests before and after treatment. Spontaneous imbibition rates are proportional to the capillary pressures in the pore network which are directly related to the wettability of the system. Other factors, such as pore size, liquid viscosities and the size and shape of the samples have also been noted to have a significant impact upon imbibition rates (Jadhunandan and Morrow, 1991). In comparing treated and untreated samples of the same type, we keep these variables essentially constant while isolating wettability as the main factor influencing changes in imbibition rates.

Imbibition data were acquired by immersing an air saturated sample in water and measuring the weight of the sample as a function of time (Denekas et al., 1959). The
experiments were conducted by suspending the samples, with vertical orientation, by a thin filament into a 600 ml beaker filled with 500 ml of water. The cores were suspended from a bottom loading scale, which was interfaced with a computer. Weight measurements were then made as a function of time for 24 hours. The weights were then converted to saturation level.

It should also be noted that in using water to displace air, the density contrast between these fluids results in a hydrostatic gradient across the samples, which is a driving force for increasing water saturation level. To assess the extent to which this has influenced the results, a second imbibition test was conducted, that of capillary rise. The core samples were placed, vertically oriented, in contact with an interface of water. The base of samples were approximately one to two millimeters beneath the surface of the water. After ten days there were no significant weight changes in the samples and the saturation level at this point was recorded. In this case the effect of gravity on hydrostatic pressure is opposite to the previous test: gravity will tend to resist the capillary rise.

It should be emphasized that these are only qualitative wettability tests. However, it is considered to be sufficient for the purposes of this study to establish that the wettability has been significantly altered by the treatment process.

3.4 Experimental Results and Discussion

In the following section the experimental results will be presented and discussed. Due to the similarity in form of the results for Berea 100 and 300, the results for both samples will be discussed simultaneously. The hydrophilic case will be presented first, followed by the results for the hydrophobic case.
3.4.1 Hydrophilic Samples

Vp and Vs in Berea 100 during imbibition and drainage cycles are shown in Figure 3.4; the bulk and shear moduli are shown in Figure 3.5. For Berea 300, Vp and Vs data can be found in Figure 3.6; the bulk and shear moduli are in Figure 3.7.

The drainage results for the Berea 100 and 300 samples are discussed in detail in Chapter Two. In both samples there was a strong decrease in bulk modulus with Sw in the upper ranges of saturation. This is followed by a period over which the modulus was insensitive to changes in saturation level until, at lower saturation levels the modulus began to decrease sharply with decreasing Sw. As Sw was reduced further the bulk modulus increased sharply in Berea 300 and leveled off in Berea 100. The shear modulus followed a similar pattern to the bulk modulus, with the variations being less pronounced in the upper ranges of saturation.

As Sw was increased through adsorption, the bulk modulus decreased sharply and then increased, leaving a substantial amount of hysteresis between the adsorption and drying results. Subsequent imbibition through immersion produced only a modest increase in bulk modulus for Berea 100 while for Berea 300 it was essential flat throughout most of the saturation range. At high saturations, the bulk modulus increased sharply in Berea 300. The lack of a sharp increase in bulk modulus in Berea 100 towards higher saturation levels is attributed to an inability to increase the saturation to a sufficiently high level by means of immersion imbibition. The shear modulus follows a similar pattern though the magnitude of the variations is less pronounced than in the bulk modulus.

During drying it was interpreted that pore bodies drained in the upper ranges of saturation and the removal of bulk and adsorbed water from grain contacts was responsible for velocity variations in the lower ranges of saturation. During adsorption, the results
Figure 3.4. Velocities in Berea 100 during imbibition and drainage.
Top: Vp; Bottom: Vs.
Figure 3.5. Moduli in Berea 100 during imbibition and drainage.
Top: Bulk modulus; Bottom: Shear modulus.
Figure 3.6. Velocities in Berea 300 during imbibition and drainage.
Top: Vp; Bottom: Vs.
Figure 3.7. Moduli in Berea 300 during imbibition and drainage.
Top: Bulk modulus; Bottom: Shear modulus.
indicate that grain contacts are filling with water. Variations in velocity as water saturation level is increased above the point of maximum adsorption is therefore attributed to the filling of the remainder of the porosity, such as pore bodies and throats. It appears then that crack-like porosity at grain contacts is the last to drain during drying and the first to fill during imbibition. In the upper ranges of saturation, variations in velocity are attributed to changes in the saturation state of pore bodies and throats.

Hysteresis is evident in the bulk and shear moduli in both the upper and lower saturation ranges. The hysteresis at low saturations was explained the previous chapter in terms of sample scale saturation heterogeneities that evolve during the later stages of drying. At higher saturations it is proposed that the hysteresis can be explained by differences in the distribution of fluids in the pore bodies that evolve between the imbibition and drainage processes. During drainage it was interpreted that pore bodies drained sequentially leaving behind partially drained pores with a connected liquid phase. This was followed by a period over which the partially drained pores drained further until the liquid phase became hydraulically disconnected. During imbibition it is interpreted that partial saturation is maintained at a pore scale until a higher saturation levels. This is followed by a period over which the remainder of gas in pore bodies is displaced by water. These scenarios are consistent with the interpretations of Knight and Nolen-Hoeksema (1990) and Cadoret et al. (1992a,b).

3.4.2 Hydrophobic Samples

As with the hydrophilic sample, an examination of the drying rates can provide important insights into the distribution of fluids within the samples during the drying process. Drying rate data for the treated and untreated samples are shown in Figure 3.8 for Berea 100 and in Figure 3.9 for Berea 300. The data are remarkably similar for both the treated and
Figure 3.8. Comparison of drying rates in hydrophilic (top) and hydrophobic (bottom) Berea 100 samples.
Figure 3.9. Comparison of drying rates in hydrophilic (top) and hydrophobic (bottom) Berea 300 samples.
untreated cases. Initially, there is a sharp decrease in rate that is followed by a period of constant rate. The constant rate period ensues until Sw = 0.33 in Berea 100 and Sw = 0.24 in Berea 300. The rates then decrease as Sw is reduced towards zero. It should be noted that no significance is attached to the absolute value of the drying rate during the constant rate period since it can be influenced by environmental factors such as temperature and humidity.

The effect of wettability on drying rates appears not to have been explicitly studied. It follows from the background theory presented in section 2.3 that for capillary transport to exist when water is being displaced by air during the evaporative drying process, water must behave as a wetting fluid. That is, the receding contact angle must be at least less than 90° for capillary pressure to exist such that it favors the removal of water through capillary mechanisms. The presence of the constant rate period during the drying of the hydrophobic samples is therefore interpreted to indicate that capillary transport is the dominant transport mechanism, which in turn implies that when air is displacing water in the evaporative drying process, water behaves like a wetting fluid. As with the water-wet samples, this suggests that grain contacts and cracks will tend to remain saturated until below the CMC.

The effects of wettability on the imbibition process can be qualitatively assessed by examining the relative changes in the imbibition versus time data. Figures 3.10 and 3.11 show plots of Sw versus time before and after treatment for Berea 100 and 300 respectively. For both Berea 100 and 300, the untreated samples show a sharp increase in saturation upon initial immersion, indicating high imbibition rates. The curves then begin to level off. For the treated samples, the saturation level increases very slowly throughout the course of measurement. These results suggest that the wettability of the samples with respect to water in an air-water system has been substantially reduced when water is displacing air.

It was also noted that the contrast in density between the air and water could give rise
Figure 3.10. Sw versus time for hydrophobic and hydrophilic Berea 100 samples during spontaneous imbibition.
Figure 3.11. Sw versus time for hydrophobic and hydrophilic Berea 300 samples during spontaneous imbibition.
to a hydraulic gradient along the length of the sample that would effectively enhance the imbibition process. Using the capillary rise experiments it was found that the hydrophilic Berea 100 sample reached a saturation level of 0.71 while hydrophobic Berea 100 sample reached a saturation of $Sw = 0.08$. Similarly hydrophilic Berea 300 sample reached $Sw = 0.74$ while hydrophobic Berea 300 reached $Sw = 0.06$. These experiments not only suggest that the wettability has been substantially reduced by the treatment process but also that the hydrostatic gradient was probably a significant factor in contributing to increasing the saturation level in the hydrophobic samples during immersion imbibition. That is, water will tend to be forced into the pore spaces during the immersion process.

In contrast to the similarity of the hydrophilic and hydrophobic drying rate curves, the treatment process has produced significant changes in the imbibition test results. This suggests that the imbibition process was more significantly affected by the change in wettability than was the drainage process. Given this information about the influence of wettability on the imbibition and drainage processes, it would now be appropriate to examine the velocity data.

$Vp$ and $Vs$ for Berea 100 during drying, before and after treatment, are show in Figure 3.12. The Berea 300 velocity data are shown in Figure 3.13. One difference between the treated and untreated samples that is immediately apparent is that, at any given saturation level, the velocities in the treated samples are higher than those in the untreated samples. Since the treatment process has chemically altered the surfaces of the rock, it seems reasonable to assume that it has affected the chemical state of the solid/solid interface at the grain contacts. It appears then that the chemical treatment has resulted in a higher degree of adhesion between the grain contacts.
Figure 3.12. Comparison of velocities in hydrophilic and hydrophobic Berea 100 sample.

Top: Vp; Bottom: Vs.
Figure 3.13. Comparison of velocities in hydrophilic and hydrophobic Berea 300 sample.
Top: Vp; Bottom: Vs.
For the treated Berea 100 sample, Vp and Vs during increasing and decreasing saturation cycles are shown in Figure 3.14; the bulk and shear moduli are shown in Figure 3.15. Similarly for the treated Berea 300 sample, Vp and Vs during increasing and decreasing saturation cycles are shown in Figure 3.16; the bulk and shear moduli are shown in Figure 3.17. In both of the treated Berea samples, the bulk modulus decreases steadily with saturation until Sw = 0.20 in Berea 100 and Sw = 0.40 in Berea 300. After this point the slope begins to level off in Berea 300. Below Sw = 0.20 in Berea 100 and Sw = 0.10 in Berea 300, the bulk moduli drops off steeply. At very low saturations the Berea 100 bulk modulus then levels off while the Berea 300 bulk modulus increases slightly. The shear modulus can be seen to decrease slightly with water saturation until Sw = 0.30 in Berea 100 and 0.18 in Berea 300. The moduli then decrease steeply until Sw = 0.04 in Berea 100 and Sw = 0.02 in Berea 300. As Sw is reduced towards zero, the shear modulus then increases steadily.

During adsorption, the bulk modulus shows a modest decrease until Sw = 0.03 in Berea 100 and Sw = 0.02 in Berea 300. As the saturation level is increased further, the bulk modulus increases gradually until Sw = 0.75 in Berea 100 and Berea 300. This is followed by an increase in modulus towards the point of maximum saturation. As with the bulk modulus, the adsorption of water to the dry rock also produces a decrease in the shear modulus until the maximum point of adsorption. This is followed by a gradual increase in modulus until the point of maximum saturation. The increase that was observed at high saturations in bulk modulus did not occur in the shear modulus.

The form of the relationship between velocities and saturation during evaporative drying of the hydrophobic rocks closely resembles that of the hydrophilic rock in the upper ranges of saturation. In both the treated and untreated cases there is a region of steep decrease in bulk modulus followed by a leveling off. The decreases in bulk moduli are accompanied
Figure 3.14. Velocities in hydrophobic Berea 100 during imbibition and drainage.

Top: $V_p$; Bottom: $V_s$. 
Figure 3.15. Moduli in hydrophobic Berea 100 during imbibition and drainage.
Top: Bulk modulus; Bottom: Shear modulus.
Figure 3.16. Velocities in hydrophobic Berea 300 during imbibition and drainage.

Top: $V_p$; Bottom: $V_s$. 
Figure 3.17. Moduli in hydrophobic Berea 300 during imbibition and drainage.

Top: Bulk modulus; Bottom: Shear modulus.
by gradual decreases in shear modulus over the upper ranges of saturation, which is consistent with the interpretation that pore bodies are draining. As with the hydrophilic case, it is interpreted that grain contacts remain saturated until the lower ranges of saturation.

The earlier onset of decrease in shear modulus relative to the bulk modulus can be explained in terms of the way in which velocities are measured, keeping in mind that $V_s$ is affected by the shear modulus and $V_p$ is affected by both the bulk and shear modulus. The transducers generate $P$ waves that effectively sample the entire radius of the rock. In contrast, the amplitude of the torsional shear waves must be zero at the center of the sample, and they will therefore tend to preferentially 'sample' towards the outside of the sample. Since the outside of the sample is likely to have a lower saturation than the inside of the sample, it seems reasonable to assume that the earlier onset of the decrease in shear modulus can be attributed to these saturation heterogeneities.

During imbibition, the results for the hydrophobic samples are substantially different from those for the hydrophilic samples. The decrease in moduli that occurred with the adsorption of water is attributed to the reduction in surface free energy of the solid surfaces leading to a decrease in contact adhesion. The fact that the magnitude of the drop is smaller in the hydrophobic samples is attributed to a chemical alteration of the grain contact regions. In the hydrophilic rocks there was a sharp rise in moduli towards the later stages of adsorption that was attributed to capillary condensation leading to the filling of grain contacts with water. This was followed by a period over which moduli were relatively constant, which is consistent with the hypothesis that the saturation level in pore bodies was increased, though partial air saturation was maintained at a pore scale. In contrast, the moduli of the hydrophobic rock rise gradually over a large range of saturation. This clearly indicates the existence of fundamental differences in the distribution of fluids between the hydrophilic and hydrophobic rocks during the imbibition process.
There are two possible scenarios for the distribution of fluids in the hydrophobic sample during imbibition. The first is based on the assumption that the increases in moduli during the period of gradual increase are due to the filling of grain contacts. In this case grain contacts fill with water over a large range of saturation while pore bodies maintain partial saturation until high saturation levels. The second scenario is based on the assumption that the increases in moduli during the middle ranges of saturation are due to the filling of pore bodies with water. In this case pore bodies fill sequentially and fully while grain contacts remain unsaturated until high saturation levels.

In comparing the relative changes in shear modulus with Sw at both high and low saturation levels during drying, it can be seen that, at high saturations, there is a modest change in moduli associated with changing saturation state of pore bodies while at low saturations, there is a more substantial change associated with altering the saturation state of grain contacts. During imbibition, there is a modest increase in shear modulus throughout most of the range of saturation until, at the point of maximum saturation it remains a substantial amount below its value at Sw = 1. These data support the second hypothesis, that the increases in moduli are due to the sequential and complete filling of pore bodies while grain contacts remain air filled until high saturation levels. A similar analysis of the bulk modulus produces ambiguous results, since the relative changes in bulk modulus that are associated with the removal of water from pore bodies are similar in magnitude to those associated with the removal of water from grain contacts. It is also notable that one of the controlling factors of the behavior of menisci in porous media is their tendency to remain 'caught' on sharp edges and inhibited from moving further (e.g., Anderson, 1987b). Qualitatively, it seems reasonable that this phenomenon might make the entry of menisci into grain contact porosity more difficult, which would also support that latter hypothesis.

In either case, it is evident that the fluid distribution occurring during the imbibition process in the hydrophobic rock differs substantially from that in the hydrophilic case. Based
on the above arguments, the scenario in which grain contacts remain air filled until high saturation levels is preferred and will be adopted for the purposes of modeling.

It is also interesting to compare these findings with those of Morrow and Mungan (1974) and Morrow (1976). It was found that capillary-pressure-drainage curves were less sensitive to variations in the wettability of the system than were imbibition capillary pressure curves. In this study, it was found that during evaporative drying, both the drying rate curves and the form of the relationship between velocity and saturation were not very sensitive to the wettability being altered. In contrast, during imbibition it was found that the imbibition rate tests and the form of the velocity-saturation relationship were substantially affected by altering the wettability of the system.

3.5 Velocity Modeling

To assess the validity of the proposed fluid distribution scenarios, the modeling routine of Endres and Knight (1989) was used to model the form of the relationship in Berea 300. This sample is used since the data set during imbibition is more complete. In the first chapter the intention was to model general trends in the form of the velocity-saturation relationship, based on qualitative estimates of the pore spectrums. In this chapter a more accurate estimate of the pore spectrum for Berea sandstone is used, based on the model of Cheng and Toksoz (1979). To calculate this pore spectrum, Cheng and Toksoz (1979) used velocity versus pressure data to calculate moduli versus pressure relationships. It was then assumed that pressure applied to the rock will result in closure of pores. Compliant porosity, represented by low aspect ratio pores will close first at low pressures; higher aspect ratio pores close at higher pressures. By inverting the pressure versus velocity data and assuming that different aspect ratio ellipsoidal pores close at different pressures, a pore spectrum was calculated. It should be emphasized that when interpreting the results of this model it must be taken into consideration that the complex pore space of Berea sandstone has been approximated by assuming a specific idealized geometry.
The pore spectrum used to approximate the porosity of the Berea 300 sample is shown in table 3.1 and was based on one calculated by Cheng and Toksoz (1979) for a 16.3% porosity Berea sample. The aspect ratio concentrations were linearly scaled to account for the higher porosity of the sample used in this study. A small reduction (0.008% of absolute porosity) in the concentration of 0.0003 aspect ratio cracks was also made. This is justified by the thin section analysis, which qualitatively indicates a lower concentration of grain contact porosity in Berea 300 than in Berea 100.

<table>
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</table>

Table 3.1 Pore Spectrum used to model Berea 300.

As was noted in Chapter Two, the model of Endres and Knight (1989) approximates the effects of the bulk properties of pore fluids on the moduli. Effects due to variations in surface free energy that result when fluids are adsorbed to the solid matrix cannot be accounted for by this model. The water contained within the pore space is therefore divided into two types: surface water and bulk water (Endres and Knight, 1991). Surface water will
be considered to be associated with decreases in the bulk and shear moduli that occur during the early stages of adsorption. Bulk water will be considered to comprise the remainder of the water. The saturations used in this section will refer to the bulk water saturation, \( S_{wb} \), which is related to the surface water saturation, \( S_w \), and the overall saturation through the following relationship:

\[
S_{wb} = \frac{S_w - S_{ws}}{1 - S_{ws}} \quad (3.2)
\]

The division of \( S_w \) into surface water and bulk water for Berea 300 is shown in Figure 3.18. The maximum surface water saturation level was selected to be \( S_w = 0.07 \), which corresponds to the point at which the bulk and shear modulus begin to increase during the adsorption stage.

Figure 3.19 shows the proposed fluid distribution scenario during imbibition and drainage for the hydrophilic rocks. During drainage, intermediate and high aspect ratio pores, representing pore bodies, are sequentially and partially drained over a range of saturation. This is followed by a period over which the saturation level in these pores is reduced further. At low saturation levels, the remainder of the water is drained from the intermediate and high aspect ratio pores, which represents the removal of disconnected bulk water from the pore bodies, as well as from the lowest aspect ratio pores, which represent the grain contact porosity. This scenario is depicted in Figure 3.20. It was found that classifying pores with aspect ratios less than or equal to 0.001 as cracks produced the best agreement between the model and data. It is also notable that the pore spectrum calculated by Cheng and Toksoz (1979) was based on a vacuum dry sample. To take into account the reductions in moduli that are associated with the adsorption of water to the dry rock, the moduli the values for the solid matrix bulk and shear moduli were reduced by 31 and 44 percent respectively, a procedure used by Toksoz et al. (1976) and Endres and Knight (1991). These values are comparable to the reductions in bulk and shear moduli observed as water was adsorbed to the dry rock.
Figure 3.18 Defining the wetted frame for Berea 300. 'S' indicates the region of Sw that is associated with surface water. 'B' indicates the region of Sw that is associated with Bulk water effects.
Figure 3.19 Pore saturation scenario during drainage. A to D: Sequential drainage of large and intermediate aspect ratio pores; D to E: Drainage of connected water in partially drained pores; E to F: drainage of cracks and disconnected surface water. Black=water, White= air.
Figure 3.19 Pore saturation scenario during drainage. A to D: Sequential drainage of large and intermediate aspect ratio pores; D to E: Drainage of connected water in partially drained pores; E to F: drainage of cracks and disconnected surface water. Black=water, White=air.
Figure 3.20 Pore saturation scenario during imbibition. A to D: Grain contacts fill and surface moisture accumulates; B to C: Pore bodies fill to a partially saturated state; D to F: The remainder of gas in pore bodies is replace sequentially with water. Black=water, White= air.
The model and data are compared for imbibition and drainage cycles in Figures 3.21 and 3.22 for the bulk and shear moduli respectively. The model and data are very similar in form: both the hysteresis at high saturation levels and the drop in moduli at low saturations are reproduced in the model. The most notable difference is in the absolute magnitude of the shear modulus, which is higher in the model than it is in the data. Such a difference is not surprising since the rock used to derive the pore spectrum had a much lower porosity, which suggests that differences in the mechanical behavior of the pore structure might also exist.

The interpretations of the fluid distributions in the hydrophobic samples will now be evaluated using numerical modeling. The division of Sw into surface and bulk water is shown in Figure 3.23. The proposed scenario for drainage is the same as that for the hydrophilic case. Large and intermediate aspect ratio pores, representing pore bodies, are drained in the upper ranges of saturation. At low saturations the lowest aspect ratio pores drain. In contrast, the model for imbibition, shown in Figure 3.24, begins by sequentially and completely filling intermediate and high aspect ratio pores. The lowest aspect ratio pores, representing grain contacts, are the last to fill with water. Since the treatment process also affected magnitude of moduli decreases associated with the adsorption of water to the dry rocks, the solid matrix values were also changed. The bulk and shear solid matrix values were reduced by 31 and 27 percent respectively, which are close to the observed reductions in moduli as water was adsorbed to the dry rock.

The model and data are compared in Figure 3.25 for the bulk modulus and 3.26 for the shear modulus. As with the water-wet rocks, the form of the data is reproduced by the model. The most notable difference is that the flat portion of the drainage curve in the model, between Sw = 0.20 and 0.50, is a downward slope in the data. Also, the absolute magnitudes are higher in the model, particularly of the shear modulus. Overall however, the agreement in form, which was the primary objective of the modeling process, is quite good.
Figure 3.21. Comparison of bulk moduli model and data for hydrophilic Berea 300.

Top: model; Bottom: data.
Figure 3.22. Comparison of shear moduli model and data for hydrophilic Berea 300.

Top: model; Bottom: data.
Figure 3.23 Defining the wetted frame for Berea 300. 'S' indicates the region of Sw that is associated with surface water. 'B' indicates the region of Sw that is associated with bulk water effects.
Figure 3.24 Pore saturation scenario in hydrophobic sample during imbibition.  
A to D: Filling pore bodies with water, sequentially and fully;  
D to E: Grain contacts filling with water. Black=water, White= air.
Figure 3.25. Comparison of bulk moduli model and data for hydrophobic Berea 300.
Top: model; Bottom: data.
Figure 3.26. Comparison of shear moduli model and data for hydrophobic Berea 300.
Top: model; Bottom: data.
The agreement between the form of the data and models for both the hydrophilic and hydrophobic samples indicate that the proposed fluid distribution scenarios are plausible.

When interpreting the results of any model it is important to recognize its limitations. In this model, the two primary limitations are the assumption that the effects of fluid communication will be negligible and the potential oversimplification of pore space microgeometry. While it is not the focus of this thesis to evaluate the general validity of these assumptions, it would be appropriate to examine how these factors may affect the interpretation of the results. Two scales of fluid communication are possible: macroscopic flow, occurring at a scale much larger than the average pore size, and local flow, occurring at the pore scale due to pore-scale pressure gradients. The recent work of Akbar et al. (1993) and Gist (1994) suggests that macroscopic flow would not occur at ultrasonic frequencies. The impact of local flow is more difficult to evaluate, since it is dependent upon the specific geometries of the pore space.

The drop in moduli at lower saturation levels was attributed to the drainage of crack-like porosity at grain contacts. This was supported by the drying data, the adsorption data and by the fact that both the bulk and shear moduli were substantially altered. The fluid in these regions therefore appears to have remained isolated from the rest of the pore space and the assumption of no fluid communication appears to be valid. Additionally, approximating these compliant regions by very low aspect ratio pores appears to be reasonable.

The remainder of the porosity is comprised of complex pore geometries, frequently consisting of rounded pore bodies that taper towards the grain boundaries. Mavko and Nur (1978) noted that very low aspect ratio ellipsoids are required to approximate the mechanical behavior of thin pores that are tapered at their ends. Mendoza (1987), using numerical modeling, found that pores composed of larger, high aspect ratio bodies that were tapered towards the edges were highly compressible. It seems plausible then that the inversion
process has approximated the mechanical behavior of these pores in terms of a combination of intermediate and high aspect ratio ellipsoidal inclusions. Keeping these points in mind, the use of the model to support the general interpretations that the drops in the lower ranges of saturation are due to the drainage of grain contacts and those in the upper ranges of saturation are due to the rest of the porosity seems justified.

3.6 Summary

The differences that were found to exist between the results for hydrophilic and hydrophobic samples indicate that wettability can have a substantial impact upon the relationship between velocities and saturation. From these results, it is apparent that fundamental differences in the nature of fluid distributions can exist between the hydrophilic and hydrophobic samples at partial saturation levels. In the hydrophilic rocks it was interpreted that the cracks are the first to fill with water and the last to drain of water. As Sw was decreased, the form of the results were similar for both the hydrophilic and hydrophobic samples. However, as Sw was increased in the hydrophobic samples, the data indicated that water did not fill the cracks until higher saturation levels. These data suggest that wettability is another factor that may have to be taken into consideration when interpreting measured relationships between elastic wave velocities and saturation level.
The objective of this thesis was to examine the influence of pore space microgeometry, saturation history and wettability on the relationship between velocities and water saturation level. Two specific areas of these problems were explored. In Chapter Two, the evaporative drying process, pore-space microgeometries and their interrelated influence on the form of dependence of velocities on saturation level was investigated. In Chapter Three, the effect of wettability on the relationship between velocities and saturation level was explored.

Elastic wave velocity and drying rate measurements were made on three different rock types as saturation level was reduced through evaporative drying. The samples possessed three distinctly different pore-space microgeometries and exhibited three different forms of velocity-saturation relationship. Using drying rate curves and simplified versions of the pores spaces based on thin section analysis, fluid distribution scenarios were proposed to model the form of the relationships and these were found to be in good agreement with the data. This suggests that the application of these methods can be of considerable use in interpreting the relationship between ultrasonic velocities measured in non-hygrosopic capillary porous rocks during evaporative drying. The results for the limestone and Berea sandstone samples also suggest that two regions of velocity decreases were evident: one with the drainage of pore bodies and the second associated with the removal of pendular water which was held in cracks until low saturation levels.

Wettability was also shown to have a significant impact on the relationship between velocities and saturation history. In particular, the main difference found was that in the hydrophobic rocks, water tended to be excluded from grain contacts until higher saturation levels during imbibition. These results suggest that wettability could be a significant factor.
that may have to be taken into consideration when interpreting the results of velocities that
are measured as a function of saturation in rocks.

As was noted in the introduction, the state of liquid connectivity and rock surface
wettability can be of primary importance in determining the transport properties of rocks. The
ability to seismically monitor these properties would therefore be of considerable use. The
results of this study indicate that both pendular water and wettability can have a significant
influence on measured ultrasonic elastic wave velocities. When considering the application of
these results to the interpretation of seismic and sonic well logging surveys of partially
saturated geologic formations a key issue is frequency dispersion. In particular, it should be
noted that further investigation is necessary to determine if the mechanisms that are
responsible for the observed velocity variations at ultrasonic frequencies are still important at
lower frequencies.
REFERENCES


Cadoret, T., Marion, D., and Zinszner, B., 1992a, 1 kHz elastic wave velocities in partially saturated limestones: Evidence of fluid distribution effect, 62nd Annual SEG meeting Expanded Abstracts, 658-661.


Denekas, M. O., Mattax, C. C., and Davis, G. T., 1959, Effect of crude oil components on rock wettability, Trans. AIME, 216, 330-333.


Israelachvili, J. N., 1985, Intermolecular and surface forces with application to colloidal and biological systems, Academic, San Diego, Calif..


Knight, R., 1992, Hysteresis in the electrical resistivity of partially saturated sandstones, Geophysics, 56, 2139-2147.


Whitaker, S., 1985, Moisture transport mechanisms during the drying of granular porous media, Drying 85, A. S. Mujumdar editor.


