

A generalized Archie's law for n phases

Paul W. J. Glover¹

ABSTRACT

Archie's law has been the standard method for relating the conductivity of a clean reservoir rock to its porosity and the conductivity of its pore fluid for more than 60 years. However, it is applicable only when the matrix is nonconducting. A modified version that allows a conductive matrix was published in 2000. A generalized form of Archie's law is studied for any number of phases for which the classical Archie's law and modified Archie's law for two phases are special cases. The generalized Archie's law contains a phase conductivity, a phase volume fraction, and phase exponent for each of its n phases. The connectedness of each of the phases is considered, and the principle of conservation of connectedness in a three-dimensional multiphase mixture is introduced. It is confirmed that the general law is formally the same as the classical Archie's law and modified Archie's law for one and two conducting phases, respectively. The classical second Archie's law is compared with the generalized law, which leads to the definition of a saturation exponent for each phase. This process has enabled the derivation of relationships between the phase exponents and saturation exponents for each phase. The relationship between percolation theory and the generalized model is also considered. The generalized law is examined in detail for two and three phases and semiquantitatively for four phases. Unfortunately, the law in its most general form is very difficult to prove experimentally. Instead, numerical modeling in three dimensions is carried out to demonstrate that it behaves well for a system consisting of four interacting conducting phases.

INTRODUCTION

Archie's law has been the standard method for relating the conductivity of a clean reservoir rock to its porosity and the conductivity of the fluid saturating its pores for over 60 years. Initially an empirical relationship for a narrow range of rocks and porosities, it has

found wide application. It has been verified recently by analytical methods for certain special cases (e.g., [Sen et al., 1981](#); [Mendelson and Cohen, 1982](#)), and has been extended for use when the surface conduction is significant, such as at low salinities and in clay-bearing lithofacies (e.g., [Tiab and Donaldson, 2004](#)).

One form of the traditional Archie's law can be expressed as ([Glover, 2009](#))

$$\sigma = \sigma_f \phi^m = \frac{\sigma_f}{F}, \quad (1)$$

where σ is the bulk effective conductivity of the rock; σ_f is the conductivity of the fluid occupying the pores; ϕ is the porosity, which is assumed to be fully saturated (i.e., identical to the volume fraction of the fluid phase); and m is the cementation exponent. The ratio of the conductivity of the pore fluid to that of the rock (or of the resistivity of the rock to that of the pore fluid) is called the formation factor ([Archie, 1942](#)).

$$F = \frac{\sigma_f}{\sigma} = \frac{\rho}{\rho_f}. \quad (2)$$

The term "formation factor" was originally used because it was approximately constant for any given formation. The formation factor varies from unity, $F = 1$, which represents the case where $\sigma = \sigma_f$ (i.e., when $\phi \rightarrow 1$) and increases as the porosity decreases, with $F \rightarrow \infty$ as $\phi \rightarrow 0$. It was Archie's experimental work that led to the empirical finding that

$$F = \phi^{-m}. \quad (3)$$

Archie called the exponent in equation 3 the cementation exponent (factor or index) because he believed it to be related to the degree of cementation of the rock fabric. In fact, the advantage that Archie's law has always had over other mixing laws such as the Hashin-Shtrikman bounds ([Hashin and Shtrikman, 1962](#)); Waff's model ([Waff, 1974](#)); the parallel, perpendicular, and random models ([Glover et al., 2000a](#)); and the modified brick-layer model ([Schilling et al., 1997](#)) is that it contains a "variable" parameter, the cementation exponent, that gives it flexibility of application ([Glover et al., 2000a](#)). Table 1

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¹Université Laval, Département de géologie et de génie géologique, Québec, Canada. E-mail: paglover@ggl.ulaval.ca.

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Table 1. Some of the most common mixing models for electrical conductivity in porous media.

Name	Conducting phases		Equation	Reference	Notes
	Min	Max			
Models without variable exponents					
Parallel model	1	Many	$\sigma_{\text{eff}} = \sum_{i=1}^n \phi_i \sigma_i$	Guéguen and Palciauskas (1994), Luo et al. (1994), Somerton (1992)	Arithmetic mean. Parallel layers of constant arbitrary thickness with conductivity σ_i arranged axially to current flow.
Perpendicular model	1	Many	$1/\sigma_{\text{eff}} = \sum_{i=1}^n \phi_i / \sigma_i$	Guéguen and Palciauskas (1994), Luo et al. (1994), Somerton (1992)	Harmonic mean. Parallel layers of constant arbitrary thickness with conductivity σ_i arranged normally to current flow.
Random model	1	Many	$\sigma_{\text{eff}} = \prod_{i=1}^n \sigma_i^{\phi_i}$	Guéguen and Palciauskas (1994), Luo et al. (1994), Somerton (1992)	Geometric mean. Arbitrary shaped and oriented volumes of conductivity σ_i distributed randomly.
Hashin-Shtrikman upper bound	2	2	$\sigma_{\text{eff}}^+ = \sigma_2 \left(1 - \frac{3(1-\phi_2)(\sigma_2 - \sigma_1)}{3\sigma_2 - \phi_2(\sigma_2 - \sigma_1)} \right)$	Hashin and Shtrikman (1962)	Commonly denoted HS+. Derived from effective medium considerations.
Hashin-Shtrikman lower bound	2	2	$\sigma_{\text{eff}}^- = \sigma_1 \left(1 + \frac{3\phi_2(\sigma_2 - \sigma_1)}{3\sigma_1 + (1-\phi_2)(\sigma_2 - \sigma_1)} \right)$	Hashin and Shtrikman (1962)	Commonly denoted HS-. Derived from effective medium considerations.
Waff model	2	2	$\sigma_{\text{eff}} = \frac{\sigma_2 + (\sigma_1 - \sigma_2)(1 - (2\phi_2/3))}{1 + (\phi_2/3)(\sigma_1/\sigma_2 - 1)}$	Waff (1974)	Based on concentric spheres of varying sizes with volume of core (fractional volume of phase 1) to volume of shell (fractional volume of phase 2) ratio constant. Functionally equivalent to HS+.
Modified brick-layer model	2	2	$\sigma_{\text{eff}} = \frac{\sigma_2(\sigma_2(\phi_1^{2/3} - 1) - \sigma_1\phi_1^{2/3})}{\sigma_1(\phi_1 - \phi_1^{2/3}) - \sigma_2(\phi_1^{2/3} - \phi_1 - 1)}$	Schilling et al. (1997)	Modified to allow validity to be extended to cover the range $0.00 \leq \phi_1 \leq 1.00$ (0%–100%). Almost coincident with HS+.
Models with variable exponents					
Lichtenecker-Rother equation	1	2	$\sigma_{\text{eff}} = (\sigma_1^{1/m}(1 - \phi_2) + \sigma_2^{1/m}\phi_2)^m$	Lichtenecker and Rother (1936) Korvin (1982)	Derived from the theory of functional equations under appropriate boundary conditions. Formally the same as Archie's law if $\phi_1 = 0$.
Lichtenecker-Rother equation (generalized)	1	Many	$\sigma_{\text{eff}} = \left(\sum_{i=1}^n \sigma_i^{1/m} \phi_i \right)^m$	Lichtenecker and Rother (1936) Korvin (1982)	Logical extension of the Lichtenecker and Rother model made in this work.
Bussian equation	2	2	$\sigma_{\text{eff}} = \sigma_2 \phi_2^m \left(\frac{1 - \sigma_1/\sigma_2}{1 - \sigma_1/\sigma_{\text{eff}}} \right)^m$	Bussian (1983)	Derived from effective medium theory.
Conventional Archie's law	1	1	$\sigma_{\text{eff}} = \sigma_2 \phi_2^m$	Archie (1942)	Derived empirically, but provable analytically for special cases.
Modified Archie's law	1	2	$\sigma_{\text{eff}} = \sigma_1(1 - \phi_2)^p + \sigma_2\phi_2^m$ where $p = \frac{\log(1 - \phi_2^m)}{\log(1 - \phi_2)}$	Glover et al. (2000a)	Derived from the conventional Archie's law by considering boundary conditions implied by geometrical constraints.
Generalized Archie's law	1	Many	$\sigma = \sum_{i=1}^n \sigma_i \phi_i^{m_i}$ where exact solution $m_j = \log(1 - \sum_{i \neq j} \phi_i^{m_i}) / \log(1 - \sum \phi_i)$ first order approximation $m_j = \sum_{i \neq j} \phi_i^{m_i} / \sum_{i \neq j} \phi_i$	This work	Derived from the conventional Archie's law by considering boundary conditions implied by geometrical constraints.

summarizes the main electrical conductivity mixing models that are currently available.

It is important to note that Archie's law was derived from empirical observations for a relatively small number and type of rocks and for a relatively small range of fluid conductivities and porosities (Archie, 1942). Strictly speaking, Archie's law should not be used outside of these ranges. However, it has been commonly used outside of these ranges for over 60 years with a great degree of success.

In 1936, [Lichtenecker and Rother \(1936\)](#) derived a relationship for the calculation of the effective value of a physical property of a heterogeneous medium A that contains n distinct phases each having a value of the physical property A_i and each having a volume fraction ϕ_i .

$$A = \left(\sum_{i=1}^n \phi_i A_i^b \right)^{1/b} \quad \text{when } b \neq 0, \quad (4)$$

and

$$A = \exp \left(\sum_{i=1}^n \phi_i \ln A_i \right) \quad \text{when } b = 0. \quad (5)$$

By writing $m = 1/b$ and applying equation 4 for the conductivity of a heterogeneous porous medium, it is possible to obtain

$$\sigma = (\phi_1 \sigma_1^{1/m} + \phi_2 \sigma_2^{1/m})^m \quad \text{for } m \neq \infty. \quad (6)$$

For a sedimentary rock with an insulating matrix ($\sigma_1 = 0$) and a porosity $\phi_2 = \phi$, which is completely saturated with a fluid of conductivity $\sigma_1 = \sigma_f$, equation 6 becomes

$$\sigma = \sigma_f \phi^m, \quad (7)$$

which amounts to a direct proof of Archie's law and relates the cementation exponent to the Lichtenecker and Rother mixing coefficient.

The range of values for the cementation exponent is relatively small. A value of $m = 1$ is not observed for real rocks and represents a porous medium composed of a bundle of capillary tubes that cross the sample in a straight line. Rocks with a low porosity but a well-developed fracture network sometimes have cementation exponents that approach unity because the network has flow paths that are fairly direct. A cementation exponent equal to 1.5 represents the analytical solution for the case in which the rock is composed of perfect spheres ([Sen et al., 1981](#); [Mendelson and Cohen, 1982](#)). Most porous arenaceous sediments have cementation exponents between 1.5 and 2.5 ([Glover et al., 1997](#)). Values higher than 2.5 and as high as 3 are usually found in carbonates in which the pore space is less well connected ([Tiab and Donaldson, 2004](#)). In general, the value of the cementation exponent increases as the degree of connectedness of the pore network diminishes. The concept of connectedness is fully defined in the next section and in [Glover \(2009\)](#).

Archie's law does not take account of surface conduction. In clean rocks, if the concentration of the pore fluid is greater than approximately 0.01 mol/L, it does not matter because the surface conduction is small compared with that provided by the pore fluid. However, it was recognized early on that formations that contain significant amounts of clay minerals may have a significant surface conduction even if the pore fluid is relatively saline ([Glover et al., 2000a](#)). Several empirical adjustments have been proposed for this scenario and

are commonly used by the oil industry. One of the most important is probably that of [Waxman and Smits \(1968\)](#),

$$\sigma = \frac{1}{F^*} (\sigma_f + B Q_v), \quad (8)$$

where F^* is the shaly sand formation factor and the additional term includes the factor B , which is the average mobility of the counterions close to the grain surface ($S \text{ m}^2/\text{meq}$), and Q_v , which is the ionic concentration per unit pore volume (meq/m^3), in which 1 milliequivalent is a measure of ionic concentration. Another important model for shaly sands has been the Dual-Water model ([Clavier et al., 1984](#)). It should be noted that these models represent a method of empirically compensating for the surface conduction rather than representing conductivity mixing laws in their own right. Moreover, as pointed out by [Devarajan et al. \(2006\)](#), these models are not explicit in their predictions of electrical conductivity with respect to rock structure, spatial fluid distribution in the pore space, wettability, or clay mineral distribution.

Even when it is modified to take surface conduction into account, the classical Archie's law is only applicable to the scenario in which there is a nonconductive matrix and in which the only conducting phase is a liquid (or solid) that completely saturates the pore space. It is not applicable if there are two conducting phases or if the conducting phase does not completely fill the pore space.

Archie addressed the second of these issues by deriving a second Archie's law that describes how the resistivity of a partially saturated rock varies with water saturation. He did not address the problem of having two or more conducting phases.

In 2000, [Glover et al. \(2000a\)](#) published a modified Archie's law for a rock with two conducting phases in response to the need for a conductivity mixing model with a variable mixing parameter when there was a conductive fluid occupying a matrix that was sufficiently hot to also be considered conductive.

The modified Archie's law takes the form

$$\sigma = \sigma_1 \phi_1^p + \sigma_2 \phi_2^m, \quad (9)$$

where σ is the bulk effective conductivity of the rock, σ_1 and σ_2 are the conductivities of the two conductive phases, ϕ_1 and ϕ_2 are the volume fractions of the two conductive phases, and p and m are the exponents of each phase. By convention, when one of the phases is a conductive fluid occupying the pore space, phase 2 is used to represent it so that ϕ_2 is the porosity of the rock, m is the cementation exponent, and σ_2 is the conductivity of the fluid just as it was in the traditional Archie's law. If either the matrix is nonconducting (i.e., $\sigma_1 = 0$) or the porosity is 100% (i.e., $\phi_1 = 0$), the modified Archie's law (equation 9) collapses to the classical Archie's law (equation 1).

If an electrolyte saturates a rock matrix and the whole matrix is conductive, equation 9 becomes

$$\sigma = \sigma_1 (1 - \phi_2)^p + \sigma_2 \phi_2^m, \quad (10)$$

with $\sigma_1 \neq 0$. The matrix exponent p can be calculated from the porosity and cementation exponent m using a relationship that takes into consideration the 3D topological arrangement of the two phases,

$$p = \frac{\ln(1 - \phi_2^m)}{\ln(1 - \phi_2)}. \quad (11)$$

It should be noted that for a typical rock with a typical porosity and

cementation exponent, the value of the p exponent will be less than unity. For example, if the porosity $\phi_2 = 0.1$ and $m = 2$, then $p = 0.095$. The low value represents the great degree of connectivity that the matrix phase enjoys. Thus, exponent values less than unity do have a physical interpretation. If such a rock is at low temperatures, the overall conductivity of the rock will be controlled by the pore fluid because the pore fluid will generally have a conductivity much greater than the matrix although it has a low connectedness. However, at higher temperatures (or at low temperatures if the matrix contains sufficient conductive minerals) the matrix controls the overall conductivity of the rock because it has a much higher connectedness. If the porosity $\phi_2 = 0.1$, $m = 2$, and the conductivities of the fluid and the matrix are the same, it is a trivial result that $\sigma = \sigma_1 = \sigma_2$; however, 99% of the conductivity is contributed by the matrix, whereas only 1% is contributed by the pore fluid.

A summary of electrical conductivity mixing models is given as Table 1. A comparison of many of these models with the modified Archie's law for two conducting phases is given in Glover et al. (2000a).

The two-phase Archie's law has been used successfully in the modeling of enhanced porosity concretes that have significant matrix conductivity (Neithalath et al., 2006; Neithalath, 2007), rock melt fractions in which the temperature is high enough to induce a conductivity in an otherwise low-conductivity rock matrix (Glover et al., 2000b), the distribution of crustal fluids (Mishina, 2009), the electrical conductivity of partially crystallized basaltic samples (Gaillard and Marziano, 2005), the prediction of a possible magma chamber beneath Mount Vesuvius (Pichavant et al., 2007), and even in the electrical treatment of food materials for preservation (Lebovka et al., 2002) and the design of membranes for fuel cells (Munakata et al., 2008).

The purpose of this paper is to extend Archie's law to its most general form; that for n -phases, any of which may or may not be conductive.

CONNECTEDNESS AND CONNECTIVITY

Each of the n phases that occupy a 3D rock must share the same total space. Hence, an increase in the connectedness of one of the phases must lead to a reduction in the connectedness of at least one of the other phases. Here we deliberately use the phrase "connectedness" instead of "connectivity" because they are two different entities.

The connectedness of a porous medium G was defined by Glover (2009) as the physical availability of pathways for transport and mathematically as the ratio of the conductivity of the rock to the conductivity of the pore fluid (i.e., the inverse of the formation resistivity factor)

$$G \equiv \frac{\sigma}{\sigma_f} = \frac{1}{F} = \phi^m. \quad (12)$$

Hence, the connectedness of a given phase is a physical measure of the availability of pathways for conduction through that phase that is based on the ratio of the measured conductivity to the maximum conductivity possible with that phase (i.e., when that phase occupies the whole sample). This implies that the connectedness of a sample composed of a single phase is unity.

By contrast, the connectivity is defined as the measure of how the pore space is arranged. The connectivity is given by

$$\chi = \phi^{m-1} \quad (13)$$

and depends on the porosity and the cementation exponent m . It should be noted that the connectedness is also given by

$$G = \phi\chi, \quad (14)$$

and it is clear that the connectedness depends on the amount of pore space (given by the porosity) and the arrangement of that pore space (given by the connectivity).

AN ARCHIE'S LAW FOR N -PHASES

The porosity of a rock is defined as the fractional amount of pore space. The porosity represents just one phase of many that are distributed within the rock. The sum of the fractions of all of the phases present must therefore always equal unity

$$\sum_{i=1}^n \phi_i = 1, \quad (15)$$

where there are n phases.

Archie's law can be expanded in the following form:

$$\begin{aligned} \sigma &= \sigma_1 \phi_1^{m_1} + \sigma_2 \phi_2^{m_2} + \sigma_3 \phi_3^{m_3} + \dots + g(\sigma_i, \Theta_k) \\ &= \sum_i^n \sigma_i \phi_i^{m_i} + g(\sigma_i, \Theta_{ij}), \end{aligned} \quad (16)$$

where each phase is represented by a term of the form $\sigma_i \phi_i^{m_i}$, and the function $g(\sigma_i, \Theta_{ij})$ is the sum of the Stieltjes integrals that represent the interactions between the phases and Θ_{ij} represents the resonance density functions between each pair of phases. The Stieltjes integral between any pair of phases is given as (e.g., Glover et al., 2000a)

$$f(\sigma_i, \sigma_j, \Theta_{ij}) = \int_0^\infty \left(\frac{\Theta_{ij}(y)}{(1/\sigma_i + y/\sigma_j)} \right) dy. \quad (17)$$

In full, equation 16 becomes

$$\sigma = \sum_i^n \sigma_i \phi_i^{m_i} + \sum_{i \neq j} \int_0^\infty \left(\frac{\Theta_{ij}(y)}{(1/\sigma_i + y/\sigma_j)} \right) dy, \quad (18)$$

which involves three independent terms for each of the n phases (conductivity, volume fraction, and phase exponent) as well as $n(n-1)$ resonance density functions. It was discussed in Glover et al. (2000a) that little was known about the properties of the Stieltjes integral and that it is commonly regarded to be negligible as a first-order simplification. We follow the same approach in this paper. Equation 18 then becomes

$$\sigma = \sum_i^n \sigma_i \phi_i^{m_i}, \quad (19)$$

with

$$\sum_{i \neq j} \int_0^{\infty} \left(\frac{\Theta_{ij}(y)}{(1/\sigma_i + y/\sigma_j)} \right) dy = 0, \quad (20)$$

provided that either the Stieltjes integrals are negligible or that their matrix is symmetric (i.e., they cancel each other out).

In equation 19, each of the phases has an electrical conductivity σ_i and a volume fraction ϕ_i . Because each phase is distributed differently in the porous medium, each also has its own individual connectedness $G_i = \phi_i^{m_i}$ and connectivity $\chi_i = \phi_i^{m_i-1}$; hence, each will have its own phase exponent m_i . It should be noted that equation 19 can be written as $\sigma = \sum_i^n \sigma_{ci}$ where σ_{ci} are the individual conductivity contributions from each phase calculated in isolation. Hence, equation 19 contains the implicit assumption that the sum of the interactions between the phase components is zero, which is a restatement of equation 20.

Because there is no physical meaning in the word ‘‘cementation’’ for the i th phase of a complex multiphase mixture, from this point forward the term ‘‘phase exponents’’ or just ‘‘exponents’’ will be used when referring to the exponents of the generalized model and ‘‘cementation exponent’’ will be reserved for referring to the exponent in the classical Archie's law.

In the generalized law, the phase exponents can take any value from zero to infinity. Values less than unity represent a phase with an extremely high degree of connectedness, such as that we would recognize as belonging to the solid matrix of a rock. Connectedness decreases as the phase exponent increases. Phase exponents of approximately 2 represent the degree of connectedness that one might find associated with the pore network in sandstone, whereas higher values represent lower connectedness such as that in a vuggy limestone. Higher phase exponents would tend to be related to lower phase fractions, although this form of the generalized law does not impose such a restriction.

Although equation 19 seems like an intuitive extension of the classical Archie's law, it is important to point out some subtle but important differences in the physical meaning of the exponents. Examining the two Archie exponents and then the generalized law exponent, we find that

- 1) The classical Archie cementation exponent m is the exponent applied to the volume fraction of pores (porosity) in the rock assuming the pores to be full of a single phase (water) with a characteristic conductivity.
- 2) The classical Archie saturation exponent n is the exponent applied to the water saturation, which is not the fraction of the water in the rock but of that in the pores; hence, it is the exponent applied to the volume fraction of a volume fraction of the rock.
- 3) Each of the exponents in the generalized law m_i is the exponent applied to the volume fraction of that phase in the rock assuming that phase to have a characteristic conductivity.

It is clear that the classical and generalized laws share the property that the exponents modify the volume fraction of the relevant phase with respect to the total volume of the rock. However, the exponents on the generalized law differ from the classical exponent in that some of them have values that are not measurable because the phase to which they refer has a negligible conductivity. Despite this, each phase has a well-defined exponent providing (1) it has a non-zero volume fraction and (2) the other phases are well defined.

The classical Archie's law can be derived from the generalized

law by considering a three-phase system in which equation 19 can be rewritten explicitly as

$$\sigma = \sigma_1 \phi_1^{m_1} + \sigma_2 \phi_2^{m_2} + \sigma_3 \phi_3^{m_3} = \sigma_m \phi_m^{m_m} + \sigma_g \phi_g^{m_g} + \sigma_f \phi_f^{m_f}, \quad (21)$$

where phases 1, 2, and 3 have been assigned to mineral matrix, gas, and pore fluid, respectively.

Assuming that the mineral is not conductive, $\sigma_m = 0$, and the pore space is fully saturated with water $\phi_g = 0$, equation 21 becomes

$$\sigma = \sigma_f \phi_f^{m_f}. \quad (22)$$

Note that the gas phase can take any conductivity in this analysis.

Because $\phi = \phi_g + \phi_f$ and $\phi_g = 0$, we have $\phi = \phi_f$ and equation 22 becomes the classical Archie's law

$$\sigma = \sigma_f \phi^m. \quad (23)$$

This is a trivial result analytically, yet important for two reasons. First, it shows that the classical Archie's law can be generated from the generalized law. Second, it shows that each of the exponents in the generalized law share the same physical meaning as those in the classical Archie's law because the same result is possible by setting any combination of two phases to zero conductivity and noting that the same logic applies to n phases.

It is important to state that all of the results and theoretical development in this paper depend upon equation 20 being true for porous media. We have stated but not proven that the hypothesis that the sum of the Stieltjes integrals for n interacting phases in a porous medium is zero because of its nontrivial nature. However, it should be acknowledged that, since its initial proposal (Bergman, 1978; 1980; 1982; McPhedran et al., 1982; McPhedran and Milton, 1990; Milton, 1980; 1981), the use of a Stieltjes approach has been developed (e.g., Zhang and Cherkaev, 2008; 2009; Cherkaev and Zhang, 2003) and applied particularly to the calculation of the frequency-dependent dielectric permittivity of multiphase mixtures (Zhang and Cherkaev, 2008). Although I have not found any application to mixtures of electrical conducting phases, the apparent success of this approach leads me to be hopeful that further research into the Stieltjes approach might (1) show that equation 20 is exactly or approximately true or (2) provide an expression for the interaction between the phases that will improve the model. The use of the Stieltjes approach to calculate the frequency-dependent dielectric permittivity of mixtures (Zhang and Cherkaev, 2009) holds the hope that it might also be used to calculate the frequency-dependent electrical conductivity of multiphase systems.

PRINCIPLE OF CONSERVATION OF CONNECTEDNESS

We have already stated in equation 15 the classical result that the sum of the volume fractions of all of the phases in a porous medium must equal unity. Now we consider an analogous result for the connectedness. We have already shown that the connectedness of a system that contains only one phase is unity as a result of equation 12. Intuitively, it seems reasonable that as one or more phases increase their connectedness, other phases must lose connectedness. This idea leads to the hypothesis that there is a fixed maximum amount of connectedness possible in a 3D sample. It is possible to distribute it between whichever phases are present in an infinite number of ways,

but the total connectedness must not exceed some maximum value that is defined by the topology of the 3D space.

Equation 19 must be valid for all combinations of the conductivity of the phases that are present. Hence, we can use the special case where $\sigma_i = \sigma$ for any value of i to generate the relationship

$$\sum_i^n \phi_i^{m_i} = \sum_i^n G_i = 1. \quad (24)$$

Now it is possible to say not only that the sum of the volume fractions of the phases composing a 3D medium is equal to unity, but so is the sum of the connectednesses of those phases. In other words, equation 24 is a statement of the principle of conservation of connectedness. In a multiphase system, the decrease in connectedness of one phase is balanced by increases in the connectedness of the other phases such that the overall connectedness remains unity.

CALCULATION OF PHASE EXPONENTS

In the application of equation 19, one assumes that the conductivity of the individual phases and their fractions are known. The question arises whether it is possible to find a relationship for the calculation of the phase exponents along the same lines as that in Glover et al. (2000a). Equation 19 is symmetric in the sense that no phase holds a special place in the relationship. Therefore, it can be rewritten as

$$\sum_{i \neq j} \phi_i^{m_i} + \left(1 - \sum_{i \neq j} \phi_i\right)^{m_j} = 1, \quad (25)$$

and therefore

$$\left(1 - \sum_{i \neq j} \phi_i^{m_i}\right) = \left(1 - \sum_{i \neq j} \phi_i\right)^{m_j}; \quad (26)$$

hence, we arrive at

$$m_j = \log\left(1 - \sum_{i \neq j} \phi_i^{m_i}\right) / \log\left(1 - \sum_{i \neq j} \phi_i\right). \quad (27)$$

which is the exact solution of equation 26 for the phase exponent of the j th phase in an ensemble of n phases.

Provided that the sum of all of the phases except the j th is significantly less than unity (i.e., $\sum_{i \neq j} \phi_i \ll 1$), it is possible to expand the right-hand side of equation 26 in the form

$$(1+x)^a \approx 1 + \frac{ax}{1!} + \frac{a(a-1)x^2}{2!} + \dots, \quad (28)$$

from which we find that

$$m_j = \frac{\sum_{i \neq j} \phi_i^{m_i}}{\sum_{i \neq j} \phi_i} = \frac{\sum_{i \neq j} G_i}{\sum_{i \neq j} \phi_i} = \frac{\sum_{i \neq j} \phi_i \chi_i}{(1 - \phi_j)}. \quad (29)$$

Hence, the phase exponent of a particular phase is the sum of the connectednesses of all of the other phases divided by the sum of their fractions.

Because $m_j = \log(\phi_j^{m_j}) / \log(\phi_j) = \log(G_j) / \log(\phi_j)$, equation 29 may also be stated as

$$\frac{\log(\phi_j^{m_j})}{\log(\phi_j)} = \frac{\sum_{i \neq j} \phi_i^{m_i}}{\sum_{i \neq j} \phi_i}, \quad \text{and} \quad (30)$$

$$\frac{\log(G_j)}{\log(\phi_j)} = \frac{\sum_{i \neq j} G_i}{\sum_{i \neq j} \phi_i}. \quad (31)$$

Although these results are attractively elegant, they are only a first-order approximation of equation 26 that is valid for $\sum_{i \neq j} \phi_i \ll 1$.

For two phases, we can easily also derive a second-order approximation of equation 26 using the expansion of the sum given by equation 28. Equation 26 can be written as

$$1 - \sum_{i \neq j} G_i = \left(1 - \sum_{i \neq j} \phi_i\right)^{m_j}, \quad (32)$$

which for two phases becomes

$$1 - G_1 = (1 - \phi_1)^{m_2}. \quad (33)$$

Application of the second-order approximation of the expansion equation 28 gives

$$\left(-\frac{\phi_1^2}{2}\right)m_2^2 + \left(\phi_1 + \frac{\phi_1^2}{2}\right)m_2 - \phi_1^{m_2} = 0, \quad (34)$$

from which the roots m_2 can be calculated

$$m_2 = \frac{-\left(\phi_1 + \frac{\phi_1^2}{2}\right) \pm \left(\left(\phi_1 + \frac{\phi_1^2}{2}\right)^2 - 4\left(-\frac{\phi_1^2}{2}\right)(-\phi_1^{m_2})\right)^{1/2}}{-\phi_1^2} \quad (35)$$

and

$$m_2 = \frac{-(4\phi_1 + 2\phi_1^2) \pm (4\phi_1^2 + 4\phi_1^3 + \phi_1^4 - 8\phi_1^2\phi_1^{m_2})^{1/2}}{-4\phi_1^2}. \quad (36)$$

It is the positive root that provides the physical solution.

PHASE AND SATURATION EXPONENTS

We start once more by writing equation 19 explicitly for three defined phases as in equation 21. This time, we assume that neither the mineral nor the gas is conductive, i.e., $\sigma_m = 0$ and $\sigma_g = 0$, but we allow the pore space to be partially saturated with water such that $\phi_g \neq 0$. Equation 21 now becomes

$$\sigma = \sigma_f \phi_f^{m_f}. \quad (37)$$

This is the same equation as equation 22 but is valid for a different set of scenarios:

- 1) Equation 37 is valid for $\phi_g \neq 0$, whereas equation 22 is valid only for $\phi_g = 0$.

2) Equation 37 requires that $\sigma_g = 0$ but equation 22 does not.

The distinction may be deemed trivial, but it is formally necessary for the analysis.

Because $\phi_g \neq 0$, the pore space is partially saturated with gas and partially saturated with water. It is possible to write

$$\begin{aligned} \phi_f &= \phi S_w \quad \text{and} \\ \phi_g &= \phi(1 - S_w) \quad \text{where} \\ S_w &= \frac{\phi_f}{\phi} \end{aligned} \quad (38)$$

Equation 37 can then be rewritten as

$$\sigma = \sigma_f \phi_f^{m_f} = \sigma_f (\phi S_w)^{m_f} = \sigma_f \phi^{m_f} S_w^{m_f}. \quad (39)$$

Comparison with the classical second Archie's law, which can be written as (Tiab and Donaldson, 2004)

$$\sigma = \sigma_f \phi^m S_w^n, \quad (40)$$

shows structural similarity. However, equation 39 is expressed relative to the phase volume fraction of the fluid in the rock whereas the classical second Archie's law is expressed relative to the porosity of the rock. Note also that there is no constraint on the value that the saturation exponent n can have at this stage.

By setting 39 equal to 40 and invoking equation 12 we can write

$$\phi^m = \phi^{m_f} S_w^{(m_f - n_f)}, \quad (41)$$

$$G_{\text{pore}} = G_f S_w^{-n_f}, \quad (42)$$

$$G_f = G_{\text{pore}} S_w^{n_f}, \quad (43)$$

$$G_g = G_{\text{pore}} S_g^{n_g}, \quad (44)$$

and

$$G_i = G_{\text{pore}} S_i^{n_i}. \quad (45)$$

In equations 41–45, we have recognized that (1) the classical Archie saturation exponent refers to saturation with water and is hence renamed as n_i , and (2) the symmetry of the system allows us to write equivalent equations for the gas phase (and any other phase that may be present), with a gas saturation exponent n_g that acts on the gas saturation S_g , where

$$\begin{aligned} \phi_g &= \phi S_g \quad \text{and} \\ \phi_f &= \phi(1 - S_g) \quad \text{where} \\ S_g &= \frac{\phi_g}{\phi} \end{aligned} \quad (46)$$

Equation 42 states that the connectedness of the pore volume G_{pore} (no matter what material occupies it) is equal to the connectedness of the water phase G_f multiplied by a factor that depends on the fractional water saturation of the pore space S_w . Rearrangement of equation 42 gives equations 43 and 44, which describe the relationships between the connectedness of each phase and the connectedness of the volume that the phases occupy. If the two phases occupy the pore space exclusively (i.e., $S_w + S_g = 1$, or $\phi_f + \phi_g = \phi$), the sum of their connectednesses is constant $G_f + G_g = G_{\text{pore}}$, which is less than

unity because there is a finite and non-negligible connectedness associated with the (here nonconducting) mineral phase. We have generalized equations 43 and 44 to give the equation 45, which is true for any number of phases occupying the pore space.

Note that equations 43–45 are an intuitive extension of the classical Archie's law. We can write Archie's law using our new nomenclature as

$$\sigma = \sigma_f \phi^m S_w^{n_f}, \quad (47)$$

which is the same as

$$G_f = \phi^m S_w^{n_f} = G_{\text{pore}} S_w^{n_f}. \quad (48)$$

All one needs to do is replace G_f with G_i , n_f with n_i , and S_w with S_i to obtain equations 42–44. Hence, the new approach is also consistent with Archie's second law.

Equation 45 implies that the term $S_i^{n_i}$ is always less than or equal to unity (i.e., $S_i^{n_i} \leq 1$), which constrains the values of the saturation exponents n_i to be positive (in the range 0 to $+\infty$).

If we combine equation 45 with equation 24, we obtain

$$1 = \sum_{i=1}^n G_i = G_m + \sum_{i=1}^{n-1} G_i = G_m + \sum_{i=1}^{n-1} G_{\text{pore}} S_i^{n_i}, \quad (49)$$

where the n th phase is the mineral matrix and $G_m + G_{\text{pore}} = 1$, allowing us to write

$$\sum_{i=2}^n S_i^{n_i} = 1. \quad (50)$$

Hence, the application of the generalized model within an $n - 1$ subset of the n phases in the multiphase system provides a form of the generalized model that is expressed relative to the saturations S_i of each of the phases within the subset volume with the saturation exponent for each phase replacing the phase exponent. Here $S_i = \phi_i / \sum_{i=1}^{n-1} \phi_i$, which is a generalized form of equations 38 and 46.

We can map equation 24 to equation 50 and find that

$$\begin{aligned} \phi_i &\leftrightarrow S_i \\ m_i &\leftrightarrow n_i. \end{aligned} \quad (51)$$

This is equivalent to saying that suppose we take a multiphase medium described by equation 24 and we dissolve, discount, or otherwise remove one phase, the behavior of the other phases can be written as equation 50 relative to the original medium or by using equation 24 and acting as if the removed phase never existed. Hence, equations 24 and 50 are formally equivalent but are valid in two different frames of reference. The frame of reference for equation 24 is that where the phases being considered compose the whole multiphase medium. The frame of reference of equation 50 is that where the phases being considered compose a subset of a multiphase medium with at least one more phase than those being considered.

Comparison of equations 24 and 50 is remarkable in that it shows that the generalized Archie's law as formulated in this paper is truly general in that it leads to (1) the classical Archie's law for 100% water saturation and (2) the classical Archie's second law for partial saturation. The generalized Archie's law provides a deeper underlying symmetry from which the classical laws can be derived as special cases and in which the concept of connectedness is embodied. Equation 24 describes the conservation of connectedness in an n -phase medium and is expressed relative to volume fractions, whereas

equation 50 describes the same conservation of connectedness in an $n - 1$ phase medium and is expressed relative to fractional volume saturations instead. Although one could distinguish between the phase volume connectedness $G_i = \phi_i^{m_i}$ and, say, the phase saturation connectedness $H_i = S_i^{m_i}$ depending on in which regime one wants to work, the two are essentially interchangeable and depend only on the frame of reference being used.

One might even envisage a process of “phase erosion” being carried out recursively. In this process, equation 24 would be applied to a given n -phase medium, and equation 50 would be used to describe the behavior of an $n - 1$ phase subvolume of it. The relationships in equation 51 would then be used to describe the $n - 1$ phase subvolume as a complete multiphase medium in its own right (i.e., discounting the first phase), to which equation 24 now applies, with the new phase exponent being the previous saturation exponent. Equation 50 could then be used again on an $n - 2$ phase subset by discounting a further phase, and the procedure would then be carried further, recursively. The implications of and applications for this procedure are still to be worked out.

Although further work will need to be done to ascertain why real rocks seem to prefer saturation exponents near 2, which may be linked to the classical exponent value close to the percolation threshold (Montaron, 2009), we now have a theoretical link between the phase (cementation) exponents for a given set of phases and their saturation exponents.

PERCOLATION

It is interesting to consider the role of percolation effects within the generalized model. In percolation theory, the bulk value of a given transport property is only perturbed by the presence of a given phase with a well-defined phase conductivity after a certain phase volume fraction has been attained. This critical volume fraction is called the percolation threshold.

This works well for a two-phase system when one phase is non-conductive. The Kirkpatrick effective medium theory model, which was the first to consider percolation effects in porous media (Kirkpatrick, 1973), is in good agreement with Monte Carlo simulations of conductivity for a random resistor network on a simple 3D cubic grid representing a bond and site model (Montaron, 2009). The Kirkpatrick model has a percolation threshold of 0.342, which compares with the theoretical value for a two-phase cubic block model of 0.3116 (Montaron, 2009). For such a system (one nonconducting phase and one conducting) the conductivity depends on the conductivity of the conducting phase, its volume fraction, and how connected it is. It is intuitive that there will exist a phase volume fraction below which the conducting phase is not connected and the bulk conductivity will be zero.

What happens then, when we introduce another conducting phase that is in electrical contact with the first phase at certain points? The percolation idea is not applicable to individual phases anymore because current is shared between the two phases as it crosses the sample. Perhaps we can apply percolation ideas to the combined two conducting phase system, but we would have to take into account the variable conductivity of the phase combination.

At first sight, it might be apparently reasonable to ask what happens when all conductive phases have volume fractions smaller than the percolation threshold. However, the question itself presupposes that all transport phenomena in rocks operate within a fixed and inert (noncontributing) mineral framework. This is an assumption that

comes from our long habit of using the classical Archie’s law. In the generalized model, the mineral framework is one (or more) of the phases. In this conceptual approach, it is not possible that all conductive phases have volume fractions smaller than the percolation threshold because if all but one have phases less than their percolation threshold, the remaining phase, by definition, is extremely well connected. We could define individual percolation thresholds for each of n phases in isolation by considering all other phases to have zero conductivity, but the procedure would be academic — as soon as two (or more) of such phases are combined in a real sample, the interchange of current between the phases makes the calculated percolation thresholds meaningless.

It becomes clear that if we have more than two phases in which each has a non-zero conductivity, the applicability of the percolation ideas becomes unclear. Furthermore, it may be that the statement that $\sum_i^p G_i = 1$ (i.e., equation 24) in the generalized model contains enough information to make the explicit inclusion of percolation effects unnecessary. This is a hypothesis that will need to be tested robustly before it can be considered to be valid.

EXAMPLE OF THE USE OF THE GENERALIZED LAW

Let us assume that we have an arbitrary 3D medium with four distinct phases as set out in Table 2. In this example, phases 1, 2, and 3 have well-defined fractions, conductivities, and phase exponents from which their connectednesses and connectivities can also be calculated. Phase 4, although having a well-defined electrical conductivity, has a volume fraction, phase exponent, connectedness, and connectivity that depend on the other three phases. In the table, the defined values are shown in bold type, while the values calculated from the equations developed in this paper are shown in normal type.

In this example, phase 1 represents the fluid-filled pore space, with a phase volume fraction of $\phi_1 = 0.1$, a phase exponent of $m_1 = 2$, and has been filled with a hypothetical electrolyte with a conductivity of $\sigma_1 = 10$ S/m. These values are similar to that which one might use in an application of the classical Archie’s law.

Phase 2 represents the electrical double layer. This has been assigned an arbitrary conductivity of $\sigma_2 = 50$ S/m and a phase exponent of $m_2 = 2$ (equal to that of the pore fluid). There is no reason why phase 2 should not have a different phase factor from that of the phase 1; however, it is likely to be similar because the complexities of the pore network and the surface of that pore network are likely to be similar. The electrical double layer (phase 2) has been assigned a phase volume fraction of $\phi_2 = 0.05$, which implies that the total porosity of the rock is $\phi = 0.15$, but the mobile pore fluid has a fraction between 0.10 and 0.15. There are no fundamental theoretical difficulties that arise from considering the electrical double layer volumetrically as in this example. However, if the reader finds it awkward, he/she could imagine phase 2 as a conductive mineral coating instead.

Phase 3 represents that part of the rock matrix that is iron pyrites, FeS_2 . A high-volume fraction ($\phi_3 = 0.2$) has been assigned arbitrarily to phase 3 together with a phase conductivity of $\sigma_3 = 100$ S/m (Lide, 2009). This phase was considered to be dispersed throughout the rock with a low connectivity; hence, it has been assigned a higher phase exponent than phases 1 and 2. A phase exponent value of $m_3 = 4$ was used initially.

The remainder of the rock is composed of quartz for which an arbitrary and very low conductivity has been assigned (σ_4

$= 10^{-20}$ S/m). Neither the fraction nor the phase exponent of the quartz phase has been assigned. However, they can be calculated from the equations developed in this paper.

In the first part of Table 2, we can see that the phase exponent of the quartz phase is $m_4 = 0.03296$ using equation 27 (exact solution)

and $m_4 = 0.0403$ using equation 29 (first-order approximation). In both cases, this is less than unity because the quartz phase is by far the best connected phase of all of those present although it does not contribute to the overall conductivity of the rock. This is demonstrated by its calculated connectedness $G_4 = 0.9859$ and 0.9828 and its

Table 2. Example using the generalized law.

Phase i (-)	Type (-)	Fraction ϕ_i (-)	Phase conductivity σ_i (S/m)	Phase (cementation) exponent m_i (-)	Connectedness G_{ig} (-)	Connectivity χ_i (-)	Conductivity contribution σ_{ci} (S/m)	Percent contribution (-)
Scenario 1 — base case								
Exact solution (equation 27)								
1	Fluid	0.1	10	2	0.01	0.1	0.1	25.97
2	EDL	0.05	50	2	0.0025	0.05	0.125	32.47
3	FeS ₂	0.35	100	4	0.0016	0.008	0.16	41.56
4	Quartz	0.50	10⁻²⁰	0.03296	0.9859	1.517	9.86×10^{-21}	2.56×10^{-18}
Sum		1			1		0.385	
First approximation (equation 29)								
1	Fluid	0.1	10	2	0.01	0.1	0.1	25.97
2	EDL	0.05	50	2	0.0025	0.05	0.125	32.47
3	FeS ₂	0.35	100	4	0.0016	0.008	0.16	41.56
4	Quartz	0.50	10⁻²⁰	0.0403	0.9828	1.512	9.83×10^{-21}	2.55×10^{-18}
Sum		1			0.9969		0.385	
Scenario 2 — increasing the phase 3 volume fraction, $\phi_3 = 0.35\%$								
Exact solution (equation 27)								
1	Fluid	0.1	10	2	0.01	0.1	0.1	5.79
2	EDL	0.05	50	2	0.0025	0.05	0.125	7.24
3	FeS ₂	0.35	100	4	0.0150	0.0429	1.500	86.96
4	Quartz	0.50	10⁻²⁰	0.0402	0.9725	1.9449	9.724×10^{-21}	5.6356×10^{-19}
Sum		1			1		1.726	
First approximation (equation 29)								
1	Fluid	0.1	10	2	0.01	0.1	0.1	5.79
2	EDL	0.05	50	2	0.0025	0.05	0.125	7.24
3	FeS ₂	0.35	100	4	0.0150	0.0429	1.500	86.96
4	Quartz	0.50	10⁻²⁰	0.0550	0.9625	1.9252	9.6259×10^{-21}	5.5782×10^{-19}
Sum		1			0.9901		1.726	
Scenario 3 — increasing the phase 3 volume fraction to $\phi_3 = 0.35$ and reducing m_3 to $m_3 = 3$								
Exact solution (equation 27)								
1	Fluid	0.1	10	2	0.01	0.1	0.1	2.22
2	EDL	0.05	50	2	0.0025	0.05	0.125	2.77
3	FeS ₂	0.35	100	3	0.0429	0.1225	4.288	95.01
4	Quartz	0.50	10⁻²⁰	0.0822	0.9446	1.8892	9.4463×10^{-21}	2.0934×10^{-19}
Sum		1			1		4.5125	
First approximation (equation 29)								
1	Fluid	0.1	10	2	0.01	0.1	0.1	2.22
2	EDL	0.05	50	2	0.0025	0.05	0.125	2.77
3	FeS ₂	0.35	100	3	0.0429	0.1225	4.288	95.01
4	Quartz	0.50	10⁻²⁰	0.1108	0.9261	1.8522	9.2611×10^{-21}	2.0523×10^{-19}
Sum		1			0.9815		4.512	

connectivity $\chi_4 = 1.517$ and 1.512 for the exact solution and the first-order approximation, respectively. It should be noted that the sum of the connectednesses of all of the phases is exactly unity when using equation 27, which is the value predicted theoretically. The sum of all of the connectednesses is 0.9969 if the first-order approximation is used, which is close to unity and shows that the first-order approximation is a reasonable solution in this example. The last two columns of Table 2 show the conductivity contributions (σ_{ci}) from each phase as an absolute value and as a percentage. The calculated bulk effective conductivity is $\sigma = 0.385$ S/m and it is clear that there are significant contributions from phases 1, 2, and 3 (25.97%, 32.47%, and 41.56%, respectively). However, the conductivity contribution from phase 4 is negligible despite phase 4 having the greater fraction, connectedness, and connectivity. In this example, each of phases 1-3 contribute significantly to the conductivity of the rock despite some having a low connectedness (i.e., phase 3), and others, such as phase 1, having a relatively low conductivity.

If we increase the volume fraction of the iron pyrites to 35% ($\phi_3 = 0.35$) at the expense of the quartz, which then has a volume fraction of 50% ($\phi_4 = 0.50$), (Table 2, second part) we can recalculate the phase exponent of the fourth phase, obtaining $m_4 = 0.0402$ and 0.0550 using the exact solution (equation 27) and the first-order approximation (equation 29), respectively. This is still considerably less than unity because the quartz phase remains by far the best connected phase of all of those present as shown by its calculated connectedness $G_4 = 0.9725$ and 0.9625 and its connectivity $\chi_4 = 1.945$ and 1.926 for the exact solution and the first-order approximation, respectively. It should be noted that the sum of all of the connectednesses remains exactly unity when using equation 27, as before, and is 0.9901 if the first-order approximation is used, which is also close to unity. It is clear that there are not insignificant conductivity contributions from phase 1 and phase 2 (5.79% and 7.24%, respectively), but now phase 3 (the iron pyrites) is dominant, contributing 86.96% of the bulk conductivity. The bulk conductivity has risen to $\sigma = 1.7256$ S/m. The phase 3 contribution is now approximately 10 times what it was for the initial scenario ($\phi_3 = 0.2$, $m_3 = 4$, $\phi_4 = 0.65$) and over 10 times the contribution from phase 1 or phase 2. The conductivity contribution from phase 4 remains negligible despite it continuing to have the largest volume fraction ($\phi_4 = 0.50$), connectedness ($G_4 = 0.9725$ and 0.9626 , for the exact and first-order solution, respectively), and connectivity ($\chi_4 = 1.945$ and 1.925 , respectively). The increase of the volume fraction of the iron pyrites from 20% to 35% has overcome its lower phase exponent ($m_3 = 4$) to become the main conduction contributor.

In the above discussion (second part of Table 2), we increased the volume fraction of the iron pyrites from 20% to 35% but did not change its phase exponent. We would expect such an increase in phase volume fraction to result in a lower phase exponent because of an increase in the connectedness of the phase. If the phase exponent of the iron pyrites had dropped from 4 to 3 because of its increased phase volume fraction (Table 2, third part), we find that the phase exponent of the fourth phase becomes $m_4 = 0.0822$ for the exact solution (equation 27) and $m_4 = 0.1108$ for the first-order approximation (equation 29), which are still much less than unity because the quartz phase remains by far the best connected phase with a connectedness $G_4 = 0.9446$ and 0.9261 and connectivities $\chi_4 = 1.8892$ and 1.8522 for the exact and first-order approximation solution, respectively. The sum of the connectednesses of all phases remains exactly unity when using equation 27, as before, and is 0.9814 if the first-order approximation is used. The bulk effective conductivity has risen again

and is now $\sigma = 4.51$ S/m. The conductivity contribution from phase 3 is now much the most dominant, amounting to 95% of the bulk conductivity, which is 27 times its value for the initial scenario ($\phi_3 = 0.2$, $m_3 = 4$, $\phi_4 = 0.65$). Now the contributions from phases 1 and 2 each remain smaller than 3% of the bulk conductivity (2.22% and 2.77%, respectively), and that of phase 4 remains negligible.

An example such as that shown in Table 2 is useful in a semi-quantitative fashion but represents only one set of scenarios. We have examined the behavior of the generalized Archie's law theoretically and in more detail in the following two sections.

APPLICATION TO TWO PHASES

The first test of the generalized Archie's law should be against the original. However, it is immediately extremely clear that this process is a triviality with no meaning because it is clear from equations 19–23 that the generalized Archie's law collapses to give the original Archie's law if one considers a single phase.

A more interesting test is a comparison of the generalized Archie's law with the results of the modified Archie's law for two phases (Glover et al., 2000a). However, in such a procedure it is wise to remember that the generalized Archie's law and the modified Archie's law for two phases are derived in a similar manner. A distinction should also be made among (1) the formal statement of the generalized Archie's law as embodied in equation 19 with equation 27, (2) the first-order simplification of the expansion of the sum described by equation 19 with equation 29, and (3) the second-order or higher simplifications.

Figure 1 shows the results of using the generalized Archie's law and the modified Archie's law for a suite of two phase systems in which phase 2 has a fixed conductivity ($\sigma_2 = 1$ S/m) whereas phase 1 has been assigned a range of conductivity values that vary from $\sigma_1 = 0.01$ to 1000 S/m. The figure has six parts, which are arranged in pairs according to the phase 2 exponent, $m_2 = 1, 2$, and 3. Parts a, c, and e show the change of conductivity on a log scale as a function of the fraction of phase 2 for all values of the conductivity of phase 1. Parts b, d, and f show the change of conductivity on a linear scale as a function of the fraction of phase 2 but for only those values of the conductivity of phase 1 that are less than unity. This has been done to accentuate the very small differences between the curves when $\sigma_1 < 1$ S/m. Each panel contains four different calculated bulk conductivity curves: (1) that calculated using the modified Archie's law from Glover et al. (2000a) as a solid line, (2) that calculated using the exact solution of the generalized Archie's law (equation 19 with the phase exponent of phase 1 calculated from equation 27) also as a solid line, (3) that calculated using the first-order simplification of the generalized Archie's law (equation 19 with the phase exponent of phase 1 calculated from equation 29) as a dotted line, and (4) that calculated using the second-order simplification of the generalized Archie's law (equation 19 with the phase exponent of Phase 1 calculated from equation 36) as a dashed line.

The most important observation is that the result of the exact solution of the generalized Archie's law is exactly the same as the solution of the modified Archie's law from Glover et al. (2000a) for all tested values of (1) the phase exponent of phase 2, (2) the relative conductivity of the two phases, and (3) the relative volume fraction of the two phases. This is demonstrated in Figure 1 by the solutions of both approaches being colinear (i.e., producing one indistinguishable solid line for all values of ϕ_1 , ϕ_2 , m_2 , σ_1 , and σ_2).

Furthermore, for $m_2 = 1$ (parts a and b), all of the solutions are the

same, which represents a trivial solution to equation 27 that results in the connectedness of each phase being equal to the volume fraction of that phase.

For $m_2 \neq 1$, the question arises whether an approximation of equation 26 can provide sufficiently good results. Although the second-order approximation performs better than the first-order approximation, as expected, the first-order approximation itself provides a sufficiently good solution providing that (1) the conductivity of the phase with the unknown exponent (here phase 1) is smaller than that of the other phase by at least 1 order of magnitude, or (2) the volume fraction of phase 2 remains less than approximately 40% (less than approximately 60% for the second-order approximation solution).

Figure 2 shows the calculated phase exponents of phase 1 as a function of the same exponent calculated with the modified Archie's law for two phases using the exact generalized Archie's law and the two approximations to it. These results do not change with varying relative conductivity of the two phases but do vary with the phase exponent of phase 2. All values are colinear for $m_2 = 1$, and the result of the exact generalized law is colinear with the modified Archie's law for all values of m_2 . However, increasing m_2 induces errors in the solutions from the first and second approximation methods, with the errors being larger for the first-order approximation method, for small volume fractions of phase 1, and for large values of m_2 .

Although the conclusions that can be drawn from the application of the generalized law to a two-phase system are limited, it has become clear that the exact solution performs perfectly (i.e., the use of equation 19 with the phase exponent of phase 1 calculated from equation 27), whereas there are large ranges of parameters for which the approximations to the calculation of the missing exponent are approximately valid (i.e., using equation 19 with the phase exponent of phase 1 calculated from equation 29 for the first-order approximation or equation 36 for the second-order approximation).

APPLICATION TO THREE PHASES

It is instructive to examine the behavior of the general model for three phases. The problems that appear are not caused so much by complications in the model as in finding a reasonable way to represent the results of the model. The root of this problem arises from the fact that although the sum of the connectednesses of all phases is unity, the connectednesses depend on the phase fraction and the phase exponent, and all three phase fractions and the three phase exponents are inter-related. To examine a model, we would normally fix a given exponent and then examine how the calculated conductivity varies with the phase fraction. To begin, we will show that such an approach is not instructive when attempting to de-

scribe the behavior of three interacting phases (with Figure 3), and then we will describe an alternative and more instructive way of representing the data (in Figure 4).

We begin with phase 1 and define a constant phase fraction ($\phi_1 = 0.1$), a constant phase conductivity ($\sigma_1 = 0.02$), and a constant phase exponent ($m_1 = 2$), from which a constant phase 1 connectedness ($G_1 = 0.01$) and constant connectivity ($\chi_1 = 0.1$) can be calculated. These values represent an unchanging conducting phase that is distributed through the rock. These parameters also allow us to com-

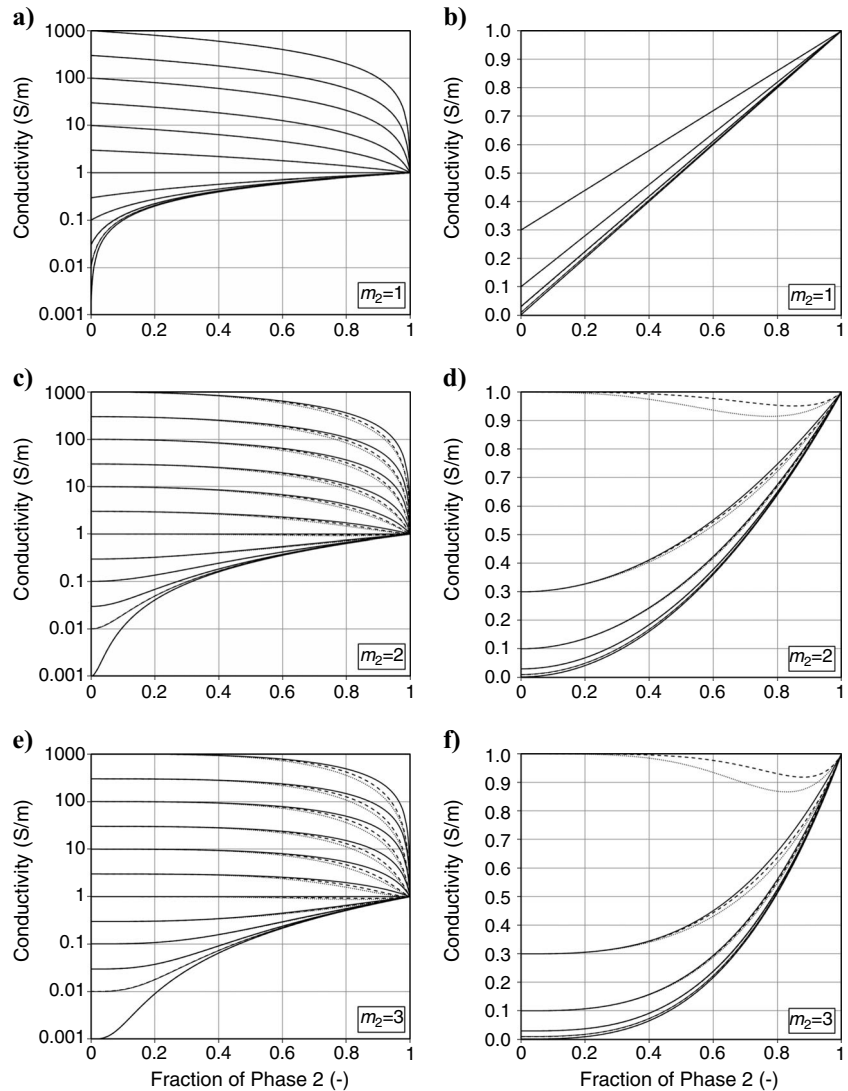


Figure 1. The variation of total conductivity as a function of the volume fraction of phase 2 for the generalized Archie's law applied to a two-phase system for three different values of m_2 . In all cases, the conductivity of phase 2 is constant and equal to 1 S/m. Calculations have been carried out for 12 different values of the conductivity of phase 1 (0.001, 0.01, 0.03, 0.1, 0.3, 1, 3, 10, 30, 100, 300, and 1000 S/m), which can be read on the y-axis when $\phi_2 = 0$. Panels a, c, and e show the full variation on semi-log axes. Panels b, d, and f show the same data on linear axes to better show the variation when the conductivity is less than 1 S/m. Solid lines represent the exact solution of the generalized Archie's law (equation 27) and the solution of the modified Archie's law for two phases (Glover et al., 2000a), which are colinear. The dotted lines represent the first-order solution of the generalized Archie's law (equation 29), and the dashed lines represent its second-order solution (equation 36).

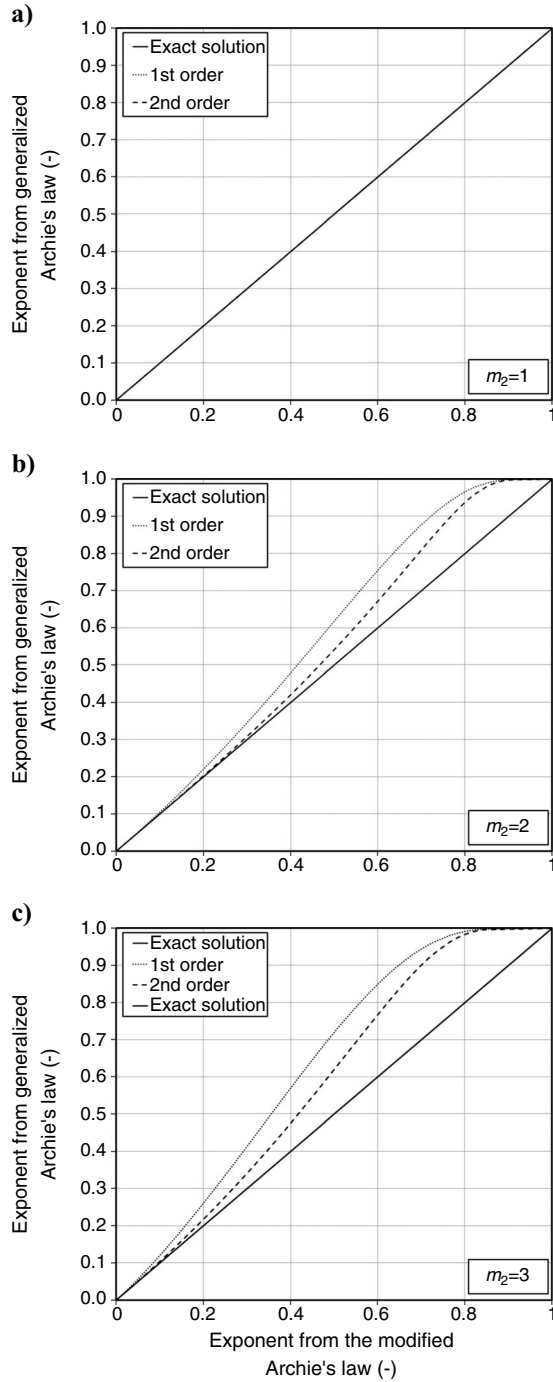


Figure 2. A comparison between the results of the exponent of phase 1 calculated with the generalized Archie's law (y-axis, this paper) and the modified Archie's law (x-axis, Glover et al., 2000a) for three defined values of the imposed exponent of phase 2. (a) $m_2 = 1$, and all three solutions of the generalized Archie's law are colinear and exactly the same as the solution of the modified Archie's law. (b) $m_2 = 2$, and the exact solution of the generalized Archie's law is exactly the same as the solution of the modified Archie's law but there is a discrepancy in the first- and second-order approximate solutions. (c) $m_2 = 3$, and the exact solution of the generalized Archie's law is exactly the same as the solution of the modified Archie's law but there is a larger discrepancy in the first- and second-order approximate solutions.

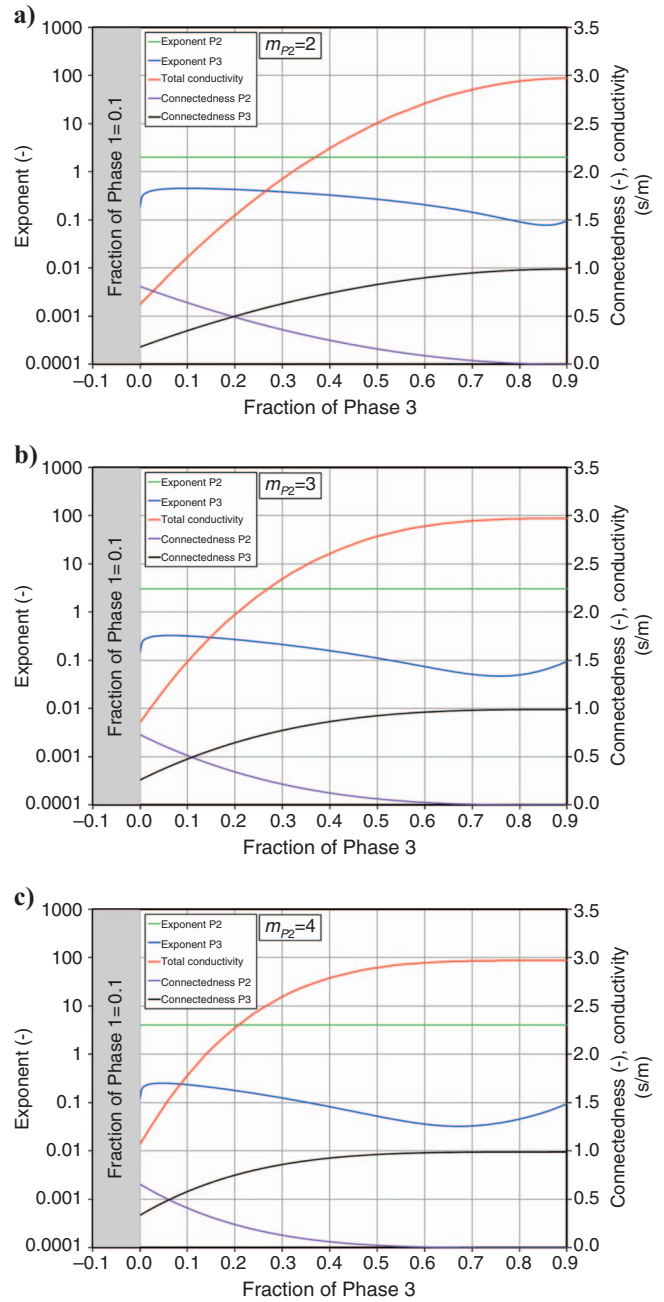


Figure 3. The solution of the generalized Archie's law for three phases for constant values of the exponent of phase 2. The variation of connectednesses and exponents of phases 2 and 3 together with the total resulting conductivities are shown as a function of the volume fraction of phase 3. Green = m_2 , blue = m_3 , purple = G_2 , black = G_3 , and red = total conductivity (S/m). Values common to all parts of the graph: $\sigma_1 = 0.02$ S/m, $\sigma_2 = 0.1$ S/m, $\sigma_3 = 3$ S/m, $\phi_1 = 0.1$, $m_1 = 2$, $G_1 = 0.01$, $0 \leq \phi_2 \leq 0.9$, $0.9 \geq \phi_3 \geq 0$. (a) $m_2 = 2$, (b) $m_2 = 3$, and (c) $m_2 = 4$.

pute the contribution to the total conductivity of the sample provided by phase 1 ($\sigma_{c1} = 0.0002$). In the remainder of this paper, the symbols σ_{ci} are used to represent the conductivity contribution from each of the i phases.

The remaining volume fraction of the rock is considered to be split into two parts (phase 2 and phase 3). The phase 2 fraction ϕ_2 varies between zero and 0.9 and has a constant phase conductivity ($\sigma_1 = 0.1$). We will, for the time being, define a constant phase 2 exponent $m_2 = 2, 3, \text{ or } 4$. As before, we can calculate the phase 2 connectedness G_2 , connectivity χ_2 , and hence a phase 2 conductivity contribution σ_{c2} that all vary with the phase 2 volume fraction ϕ_2 .

The phase 3 parameters can now be calculated. The phase 3 fraction ϕ_3 varies between 0.9 and zero and is calculated with equation 15. The phase 3 conductivity has been taken to be $\sigma_3 = 3$. The phase 3 exponent m_3 can then be calculated directly and exactly using equation 27 or by using the first approximation (equation 29). If the first approach is taken, then the connectedness of phase 3 can be readily calculated and then it can be confirmed that the sum of all three connectednesses is unity. If the second approach is taken, the sum of all of the connectednesses must be calculated to confirm that the first approximation method is valid for the parameter set being used. We recommend that the sum of all connectednesses should conform to the limits $0.95 \leq \sum_i^n G_i \leq 1$ for the first approximation method to be considered satisfactory. Finally the phase 3 connectivity χ_2 and phase 3 conductivity contribution σ_{c3} can be calculated as a function of the phase 3 volume fraction ϕ_3 .

The total conductivity of the system is the sum of the individual contributions according to equation 19 (i.e., $\sigma = \sigma_{c1} + \sigma_{c2} + \sigma_{c3}$). Figure 3 shows the results of this calculation. In each case, the connectednesses and exponents of phase 2 and phase 3 and the total conductivity are shown as a function of the volume fraction of phase 3. The conductivity contribution from phase 1 is very small. As the volume fraction of phase 3 increases from zero to 0.9, the conductivity increases nonlinearly until it reaches a value of 2.97 S/m at $\phi_1 = 0.1$ and $\phi_3 = 0.9$, irrespective of the value of m_2 . As the fraction of phase 3 increases from zero to 0.9 and that of phase 2 decreases from 0.9 to zero, the connectedness of phase 3 increases and the connectedness of phase 2 decreases concomitantly. The exponent of phase 2 is constant and greater than unity, whereas that of phase 3 describes a complex shape and is less than unity. At first sight all seems correct. However, there are various issues that will be described for the case where $m_2 = 2$ (Figure 3a) but have analogues for all other sets of the input parameters.

- 1) The value of the total conductivity at $\phi_1 = 0.1$ and $\phi_3 = 0.0001$ (solution at exactly zero is not possible) is approximately 0.622 when it should be 0.0812. This is because the connectedness of phase 3 at $\phi_1 = 0.1$ and $\phi_3 = 0.0001$ is 0.18018 when it should be close to zero.
- 2) The calculated exponent of phase 3 has a complex form that is difficult to interpret physically.

These two observations are not caused by failures in the general law or of the analytical method that

was used to derive it; rather, they arise because we have made an assumption in its application that is not correct for real porous media. The false assumption is that the exponent of phase 2 remains constant (here at $m_2 = 2$) for all values of the phase volume fraction of phase 2. This is clearly an unreasonable expectation because we may imagine that even a small decrease (increase) in the volume fraction of a given phase will lead to a reduction (increase) in its connectedness and consequently a reduction (augmentation) of the relevant phase exponent. A description of the relationships between connectivity and porosity is given in Glover and Walker (2009).

The relationship between the exponents of the phases that compose a given porous medium and their volume fraction are fundamental properties of the porous medium and are defined by the arrangement of its various components. For a porous medium consisting of n phases in which each phase has a volume fraction ϕ_i , there exists a set of functions $f_i(\phi_i) = m_i$ that obey two sets of constraints. The first set arises from the generalized Archie's law and are $\sum_{i=1}^n \phi_i = 1$ and $\sum_{i=1}^n \phi_i^{m_i} = 1$. The second set results from the necessary boundary conditions that $\lim_{\phi_i \rightarrow 0}(\phi_i^{m_i}) = 0$ and $\lim_{\phi_i \rightarrow 1}(\phi_i^{m_i}) = 1$ as well as $\lim_{\phi_i \rightarrow 1}(f_i(\phi_i)) = 0$. The constraint that $\lim_{\phi_i \rightarrow 0}(f_i(\phi_i)) = \infty$ that might be imagined also to exist is not necessary because the phase exponent may take any value in the previously defined limit $\lim_{\phi_i \rightarrow 0}(\phi_i^{m_i}) = 0$. The solution of the problem $f_i(\phi_i) = m_i$ is in the domain of mathematicians and will be the subject of a further paper.

For the moment, let us keep the phase 1 parameters constant ($\phi_1 = 0.1$ and $f_1(\phi_1) = m_1 = 2$) and impose a general condition for phase 2 that $\phi_2 \in [0, 0.9]$ with the exponent function defined arbitrarily as

$$f_2(\phi_2) = m_2 = C - A(\phi_1 + \phi_2)^B. \tag{52}$$

For example, if we take $A = 9.905$, $B = 2$, and $C = 10$, the exponent of phase 2 varies nonlinearly from 0.095 to 10 as the volume fraction of phase 2 varies from 0.9 to zero (i.e., phase 3 varies from zero to 0.9).

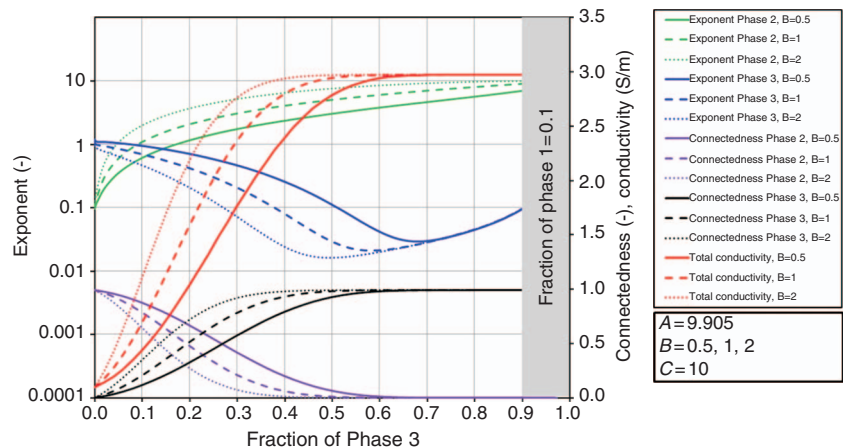


Figure 4. The solution of the generalized Archie's law for three phases for a variable phase 2 exponent. The variation of connectednesses and exponents of phases 2 and 3 together with the total resulting conductivity are shown as a function of the volume fraction of Phase 3. Green = m_2 , blue = m_3 , purple = G_2 , black = G_3 , and red = total conductivity (S/m). Values common to all parts of the graph: $\sigma_1 = 0.02$ S/m, $\sigma_2 = 0.1$ S/m, $\sigma_3 = 3$ S/m, $A = 9.905$, $B = 0.5$ (solid line), 1 (dashed line) and 2 (dotted line), and $C = 10$, where $m_2 = C - A(\phi_1 + \phi_2)^B$, $\phi_1 = 0.1$, $m_1 = 2$, $G_1 = 0.01$, and $0 \leq \phi_2 \leq 0.9, 0.9 \geq \phi_3 \geq 0$.

This is much more realistic for a real porous medium and is shown in Figure 4. In this figure, all parameters are shown as a function of the volume fraction of phase 3. The phase 1 parameters are kept constant ($\phi_1 = 0.1$ and $m_1 = 2$). In other words, phase 1 remains physically unchanged no matter what variations occur to the other parts of the porous medium. The exponent function of phase 2 is defined by equation 52 with $A = 9.905$, $C = 10$, and B taking values of 0.5, 1, and 2, shown by the green curves in the figure.

The purple curves show how the connectedness of phase 2 behaves, starting at a value near unity (0.99, 0.9989, and 0.9898 for the three values of B , respectively) for $\phi_1 = 0.1$ and $\phi_2 = 0.8999$, and decreases sigmoidally as the volume fraction of phase 2 decreases (phase 3 increases) until it becomes zero for all curves at $\phi_1 = 0.1$ and $\phi_2 = 0$.

The black curves show the variation of the connectedness of phase 3, which mirrors that of phase 2 because the constraint that the sum of all connectednesses is unity. Hence, the connectednesses of phase 3 are all equal to 0.99 at $\phi_3 = 0.9$ (the connectedness of phase 1 is 0.01, which ensures the unity sum) and become almost zero when $\phi_1 = 0.1$ and $\phi_3 = 0.0001$ (2.15×10^{-5} , 7.32×10^{-5} , and 1.77×10^{-4} , respectively, for the three values of B). This represents a much more reasonable physical behavior than was encountered in Figure 3.

Consequently, the total conductivity (red curves) also behaves more reasonably. The total conductivity at $\phi_1 = 0.1$ and $\phi_3 = 0.0001$ is 0.099262 S/m, 0.099412 S/m, and 0.099712 S/m for $B = 0.5, 1$, and 2, respectively, which are close to the theoretical value (0.09918 S/m).

The shape of the exponent of phase 3 (blue curves) is still complex, but it is now possible to attempt to interpret it. The initial decrease in the exponent of phase 3 (between $\phi_3 = 0$ and 0.65) represents an increase in the number of pathways of conduction available in phase 3, which mirrors the increase in the connectedness of phase 3 (black curves). This augmentation of pathways of conduction available to phase 3 happens at the expense of those for phase 2, and it can be seen that this is represented by a concomitant increase in the phase exponents of phase 2 (green curves) and a diminution in its connectedness (purple curves). The subsequent increase in the exponent of phase 3 (between $\phi_3 = 0.65$ and 0.9), which occurs while the phase exponent of phase 2 continues to increase, results from the conversion of phase 2 to phase 3 without significant increase in the number of pathways available to phase 3.

Modeling has been carried out for combinations of $\phi_1 = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8$, and 0.9; $m_1 = 1, 2, 3, 4$, and 5; and for relative values of the electrical conductivity of each phase as well as for combinations of values of A, B , and C . In each case, the results were found to behave in a consistent manner. Unfortunately there is insufficient space to display all of the results here. Figure 5 shows some of the results that indicate the importance of minor phases. In each part of this figure we have plotted the exponents and connectednesses of phases 2 and 3 together with the total conductivity. As in Figure 4, there are three curves for each parameter that represent $B = 0.5, 1$, or 2. The other phase 2 exponent coefficients are different from Figure 4 ($A = 4.9$ and $C = 5$). Figure 5a and b shows the results when $\phi_1 = 0.1$ and $m_1 = 2$ and for when $\phi_1 = 0.1$ and $m_1 = 3$. The effect of changing the exponent of phase 1 from 2 to 3 makes the connectedness of phase 1 10 times smaller (going from 0.01 to 0.001), which allows the connectedness of phase 3 to be higher at any given phase 3 fraction and hence allows the exponent of phase 3 to be smaller. In

other words, a larger phase 1 exponent allows more flexibility in the arrangement of the other two phases.

Figure 5c-f shows the effect of increasing the volume fraction of phase 1. Figure 5c is the same as Figure 5a except the volume fraction of phase 1 has been doubled to 0.2. The differences are subtle but important: The exponent of phase 3 does not reach such low values as in Figure 5a because it is constrained by the greater volume of phase 1. More importantly, the phase 3 exponent curves do not extend all of the way across the diagram. Why is this? The missing phase 3 exponent curves for values of the phase 3 volume fraction less than approximately 0.05 is entirely consistent with the generalized Archie's law. It indicates that there is no solution of the law for $\phi_1 = 0.2, m_1 = 2, m_2 = 5 - 4.9(\phi_1 + \phi_2)^B$ when $\phi_3 \leq 0.05$ (i.e., $\phi_2 \geq 0.75$) because the sum of the connectednesses $\sum_i^n \phi_i^{m_i} > 1$. In other words, phases 1 and 2 take up so much connectedness that there is no room for phase 3 although the requirement that $\sum_{i=1}^n \phi_i = 1$ demands it. However, if one increases the exponent of phase 1 to, say, 3 as in Figure 5d, the connectedness of phase 1 once again diminishes sufficiently for the phase 3 exponent to be well defined for the entire range of its volume fraction. Figure 5e and f shows the same effect but for $\phi_1 = 0.3$. The missing curves imply that for Figure 5c and e our imposition that $m_2 = 5 - 4.9(\phi_1 + \phi_2)^B$ is not consistent with the other parameters in the model.

Having analytically examined the behavior of the generalized Archie's law, it would be best to validate the law experimentally. Unfortunately the experimental substantiation of equations 19, 24, 27, and 29–31 requires a suite of experiments that would be unmanageably vast and technically extremely difficult, as discussed in the next section.

CONCERNING EXPERIMENTAL DATA

Ideally it would be possible to provide experimental validation for the generalized law in the same manner as for the modified law for two phases (Glover et al., 2000a). However, a broadly ranging review of the literature covering all sciences has not found any database that we could use for such a validation.

One might say that reservoir engineers have large amounts of three-phase data for the rock/air/water system. Unfortunately, these data are not helpful because although this is a three-phase material system, it is only a two-phase conductivity system, with the conductivity of the rock matrix and the air being zero.

The validation of this model in a true three-phase conductivity system is a large body of work that we have begun and to which we would invite anyone interested to cooperate or to carry out in parallel. In this section, I outline some of the technical difficulties that are involved.

To validate the generalized law experimentally for each of the n phase systems (i.e., 3, 4, 5, etc.), it is necessary to measure independently the volume fractions, the exponents, and the conductivities of all of the phases.

There are three possible independent variables: (1) the phase volume fraction, (2) the phase conductivity, and (3) the phase connectedness. Of these three, the first two may be controlled. Hence, it is best to carry out tests as a function of phase conductivity and phase volume fraction, deriving in each case a measure of the phase connectedness (e.g., G_i or m_i) that can then be compared with that predicted by the model (and other models if they exist). For example, for a three-phase system, it is sufficient to confirm that (1) the measured bulk effective conductivity as a function of the conductivity of

each of the phases matches that obtained from the model (equation 19), and (2) the use of equation 24 produces predicted values of the missing exponent that matches calculated from experimental data using the equation $m_3 = (\log(\sigma - \sigma_1\phi_1^{m_1} - \sigma_2\phi_2^{m_2}) - \log(\sigma_3))/\log(\phi_3)$. Effectively, this is the same scheme that was used in the validation of the modified Archie model for two phases (Glover et al., 2000a) but extended to three phases.

The difficulty lies in the creation of valid 3D samples in which each phase is sufficiently mechanically stable for its phase volume

fraction and phase exponent to be measured independently. A broad approach to this problem might take the following form:

- 1) Take a cylindrical sample space.
- 2) Create within it a solid framework of material A with conductivity σ_A (measured independently).
- 3) Calculate the volume fraction of material A using the density and weight of the material used and the volume of the sample space.

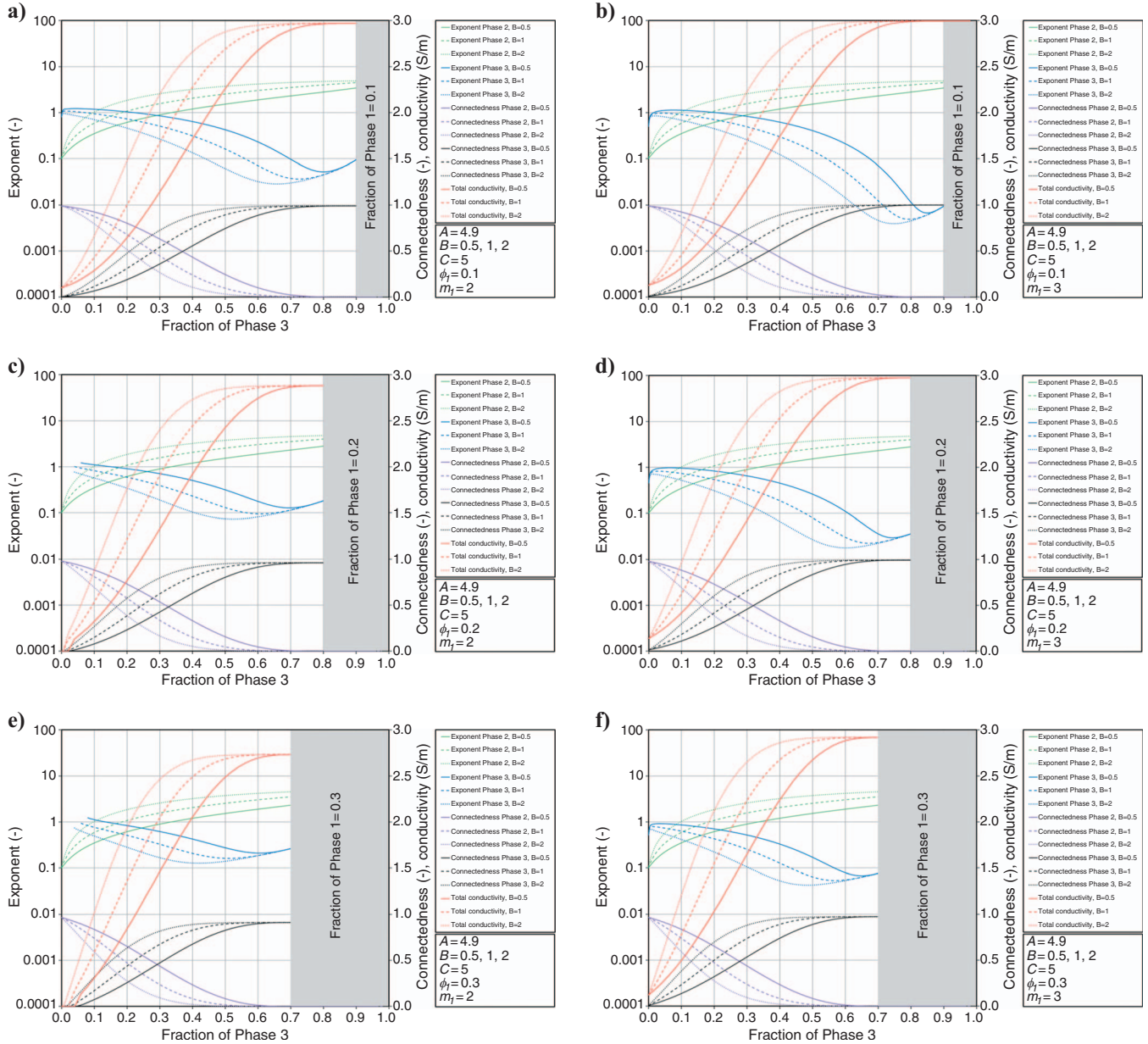


Figure 5. The solution of the generalized Archie's law for three phases: The effect of changing the volume fraction and exponent of Phase 1. The variation of connectnesses and exponents of phases 2 and 3 together with the total resulting conductivity are shown as a function of the volume fraction of phase 3. Green = m_2 , blue = m_3 , purple = G_2 , black = G_3 , and red = total conductivity (S/m). Values common to all parts of the graph: $\sigma_1 = 0.02$ S/m, $\sigma_2 = 0.1$ S/m, $\sigma_3 = 3$ S/m, $A = 4.9$, $B = 0.5$ (solid line), 1 (dashed line) and 2 (dotted line), and $C = 5$, where $m_2 = C - A(\phi_1 + \phi_2)^B$. (a) $\phi_1 = 0.1$, $m_1 = 2$, $G_1 = 0.01$, $0 \leq \phi_2 \leq 0.9$, $0.9 \geq \phi_3 \geq 0$; (b) $\phi_1 = 0.1$, $m_1 = 3$, $G_1 = 0.001$, $0 \leq \phi_2 \leq 0.9$, $0.9 \geq \phi_3 \geq 0$; (c) $\phi_1 = 0.2$, $m_1 = 2$, $G_1 = 0.04$, $0 \leq \phi_2 \leq 0.8$, $0.8 \geq \phi_3 \geq 0$; (D) $\phi_1 = 0.2$, $m_1 = 3$, $G_1 = 0.008$, $0 \leq \phi_2 \leq 0.8$, $0.8 \geq \phi_3 \geq 0$; (E) $\phi_1 = 0.3$, $m_1 = 2$, $G_1 = 0.09$, $0 \leq \phi_2 \leq 0.7$, $0.7 \geq \phi_3 \geq 0$; (F) $\phi_1 = 0.3$, $m_1 = 3$, $G_1 = 0.027$, $0 \leq \phi_2 \leq 0.7$, $0.7 \geq \phi_3 \geq 0$. ($\sigma_1 = 0.1$ S/m, $0.1 \leq \phi_2 \leq 1$, $\sigma_2 = 0.1$ S/m, $m_2 = A\phi_2^B$, $1 \geq \phi_3 \geq 0.1$, $\sigma_3 = 3$ S/m). (A) $\phi_1 = 0.1$, $m_1 = 1, 2, 3$, (B) $\phi_1 = 0.2$, $m_1 = 1, 2, 3$, (C) $\phi_1 = 0.3$, $m_1 = 1, 2, 3$, (D) $\phi_1 = 0.4$, $m_1 = 1, 2, 3$, (E) $\phi_1 = 0.5$, $m_1 = 1, 2, 3$.

- 4) Measure the effective conductivity of the material A/air two-phase system.
- 5) Calculate the exponent of phase A.
- 6) Create a solid framework of material B with conductivity σ_B (measured independently) within the sample space and interpenetrating phase A.
- 7) Ensure that there is reasonable electrical connection between phase A and B.
- 8) Gravimetrically calculate the volume fraction of material B as before.
- 9) Measure the effective conductivity of the material A/material B/air three-phase system.
- 10) Calculate the volume fraction of void space.
- 11) Calculate the exponent of phase B.
- 12) Fill remainder of sample space with material C (a set of aqueous electrolytes $\sigma_c \approx 10^{-4} \leq \sigma_f \leq 10$ S/m, measured independently).
- 13) Measure the effective conductivity of the material A/material B/electrolyte three-phase system for several different electrolyte conductivities.
- 14) Confirm that the effective conductivity as a function of phase C conductivity data is well fitted by equation 19.
- 15) Calculate the phase exponent of phase C from the experimental data.
- 16) Predict the phase exponent of phase C from the generalized model (equation 19) and compare with the experimentally obtained value.

It would be necessary to carry out the above procedure for many samples composed of different volume fractions and arrangements of material A and B.

There are several significant technical hurdles to be passed also, including sourcing material A and material B, which should be mechanically stable, chemically inert, insoluble in water, and with constant electrical conductivities that are sufficiently different to be distinct, while both being within the range of values taken by the NaCl electrolyte ($10^{-4} \leq \sigma_f \leq 10$ S/m).

In the face of such experimental difficulties, we have chosen to test the equations using numerical modeling, with the warning that a full validation of these equations by modeling represents a much greater corpus of work than it would be possible to include in a single paper.

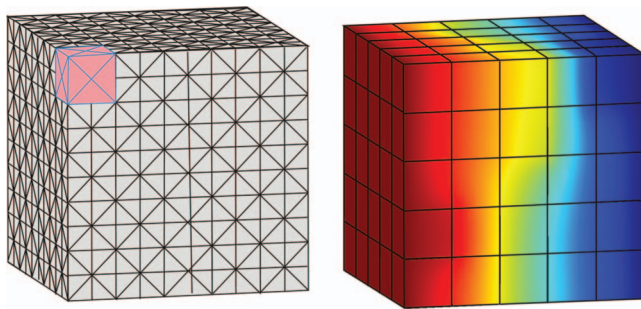


Figure 6. (a) Geometry of the numerical model (here a $5 \times 5 \times 5$ model is shown for simplicity; the real size was $20 \times 20 \times 20$) and the tetragonal grid used in the numerical modeling (red = 10 V). (b) An example of a numerical solution of electrical potential across the cube (blue = 0 V).

NUMERICAL MODELING METHODOLOGY

In a stationary coordinate system, the point form of Ohm's law states, in its most general form, that

$$\mathbf{J} = \sigma \mathbf{E} + \mathbf{J}_e, \quad (53)$$

where \mathbf{J} is the total current density, σ is the conductivity, \mathbf{E} is the electric field, and \mathbf{J}_e is an externally imposed current density (if present). The static form of the equation of continuity then gives us

$$\nabla \cdot \mathbf{J} = -\nabla \cdot (\sigma \nabla V - \mathbf{J}_e) = Q_j, \quad (54)$$

where Q_j is an externally generated current source (if present). In this modeling, there is no externally imposed current; hence, $\mathbf{J}_e = 0$ and $Q_j = 0$.

The model is composed of 8000 cubic blocks ($20 \times 20 \times 20$). Thus, each percentage of the volume fraction is represented by 80 blocks. The conductivity (isotropic or anisotropic) for each block can be specified. An example of the geometry of the model is shown in Figure 6a, but for a $5 \times 5 \times 5$ grid for simplicity.

At the input face to the 3D model, we have specified inward current flow according to

$$-\mathbf{n} \cdot \mathbf{J} = J_n, \quad (55)$$

where the normal component J_n is positive representing current flow into the model. The opposite face of the model we have specified as grounded (i.e., $V = 0$). All other faces of the model are specified as insulating, where $\mathbf{n} \cdot \mathbf{J} = 0$ (i.e., that there is no current flowing across the boundary). All interior boundaries are conservative (i.e., continuity boundary conditions),

$$\mathbf{n} \cdot (\mathbf{J}_1 - \mathbf{J}_2) = 0. \quad (56)$$

The relevant interface condition at interfaces between two different phases is $\mathbf{n}_2 \cdot (\mathbf{J}_1 - \mathbf{J}_2) = 0$, where \mathbf{n}_2 is the outward normal from phase 2 and \mathbf{J}_1 and \mathbf{J}_2 are the current densities in each of the two adjoining phases. This is fulfilled by the natural boundary condition

$$\mathbf{n} \cdot [(\sigma \nabla V - \mathbf{J}_e)_1 - (\sigma \nabla V - \mathbf{J}_e)_2] = -\mathbf{n} \cdot (\mathbf{J}_1 - \mathbf{J}_2) = 0. \quad (57)$$

The electrical potential was solved using Comsol's Femlab 3.0 on a finite element mesh, which consisted of tetrahedra created by constrained Delaunay triangulation. The mesh consisted of 768,000 tetrahedra, which provides 96 tetrahedra per cubic block such that each tetrahedron represents approximately 1.3×10^{-6} of the total volume fraction. Figure 6a shows a typical mesh, but for a $5 \times 5 \times 5$ grid for simplicity. The electrical potential at the input and output faces was calculated using the integration functions that are built into the Femlab software.

Initially, all blocks were set to the same conductivity. Several adjoining cells were chosen stochastically to create a set of pathways across the model with a predefined fraction and a predefined exponent. The predefined exponent cannot be simply forced on the model; we have to try several pathways until the calculated exponent is the desired value. The only constraint imposed was that all pathways, whether dead ends or not, were initially continuous, with their component cubes making contact face to face, not edge to edge or vertex to vertex. This was called phase 1 and was kept constant during the subsequent modeling.

The other cubes represent the volume occupied by the other three phases. Several of these cubes were chosen stochastically to create a

second set of pathways across the model with a predefined fraction and a predefined exponent as before. The same face to face contact constraint was imposed again. This was called phase 2, and was also kept constant during the subsequent modeling.

The remaining cubes represent the volume occupied by the remaining two phases. Again, several of these cubes were chosen stochastically using the same constraints to create a third set of pathways across the model with a predefined fraction and a predefined exponent as before. This was called phase 3 and was changed during the subsequent modeling. All cubes not assigned to phase 1, 2, or 3 were automatically assigned to phase 4.

The conductivity of each of the cubes composing each of the phases was then assigned to give the initial starting conditions for each set of model solutions. At this point, the conductivity and fraction of each phase is known, but their exponents are not. The exponent of each phase was measured separately by solving equation 53 across the model with the conductivity of the other phases set to zero. The finite element solution of the electrical potential may then be carried out throughout the model. The potentials and current at each face were then calculated by integrating their values over each face; hence, the modeled conductivity was calculated.

Several cubes of phase 3 were then transformed into phase 4 by re-allocating their conductivities to increase the fraction of phase 4 by approximately 1% and reduce the fraction of phase 3 by the same amount (i.e., 80 cubes). Although the choice of the reallocated cubes was random, two constraints were applied. These were that the positions of the new phase 4 cubes were (1) in face-to-face contact with existing phase 4 cubes, and (2) were not in contact with more than two pre-existing phase 4 cubes. The first constraint avoids the development of infinite current densities at vertex-to-vertex contacts, whereas the second ensures that the reallocated cubes significantly change the connectedness of the phase instead of just "filling in the gaps."

The exponents of phases 3 and 4 were then recalculated with the same method as before (the exponents of phase 1 and phase 2 do not change because their geometry has not changed). The model was

then solved again before the fraction of phase 4 was increased once more in the same manner. This process was reiterated until phase 3 was exhausted (approximately 20 realizations per suite of measurements). Figure 6b shows a typical electrical potential solution for a $5 \times 5 \times 5$ geometry for simplicity. The results described below were carried out on a $20 \times 20 \times 20$ grid.

It should be noted that this type of numerical simulation is extremely costly on processor time and on memory. We carried out our simulations on a standard desktop PC (2.4 GHz, 4 core, 3 Gb RAM) running Comsol's Femlab 3.0 (now Comsol Multiphysics 3.5a) and found that the $20 \times 20 \times 20$ grid took almost 2 h to solve and used almost all of the available memory. Although the solutions were generally stable, we found it was not possible to increase the size of the grid within our computing resources.

NUMERICAL MODELING RESULTS

Three suites of measurements were carried out in total. Table 3 shows their starting and finishing conditions.

Figure 7 shows the results of the modeling as plots between the conductivity predicted from numerical modeling and those predicted from the generalized Archie's law and the traditional Archie's law (which in this case is the same as applying the Archie's law modified for two phases because phase 4 has such a low conductivity). The results of the generalized Archie's law agree very well with the numerical results and have been taken to validate, at least in part, the equations developed in this work.

When the traditional Archie's law is used, there are errors that are because the conductivity contributions from phases 1 and 2 have not been taken into consideration. The constant difference between the results of the traditional Archie's law and the generalized Archie's law in Figure 7 arises because we kept phases 1 and 2 geometrically and electrically constant within a suite of modeling results but differ between each suite. The sensitivity of the final results to small changes in the parameters describing phases 1 and 2 indicates how

Table 3. Conditions associated with the numerical modeling.

Phase	Fraction	Number of cubes	Type	Conductivity	Exponent	Connectedness
Suite 1						
1	0.05	800	EDL	10	2.3	0.00102
2	0.1	400	Fluid	50	2.1	0.00794
3	0.2–0	1600–0	FeS ₂	100	3–4.75	0.008–0
4	0.65–0.85	5200–6800	Quartz	10 ⁻²⁰	0.0397–0.0554	0.9830–0.9910
Suite 2						
1	0.06	480	EDL	10	2.2	0.00205
2	0.09	720	Fluid	50	2.2	0.0050
3	0.2–0	1600–0	FeS ₂	100	3–4.33	0.008–0
4	0.65–0.85	5200–6800	Quartz	10 ⁻²⁰	0.0352–0.0436	0.9849–0.9929
Suite 3						
1	0.03	240	EDL	10	2.5	0.000156
2	0.12	960	Fluid	50	2	0.0144
3	0.2–0	1600–0	FeS ₂	100	3–3.78	0.008–0
4	0.65–0.85	5200–6800	Quartz	10 ⁻²⁰	0.0529–0.0902	0.9774–0.9854

Single values indicate a constant during a suite of measurements; a range of values indicates a starting and finishing value.

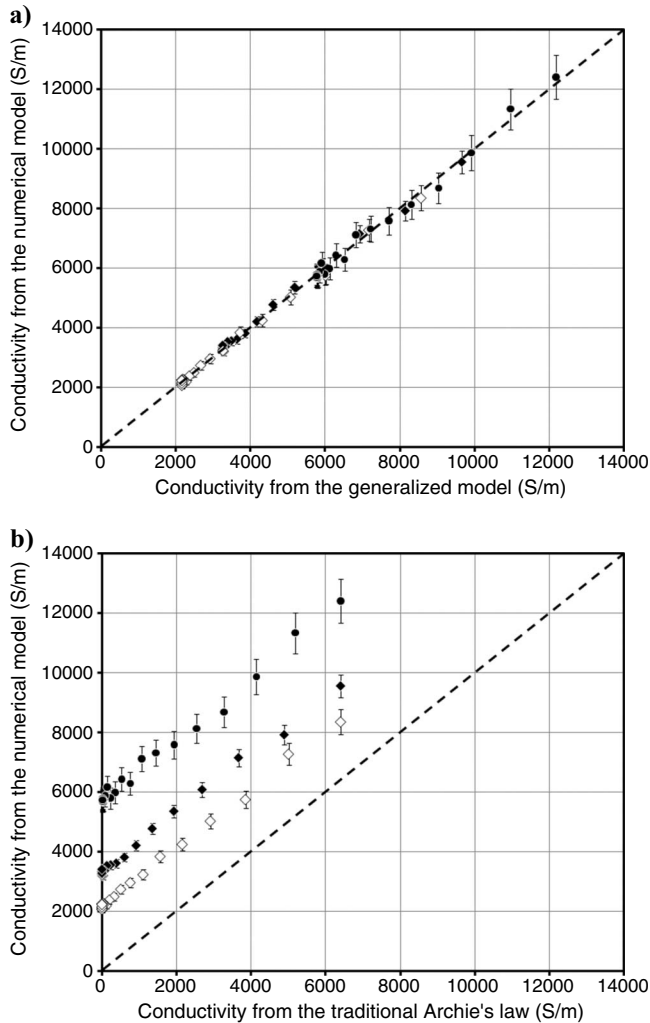


Figure 7. Results of numerical modeling of a four-phase system. (a) Conductivity from the numerical modeling as a function of that predicted from the generalized Archie's law for the three suites of modeling results. (b) Conductivity from the numerical modeling as a function of that predicted from the traditional Archie's law for the three suites of modeling results. Note that because the conductivity of phase 4 is so low, this diagram is also a plot of the conductivity from the numerical modeling as a function of that predicted from the modified Archie's law for two phases (Glover et al., 2000a).

important it is to control the contributions from all phases in the multicomponent system.

SUMMARY

The main findings of this paper can be summarized by saying that a 3D medium composed of n phases has the following properties:

- 1) The sum of the fractions of all of the phases is equal to unity, $\sum_{i=1}^n \phi_i = 1$.
- 2) The sum of the connectednesses of all of the phases is equal to unity, $\sum_{i=1}^n G_i = \sum_{i=1}^n \phi_i^{m_i} = 1$.
- 3) Connectedness is conserved — loss of connectedness for one phase is balanced by gains of connectedness in the other phases that compose the rock.

- 4) The generalized Archie's law for n phases takes the form $\sigma = \sum_{i=1}^n \sigma_i \phi_i^{m_i}$.
- 5) The phase exponent of the j th phase can be calculated using the equation $m_j = \log(1 - \sum_{i \neq j} \phi_i^{m_i}) / \log(1 - \sum_{i \neq j} \phi_i)$.
- 6) The phase exponent of the j th phase can also be calculated using a first-order approximation by the equation $m_j = \sum_{i \neq j} G_i / \sum_{i \neq j} \phi_i$.
- 7) An $n - 1$ subset of phases has the property that $\sum_{i=1}^{n-1} S_i^{n_i} = 1$, where the saturation of each phase is $S_i = \phi_i / \sum_{i=1}^{n-1} \phi_i$ and n_i is the saturation exponent of each phase. This equation represents a form of the equation for the sum of connectednesses but with reference to an $n - 1$ subset of the original n -phase medium.

The classical Archie's law for 100% fluid saturation and Archie's second law for partial saturation can be derived from the generalized model as special cases. Examination of the exact solution of the generalized Archie's law for n phases shows it to also be formally the same as the modified Archie's law for two phases.

There exist at least two approximations of the generalized law. Of these, the second-order approximation performs better than the first-order approximation, as expected, and there is a wide range of parameters in which the approximations provide a good estimate of the exact solution of the generalized law.

It may be that the generalized law as set out in this paper is too complex for general use. However, its applications should grow depending on the growth of the requirement to model increasingly complex rock mixtures, something that is becoming more common as nonconventional hydrocarbon resources are exploited. On a more fundamental level, its immediate contribution is more likely to be in the sphere of improving our seminal understanding of why empirical laws such as Archie's seem to work so well.

It is conceptually extremely difficult to imagine a method for experimentally verifying this generalized law, let alone to find data sets that are sufficiently comprehensive. Here, the generalized law has been partially verified by 3D numerical modeling and found to work well for four phases that were subject to the constraints that we applied to the modeling. I urge other researchers to carry out further and more exhaustive testing of the model experimentally and using numerical modeling with larger grids.

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