

# A modified Archie's law for two conducting phases

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## Abstract

Many types of mixing model are used widely within the earth sciences to determine the electrical properties of porous media consisting of solid and fluid phases of known conductivities, volume fractions and distributions (i.e. phase connectivities). Most models are valid for two or more conducting phases. However, of the simple models only Archie's law includes a variable term, the Archie cementation exponent  $m$ , that describes the connectivity of the phases. Unfortunately, Archie's law is only valid for one conducting phase distributed within a non-conducting phase, which makes it inapplicable in instances where the rock matrix has a significant conductivity such as for clay-rich rocks and in calculations involving partial melting. More complex models exist which account for multiple conducting phases and control over phase conductivity. We have adapted the conventional Archie's law to produce a simple modified Archie's law that can be used with two conducting phases of any conductivity and any volume fraction, while retaining the ability to model variable connectivities within those phases that result from variations in their distribution. The modified model has two exponents ( $m$  and  $p$ ) that describe the connectivity of each of the two phases. The exponents are related through an equation that depends also on the volume fractions of the two phases. The modified and the conventional versions of Archie's law have been tested on a granular analogue porous medium with a conducting matrix and a pore space saturated with a range of saline fluids with different salinities and conductivities. The new model describes the experimentally determined electrical behaviour of the system extremely well, improving greatly on the conventional Archie's law. © 2000 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

The electrical conductivity of a porous medium containing a single conducting fluid phase de-

pends upon the electrical conductivities ( $\sigma_i$ ) and relative volumes ( $x_i$ ) of the matrix and the fluid (e.g. [1]). The bulk conductivity depends also upon the geometrical distributions of the matrix and the fluid, which control the connectivity of paths for current flow in the porous medium [1].

In porous media, the prediction of bulk conductivity is a non-trivial problem as a result of the complex distribution of solid and fluid phases each of which have different conductivities, volume fractions and connectivities. A large number

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of mixing models have been published in the attempt to solve this problem [1–24], many of which are valid only for particular well defined simple geometric distributions of the solid and fluid phases, and hence implicitly assume a fixed electrical connectivity. For example, one simple model describes alternating layers of matrix and fluid parallel to an applied external potential, where the connectivity of both phases is unity, and where the bulk conductivity is given by the arithmetic mean of the conductivities of each phase weighted by their volume fractions [1–3]. The geometrical opposite is the scenario where there are alternating layers of matrix and fluid perpendicular to the applied external potential, where the connectivity of both phases is zero, and where the bulk electrical conductivity is given by the harmonic mean of the conductivities of each phase weighted by their volume fractions [1–3]. These parallel and perpendicular models are sometimes known as the Wiener bounds [3,4]. Another simple model is valid for a random distribution of each of the phases within the porous medium. Here the connectivity is not known and the bulk electrical conductivity is given by the geometric mean of the conductivities of each phase weighted by their volume fractions [5,6]. There are a number of models that take account of more complex geometries of the two phases. One example is the mixture (simple summation) of the parallel and perpendicular bounds employed by Luo et al. [2].

There have been many attempts at analysing a two phase conducting mixture with effective medium theory. One of the earliest effective medium models for the conductivity of spheres dispersed in a continuous medium was proposed by Maxwell [7] and was extended and applied to complex conductivities by Wagner [8]. The Maxwell model has also been extended for use with other particle shapes [9]. Subsequently there have been many studies on the effective conductivity of mixed media using the effective medium approach. The best known of these is the work of Hashin and Shtrikman [10], who produced new upper and lower bounds on the effective conductivity known as HS+ and HS– [10]. Another important model derived from effective medium theory is that of Waff [11]. This model assumes that the medium

is composed of composite spheres of varying size. Each sphere has a spherical core of conducting phase 1 with a conductivity  $\sigma_1$ , and is completely covered by an outer shell of conducting phase 2 with conductivity  $\sigma_2$  in such a way that the volume ratio of the phases is the same for each sphere and independent of sphere size. Since the outer shells (phase 2) of all the composite spheres are in contact, there is high connectivity for phase 2. Conversely, phase 1 is not connected.

Another approach is to suppose that a given medium composed of two conducting phases has some distribution of phases that falls between the extreme cases of the series and parallel models. It is then assumed that some combination of the series and parallel models represented by resistor/capacitor equivalent circuits will describe the effective conductivity of the medium. This approach is the basis of the conventional brick-layer model [12–15]. Although this model is an elegant and flexible solution, it has been noted to be valid only up to several percent of a conductive boundary phase [16]. Partzsch [17,18] has modified the brick-layer model to enable it to be used for conductive boundary phases up to 100%.

All of the models introduced above are valid for a particular geometry and represent a single degree of connectivity of the conducting phases. Many of these methods are correct to the first term of an expansion of terms that is implicit in the model. There have been studies that attempt to generalise the problem by solving it to further terms, but these are only valid for spherical particles dispersed randomly in a continuous medium. Examples of the latter include the work of Jeffrey [19], whose results are only valid for a dilute suspension of conducting spheres in a conducting medium, and Batchelor and O'Brien [20] who extend the approach to the limit where the spheres have a sufficiently high volume fraction to be in contact. Milton and Bergman [21,22] have taken the work of Hashin and Shtrikman and generalised it for use with complex dielectric constants, while Korrington and LaTorraca [23] use the Milton–Bergman approach to constrain the conductivity of a porous medium as a function of frequency. This last work is of particular interest because it prepares the way for extracting useful

geometric information from impedance spectroscopy measurements carried out on fluid saturated rocks in the laboratory.

Although it was derived empirically, Archie's law is the only simple model which contains a variable parameter describing the connectivity of the conducting (usually fluid) phase [1,24]. However, Archie's law is only valid strictly for a conducting phase saturating a non-conducting matrix. In practice, at shallow depths and low temperatures, the rock matrix conductivity can be assumed to be negligible, which makes Archie's law extremely useful in the calculation of water and hydrocarbon saturations in oil reservoirs composed of clean formations, where it is routinely applied. However, when the matrix conductivity has a significant conductivity, the conventional Archie's law is invalid, as will be shown in this paper.

Recently, there has been much interest in the calculation of the bulk electrical conductivity of partially molten rocks in order to explain high electrical conductivities observed by magneto-telluric measurements in various locations around the globe [17,18,25–28]. The main aims of these studies are to ascertain whether partial melting has the potential for explaining the observed high conductivities and to provide information about the conductivity, fractional volume and connectivity of the melt. Archie's law could be a useful tool in such studies because of its ability to vary the connectivity by varying its exponent. However, at the depths, pressures and temperatures where partial melting occurs, the conductivity of rock matrix is not negligible, leading to errors if the conventional Archie's law is used.

In this paper, we present a modified form of Archie's law that takes full account of the conductivity and relative volumes of both the fluid phase and the matrix phase, and that is valid for all values of the Archie exponent (i.e. degrees of connectivity).

## 2. Mixing models

Reviews of mixing models are available in the literature (e.g. [1,18,25]), and this material is not

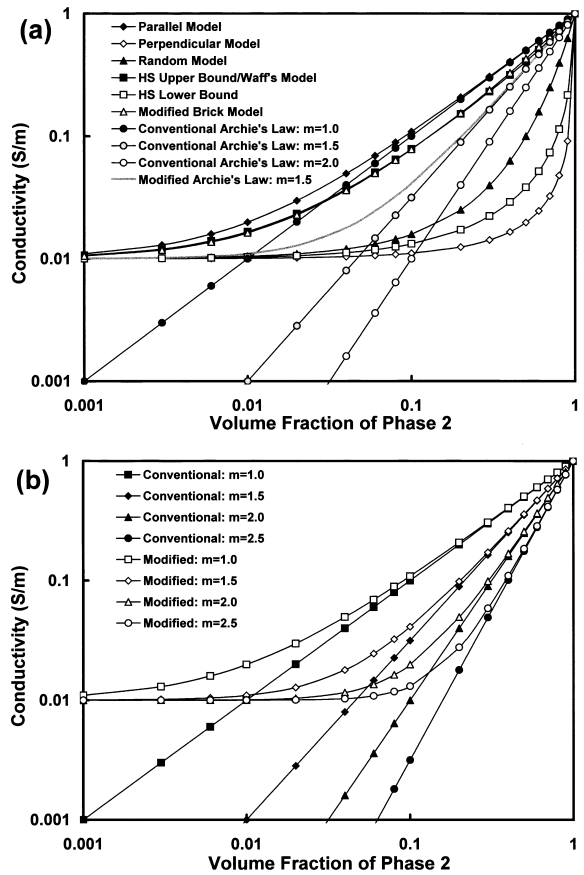


Fig. 1. (a) Various mixing models as a function of the volume fraction of phase 2 for  $\sigma_1 = 0.01$  S/m and  $\sigma_2 = 1.0$  S/m. (b) The conventional and modified Archie's law for various  $m$  values as a function of the volume fraction of phase 2 for  $\sigma_1 = 0.01$  S/m and  $\sigma_2 = 1.0$  S/m.

repeated here. However, the commoner mixing models are summarised in Table 1 with relevant references. A selection of the mixing models shown in Table 1 are also shown in Fig. 1a for two phases ( $\sigma_1 = 0.01$  S/m,  $\sigma_2 = 1$  S/m) as a function of the volume fraction of phase 2. Fig. 1a shows that the modified brick-layer model is almost coincident with HS+ over the whole range of volume fractions of phase 2.

Archie's formulation [24] for the mixing of a conductive fluid in an insulating matrix is somewhat different from these previous relationships. The most important difference is that it was initially derived empirically for saline solutions saturating a clean porous sandstone in contrast with

Table 1  
Summary of some commoner mixing models for electrical conductivity

Name	References	Conducting phases		Equation	Notes
		Min.	Max.		
Parallel model	[1–3]	1	Many	$\sigma_{\text{eff}} = \sum_{i=1}^N \chi_i \sigma_i$	Parallel layers of constant arbitrary thickness with conductivity $\sigma_i$ arranged axially to current flow. Arithmetic mean.
Perpendicular model	[1–3]	1	Many	$\frac{1}{\sigma_{\text{eff}}} = \sum_{i=1}^N \frac{\chi_i}{\sigma_i}$	Parallel layers of constant arbitrary thickness with conductivity $\sigma_i$ arranged normally to current flow. Harmonic mean.
Random model	[5,6]	1	Many	$\sigma_{\text{eff}} \prod_{i=1}^N \sigma_i^{\chi_i}$	Arbitrary shaped and oriented volumes of conductivity $\sigma_i$ distributed randomly. Geometric mean.
Hashin–Shtrikman upper bound	[1,10]	2	2	$\sigma_{\text{eff}+} = \sigma_2 \left( 1 - \frac{3(1-\chi_2)(\sigma_2-\sigma_1)}{3\sigma_2-\chi_2(\sigma_2-\sigma_1)} \right)$	Commonly denoted HS+. Derived from effective medium considerations.
Hashin–Shtrikman lower bound	[1,10]	2	2	$\sigma_{\text{eff}-} = \sigma_1 \left( 1 + \frac{3\chi_2(\sigma_2-\sigma_1)}{3\sigma_1+(1-\chi_2)(\sigma_2-\sigma_1)} \right)$	Commonly denoted HS-. Derived from effective medium considerations.
Waff model	[11]	2	2	$\sigma_{\text{eff}} = \frac{\sigma_2 + (\sigma_1 - \sigma_2)(1 - (2\chi_2/3))}{1 + (\chi_2/3)(\sigma_1/\sigma_2 - 1)}$	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	[18]	2	2	$\sigma_{\text{eff}} = \frac{\sigma_2(\sigma_2(\chi_1^{2/3}-1) - \sigma_1\chi_1^{2/3})}{\sigma_1(\chi_1 - \chi_1^{2/3}) - \sigma_2(\chi_1^{2/3} - \chi_1 - 1)}$	Modified to allow validity to be extended to cover the range $0.00 \leq \chi_1 \leq 1.00$ (0–100%). Almost coincident with HS+.
Conventional Archie's law	[1,24]	1	1	$\sigma_{\text{eff}} = C\sigma_2\chi_2^m$	Derived empirically, but provable analytically for special cases.
Modified Archie's law	This work	1	2	$\sigma_{\text{eff}} = \sigma_1(1-\chi_2)^p + \sigma_2\chi_2^m$ where $p = \frac{\log(1-\chi_2^m)}{\log(1-\chi_2)}$	Derived from the conventional Archie's law by considering boundary conditions implied by geometrical constraints.

Notes:  $\sigma_{\text{eff}}$  is the effective conductivity of the rock consisting of  $N$  different phases with individual conductivities  $\sigma_i$ , each present in volume fractions  $\chi_i$ . For single and dual conducting phase models, the subscripts refer to the phase number. The values  $l$ ,  $m$  and  $C$  are constant for any given porous medium/fluid system.

the previous formulations which were derived analytically from geometrical or effective medium considerations. It should be noted, however, that it is possible to derive Archie's law from first principles using a differential effective medium approach in some special cases, such as for granular porous media [29,30].

Archie's law implicitly assumes that there is only one conducting phase, which is distributed in some manner between a non-conductive matrix. This restriction is fulfilled (i) for the uppermost few kilometers of the crust, where temperatures and pressures are sufficiently low for major rock forming minerals to have negligible matrix conductivity, and (ii) for clean rock formations with no or very low fractions of conductive clay minerals. The oil and water industries commonly and routinely apply the conventional Archie's law for clean formations at shallow depths, and use traditionally a range of different empirically derived equations to account for the additional conductivity contributed if clays are present in any significant volume [31]. However, in the last few years, there have been a number of breakthroughs in the understanding and analytical description of the nature of surface conduction thanks to the work of Revil [32], which has led to improved models of conduction where both pore fluid-mediated and surface-mediated conduction contribute to the bulk conductivity [32–35]. This approach involves the analysis of the electrically conducting double layer that mediates the clay surface conduction from first principles, and uses the results together with the model of Bussian [36] to produce a mathematically complex but precise method for analysing the conductivity of shaly rocks incorporating the contributions to the bulk conductivity from the pore fluids and the clay surface conduction.

The conventional Archie's law is most conveniently expressed as:

$$\sigma_{\text{eff}} = C\sigma_2\chi_2^m \quad (1)$$

where  $\sigma_2$  is the conductivity of the single conducting phase and  $\chi_2$  is the volume fraction of the conducting phase. Archie's law has been implemented in Fig. 1a, and it is clear that this single

phase model differs from the other models significantly, especially at small volume fractions of the conducting phase where  $\sigma_{\text{eff}} \rightarrow 0$  as  $\chi_2 \rightarrow 0$ , which contrasts with the physically justified boundary condition that  $\sigma_{\text{eff}} \rightarrow \sigma_1$  as  $\chi_2 \rightarrow 0$ .

Unlike the previous formulations, Archie's law contains two variable terms, the Archie cementation exponent  $m$  and the Archie constant  $C$ , both of which are medium dependent. For example, Roberts and Tyburczy [25] use the simple Archie relationship to describe the conductivity of a rock containing a conductive partial melt fraction, and find from their experimental work that  $C = 0.73 \pm 0.02$  and  $m = 0.98 \pm 0.01$ . However, examination of Eq. 1 shows that the Archie constant  $C$  is not physically justified, and that at 100% melt,  $C = 1.0$  whatever the value of  $m$ . The observation of values of  $C \neq 1$  by Roberts and Tyburczy [25] and many other workers may therefore be an indication that either the conventional Archie's law is an oversimplification of the system that they are studying, or that the 'constant'  $C$  is actually a function of  $\chi_2$ , where  $C(\chi_2) \rightarrow 1$  as  $\chi_2 \rightarrow 1$ . Perhaps the non-unity values of  $C$  are not surprising in the case of Roberts and Tyburczy [25], since at the temperatures and pressures where a partial melt occurs, it is invalid to assume that the rock matrix has negligible conductivity, and hence it is expected that the conventional Archie's law is an oversimplification of the system. Significantly, non-unity values of  $C$  are also reported in oil industry applications where the conventional Archie's law is used on shaly rocks that contain conductive clays in the matrix.

The most useful aspect of Archie's law is the variable Archie cementation exponent  $m$ . It is recognised that this exponent is related to the electrical connectivity of the conductive phase within the porous medium. However, because Archie's law was derived empirically, and because the connectivity of a complex rock is difficult to quantify, the mechanistic relationship between  $m$  and the electrical connectivity remains poorly understood in most cases. There are some instances where the connectivity is very well understood; these are related to the previously mentioned special cases where Archie's law can be proven analytically

[29,30]. Comparison of Archie's law with the parallel model indicates that full connectivity of the conductive phase is achieved when  $m=1$ , when Archie's law becomes formally identical to the parallel model, and  $m \rightarrow 0$  as 100% conductive phase is approached. For values of  $m > 1$ , the effective conductivity of the porous medium decreases as the connectivity of the conducting phase reduces and the tortuosity of conduction paths increases. Values  $1.5 < m < 2.5$  are common for sedimentary rocks containing saline aqueous fluids in upper crustal basins. Fig. 1a shows effective conductivity curves for  $m=1$ , 1.5 and 2.0 as examples, where  $m=1$  is identical with the parallel model with one conducting phase and one insulating phase.

### 3. Modification to the Archie's law mixing model

We consider a porous medium consisting of two phases (solid, liquid or gas) with conductivities  $\sigma_1$  and  $\sigma_2$ , that are present in volume fractions  $\chi_1$  and  $\chi_2$  (where  $\chi_1 + \chi_2 = 1$ ). The conventional Archie's law can be written as:

$$\sigma_{\text{eff}} = \frac{\sigma_2}{F_2} = \sigma_2 \chi_2^m \text{ if } \sigma_1 = 0 \quad (2)$$

and:

$$\sigma_{\text{eff}} = \frac{\sigma_1}{F_1} = \sigma_1 \chi_1^p \text{ if } \sigma_2 = 0 \quad (3)$$

where  $F_1$  and  $F_2$  are the electrical formation factors when phase 1 and phase 2 are taken to be insulating, respectively. Note that we are using Eq. 1 and setting  $C \equiv 1$ , and we have introduced two exponents;  $m$  to represent the connectivity of phase 2 and  $p$  to represent the connectivity of phase 1. The most general form of Archie's law for a two phase system is the sum of Eqs. 2 and 3 with an additional term [21–23]:

$$\sigma_{\text{eff}} = \sigma_1 \chi_1^p + \sigma_2 \chi_2^m + \int_0^{\infty} \left( \frac{\Theta(y)}{1/\sigma_1 + y/\sigma_2} \right) dy \quad (4)$$

The additional integral term is known as Stieltjes integral [37], and contains the parameter

$\Theta(y)$ , which is known as the resonance density, and is always positive. The electrical formation factors  $F_1 = \sigma^{-p}$ ,  $F_2 = \sigma^{-m}$  and  $\Theta(y)$  are all dependent upon the topology of the two component phases. Little is known about the resonance density, and it is a common feature of a number of studies that it is assumed to be negligible as a first order simplification. In this paper, we also neglect the Stieltjes integral, assuming that the dependence of effective conductivity upon the relative distributions of the two phases can be accounted for purely by the two electrical formation factors (i.e. through the exponents  $m$  and  $p$ ). Hence:

$$\sigma_{\text{eff}} = \sigma_1 \chi_1^p + \sigma_2 \chi_2^m \quad (5)$$

Each of the phases has its own distribution in the porous medium, resulting in each phase having an electrical connectivity and an electrical tortuosity. Each phase will therefore also have a representative exponent ( $m$  and  $p$ ), and although these exponents may be the same they will generally differ. Large exponents ( $> 2$ ) occur for low connectivity phases and small exponents ( $< 2$ ) occur for high connectivity phases. We also expect the exponents to be a function of the fractional volumes of each phase because low phase connectivities are likely to be associated with small volume fractions and high phase connectivities are likely to be associated with large volume fractions.

Consider a porous rock described by Eq. 5, where the conductivities and volume fractions of each phase remain constant. If the three dimensional distribution of the phases is modified such that the electrical connectivity of phase 2 increases, then the electrical connectivity of phase 1 would be expected to decrease (i.e. the electrical connectivities of each phase are interrelated). This relationship is imposed on the system by the limited volume in the porous medium that can be occupied by three dimensional distributions of the two phases. As the exponents  $m$  and  $p$  are functions of the phase connectivities, we should also expect them to be interrelated in real two phase porous media. The relationship between  $m$  and  $p$  can be solved for two phases by considering the appropriate boundary conditions.

Considering the boundary conditions ( $\sigma_{\text{eff}} = \sigma_1 = \sigma_2$ )  $\forall (\chi_1$  and  $\chi_2)$  applied to Eq. 5 gives:

$$1 = \chi_1^p + \chi_2^m \tag{6}$$

This type of boundary condition is known as the isoconductivity point, and is not generally valid. However, it is known to be valid for granular porous media such as rocks containing conductive fluids [32–35]. The use of this boundary condition restricts the derived relationships to use with granular porous media.

Eq. 6 can be rearranged to obtain the exponent  $p$  for phase 1 in terms of the exponent  $m$  for phase 2 and the volume fraction of phase 2:

$$p = \frac{\log(1 - \chi_2^m)}{\log(1 - \chi_2)} \tag{7}$$

Combining Eqs. 5 and 7 allows a mixing relationship for two conductive phases to be expressed in terms of only one exponent and volume fraction. In this case (Eq. 8), we have written it in terms of the exponent and volume fraction for phase 2, but it can easily be rewritten in terms of phase 1 parameters:

$$\sigma_{\text{eff}} = \sigma_1(1 - \chi_2)^{(\log(1 - \chi_2^m) / \log(1 - \chi_2))} + \sigma_2 \chi_2^m \tag{8}$$

Fig. 1a includes an example of the modified Archie’s law for  $m=1.5$ , and it is immediately clear that the new modification provides a mixing curve where  $\sigma_{\text{eff}} \rightarrow \sigma_1$  as  $\chi_2 \rightarrow 0$ , and  $\sigma_{\text{eff}} \rightarrow \sigma_2$  as  $\chi_2 \rightarrow 1$ , in the same fashion as all the mixing models other than the conventional Archie’s law. However, the modified form of Archie’s law retains the  $m$  exponent as a measure of connectivity of the second phase, and can be implemented for different values of  $m$ . Fig. 1b shows the conventional and modified Archie’s laws implemented for the range of  $m$  values that is most commonly encountered. It should be noted that for the case where  $m=1$ , the new model is identical to the parallel model, and that the new model approximates to the HS upper bound and the modified brick-layer model at  $m \approx 1.15$ . There are no values of  $m$  where it may reasonably be said that the model approximates to the ran-

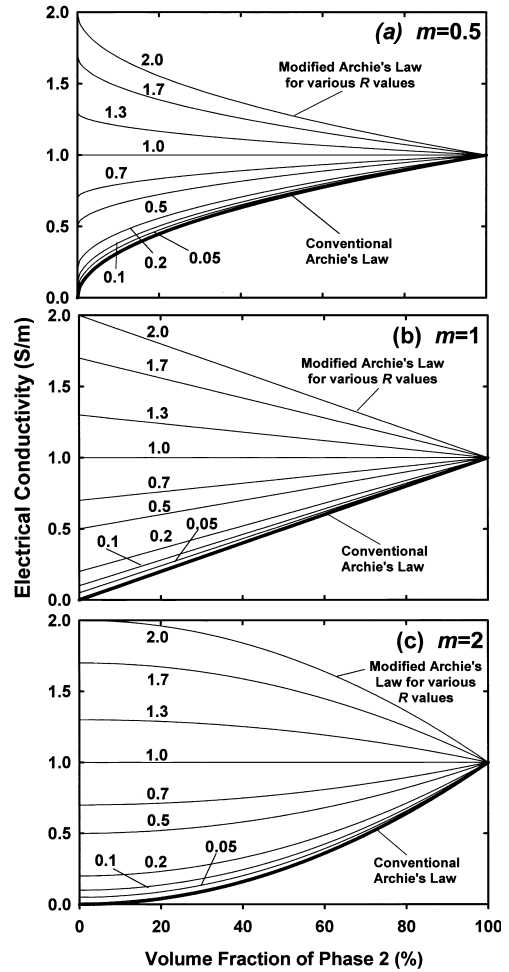


Fig. 2. The conventional (thick lines) and modified Archie’s law (thin lines) as a function of the volume fraction of phase 2 for various values of  $R = \sigma_1/\sigma_2$ , and for (a)  $m=0.5$ , (b)  $m=1.0$  and (c)  $m=2.0$ .

dom model, HS lower bound or perpendicular models.

It should be noted that Eqs. 5 and 8 are symmetrical, hence the allocation of which physical phase is represented by each of the mathematical phases described in these equations is arbitrary. This also implies that Eq. 8 is valid for all values of  $\sigma_1$  and  $\sigma_2$ , providing that the assumption that the Stieltjes integral can be neglected holds. Hence, the modified equation is also valid for porous media where the matrix is relatively conductive compared to a saturating insulating fluid.

The modified model and the conventional Archie's law are shown in Fig. 2 for a range of  $m$  values and a range of conductivities of each of the two phases present. The relative conductivities of the two phases are represented by the parameter  $R$ , where  $R = \sigma_1/\sigma_2$ , and where the conductivity of phase 2 is fixed for all curves at  $\sigma_2 = 1.0$  S/m. Fig. 2 shows curves for both low connectivities ( $m \geq 2$ ) and high connectivities ( $m \leq 1$ ) of phase 2, as well as conductivities of phase 1 that are larger and smaller than the corresponding conductivities for phase 2.

It should be noted that the new model can be viewed both as an extension of Archie's law to include a second conducting phase as well as a modification of the parallel model taking account of the connectivity of the conducting phases by the incorporation of exponential weightings to each of the volume fraction terms.

#### 4. Testing the new model

##### 4.1. Testing methodologies

The new model has been tested for a porous medium analogous to a saturated rock but with a moderately conductive matrix. A conducting matrix was chosen to ensure that the new model was tested in a scenario with two non-negligible conducting phases. Testing on partially molten rocks was not attempted due to their experimental difficulty and our requirement for obtaining extremely accurate determinations of conductivity on a well controlled experimental system. Testing the new model on rocks with a clay matrix was also not attempted because these rocks have three conducting phases (matrix, surface conduction and fluid conduction), and treating the clay matrix and surface conductivity as if it were one phase may have upset the geometrical balance between  $p$  and  $m$  that is the basis for the new mixing equation.

##### 4.2. Testing procedure

We have used copper oxide ( $\text{Cu}_2\text{O}$ ) as the matrix material to ensure that the test is valid and

robust for matrix materials with a conductivity that is not negligible. This material, which is found in nature as cuprite, is a semiconductor and has a conductivity between 0.1 and 0.02 S/m. We have created a suite of 10 samples with different matrix volume fractions and porosities. It was possible to create samples with porosities ranging from approximately 4% to 44% by using grains of  $\text{Cu}_2\text{O}$  of different size fractions and roundness, and subjecting the sample to various degrees of hydrostatic confining pressure. Each sample was formed by adding the grains to a Viton<sup>®</sup> sleeve plugged at the bottom end with a stainless steel end-piece with a sandwich of filter paper and blacked platinum gauze to act as an electrode. A further stainless steel end-piece, filter paper and electrode was used to close the system. The sample arrangement was inserted into a hydrostatic pressure vessel and raised to different confining pressures depending upon the required final porosity. The samples were carefully removed from the hydrostatic cell, and placed in a Hassler cell, before being subjected to helium porosimetry. Each sample was carefully saturated with distilled water using a flow-through technique with a fluid back-pressure of 200 psi to ensure that all gas was expelled from the porous medium and replaced by the fluid. The finished samples had a diameter of approximately 38 mm and lengths varying from 40 mm to 60 mm. The friable nature of the samples required that they remained enclosed in the sleeve and end-piece arrangement during porosimetry and saturation and for the remainder of the experiment. The enclosed saturated samples were then inserted in a pressure vessel and subjected to a confining pressure of 500 psi.

Measurements were made of the complex electrical impedance of the sample for 50 frequencies from 50 Hz to 500 kHz using a QuadTech 7400 impedance analyser for the original distilled water and six NaCl brine salinities, whose conductivities ranged from approximately  $2 \times 10^{-3}$  to 15 S/m in approximately order of magnitude increments. Brines were changed by a flow-through technique, with 100% saturation of the new brine being accepted when changes in the electrical response of the system had ceased. The samples were then



dried using dry nitrogen, before being resubjected to a helium porosimetry to check whether the porosity had remained the same during the measurements. A slight decrease in porosity, amounting to approximately a 2% reduction, was found in most samples. This was attributed to slight compaction resulting from the confining pressure applied during measurement. The porosity at the end of the experiment was therefore used in all calculations, and is given in Table 2.

The conductivities of the brines used in the experiments were measured using the same instrument as for measuring the samples with the same frequencies and currents. Aliquots of the fluids emerging from the sample towards the end of each brine change-over were placed immediately in a glass brine conductivity cell equipped with two blacked platinum electrodes for the conductivity measurements. The cell was clamped close to the Hassler cell containing the sample and not handled during measurement to ensure that the fluids retained the same temperature as the sample. The in-phase brine conductivities at 1 kHz are

given in Table 2 together with the brine temperature.

#### 4.3. Analysis and validation

All analysis was carried out for the in-phase electrical conductivity at 1 kHz. This frequency was chosen to minimise any small electrode polarisation effects that were not eliminated by the use of blacked platinum electrodes, and because it is a common frequency used for electrical conductivity measurements in petrophysics. Initially, the measured conductivity data for each sample were plotted against fluid conductivity on a bi-logarithmic scale. Eq. 5 was fitted to the data for each of the samples using the Marquardt–Levenberg non-linear regression algorithm implemented in SigmaPlot<sup>®</sup> 5.0, as shown in Fig. 3a. This procedure gives values for the matrix conductivity  $\sigma_1$ ,  $m$  and  $p$ , which are given in Table 2. There is an extremely good fit of Eq. 5 to the measured data (coefficients of determination  $R^2 \geq 0.99$ ), which validates the use of Eq. 5 as a

Table 2  
Experimental parameters

Sample	Volume fractions		Modified Archie's law			Archie's law
	$\chi_{\text{matrix}}$	$\chi_{\text{pores}}$	$m$	$p$	$\sigma_{\text{matrix}}$ (S/m)	$m$
A1	0.959	0.041	2.403	0.031	0.0298	1.82
A2	0.926	0.074	2.230	0.030	0.0321	2.00
A3	0.889	0.111	2.292	0.061	0.0297	2.14
A4	0.869	0.131	2.246	0.070	0.0297	2.14
A5	0.847	0.153	1.972	0.147	0.0299	1.92
A6	0.802	0.198	1.513	0.381	0.0294	1.50
A7	0.769	0.231	1.403	0.566	0.0313	1.39
A8	0.711	0.289	1.412	0.552	0.0320	1.40
A9	0.638	0.362	1.184	0.786	0.0320	1.18
A10	0.561	0.439	1.095	0.893	0.0313	1.09
Phase	Salinity (M)	Temperature (°C)	Conductivity (S/m)			
Distilled	0	25.4	$3 \times 10^{-8}$			
NaCl brine	0.0001	25.3	0.00126			
NaCl brine	0.001	25.0	0.01237			
NaCl brine	0.01	25.3	0.11850			
NaCl brine	0.1	24.7	1.06750			
NaCl brine	1	25.1	8.57614			
NaCl brine	2	24.6	14.9426			

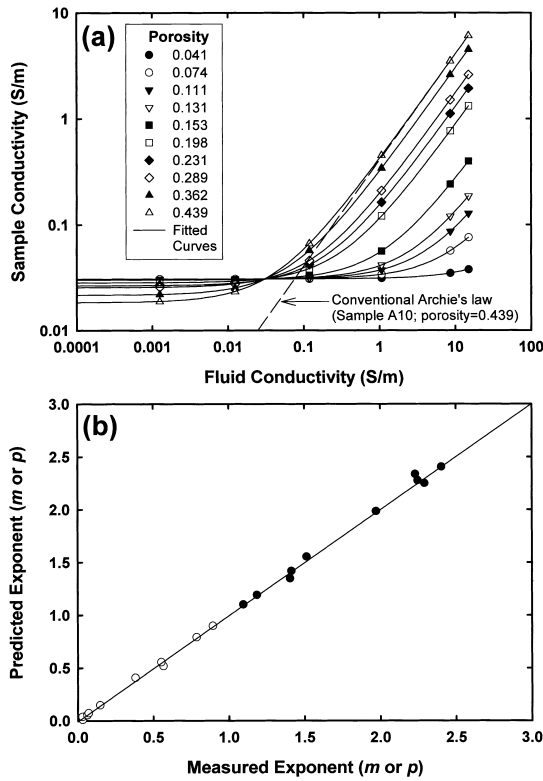


Fig. 3. (a) Sample conductivity as a function of fluid conductivity for 10 samples whose matrix was composed of  $\text{Cu}_2\text{O}$ , with various porosities: symbols represent measured values, and solid lines represent the fit of Eq. 5. (b) Predicted values of  $m$  and  $p$  plotted against  $m$  and  $p$  measured in the experiment for each sample. Open symbols represent  $p$  values predicted from measured  $m$  values using Eq. 7, plotted against measured  $p$  values. Solid symbols represent  $m$  values predicted from measured  $p$  values using Eq. 7, plotted against measured  $m$  values. Validity of Eq. 7 is shown by the 1:1 straight line relationship.

mixing model for a two phase system such as this. The extremely good fit that was achieved has also been attributed to the fine temperature control implemented during fluid conductivity measurements.

However, validation of Eq. 5 is not a test of Eq. 8. To validate Eq. 8 fully, we need to check that the relationship between  $m$  and  $p$  given in Eq. 7 is also true. The 'measured' values of  $m$  and  $p$  for each sample were obtained during the non-linear regression procedure (Table 2), so it is an easy task to check whether these values obey Eq. 7 for the given sample porosities. We have taken

the measured value of  $m$  and porosity for each sample and used Eq. 7 to predict the corresponding  $p$  values. We have plotted the predicted  $p$  values as a function of the measured  $p$  values. We have also carried out this procedure in reverse by predicting the  $m$  values from the measured  $p$  values and plotting them against the measured  $m$  values. The plotted points will fall on a 1:1 straight line only if Eq. 7 is valid. Reference to Fig. 3b shows this to be the case. We can therefore say that for the system studied here, Eqs. 5 and 7 are valid, therefore it follows that Eq. 8 has also been validated. The parameter ranges for this validation of the modified Archie's law are:

$$\begin{aligned} \sigma_1 &\approx 3.08 \times 10^{-2} \text{ S/m (matrix conductivity for the } \text{Cu}_2\text{O} \text{ derived from the non-linear fitting).} \\ 3 \times 10^{-8} &\leq \sigma_2 \leq 14.94 \text{ S/m (the range of fluid conductivities).} \\ 0.561 &\leq \chi_1 \leq 0.959 \text{ (the range of matrix volume fractions).} \\ 0.041 &\leq \chi_2 \leq 0.439 \text{ (the range of pore volume fractions).} \end{aligned}$$

It should be noted, however, that the symmetry inherent in the model and the limiting behaviours of the model indicate that it should be valid for the full range of these parameters, providing the assumption that the Stieltjes integral can be neglected holds.

The conventional Archie's equation has also been fitted to the data, and the derived  $m$  value is given in Table 2 for comparison. The dotted line in Fig. 3a shows the fitted conventional Archie equation for sample 10 and indicates how badly the conventional Archie's law fits effective conductivity data where the matrix has a non-negligible conductivity.

## 5. Some geophysical implications

For most upper crustal oil and water industry related problems,  $\sigma_1 \approx 0$  S/m,  $1.0 \leq \sigma_2 \leq 25.0$  S/m,  $0 \leq \chi_2 \leq 0.25$  and  $1.5 \leq m \leq 2.5$ . The parameter  $R=0$  for these values of conductivity and the modified model approaches the conventional Archie's law for all values of  $p$ ,  $m$ ,  $\chi_1$  and  $\chi_2$  (Fig. 2).

However, application of the conventional Archie’s law leads to large errors if the two phases have similar conductivities. This will occur if the rock matrix has a significant conductivity arising from (i) high temperatures such as those encountered in the lower crust or in rocks which are partially molten, or (ii) the presence of unusually high conductivity minerals such as clays, graphite or sulphides at low temperatures. Examples are given here for high conductivities arising from partially molten lower crustal rock and arising from the presence of clays in a sandstone.

5.1. Partially molten rock

In the case of partially molten rock, we use an example from the lower crust beneath the Pyrenees. At depths between 55 km and 80 km below the Pyrenees, the temperature increases from 1035°C to 1350°C and the lithostatic pressure increases from 15.91 kbar to 23.09 kbar [28]. At these depths, it is suspected that the granulite facies rocks undergo partial melting [26,27]. Laboratory experiments indicate that the conductivity of the solid matrix,  $\sigma_1$ , is between 0.01 S/m and 0.015 S/m [38], while other laboratory experiments indicate that the melt conductivity occupies the range  $0.1 \leq \sigma_2 \leq 5$  S/m [25,39]. As an example, we take  $\sigma_1 = 0.015$  S/m,  $\sigma_2 = 0.3$  S/m, which gives  $R = 0.05$  (i.e. the rock matrix conductivity is only 5% of the conductivity of the melt), and assume that the connectivity of the melt is moderately well connected ( $m = 2$ ). For these parameters, a 10% melt fraction gives an effective conductivity of the system  $\sigma_{\text{eff}} = 0.003$  S/m from the conventional Archie’s law (Figs. 2 and 4). This is clearly invalid as it is less than both  $\sigma_1$  and  $\sigma_2$ , falling in the lower zone of disallowed conductivities shown in Fig. 4a. By comparison, the new model gives an effective conductivity for the system as  $\sigma_{\text{eff}} = 0.0178$  S/m, which is much more realistic since it lies between  $\sigma_1$  and  $\sigma_2$ , and hence is an allowed conductivity (Fig. 4a). If we assume the melt to be perfectly connected ( $m = 1$ ), the conventional Archie’s law gives an effective conductivity of the system  $\sigma_{\text{eff}} = 0.03$  S/m, which does fall between the bounding values  $\sigma_1$  and  $\sigma_2$ , but is significantly less than the value calculated with the

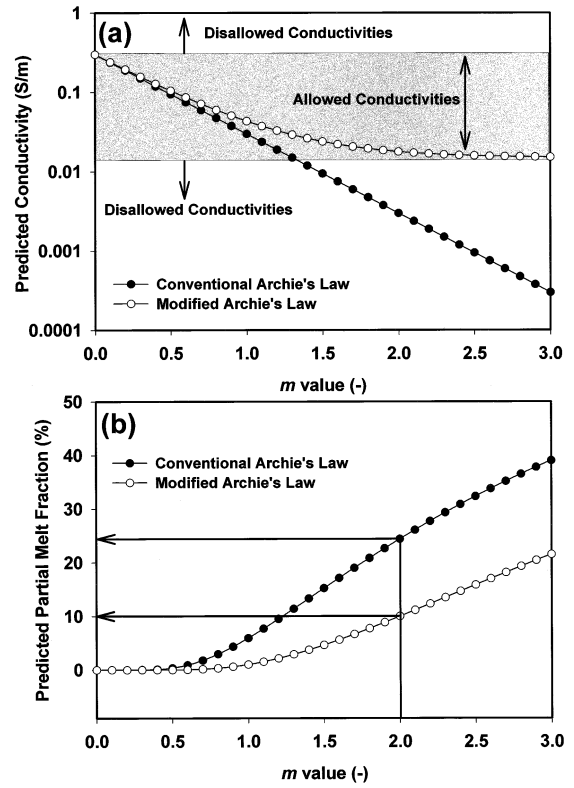


Fig. 4. (a) Predicted conductivity as a function of  $m$  for the conventional and modified Archie’s laws for  $\sigma_1 = 0.015$  S/m,  $\sigma_2 = 0.3$  S/m and  $\chi_2 = 0.1$  (10%). (b) Predicted melt fraction as a function of  $m$  for the conventional and modified Archie’s laws for  $\sigma_1 = 0.015$  S/m,  $\sigma_2 = 0.3$  S/m and  $\sigma_{\text{eff}} = 0.0178$  S/m.

modified Archie’s law ( $\sigma_{\text{eff}} = 0.0435$  S/m), representing approximately a 25% underestimation of the conductivity due to the failure of the conventional Archie’s law to take into consideration the conductivity of the rock matrix. For lower values of  $m$ , the two models converge, but the conventional Archie’s law always gives conductivities which are lower than the modified Archie’s law.

Even more significant errors occur if the conventional Archie’s law is used to calculate the partial melt fraction from knowledge of the effective conductivity of the rock and the conductivities of its matrix and melt phases. If we know the effective conductivity of the rock/melt system at depth, say from magneto–telluric measurements, to be  $\sigma_{\text{eff}} = 0.0178$  S/m, the use of the modified

Archie's law with  $\sigma_1 = 0.015$  S/m and  $\sigma_2 = 0.3$  S/m gives a 0.1 volume fraction of melt (10%), while application of the conventional Archie's law gives 0.244 (24.4%), as shown in Fig. 4b. It is also clear from this figure that the degree of error is small at low values of  $m$  and increases as the value of  $m$  increases. However, even at  $m = 1$ , when the melt is connected to the same degree as in the parallel layer model, the conventional Archie's law calculates a predicted partial melt fraction  $\chi_2 = 5.95\%$ , which is significantly higher than that provided by the modified law ( $\chi_2 = 1.00\%$ ). Hence, the use of the conventional Archie's law for estimating the partial melt fraction at depth from the conductivities of the matrix, melt and the bulk rock can grossly overestimate the partial melt fraction present, resulting from the conventional Archie's law not taking the contribution of the matrix con-

ductivity to the effective conductivity into account.

It should be remembered that the previous examples are for  $R = 0.05$ , where the matrix conductivity is only 5% of that of the more conductive (melt) phase. Even larger errors are possible if the matrix conductivity is higher and closer to the conductivity of the other (melt) phase.

## 5.2. Clay-rich sandstones

Application of the modified form of Archie's law to situations where the bulk rock conductivity is enhanced by the presence of surface conduction along clay surfaces is not simple. This is because the additional surface conduction supplied by the clays has a geometric distribution that is not the same as that of the matrix. It is probably better to

Table 3

Comparison of the modified Archie's law with data from Waxman and Smits [31] for shaly sandstones

Sample	From Waxman and Smits [31]					From this paper			
	Porosity (–)	$Q_v$ (meq/cm <sup>3</sup> )	$BQ_v$ (S/m)	$F^*$ (–)	$m$ (–)	$\sigma_1$ (S/m)	$F^*$ (–)	$m$ (–)	$p$ (–)
1	0.239	0.017	0.232	12.28	1.752	0.008	12.23	1.749	0.312
2	0.212	0.052	0.264	14.19	1.710	0.012	14.14	1.708	0.308
3	0.231	0.052	0.268	11.26	1.652	0.012	11.20	1.648	0.356
4	0.080	0.260	0.287	48.47	1.537	0.004	47.87	1.532	0.253
5	0.154	0.200	0.412	14.85	1.442	0.020	14.74	1.438	0.420
6	0.215	0.095	0.415	18.68	1.905	0.016	18.61	1.902	0.228
7	0.171	0.053	0.589	26.87	1.863	0.014	26.69	1.860	0.204
8	0.171	0.053	0.584	25.72	1.839	0.013	25.53	1.835	0.213
9	0.199	0.085	0.443	18.14	1.795	0.019	18.05	1.792	0.257
10	0.125	0.253	1.376	160.75	2.443	0.005	158.10	2.435	0.048
11	0.125	0.253	0.857	173.27	2.479	0.003	170.19	2.470	0.044
12	0.110	0.280	1.243	44.40	1.719	0.021	43.87	1.713	0.198
13	0.110	0.280	1.617	45.57	1.730	0.025	44.46	1.719	0.195
14	0.110	0.280	1.384	32.58	1.578	0.032	32.17	1.573	0.271
15	0.092	0.410	2.433	155.75	2.116	0.010	151.24	2.103	0.069
16	0.103	0.670	2.898	62.03	1.816	0.037	59.74	1.799	0.155
17	0.140	0.330	2.947	44.68	1.933	0.053	43.06	1.914	0.156
18	0.259	0.590	2.354	18.37	2.154	0.107	17.99	2.139	0.191
19	0.259	0.590	1.853	16.94	2.094	0.085	16.65	2.082	0.207
20	0.259	0.590	1.463	13.12	1.906	0.092	12.97	1.897	0.268
21	0.238	0.290	0.872	14.81	1.878	0.053	14.64	1.870	0.260
22	0.225	0.720	3.740	35.32	2.390	0.094	34.74	2.378	0.115
23	0.242	1.040	4.540	26.92	2.321	0.142	25.60	2.285	0.144
24	0.216	0.810	5.260	44.29	2.474	0.103	43.03	2.455	0.097
25	0.187	1.270	7.240	55.90	2.400	0.128	55.46	2.395	0.088
26	0.229	1.470	7.710	41.18	2.522	0.168	39.32	2.491	0.099
27	0.209	1.480	7.830	44.41	2.423	0.179	44.12	2.419	0.098

assume, as Waxman and Smits [31] have done, that the conduction pathways for surface conduction are the same as the conduction pathways through the pore fluid.

Waxman and Smits [31] fitted an equation to data from 27 samples of clay-rich sandstones (table 7 in [31]). These data are in the form of effective rock conductivity as a function of the conductivity of the aqueous fluid occupying the pores of the rock. The Waxman and Smits equation implicitly assumes that the conduction pathways taken for the clay surface conduction are the same as that through the pore fluid, and can be written as:

$$\sigma_{\text{eff}} = \frac{1}{F^*}(\sigma_{\text{clay}} + \sigma_{\text{fluid}}) = \frac{1}{F^*}(BQ_v + \sigma_{\text{fluid}}) \quad (9)$$

Here  $Q_v$  is the volume concentration of clay exchange cations (equivalents/l),  $B$  represents the mobility of surface cations, and  $\sigma_{\text{clay}} = BQ_v$  (S/m) represents the contribution to the overall conductivity due to the surface conduction at the clay mineral–fluid interface. Waxman and Smits [31] calculated the shaly sand formation factor,  $F^*$ , from the inverse gradient of the linear fit, and  $BQ_v$  from the ordinate intercept divided by  $F^*$ . However, the data are not linear and diverge at low fluid conductivities. This is because  $\sigma_{\text{clay}} = BQ_v$  is not constant, but is itself dependent upon the fluid conductivity  $\sigma_{\text{fluid}}$ . To overcome this problem, Waxman and Smits used only the linear portion of the data (at the higher values of fluid conductivity) in their fitting procedure.

We have fitted Eq. 8 to the same data. This procedure allows us to obtain values of the formation factor for shaly sands,  $F^*$ , the classical cementation exponent,  $m$ , the newly introduced exponent,  $p$ , and the effective conductivity of the rock matrix,  $\sigma_1$ . These values are given in Table 3 together with values of  $F^*$ ,  $m$ ,  $Q_v$  and  $BQ_v$  given in or derived directly from [31]. The fit was good in all cases, with the coefficient of determination  $R_2 > 0.98$ . The fitted values of  $F^*$  agree closely with those obtained by Waxman and Smits [31] (Fig. 5a). However, the values of  $BQ_v$  from the Waxman and Smits model do not coincide with our values of matrix conductivity  $\sigma_1$ . This is because the Waxman and Smits model assumes that

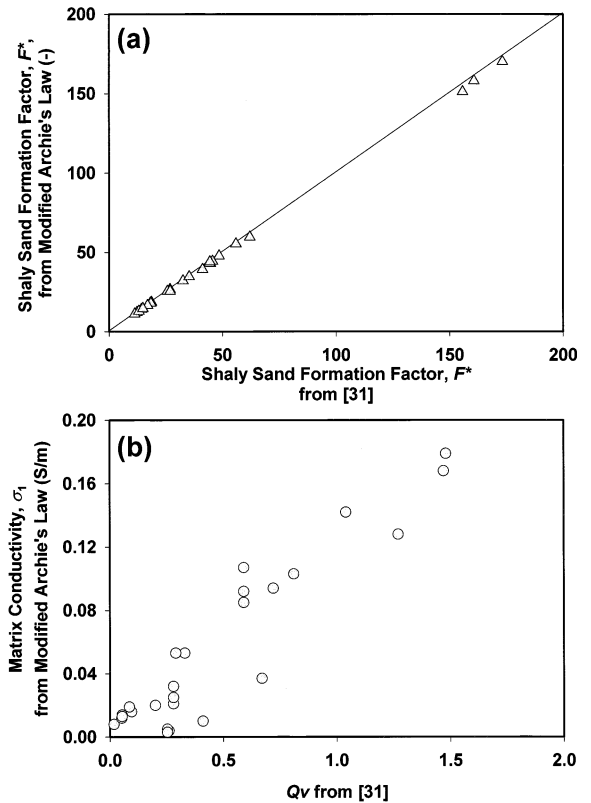


Fig. 5. (a) Shaly sand formation factor,  $F^*$ , obtained from fitting the modified Archie's law to the data from [31] as a function of the shaly sand formation factor,  $F^*$ , obtained by fitting the Waxman and Smits [31] model to the same data. (b) Matrix conductivity obtained from fitting the modified Archie's law to the data from [31] as a function of values of  $Q_v$  from [31].

the additional conduction provided by the presence of clay minerals occurs along conduction paths of equal tortuosity to conduction through the pore fluid, whereas the modified Archie's law assumes that the conduction occurs through the entire matrix. Hence, one would expect that the values of the matrix conductivity (sand and clay) obtained from fitting the modified Archie's law to the data to be consistently lower than the value of  $BQ_v$  obtained by Waxman and Smits, which is the case. Even though the geometric distribution of the clays is assumed to be different by the two approaches, we would also expect to see an approximate relationship between the matrix conductivity from the fitting of the modified Archie

law and the value of  $Q_v$  for the samples. This has been carried out and shows that a reasonable linear correlation between these two parameters exists (Fig. 5b). The scatter is due to the unknown distribution of clay minerals amongst the sand grains.

## 6. Conclusions

Archie's law was formulated empirically in 1942 to describe the conductivity of a porous medium consisting of an insulating porous solid matrix with a conductive fluid phase completely filling the pores, and includes an exponent term that describes, in some currently unknown way, the connectivity of the conducting phase.

We have modified Archie's law to enable it to operate in circumstances where the matrix phase and the fluid phase can have any conductivity. The modified model retains the exponent term describing the connectivity of the fluid phase, and introduces another exponent describing the connectivity of the matrix phase. We have derived an expression that links the two exponents in a two phase system, such that only one is necessary for the operation of the modified law.

The new model has been tested on 10 samples of a porous medium with various porosities. The samples consist of a semiconducting matrix and a connected pore space that can be saturated with saline fluids with various conductivities. It was found that the new model (Eqs. 5–8) provides an extremely good fit to the experimental data, and that the relationship between  $m$  and  $p$  (Eq. 7) is valid. The ranges over which the new model has been tested are: phase 1 (matrix) conductivity,  $\sigma_1 \approx 3.08 \times 10^{-2}$  S/m; phase 2 (fluid) conductivity,  $3 \times 10^{-8} \leq \sigma_2 \leq 14.94$  S/m; matrix volume fractions,  $0.561 \leq \chi_1 \leq 0.959$ ; and pore volume fractions,  $0.041 \leq \chi_2 \leq 0.439$ . However, there are no physical or mathematical reasons why the model should not be valid for wider ranges providing Stieltjes integral can be assumed to be zero.

The modified Archie's law represents a new mixing model that can be viewed as both a generalisation of Archie's law for two conducting phases, and as a generalisation of the parallel

model to incorporate variable connectivity of each of the phases. While it is expected that this model will not provide significant improvements over the conventional Archie's law in the analysis of clean formations at low temperatures, it is a large improvement if the matrix of a rock is significantly conductive, such as in partial melt modelling, or in the analysis of clay-rich reservoir rocks.

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