A STUDY OF THE FREQUENCY DOMAIN INDUCED POLARISATION EFFECTS DISPLAYED BY CLAY AND BY CATION EXCHANGE RESIN, MODEL SOIL SYSTEMS

Submitted for the

Degree of Master of Science in Chemistry at Victoria University of Wellington.

May 1972.

ABSTRACT

Work is reported of the development of clay and resin model soil systems for the observation of induced polarisation phenomena. A measuring technique is developed to determine impedance spectra of such models over the frequency range of 10^{-3} to 10^4 Hz, and a variety of model cells tested varying such parameters as temperature, electrolyte type and concentration, and bead size of resin.

An increase in impedance with decrease in frequency is observed, consistent with field observation of the induced polarisation phenomenon associated with moist, non-mineralised soils, and a number of empirical observations of the form of this are made.

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INTRODUCTORY MATERIAL

CHAPTER 1

INTRODUCTION TO INDUCED POLARISATION

i) Background

When an electric current passing into the earth through ground electrodes is suddenly interrupted, a potential can be measured between these or nearby electrodes for some time after the applied current stops (12). This decay is not exponential but roughly fits a hyperbolic expression (54).

$$V = \frac{K}{(C + t)^{X}}$$

where V is the induced voltage

t is the time

C, K and x are constants.

Nevertheless a time constant is often assigned and this is observed to have an order of seconds or tens of seconds.

Such a polarisation effect was known to Schlumberger as early as 1912 (51) and called by him " provoked polarisation", however when attempting to use this effect to prospect for the metallic ores he believed responsible, Schlumberger found that the effect of wet soils completely masked the effect he expected from metallic sulfides.

Over the years this phenomenon has come to be known as the Induced Polarisation (I.P.) effect from an analogy with polarised

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electrodes, but in confirmation of Schlumberger's observations, an electrode polarisation like model is now known to be responsible for only some observed I.P. phenomena. The term "over-voltage" again referring to an analogy with polarised electrodes has been used by Brant (7), and the perhaps more nearly correct term "Interfacial Polarisation" was recommended by Von Hippel (56) but is little used.

Investigators subsequent to Schlumberger (5,8, 38, 58) have found that while all soils do display a so-called "Normal effect" this background effect rarely is of the same order of magnitude as the polarisation effect of commercial metallic sulfide bodies. The I.P. technique has been used extensively since about 1950 to prospect for such deposits, the primary advantage of I.P. over resistivity surveying being the greater sensitivity and discrimination of the former in areas where the low resistance, electron conductive body, is highly disseminated or where there exists a highly conductive overburden or a well-defined fracture zone. The superior resolving power of I.P. over resistivity surveying in these circumstances is well documented in many case histories (35, 45).

The predominant cause of induced polarisation in geologic materials is believed to be the polarising of metallic minerals within the rock. Grains of electronic conductor* are considered to polarise

* Electronic conductors include not only metallic sulfides but also graphite, magnetite, and pyrolusite, which are all observed to give identical I.P. effects (38).

by the setting up of overvoltages at their surface as a current is passed. On this (microscopic) scale the Warburg treatment adequately describes the polarisation (36), but the derivation of a macroscopic model is the subject of some controversy. Since it takes a finite time to build up these overvoltages, one finds that the impedance decreases with increasing frequency. Qualitatively these effects behave somewhat as the ordinary dielectric properties of the material, and Keller and Licastro (25) conducted research into the frequency dependent conductance of core samples, expressing their data in terms of (large) dielectric "constants". These effects, however, occur at audio and sub-audio frequencies which are much too low for ordinary displacement currents to be of any significance (3).

In fact "time domain" measurements (so called because of the use of time as the prime variable) involving the observation of the secondary current or voltage decay in time, after the primary current ceases, are mathematically equivalent to the measurement of impedance as a function of frequency, through the Fourier transform provided the medium is linear. Measurements made with frequency as the prime variable are said to be made in the frequency domain, and such determinations have a conceptual advantage over similar time domain measurements in that the parameter observed (impedance) is the one commonly used in describing electrical phenomena.

Since Schlumberger's observation of the "provoked polarisation" effect of moist soils (51) it has been realised that the I.P. phenomenon is not exclusively caused by the presence of pore blocking electronic

conductors, and Mayper has shown (41) that the ubiquitous background effect of non-mineralised regions can be associated with the presence of clays. Marshall and Madden in a series of papers on the topic (35,36,37,38,39) have shown that the I.P. effect of clays results from their membrane properties, and that commercial ion exchange resins can be made to display an I.P. effect which is large, but similar in form, to that of clay systems.

ii) Field of Study

It is intended in this thesis to study exclusively the membrane polarisation phenomenon associated with model soil systems. It is hoped that ultimately a physical model of the membrane I.P. effect can be constructed which is applicable to the field of exploration geophysics, but the scope of this thesis is rather more limited (see p. 37). The usefulness of such a model, if applicable to the earth, is varied. Some applications are as follows:

1) In mineralised regions, by making a separate test of chemical properties of the soil, it may be possible to remove from the results of an I.P. survey that effect attributable to clays, leaving a residual I.P. effect due only to the mineral content. This would increase the sensitivity of I.P. surveys and enable hitherto undetectable mineral deposits to be prospected for.

2) I.P. surveys have been successfully conducted to find ground water (54), utilising the observation that wet clays have a considerably larger I.P. effect than dry clays. A more precise knowledge of the

effect of water amount on the observed I.P. response would, however, greatly aid the search for ground water.

3) The properties of a geothermal area which make it suitable for power generation are high temperature and high porosity, and thus resistivity surveys are highly suited as a method of prospecting for such zones (17). If a model for the I.P. response of clays could be extended to temperatures and pressures of the order of those found in geothermal regions, it is possible that a significant impetus could be given to the prospecting for exploitable steam reservoirs if I.P. surveys were conducted as well as or instead of resistivity surveys.

The practical advantages of an understanding of membrane polarisation are sufficiently great that further research in this poorly understood field seems justified.

iii) Parameters

A number of parameters have been evolved to describe both frequency and time domain data. These various single valued parameters describe a particular property of the I.P. response of a system, although none accurately describes the I.P. effect (see page 125). Nevertheless a number of parameters are widely used in the literature and to a limited extent to describe data in this thesis, and a description of the most common parameters must be given. Although this thesis involves (with only one exception) frequency domain determinations, much of the literature describes time domain data and a knowledge of the parameters used in both domains is necessary. When measurements are made in the time domain three parameters are commonly used to express the I.P. effect.

to the primary voltage 1) The ratio of the decay voltage/at a given time after the primary voltage is shut off, expressed in millivolts per volt. This is usually known as the mV/V parameter.

2) The ratio of the area under the decay curve from time t = t'to $t = \infty$ to the primary voltage. This is commonly expressed in millivolt seconds per volt (mV-sec/V) and is known as the polarisability.

3) Despite the non-exponential form of the decay curve a time constant is often assigned, being the time taken for the secondary voltage to decay to 1/e of the value assumed immediately upon shut off of the primary voltage.

If measurements are made in the frequency domain a complex impedance is measured which may be expressed as a function of frequency. In order to facilitate correlation of data from different systems the impedance (or the magnitude of the impedance) is often normalised by dividing the value at frequency f by the value at frequency F_0 , usually taken as the high frequency limit where the impedance is a minimum. In addition to these frequency dependent parameters two single valued parameters are often used by exploration geophysicists.

1) The frequency effect, f.e. (or the frequency effect per decade, F, as defined in Table 1). The frequency effect of the impedance is defined

f.e. =
$$\frac{Z_{Low} - Z_{High}}{Z_{Low}}$$

Where Z_{High} and Z_{Low} are the high and low frequency limits of the impedance respectively. In fact Z_{High} and Z_{Low} are often used as two frequencies for which the impedance need not have a limiting value, one being higher than the other.

The percent frequency effect is often used and describes the percent decrease of the impedance at frequency f from the D.C. limit. This is defined

% f.e. =
$$\frac{Z_{D.C.} - Z_F}{Z_{D.C.}} \times \frac{100}{1}$$

 \mathcal{F}) 3 The frequency effect parameter has the disadvantage of being strongly dependent on the magnitude of the shunt resistance, and in mineralised systems where the metal ore blocked pore may be shunted by pores containing electrolyte only, the frequency effect is a function of the concentration of electrolyte as well as the percentage of metal ore. For such systems the metal factor (M.F.) was defined to eliminate the effects of pore resistive shunts.

$$M \cdot F \cdot = (G_{\text{High}} - G_{\text{Low}}) 2 \pi \times 10^5$$
$$= \frac{Z_{\text{Low}} - Z_{\text{High}}}{(Z_{\text{Low}})(Z_{\text{High}})} \times 2 \pi \times 10^5$$
$$(= 2 \pi \times 10^5 \text{ f.e.}/Z_{\text{High}})$$

where G, the conductance, is equal to 1/Z.

Because of the inter-relation of time and frequency domain data through the Fourier transform (for a linear medium), one can in fact derive frequency information from transient measurements and vice versa. There is not an exact one to one correspondence between a point in a frequency domain and a point in a time domain, but there is often an approximate one. The percent frequency effect and the millivolt per volt parameters have been found by Marshall and Madden (36) to be related roughly by the equation

% f.e. at frequency f - 0.1 x mV/V value at time t = $1/2 \pi F$

This "rule of thumb" has proved very useful for determining similarities in general trends of frequency and time domain data, but cannot be relied on to give quantitative information. Such information can be obtained by performing a Fourier transform and Marshall and Madden (36) describe in detail the mathematics involved in such a transform. In practice the large amount of data handling necessitates the use of a computer. CHAPTER 2

LITERATURE SURVEY

i) Introduction

It has not been possible to review here the literature in a wide range of topics, primarily biophysical, which are related to membrane polarisation phenomena. In fact throughout the literature there appeared to be no study reported dealing with the frequency dependent impedance or transient response of membranes. An extremely brief section on the membrane properties of resin beads is included in the next chapter, and a slightly more detailed survey of the properties of clay (specifically montmorillonite) is presented in chapter 8.

The following is a survey first of the electrical properties of clays (Self Potential and excess conductivity) and secondly of the work done on the Induced Polarisation of clay systems.

Only three major surveys have been conducted into the membrane polarisation effect, those of Vacquier et al (54), Keller et al (2,25,26,27), and Marshall and Madden (35,36,37,38,39); with Vacquier making studies and reporting data in the time domain, Keller in a "dielectric" type, ratio frequency, frequency domain, and Marshall and Madden at lower frequencies in the frequency domain. As such the data cannot easily be compared between these surveys, and only on a few points can correlations of the observations be made. With this in mind, rather than presenting a critical review of the subject, each of these bodies of work is considered individually.

ii) The electrical properties of clays

Early models of the effect of clays on the soil conductivity were proposed to explain the abnormal conductance found in shaly reservoirs containing electrolyte, in electric well logging, and to explain the self potential observed associated with clays in shaly zones.

3

McCardell and Winsauer (42-1953) conducted research into such self potentials and proposed a model of the shale as a mass of clay particles or aggregates of clay, which enclose a network of interconnecting pores. When electrolyte saturates the pore channels the total concentration of mobile positive ions is higher than that of mobile negative ions due to the presence of a layer of fixed negative exchange sites on the clay surface which is balanced by a diffuse double layer of cations (15,16). The authors consider self potential to be the result of a Nernst type potential occurring at the boundary between the pore network and the electrolyte solution with which it is in contact.

In a second paper Winsauer and McCardell (60 - 1953) consider the anomalously low resistivity factor* observed in shaly sands. The authors attribute this excess conductivity of shales to the double layer at clay surfaces in which the concentration of cations near the clay

* The resistivity factor is defined as the resistivity of the rock when completely saturated with electrolyte, divided by the resistivity of the electrolyte itself.

surfaces (in which the concentration of cations near the clay surface may be much greater than in the bulk solution.

A plot of ionic concentration versus distance from the double layer indicates that the excess concentration of cations varies markedly with surface potential, and that although there are fewer mobile negative ions in the double layer than in the bulk solution, the difference in the two anion concentrations is not great. As a result the number of mobile ions in the double layer is greater than in the bulk solution. In terms of ion exchange the clay can be thought of as having a number of fixed negative sites, which in the dry shale are balanced by weakly bonded cations. When the clay is saturated with electrolyte these cations become very loosely associated and form a double layer, from which they may be exchanged by other cations giving rise to a cation exchange capacity, or they may contribute to the conductivity of the system giving rise to a surface conductivity phenomenon. Since the same cations are involved in exchange as in the excess conductivity. the number of cations participating can be deduced from the cation exchange capacity.

McKelvey, Southwick, Spiegler and Wyllie (43 - 1954) proposed a three element model for the S.P. and resistivity phenomena characteristic of dirty sands, on the basis of conductance measurements of natural and synthetic dirty sands, the latter consisting of mixtures of synthetic ion exchange resins and glass beads. The model proposed represents the electrical conductance of a plug of electrolyte saturated resin as the sum of three conductance elements, the first being an element of solution and particle conductance in series, the

second an element of particles only and the third an element of solution only (see Figure 1a).

While the mathematics is not directly applicable to I.P., the concept of parallel conductive elements may possibly be of some value. Still more important, this work apparently represents the first use of ion exchange resins as model clays in electrical studies.

iii) Induced polarisation studies

Vacquier et al (54 - 1957) performed a number of time domain I.P. studies on clay/sand mixtures in open troughs, saturated with a variety of electrolytes. Measurements of the decay voltage and of the electronically integrated decay were made and correlated with a number of parameters. These observations are far from conclusive in proving the model proposed by Vacquier, but are valid experiments and give an indication of some of the properties of the I.P. phenomenon in the time domain.

Some experimental determinations made are as follows.

1) Clean quartz sand and "water" displayed "almost no I.P. effect" and a clay slurry was likewise unpolarisable even with dry quartz sand added. Polarisable samples were prepared by drying a sand/clay slurry and re-wetting (see p.95).

It is not clear even now, whether the clay must be fixed to a matrix in order for an I.P. effect to be observed, or whether no I.P. effect is obtained from homogeneous clay suspensions simply because they are homogeneous and individual clay particles interact identically with all their colloid neighbours.

FIGURE 1



 The polarisability of a given sand/clay/electrolyte system (mV-sec/V), is independent of the charging voltage gradient.

3) For a given specimen and excitation time the polarisability is exactly proportional to the density of the charging current.

4) The magnitude of the polarisability (mV-sec/V) and mV/V parameters depend in some complicated (and as yet undetermined) fashion on

a) The concentration of the electrolyte. A number of studies in both the time and frequency domain in Vacquier's and subsequent works (including this thesis), have shown the I.P. effect to increase with decreasing concentration (39,52), but the form of this increase is not known.

b) The particular ion saturating the clay. Again a number of time and frequency domain studies have been made of the dependence of I.P. on the saturating cation (35,36,37,38,52), but apart from a possible trend of decreasing effect with increasing rate of exchange (see p.16) the form is not known.

c) The amount and kind of clay present. Extremely simpleminded and implausible considerations of Anderson and Keller (2) suggest that the I.P. effect should maximise when the concentration of anions (a) is twice the concentration of exchange sites (a') - determined by the amount and type of clay. Determinations by them show such a maximum, but whether or not it occurs for a' = a/2 is not known.

5) Using an isotopically labelled NaCl electrolyte it was found that the magnitude of the polarisation increases with sodium

content on the clay*, and decreases with the ion concentration in the electrolyte. Vacquier states that "the interplay of these factors combine to product an approximately linear variation of polarisability with resistivity of electrolyte", however equally valid experiments of Schufle (52 - 1959) have shown that the rate at which polarisability increases with resistivity becomes less rapid as the solution becomes more dilute.

6) On percolation with HCl the Na population on the clay drops to zero, and the polarisability drops to a value about one third as large as for NaCl. Vacquier states that a possible explanation for the residual effect is the clogging of exchange positions with aluminium ions and cites Grim (15) as stating "it is substantially impossible to prepare a clay in which all exchange positions are occupied by H⁺, since Al⁺⁺⁺ moves from the lattice into exchange positions before saturating with HCl becomes complete." Vacquiers hypothesis, however, seems an unlikely and an unnecessary one, since there is no reason to assume that H⁺ ions behave dissimilarly from other exchangeable cations and produce no I.P. effect, nor is it likely that 37% of the exchange sites of Vacquier's kaolin are clogged with Al⁺⁺⁺.

- * The clay under study was kaolin, initially in the hydrogen form by electrodialysis.
- ** According to Mukherjee et al (49 1946) kaolinite is only slightly susceptible to clogging of its exchange site by the withdrawal of Al or Mg from the sheet structure into exchange positions.

7) The rate of decay of the induced potential is independent of the electrolyte and not greatly influenced by the type of clay, and seems to be principally influenced by the grain size of the sand. Since the thickness of the double layer is strongly dependent on the nature of the electrolyte, this result suggests that the decay time is independent of the double layer thickness.

8) The induced polarisation observed in the field of dry soils (dry in the geologic sense that they contain no interstitial water), while being smaller in magnitude, has a similar decay time to that observed in saturated alluvium.

On the basis of these observations Vacquier et al conclude that induced polarisation is a result of local electrodialysis of the clay across semipermeable partitions formed by adjacent sand grains. More specifically, their model states that the I.P. voltage is a result of a concentration cell being set up in a region where two sand grains are close together through which the electric field gradient is increased due to constriction (see fig. 1b). In such a zone conduction occurs through the double layer affecting the concentrations of ions in the double layer. Thus the function of the clay is to provide a source of sink for ions, which relax to their equilibrium positions upon termination of the applied field.

In fact this model does little to increase the understanding of I.P. phenomena since the mechanisms of "local electrodialysis" are unknown. Nevertheless it is possible to make a number of predictions from the model as follows.

The decay time should increase with grain size since (assuming spherical grains), the greater the grain size the greater distance the double layer overlap is operative, and hence the greater the distance the ions must travel, and the longer the decay time. This is observed by Vacquier, a plot of log (polarisation voltage at 5 seconds/ polarisation voltage at 20 seconds)* versus log grain diameter being linear with a negative slope.

The model in its simple form should, however, predict a marked dependence of the decay time on the double layer thickness, since (again assuming spherical grains and a uniform coating of clay) the distance of the double layer overlap would be strongly dependent on the thickness of the double layer. Vacquier's observations are contrary to this (see 7 above).

The polarisability should vary with the rate of exchange of a particular saturating cation since the more firmly bound the cation is to the exchanger, the less the equilibrium configuration in the double layer will be disturbed by the passage of diffusing ions. All other factors being equal, the higher the valence of the cation, the more firmly it is bound to the exchanger (31). Schufle (52) measured the time domain I.P. effect of NaNO₃, Ca(NO₃)₂, La(NO₃)₃, Th(NO₃)₄ over a concentration range of 0.00004 to 0.01 Normal (N). He observed some difficulty in forming reproducible clay/sand beds,/measurements were made on mixtures of $\frac{1}{50}$ cation exchange resin and 95% sand by volume, both 20-30 mesh.

* This parameter is a function of the reciprocal decay time.

Schufle's results are plotted as graphs 1 of mV-sec/V versus log concentration, and 2 of mV-sec/V versus cation valence. Graph 2 shows the expected decrease of polarisability with cation valence, but this is regular only for 0.005N electrolyte. Graph 1 of polarisability versus log concentration, except for the Na plot, shows an increase of I.P. with decrease in concentration, but quite clearly the concentration effect is different for different cation valences.

In all it would seem that while insufficient information is available to prove Vacquier's model, and certain inconsistencies do exist, the model cannot be dismissed.

Keller and Licastro (26, 27, 28 - 1959) conducted research into the conductance and capacitance of core samples equilibrated with tap water, expressing the capacitance in terms of a dielectric "constant" (see p. 3), in the frequency range 50 to 3×10^7 Hz. The authors observe that the water content seems to be the controlling factor, high resistivities being associated with low water content, and high "dielectric constants" with high water content. The model proposed to explain these observations considers the rock to be a semipermeable membrane with fixed negative charges scattered through it whereby the negative ion flow is impeded more than the positive. A typical pore structure is considered to be a series of large spherical voids connected by thin fibrous channels (Fig. 2a). Clay particles in the constrictions of the interconnecting channels impede the migration of mobile negative ions if these are forced by constriction to travel





FIGURE 2

a) Idealised Pore (Keller and LICASTRO)



Ion concentrations



through the double layer and thus within the repulsive force field of the fixed negative surface layer on the clay.

In this model the positive ions are free to move through the rock under the influence of an external field, but the anions may proceed only until they come to a constricted pore occupied by a clay particle bearing a surface charge. At this point anions will start to accumulate and will achieve a concentration in excess of their mean concentration after a prolonged unidirectional field has been applied. Upon termination of the field this anion concentration is considered by the authors to relax non-symmetrically to its equilibrium configuration producing a current accompanied by a potential, observed as I.P.

A model suggested by Dakhnov et al (11 - 1952) to explain the large polarisation in non-metalliferous rock material, is the storage of charge by electro-osmosis. When a voltage is applied across a rock the fluid in the pores may be carried along parallel to the clay double layer coupled with the electric current. If this pore fluid is richer in one sign of ion than the other then there will be an electrical current flow associated with the fluid flow, which will continue when the exciting current is removed due to the inertia of the water. This current may appear as an I.P. signal, decaying proportional to the sum of the exponential slowing of the fluid in each pore due to friction.

The induced polarisation effect is most pronounced in rocks containing graphite and disseminated sulfides (39, 46, 58), and a

moderate I.P. effect is observed in clay bearing rocks (25,54), but in fact a low frequency polarisation is observed in every natural rock material. This latter ubiquitous effect is called by Mayper the "Normal Effect", and a number of possible explanations have been presented for its occurrence, being due to the following:

1) The electrokinetic response of air bubbles in the rock pores.

- 2) To other more obscure electrokinetic effects in the mobile part of the double layer (of clays) in the pore structure, as for example Dakhnov's model.
- 3) To electrically induced ion-exchange disequilibria (or to other electrochemical reaction gradients) in particles (specifically clays) in the rock pores, as for example Vacquier's model.
- 4) To surface conduction phenomena on the mineral crystals.
- 5) To "non-conducting" minerals which actually have the small conductivity required to act as good conductors with respect to electrochemical polarisation.
- 6) To the presence of otherwise undetectably small amounts of electronic conductor within a very tight pore structure, acting to produce an electrode polarisation type I.P. response.

In a series of experiments designed to differentiate between these, Mayper (41 - 1959) made tests of the time domain I.P. response of core samples and of artificial "clean" porous material. He found that the I.P. response of a variety of porous glass and porcelain normals in 0.01M CuSO₄ solution was zero, and took this to indicate that electrokinetic effects involving the double layer (point 2 above)

are not important, arguing that such clean material has a double layer yet does not display an I.P. effect. Mayper does not consider the substantial modification to the double layer configuration in pores caused by the discrete deposits of clay almost certainly present in natural specimens, and his argument is not reasonable.

Mayper gives proof that the normal effect is indeed due to the presence of clays in rock samples, by measuring the I.P. effect after various degrees of heating.* Strangely, many samples display a maximum I.P. response after heating to about 500°C, but the rapid decline of the I.P. of all samples after heating above 600° is strong proof that clay is responsible for a large part of the normal effect. (Still, the presence of a very small percentage of fine grains of electronic conductor in a tight pore structure, point 6 above, may well be responsible for a large part of the normal response, since as long as the metallic grain blocks a pore, its size, and thus the volume percentage, is irrelevant).

The surface conductor and non-conductor theories (points 4 and 5 above) are not entirely disproved by Mayper, but their effects are considered to be small.

An interesting effect is observed by Mayper regarding the presence of air bubbles, that these were responsible for erratic, sometimes high I.P. responses in artificial "clean" samples. It is suggested by Mayper that elaborate precautions be taken to exclude air bubbles in laboratory experiments, but that the electrokinetic

* Interestingly rock samples showed practically no variation in I.P. response with temperature between 20 and 70°C.
response of air bubbles does not constitute a significant part of the normal effect.

Despite Mayper's assertions to the contrary it would seem, however, that both ion exchange disequilibria and electrokinetic phenomena associated with clays are possible causes of appreciable I.P. responses in geologic materials.

Madden and Marshall and co-workers in a series of papers (35,36, 37,38,39) dating from 1957, describe an extensive research into induced polarisation of both electrode and membrane origin, observed in the frequency and time domains. Unfortunately until recently only the last of these was available. In this series of papers the authors develop the only comprehensive model relating to the I.P. effect of membrane systems presented to date, but fail experimentally to prove the validity of this model.

Madden and Marshall consider membrane induced polarisation to be due to a coupling of flows, and after rejecting EM coupling as being negligible under about 10 Hz, set up equations describing a general electrolyte with coupling, after the manner of the Thermodynamics of Irreversible Processes (T.I.P.). These equations may be represented by the following matrix.

Flow of cations =
$$\begin{bmatrix} J_p \\ J_n \\ J_s \end{bmatrix}$$
 = $\begin{bmatrix} L_{11} & L_{12} & L_{13} & L_{14} \\ L_{21} & L_{22} & L_{23} & L_{24} \\ L_{31} & L_{32} & L_{33} & L_{34} \\ L_{41} & L_{42} & L_{43} & L_{44} \end{bmatrix} \begin{bmatrix} -\nabla \mathcal{M}_p & -F & Z_p \Delta \vec{p} \\ -\nabla \mathcal{M}_n & -F & Z_n \Delta \vec{p} \\ -\nabla \mathcal{M}_n & -F & Z_n \Delta \vec{p} \\ -\nabla \mathcal{M}_n & -\nabla P \end{bmatrix}$

where ϕ = electric potential

M = chemical potential
P = pressure
T = temperature
F = Faraday's constant
Z = ion valence
L_ij = L_ji

On the basis of this Marshall and Madden reject Electro-osmotic and Thermoelectric coupling as producing negligible effect under geologic conditions. As such, when considering Diffucion Coupling, the cross terms in the matrix equation may be considered to be zero, and when the diagonal terms relating the flow of cations to the potential experienced by the anions (L_{12}) and vice versa (L_{21}) are removed, the equation becomes

$$J_{p} = -L_{11} \nabla \mathcal{M}_{p} - L_{11} F Z_{p} \nabla \emptyset$$
$$J_{n} = -L_{22} \nabla \mathcal{M}_{n} - L_{22} F Z_{n} \nabla \emptyset$$

or, in more familiar terms, replacing the coefficients L with the diffusion and mobility coefficients,

$$J_{p} = - D_{p} \frac{\mathbf{\delta} P}{\mathbf{\delta} x} + U_{p} P E$$
$$J_{n} = - D_{n} \frac{\mathbf{\delta} N}{\mathbf{\delta} x} - U_{n} N E$$

where U = mobility

D = diffusion coefficient

P = cation concentration

N = anion concentration

E = Electric field

 t^{+} = cation transference number = $U_p/(U_p+U_n)$ t = anion transference number = 1-t⁺

If t⁺ should vary along the current path, a divergence will result in the flow of ions, causing concentration gradients.

On the basis of this Marshall and Madden propose a model for membrane polarisation involving a pore containing strongly cation selective zones (II - see fig. 2b) interspersed with neutral zones (I) having no selectivity. Because of its selective transference properties the current in zone II is largely carried by cations, and a surplus of these ions will be found at the end of such a zone. The anion flow will also be unbalanced and the build-up of anions will be equal to that of the cations. The resulting concentration gradients will modify the ion flow until a steady state is reached under which conditions the net flows of cations and anions in zone II will equal those in zone I

- (1) $J_{\mathbf{PI}} = J_{\mathbf{PII}}$
- (2) $J_{NI} = J_{NII}$

The impedance will be modified by the diffusion potentials associated with the concentration gradients developed.

The cation and anion concentrations can be considered as equal

(3) P = N

The electric field is assumed to be constant in each zone, so the total potential difference across a pair of zones is given by

$$(4) \quad \emptyset = - \mathbb{E}_{I} \Delta \mathbb{L}_{I} - \mathbb{E}_{II} \Delta \mathbb{L}_{II}$$

Since P and N will be continuous across the boundaries, if succeeding zones repeat the same geometry and electrical properties, we can put

> (5) $P_I = - P_{II}$ (6) $N_I = - N_{II}$

Assuming the concentration gradients are constant in each zone, a solution of (1), (2), (3), (5) and (6) for the steady state conductivity $\sigma_{D.C.}$ is

$$\sigma_{\text{D.C.}} = \frac{\text{F U}_{\text{PI}} \text{ C } \left(\frac{1}{\text{t}_{\text{II}}} + \frac{\text{A}}{\text{B} \text{t}_{\text{T}}}\right) \text{ S}_{\text{I}} \text{ S}_{\text{II}}}{\Delta \text{L}_{\text{I}} \left[\text{S}_{\text{I}}(1+\text{B/A}) + \text{S}_{\text{II}}(1+\text{A/B})\right]}$$

where C = net concentration

$$A = \Delta L_{I} / \Delta L_{II}$$
$$B = D_{PI} / D_{PII}$$
$$S_{i} = t_{i} / t_{i}^{+}$$
$$\Delta L_{i} = \text{length of zone i}$$

At the high frequency limit no concentration gradients develop, and the only unknowns are the potential gradients, Using (4) a solution is

(7)
$$\sigma_{A.C.limit} = F U_{PI} C A/\Delta L_{I} (A t_{I}^{+} + B t_{II}^{+})$$

and the maximum frequency effect that diffusion coupling can create is

(8)
$$\sigma_{A.C.} / \sigma_{D.C.} = \frac{(A+B) \left[\frac{A}{t_{I}} + \frac{B}{t_{I}} + \frac{B}{t_{I}} + \frac{B}{t_{I}}\right]}{\left[\frac{A}{t_{II}} + \frac{B}{t_{I}}\right] \left[\frac{A}{t_{I}} + \frac{B}{t_{I}}\right]}$$

The authors have shown that under geologic conditions diffusion coupling is capable of producing a considerable frequency effect by the above model.

It is interesting to note that if zones of positive ion blocking capacity exist as well as negative ion blocking zones (such as is the case with some synthetic **ion** exchange resins) then the frequency effect could increase without limit.

Also important is the dependence of the I.P. effect on the length ratio A. If a material has zones of very high cation transference number (t^+) but the zones are too numerous so that the conduction path lies primarily within these zones, little polarisation will result. This is a possible explanation for the small I.P. effect of massive clay banks observed by Vacquier (54 - 1957), and the reason why he could get an I.P. effect only when his clays were coated on sand grains.

Using Poisson's equation Marshall and Madden derive an expression for the membrane impedance,

$$Z = \frac{\Delta L_{I}}{U_{PI} CF} \left[t_{I}^{+} + \frac{B\Delta L_{II}^{+}}{A} + \frac{(S_{II} - S_{I})^{2}}{\frac{X_{I} S_{I}}{(t_{II}^{+})^{2} t_{I}^{+} \tanh X_{I}} + \frac{A X_{II} S_{II}}{B t_{II}^{+} (t_{I}^{+})^{2} \tanh X_{II}} \right]$$

where
$$X_i = (j w/2 D_{pi} t_i)^{\frac{1}{2}} \Delta L_i/2$$
.

This equation is derived using a number of approximations to obtain a solution of the differential equations. One of these is the dropping of terms of powers greater than one, and Marshall and Madden consider this assumption to be valid at low current densities.

The complexity of this equation does not make it easy to visualise the form of the impedance, however, the equation can be considered at the high and low frequency limits, and the impedance is found to have an asymptotic shape. At very low frequencies, we can expand the hyperbolic tangents in their power series with the result that the impedance looks like that of a parallel RC circuit. The frequency range over which this is expected, however, is so low that the parallel capacitor has essentially no effect, and the lower asymptote occurs. At the higher frequency limit tanh X approaches unity and the upper asymptote is reached.

Assuming appropriate values for some of the parameters*, Marshall and Madden plotted hypothetical impedance versus frequency plots, varying the remaining parameters to determine the effect of these. Their graphs show in all cases a transition between the high and low frequency limits that is about 95% complete in 3 decades. A decrease in the zone length ratio (A) from 11.3 to 1 is shown to move the point of inflection to higher frequencies by about 2 decades, as well as to

* The parameters assumed are a selective zone length of

$$\Delta$$
 L_{II} = 3.2x10⁻⁴ cm

and a non-selective zone transference number ratio of

$$S_{T} = 1.00.$$

decrease the frequency effect. Until the existence of discrete selective and non-selective zones has been proved, and the dependence of the length ratio of such zones on the gross features of the membrane system is determined, A must remain a quasi-empirical parameter and its effect on Z cannot be measured directly.

As expected from the basic proposition of the model, the effect of decreasing S_{II} (the transference number ratio in the selective zone) is to increase the I.P. effect. Again, the transference numbers cannot be assessed in the membrane, and S_{TT} is semi-empirical.

The effect of B (the ratio of the cation diffusion constants in zones I and II) is also shown to be an inverse one with I.P. effect; as B is increased the frequency effect is decreased. Thus the model predicts that an increased mobility of the cation in zone II with respect to that in zone I, will increase the frequency effect.

The variation of frequency effect with A, B and S may be seen from the following.



As a test of their model Marshall and Madden made both frequency and time domain observations on clay and ion exchange resin systems.

1) Clays

(mostly kaolinite) to pressures of from 1 ton/ft² to 250 tons/ft² using

a plastic piston. Dispersed samples were also prepared by adding 0.02% by weight of trisodium phosphate per gram of supernatant fluid. The transient measurements of these systems gave frequency domain information at 0.1. 1 and 10 Hz through a Fourier transform, and the frequency domain measurements from 10 to 20,000 Hz. The frequency effects observed were quite large, some being of the order of 6%/decade, but the spectra are spread out over a tremendous range compared with the model. This is not surprising considering the distribution of lengths expected for clay particles. There is little evidence of an asymptotic behaviour on any of the spectra for the five decades observed, 0.1 to 10.000 Hz. except that of compacted natural kaolinite in distilled water, for which a possible inflection point was observed. Based on this inflection point, and assuming a value for A of unity, Marshall and Madden calculate from their model a selective zone length of 20,000 Angstroms, which, according to Lambe (33) is of the order of the long axis of kaolinite particles. It would appear then that the I.P. technique was sampling the fine details of the clay structure.

This calculation raises the interesting point that, since kaolinite particles are the largest among the common clay types (illite and montmorillonite being perhaps ten times smaller in size), that if the model is correct, an inflection point for these other clays might occur at frequencies as high as 10⁵ Hz. This is out of the range of geological interest (see p.38), but Marshall and Madden suggest that it may be necessary to perform experiments on montmorillonite into the megahertz region in order to test the model, although they do not do so.

The authors observe that the impedance spectrum for natural kaolinite flocculated in distilled water is dramatically different from that for flocculated samples of sodium clay in 0.0001M NaCl. Since the model predicts no change in f.e. with conductivity of electrolyte, the authors seek to explain this effect on the basis of the large percentage of calcium found at the exchangeable sites of natural kaolinite. In order to check the possible influence of calcium ions, a system of kaolinite homoionic to Ca and of 0.01M CaCl₂ was tested and found by Marshall and Madden to exhibit no frequency effect. This last observation is very strange in view of the large I.P. effect observed by Vacquier (54) of 5% calcium from kaolinite/80-100 mesh sand grains/7.7 ohm-meter CaCl₂.

2) <u>Resins</u>

Marshall and Madden conducted a limited number of I.P. investigations on cation exchange resins (Dowex 50, 20-40 mesh and smaller than 400 mesh) and on mixed beds of cation and anion exchange resins (50% Dowex 50 and 50% Dowex 1, both larger than 100 mesh) in a column, partially enclosed with a heating jacket. Silver/silver chloride electrodes were inserted at the ends of the column, and the impedance of the column measured by a two terminal technique at audio and sub-audio frequencies. The current density used was of the order of $3x10^{-5}$ Amps/cm² which the authors consider to be low enough to insura linear behaviour. Spectra were run using resin equilibrated with. 0.012M NaCl and 0.010M KCl (which electrolytes have the same conductivities), at 25 and 45^o C. The results although containing considerable inaccuracy, show an impedance spectrum of approximately asymptotic form for NaCl and KCl, the impedance level decreasing with temperature for NaCl/resin, and increasing for KCl/resin.

Using this data in their model, Marshall and Madden calculate an effective selective zone length of 0.0003 to 0.003 cm. These values do not correlate with any apparent property of the resin. The resin particles themselves are much larger than this (0.042 to 0.084 cm) and it is generally agreed on the basis of electron microscopy, X-ray and other data (31, 32, 50) that individual particles are essentially a homogeneous network of molecules, and that irregularities occur on the molecular scale.

Interestingly, observations of smaller than 400 mesh resin (0.0037 cm diameter) failed to show any impedance variation from 0.01 to 1,000 Hz.

A measurement of a 50:50 mixture of larger than 100 mesh anion and cation exchange resin exhibited a larger frequency effect between 0.01 and 10,000 Hz than the sum of the effects of the resins taken separately. This result supports the model of Marshall and Madden that the I.P. effect is due to a change in transference number between alternate zones. The f.e. is not larger since (assuming a close packed mixture of resins) one would expect any sphere to be surrounded by 50% of its own kind and 50% of the opposite, and only in $\frac{1}{2}$ of the cases will a test particle proceed from a cation selective zone (via a non-selective zone) to an anion selective zone.

. 30.

The results of the experiments of Marshall and Madden fail to provide conclusive evidence for or against their model. This is partly because the experiments were far from exhaustive, but chiefly because the large number of indeterminate parameters in the model make it impossible to correlate results with a separately determinable parameter. Assuming the mobility and transport properties of the non-selective zone to be determinable from the external electrolyte, then only one parameter of the non-selective zone, its length (ΔL_{I}), and three independent properties of the selective zone, the cation transference number (t_{II}^{+}) , the cation diffusion coefficient (D_{PII}) and the length (ΔL_{II}), remain indeterminate. All four parameters are essentially independent and each is conceivably variable over quite a wide range, this indicating an almost total lack of ability of the macroscopic model to predict any more than general trends without a further microscopic model or an applicable set of boundary conditions for the four unknowns.

A further failing of this model is the inability to predict the gross two terminal impedance of a membrane system. The model describes the impedance of a single series of alternating zones, but in fact such zones will be shunted by pure resistive electrolytic paths and by other impedances. Further, the alternating pairs will not be identical, and the four indeterminate parameters will in fact vary from zone to zone. These complications can only be taken into consideration statistically and as yet no such analysis has been made. Marshall and Madden assumed that the effect of having a distribution of zone parameters was to spread out the frequencies of the impedance spectrum, but it is unlikely that this is the only effect. L.S. Collett (10 - 1959) made time and frequency domain measurements on both mineralised and non-mineralised andesite particles of diameters 2.0 to 0.84 mm, varying

- a) The primary or exciting voltage
- b) The amount of electrolyte
- c) The type of electrolyte
- d) The concentration of electrolyte
- e) The temperature

in order to assess the degree of linearity of such systems (see Ch. 5, part iii) and to determine the similarity of the I.P. response due to clay and to electronic conductors.

The results obtained by Collett are summarised as follows:

a) Linearity

In the voltage range 10 to 20 volts the samples tested were only approximately linear.

b) Electrolyte Amount

For the non-mineralised (NM) specimen the I.P. effect appeared to maximise for about 2% electrolyte amount.

The mineralised (M) specimen showed no significant change in the shape of the decay curve for electrolyte amounts from 1 to 10%.

c) Electrolyte Type

NM - the decay curve is independent of type

M - the decay curve is essentially independent of type.

- d) Concentration of NaCl
 - NM the decay curve shows a uniform upward shift with increasing concentration* except for an anomalous curve for 0.005M.
 - M varying the concentration influences both the magnitude and slope of the decay curve, but there is general increase in magnitude with decrease in concentration.
- e) Temperature
 - NM the secondary response increases with increasing temperature.
 - M the secondary response decreases with increasing temperature.

Fraser, Keevil and Ward (13 - 1964) in a study of the frequency dependent conductivity of a number of core samples have utilised the shape of the conductivity spectrum to deduce the nature of the polarising species within the rock. The electrical response of 43 specimens was studied as a function of the frequency between 0.1 and 1,000 Hz and it is observed that while the log conductivity spectra of mineralised samples are concave up or sensibly linear, spectra for clay-containing sandstone samples are slightly convex up. Because of the rather restricted frequency range examined by Fraser, Keevil and Ward, it is still possible that the form of the conductivity spectrum is asymptotic, consistent with Marshall and Madden's model, and that only the high frequency portion is being observed.

* This is in direct contrast with Vacquier's (54) observations, and of all subsequent observations of the membrane I.P. effect, and must be viewed with some suspicion.

Henkel and Collins (19 - 1961) consider two models of induced polarisation in clay/electrolyte systems, described as the dipole layer model and the clay conductor model.

In the dipole layer model (DLM) it is assumed that the clay particles have charge surfaces in contact with an electrolyte solution, and that the electric field arising from the charged surfaces gives rise to polarised layers of molecules adjacent to the surface (Fig. 3a). Upon application of an external electric field, the total fields at the clay surfaces change, and subsequently the polarisation of the polarised layers change. A mathematical expression is derived for this (ref. 19).

In the elementary clay conductor model (CCM) it is assumed that the current flows across clay/solution boundaries, that the cell consists of a solution region and a clay region (Fig. 3b) and that the current may take one of two paths through the cell - either through solution only, or through solution, across a solution/clay boundary, and through the clay.

According to Henkel and van Nostrand (20), the polarisation induced at a solution/conductor boundary is inversely proportional to the effective electrolyte concentration, and proportional to the current density

$$V = g I_{cs} r_{s}$$

- where V = Induced Polarisation
 - g = proportionality constant
 - I cs = Normal current density flowing across conductor/ solution interface

r = solution resistivity



and and a second second

$$V/V' = H r_{s}/(r_{s} + B)$$
 where $H = g/h$
(= mV/V parameter/1000)

In an attempt to decide between the two models, determinations of V/V' were made for NaCl saturated core samples, at concentrations ranging from 0.005 to 0.5 M. This data showed a reasonable fit for a theoretical curve of $r_{\rm s}/(r_{\rm s} + B)$, but the DLM failed almost completely to describe the observations.

iv) Discussion

The literature concerning induced polarisation describes experiments performed on clay and ion exchange resin systems as follows.

1) Clay-containing core samples

a) Time domain: Keller (2, 25, 26, 27) Mayper (41) Collett (10) Henkel and Collins (19)
b) Frequency domain: Fraser, Keevil and Ward (13)

2) Clay bonded to an inert matrix

a) Time domain: Vacquier (54)

- b) Frequency domain: None
- 3) Compressed clay systems

a) Time domain:)
b) Frequency domain:)
b) Frequency domain:)

4) Ion exchange resin systems

- a) Time domain: Schufle (52), Marshall and Madden
- b) Frequency domain: Marshall and Madden (35, 36, 37, 38, 39).

For the purposes of constructing a detailed model of the membrane polarisation effect, observations of core samples are useless, since there can be almost no control on the pore configuration, and the electrode polarisation effects of a very small amount of metallic contaminant may produce large errors (41).

This study is to be performed primarily in the frequency domain, in pursuit of the membrane polarisation properties of clays, but for a variety of reasons (see p.39), initial observations were made of resins, which have previously only received a cursory frequency domain study by Marshall and Madden. For clay determinations the perhaps more geologically realistic system of clay/inert matrix was chosen, this system having previously received no attention in the frequency domain. CHAPTER 3

INTRODUCTION TO THESIS

A) Aims

The aims of this thesis are as follows:

1) To determine the optimum cell design for the study of possible frequency dispersion of the impedance of its contents. The features which must be considered are the gross shape of the cell in respect of the accessibility of its contents, the ease with which the cell may be cleaned, and the situation of the contents with respect to the electrodes; and the type, configuration and accessibility of the electrodes.

2) To determine what if any dispersion effects occur with clays, ion exchange resins and glass beads, and what general form this dispersion takes. In this endeavour a method must be found of correlating data from different cells in order to assess the similarities and differences between the response of varied systems.

A sub objective under this heading is to construct a resin/glass bead system which behaves as a clay system does, and to use this resin system in an attempt to explain the clay dispersion phenomenon.

3) To extend the frequency spectrum to as wide a useful range as possible. This "useful" range is bounded at the low frequency end by noise problems and the limit imposed by the allowable length of the experiment, and at high frequencies by problems of electro-magnetic (E-M) coupling and skin depth. At 10 k Hz the free air wavelength of EM radiation

 $= 3 \times 10^4$ meters

and E-M coupling can be ignored for a cell whose dimensions are of the order of 10 cm but not for a field resistivity survey whose spread may be of the order of 10^3 meters. Thus extending the frequency spectrum above 10^4 Hz does not extend the range for which model determinations are applicable to the earth.

The skin depth also is a frequency dependent parameter which must be considered in the earth but may be ignored in model determinations.*

B) Ion Exchange Resins

i) Precedent

Several earlier investigations have used ion exchange resins as model soil systems both in studies of the transient response with regard to I.P. phenomena (38, 52) and of the electrical resistivity with regard to well logging problems (43). In each case no rigorous attempt was made to justify either experimentally or theoretically the use of resins in a model system, but the tacit assumption which underlies their use as model clays in I.P. investigations is that the phenomenon is caused exclusively by the presence of bound negative sites on an

* The skin depth (d) is that distance below the surface of a conductor where the current density has diminished to 1/e of its value at the surface. d $\propto 1/f^{\frac{1}{2}}$

38.

otherwise inert matrix. It is these sites which, if situated in a suitable pore system, give both clays and resins their membrane properties of semipermeability.

Vacquier's model of "local electrodialysis across semipermeable partitions" involving a disequilibrium among the exchangeable cations caused by conduction over the clay in restricted zones when a (charging) current is applied, involves exclusively the properties of the clay which determine its membrane properties and treats the rest of the clay/sand/electrolyte system as inert, acting only as a shunt resistance. As such, Vacquier's model may be considered as a membrane system and any system having semipermeable zones should display an I.P. effect. Marshall and Madden (35, 39) specifically consider the I.P. phenomenon to be due to the membrane properties of clay and develop a mathematical model based on alternating ion selective and non-selective zones which results in a frequency dispersion of the form observed, under some conditions.

ii) The Use of Resins

Several reasons exist for using resin models instead of the clays themselves in the preliminary investigations.

These are as follows: -

1) The ease of obtaining, of handling and of exchanging resins as opposed to clays.

2) The considerably greater reproducibility of pore structure possible with resin systems.

3) The larger impedance dispersion effect of resins primarily due to their higher exchange capacities (15,16,31,32,35,43).

The exchange capacities of the resins used in this work were about 5 meg/g and for kaolinite, 0.1 meg/g.

4) The highly stable, well characterised, simple structure of resins facilitates any mathematical treatment of the data.

The use of resins in this work is firstly with the view of testing such membrane models as have been proposed to date, and secondly to set up a resin system that behaves as a clay system, with the intention of using this system to develop instrumentation to study the frequency dispersion of resins, clay systems, core samples and soil in situ.

iii) The resins used in this work were as follows:20-50 British Standard Mesh "Dowex" 50W-X8
100-200 " " A.G. 50W-X12
200-400 " " A.G. 50W-X12

all being "Dowex" cation exchange resins consisting of a copolymer matrix of polystyrene chains crosslinked with divinylbenzene (D.V.B.)

Terminology

The percent cross linkage is denoted by the "X" factor thus: X8 implies 8% D.V.B. X12 implies 12% D.V.B.

A.G. indicates Analytical Grade, the 20-50 mesh resin being simply of commercial grade. 50W designates a strongly acidic cation exchange resin

composed of sulfonic acid exchange groups attached to the styrene - D.V.B. polymer lattice.

Specifications

The distributors (Bio-Rad) describe the physical form of the resin as "symmetrical spheres" and describe the thermal stability as "good up to 150°C". The stability in organic solvents and towards reducing agents is described as "very good". The order of selectivity of monovalent cations is given as

Ag > Rb > Cs > K > NH_L > Na > H > Li

with the selectivity of Na over 1.1 specified as 1.2 for the X8 resin for divalent ions.

Zn > Cu > Ni > Co

This series is very similar to that found by Mattson (40), Jenny (24), and Weigner (59) for clays and silicates.

iv) Cation Exchange Kinetics

It was demonstrated by Kunin and Myers that the cation exchange capacity of the various sulfuric acid cation exchange resins may be quite accurately accounted for by the sulfur content of these resins. This indicates quite strongly that the exchange of ions with these resins takes place throughout the whole gel structure of the resin and is not limited merely to the surface. Ion exchange resins may thus be considered to be gel-like particles whose exchange groups are randomly distributed throughout each particle (6,31,65), and the overall exchange process may be divided into five distinct steps.

1) Diffusion of the ions through the solution to the surface of the exchange particle.

2) Diffusion of the ions through the gel-like particle.

- 3) The exchange of these ions with those already on the exchanger.
- 4) Diffusion of these displaced ions out through the gel.
- 5) Diffusion of these latter ions away through to solution.

The work of Boyd et al (6) and Adamson (1) indicates that the rate is diffusion controlled, and Boyd et al have distinguished between two diffusion processes. First, at concentrations less than about 0.003M, the diffusion of ions through the film of solution about each particle is considered to be rate determining. Second, at concentrations greater than about 0.1M the diffusion of ions through the gel becomes rate determining.

The fact that the rates of exchange in cation exchange resins increase with decreasing particle size and increasing temperature (66) in a manner required by the diffusion law is strong evidence for a diffusion controlled reaction. However there are certain exceptions which must be considered. For example it is possible that some resins may be so tightly cross linked that diffusion of large ions is impeded. For such cases, resin diffusion may not be rate controlling at all. With the resins used in this study this is unlikely to be the case as although the effective pure size of the X12 resin is described as small, it is almost certainly large enough to pass even hydrated Na and Ca ions. For sulfonic acid resins the exchange rates have been shown (6) to be extremely rapid.

The above points are of some importance in view of the fact that some difficulty was observed in attaining an equilibrium of resins with electrolyte at a later stage in this work.

v) The Exchange Procedure

In each case the resin was obtained in the hydrogen form and had to be exchanged to the form desired (either Na or Ca). This was accomplished by passing several bed volumes of strong electrolyte (in the case of Na, 1M NaOH was used and for Ca 1M CaCl2) in a column, with an elution rate of about two drops per second. For the finer resins a slight vacuum had to be applied to attain this rate and with the coarser resin a stopcock was used to slow the elution rate. In all cases and especially with the commercial grade 20-50 mesh resin the resin was observed to "throw" a pink coloration as the first volume of exchanging electrolyte passed. This was assumed to be a high molecular weight sulfonate formed by the hydrogen resin on standing, as is specified by the distributors, and was not a problem. Following exchange the beds were flushed with several litres of distilled water. In the case of the sodium resin using 1M NaOH as the exchanging electrolyte, the resin was flushed until universal indicator showed a pH of 7. It was found that if such a "flushed" resin was left standing overnight in distilled water, the following morning the pH of the elutant water was often as high as 11 even though it had been 7 the day before. This effect is believed to be due to the take-up of OH ions by the glass of the column, and the subsequent release of these.

PRELIMINARY EXPERIMENTAL

CHAPTER 4

A.C. BRIDGE MEASUREMENTS

i) Description of Apparatus

A.C. bridge measurements of the equivalent parallel conductance and capacitance were made using a Wayne Kerr needle balance bridge (B221) at 1592 Hz, and the bridge in conjunction with a Wayne Kerr oscillator (S121) and Wayne Kerr waveform analyser (A321) as an external detector, over the frequency range from about 60 Hz to 20,000 Hz. The upper boundary is that of the oscillator, and the lower limit is imposed by two effects of the detector. First the frequency dependent response of the detector amplifiers coupled with the diminished out of balance signal from the bridge at low frequencies results in a signal at the detector meter too small for precise balance below about 80 Hz. Secondly the detector has an internal zero Hz calibration peak which has considerable band width, the signal at the meter being larger than the out of balance signal from the bridge up to about 60 Hz. Attempts were made to decrease the low frequency limit by using a Wayne Kerr "magic eye" bridge (B221A) to which a greater oscillator voltage may be applied, and by using an oscilloscope as a detector, since its amplifiers are D.C. coupled. It was found, however, that the decreased sensitivity of the magic eye

bridge more than offset the advantage of increased voltage, and that using the oscilloscope, the observed out of balance voltage had a non-simple form, and no configuration could be found which corresponded to a null output from the bridge.

ii) Concentrations and preparation of electrolytes

Throughout this work concentrations were described in molarities (M), and all solutions were prepared using Analar reagents and distilled or double distilled water. No real attempt was made to use a high grade of conductance water.

The upper limit of concentration used in the preliminary survey was 0.1M (6,000 ppm), this being the upper limit of concentration usually found in the ground even in hydrothermal regions. [Soils saturated with sea water have rather larger concentrations of ions, the concentration of Cl⁻ being 19,000 ppm (0.4 M) and of Na⁺, 10,000 ppm (0.2 M)]. Concentrations of 0.01 M or less were used most extensively as being more typical of ground water electrolyte concentrations.

iii) Cell 1

The cell used for the first series of determinations consisted of a large vessel with narrow neck (as shown in Fig. 4) with two platinum wire electrodes. Runs were made* to determine the equivalent parallel

* Unless otherwise stated, a run consists of a measurement three times per decade at 2, 5 and 10, between the limits of frequency specified.



centimeters

conductance (G) and capacitance (C) between 100 and 20,000 Hz for the cell containing 0.1 M NaCl then 0.01 M NaCl with the initial bright platinum electrodes, and then for the cell containing 100-200 mesh sodium form resin equilibrated with 0.01M NaCl. The electrodes were then platinised (by the method described in Appendix I), and a series of similar determinations made. The results are as follows:

| Electrode | Medium Co | nc. NaCl | ^G 20,000 ^{/G} 100 Hz (milli mho) | ^C 20,000 ^{/C} 100 Hz (micro Farads) |
|----------------------------|--------------------------------------|------------------------|---|--|
| Bright (Platinum (| NaCl only NaCl only Resin/NaCl | 0.1M 0.01M 0.01M | 15•15/3•44 1•58/0•795 8•47/0•39 | 0.005/3.26 0.0001/1.01 0.0033/2.59 |
| Platinised (Platinum (| NaCl only NaCl only Resin/NaCl | 0.1M 0.01M 0.01M | 14.80/14.60 1.64/1.64 8.63/7.08 | 0/0.56 0/0.0044 0.0008/1.195 |

These results indicate that platinised platinum electrodes are much more suitable than bright platinum, and a further series of determinations was made in cell 1 with platinised platinum electrodes, of five electrolyte concentrations between 0.004 and 0.1 M NaCl for cells containing electrolyte only, ground glass/electrolyte, 100-200 mesh resin/electrolyte, 200-400 mesh resin/electrolyte. For cells containing no resin the dispersion of G and C was negligible between 100 and 20,000 Hz. compared with the resin determinations. The results of the resin cell determinations are presented graphically and described in Chapter 13, part ii.

iv) Cell 2A

A second cell was designed as shown in Figure 5 to provide a long ion path, the resin being contained between sinters in a cylindrical tube to provide a reproducible and well defined geometric boundary. A large electrode separation was chosen to minimise parallel plate capacitance and the electrodes have a large surface area to minimise frequency dispersion due to double layer effects. A third electrode was included to enable the conductance and thus concentration of the electrolyte to be determined in situ.

A comparison of the free air parallel plate capacitance of cells 1 and 2A was made using the Wayne Kerr apparatus after both cells had been washed in acetone and dried in an oven. The results are as follows,

| | ^G 20,000 Hz ^{/G} 110 Hz | ^C 20,000 Hz ^{/C} 110 Hz |
|---------|---|---|
| | (nano mho) | (pico Farads) |
| Cell 1 | 4.43/1.27 | 0.4015/0.38 |
| Cell 2A | 0/0 | 0.0165/0.0165 |

indicating that cell 2A has a considerably better free air response.

A series of runs was made primarily with 0.01 M NaCl between 10,000 and 110 Hz using cell 2A to determine the usefulness of this cell. The results are shown in Table 1 from which it can be seen that the frequency effect of R per decade and the dispersion of the capacitance is very much greater for cell 1 containing resin than for cell 2A. Reasons for this are discussed in Chapter 5, part i.

Figure 5





Centimeters



TABLE 1

Wayne Kerr Determinations, Cell 2A

| Medium | ^G 10,000Hz ^{/G} 110Hz (micro-mho) | C _{10,000Hz} /C _{110Hz} (nano-farads) | 10,000 _{F*} 110 ^F R |
|--|--|--|--|
| NaCl only 0.01M | 38.52/38.58 | 0/0 | -0.000778 |
| 100-200 mesh resin**/0.01M NaCl | 64.78/64.25 | 0.012/0.270 | 0.00536 |
| 100-200 mesh resin/0.125M NaCl | 469.3/466.8 | 0.13/3.0 | 0.00266 |
| 200-400 mesh resin/0.01M NaCl | 56.79/55.73 | 0.004/0.984 | 0.00935 |
| Approximately 50:50 100-200 mesh resin: 100-150 mesh glass /0.01M NaCl | 44.64/44.1 | 0/1.05 | 0.00605 |

* ^a_F is the frequency effect of R per decade where R = 1/G, and the frequency effect is defined on page 6, between the limits of frequency a and b.

** AG 50W - X12.

CHAPTER 5

LOW FREQUENCY IMPEDANCE MEASUREMENTS

Because of the E.M. coupling and skin effect considerations discussed previously, and because previous time and frequency domain studies have shown the I.P. effect to be primarily associated with low and very low frequencies, no attempt was made at this stage to extend the frequency range above 20,000 Hz. Instead attempts were made to obtain a technique suitable for determining small impedance changes at frequencies below 100 Hz.

i) Two Terminal Measurements

The first technique attempted involved a series circuit as shown in Fig. 6a. The oscillator used was a Philips Function Generator (PM 5168) with a frequency span of 0.0005 to 5,000 Hz, capable of producing sine, saw tooth, or square wave of continuously variable amplitude up to 6 V_{pp} into an infinite resistance (3 V_{pp} into 600 **f**.). The A.C. output may be superimposed on a D.C. level continuously variable from + to -1.5 V. The output impedance of the generator is 600 ohms, and the output signal is with respect to ground. The resistance shown as R_R is a Sullivan non-reactive decade box 10⁶ ohms maximum, and Z_c is the impedance of the cell. In this series configuration the same current passes through both the cell and the non-reactive (N.R.) resistance, and the voltages AB and AC were observed on each channel of a Tektronix type 549 two channel storage oscilloscope. After calibration of the oscilloscope to ensure that each voltage range and both channels responded identically to a standard signal, channel 1

Figure 6



1) Electrode impedance and the resistance of the electrolyte path between the electrode and the sinter.

2) Large resistance associated with the sinters.

3) Impedance associated with the contents of the cell (contained between the sinters). was used on the 0.1 V/cm range and channel 2 on the 0.2 V/cm scale, and R_R adjusted until the magnitudes of the signals on the two channels were the same. With the magnitudes equal,

 $\begin{bmatrix} \mathbf{E}_{AB} \end{bmatrix} = \frac{1}{2} \begin{bmatrix} \mathbf{E}_{A\mathbf{C}} \end{bmatrix}$ But $\begin{bmatrix} \mathbf{E}_{AB} \end{bmatrix} = \begin{bmatrix} \mathbf{I} \end{bmatrix} \begin{bmatrix} \mathbf{R}_{R} \end{bmatrix}$ and $\begin{bmatrix} \mathbf{E}_{AC} \end{bmatrix} = \begin{bmatrix} \mathbf{I} \end{bmatrix} \begin{bmatrix} \mathbf{Z}_{c} + \mathbf{R}_{R} \end{bmatrix}$ thus $2\begin{bmatrix} \mathbf{R}_{R} \end{bmatrix} = \begin{bmatrix} \mathbf{Z}_{c} + \mathbf{R}_{R} \end{bmatrix}$... (1)

Now we can express the impedances ${\rm R}_{\rm R}$ and ${\rm Z}_{\rm c}$ in the form

Z = R' + j X'i.e. $R_{R} = R' + j X'$ but $R_{R} \text{ is non-reactive so } X' = 0$ thus $R_{R} = R'$ and $Z_{c} = R'' + j X'' .$ Now $[Z] = [R^{2} + X^{2}]^{\frac{1}{2}}$ thus $[R_{R}] = [R'^{2} + 0^{2}]^{\frac{1}{2}}$ = R'

and
$$[Z_{c} + R_{R}] = [R" + R_{R} + X"]$$

= $[(R" + R_{R})^{2} + X"^{2}]^{\frac{1}{2}}$

(1) becomes

$$2 R_{R} = [(R^{"} + R_{R})^{2} + X^{"2}]^{\frac{1}{2}}$$

or
$$4 R_{R}^{2} = (R^{"} + R_{R})^{2} + X^{"2}$$
$$3 R_{R}^{2} - 2 R^{"} R_{R} - R^{"2} = X^{"2}$$
$$(3 R_{R} + R^{"}) (R_{R} - R^{"}) = X^{2} \qquad \dots (2)$$

The two unknowns (X" and R") can be solved by observing the phase shift between E_{AB} and E_{AC} . [This was done by inspection of the wave forms on the oscilloscope, and the accuracy with which \emptyset can be determined is only about $\stackrel{+}{=} 2.5^{\circ}$, which is of the order of the phase shifts generally observed].

This implies that the phase shift E_{AC} with respect to E_{AB} (which is observed) is the phase shift of E_{AC} with respect to I, since the current is in phase with the voltage across a non-reactive resistor.

$$\varphi'_{AC} = \tan^{-1} \frac{X}{R'' + R_R} \qquad \dots (3)$$

(2) and (3) are two independent equations containing two determinable parameters (p'_{AC} and R_R) which may be solved for X" and R".

PRACTICAL

At the start of each run the magnitude of the two signals was adjusted to as near full scale as is feasible, by adjustment of the oscillator voltage, in order to give maximum accuracy. Determinations were made from 5000 Hz down to 0.01 Hz at three frequencies per decade (2, 5 and 10). At each frequency R_R is adjusted so that $[E_{AB}] = \frac{1}{2} [E_{AC}]$ and R_R recorded, and the phase shift of E_{AC} with respect to E_{AB} determined by inspection of the fraction of the wavelength that the peaks are shifted. The lower frequency limit is imposed by the maximum sweep time of the oscilloscope.

A great number of problems were encountered using this technique, some of these are listed below.

1) A very high level of 50 Hz noise was observed on both signals - sometimes approaching 10%. This is due in part to the difficulties experienced in shielding the cell and to the lack of common mode rejection of the oscilloscope. [A degree of common mode rejection can be achieved by using the oscilloscope on a differential mode. With the Tektronix this can be achieved by adding the signal appearing at one probe with respect to an arbitrary ground, to the inverted signal appearing at the other probe with respect to the same ground. Thus the same signal applied to both probes will cancel on the oscilloscope display. This is in effect a three terminal measurement and requires the use of both channels.]

2) Table 2 represents data taken by this technique on various cells. It can be seen that the frequency effect of resin in Cell 1
| Medium | Frequency (Hertz) | [Z]* (ohms) | 100 0.1 ^F [Z] | ø (degrees) |
|--|--------------------------------|--|-----------------------------|---------------------------|
| Cell 2A 200-400 mesh resin/0.01M NaCl | 100 10 1 0.1 | 15,100) 15,300) 15,550) 15,700) | 0.013 | |
| Cell 1 200-400 mesh resin/0.01M NaCl | 100 10 1 0.1 0.01 | 140) 165) 240) 380) 460) | 0.21 | 0 10 20 35 76 |
| Cell 1 0.01M NaCl electrolyte only | 100 10 1 0.1 0.025 | 550) 560) 650) 1,830) 4,530) | 0.23 | 0 11 30 53 58 |
| Cell 1 200-400 mesh resin/0.1M NaCl | 100 10 1 0.1 0.025 | 50) 60) 170) 1,060) 3,465) | 0.29 | 2 26 44 57 72 |
| Cell 1 O.1M NaCl electrolyte only | 100 10 1 0.1 | 65) 75) 190) 1,180) | 0.32 | 0 13 43 50 |
| Cell 1 200-300 mesh ground glass /0.1M NaCl | 100 10 1 0.1 | 200) 220) 350) 1,550) | 0.29 | 2 9 32 50 |

Two Terminal Oscillator/Oscilloscope Determinations

* The magnitude of the impedance

TABLE 2

is a factor of ten greater than that for resin in Cell 2A. This also was observed with the A.C. bridge determinations, and is due at least partly to the presence of the sinters which act as large resistors in series with the resin in Cell 2A. Ignoring electrode effects Cell 2A may be represented by the model shown in Fig. 6b where

$$z_{sinter} \gg z_{resin} \approx R_{electrolyte}$$

A measure of the order of Z_{sinter} over R_{electrolyte} may be obtained from the bridge measurements of Cell 2A containing 0.01 M electrolyte only, between the two end electrodes (AC) and between AB (see Fig. 6b).

 G_{AC} at 1592 Hz = 39.5 micro mho G_{AB} at 1592 Hz = 660.4 micro mho

thus

 $R_{AC} = 25,300$ ohms $R_{AB} = 1,500$ ohms.

The conduction path from A to B is roughly 1/4 of the ionic path from A to C ignoring the sinters, thus the total resistance of the electrolyte is about 6,000 ohms, leaving 19,000 ohms to be associated with the sinters. The frequency effect of the resistance is diminished because one has to observe a small change in resistance in a high resistance circuit. 3) Cell 1 exhibits a considerable frequency effect of the resistance with the cell containing electrolyte only both at 0.1 and 0.01 N NaCl (see Table 2), suggesting that the electrodes are polarising and that a four terminal system, where the potential electrodes do not have to pass any appreciable current, is necessary.

ii) Four Terminal Measurements

Cell 2A was modified to include two 1 mm silver wire electrodes as shown in Fig. 7. These silver electrodes were chloridised in situ as described in Appendix II, Ag/AgCl electrodes being chosen for their reversibility to Cl⁻ and because of an effect observed by D. Wright (61) of a large rapidly changing asymmetry potential associated with platinised platinum wire electrodes in electrolyte. Especially at low frequency this effect could substantially modify the form of a sine wave applied to such electrodes.

Using the Tektronix oscilloscope it is impossible to observe simultaneously the voltages between two pairs of points that do not contain a common point, since both signals are referred to a common ground. As such, in a four terminal cell, the voltage drop across R_R and across the potential electrodes can be observed alternately and their magnitudes recorded, but no determination of the phase shift between the voltages can be made without the use of at least one differential input. At this time no two channel oscilloscope was available with one differential channel and direct observations of the phase shift were impossible. Ignoring the phase shift an attempt was made to determine the behaviour of the magnitude of the impedance







0

between the potential electrodes, $[\rm Z_{XY}]$.

Since only one voltage measurement is to be made at a time the Tektronix could be used in a differential mode (and indeed had to be since neither of the potential electrodes is at ground potential), thus helping to alleviate the noise problem noted above. Also since the potential measurement of the resins is made inside the sinters, the effect of these sinters as large series resistances is removed.

Using the circuit shown in Fig. 8 the peak to peak voltages E_{AB} and E_{XY} were determined from direct observation of the signals on the oscilloscope.

Prior to each run R_{AB} was adjusted to give a desired current density through the cell, but no attempt was made to adjust R_{AB} to give equal amplitudes of E_{AB} and E_{XY} at each frequency because of a previously observed difficulty of doing so at very low frequencies.

 $[E_{AB}]$ and $[E_{XY}]$ were recorded at each frequency three times per decade from 5,000 to 0.01 Hz.

$$\begin{bmatrix} \mathbf{E}_{AB} \end{bmatrix} = \begin{bmatrix} \mathbf{I} \end{bmatrix} \begin{bmatrix} \mathbf{R}_{AB} \end{bmatrix} = \begin{bmatrix} \mathbf{I} \end{bmatrix} \begin{bmatrix} \mathbf{R}_{AB} \end{bmatrix}$$
$$\begin{bmatrix} \mathbf{E}_{XY} \end{bmatrix} = \begin{bmatrix} \mathbf{I} \end{bmatrix} \begin{bmatrix} \mathbf{Z}_{XY} \end{bmatrix}$$
$$\begin{bmatrix} \begin{bmatrix} \mathbf{E}_{XY} \end{bmatrix} = \frac{\begin{bmatrix} \mathbf{I} \end{bmatrix} \begin{bmatrix} \mathbf{Z}_{XY} \end{bmatrix}}{\begin{bmatrix} \mathbf{I} \end{bmatrix} \begin{bmatrix} \mathbf{R}_{R} \end{bmatrix}}$$
$$\begin{bmatrix} \mathbf{Z}_{XY} \end{bmatrix} = \frac{\begin{bmatrix} \mathbf{E}_{XY} \end{bmatrix} \begin{bmatrix} \mathbf{R}_{R} \\ \begin{bmatrix} \mathbf{E}_{AB} \end{bmatrix}}$$

Thus the magnitude of the impedance of the sample can be determined from observations of $[E_{XY}]$, $[E_{AB}]$ and R_{R} .



iii) Linearity

In time domain I.P. measurement, the degree of linearity of a sample is of considerable importance since current independent parameters are sought. Collett (10) defines a linear medium as one in which the response of the system is directly proportional to the applied force, and states, concerning induced polarisation; "The most fundamental test for phenomena of this kind is for linearity". In fact, while the I.P. phenomena is known to be a linear one in the field, the very much higher current densities used in the laboratory are often sufficient to drive the I.P. system into a non-linear region. Vacquier (54) observed that for a given specimen and excitation time the induced polarisation (mV - sec/V) is exactly proportional to the density of the charging current, but cautions against the use of "high current densities" without defining this term. Collett (10) made observations of core samples in the time domain, applying a primary voltage in steps and observing the decay curves of the secondary voltage. He concluded that the samples tested were only approximately linear in the voltage range 10-20 V (but fails to give sufficient information to determine a current from these voltages), and suggests that one should exercise great caution in extrapolating laboratory results to the earth, noting that the current densities used in the field are of the order of 10⁻² times those used in the laboratory.

Linearity is of prime importance in both time and frequency domain measurements since it will often be desirable to transform from one domain to the other. Only when the phenomenon is linear can the Laplace analysis be used to handle this transform.

iv) Ohmic behaviour

For practical reasons* ohmic behaviour is of great importance in all frequency domain measurements. The theoretical considerations of Marshall and Madden (39) result in an impedance directly proportional to the current, but suggest that this behaviour may not extend to high current densities. Marshall and Madden select a current density of $3x10^{-5}$ Amps/cm² for their core samples, and consider the media tested to behave ohmically in this region.

To ensure ohmic behaviour, frequency spectra of $[Z_{XY}]$ were run at a range of current densities for a variety of cells, and this data graphed as an E vs. I plot (Graphs 3 to 8). In the absence of a more fundamental test, ohmic behaviour of these plots (a straight line passing through the origin) was taken to indicate linearity.

v) <u>Results</u>

Impedance spectra were run for a range of current densities on each of the following systems, all in Cell 2B.

- a) 0.01M NaCl, electrolyte only
- b) 0.01M NaCl/200-300 mesh ground glass
- c) 0.01M NaCl/200-400 mesh sodium form ion exchange resin
- * In the absence of a constant current oscillator, as the impedance of the cell changes (with frequency) so will the current, and unless the impedance is independent of the current, a meaningful value of Z cannot be assigned from a single measurement of E and I.

- e) 0.05M NaCl, electrolyte only
- f) 0.05M NaCl/200-400 mesh sodium resin.

The results are too numerous to reproduce. Instead, for each system, plots 3 to 8 of $[E_{XY}]$ vs. I were made. Only in the case of the cells containing resin is there any significant dispersion of $[Z_{XY}]$ with frequency, and for these plots of E vs. I were drawn for decade frequencies between 0.1 and 1,000 Hz. For each system and each frequency the slope of the E, I plot gives a more accurate value of the impedance that for any one current density. Impedances were determined in this fashion and used to plot graphs 9 to 11 of $[Z_{XY}]$ versus log frequency for the resin cells (c, d and f).

This series of determinations has made apparent the following points regarding the magnitude of the impedance.

1) Within experimental error the four terminal cell shows no dispersion of $[Z_{XY}]$ over the five decades from 0.01 to 1,000 Hz, either when filled with electrolyte (0.01 and 0.05M NaCl) only, or with 200-300 mesh ground glass saturated with electrolyte (0.01 and 0.05M NaCl).

2) A plot of E vs. I is linear and passes through the origin for

0.01M NaCl electrolyte only - up to I = 3.6×10^{-4} Amps 0.01M NaCl/200-300 mesh glass - up to I = 2.5×10^{-5} Amps 0.05M NaCl electrolyte only - up to I = 2.0×10^{-4} Amps

3) An E, I plot for Cell 2B containing 200-400 mesh AG 50W - X12 resin equilibrated with 0.05 or 0.0005M NaCl exhibits no non-linearity in the current range tested (up to 4×10^{-5} and 6×10^{-4} Amps respectively).













4) An E, I plot for 0.01M NaCl equilibrated with 200-400 mesh resin exhibits no non-linearity from 1.2×10^{-5} to 7.0×10^{-5} Amps, but for frequencies of 0.1, 1, 10 and 100 Hz, there is an approximately 15% deviation from the low current line extrapolated, at 1.8×10^{-4} Amps.* 5) There is a marked frequency dispersion for 200-400 mesh resins equilibrated with 0.0005, 0.01 and 0.05M NaCl. In each case the impedance increases from 1000 to 1 Hz and remains roughly constant at lower frequencies. Graphs 9 to 11 of $[Z_{XY}]$ (determined from the slope of E,I plots 5, 6 and 8) versus log frequency show this form. There seems also to be some evidence in the shape of the spectra for different concentrations that what is being observed is a curve of the general form shown by graph 12, and that this curve is more spread out at lower concentrations. Thus with resin/0.0005M NaCl, AB is observed, with resin/0.01M NaCl, AC is observed and with resin/0.05M NaCl, AD.

* Point 3 above suggests that this non-linearity might not be in the sample, but rather is an artifact of the measuring system. Since the 1.8x10⁻⁵ Amp determination was the first made it is possible that the impedance, [Z_{XY}], was higher than its equilibrium value. A perhaps more likely possibility is that this anomalous result is due to poor calibration amongst the oscilloscope voltage ranges, since this was the only determination made using the 0.05 V/cm range - all others were made using the 0.02 V/cm range.

$$I_{2xy1} versus Frequency
Cell 2B
0.05 M Nrcl / Result
data derived from slope of EwI plot, graph 8
$$I_{2xy1} (\Omega)$$

$$I_{2xy1} (\Omega)$$

$$I_{300}$$

$$I_{300}$$$$



$$\frac{G_{RAPH} 11}{2,700} \frac{G_{RAPH} 11}{2xy1} \frac{G_{RAPH} 11}{G_{RAPH} 11}$$

$$\frac{G_{RAPH} 11}{G_{RAP} 11}$$

$$\frac{G_{RAPH} 11}{G_{RAP} 11}$$

$$\frac{G_{RAPH} 11}{G_{RAP} 11}$$

$$\frac{G_{RAPH} 11}{G_{RAP} 11}$$

$$\frac{G_{RAP} 11}{G_{RAP} 11}$$

$$\frac{G_{RAP} 11}{G_{RAP} 11}$$

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CHAPTER 6

FOUR TERMINAL MEASUREMENTS OF THE MAGNITUDE OF THE IMPEDANCE, AND OF THE PHASE SHIFT

i) Introduction

At this point a Telequipment type DM53A storage oscilloscope with one plug in "type K" differential channel, and one "type A" non-differential channel became available. This was used to make observations of both $[Z_{XY}]$ and the phase shift (\emptyset) of a number of resin sizes and electrolyte concentrations, and of cells containing electrolyte only. Since now both waveforms can be displayed simultaneously, the magnitudes of the cell and reference voltages can be observed without switching, and the phase shift can be determined by inspection.

ii) Technical difficulties

Two points became immediately apparent.

1) An anomalous phase shift occurred due to a significant reactance in the "non-reactive" decade box used as a reference. Sullivan non-reactive resistors whose equivalent parallel resistance and capacitance had been determined on the Wayne-Kerr bridge, were used instead.

2) Miss-matching of the two oscilloscope channels resulted in an anomalous phase shift and a tail up of $[Z_{XY}]$ at frequencies above about 500 Hz. This has the form shown in Fig. 9 and is almost independent of the nature of the cell.



Attempts were made to match the channels, initially by connecting a Hewlett-Packard variable capacitance in parallel with the potential electrodes and the differential (type K) channel (Fig. 10). Graphs 13 and 14 show results of $[Z_{vv}]$ and \emptyset determinations made on Cell 2B containing 0.01M NaCl only, at various settings of the parallel capacitance. Four values of capacitance are shown, zero, 1.8x10⁻¹⁰, 7.65×10^{-10} and 6.52×10^{-10} , the last being selected as the value for which the best superimposition of the signals on the two channels could be obtained when a square wave was applied to the circuit. Similar determinations using 0.1 and 0.001M NaCl only indicate that a value of the parallel capacitance may be found by the best superimposition of square waves, for which the phase shift is apparently zero. at which time the linear region of a non-dispersive element* is extended from about 500 to 2,000 Hz. That both the phase shift and the impedance dispersion cannot be held at zero simultaneously for any value of parallel capacitance, indicates that the circuit required to match the two channels is rather more sophisticated than a simple parallel resistance. In addition to the added complexity of the "best superimposition" technique, the presence of a parallel capacitor reduces the observed impedance and introduces an error which must be corrected for. These points, the difficulty of deciding what values of capacitance to use for resin systems which may display a significant phase shift themselves, and the relatively small increase in the upper useful frequency, resulted in the eventual discarding of the parallel capacitance.

* That cells containing electrolyte only are effectively non-dispersive/the range of frequencies under consideration, is indicated by Wayne-Kerr measurements of these cells.

Figure 10

FOUR TERMINAL IMPEDANCE MEASUREMENT

VARIABLE CAPACITOR USED IN AN ATTEMPT TO OSCILLOSCOPE INPUTS. MATCH



TELEQUIPMENT OSCILLOS COPE

GRAPH 13

GRAPH 14 PHASE SHIFT VOISUS FRequency VARIOUS settings of parallel capacitance Cell 2B 30 0.01 M Nacl only \$ (degrees) 20 ----X--- No parallel capacitor 10 IN PARAllel 0 10 100 Frequency (H2) -> 1,000

10,000

Experiments were conducted to find a more suitable R.C. matching circuit, but these failed and were abandoned.

iii) Cell 3

Gell 3 was constructed as shown in Fig. 11a. Connections to the electrodes are sheathed in glass to a height of 15 cm so the entire cell can be immersed in a water bath. This is necessary in order to keep the cell at a constant and reproducible temperature, and to enable the temperature dependence of the dispersion of the impedance to be studied. The cell has two pairs of potential electrodes, one pair inside and one outside the sinters which contain the resins. The purpose of this duplication is to enable an assessment of the effects of the sinters to be made, and to determine if there is any direct interaction between the inside electrodes and the resins they are in contact with. The platinum foil end electrodes were platinised as described in Appendix I, and the silver wire potential electrodes were chloridised in pairs as described in Appendix II. After chloridising an anomalously large asymmetry potential was found associated with electrode Z (see Fig. 11).

iv) The interaction of the potential electrodes with resin particles

In order to determine the dispersion of the impedance of each pair of potential electrodes, frequency spectra of [Z] and \emptyset were run for Cell 3 filled with 0.005M NaCl only, using the Telequipment



oscilloscope and Philips Function generator, and the circuit shown in Fig. 11b. Spectra were run for both the inner (XY) and outer (WZ) pairs of potential electrodes, and in each case for two values of parallel capacitance - one zero and the other determined by a best superimposition of square waves. The results are shown in Table 3 and show no dispersion of [Z] or \emptyset for either pair of electrodes.

In an attempt to determine if the inner potential electrodes (XY). have any direct interaction with the resin beads in which they are immersed that might affect the observed impedance of the cell when resins are being studied, frequency spectra of Cell 3 containing 20-50 mesh Dowex 50W - X8 equilibrated with 0.005M NaCl were run for both the inner and outer pairs of potential electrodes. From 0.01 to 5,000 Hz the Telequipment oscilloscope/Philips Function generator circuit was used, and from 100 to 20,000 Hz the Wayne-Kerr bridge. The results, shown in Table 3, indicate that the impedance between the outer potential electrodes ($[Z_{WZ}]$) is very much greater than that between the inner ($[Z_{\chi Y}]$), (2.3x10⁴ as opposed to 1.6x10³ ohms). This additional impedance is primarily due to the sinters, and an impedance of about 1.07x10⁴ ohms may be associated with each sinter at 1592 Hz, while the total change of impedance of the resin, as observed at the inner electrodes, is no more than 1.0x10³ ohms. Since the resistance of the sinters appears to the outer potential electrodes to be in series with the impedance of the resin, their effect may be removed by subtracting from the impedance at the frequency f, the value of the



TABLE 3

Determinations on Cell 3

a) Cell 3 containing 0.005M NaCl only - oscillator/oscilloscope determinations

| Frequency | [Z _{XY}] | [z _{xy}]*1 | Ø _{XY} | Ø ^{**1} XY |
|-------------------------|--|--|---------------------------------|-------------------------------------|
| (Hertz) | (Ohms) | (Ohms) | (Degrees) | (Degrees) |
| 1,000 100 10 1 | 9.12x10 ³ 9.01 " 9.01 " 9.01 " | 8.79x10 ² 8.79 " 8.79 " 8.79 " | 7 0 0 | 0 0 0 |
| | $[\mathbf{z}_{WZ}]$ (0hms) | $\left[z_{WZ} \right]^{*2}$ (Ohms) | ${ m \not p}_{_{MZ}}$ (Degrees) | ${\it g}_{_{ m WZ}}^{*2}$ (Degrees) |
| 1,000 100 10 | 3.13x10 ⁴ 3.13 " 3.13 " | 3.13x10 ⁴ 3.13 " 3.15 " | 3.5 | 0 0 |
| 1 | 3.13 " | 3.15 " | 0 | 0 |

* Capacitor connected in parallel with potential electrodes (see Fig. 10), the value being selected by a best superimposition of square wave technique.

1 0.001866 micro-farads 2 0.000558 micro-farads

b) Cell 3 - 0.005M NaCl/20-50 mesh 50W-X8

i) Wayne Kerr determinations

| Frequency | [Z _{XY}] | $[z_{WZ}]$ | 10,000 _H * | 10,000 _H _{WZ} |
|-----------|-----------------------|-----------------------|-----------------------|-----------------------------------|
| (Hertz) | (Ohms) | (Ohms) | (Ohms) | (Ohms) |
| 10,000 | 1.523×10^{3} | 2.283x10 ⁴ | 0x10 ³ | 0x10 ³ |
| 5,000 | 1.546 " | 2.286 " | 0.023 " | 0.03 " |
| 2,000 | 1.579 " | 2.292 " | 0.056 " | 0.09 " |
| 1,000 | 1.611 " | 2.296 " | 0.088 " | 0.13 " |
| 500 | 1.645 " | 2.299 " | 0.122 " | 0.16 " |
| 200 | 1.697 " | 2.308 " | 0.172 " | 0.25 " |
| 150 | 1.714 " | 2.309 " | 0.191 " | 0.26 " |

/continued...

* Defined on page 63.

Table 3 continued

ii) Oscillator/Oscilloscope determinations

| Frequency (Hertz) | [Z _{XY}] (Ohms) | [Z _{WZ}] (Ohms) | 100 _H XY (0hms) | 100 _H WZ (0hms) |
|----------------------|------------------------------|------------------------------|-------------------------------|----------------------------------|
| 100 | 1.08×10^3 | 2.13x10 ⁴ | 0x10 ³ | 0x10 ³ |
| 10 | 1.19 " | 2.13 " | 0.11 " | 0 ** |
| 1 | 1.39 " | 2.18 " | 0.31 " | 0.5 " |
| 0.1 | 1.59 " | 2.18 " | 0.51 " | 0.5 " |
| 0.01 | 1.72 " | 2.18 " | 0.64 " | 0.5 " |

1

impedance at some arbitrary frequency, a. Assuming the impedance of the sinters to be non-dispersive*, the parameter $[Z_{WZ}]_{f} - [Z_{WZ}]_{a}$ (defined as ${}^{a}H_{WZ}$) should have identical values to ${}^{a}H_{XY}$ at all frequencies, if the electrodes X and Y have no direct interaction with the beads with which they are in contact that in any way effects the impedance dispersion of the resin system as a whole, or the voltage, V_{YY} , used to determine this impedance.

For the Wayne-Kerr measurements, the bridge is fully calibrated between ranges, and is highly accurate. The means of determining [Z] is the same for both electrode pairs, and from Table 3 it is clear that ${}^{10,000}\text{H}_{XY}$ and ${}^{10,000}\text{H}_{WZ}$ are indeed identical within experimental error at all frequencies, thus suggesting that the electrodes do not interact appreciably with the resin beads.

In the lower frequency range, 0.01 to 5,000 Hz, the oscillator/ oscilloscope technique gives much less accurate results than does the Wayne-Kerr bridge at higher frequencies. As such, the total impedance change observed between the outer electrodes is only twice the experimental error, and although the trend of ${}^{100}\text{H}_{WZ}$ is the same as that of ${}^{100}\text{H}_{XY}$, no statement that a point to point correlation exists can be made. Nevertheless it would seem that the fact that the inner electrodes are immersed in resin beads has a negligible effect on the observed potential.

* Observations of cells containing electrolyte only indicate that the impedance of the sinters is constant, and the phase shift zero, within experimental error.

v) Low frequency [Z] and Ø measurement

Graphs 15 to 17 show the phase and impedance dispersion of cell 3 containing 20-50 mesh ion exchange resin equilibrated with 0.005M NaCl, observed between the inner potential electrodes using both the oscillator/oscilloscope and Wayne-Kerr techniques.

For the impedance spectrum the four terminal and Wayne-Kerr data do not coincide (Graph 15). There are two possible causes for this.

1) The bridge measurements were made 24 hours after the oscilloscope determinations and display a consistently higher resistance. It is therefore possible that for the initial measurement the resin and electrolyte were not in equilibrium, and that continued equilibration has resulted in the ions being more closely associated with the resin, and less free to move. Since it is not possible to calculate the effects of such an ion de-mobilisation on the impedance, a correction for this effect cannot be made.

2) The two voltages V_{XY} and V_{AB} (see Fig. 11b) used to determine $[Z_{XY}]$ were observed on widely varying voltage ranges (10 mV/cm and 1 V/cm respectively), as well as different channels. Although both channels of the oscilloscope respond linearly to an applied voltage within a particular volts/cm range, in general each channel is not linear amongst voltage ranges. Thus the voltage applied to the type "A" channel (V_{AB}) is only proportional to the voltage appearing on the oscilloscope (V_A),

$$V_{AB} = n V_{A}$$
.

SRAPH 15 VERSUS FREqueNcy 12xy ٢ Cell 3 12xy (() 0.005 M Naci / 20-50 mesh 50W-X8 2,200 O Magnitude of impedence as determined using the WAYNE - Kern bridge two terninal technique 2,000 X 12xyl From oscillator / oscilloscope, 4 Ternival determination 1,800 1,600 1,400 1,200 1,000 0.1 0.01 1,000 10,000 100 10 Frequency (Hz)

Likewise the voltage applied to the type "K" channel (V_{XY}) is proportional to the oscilloscope display (V_K)

 $\mathbf{V}_{\mathbf{X}\mathbf{Y}}$ = m $\mathbf{V}_{\mathbf{K}}$

Now

$$\mathbf{Z}_{\mathbf{X}\mathbf{Y}}] = \frac{\mathbf{V}_{\mathbf{X}\mathbf{Y}} \mathbf{R}_{\mathbf{A}\mathbf{B}}}{\mathbf{V}_{\mathbf{A}\mathbf{B}}} = \frac{\mathbf{m} \mathbf{V}_{\mathbf{K}}}{\mathbf{n} \mathbf{V}_{\mathbf{A}}} \times \mathbf{R}_{\mathbf{R}}$$

and in general $m \neq n$.

The impedance observed

$$\begin{bmatrix} Z_{XY} \end{bmatrix}_{Apparent} = \frac{V_K}{V_A} \times R_R$$
$$= (n/m)(m/n)(V_K/V_A)R_R$$
$$= (n/m)(V_{XY}/V_{AB})R_R$$

Thus

$$[Z_{XY}]_{Apparent} = (n/m) [Z_{XY}]_{Actual}$$

The effect of this error on the observed impedance is simply removed by multiplying the apparent impedance at each point by a constant (m/n) to obtain the actual impedance, provided of course the voltage ranges are not changed.

Graph 16 shows oscillator/oscilloscope data corrected to be contiguous with Wayne-Kerr data, by two methods - the addition of a constant, and multiplying by a constant. There is, however, insufficient overlap of the two frequency ranges to determine which is most applicable.

Graph 17 is a plot of phase shift versus frequency and represents the first observation of a phase shift directly attributable to the
GRAPH 16 12xy 1 VERSUS FREquency Cell 3 12xy1 (1) 0.005 M NACI / 20-50 mesh 50W - X8 2,700 x- x 12xyl, (2 TermiNal) WAYNE - KERR 0 12xy | x (1.626), (4 Terminal) Osc. / Osc. X 2,500 ×, '× 12xy 1 + (690-2), (4 TERMINAI) OSC. / OSC. + 2,300 ×′ 2,100 1,900 · · · · · 1,700 1,500 0-0.01 0.1 100 1,000 10 Frequency (HE) 10,000



presence of the resin. A significant phase shift is observed above 200 Hz, however, which is associated with the miss-matching of the two oscilloscope channels, and disappears when 0.011858 micro Farads (selected by the best superimposition of square waves) is connected in parallel with the type "K" differential channel. The presence of this large capacitance in parallel has a large effect on the observed impedance and it cannot be left in place while determinations of $[Z_{XY}]$ are made (see Table 3). Below 200 Hz a phase shift occurs in the opposite direction to that observed above. As far as was determined, this phase shift at low frequencies has an identical form whether the parallel capacitance is in place or not. Phase shifts calculated from Wayne-Kerr measurements are of the same order of magnitude as the error in the oscilloscope determinations, but are negative, and increasingly so at low frequencies.

Measurements made on Cell 3 containing 0.005M NaCl electrolyte only, show a positive phase shift due to miss-matching, which does not entirely disappear until below 10 Hz (see graph 17). No phase shift is observed at low frequencies.

The pronounced peak in the negative phase shift, centered at 5 Hz is the most obvious feature of the low frequency phase spectrum, and has a form incompatible with any simple parallel or series RC model circuit used to represent the resin/electrolyte system.

vi) Preliminary clay measurements

Since one of the aims of this project is to make observation of the frequency dispersion of clays, it was felt desirable at this stage of the development of a suitable experimental technique, to make a trial measurement on a clay/electrolyte system to determine what effect, if any, the clays display, and what sensitivity is required by the measuring device. Such measurements were made on a cell supplied by D. Wright, currently engaged in observations of the transient response of clay/electrolyte systems at the Victoria University of Wellington. This cell consists of a cylindrical glass sinter constructed from ground pyrex particles between 50 and 100 mesh, having about a 40% porosity, supported in a pyrex cell as shown in Fig. 12. A calcium form bentolite had been bonded to this sinter, and the whole equilibrated with 0.005M NaCl. Spectra of [Z] and ${oldsymbol arphi}$ were run using the Wayne-Kerr and oscilloscope techniques as for the previous cell. Graph 18 is a plot of $[Z_{yy}]$ versus log frequency and shows an increase of the magnitude of the impedance towards low frequency for both the oscilloscope and Wayne-Kerr determinations. As with the resin, the dispersion as measured by the two techniques is discontinuous, the impedance calculated from Wayne-Kerr data being about 46 higher. Assuming $[Z_{yy}]$ to be a continuous function of frequency and the point (4.39x10⁴ ohms, 100 Hz) to lie on the curve, the oscillator data has been corrected by multiplying each point by a constant (1.062).





The oscilloscope data show a positive phase shift associated with miss-matching, above 100 Hz, but no phase shifting is observed at lower frequencies. The phase shift calculated from Wayne-Kerr measurements is less than 1 degree between 20,000 and 100 Hz.

At this time no sinters were available that did not contain clay, and thus the normal effect of a blank sinter/electrolyte system was not determinable, however subsequent determinations indicate that the dispersion of both [Z] and \emptyset for clay free sinter/electrolyte systems is in fact zero.

An impedance dispersion of the order of 20% can thus be associated with the presence of clay on the sinter, and, using the oscilloscope/oscillator technique the accuracy with which [Z] can be determined is about $\pm 2\%$. The phase shift, however, is only of the order of 1 degree while the sensitivity of the oscilloscope is of the order of 3 degrees.

vii) The dispersional effects of Ag/AgCl electrodes

To this point the normal response of Cell 3 containing electrolyte only has not been determined using the A.C. bridge. Measurement of the frequency dispersion of $[Z_{XY}]$ were made with Cell 3 containing 0.025M NaCl only, over the entire frequency range from 0.01 to 20,000 Hz, and the results are given in table 5. Graph 19 is a plot of $[Z_{XY}]$ versus log frequency as determined from Wayne-Kerr data, and shows a linear increase of $[Z_{XY}]$ with logarithmic decrease of frequency. Similar measurements conducted six hours later result in a parallel line (shown

TABLE 5

Dispersion of Electrodes in 0.025M NaCl Only

a) Cell 3/0.025M NaCl only

i) Wayne Kerr determinations

| Electrodes | Frequency | C | R | % f.e./ | decade |
|------------|-----------|---------------|---------------------|---------|--------|
| | (Hertz) | (Nano-farads) | (Ohms) | | |
| Inner (XY) | 10,000 | 0.093 | 2.417×10^3 | 1.9% | |
| Ag/AgC1 | 1,000 | 0.928 | 2.464 " | 2.0% | 1.95% |
| Potential | 100 | 11.0 | 2.514 " | 2.0,0 | |
| Outer (WZ) | 10,000 | 0 | 7.848 " | 1.6% | |
| Ag/AgCl | 1,000 | 0.342 | 7.974 " | 3.3% | 2.2% |
| Potential | 200 | 2.336 | 8.152 " | J•J/• | |
| Platinised | 10,000 | 0 | 9.096 | 0% | |
| Platinum | 1,000 | 0 | 9.096 | -0.00% | -0.02% |
| Current | 100 | 0 | 9.092 | -0.0440 | |

ii) Oscillator/Oscilloscope determinations

| Frequency (Hertz) | [Z _{XY}] (Ohms) | [Z _{WZ}] (Ohms) | Ø _{XY} (Degrees) | \emptyset_{WZ} (Degrees) |
|----------------------|------------------------------|------------------------------|------------------------------|----------------------------|
| 1,000 | 2.0x10 ³ | 6.75×10^{3} | 7 | 0 |
| 100 | 2.0 " | 6.75 " | 0 | 0 |
| 10 | 2.0 " | 6.75 " | 0 | 0 |
| 1 | 2.0 " | 6.75 " | 0 | 0 |
| 0.1 | 2.0 " | 6.75 " | 0 | 0 |
| 0.01 | 2.0 " | 6.75 " | 0 | 0 |

b) Ag/AgCl electrodes in a beaker of 0.025M NaCl only

| | Frequency (Hertz) | C (Nano-farads) | R (Ohms) | % f.e./decade |
|---------|----------------------|--------------------|-------------|---------------|
| | 10,000 | 0.6 | 8.046 | 1.3% |
| Ag/AgC1 | 1,000 | 62.8 | 8.152 | 3.3% |
| | 300 | 556.0 | 8.458 | 1.5% |



dotted on graph 19) shifted to lower resistance possibly as a result of the concentrating effect of evaporation. For both lines the slope is -48 ohms/decade.

Determinations of $[Z_{XY}]$ using the oscilloscope/oscillator technique show no dispersion below 1,000 Hz, but the accuracy of this method is $\stackrel{+}{=} 2\%$ (or $\stackrel{+}{=} 40$ ohms), and although one can be sure that the linear increase of $[Z_{XY}]$ with decade decrease of frequency does not extend to 0.01 Hz, the expected increase of 48 ohms between 1,000 and 100 Hz could easily be undetected on the oscilloscope.

The impedances between the outer (WZ) potential electrodes and the platinised platinum current electrodes were also determined using the Wayne-Kerr apparatus (results - Table 5) for Cell 3 containing 0.025M NaCl only, and graph 20 shows $[Z_{WZ}]$ versus log frequency. That this graph is no longer linear suggests that the sinters display some dispersion effect above about 5,000 Hz or else, more simply, the dispersional effects of the inner and outer pairs of potential electrodes is not the same.

The maximum impedance dispersion observed using the Wayne-Kerr apparatus for the three pairs of electrodes is as follows:

Inner Ag/AgCl (XY) = + 4.4%Outer Ag/ÁgCl (WZ) = + 4.2%Platinised platinum (PQ) = -0.1%

Platinised platinum electrodes are well known to display very little dispersion at A.C. frequencies (23) and for Cell 3 little dispersion is in fact observed between the current electrodes indicating



that these electrodes and the Wayne-Kerr bridge are behaving as they should, and that the cell has no inherent dispersional effect. The results thus suggest that there is a considerable and non-uniform dispersion of [Z] associated with Ag/AgCl electrodes in the frequency range 100 to 20,000 Hz, but that no significant dispersion is observed in four terminal measurements below about 1,000 Hz.

A pair of Ag/AgCl electrodes were prepared as described in Appendix II, and a series of Wayne-Kerr measurements made of these clamped in beakers of various concentrations of NaCl electrolyte. These measurements indicate a considerable dispersion effect to be associated with Ag/AgCl electrodes at all concentrations tested (0.005, 0.01, 0.025, 0.1M NaCl).

viii) The use of plug in electrodes

In view of the dispersion effects observed at Ag/AgCl electrodes, and the difficulty of cleaning or replacing these in the present cell, Cell 3 was modified by removing the four potential electrodes and replacing the inner two only with B5 ground glass sockets (see Fig. 13). Electrodes can thus be prepared in a more convenient vessel than the cell itself, using a B5 ground glass plug, and inserted into the cell. Using this system, Ag/AgCl electrodes can be replaced at will when, with age, their asymmetry potentials become intolerable. The possibility also exists of using plug in platinised platinum electrodes for Wayne-Kerr measurements, and Ag/AgCl for four terminal low frequency determinations.



PLUG-IN POTENTIAL ELECTRODE

CELL 3

One pair of Ag/AgCl electrodes were prepared from silver wire mounted via platinum wire to a B5 plug, and a pair of platinised platinum electrodes were prepared from 0.5 mm Pt wire mounted on a B5 plug. A series of determinations of the dispersion observed at these electrodes in electrolyte only and electrolyte/20-50 mesh resin systems, were made using the Wayne-Kerr and oscillator/oscilloscope techniques. Three concentrations, 0.005, 0.025 and 0.125M NaCl were used, and impedance and phase spectra run. Table 6 gives results of the change of impedance per decade (Δ [Z]_n), and of this change as a percentage of the impedance (% f.e/decade).

It can be seen that the large platinised platinum disc electrodes at the ends of the cell, display no dispersion in electrolyte only, and dispersion only of the order of the experimental error when resin is present. This small frequency effect for resins observed at the end electrodes is due to the large, non-dispersive, series resistance, associated with the sinters, and to a lesser degree, the electrolyte path between these electrodes and the sinters. While the absolute change in impedance (Δ [Z]) should be constant no matter where it is observed from (outside the sample), division by the impedance (which consists mainly of the impedance associated with the sinters) to obtain a percent change, results in a smaller value for electrodes situated outside than inside the sinters.

The plug in platinised platinum wire electrodes show a negative dispersion* in 0.0005M NaCl about 7 times larger than the precision of

^{*} Negative dispersion implies the magnitude of the impedance decreases with decreasing frequency.

| CT1 | ٨ | DI | 67.7 | 1 |
|-----|---|----|------|---|
| T | Н | D. | 414 | C |

Dispersion of Plug-in Electrodes in Cell 3 (Modified)/Electrolyte Only

a) 0.005M NaCl (Wayne Kerr)

| Electrode | Frequency (Hertz) | [Z] (Ohms) | [Z] _n (Ohms) | % f.e./decade |
|---------------------------------------|------------------------|---|----------------------------|-------------------------|
| Ag/AgCl Plug-In Potential | 10,000 1,000 200 | 1.072x10 ⁴ 1.080 " 1.081 " | 80 10 | 0.74% 0.49% 0.13% |
| Platinised Pt Plug-In Potential | 10,000 1,000 200 | 1.032 " 1.028 " 1.029 " | -40 10 | -0.39% -0.14% +0.14% |
| Platinised Pt End Current | 10,000 1,000 200 | 4.262 " 4.246 " 4.244 " | -16 - 2 | -0.04% -0.007% |

b) 0.025M NaCl (Wayne Kerr)

| Ag/AgCl | 10,000 | 2.609x10 ³ | 838 | 1 1.3% | |
|-----------|--------|-----------------------|-----|--------|-------|
| Plug-In | 1,000 | 2.647 " | 52 | 2 76% | 1.96% |
| Potential | 200 | 2.699 " | | 2.10/0 | |

c) 0.125M NaCl (Wayne Kerr)

| Ag/AgCl | 10,000 | 5.906x10 ² | 71 | 10.7% | |
|---------------|--------|-----------------------|----|----------|-------|
| Plug-In | 1,000 | 6.615 " | 20 | 16 76 | 12.1% |
| Potential | 500 | 7.008 |)) | 10 • //0 | |
| Platinised Pt | 10,000 | 1.995x10 ³ | 0 | 0% | |
| End | 1,000 | 1.995 " | 1 | 0.15% | 0.04% |
| Current | 500 | 1.996 " | | | |

the bridge, but of the same order of magnitude and sign as the dispersion at Ag/AgCl electrodes. It was quickly realised when using these electrodes that exchanging plug in electrodes (Pt for Ag) could not be accomplished without seriously disturbing the system under consideration. Since the performance of the Pt plug in electrodes was not appreciably better than that of Ag/AgCl, they were discarded.

ix) <u>Cell 4</u>

The electrode configuration in the modified Cell 3 is rather an awkward one since the potential electrodes are mounted at the side (Fig. 13) and tend to break off. As such a new cell was designed with potential electrodes plugging into B5 sockets on the top, and current electrodes mounted with B19 plugs, designed to be removable (see Fig. 14a). Removable current electrodes permits their use on other cells, and a number of cells containing sinters* (as shown in Fig. 14b) were constructed for subsequent use with clays.

* The sinters are those described in Chapter 9A.





CHAPTER 7

THE EFFECTS OF TEMPERATURE

i) Procedure

Perhaps the most fundamental parameter in all diffusional and relaxational processes is temperature, and it was considered desirable to determine the effects of temperature on Cell 4 containing resin.

In order to perform high temperature measurements, a water bath designed to thermostat at 25°C had to be modified to operate at temperatures up to about 80°C. This was done by the addition to the bath of two 1,000 watt heaters and increasing the value of the two light bulb heaters to 120 watts each. A cooling coil consisting of a spiral of 0.6 cm diameter copper tubing through which tap water may be passed was provided to speed up the cooling process, and a layer of broken pieces of polystyrene foam was placed on the surface of the water to minimise undesired heat loss. The bath was stirred by a stirrer connected to an electric motor via a belt, thus minimising conductive heat loss and preventing the motor from overheating.

Measurements of $[Z_{XY}]$ and \emptyset were made on Cell 4 containing 0.025M NaCl/20-50 mesh sodium form Dowex 50W - X8 at temperatures from 64 to 14 degrees Centigrade.

A 25.16 degrees C determination was made first, then the bath and cell heated to 64 degrees and that determination made. The bath and cell were then allowed to cool, and the first 50 degree C determination made. The bath was turned off and left over the weekend,

the two central ports of the Cell 4 being corked. On the following Monday the bath and cell were reheated to 50 degrees C and a determination made, then allowed to cool to 45 degrees and a determination made, then to 22 degrees and a determination made. Ice was then added to the bath water and at 14 degrees C a further series of readings taken. At each temperature the cell was allowed to equilibrate for about 15 minutes, the bath temperature being kept constant by manual control of the light bulb heaters and by simmerstatic control of the elements.

The total time elapsed from the 25 degrees C determination to the 14 degrees C readings was about 84 hours, and although when a run was not in progress the larger vents of the cell were corked, during each run the cell was uncorked and appreciable evaporation loss was observed.

ii) <u>Results</u>

The results of the determinations of $[Z_{XY}]$ and \emptyset are plotted in graph 21 of \emptyset versus log frequency, and graph 22 of $[Z_{XY}]$ versus log frequency.

Graph 21 shows that in all cases except the 25.16 degree run, the observed negative phase shift at low frequencies is zero or only of the order of the experimental uncertainty. For all temperatures the general form is of zero phase shift above 100 and below 0.01 Hz, with the phase shift maximising between 1.0 and 10 Hz in all cases except the 25.16 degrees C run which maximises at 0.1 Hz. Little can be deduced from this form because of the high percentage error. It



12 my US. Frequency 25.16 ° C 63.5° C 49.78° C × ▲ GRAPH 22 3500 0.025 M NACI Ŷ 10 FINIL determination ONE WEEKEND LATER 20-50 MESH TIME 12AY (.2.) 44.5°C DOWEX 50W-X8 21.8°C 3000 \odot 13.9 ° C 2500 2000 14 6 25 0 6 \odot 0 1500 22° C 1000 45°C 5000 Lowe - 50°C 500 0 10,000 1000

I

4 V(H2) 10

100

.01

is clear, however, that the 25.16 degree determination is anomalous.

Graph 22 shows the impedance spectra at each temperature, and has two points of interest.

1) At any given frequency, the impedance varies with temperature in a seemingly erratic fashion.

2) The spectra at different frequencies are very similar to each other and differ only in absolute level.

In order to further examine point (1) above, $[Z_{XY}]$ was measured directly off graph 22 for each temperature at a given frequency. Graph 23a shows the general form of $[Z_{XY}]$ versus temperature for the five frequencies 0.01, 0.1, 1, 10 and 100 Hz. Apart from the 25.16 degree determination, the data all falls on smooth constantly decreasing curves as shown by graph 23b which is drawn as for 23a with the 25.16 degree data removed. Again it seems that the 25.16 degree C determinations are anomalous.

In order to reduce the impedance spectra to a common level and thus ascertain how similar the spectra are (point (2) above), each was divided by the value at 100 Hz, chosen because for each spectrum this was a minimum. This normalised impedance $([Z_{XY}]_F / [Z_{XY}]_{100 Hz})$ is plotted versus log frequency as graphs 24a and b.

Taking the uncertainty shown into consideration, the 7 plots on graphs 24 may be divided into three groups as follows.

1) The three spectra on graph 24a taken at 25.16, 64 and 50 degrees C on the Friday.







and the second sec





2) The three spectra on graph 24b taken at 50, 45 and 22 degreesC on the following Monday.

3) The spectrum taken at 14 degrees C on Monday (graph 24b).

Graph 25 shows generalised plots of the spectra of these three groups.

iii) <u>Discussion</u>

ction raise the points expressed

degrees C. ns exhibit a phase shift more t at any other temperature studied. .005 and 100 Hz, [Z_{XY}] for the y high when referred to the smooth her temperature points on a [Z_{xY}]

lised impedance spectrum, frequency effect may be determined

rm.), is closely comparable rees C, taken on the same day. t that either the temperature eal, and that a determination hers would show a similar effecThe data and graphs in this se and discussed below.

The anomalous behaviour at 25.16
 a) The 25 degree determination
 than twice as large as the phase shift

25 degree determination is anomalousl curve which passes through the six of versus temperature plot.

c) At 25 degrees 0, the norma $[Z_{XY}]_F / [Z_{XY}]_{100 \ Hz}$ (from which the by

 $f_{\bullet}e_{\bullet} = 1 - 1/[Z]_{No}$

with similar spectra at 64 and 50 deg Points a, b and c above sugges effects observed on $[\Sigma_{XY}]$ and \emptyset are r made at 25 degrees C after all the of

SRAPH 25 12×410 US. FREQUENCY RESIN 20-50 MESM NACI 0.025 N 12xy 1 100 HZ 1.7 12 xy 1 12 AY 1 100 H2 For 25.11° C 50°C & 66°C 1 CURUE Severalised 1.6 Friday . dATA 0~ LAKEN , so'c local curve for 22°C, 45°C baken on following monday Severalised 1 2 dara on monday (3) 14°C data baken 1.5 1.4 1.3 1.2 1.1 1.0 .1 .001 .01 100 10 ~ V (H2) 1000 1

(which is extremely unlikely since this would require an increase in \emptyset from virtually zero to -10 degrees, and an increase in $[Z_{XY}]$ by a factor of 1.15 between 22 and 25 degrees C); or else, whatever produces the anomaly has a multiplicative effect on the impedance spectrum which is removed by normalising. This latter is entirely consistent with a transfer of ions from the resin to the solution (i.e. to the mobilisation of ions formerly held immobile at the membrane surface), since removing cations from the double layer would lead to a decreased capacitive effect, and the presence of more mobile cations would reduce the resistance without necessarily affecting the dispersion.

In fact the 25 degree determination was made first, only one hour after the cell had been filled, and the 64 degree determination second, six hours later. Thus, if a latent ion release does occur, it might be a result of continued equilibration of the resin/electrolyte system*, or due to some effect of heating the resin for the first time.

Since the normalised impedance spectrum for the 25 degree determination is not anomalous, if the hypothesis is correct it

* It should be pointed out that equilibration of the resins with the electrolyte under consideration was done in all cases of resin cells by rinsing the resins with at least ten 100 ml aliquots of electrolyte, over a period of not less than 15 minutes.

Despite the fact that Kunin and Myers (31) describe the equilibration rates of sulfonic acid exchangers as "rapid", it is possible that for the systems under consideration times of the order of hours are required.

suggests that the effect of an effective transfer of ions from the resin to the electrolyte may be represented simply as a constant term multiplying $[Z_{\chi\gamma}]$ at each frequency.

2) The effect of temperature on $[Z_{XY}]$

Graph 23b of $[Z_{\chi Y}]$ versus temperature drawn ignoring the initial 25.16 degree data, shows a smooth increase of $[Z_{\chi Y}]$ with decreasing temperature. Regrettably at the time of writing no reliable data could be found concerning the conductance of aqueous NaCl solutions as a function of temperature, but data for aqueous KCl was obtained from the work of Grinnel Jones (62), for temperatures 0, 18 and 25 degrees C. This was converted to a resistance normalised to 1,400 ohms at 25 degrees C, and plotted on graph 23b.

Lakshminarayanaiah (32) states regarding the conductance of membranes that "The temperature coefficient of conductance is of the same order as that observed in aqueous solutions (about 2%/degree C)". A "reasonable" point (1000 ohms, 70 degrees C) was chosen, and a curve plotted on graph 23b for the equation

 $[Z_{XY}] = (1000) (1.02)^{(70-T)}$

which describes a conductance increase of 2% per degree.

It can be seen from graph 23b that the 2%/degree conductance increase curve closely parallels the data for aqueous KCl, but that the resin data display a less steep resistive decrease with temperature above about 25 degrees C, and a considerably steeper resistive decrease below 25 degrees. Graph 23c of log $[Z_{XY}]$ versus temperature emphasises the dissimilarity between the temperature effect on the impedance of the resin bead system and that for the aqueous resistance of KCl, and the resistance of membranes expected by Lakshminarayanaiah; only the resin displaying any curvature on the semi-log plot.

The form of the temperature dependence of $[Z_{XY}]$ for the resin cell is not simple, and cannot be represented by the standard forms R $\propto \exp(B T)$ or R $\propto \exp(B(T-T_0))$, nor is this curve linear on a log log plot. Clearly the temperature effect on the magnitude of the impedance is more complex than that expected by Lakshminarayanaiah, and possibly warrants further investigation.

iv) Geophysical Implications

It is apparent from this study of temperature dependance that above 20 degrees C, the normalised impedance is essentially independent of the temperature. This is of some importance in the possible application of induced polarisation effect to geothermal prospecting since

f.e. =
$$\frac{\left[Z\right]_{Low} - \left[Z\right]_{High}}{\left[Z\right]_{Low}}$$
$$= 1 - \frac{\left[Z\right]_{High}}{\left[Z\right]_{Low}}$$
$$= 1 - \frac{1}{\left[Z\right]_{Low}}$$

= constant.

Thus the frequency effect is constant provided no property other than temperature is changed.

The other parameter commonly used by field geophysicists is the metal factor.

$$M.F. = \frac{[Z]_{Low} - [Z]_{High}}{([Z]_{Low})([Z]_{High})} = f.e./[Z]_{High}$$

But the temperature dependence of [Z] is given by graph 23b, and the metal factor must have the form of the reciprocal of this since the frequency effect is constant (see graph 26 of MF vs T). This plot displays a sharp curvature below about 30 degrees C, but becomes nearly level at high temperatures, suggesting that the metal factor too is a poor parameter for geothermal prospecting.

It should be remembered that only the effects of temperature on resin systems have been studied here, and that the effects of pressure and the applicability of resin models to geothermal situations have not been investigated.

SRAPH 26 METAL FACTOR VENSUS TEMPERATURE 7 × 10-4 derived from curves (D), (D) and (D) of graph 25, and the 100 Hz curve of graph 23 b r 6 " M.F. (1/1) M.F. = (1-1/F.e.)/(121100 H2) -40 TEMPERAture (degrees C.)

80a.

CHAPTER 8

CLAYS

A) Description

Throughout the preliminary investigations the clay chosen was a Wyoming bentonite, selected for its large ion exchange capacity, ease of procurement, and its well catagorised structure.

The term bentonite was first applied by Knight (30) to a particularly high colloidal, plastic clay found near Fort Benton in the Cretaceous beds of Wyoming. It has the unique characteristic of swelling to several times its original volume when placed in water, and it forms thixotropic gels with water even when the amount of bentonite in such gels is relatively small. Bentonites are particularly widely distributed in the Tertiary (occurring in Tertiary beds in New Zealand), and in the Upper Cretaceous.

The dominant clay mineral component of bentonites is smectite*. Other clay minerals, particularly illite and kaolinite, are present in many bentonites, sometimes in amounts up to about 50% of the total clay content.

Grim (15) states that "with regard to exchangeable cations, most bentonites that have been described carry Ca^{++} as the most abundant ion.

* The term smectite is used as a group name for all clay minerals with an expanding lattice, except vermiculite, while montmorillonite is a species name, specifically indicating a high-alumina end member of the smectite group with some slight replacement of Al³⁺ by Mg²⁺ and substantially no replacement of Si⁴⁺ by Al³⁺.
Only a few are known to carry Na⁺ as the dominant ion, and of these Wyoming bentonite is the main example". Grim attributes the very large variation in properties observed amongst bentonites, partly to the nature of the exchangeable cation, and states:- "The very high swelling and highly colloidal bentonites carry Na⁺ as the principle exchangeable cation. The Wyoming bentonite is an example of such a bentonite."

In Chapter 7 of his book "Clay Mineralogy" Grim gives an excellent discussion of the factors affecting ion exchange in clays. Some pertinent points made by him are reproduced below.

The clay minerals have the property of sorbing certain anions and cations, and retaining them in an exchangeable state. The exchange reaction proceeds with very little heat evolved, usually of the order of 2 kcal/mole. The exchange reaction generally does not affect the structure of the silica-alumina clay mineral structural unit.

Smectites have cation exchange capacities between 70 and 150 $meq^*/100g$ determined at neutrality, and the value for Wyoming bentonite is around 77 meq/100g (16). Grim ascribes the majority of the cation exchange capacity of smectites to substitution within the lattice of Mg^{2+} for Al³⁺ and to a lesser extent Al³⁺ for Si⁴⁺. Broken bonds at the particle edges account for about 20% of the exchange capacity while exchange of the hydrogens of exposed hydroxyls is not considered important for smectites.

* milli equivalents per 100 grams of clay.

Clay concentration

Grim observed that the cation exchange capacity of montmorillonite may vary with the concentration of the clay, particularly at relatively high concentrations. Mitra et al (47) show the cation exchange capacity of Indian bentonite to increase from 81 to 103 meg/100 g as the clay concentration increased from 0.25% to 8.80%.

Cationic form

The ion exchange capacity may also vary with the nature of the cation, and data of Mitra et al (47) shows a considerably larger exchange capacity when determined with Ca^{2+} than with Na⁺ for Indian bentonite.

Mering and Glaeser (44) point out that the negative charges on the clay mineral can be neutralised locally only by monovalent cations. Thus saturation of the mineral by divalent or polyvalent cations inevitably creates deficiencies of local neutralisation. The cations can solvate or hydrate only when they are detached from the silicate units, and the cations can detach themselves only when they do not participate in local neutralisation. Monovalent cations cannot detach themselves and therefore cannot solvate. As a consequence, clay saturated with polyvalent cations has relatively greater stability in the solvated states. These authors showed that when there is less than about 30% calcium on a montmorillonite containing Ca²⁺ and Na⁺, the Ca²⁺ ion is not effective; in other words the clay acts as if completely saturated with sodium.

A sample of Wyoming bentonite analysed by Grimshaw (16) has a total cation exchange capacity of 76.5 meg/100g with cations present in

the following percentages.

| Ion | Ca ²⁺ | Mg ²⁺ | Na | к + | H+ | Total |
|-----|------------------|------------------|------|------------|-----|--------|
| % | 23.2 | 19.4 | 50.7 | 4.3 | 2.5 | 100.1% |

Particle size

According to Grimshaw (16) bentonites are, for the most part, of extremely small size. The larger proportion of clay particles are less than 0.05 microns and those that are above this size are probably agglomerates. In watery suspension, the ultimate size of montmorillonite particles is probably only a few Angstroms. Commercial bentonites often contain a proportion of non-plastic material which is of comparatively large particle size.

The effects of grinding

Kelley and Jenny (29) show that grinding clay minerals as well as non-clay minerals causes an increase in cation exchange capacity.

This effect is quite marked and it would appear that in order to prepare reproducible clay systems, any stirring must be done carefully to avoid grinding the clay.

The effect of heating

In general montmorillonite appears to display a small negative temperature coefficient of the cation exchange capacity. The nature of the exchangeable cation has a marked effect on the high temperature behaviour, and Grim quotes the work of Hofmann(21,22) in which the temperature effect of the cation exchange capacity of Ca, Na and Li montmorillonite was studied. Hofmann's data indicates a gradual loss of cation exchange capacity on heating to 300°C for the calcium montmorillonite and an abrupt drop between 300° and 390°C. The sodium clay shows a very slight drop to 300°C and only a moderate one between 300° and 390°C, but the lithium montmorillonite shows a marked decrease in the cation exchange capacity on heating to only 105°C. Hofmann interprets this data to mean that when a clay is heated the exchangeable cations tend to move inside the montmorillonite lattice. Lithium is a small ion and can fit easily into the structure, possibly into vacancies in the octahedral sheet, and consequently only a small temperature is required for the shift into the structure (14). Because Na⁺ and Ca²⁺ are large ions and would fit with great difficulty into the structure , a high temperature would be required for the move.

This property of montmorillonites to "fix" small cations within the lattice at elevated temperatures suggests that a useful experiment in the study of the frequency dispersion of clay systems might be to observe the frequency spectrum of a lithium montmorillonite to temperatures of the order of $105^{\circ}C$ (at an elevated pressure).

Clogging of exchange positions

The development of aluminium on the exchange positions reduces the exchange capacity of montmorillonite clays. This is in part due to damaging of the lattice, but also in part to clogging of the exchange positions by Al^{3+} . Grim points to unpublished work by G. Michelson as suggesting that the movement of Al^{3+} from positions on the lattice to exchange positions is facilitated by drying. So long as the sample is not dried, the amount of movement is relatively small.

Unfortunately the bentonite sample used in this thesis was dry, and may have been dry for a number of months or years. The preparation of clay/sinter systems (Chapter 9) also, necessarily involves a wetting and drying to bond and weigh the clay on the sinter. Thus the exchange positions of the clay under study may well be extensively clogged with aluminium, and its exchange capacity so reduced. Before any quantitative analysis of data from clay cells can be made, it will be necessary to determine the exchange capacity of the clay in question.

Replaceability of exchangeable ions

The matter of cation replaceability is of great importance, both in the preparation of clays and with regard to I.P. effects. Briefly, some of the factors which affect replaceability are as follows.

The effect of concentration is complex. Kelley (28) states: "With cation pairs of about similar replacing power and of the same valence, such as K^+ and NH_4^+ , or Ca^{++} and Ba^{++} , dilution has relatively little effect on exchange, while with cations of different replacing power and different valence, for example Na^+ vs. Ca^{++} , or NH_4^+ vs. Ca^{++} , dilution produces marked effects on exchange."

Both the nature and number of the complementary ions filling the remainder of the exchange positions have an effect on the exchange kinetics. This too is complex, but for calcium, the smaller the concentration of exchangeable cation on the exchange positions, the more difficult the calcium is to release. For sodium the reverse occurs. Thus it seems that it would be easier to prepare a calcium montmorillonite from one containing exchangeable sodium, than to prepare the sodium form

from a clay partly in the calcium form.

Numerous investigators have found that the replaceability of a given ion varies with the nature of the anion that might be present.

In general, also, the replacing power of a cation tends to increase with the valence and size of the ion, and a rough guide to replacing powers in clays is given by the following series.

Mg > Ca > K > Na > Li

Anion Exchange

The exchange of crystal lattice anions as well as cations is also quite possible, and in certain cases the exchange of both anions and cations may occur in the same crystal. Substances exhibiting the latter **phenomenon** are called amphoteric exchangers. Grim gives a value of 23 meq/100g for the anion exchange capacity of Wyoming bentonite, this indicating a ratio of cation to anion exchange capacity of about 6.7. It is important to realise that this amphoteric behaviour exists, and that clays are fundamentally different from ion exchange resins in displaying an anion exchange capacity.

B) Preparation

i) Cleaning

The sample of Wyoming bentonite used in the preliminary investigations was received dry, and consisted of a light yellow powder interspersed with about 0.1% sand. To remove this sand the technique shown in Fig. 15 was developed. Sand free clay was placed in vessels and the clay allowed to

Figure 15

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VIBRATOR



CLAY SUSPENSION

Air from a compressor is passed through acetone, alcohol and water, to remove oil, and then passed gently through a thin clay/sand slurry in

a large separating funnel. Sufficient

disturbance is created by the passage of air bubbled to keep the clay dispersed, but the sand settles slowly out. Vibration is accomplished using a variable speed electric motor fitted with an eccentric bit, its purpose being to let the sand particles that settle on the sides of the vessel pass to the bottom by reducing the coefficient of friction between the sand and the glass. An estimated 90% of the sand is removed by this process if allowed to continue for 48 hours. settle out over a period of weeks, after which time most of the water could be decanted off leaving a thick clay slurry.

ii) Exchanging of clays

The foregoing discussion indicates the necessity of finding a technique suitable for exchanging the Wyoming bentonite sample into a reproducible cationic form. The clay itself cannot be percolated with electrolyte as the clay either passes through or completely blocks any sieve designed to retain it. Normally clays are bonded to sand, and exchanged by percolation in a column, but this was considered impractical since the clay must be removed from the sand and collected again somehow. Exchange cannot be accomplished by decantation of several volumes of electrolyte, as the clay takes several weeks to settle.

The technique adopted was to exchange a quantity of 20-50 mesh Dowex 50W - X8 ion exchange resin to the desired cationic form, add to this a slurry of about 5% clay in either the desired electrolyte or distilled water, and stir gently for 24 hours. The amounts of clay and resin used were calculated such that the number of cation exchange sites on the resin was greater than ten times that on the clay, based on values of 5 meg/g for the resin and 0.1 meg/g for the clay.

To test the effectiveness of this method of exchange, D. Wright (61) performed atomic absorption experiments on a montmorillonite believed to be Wyoming bentonite. The percentage calcium and sodium in the clay (assumed to be only at exchange sites) was determined before and after a sample was exchanged by the method described above. (The slurry was in distilled water). The results are as follows.

| | Na | Ca | |
|-----------------|---------------|---------------|--|
| before exchange | 7.74 meg/100g | 28.4 meg/100g | |
| after exchange | 64.5 meg/100g | 0.2 meg/100g | |

Thus the exchanged sample has gained

and has lost

$$28.4 - 0.2 = 28.2 \text{ meq Ca}^+$$

= 56.4 meq "Ca⁺"

The exchanging process has exchanged all calcium for sodium within (100)(0.4)/(56.8) = 0.7%. Although not tested, it was assumed that exchanging in an electrolyte containing the desired cations would further assist the exchange process. Also, as stated on p.85, the reverse process of exchanging calcium for sodium should go to completion even more readily.

CHAPTER 9

PREPARATION OF SINTER/CLAY SYSTEMS

A) Preparation of Sinters

i) Introduction

Vacquier (54) has stated that little or no I.P. effect was observed for clay slurries or massive clays, and that an effect was obtained only after a slurry was dried onto an inert framework, and the whole rewetted with electrolyte. It is necessary that the framework provided be reproducible and be available in a range of pore dimensions in order to study the effect of this parameter. Vacquier accomplished this by using various mesh sizes of sand, in beds, but the lack of reproducibility and the possibility of disruption of the matrix during re-equilibration with different electrolyte concentrations, has prompted the use in this thesis, at least initially, of glass sinters onto which clay may be emplaced.

ii) External dimensions of sinter framework

It is reasonable to suppose that the I.P. effect of a clay/ sinter/electrolyte system behaves as Conrad Schlumberger (51) observed the I.P. effect in the field to behave, the normal effect of wet soils being a bulk property of the soil, and not due to the interaction of the earth with the electrodes. That is, within certain other boundary conditions, the larger the clay/sinter system, particularly the longer the current path, the larger the effect expected. There are two reasons why the optimum sinter should be highly resistive, and thus why the sinter should be thin as well as long. In the first place it is desirable to minimise the effacts of series resistances, primarily that of the electrolytic path between the sinter and the potential electrodes, by maximising the resistance of the sinter. This may be accomplished either by increasing the length or decreasing the cross section. Secondly, since the determination of impedance is made by observing the voltage across the sinter, and since the I.P. effect is suspected of behaving in a non-linear fashion at high current densities (39,54) it is desirable to have a highly resistive sinter and thus ensure a measurable voltage at low current densities. To minimise the current density, for a given voltage response the length must be increased.

It is also desirable to have a highly symmetric sinter in order to simplify any mathematics involving the distribution of current.

In consideration of the points above, the shape of sinter selected was a long axis right cylinder.

iii) Practical

The actual preparation of sinters was based on unpublished work by C. D. Taylor (53). Sinters are prepared by grinding pyrex glass and firing this in a mould. Taylor stresses the importance of maintaining a uniform quality of pyrex glass in the ground glass and in the cylinder into which the sinter is to be sealed. It is necessary to grind fresh, clean glass, as an aging process in the glass (possibly devitrification)

prevents a good seal being made with the new tubing. Grinding was accomplished in an N. V. Tema T100 iron ring inertial grinder, grinding for a few seconds at a time / sieving each time through a 52 B.S.M. sieve, the coarser particles being returned for further grinding until a considerable quantity of ground glass was obtained. This ground glass was sieved through five standard sieves of British Standard Mesh, 52, 100, 150, 200, 300, by far the greatest amount being of particle size smaller than 300 mesh. The ground glass so obtained contained a large amount of visible impurities, possibly some of which were iron contaminants derived from the Tema. A comprehensive cleaning process was employed for each mesh size as follows. The glass was first washed in several aliquots of tap water to remove any floating or very light particles by decantation. Several aliquots of concentrated hydrochloric acid were then added, the whole being heated to remove any metallic contaminants. A conc. $H_2SO_{L}/alcohol$ mixture was used to remove oxidisable contaminants. When the glass could not be cleaned completely by this process, a strong sodium hydroxide solution was used in which the insoluble material could usually be suspended sufficiently to make decantation possible. Acetone then alcohol were used to remove organic contaminants on the glass surface, and the glass finally washed with several litres of distilled water by percolation in a column.

The initial sinters (numbers 1 and 2) were prepared in a mould made of brass (Fig. 16a), because of the ease with which this metal may be worked, and these were cylinders approximately 3.2 cm long by 1 cm diameter. Since the zinc content oxidises at temperature and invariably



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discolors the surface of the sinter, another somewhat larger mould was prepared from stainless steel, having the shape shown in Fig. 16b.

The moulds were filled with cleaned, graded ground glass, packed as tightly as possible. Initially this was accomplished by simply tapping the mould sharply, but with the larger stainless steel mold this was thought not to produce sufficient settling, and the mould was filled by pouring a glass/alcohol slurry into it. The glass was then settled by pouring alcohol through the mould while gently shaking the mould from side to side. Before firing, the alcohol had to be entirely removed by evaporation substantially below its boiling point to prevent the formation of vapour bubbles.

Taylor conducted experiments to determine the effects of time and temperature on the sintering process and concluded that "in all cases a change of a few degrees in temperature had more effect than even doubling the time. As a result the standard time chosen for all grades of glass was 15 minutes, chosen since this length of time was not tiresome, and it allowed well for inequalities of temperature, either locally in the furnace or due to lag in heating elements, both being factors of great importance when temperature control is critical." He gives optimum firing temperatures as follows,

British Standard Mesh

Temperature, degrees C

| 100-150 | 810 |
|---------|-----|
| 150-200 | 800 |
| 200-275 | 790 |
| 275-325 | 780 |

for sinter discs. These temperatures were found by experiment to be roughly applicable to the long axis cylinders under consideration.

Figure 17 shows the oven system used to fire all except the preliminary brass mould sinters. The thermostat and temperature thermocouples are separate, the temperature being continuously recorded on a Honeywell "Elektronik 15" recorder using a Ni/Cr v Ni/Al thermocouple with ice-water cold junction, situated near the top of the mould to register the maximum temperature.

Sinters 1 and 2 were prepared from 52-100 mesh ground pyrex, fired in the brass mould at 845 degrees C for fifteen minutes. The porosities of these sinters were determined by comparing the weight in air with that in water after all the air had been removed by evacuation, and for each the porosity was of the order of 40%. The sinters were mounted in the configuration shown in Fig. 14a, and are henceforth referred to as sinter cells 1 and 2 respectively.

Sinters 3 and 4 were prepared in the stainless steel mould, the mould being packed with 100-200 mesh ground pyrex using alcohol. Each was left in the furnace for about 22 minutes until the temperature reached 810 and 805 degrees C respectively. These cells were cut to a uniform size using a diamond saw, and sinter cells 3 and 4 prepared as shown in Fig. 14b. The porosity of each was determined as before and sinters 3 and 4 show 41 and 42% porosities respectively.

Sinters prepared in both the brass and stainless steel moulds show considerable surface pitting in all cases except one sinter prepared from



52-100 mesh spheres of soda glass*, probably due to the rather large amount of force necessary to remove sinters from the moulds. For both moulds the force required when cold was greater than that when the mould was as hot as was practical, and this effect was ascribed to the much greater thermal expansivity of both brass and stainless steel, than glass. Even with the mould as hot as it could conveniently be handled the force required to remove the sinters frequently resulted in broken sinters and always in surface pitting.

In an attempt to circumvent expansion problems, a mould was constructed from pyrophyllite - selected for its high mechanical strength on firing, and its extremely low coefficient of thermal expansion. While none were in fact used, this mould was found to produce excellent sinters displaying a high strength and negligible surface pitting. Considerably less force was required to remove these sinters than from metal moulds. It is suggested therefore that ceramic moulds be used in future preparations of sinters.

* Regrettably soda glass sinters could not be used with the present cell design as ground glass joints were only available in pyrex glass, the difference in thermal properties between the two being so great as to make bonding impossible. In all other respects, however, the soda glass sphere sinter behaved ideally, its mechanical strength being several times greater than that of ground pyrex sinters, while the porosity was about the same (3%). The fact that the sinter was composed of glass spheres, too, means that the pores have a far better defined shape than do those in a sinter of fragmented glass. In future work it would be highly desirable to use sinters prepared from spheres.

B) Bonding of Clays to a Sinter Framework

Grim (15) has observed that "in the case of sand-clay-water systems, the maximum bonding force is developed when the sand and clay are wet with an extremely restricted amount of water. With a very small amount less or more than the optimum amount of water, the bond is greatly reduced." In spite of this Vacquier (54) used, apparently successfully, three methods of bonding clay to sand, each having little control on the water content of the clay. The first of these is to mix dry, weighed amounts of clay and sand by tumbling, which apparently causes the clay to stick sufficiently to the sand so that when the sample is wet it immediately exhibits an I.P. effect. The second method, used when the clay makes a homogeneous slurry, is to force a slurry through the sand with an aspirator, let the whole dry, break up the resulting cake, place in a sample holder and re-wet. The third method is simply to wet a clay/sand mixture with distilled water, let it dry then re-wet with the electrolyte under consideration.

Fortunately Wyoming bentonite forms a homogeneous slurry and Vacquier's second method can be used to introduce clay to the sinter, but the others cannot. Nor can Grim's method be used since a clay with an "extremely restricted" amount of water cannot be made to pass into a sinter.

The practical considerations involved with the preparation of clay/sinter systems are as follows.

i) Thickness of slurry and method of introduction

When situated in a cell (as shown in Figure 14b) a thin slurry of about the viscosity of milk could be poured through the sinters at the rate of about one drop per second with no apparent filtering out of clay. Slurries much thicker than this do not pass at all, and when attempts were made to suck thick slurries through a sinter under vacuum, the suspension passed for a few seconds then ceased as an impermeable layer of clay was deposited on the top face of the sinter. The best method of introducing clay was found to be by immersing the sinter in a cleaned clay suspension of about 56 by weight in a desiccator, and evacuating. In this way the suspension was able to penetrate all the pore volume of the sinter, ensuring a uniform deposition on drying.

ii) Drying temperature and time

The data in Grim (15) suggests that the cation exchange capacity and structure of sodium and calcium Wyoming bentonite is substantially unaffected by prolonged heating to temperatures of the order of 150 degrees C, (but that, particularly hydrogen form clays, might be susceptible to clogging of exchange sites by Al when dried). As such the first three cells were prepared by drying clay in the Na or Ca form at 160 degrees C, to constant weight (normally about 12 hours), however subsequent experiments show that the frequency dispersion might be seriously diminished by such temperatures, and the final cell was dried at 90 degrees C for 12 hours.

iii) Cationic form of the clay

Grim (15) has observed that a major cause of the wide variation in properties observed among bentonites is the nature of the exchangeable ion, and notes a tendency towards dispersion of sodium form Wyoming bentonite.

Vacquier (54) observed a diminished tendency of clays to bond in the sodium form and states: "A strong salt solution can be used to saturate the clay with a particular metallic ion as long as the solution does not contain sodium or potassium. In the case of Na or K dispersion of the ion saturated clay occurs when dilute solutions are introduced later into the solution." This effect was in fact observed, and greater quantities of clay were bonded to identical sinters when the clay was in the Ca rather than Na form.

iv) Nature of re-wetting electrolyte

It is known that uptake of sodium by Wyoming bentonite in the exchange positions causes the clay to swell, and that the sodium Wyoming bentonite has considerably more colloidal character than the calcium form. As such, since the re-wetting of a calcium clay with NaCl electrolyte would cause an equilibrium exchange reaction, a number of changes would occur in the clay, possibly involving swelling, strain, fragmentation and dispersion. It is proposed to eliminate this complexity in the initial experiments by re-wetting with electrolytes of the same cation as the clay predominantly holds in the exchange positions.

MORE SENSITIVE MEASURING TECHNIQUES

CHAPTER 10

THE NEED FOR MORE SENSITIVE MEASUREMENT OF [Z] AND Ø

i) The dispersion of clay/sinter/electrolyte systems

The impedance spectrum of sinter cell number 1 containing no clay was run as a normal using the oscillator/oscilloscope technique. The sinter was filled by evacuating the cell in 0.025M NaCl in a desiccator, and the following response was observed in that electrolyte. No negative phase shift attributable to the cell was observed between 0.005 and 500 Hz, but a positive phase shift was observed above 500 Hz due to miss-matching of the oscilloscope channels. $[Z_{XY}]$ was constant within experimental error at a value of 1.1 x 10⁴ ohms \div 5% between 0.005 and 1,000 Hz.

This cell was then treated with clay by evacuating in a 2% slurry of cleaned clay in the form as received and drying in an oven at 160 degrees C. A rather small amount of clay, estimated at about 20 mg^{*} was deposited on the sinter. This cell was then equilibrated with 0.01M NaCl in which electrolyte the frequency response of both $[Z_{XY}]$ and \emptyset was observed to be flat within experimental error using the oscillator/ oscilloscope technique between 0.005 and 100 Hz.

It is clear that if the impedance effect of this cell is to be studied, a more sensitive measuring technique must be found.

* See note on p.141.

ii) Hewlett Packard solid state voltmeter

The limit of accuracy in impedance measurement using the oscilloscope, is that with which the amplitude of the voltages can be determined (assuming the oscilloscope behaves linearly and that all ranges on both channels are calibrated). The oscilloscope display is divided into centimeter grids, being 6 cm high and 10 cm wide, and the accuracy with which the amplitude of the voltage can be read is at best \pm 0.1 cm (\pm 1.7% full scale) and typically \pm 0.2 cm (\pm 3.3% full scale).*

A Hewlett Packard (427A) solid state high impedance voltmeter was obtained which has the following advantages and disadvantages over the oscilloscope as a voltage measuring device.

Advantages

- 1) Reading accuracy of ⁺ 0.1% full scale.
- Input impedance of 10 Megohm (as compared with 1 Megohm for the oscilloscope).
- Measures both D.C. and A.C. voltages and thus can operate to infinite frequencies.

Disadvantages

1) The waveform is not displayed and thus there is no check on distortion of the sine wave or on the noise level. Also readings must

* The trace itself is approximately 0.2 cm wide and a determination of the top and bottom of the wave must be made in order to determine the amplitude.

be taken as the maximum occurs and at very low frequencies one cannot leave the machine to produce a wave and measure it later. This problem can be partially alleviated by making simultaneous oscilloscope and voltmeter determinations, but this eliminates the advantage of a higher input impedance.

2) A.C. measurements can be conducted only down to 10 Hz and D.C. up to 0.1 Hz because of the time constant of the A.C. to D.C. converter and the ballistic properties of the meter, respectively. This leaves a two decade region where no readings can be made.

3) There is only one instrument and thus readings must be made alternately across the cell and the standard resistor. For very low frequencies, several hundred seconds may pass between these two readings and accuracy may be limited by lack of stability of the oscillator voltage.

4) Single channel operation also means that no measurements of the phase shift can be made. This is not a great disadvantage since the determinations of \emptyset made on the oscilloscope are insufficiently precise even for resin cells, and a new method must be found.

The solid state voltmeter (S.S.V.M.) was calibrated extensively in the D.C. ranges using a Cambridge type 44228 potentiometer to supply standard voltages, and in the A.C. ranges using the Philips function generator with its output tapped across a Bourn "Lab-Pot".* The prime

* Effectively a linear ten turn potentiometer.

requirement of these calibrations was that the SSVM behave linearly within a voltage range, and read consistently amongst the ranges. For both the A.C. and D.C. ranges the meter was linear within the reading accuracy (\pm 0.1% full scale), and the calibration amongst ranges was of the order of a few percent full scale.

The voltage observed for a fixed potentiometer setting as the frequency was varied, changed quite considerably, and this effect was measured on both the A.C. and D.C. ranges 0.1, 1, and 3 volts full scale, for frequencies from 0.005 to 5,000 Hz. This latter calibration is in fact unnecessary as the impedance is determined by a ratio of voltages, and whatever calibration factor is involved cancels; however these measurements served to indicate the uppermost frequency at which voltages could be determined with accuracy on the D.C. ranges, and the lowest frequency on the A.C. ranges.

A number of determinations were made on both clay and resin cells using the SSVM and oscilloscope simultaneously, but it soon became apparent that although the measuring accuracy was increased about tenfold

- a) The clay/sinter/electrolyte systems currently under study showed little impedance dispersion.
- b) Measurements of voltages at very low frequencies using the SSVM in its D.C. mode were extremely time consuming and fatiguing on the eyes.
- c) The present methods of determining the phase shift were insufficiently accurate.

iii) Accuracy considerations in [Z] and \emptyset

At this stage the accuracy with which $[Z_{XY}]$ can be determined is considerably greater than that for \emptyset , and there is little point in increasing the accuracy of the determination of $[Z_{XY}]$ since any subsequent mathematical treatment of the data would be limited in accuracy by errors in \emptyset almost exclusively.

This is so since the most fundamental way of treating impedance data is to determine the real and imaginary parts of the complex impedance (see p.126)

$$Z = R + j X$$

The parameters determined in this study are,

$$[Z] = (R^{2} + X^{2})^{\frac{1}{2}}$$

 $\emptyset = \tan^{-1} (X/R)$

and X and R are related to these by

$$R = [Z] \cos \emptyset$$
$$X = [Z] \sin \emptyset$$

If a, b, r and x are the errors in [Z], \emptyset , R and X respectively, the errors in R and X caused by errors in the independent observation of [Z] and \emptyset are as follows.

 $R \stackrel{+}{=} r = ([Z] \stackrel{+}{=} a)(Cos(\emptyset \stackrel{+}{=} b))$

but $\cos(\emptyset \stackrel{+}{=} b) = \cos \emptyset \cos b \stackrel{+}{=} \sin \emptyset \sin b$

≈ Cos Ø ± Sin Ø Sin b

(if b is of the order of a few degrees as is the case for the oscilloscope determinations, $\cos b = 0.999$ and may be ignored)

$$X \stackrel{+}{=} x = ([Z] \stackrel{+}{=} a)(Sin(\emptyset \stackrel{+}{=} b))$$

Sin($\emptyset \stackrel{+}{=} b$) = Sin \emptyset Cos b $\stackrel{+}{=}$ Cos \emptyset Sin b
= Sin $\emptyset \stackrel{+}{=}$ Cos \emptyset Sin B

but

For the oscilloscope the error in [Z] is of the order of 5% and the error in $\not = 2.6$ degrees. For a (large) phase shift of 10 degrees

$$R \stackrel{+}{=} r = ([Z] \stackrel{+}{=} 5\%)(\cos 10 \stackrel{+}{=} \sin 10 \sin 2.6)$$
$$= ([Z] \stackrel{+}{=} 5\%)(0.9848 \stackrel{+}{=} 0.8\%)$$
$$r = (a^{2} + b^{2})^{\frac{1}{2}} = (25 + 0.64)^{\frac{1}{2}}$$
$$= 5.06\%$$

$$X \stackrel{+}{=} x = ([Z] \stackrel{+}{=} 5\%)(\sin \phi \stackrel{+}{=} \cos \phi \sin b)$$
$$= ([Z] \stackrel{+}{=} 5\%)(0.1736 \stackrel{+}{=} 26\%)$$
$$r = (25 + 6,760)^{\frac{1}{2}}$$
$$= 26.05\%$$

Increasing the measuring accuracy of [Z] to, say, ± 1%

$$r = (1 + 0.8)^{\frac{1}{2}}$$

= 1.34%
$$x = (1 + 6760)^{\frac{1}{2}}$$

= 26.00%.

Since X and R are equally represented in the expression for the complex impedance, for maximum accuracy in the determination of Z, x and r should have similar values, necessitating an increase in the accuracy of X (x) and hence in the measuring accuracy of \emptyset (b).

iv) Conclusions

On the basis of the considerations in this chapter, an entirely new measuring system was designed and built, with the intention of obtaining values for R and X down to 0.001 Hz and to at least 100 Hz, with an accuracy of better than 1%. CHAPTER 11

THE MEASUREMENT OF ZVV.

i) D.C. measurement of voltage

A Honeywell "Electronik 194 Single Pen Lab Recorder" was used as a voltage measuring device, the voltage being measured across a standard non-reactive resistance and the potential electrodes of the cell, alternately as for the SSVM. This model was selected for its extremely fast response time, and can be used up to about 2 Hz with very high accuracy. This recorder also has the advantage of high sensitivity (up to 0.1 mV full scale) and high measuring accuracy (± 0.2% full scale).

The input impedance of the recorder is only 2 Megohms, and since the sinter cells have an impedance of the order of 10⁵ ohms, a voltage follwer was required to ensure measuring accuracies of better than 0.1%. Since neither of the potential electrodes are at ground potential, a twin channel voltage follower was constructed which refers the potential at each electrode to ground, the difference in these voltages being taken to the chart recorder. The effective input impedance of this follower is of the order of 400 Megohms.

The circuit used to measure D.C. voltage is shown in Fig. 18. Impedances are determined by making alternate measurements of the peak D.C. voltage of the sine wave across the cell, and that across a Sullivan Non-reactive decade box* adjusted to have the same impedance

* The reactive component of this decade box was measured using the Wayne-Kerr bridge, and found to be negligible.



as the cell at about 0.5 Hz. In this way maximum accuracy may be obtained by initially adjusting the oscillator voltage to give an approximately 90% of span peak to peak sine wave for both the reference and cell voltages*. The cell and the resistive reference are connected to the follower by means of a double pole double throw (DPDT) switch, both the switch and the follower being housed in an aluminium case which acts as an electrostatic shield.

ii) Peak to peak voltage measurement

The D.C. voltage circuit (V_{DC}) operates up to 2 Hz, and the SSVM can be used to measure A.C. voltages down to 10 Hz, but it was considered desirable to measure impedance in the missing region and to provide a reasonable overlap of measuring techniques in order to determine a continuous spectrum.

The device eventually built is shown in Fig. 19. The output of the voltage follower is connected by a switch, instead of to the chart recorder, to an amplifier with gain adjustable from 2 to 100. The output of this amplifier is fed into a pair of reversed diodes, one passing the positive half cycle and the other the negative, and then into a pair of very large capacitors. Because of the high reverse resistance of the diodes, charge escapes only slowly from the capacitors, and each capacitor

* Although the chart recorder was extensively calibrated using a Cambridge type 44228 potentiometer to supply D.C. voltages, and was observed to behave linearly, the mechanical damping of the pen mount will introduce some non-linearity, and this effect is minimised by maintaining the two voltages at similar amplitudes.



Figure 19 b

LEAKAGE PATHS. 6)



1 Lenhage between capacitors through the diodes. The revenue resistance of the diodes is 6.5 ×10° A. 2 Leakage between capacitors through the recorder. The imput impedance of the chart recorder is 2×10 A, but a Vollage Follower can be used to increase this to about 4 ×10 ° A. and 4 Leakage through capacitons. The 3 equivalent parallel resistance is about 10 A.

stores the maximum value of the particular half wave voltage minus a threshold voltage (approximately 0.65 V), below which the diodes pass no forward current. The voltage that appears across each capacitor obeys the relation

$$V' = aV - V_0$$

where
$$V' = observed voltage$$

 $V = applied voltage$
 $V_o = threshold voltage$
 $a = amplification$

The voltages that appear across the cell and the reference resistor are observed alternately in this fashion, thus

$$[Z_{XY}]/R = V_{XY}/V_R$$
$$= (V'_c + V_o)/(V'_R + V_o)$$

 V_o may be determined by plotting a current versus voltage chart (graph 27) and interpolating values on this, however with only a small decrease in accuracy, a constant value of 0.65 volts can be used.

Three leakage effects combine to reduce V' with time, and thus give the system a finite (but long) time constant, limiting the lowest frequency at which the device can be operated. These leakage paths are shown on Fig. 19, however the only leakage of significance is that across each capacitor. Thus in selecting capacitors, two factors must be taken into consideration. First, the larger the leakage, the smaller is the discharge time constant. Secondly, the larger the value of the capacitor, the more coulombs it will store for a given voltage, and the smaller the



effect of a current leak will be on the stored voltage level (and thus the longer the discharge time constant). To maximise the discharge time constant, a large, low leakage capacitor is required. Unfortunately, in general, the larger the capacitor the larger is its leakage, however by experiment a capacitor was found (3200 micro farads - electrolytic) for which peak to peak voltages could be determined with precision down to 0.1 Hz, and satisfactorily down to 0.01 Hz.

Fig. 20 shows roughly the form of the voltage across the various elements of the peak to peak voltage measuring device. The solid line closely resembles the form actually observed when determinations are made at low frequency. The voltage across the capacitors is measured using the Honeywell chart recorder, and can be determined with about the same precision as for the "D.C. wave". Because of the very large value of the capacitance the charging time constant of the system is long, and the voltage measured across the capacitors on the chart recorder has a roughly exponential envelope with a time constant of the order of minutes. Observations at all frequencies down to 0.1 Hz show that the voltage seems to reach 99.9% of its final value after 10 minutes, while for 0.01 Hz a reading is best taken after an integral number of half cycles (about 18) has passed. Thus, to minimise errors (since the voltages are to be used in a ratio), readings were taken at a constant time after the capacitor was connected, and for convenience this time was selected as 10 minutes. Between each reading both capacitors were short circuited using a switch, and the chart recorder re-set to zero.

This technique was found to work well enough, but was extremely time consuming since 20 minutes must be spent at each frequency.


iii) Measurement of A.C. voltages using the Hewlett Packard SSVM

At frequencies above 10 Hz, the SSVM could be used to determine A.C. voltages across the cell and resistor alternately by using the voltage follower and switch as for the D.C. and peak to peak (V_{pp}) voltage measuring techniques.

As with V_{pp} , this system has no theoretical upper limit of frequency. For both, however, the D.C. coupled voltage follower (and for V_{pp} , the amplifier) imposes an upper frequency limit of about 1000 Hz for practical impedance measurement.

iv) Noise

In an attempt to keep noise to a minimum, when the final measuring circuit was set up all leads were shielded and all instruments housed in shielded cases, including the Sullivan non-reactive decade box and an auxiliary 10^4 ohm non-reactive resistor which was mounted in a grounded aluminium tube. The cell was mounted in an enclosed stainless steel oil bath (see p.131), which besides acting to minimise thermal effects, also served as an electrostatic shield.

What noise remained in the circuit after these precautions had been taken was mainly attributable to noise in the line voltage.

The measuring accuracy of [Z] is primarily noise limited and thus fluctuates with the noise level, however determinations of $[Z_{XY}]$ should be accurate within $\frac{1}{2}$ 1.0% for all the techniques described above.

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CHAPTER 12

THE MEASUREMENT OF PHASE SHIFT

A) Lissajous Figures

Adjusting the orientation of a lissajous figure using a standard phase shifting circuit was found to be insufficiently accurate, and extremely painstaking at low frequency. This method was abandoned.

B) Triggering Circuit

i) Construction

The most promising method seemed to be to use a point on the leading sine wave (preferably the zero cross over of this wave where the slope is a maximum) to trigger the starting gate of a clock, and to use the identical position on the trailing sine wave to stop the clock. Given the frequency, \emptyset can be determined. In order to sharpen the leading edge of the sine waves, and thus reduce any error in the time caused by variations in the threshold voltage of the gate, it was decided to amplify the sine wave by a factor of several thousand, saturating the power supply and producing an effectively square wave. Square waves derived from the input sine waves are used to trigger start and stop gates of a high frequency counter.

The first counter obtained triggered on a voltage level and not on a positive going pulse, thus as long as a voltage greater than a certain value appeared at the start gate, the gate was open. This meant the square wave had to be converted to a voltage spike, and this was done by constructing an active differentiator and connecting this to the output of the amplifiers.

A block diagram for the circuit is shown in Fig. 21.

Malmstadt and Enke (34) give an excellent discussion of the use of digital devices, and it is not proposed to discuss the operation of such instruments here, further than giving a block diagram of the digital elements used in making a determination of time in an interval bounded by a starting (A) and stopping (B) pulse (see Fig. 22)

ii) Errors

Possible sources of error in the phase shift derived from a determination of time AB using the device shown in Fig. 21 may be considered under the following headings.

1) Noise

The effect of amplification on the noise is both to increase the voltage level of the noise, and to decrease the effect of a given noise level on the determination of a given time AB. The reason for this opposing effect may be seen from Figs. 23a and b. In the linear region of the zero voltage cross over, the slope of the leading and trailing edges of the amplified sine wave is proportional to the amplification (this can be seen from Fig. 23a). The detail on Fig. 27b shows



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FIGURE 22 BLOCK DIAGRAM OF TIME INTERVAL METER Reproduced from Malmstadt and " Digital Electronics For Scientists" ENKE page 23. START SIGNAL INPUT COMPARATOR GATE CONTROL A A STOP BINARY DIRECT GATE CONTROL SIGNAL INPUT COMPARATOR COUNT COUNTER GATE ß AND В INPUT READOUT CLOCK OSCILLATOR SCALER AND PARATOR





| V/ | /t = | slo | ope | of | leading | edge |
|-----------|----------------|----------------|-----|----------------|----------|----------|
| | × | A | (+ | the | amplific | cation) |
| thus | v = | k ₁ | A I | t | | |
| But | v « | A | = | k ₂ | A | |
| Therefore | k ₂ | A | = | k ₁ | A t | |
| i.e. | | t | = | k_ | /k_ = 0 | constant |

In other words the error in the time is independent of the amplification provided there exist sufficient amplification for the leading edge to be considered linear. This last requirement can be seen from Fig. 23a to hold provided the amplification is such that the amplified sine wave is greater than about three times the power supply voltage.

2) Threshold Voltage of Gates

While amplification above a certain level does not affect the error in time due to noise, a large amplification is necessary to ensure that small fluctuations in the minimum voltage required to trip the gates do not significantly affect the measurement of time AB.

The fact that the gates trip at a non-zero voltage will have an effect on the measured time only if the threshold is different for A and B or if the output square waves from the triggering circuit have different rise times. (Observations of the leading edges of the output square waves indicate a dissimilarity of about 10 micro-seconds in the rise time and thus an error in the time determination of this order of magnitude, however the effects of (5) below completely overshadow this.) If the amplification is large, the leading edge will pass nearly vertically through zero volts, and thus reach the threshold voltage and pass through the threshold range in extremely short times.

3) Overamplification

Since the amplifiers have a finite rise time (about 1 micro-second), increasing the amplification past the point required to produce a square wave that rises to the supply voltage (18 volts) in less than 1 microsecond merely serves to increase the effect of noise which has no such upper limit. Thus noise is independent of the amplification only up to a certain maximum value, A', which may be calculated as follows.

Assuming the amplification is sufficient so that the leading and trailing edges of the "square" wave are effectively linear, the slope of this line may be calculated from the slope of the zero voltage crossing of the initial sine wave (A=1). The sine wave has the form $V = V_0 \sin \omega t$, and the slope

$$\frac{dV}{dt} = V_0 \cos \omega t$$

For V = 0, Sin $\omega t = 0$ and Cos $\omega t = 1$, thus the slope of the leading and trailing edges of the "square" wave is;

slope =
$$dV/dt$$
 = 2 π f V for A = 1

where f is the frequency in Hertz.

We can use this to evaluate the constant in

$$V/t = kA$$
 (see Figs. 23a and b)

since

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 $dV/dt = V/t for a straight line = k_1^A = 2\pi f V_0 for A = 1$

thus

and

 $k_{1} = 2\pi f V_{0}$ $V/t = (2\pi f V_{0})A$

We require to know how large A can be made such that the voltage reaches the level of the power supply (18 V) in not less than 1 micro-second.

$$18/10^{-6} \leq 2\pi f V_{0} A$$
$$A \leq \frac{18 \times 10^{6}}{2\pi f V_{0}}$$

For the maximum probable values, $V_0 = 1$ volt, f = 1,000 Hz

4) Counter Error

Since the counter operates in a strictly digital fashion to measure time AB, the only possible causes of error are in the oscillator frequency, and $\frac{+}{2}$ 1 in the last digit random counter error. Neither of these is likely to be of any concern at frequencies less than about 1,000 Hz.

5) Phase Shift Introduced by the Triggering Circuit

After the triggering circuit had been constructed it was found to have a pronounced phase response that varied with frequency (see p.137). This response is considered to be an artifact of the measuring system only, and very much diminishes the accuracy with which phase shifts can be observed at frequencies above about 1 Hz. No time however was available in which to perform the extensive modifications to the triggering circuit required to ensure that the phase response of each channel was identical at all frequencies.

In fact the effect of 5 above is responsible for by far the greatest error in phase measurement, and its effect is large enough to prevent any measurement of \emptyset above about 10 Hz, and to reduce the precision to about 0.1 degrees below 1 Hz.

iii) Heath counter

The final measuring circuit for the determination of \emptyset (and [Z]) is shown in Fig. 24. The counter used was a Heath type EU-805 digital instrument with six digit display and a crystal oscillator, and is capable of counting micro-seconds. This instrument is not only capable of measuring time AB, but can also act as a digital voltmeter (DVM), and was used in this mode to supplement the chart recorder measurements both when measuring V_{DC} and V_{pp} . Regrettably the minimum ramp time of the A to D* converter was 0.1 seconds and thus the DVM was incapable of acting as a D.C. voltmeter at frequencies much above 0.1 Hz. High input impedance and six digit precision make this instrument extremely useful as a DVM.

The features which make this counter useful as a phase shift detector are as follows.

* Analog to Digital.



1) High counting rate

Times of 1 micro-second may be measured thus the instrument is capable of measuring phase shifts of 0.3 degrees at 1,000 Hz, $3x10^{-4}$ degrees at 1 Hz, and $3x10^{-7}$ degrees at 0.001 Hz. The instrument thus has extremely high precision, especially at low frequencies.

2) Operation from square pulse

Both gates are triggered by a positive going pulse, and not a voltage level, thus the output square wave from the amplifiers need not be differentiated.

3) Positive or negative triggering

Both gates have a separate switch to enable triggering on a positive or negative going pulse. This means that the time differences between both the leading and the trailing edges may be taken, and averaged.

4) Variable attentuation

Since the gates can be triggered by a transient spike, the effect of such interference must be reduced below the gate threshold by attentuation. The counter has a switched decade attenuator from 0.1 to 100 for each channel.

5) Hold facility

Rather than the counter counting up to the appropriate time between gating pulses (in micro-second steps), the previous result may be held on the screen, to be replaced by the next result.

At high frequencies this enables an average to be taken by inspection since the only numbers appearing on the screen are results, and (assuming random noise) the average is the most commonly occurring number. When the noise level is low, an average is immediately apparent by this method down to about 10 Hz.

6) Sum facility

In the sum mode, the counter simply adds the result of the current determination to the held sum of the previous ones, thus an average can be taken by summing n determinations, and dividing the result by n.

7) Adjustable viewing window

Where the average cannot be taken by inspection using the hold mode at high frequencies, because of noise, a sample may be made at any rate from zero to infinity by adjusting the viewing time of the held result. A convenient time is found to be about twice per second and an average is taken using the sum mode. All that is required is that the number (A) of determinations be known. If each determination is to be recorded for some subsequent statistical analysis, a rather slower sample rate is necessary.

8) Frequency and period modes

Determinations of the frequency of the input signal can be made by using either the frequency or the period modes on either the A or B inputs. At high frequencies, the frequency mode is used, and at low frequencies the period mode, to give maximum accuracy.

9) Adjustable time base

Using decade scalars the counter can be made to read 10^{-6} seconds on the sixth tube, to 10^7 seconds on the first.

iv) Practical

Actual measurements of the phase shift were made as follows. The time difference between the positive going pulses (t_{++}) and the negative going pulses (t_{-}) were determined at each frequency using the circuit as shown in Fig. 24. These times are affected by both the D.C. level of the input signals and the phase shift. Four cases must be considered (Fig. 25) and in all cases it can be shown that if t_{++} and t_{--} are considered with sign, then the time between the cell and reference signals

$$t = (t_{++} + t_{-})/2,$$

irregardless of D.C. level. The phase shift is now determined in terms of $\Delta t/t$, where t is the period of the wave under consideration and may be determined either by measurement using the counter in the frequency or period modes, or read directly from the oscillator

$$\Delta t/t = (\Delta t) \times frequency$$

and is a linear parameter that becomes unity at 360 degrees. Thus,

 $\emptyset = (\Delta t) (f) (360)$ degrees

At high frequencies t_{++} and t_{--} are determined by inspection with the counter in the hold mode, at intermediate frequencies by summing and averaging a large number of observations (usually 50), using the sum





mode and a sample rate of about 0.5 Hz, and at low frequencies by observing as large a number of readings as is convenient in the time available, and taking the average.

This system is not foolproof as the attitude of one square wave to the other may change as the frequency (and thus the phase shift) is altered, or as the D.C. level drifts, and the time measured may change sign. As such it was found convenient to use a reverse switch and oscilloscope as shown in Fig. 24 to assess the approximate magnitude, and the sign of t_{++} and t_{--} before each counter determination, and to ensure that the signal on the start gate precedes that on the stop gate. Resin Cell 4 (modified)



Sinter Cell 4



Phase Shift, V_{D.C.} and V_{P.P.} Measuring

Apparatus





Oil Bath and Wayne-Kerr A.C. Bridge Apparatus





RESULTS

CHAPTER 13

RESULTS

i) Introduction

The results have been divided into two sections relating to the measuring technique employed. In the first section the results are those of a series of determinations made using the A.C. bridge apparatus described previously (p. 44), and a two terminal cell with platinised platinum electrodes. Runs were made on 100% resin beds of two mesh sizes (100-200 and 200-400 B.S.M.) using five NaCl concentrations between 0.004 and 0.1M and frequencies between 41 and 10,000 Hz.

The second section contains results of 17 determinations made using the final low frequency measuring apparatus (Fig.24) on cells containing resins, resin/glass mixtures, and clays in various forms. For the measurements in this series 0.01M was selected as a concentration of the order of those found in the soil.

ii) Section I

Two Terminal A.C. Bridge Measurements.

Using Cell 1 with platinised platinum electrodes to minimise electrode polarisation effects (p.46) and the A.C. bridge described on page 44, frequency spectra for the equivalent parallel conductance (GP) and capacitance (CP) were determined for cells of 100% sodium form resin equilibrated with NaCl solution of concentration 0.05, 0.02, 0.01, 0.004M for 100-200 mesh resin, and 0.1, 0.05, 0.01, 0.004M for 200-400 mesh resin.

In order to determine the effects of the various parameters currently in use to describe the I.P. effect, these were calculated from GP and CP. For each cell [Z] was observed to increase with frequency consistent with an I.P. effect (see p.3). There being well over 100 data points from the 8 runs, the large amount of data handling necessitated the use of a computer, and a short program was written for the IBM 1130 computer to calculate at each frequency the following parameters:

| | f.e. | Ξ | frequency effect = $([Z] - [Z]_{10,000})/[Z]$ |
|---|-------------------|---|--|
| | M.F. | = | metal factor = $f.e./[Z]_{10,000}$ |
| | RP | = | equivalent parallel resistance |
| | [Z] | = | magnitude of the impedance |
| | ø | = | phase shift of voltage with respect to current |
| Ζ |] _{Norm} | = | normalised $[Z] = [Z]/[Z]_{10,000 \text{ Hz}}$ |
| | CS | = | equivalent series capacitance |
| | R | = | equivalent series resistance |
| | Х | = | reactance |
| | log R | | |
| | log X | | |

This large amount of data also prevents its reproduction here, but graphs of the parameters versus concentration and/or log concentration, and frequency and/or log. Frequency are for the most part included. It is found in all cases that plots against frequency or concentration

are more nearly linear when an extended (log) scale is used. Also in the case of frequency, data points have been selected at logarithmic intervals and more accuracy is obtained by plotting on a log scale. This does not necessarily imply that there is any theoretical justification for expecting any parameter to be proportional to log frequency.

Graphs 28, 29 and 30 test the effectiveness of the f.e. as a parameter for describing the observed change in impedance with frequency. In fact the frequency effect appears to be a very poor parameter to use in describing an I.P. effect since it is both non-linear against frequency and log frequency, thus the frequency effect and the frequency effect per decade are both functions of the particular frequencies selected. (If. however, the frequency range is so wide that both the high and the low frequency limits of [Z] can be observed, then the frequency effect is a unique parameter independent of frequency, and describes the proportional change in impedance to the low frequency impedance). The general shape of f.e. versus log frequency plots has no simple mathematical form, but is characteristic since it is similar for both resin mesh sizes and all concentrations except 0.1M NaCl which, rather than being parallel to, crosses the 0.05M plot at a frequency of about 60 Hz. Spectra at the same concentration but different resin mesh sizes are closely parallel and almost coincident, but the 200-400 mesh systems consistently display a higher frequency effect.

Except for the 200-400 mesh resin 0.1M NaCl determination below 60 Hz, the f.e. consistently increases with decreasing electrolyte







concentration as shown by graph 30. The 100-200 mesh determinations again display a slightly smaller f.e. than the 200-400, and are roughly linear in log concentration, the slope of the line decreasing with increasing frequency. For the 200-400 mesh resin a plot of f.e. versus log concentration is not linear but a gentle curve, the mean slope of which between 0.05 and 0.004M being almost identical with the slope of the line for 100-200 mesh resin at each frequency. Extrapolation to the zero f.e. intercept results in concentrations between 0.1 and 1.0 Molar - this verifying field observations of zero or very small frequency effects from clays in saline waters (38, 54).

It is perhaps unfortunate from the point of view of geothermal prospecting that the f.e. decreases so markedly with increasing concentration near 0.1M since a characteristic of geothermal regions is their high salinity (17,18). If the f.e. were to be used as a parameter in such prospecting the method employed would be quite opposite to that in all current I.P. surveying techniques, in prospecting for a minimum effect.

The metal factor (M.F.) is a parameter ostensibly designed to remove the effects of shunt resistance when studying a rock/electrolyte system in which pore blocking polarisable zones may be shunted by pores containing electrolyte only. In this context the parameter is not directly applicable to beds of ion exchange resin, nevertheless the behaviour of the M.F. is of some significance since it is almost universally used by geophysicists to describe the I.P. phenomenon.

$$M.F. = G_{High} - G_{Low}$$

$$= 1/[Z]_{High} - 1/[Z]_{Low}$$

$$= ([Z]_{Low} - [Z]_{High})/[Z]_{Low} [Z]_{High}$$

$$= (f.e)(G_{High})$$

M.F. = f.e x Constant if the concentration is unchanged, and Thus the shape of M.F. versus log frequency is identical to that of f.e. versus log frequency (graphs 28 and 29). Also since $M_{\bullet}F_{\bullet} = (f_{\bullet}e_{\bullet})(G_{High})$ the change of metal factor with concentration will depend on the change of f.e. and GHigh with concentration. Graph 30 shows f.e. versus log concentration, and graph 31 shows G10.000 and G110 for 100-200 and 200-400 mesh resin, versus log concentration. The product of f.e. and G is shown as graphs 32 and 33 of M.F. versus log concentration for 100-200 and 200-400 mesh resins respectively. In each case the M.F. displays a maximum between 0.01 and 0.02M, this maximum moving to higher concentration with decreasing frequency as is to be expected from the increased slope of f.e. versus log concentration. The 100-200 mesh system appears to show a larger movement, but the data is insufficiently accurate to verify this. The M.F. for the 200-400 mesh resin is consistently larger than for 100-200 mesh by about 10%, due to the consistently larger frequency effect and conductance.

A significant point is the apparently rapid decline of the M.F. at concentrations greater than about 0.05M NaCl, corresponding to the approach of the f.e. to zero. This renders the M.F. as useless a parameter as the frequency effect in saline waters, and as dubious for geothermal prospecting.




0.001 CONCENTRATION (M) > 0.01

GRAPH 33 As A FUNCTION OF Frequency METAL FACTOR VERSUS CONCENTRATION Cell 1 Naci / 200 - 400 mesh AG 50 W - X12 ۱.2 7 MF. (IL) 1.0 0.5 0. 0.001 CONCENSMALION (M) + 001 0

7

Since both the frequency effect and the metal factor display a non-simple frequency spectrum it was decided to test the normalised impedance. For the 100-200 mesh resin the four concentrations (0.004, 0.01, 0.02, 0.05) display a very closely parallel set of curves when $[Z]_{Norm}$ is plotted against log frequency (graphs 34 and 35). As expected (see p.3) these curves show an increased impedance with decreased frequency. For the 200-400 mesh resin the 0.1M NaCl determination is anomalous and as with the f.e., crosses the 0.05M determination at about 60 Hz.

The phase shift of the current with respect to the voltage (\emptyset) was chosen as a frequently used parameter to represent the complex nature of the impedance. \emptyset was plotted versus log frequency (graphs 36 and 37) and is observed to have a very similar form to the impedance. The curves for various concentrations are roughly parallel and gently increasing to low frequency except for the 200-400 mesh resin/0.1M NaCl determination which crosses the 0.05M spectrum at about 200 Hz. This similarity reflects the fact that [Z] and \emptyset are not independent parameters R and X,

 $\begin{bmatrix} Z \end{bmatrix} = (R^{2} + X^{2})^{\frac{1}{2}}$ $\emptyset = \tan^{-1} (X/R)$

where X and R are defined by the general equation for the impedance

Z = R + j X.









This lack of orthogonality will hamper the search for trends in any subsequent attempt to derive an RC model for the I.P. effect, and it was decided to express the A.C. bridge data in terms of R and X.

R, log R, X and log X were plotted versus log frequency. Whether or not these plots have any fundamental significance it was immediately apparent that log log plots of R and X versus frequency (graphs 39, 40, 41 and 42) are an extremely efficient means of presenting frequency data since the plots are all very nearly straight lines of roughly similar slope. On these grounds it is recommended that A.C. bridge data be expressed in terms of R and X and be represented graphically as plots of log R and log X versus log frequency.

The plots of log R versus log frequency are not quite linear but show a tail up at low frequency. The graphs for 100-200 mesh and 200-400 mesh resin superimpose to within 0.8% for 0.004 M NaCl over the entire frequency spectrum measured, and the graphs for 0.01M and 0.05M NaCl for different mesh sizes can be made to superimpose within about 0.5% by a considerable vertical displacement. For 0.01M NaCl

 $\log R_{100-200 \text{ Mesh}} = \log R_{200-400 \text{ Mesh}} + 0.036$ thus $R_{100-200}/R_{200-400} = 1.086$.

For 0.05M NaCl

 $\log R_{100-200} = \log R_{200-400} + 0.029$ thus $R_{100-200}/R_{200-400} = 1.069.$









These resistance changes are large (approximately 7%) and are unlikely to be caused by errors in the concentrations used. Instead this must be considered as a property of the resin beds, and the 200-400 mesh system has a lower resistance than the 100-200 at 0.01 and 0.05M NaCl, but not at 0.004 Molar.

Graphs 41 and 42 of log X versus log frequency show considerable scatter reflecting the diminished precision with which X was determined*, and have a somewhat more erratic form than do the log R plots. Nevertheless, the general form is of nearly straight, nearly parallel lines, with some scatter at low frequency.**

Plots of log R and log X versus log concentration are very close to linear especially at low frequencies (graphs 43 and 44). A characteristic

* This is due to the error in measurement of CP on which X is primarily based. The Wayne-Kerr bridge has 7 decade scales which determine both GP and CP, plus a factor of ten divider for GP and CP individually. In the case of almost all measurements made using this bridge, the parallel capacitance was so small (especially at high frequency) that on a range suitable for the measurement of GP, CP could only be measured on 1, 2 or 3 of the 4 places provided - this diminishing the measuring accuracy.

** Above about 5,000 Hz, CP was almost invariably measured on the last position of the dial, the inaccuracy being perhaps of the order of 10%, decreasing with increasing CP (and thus decreasing frequency).





feature of both these plots especially log X versus log concentration is that data points for both 100-200 and 200-400 mesh resin have a best fit to the same straight line.*

Both plots show a slight variation of slope with frequency, log R diverging with frequency to low concentrations and log X to high concentrations.

The slope of log X versus log concentration varies from -0.72 at 110 Hz to -0.90 at 1000 Hz (the 10,000 Hz determination is based on data of such low precision as to be almost meaningless), suggesting a concentration dependence of the order of $-\frac{3}{4}$ to -1. Plots of X versus C⁻¹ and X versus C^{- $\frac{3}{4}$} (graphs 45 and 46) verify this and a fairly good fit to a straight line is obtained for the latter. From this graph

$$X_{110 \text{ Hz}} = 0.48 \text{ C}^{-\frac{3}{4}} + 0.8$$

 $X_{1000\text{Hz}} = 0.254 \text{ C}^{-\frac{3}{4}} - 0.6$

Similarly the slope of log R versus log concentration is -0.48.

$$\log R = -0.48 \log C$$

i.e. R $\propto c^{-0.48}$

which is very close to the relation

and a plot of R versus C^{-2} (graph 47) is very close to linear for each

* These lines are fitted by observation only. In the case of log R versus log concentration a small variation in R is observed for 0.01 and 0.05M NaCl for different mesh sizes as noted previously for graphs 39 and 40.





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frequency plotted and has the form

$$R_{110 \text{ Hz}} = 1.43 \text{ C}^{-\frac{1}{2}}$$

$$R_{1000 \text{ Hz}} = 1.17 \text{ C}^{-\frac{1}{2}} + 0.082$$

$$R_{10.000 \text{ Hz}} = 1.067 \text{ C}^{-\frac{1}{2}} + 0.115$$

These observations contrast with the behaviour of the same cell containing electrolyte only, and of an Onsager electrolyte in general, since

where
$$= (1000 \text{ k})/(\text{RC})$$

 $= \text{equivalent conductance}$
 $k = \text{cell constant}$

R = resistance

C = concentration

But,

thus

$$\Lambda \propto 1/(C^{-\frac{1}{2}})(C)$$

 $\Lambda \propto c^{-\frac{1}{2}}$

D ... 0-2

whereas for an Onsager electrolyte

$$\Lambda = \Lambda_0 - a/c$$

which is the form displayed by the cell containing electrolyte only.

Graph 48 of Λ versus $C^{-\frac{1}{2}}$ (for 110, 1,000 and 10,000 Hz) shows this linearity, however a plot of Λ versus $-C^{\frac{1}{2}}$ (graph 49) displays a pronounced curvature.



14 Equivalent Conductance versus Concentration 1/2 GRAPH 49 Cell 1 NACI / AGSOW-X12 1.2 10,000 Hz . 1 1,000 R 1,000 Hz 1.0 110 HZ X 100-200 mesh + 200-400 mesh 0.8 0.6 0.4 0.2 $C'^{h} \rightarrow$ 0.3 ·02 ·04 ·06 ·08 0·1 0.2 0

The only study in the literature of the I.P. effect of resin beds over a range of concentrations is that of Schufle (52 - see p. 16 this thesis). Schufle's study is of the time domain dependence of I.P. on electrolyte type and concentration for beds of 95% sand and 5% cation exchange resin, both 20-30 mesh. During the charging cycle resistivity measurements were made, and this value is plotted as graphs 50 and 51 versus $C^{-\frac{1}{2}}$ and $C^{\frac{1}{2}}$ respectively. Graph 50 shows a closely linear form for each electrolyte type, especially $Th(NO_3)_4$. The Onsager plot (51) on the other hand is markedly non-linear.

The results of this section (as well as of Chapter 7 of the temperature dependence of resin systems) are partly summarised in the following table which describes the effect on the parameters down the side of an increase in the variables along the top.

| | Increasing frequency | Increasing concentration | Increasing resin size | Increasing temperature |
|---------------------------|-------------------------|--|-----------------------|------------------------|
| f.e. | decrease | decrease | decrease | no effect |
| M.F. | decrease | maximises for some concentration | decrease | increase |
| [Z]/[Z] _{10,000} | decrease | decrease | decrease | decrease |
| ø | decrease | decrease | decrease | uncertain |
| R | decrease | decrease $(C^{-\frac{1}{2}})$ | no effect | not deter- mined |
| Х | decrease | decrease | no effect | not deter- mined |





iii) Section II

Four terminal low frequency measurements

In this section results are reported of 17 [Z] and \emptyset spectra made using the apparatus as shown in Fig. 24, , in the six decades between 0.001 and 1,000 Hz. The clay systems included in this section primarily represent the attempts to construct a cell in which I.P. effects of clays can be observed. The 17 systems studied are as follows all cells containing 0.01M electrolyte (either NaCl or CaCl₂), measurements being conducted in a Tampson type TEB 45 300 oil bath* at 30° C unless otherwise stated. The order is chronological.

Cell Number

1) An undetermined amount (estimated at less than 50 mg) of cleaned unexchanged** clay was deposited on a 50-100 mesh sinter (sinter cell number 2) by evacuation in a 2% clay slurry followed by drying at 160°C. This cell was equilibrated with 0.01M NaCl by percolation, and evacuated in this solution. [Z] and \emptyset were determined for the six decades between 0.001 and 1,000 Hz using the $V_{D.C.}$, $V_{P.P.}$ and triggering circuit techniques. Wayne-Kerr A.C. bridge measurements were also made from 100 to 10,000 Hz, but electrode effects render this data suspicious.

- * An oil bath was used to maintain a constant temperature, oil being selected to minimise capacitive coupling, but more importantly the enclosing stainless steel bath served as an electrostatic shield.
- ** Grim states that Wyoming bentonite in its natural form has primarily Na⁺ ions on the exchange sites (15).

2) A blank resin cell containing 0.01M NaCl electrolyte only.

3) A model circuit composed of a $10^{4}\Omega$ non-reactive resistor in place of the cell (Fig. 26a).

4) A resin cell containing 20-50 mesh sodium form resin equilibrated with 0.01M NaCl.

5) A model circuit as shown in Fig. 26b designed to test the response of the peak to peak voltage measuring device at high frequencies.

6) A resin cell containing 20-50 mesh calcium form resin, equilibrated with 0.01M CaCl₂.

7) Sinter cell number 3 composed of 100-200 mesh ground pyrex of dimensions shown in Fig. 14b. This cell was washed and percolated with 0.01M CaCl₂ then evacuated in this solution. Determinations were made on this cell containing no clay using 0.01M CaCl₂.

8) The resin cell was cut in two down the middle and fitted with a sinter joint (Fig. 27). This cell was then filled with clay that had not been treated in any way* except by the addition of sufficient 0.01M CaCl₂ to attain plasticity. The purpose of measurements on clays in this form is to simulate the properties of massive clay banks. [It should be remembered that Vacquier et al (54) observed little or no I.P. effect from massive clays.]

9) Clay was deposited on 20-50 mesh glass spheres by immersing these in a 1% suspension of cleaned non-exchanged clay in distilled water, and drying in an oven at 160°C. The clay was then exchanged by percolating the clay coated spheres with 0.01M CaCl₂ in a column. After this treatment little clay could be seen on the glass spheres but a resin

* In this form the clay includes an estimated 1% of non-colloid material.

FIGURE 26





cell was filled with these spheres, equilibrated with 0.01 M CaCl₂ and a run made.

10) Equal weights of untreated clay and 20-50 mesh glass spheres were placed in a beaker and sufficient 0.01M CaCl₂ added to attain plasticity. A cell was filled with this as for "8" above, and a run made.

11) The original intention of this measurement was to situate resin particles in the (tetrahedral) pore spaces of a matrix of glass spheres. A calculation was made assuming close packed spheres of diameter 500 microns (approximately 30 B.S.M.) and it was found that a volume percentage of 0.34% 200-400 mesh resin beads was required to fill each tetrahedral site with a resin particle. Obviously 0.17 cm³ of resin could not be measured and dispersed in 50 cm³ glass spheres, and the experiment was modified by using 5% resin by volume. A resin cell was prepared containing 2.5 cm³ 200-400 mesh sodium form resin dispersed in 50 cm³ glass spheres, and 0.01M NaCl. The resin was fairly uniformly distributed but an accumulation of resin was noticed at the ends of the cell outside the potential electrodes.

12) A second mixture of resin and glass beads was prepared from 17% 20-50 mesh sodium form resin and 83% 20-50 mesh glass spheres equilibrated with 0.01M NaCl. A run was made on a cell containing a homogeneous mixture of these proportions.

13) Clay was introduced to sinter cell 3 (used as a blank in "7" above) by immersing the cell in a 2% suspension of cleaned unexchanged clay, evacuating in a vacuum desiccator, then drying at 160°C overnight. The clay was exchanged in situ by percolation with 0.01M CaCl₂ then dried to constant weight at $160^{\circ}C$ and weighed. The amount of clay deposited on the cell was 0.1283 g.

The cell was re-equilibrated with 0.01M CaCl₂ and a run attempted, however an equipment failure (later traced to a faulty operational amplifier in the voltage follower circuit) rendered this data useless.

14) In an attempt to run a resin "normal" for 11 above a cell was filled with 200-400 mesh sodium form resin and equilibrated with 0.01M NaCl. It was during this run that the failure of the operational amplifier became apparent. The cell also developed a leak around the electrodes and the run was abandoned.

15) The instrumentation was repaired and measurements made on a cell prepared by D. Wright* which had been previously observed to display a frequency dispersion using the oscilloscope/oscillator technique. This cell consisted of a sinter onto which a bentolite had been deposited by drying at less than 100°C, and equilibrated with NaCl. Measurements conducted with 0.005M NaCl show a marked frequency dispersion below 10 Hz. Since that measurement the cell had been dried at 160°C and re-equilibrated with 0.01M CaCl₂, and the frequency effect of the impedance is observed to be markedly less than it was for the same cell before heating, using 0.005M NaCl.

16) Sinter cell number 3 as described in "13" above was re-run using 0.01M CaCl₂.

* Physics Department, Victoria University of Wellington.

17) Number "15" above suggests that either heating, equilibration of a sodium clay with $CaCl_2$, or some aging effect, substantially reduces the frequency effect of a clay/sinter system. In an attempt to determine the effects of heating on the frequency effect, and of the ionic form of the clay on the amount deposited on a sinter, sinter cell number 4 was prepared. In all gross physical characteristics sinter cells 3 and 4 are identical - both having been prepared from 100-200 mesh ground pyrex in the same mould, both having the same external dimensions and porosities, and both sinters were emplaced in an identical cell. Clay was deposited on the sinters in an identical fashion except that for number 4 the clay was exchanged to the calcium form before the cell was immersed. Sinter cell number 3 was dried at $160^{\circ}C$ and number 4 at $90^{\circ}C$ both overnight. Cell number 4 was equilibrated with 0.01M CaCl₂ and the amount of clay determined (0.2233 g).

In addition to frequency spectra of [Z] and \emptyset , a series of measurements of the transient response of this cell were also made using apparatus to be described by D. Wright (61). Observations of the decay curve after termination of a square current pulse were made and the effects of charging current density and temperature studied. At the time of writing only the 25°C data had been processed. While these results show a marked dependence of the mV/V parameter on charging current, a value of about 50 mV/V can be assigned. The decay curve is not exponential but hyperbolic in form, but a time constant of 3 to 4 seconds can be assigned.

Employing Marshall and Madden's "rule of thumb" (ref. 38, this thesis page 8) a mV/V value of 50 corresponds roughly to an f.e. of 5%.

Table 7 gives a brief summary of the nature of each of the systems above.

The results of these 17 determinations, plotted in terms of the normalised impedance and the phase shift are shown in graphs 52 to 58.

For convenience of analysis the 17 systems were divided into three groups based on the percent change of impedance with frequency.

The first group contains systems having a "large" I.P. effect - the % f.e. between 10⁻³ and 10³ Hz being greater than 20%. This group contains all the resin cells and exclusively resin cells.

The second group contains systems having an "intermediate" I.P. effect and includes only two cells, both of which are of clay bonded to a porous glass sinter plug (see p. 95) equilibrated with 0.01M CaCl₂. A bentolite (cell 15) and Wyoming bentonite (cell 17) display respectively a 5% and a 9% frequency effect.

While the first two groups contain readings for which the greater part of the observed impedance dispersion is associated with the cell contents, the third group contains runs for which the observed impedance dispersion is of the order of the experimental error in the measuring circuit (approximately \pm 1% - see p.109) and for which the existence and form of an I.P. effect is difficult to assess.

The two runs made on RC models fall into a special category since they are not cell determinations. The first of these models used a 10^4 ohm non-reactive resistor in place of the cell in order to observe the response of the measuring system to an impedance which does not change with frequency, and to a constant, zero phase shift. Measurements of the impedance using both the $V_{p.p.}$ and $V_{D.C.}$ techniques agree with the

Table 7

The Physical Properties of the Final 17 Cells

| System Number | Cell type | Resin or Clay Type | Electrolyte (0.01M) |
|------------------|--------------------------------|---|------------------------|
| 1 | Sinter Cell 50-100 mesh | Bentonite Na form | NaCl |
| 2 | Resin Cell 4 | Blank | NaCl |
| 3 | Model Circ | uit (fig. 31a) | |
| 4 | Resin Cell 4 | Resin 20-50 mesh Na form | NaCl |
| 5 | Model Circ | uit (fig. 31b) | |
| 6 | Resin Cell 4 | Resin 20-50 mesh Ca form | CaCl ₂ |
| 7 | Sinter Cell 100-200 mesh | Blank | CaCl |
| 8 | Resin Cell 4 (modified) | Massive clay, Na form | CaCl ₂ |
| 9 | Resin Cell 4 (modified) | Clay/20-50 mesh glass spheres - dried and re-wet | CaCl ₂ |
| 10 | Resin Cell 4 (modified) | Clay/20-50 mesh glass spheres - wet slurry | CaCl ₂ |
| 11 | Resin Cell 4 | 5% 200-400 mesh Na form resin/ 95% 20-50 mesh glass | NaCl |
| 12 | Resin Cell 4 | 17% 20-50 mesh Na form resin/ 83% 20-50 mesh glass | NaCl |
| 13 | Sinter Cell 3, 100-200 mesh | 0.1283g Ca form clay (deposited in Na form and exchanged) | CaCl2 |
| 14 | Resin Cell 4 | Resin 200-400 mesh Na form | NaCl |
| 15 | Sinter Cell (D. Wright) | Bentolite, Ca form | CaCl ₂ |
| 16 | As for 13 | | |
| 17 | Sinter Cell 4, 100-200 mesh | 0.2233g Ca form Bentonite | CaCl ₂ |

specified value and are constant to within 0.1% (graph 52), however the phase shift shows a considerable dispersion especially at high frequencies (graph 53). The second model circuit designed to produce a negative phase shift and impedance dispersion only at high frequencies (greater than about 100 Hz) displayed an impedance dispersion within 1% of that expected, but cursory phase measurements indicated a phase shift somewhat diminished from the value for the non-reactive model, but still positive at high frequencies.

These results indicate a large phase response inherent in the measuring circuit. This frequency response was subsequently found to be due to miss-matching of the two amplifier channels of the sine to square converter, and has a form similar to that shown in graph 53 for the non-reactive circuit. The presence of this fault effectively renders phase data at frequencies greater than about 1 Hz useless, but qualitative information can be derived from the phase data below this frequency. It is because of this last point that, despite the parameter considerations of section I, impedance data in this section is reported in terms of [Z] and \emptyset , not R and X.

All the runs made on cells display a larger impedance effect than that of the non-reactive resistor, however the blank cells (2 and 7) display impedance effects only of the order of 0.5% (graph 52) which may be an electrode effect or due to the instrumentation. This impedance effect of the order of 1% is considered to be a normal one for the various cells measured.

Measurements number 8, 9 and 10 of a massive clay, a dried and re-wetted slurry with 20-50 mesh glass spheres, and a plastic clay with
SRAPH 52 a



1.01



0.99

0.98

0.97

1,000 100 10 (Frequency (H2) 0.1 0.01 0.001

SRAPH 52 b

1.04 Impedance versus Frequency 1 121/R + Cell # 9 Call / Clay / glass spheres, dried and re-wet X Cell # 8 Call / Clay only 1.02 A Cell # 10 Call / clay / glass spheres, wet sharry

101





Impedance versus Frequency 1.04 SRAPH 52 C î 121/R Х Cell # 1 Naci / Sinter / clay. Caciz / Sinter / clay Cc11 # 16 + 1.02 1.01 Х 1.00 苶 х 0.99 0.98 0.97 1,000 100 10 + Frequency (Hz) 0.1 0.01 0.001



50% 20-50 mesh glass spheres, all show a similar dispersion of impedance (graph 52), displaying a maximum between 1 and 10 Hz, and decreasing to high and low frequency. The maximum f.e. observed is

For cells 8 and 10 a 1.0% drop in the impedance occurs between 1 and 0.1 Hz - the characteristic shape of this drop and the similarity between the two curves suggests that this is not a random effect but rather a characteristic feature of such moist clay systems.

An impedance dispersion more typical in shape of an I.P: effect is observed for cell 1, graph 52c - a clay/sinter/0.01M NaCl system which displays a f.e. of 2% with [Z] still rising at 0.001 Hz.

A second cell containing a larger volume sinter with 0.1283 g clay was tested (Cell 16, graph 52c) but the shape of the impedance spectrum was suspicious and the frequency effect only 1.1%, and the data was rejected.

The second group of determinations contains just two runs, both of clay mounted on 100-200 mesh sinters, equilibrated with 0.01M $CaCl_2$ (graph 54). Cell 17 (Wyoming bentonite) displayed a % f.e. while cell 15 (bentolite) displayed 5%. For both curves the dispersion is broad with no sign of a minimum to 1,000 Hz, and while the bentonite cell displays a maximum at about 0.01 Hz, the impedance for the bentolite cell increases smoothly over the entire frequency span from 10^3 to 10^{-3} Hz.



In contrast to this, measurements on ion exchange resins (group one) show a much less broad impedance dispersion. For cells 4, 6 and 11 the shape of the impedance spectra are very similar, but for cell 12 the spectrum is shifted to much lower frequency and the complete form cannot be observed (graph 55).

The form of the impedance spectra for resin cells is well represented by the equation

$$[Z] = A/(f + a)$$

where

- A = [Maximum frequency effect] x (constant)
- f = frequency (Hz)
- a = frequency of maximum slope of the impedance
 versus log frequency plot (and is also the
 frequency corresponding to the midpoint of such
 a plot).

This general form is shown as graph 56.

The implications of this form on a Laplace analysis will be discussed in the next chapter.

Also apparent from graph 55 is that a bed of calcium resin equilibrated with 0.01M CaCl₂ displays only 50% of the frequency effect that an identical bed of sodium resin equilibrated with 0.01M NaCl. The mid-point of the impedance spectrum is also moved to lower frequency and it is apparent that the presence of calcium ions instead of sodium both diminishes the percent change of impedance, and increases the relaxation time constant (see Chapter 14).



SRAPH 56 Impedance versus FREquency for the curve 121 = A/(F+a) (C.F. SRAPH 12) 1.0 1 121/A 0.6 0.4 0.2 0 % 4 F/a 10 0.1 10.0 1,000 0.001 100

Two measurements were made on sodium resin/glass sphere/0.01M NaCl systems. Cell number 11 5% 200-400 mesh resin 95% 20-50 mesh glass spheres 12 17% 20-50 mesh resin

83% 20-50 mesh glass spheres

For each of these the maximum percent change in the magnitude of the impedance between 10^3 and 10^{-3} Hz is 20%, however for cell 12 the impedance is still rising at 10^{-3} Hz. Cell 4 containing 100% 20-50 mesh sodium resin equilibrated with 0.01M NaCl displays a 40% frequency effect. If one attempts to correlate this percent change of impedance with ion exchange resin in cells 4, 11 and 12, it is immediately apparent that there is no correspondence between f.e. and volume of exchanger*, and very little with surface area. The best correspondence is between surface area of resin in cells 11 and 12, where the frequency effects are the same but the area of the 200-400 mesh beads is 2.5 times that of 20-50 mesh resin.

As stated previously a fault in the phase measuring circuit prevented phase determinations at frequencies greater than about 1 Hz, but qualitative information regarding \emptyset can be obtained from measurements at lower frequencies. This phase information roughly corresponds with the impedance spectrum, the maximum in the low frequency negative phase shift occurring roughly at the same frequency as the maximum slope of the impedance curve, and large phase shifts corresponding to large frequency effects.

* For a sulfonic acid exchange resin, exchange sites are distributed uniformly through the bulk of the particle (31).

Because of the apparent phase shift of a non-reactive circuit even at low frequencies, cells displaying a phase shift of the order of 0.1 degrees or less are considered to have zero phase shift. When this criterion is applied 5 cells are observed to have no phase response.

Cell number 2 0.01M NaCl/Blank resin cell

- 3 Model 10⁴ ohm non-reactive circuit
- 7 0.01M CaCl_/sinter cell 3/Blank
- 8 0.01M CaCl_/Massive clay
- 10 0.01M $CaCl_2/20-50$ mesh glass spheres/wet clay slurry (See graph 57 of \emptyset versus log frequency).

These are exactly the cells observed to display frequency effects less than 2%, with two exceptions:

Cell number 1 0.01M NaCl/Clay bonded to sinter

9 0.01M CaCl_/Clay bonded to glass spheres.

For the first of these the impedance curve is similar to that expected for an I.P. response, and although the observed f.e. is only 2% the impedance is still rising at 10^{-3} Hz. It is almost certain that the cell displays an I.P. response. This response is small probably because very little clay has been deposited on the sinter*. The second cell (9) should display an effect similar to a 20-50 mesh sinter/clay system,

* The amount of clay was not determined, but visual comparison with subsequent sinters containing known weights of clay suggests that there was less than 50 mg of clay on the sinter.

The reason for this small amount of clay is that the Wyoming bentonite was deposited in the sodium form and re-equilibrated with NaCl electrolyte, under which conditions it disperses.

however when attempting to bond clay to the spheres it was noted that very little clay had adhered to the glass. A maximum f.e. of only 0.6% suggests that there is in fact no impedance dispersion, however the observed phase shift has a maximum of 0.3 degrees, which is far from negligible. The observed response of these two cells suggests that observations of the phase shift are very sensitive to a small percent clay on an inert matrix. Large amounts of clay not bonded (cells 8 and 10) display no phase dispersion.

Table 8 is a brief summary of the [Z] and \emptyset data in this section.

That a significant phase shift occurs for clay cells only in four cases, for all of which the clay has been bonded to a matrix, is not considered to be a coincidence. These cells are

Cell number 1 0.01M NaCl/bentonite bonded to sinter

- 9 0.01M CaCl_/bentonite bonded to glass spheres
- 15 0.01M CaCl_/bentolite bonded to sinter
- 17 0.01M CaCl, bentonite bonded to sinter

(Phase response graph 57).

Previously Vacquier et al (54) have observed a similar effect, and it seems that only when clay systems are prepared for which the surface layers of clay are strongly constrained, can an I.P. response be observed.

As with the frequency effect, the maximum phase shifts for all resin cells (graph 58) are larger than those for clay cells, being 5 to 10 times larger. Perhaps by coincidence the maximum percent frequency effect and the maximum phase shift correlate almost exactly for the

| Table | 8 |
|-------|---|
|-------|---|

| The | Electrical | Properties | of · | the | Final | 17 | 7 Cells |
|--|---|------------|------|-----|---|----|---|
| and the second s | the second se | | | | and the second of the second | | and the second se |

| Group | Cell No. | Maximum % f.e. | Maximum Ø (x 1000/ 2 π, radians) | Frequency of Ø max. | Frequency of maximum slope [Z] | Form of [Z] dispersion |
|-------|-------------|-------------------|---|---------------------|--------------------------------------|------------------------------|
| III | 1 | 2.0 | -0.75 | 0.05 | | В |
| III | 2 | 1.1 | | | | |
| | 3 | Model | | | | |
| I | 4 | 40 | -15 | 1.0 | 2.0 | A |
| | | | -21 | 0.04 | | |
| | 5 | Model | | | | |
| I | 6 | 20 | -9 | 0.2 | 0.3 | A |
| III | 7 | 0.5 | | | | |
| III | 8 | 2.0 | | | | C |
| III | 9 | 0.6 | -0.9 | 0.08 | | D |
| III | 10 | 1.4 | | | | С |
| I | 1 1 | 20 | -9 | 10 | 10 | A |
| I | 12 | 20 | -9 | 0.01 | 0.008 | A |
| | 13 | | | | | |
| | 14 | | | | | |
| II | 15 | 5.0 | -0.85 | 0.1 | | В |
| III | 16 | 1.1 | | | | |
| II | 17 | 9.0 | -2.1 | 0.3 | | В |

- A) A symmetric increase of [Z] between a minimum and maximum value, with decreasing log frequency. This form is characterised by the equation [Z] = A/(f + a) where A and a are constants and f is frequency (see graph 56).
- B) A broad, almost linear increase of [Z] with decreasing log frequency.
- C) The impedance spectrum maximises between 1 and 10 Hz, with a sharp decrease between 1 and 0.3 Hz.
- D) The impedance spectrum maximises between 1 and 10 Hz but is very broad and shallow.



0.1 Frequency (Hz) 0.01

0.001

10

۱





resin cells, but this is not true amongst clay cells or between clay and resin cells. as shown by the following table.

| | Cell No. | Max. % f.e. | Max Ø (x 1000/2 π Radians) | - f.e./Ø |
|--------|----------|-------------|--------------------------------------|----------|
| resins | (4 | 42 | -21 | 2.00 |
| | (6 | 20 | - 9 | 2.22 |
| | (11 | 20 | - 9 | 2.22 |
| | (12 | 19 | - 9 | 2.11 |
| clays | (1 | 2 | - 0.75 | 2.67 |
| | (9 | 0.6 | - 0.9 | 0.67 |
| | (15 | 5 | - 0.85 | 5.88 |
| | (17 | 10 | - 2.1 | 4.76 |

The frequencies at which the impedance and the phase shift maximise are not the same, and the frequency of maximum phase shift appears to coincide with the frequency of maximum slope of the impedance spectrum. For cells 6, 11 and 12 which display single peaked phase spectra (graph 58) this correlation is immediately apparent, however for cell 4 the higher frequency peak corresponds with the maximum slope of [Z] versus log **f**. Similarly in clay cells, although the impedance spectra are so spread out as to prevent the finding of a mid-point or maximum slope, transient observations of cell 17 indicate a decay time of 3 to 4 seconds which is in almost exact agreement with the observed reciprocal frequency of the maximum phase shift (3 seconds).

These apparent correlations suggest two relations for resin cells, as follows.

(1)
$$\mathbf{\Phi}^{\circ} = -\mathbf{\pi}(f.e.)/10$$

(2) $f_{\mathbf{\Phi}^{\circ}} = f_{\text{maximum slope of f.e. versus log f}}$
where $\mathbf{\Phi}^{\circ} = \text{maximum phase shift (radians.s}^{-1})$
 $f_{\mathbf{\Phi}^{\circ}} = \text{frequency at which } \mathbf{\Phi}^{\circ} \text{ occurs.}$

To these can be added the previously observed empirical relation for resin cells,

$$(3) [Z] = A/(f + a)$$

where A and a are constants

f = frequency in Hz.

145.

CHAPTER 14

THE APPLICABILITY OF THE LAPLACE TRANSFORM

i) Introduction

It has been mentioned previously in this thesis that time and frequency domain data are equivalent through Fourier or Laplace transforms, for a linear medium. It is assumed, for all cells, that the current density employed is sufficiently low for linearity conditions to be obeyed, and it is now useful to perform an elementary transform on the primarily frequency domain data of this thesis in order to correlate this data with the more commonly observed I.P. relaxation phenomenon.

ii) Theory

Using the Laplace transform, a time function f(t) may be transformed to a complex frequency function f(s),

(1)
$$f(s) = \int_{0}^{\infty} f(t) \exp(-st) dt$$

where s is the Laplace transform variable.

$s = \sigma + j \omega$

where σ and ω have dimensions of frequency (radians/second). The complete function f(s) is thus described by a complex plane in which all absolute values of σ and ω may be employed, provided the integral in (1) converges.

Real or imaginary axis transformations of time to frequency domains may be accomplished by using the real or imaginary parts of $s (s = \sigma \text{ or } s = j \boldsymbol{\omega} \text{ respectively})$. In the case of a real axis transformation, (1) becomes

(2)
$$f(\sigma) = \int_{0}^{\infty} f(t) \exp(-\sigma t) dt$$

and for the imaginary axis

(3)
$$f(j\boldsymbol{\omega}) = \int_{0}^{\infty} f(t) \exp(-j\boldsymbol{\omega}t) dt$$

Equation (3) is the well known single sided Fourier transform, and the Fourier transform is identical to a Laplace in which the integration is made along the imaginary axis (4).

The imaginary axis transformation describes the system behaviour as if the perturbation were a steady state sinusoidal function (4). If f(t) is a causal function* then an imaginary axis transform will be possible, resulting in a complex function, $f(j\omega)$, where f is expressed in terms of the real angular frequency, ω .

Impedance of an electrochemical system can be defined validly only in an appropriate frequency domain, because of its vector and phasor properties (55). Therefore, in order to obtain an impedance function from time domain behaviour it is necessary to convert both the perturbation

* A causal function is one for which

$$f(t) = 0 \quad \text{for} \quad t < 0$$
$$\int_{0}^{\infty} [f(t)] dt < \infty$$

and the response from time functions into frequency functions and take a ratio

$$i(t) \longrightarrow I(j\omega)$$
$$v(t) \longrightarrow V(j\omega)$$
$$Z(j\omega) = V(j\omega)/I(j\omega)$$

The impedance determined in this way behaves identically to and obeys the same relationships as the impedance measured using A.C. sine wave techniques, thus

$$Z(j\omega) = R + jX$$

and the magnitude of the impedance, [Z], and the phase shift of the voltage with respect to the current, \emptyset , can be determined from the relationships

$$[Z] = (R^{2} + X^{2})^{\frac{1}{2}}$$
$$\tan \emptyset = X/R$$

iii) Practical

Transformations between time and frequency domains may be made using (3). In addition, the Borel or convolution integral theorem,

(4)
$$e(t) = \int_{0}^{t} i(\mathbf{T}) Z(t - \mathbf{T}) d\mathbf{T}$$

where \mathbf{T} is an integration variable, may be used to describe the time domain potential response, e(t), to a current excitation function, i(t), applied to an impedance.

Unfortunately the time domain data cannot be transformed into frequency domain impedances, since this data consists only of an observation of the decay voltage, and measurements of the currents associated with the diffusion processes within the sample are not made during the decay cycle.

While it would be unreasonable to assume the current behaviour in transient domain observations, it is not unreasonable, as a first approximation, to assume a constant current during frequency domain observations. Assuming this, the complex impedance derived from [Z] and \emptyset via

(5) $Z(j\boldsymbol{\omega}) = [Z] (\cos \boldsymbol{\emptyset} + j \sin \boldsymbol{\emptyset})$

is proportional to the complex voltage

(6) $V(j\boldsymbol{\omega}) = I Z(j\boldsymbol{\omega})$

which may be transformed into the time domain via (3), and there represents the transient voltage decay resulting from a Dirac current impulse*.

It was observed in Chapter 13 that

(7) [Z] = B (f.e.)/(f + a) see p.139

Also observed phase shifts are less than 7 degrees, and thus from (5)

* The transform of a constant, $I(j \boldsymbol{\omega})$, is the same constant times the unit impulse, $S_o(t)$, as defined below.

$$S_o(t) = unit impulse, also called Dirac "delta" function= 0, t \lt 0
= 0, t \rbrace 0
= ∞ , if t = 0 and $\int_{-\infty}^{\infty} S_o(t) dt = 1$$$

since

$$\cos 7^{\circ} = 0.992$$

and $\sin 7^{\circ} = 0.122$,
 $Z(j\omega) \approx [Z] (= 2\pi B(f.e.)/(\omega + 2\pi a))$

and from (6)

$$V(j\omega) \simeq 2\pi B(f.e.)I/(\omega + 2\pi a)$$

This corresponds to the transform of

$$v(t) = 2\pi B(f.e.)I \exp(-2\pi a t)$$

This represents an exponential decay with a single time constant, b = $1/2\pi a$, and pre-exponential, A = $2\pi (f.e.)I$.

Thus for the resin cells, which adhere roughly to the form of equation (7), one would expect to see an exponential decay of the voltage in the time domain, as a result of a Dirac unit current impulse. The clay cells, however, do not obey equation (7), and the dispersion effects are much more spread out. Rather than postulating that an entirely different relaxation mechanism occurs for clay than for resin systems, it seems probable that the dispersion effect of clay cells in fact results from a distribution of exponential relaxations of widely varying decay constants, resulting from the widely variant pore geometries of clay systems as compared with resin beds. CHAPTER 15

DISCUSSION OF RESULTS

i) Remarks

The work described in this thesis is of a developmental nature and the prime concern was in developing a measuring technique suitable for the observation of the impedance dispersion of model soil systems for frequencies from about 10,000 Hz to as low as is feasible. Such a system has been developed and the effects of a number of parameters on resin and clay model soil systems has been investigated and certain empirical relationships observed.

It is not possible to evaluate the models of Vacquier et al (54) or Keller (2, 25, 26, 27) in terms of the data obtained as the vague terms of these models made predictions impossible, nor to evaluate the model of Madden and Marshall (35, 36, 37, 38, 39) as four parameters of this model are indeterminate (see p. **3**).

It has been determined that a clay model system suitable for the observation of the membrane polarisation effect may be constructed by bonding a (Ca form) clay to a sinter framework. Only bonded clays display an I.P. effect.

A model is not immediately apparent to describe the observations of this thesis, and since it is intended to pursue this line of research, data has been left in its empirical form, and no real attempt has been made to fit it to a general mathematical model. In fact, precise wide frequency range impedance observations have been made on relatively

few systems (4 resin and 2 clay/sinter systems), and observations of the temperature dependence of [Z] has been made for only one resin system, and this with low precision.

The observed $C^{-\frac{1}{2}}$ dependence of R (and thus the equivalent conductance - see p.129) in resin/electrolyte systems, is of possible consequence to disciplines other than Geophysics. Plots of R versus $C^{-\frac{1}{2}}$ are linear for the NaCl data of this thesis (see p.129 and graph 47), and for NaNO₃, Ca(NO₃)₂, La(NO₃)₃, Th(NO₃)₄ data of Schufle (52), which is the only literature data for which such a plot can be made (graph 50 this thesis).

Sufficient data has been accumulated in this thesis to indicate the behaviour of model soil systems to be sufficiently anomalous to warrant further investigation. Although the application of the prepared model systems to the real earth is as yet uncertain, the form of the frequency and time domain observations, and of the Laplace transform of frequency domain data leaves little doubt that the effect under study in the model systems is in fact the phenomenon known as induced polarisation in the ground.

ii) Suggestions for further work

Observations of clay/sinter systems indicate a frequency dispersion spread out over a much wider frequency range than that employed in this study. In order to observe the impedance spectrum between its limits, it is necessary to make measurements below 10^{-3} Hz and possibly make a D.C. observation, and to extend measurements above 10^{4} Hz, possibly to as high as 10^{6} Hz.

The problem of practical interest is the I.P. effect of clays in geological situations. For a variety of reasons resins are easier to investigate than clays (p.39), and for this reason have received the majority of attention in this thesis; but clay model systems are more directly applicable to the earth. It is thus suggested that further investigation be conducted into clay model systems, varying such parameters as clay type and concentration on an inert framework, and the pore size of this framework and cationic form of the clay. The effects of both the anion and cation type in the electrolyte is as yet indeterminate, and the effects of electrolyte type and concentration should be studied bearing in mind the $C^{-\frac{1}{2}}$ dependence of R observed above. Marshall and Madden made I.P. determinations of compressed clay systems (37), and a determination of the similarity between these and clay/sinter systems would be of value.

Suggested experiments with artificial membrane systems involve wide frequency range I.P. determinations on well catagorised membranes for which the unknown parameters of Marshall and Madden's model may be assessed by additional experiment. The purpose of this experiment is to test their model. It is conceivable too, that observations of a system composed of alternating layers of anion and cation exchanger may yield extremely interesting results in view of the fact that the transference number of the cation, say, in such a system may be made to vary from nearly unity to effectively zero in alternate zones. A somewhat anomalous temperature effect was observed in Chapter 7 of the magnitude of the impedance of a resin/electrolyte system. This observation possibly warrants further

investigation in resin systems and for clays both mounted to an inert framework, and massive.

In any further work on the membrane polarisation phenomenon, the practical implications should be considered, and a successful investigation of the I.P. effect should be complemented by field observations in which the laboratory results may be applied to problems of geophysical prospecting.

PREPARATION OF PLATINISED PLATINUM ELECTRODES

Platinised platinum electrodes throughout this work were prepared by the method described in Vogel (56 - p.972) using a plating solution of 3g chloroplatinic acid, prepared by the method in Ives and Janz (23 - p.107), and 0.025g lead acetate in 100 ml of double distilled water. The electrodes to be platinised are made the cathode in this solution, and the current was not reversed. A plating current density of about 100 mA/cm² was passed for 5 to 10 minutes, the resultant coating in all cases being jet black. APPENDIX II

PREPARATION OF Ag/AgC1 ELECTRODES

Silver silver chloride electrodes were prepared primarily by chloridising 1 mm silver wire in 0.1M HCl, after the method of Brown and MacInnes (9), described in Ives and Janz (23 - 0.206). Initially pairs of electrodes were prepared in parallel, but smaller asymmetry potentials were observed when pairs of electrodes were chloridised in series (Fig. 28), and this was done for later electrodes. In all cases a current density of about 10 mA/cm² was applied for 30 minutes using silver wire counter electrodes.

Upon completion of chloridisation the electrode pairs were short circuited and left in the plating solution for at least 24 hours. The electrodes were then carefully washed in distilled water and left standing in dilute NaCl solution, still short circuited.

One pair of electrodes was prepared using 0.5 mm Pt wire as base, onto which was deposited a plating of silver by passing 8 mA/cm² for a period of about 5 hours. The plating solution was $KAg(CN)_2$, prepared as described in Ives and Janz (23 - 0.198). The electrodes were chloridised as described above. The properties of these electrodes (asymmetry potential and stability) were not appreciably different from those prepared from silver wire, and seemed not to justify the extra effort.





ACKNOWLEDG EMENTS

The practical work which is the basis of this thesis was performed with assistance from a great number of people. Specifically I would like to acknowledge the assistance of Professor F. Jacob, Sacramento State College in the design of instrumentation, of Messrs E. J. Keller, A. D. Price and C. D. Taylor in technical matters, Messrs T. S. Clarkson, H. Wong and D. P. Wright for assistance in computing problems, and to Mr P. Mackey for the illustration of cells in this thesis. Each of the above contributed much in valuable discussion.

The bentolite and Wyoming bentonite samples used in the experiments described in this thesis were supplied by Mr J. Linzey, Crown Lynn Potteries Ltd., Auckland.

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