

Reprinted from *Nonlinear Behaviour of Molecules, Atoms and Ions in Electric, Magnetic or Electromagnetic Fields*

© 1979 Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

## NONLINEAR ELECTRICAL PROPERTIES

G.R. OELHOFT

U.S. Geological Survey MS964, Box 25046 Federal Center, Denver, CO 80225 USA

### ABSTRACT

Electrical properties become nonlinear in several different ways due to a variety of mechanisms and processes. In naturally occurring materials, nonlinear behavior is dominantly caused by the charge transfer reactions accompanying either oxidation-reduction processes or ion-exchange processes. Since most nonlinearities are directly caused by specific chemical phenomena, nonlinear electrical properties may be used in the remote measurement of geochemical activity within the earth. Applications through borehole geophysics include the determination of geochemical information during solution mining of minerals, monitoring ground water chemistry for leaks around nuclear waste repositories, and measuring the buildup of clays and similar alteration products that may clog pores in geothermal systems.

---

### INTRODUCTION

Electrical properties are useful in the earth sciences in a wide variety of ways as they are one of the easiest of all physical properties to measure and they are one of the most sensitive to changes in material or environmental parameters (Keller and Frischknecht, 1966; Olhoeft, 1976). The extreme sensitivity of some electrical properties to small changes in a wide variety of parameters is sometimes a problem. As an example, a volcanic material like basalt may exhibit an electrical resistivity at a frequency of  $10^{-3}$  Hz which is  $10^{12}$  ohm-m when vacuum dry at room temperature. That same material will have a resistivity of  $10^3$  ohm-m if it is saturated with a few weight percent water or if it is raised to a temperature of  $700^\circ\text{C}$  or if it is measured at a frequency of  $10^5$  Hz. A few weight percent clay or a single monolayer of adsorbed water can alter the low frequency resistivity by an order of magnitude while not altering the high frequency resistivities at all.

To address the ambiguous and multiple nature of electrical properties, investigators measure the widest possible number of electrical parameters as functions of variables that are easily controlled by the experimenter. Typically this involves the use of frequency of measurement as a variable.

In the frequency domain, the electrical properties describing a system response

relate the input (or stimulus or excitation) to the output (or response) of the system by a multiplicative factor, the transfer function of the system. If the input to the system is an electrical field and the output is current density, then the transfer function is the complex electrical conductivity. If the input is current density and the output is electrical field, then the transfer function is the complex electrical resistivity. The complex electrical resistivity and complex electrical conductivity are reciprocals of each other and are further discussed in the appendix.

The equation relating the input and output of a system is called the system equation. If all the derivatives of the input and output in the system equation are raised to the first power only and there are no products of derivatives, then the system is said to be linear. Mathematical properties of linear systems include additivity and homogeneity (together called superposition) which are discussed in detail in Cooper and McGillem (1967). These mathematical properties of linearity result in two measurable properties of linear systems: 1) the transfer function of a linear system is independent of the amplitude of the input to the system, and 2) the output of a linear system contains no new harmonic content that did not appear in the input to the system. In the latter case, if the input to the linear system is a pure sine wave, then the output contains no harmonics.

In addition to linearity, systems are described as being causal or acausal and by being integrably transformable or not. Causal systems have outputs which are independent of future values of the input. All physically realizable systems are causal (they cannot predict the future). A system which is linear may be integrably transformable. The integral transforms of the input, output, or system transfer function do not exist unless the integrals are convergent (Sneddon, 1972). Most physically realizable waveforms are convergent in this sense, and it is always possible to choose the input to a system such that the input and the output are both convergent.

The integral transform of a causal function has a time function that is completely specified by either the real or the imaginary part of the transform (see derivation in Landau and Lifshitz, 1960). Thus, the real and imaginary parts and the amplitude and phase spectra of the transfer function are related to each other. The relation between the real and imaginary parts is called the Hilbert transform or the Kramers-Kronig relations (Landau and Lifshitz, 1960). If the real and imaginary parts of the transfer function do not obey the Hilbert transform and the input was chosen to give a convergent input and output, then the system is either acausal or nonlinear. As all physically realizable systems must be causal, such a system must then be nonlinear.

As a consequence, there are two additional measures of nonlinearity: 3) the transfer function of a system in the frequency domain is the Laplace transform of the impulse response of the system in the time domain (see Cooper and McGillem,

1967), and 4) the real and imaginary parts of the transfer function are a Hilbert transform pair. In practice the third measure of linearity is very difficult to obtain as the impulse response is difficult to measure directly. However, a similar test may be performed using the step response or by measuring and comparing the transfer functions of a system measured by using two very different waveforms of input (such as a sine-wave versus a triangular-wave). In linear systems, the transfer function is independent of the form of the input.

Thus, there are four methods of measuring nonlinearity in an electrical system:

1) Measure the electrical transfer function at two or more different values of input signal amplitude. A measure of the nonlinearity is the derivative of the transfer function with respect to amplitude of input. Note that the transfer function is a complex quantity and that amplitude and phase spectra may be independently nonlinear.

2) Measure the harmonic content of the input and output of the system. The root-mean-square (RMS) difference between the harmonics in input and output is the total-harmonic-distortion (THD) and is a measure of nonlinearity.

3) Measure the transfer function using a sine-wave and a triangular-wave input. The difference between the resultant transfer functions is a measure of nonlinearity.

4) Measure the frequency dependence of the transfer function. Use the Hilbert transform to generate new real and imaginary parts of a synthetic transfer function from the imaginary and real parts of the measured transfer function. The differences between the derived synthetic and the original measured transfer functions are measures of nonlinearity versus frequency.

Further, these four generalized measures of nonlinearity may appear in different ways. It is possible to have a complex transfer function with an amplitude nonlinearity (the amplitude or magnitude of the transfer function varies with the amplitude of the input) but without a phase nonlinearity (for example, if the nonlinearities in the real and imaginary parts of the transfer function cancel). It is also possible to have a system which exhibits the first two types of nonlinearity (amplitude and harmonic), but does not exhibit the last type of nonlinearity (Hilbert). The reverse is also possible and has been found to be common in clay minerals.

#### EXAMPLES

Nonlinear electrical properties have been studied for a number of years by electrochemists through a variety of techniques, including polarography, cyclic voltammetry, and others. These techniques are discussed in textbooks such as Bockris and Reddy (1970), Fleet and Jee (1973), Nurnberg (1974), Galus (1976), Antropov (1977), and others. The best known of the nonlinear processes is that accompanying charge transfer during oxidation-reduction reactions (for a general discussion of charge transfer, see Mathews and Bockris, 1971).

The linear equation describing electrical properties is Ohm's law, given by

$$J = \sigma E \quad (\text{see appendix})$$

where  $J$  = current density

$E$  = electric field strength

and  $\sigma$  = electrical conductivity (transfer function between  $E$  and  $J$ ).

The oxidation-reduction reaction carrying charge across an interface between a solution and an electrode is given by the nonlinear Butler-Volmer absolute rate equation

$$J = C_1 e^{\beta C_2 E} + C_3 e^{-(1-\beta) C_4 E}$$

where  $C_i$  = various constants involving chemical parameters such as diffusion coefficients, concentrations, kinetics, and so forth

and  $\beta$  = anodic transfer coefficient.

The details of the coefficients are unimportant for the purposes of describing how nonlinear behavior appears (for further discussions see Sluyters-Rehbach and Sluyters, 1970, or the electrochemistry textbooks referenced above).

The Butler-Volmer type of equation yields electrical properties which are not only nonlinear, but are also complex, frequency dependent, and asymmetrical with respect to the polarity of the input. The properties may become linear for very small perturbations of  $E$ , for frequencies of input that are higher than the speed of reaction, and for conditions which may be diffusion or otherwise limited. The properties may be asymmetrical if the constants in the equation are not equal for the anodic and cathodic terms, or if the anodic (reduction) process is not completely reversible during the cathodic (oxidation) process, or if the system stores energy and exhibits memory (a dynamic system) differently for the anodic process than for the cathodic process.

Figure 1 illustrates the plot of current versus electric potential across a pyrite/water interface. In both parts of the figure, the sample is in a three-terminal sample holder similar to the corrosion cell of Peters (1977) with 0.1 molar NaCl aqueous solution at a pH of 7. The driving waveform is a sinewave with the illustrated Lissajous patterns proceeding in a clockwise direction. The dotted lines are the actual waveforms recorded by a digital oscilloscope while the solid line in Figure 1b is a model fit based upon the Butler-Volmer equation (offset for clarity).

Figure 1a illustrates the pyrite with a freshly polished surface at a frequency of 0.1 Hz and a current density of 0.085 A/m<sup>2</sup>. Each change in slope or distortion of the pattern relative to an ellipse is indicative of a specific chemical reaction. Reactions occur at specific potentials across the interface (Milazzo and Caroli, 1978), and if the current density is not high enough to generate the required potential then the reaction will not occur. Similarly, reactions proceed at specific rates (determined by either the reaction kinetics or the speeds of diffusion, see Arvia and Marchiano, 1971, and Bernasconi, 1976), and if the

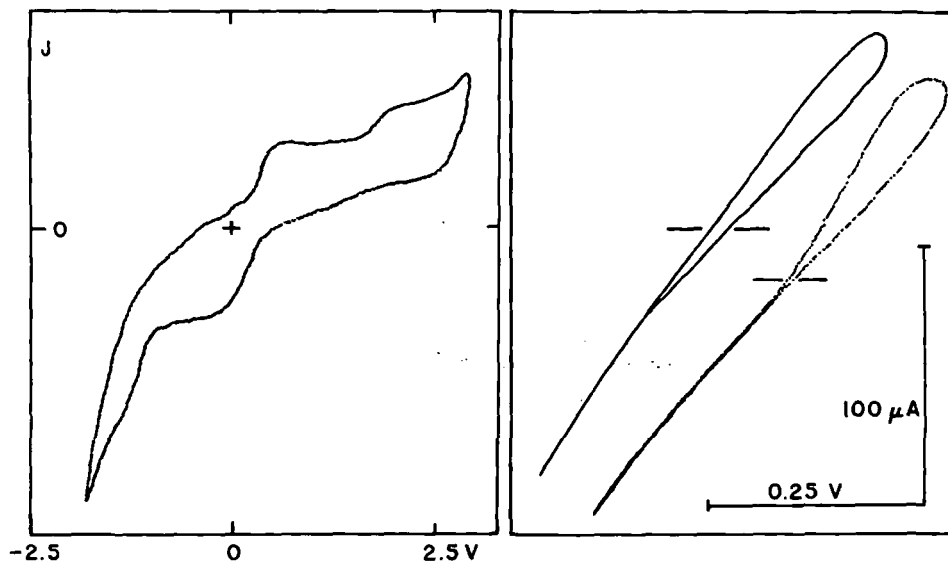


FIGURE 1: Figure 1a (left) illustrates the Lissajous pattern of current density (vertical axis) versus electrical potential (horizontal axis) across the pyrite-water interface with a 0.1 molar NaCl aqueous solution. The cross marks zero current and zero potential. The frequency is 0.1 Hz at a maximum current density of  $0.085 \text{ A/m}^2$ . Figure 1b (right) illustrates the same sample and conditions as part 1a except a frequency of 0.01 Hz and a current density of  $0.008 \text{ A/m}^2$ . At this current density, only one oxidation-reduction couple is present. The dotted curve is the actual digitized data while the solid line is a model fit based upon the Butler-Volmer equation. The two curves are offset for clarity with broken horizontal bars through each indicating zero current.

frequency of excitation is too high, the reaction will not occur. In either case of too low a current density or too high a frequency, the system becomes linear.

Figure 1a illustrates several reactions occurring with the lower left quadrant (anodic) of the plot reducing the sample and generating hydrogen gas while the upper right quadrant (cathodic) is where the sample is oxidized and oxygen may be evolved. Figure 1b illustrates the same sample at a lower current density and a lower frequency where only one reaction couple is activated. The opening of the loop in the oxidizing quadrant indicates that the sample either resists being oxidized or the oxidizing reaction is diffusion limited. As the plot does not change upon stirring the solution, the sample must be resistant to oxidation. The lower left reducing quadrant illustrates that the sample is not diffusion limited nor resistant to being reduced. For further discussion of the detailed electrochemistry of pyrite, see Peter (1977), Hall (1975), Biegler and others (1977), Scott and Nicol (1977), and Klein and Shuey (1978a, b).

Figure 2 illustrates the dependence of highly altered pyrite upon current density at 0.1 Hz in a four-terminal sample holder. The sample holder has a symmetrical arrangement with a current electrode in solution, a potential electrode near but not touching the pyrite sample, the pyrite sample potted in silicone,

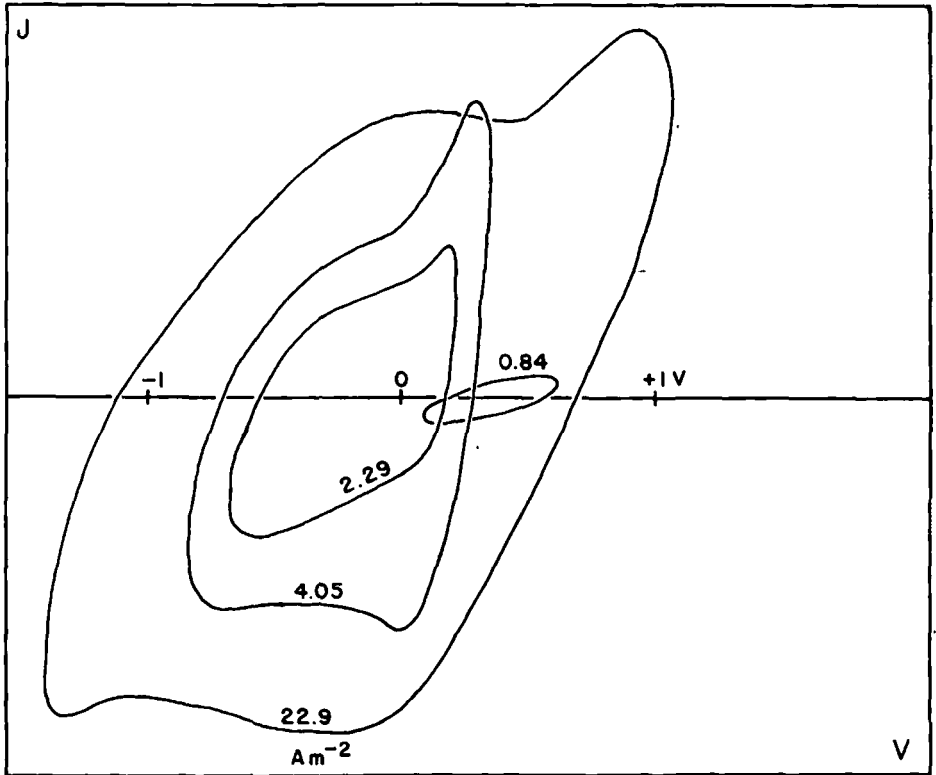


FIGURE 2: An altered pyrite-electrolyte interface under similar conditions as for Figure 1 with a frequency of 0.1 Hz and various current densities as indicated on each curve. This is a four-terminal sample holder as described in the text.

another potential electrode, and another current electrode in solution. The electrodes are all constructed of platinum mesh (bright platinum as the platinized electrodes introduce impurities and do not stay platinized over long periods of time). High input impedance ( $>>10^{11}$  ohms) electrometer amplifiers are used in the measurement of the potential electrodes so as to not draw enough current to generate significant charge transfer impedances in the potential measuring circuit. The electrode arrangement is identical with common practice for geophysical and borehole instrumentation (Keller and Frischknecht, 1966). This electrode arrangement will not produce the characteristic and asymmetrical plots of Figure 1 unless the oxidation-reduction reactions are incompletely reversible or are dynamically different at anode and cathode. In the latter case, dynamically different means the anode stores energy and exhibits memory (phase lag) in a manner different than the cathode.

Figure 2 illustrates the pyrite-electrolyte reactions as a function of current density showing the distinct asymmetry for one of the above reasons. In addition, the 0.84 A/m<sup>2</sup> current density pattern is nearly a perfect ellipse and therefore

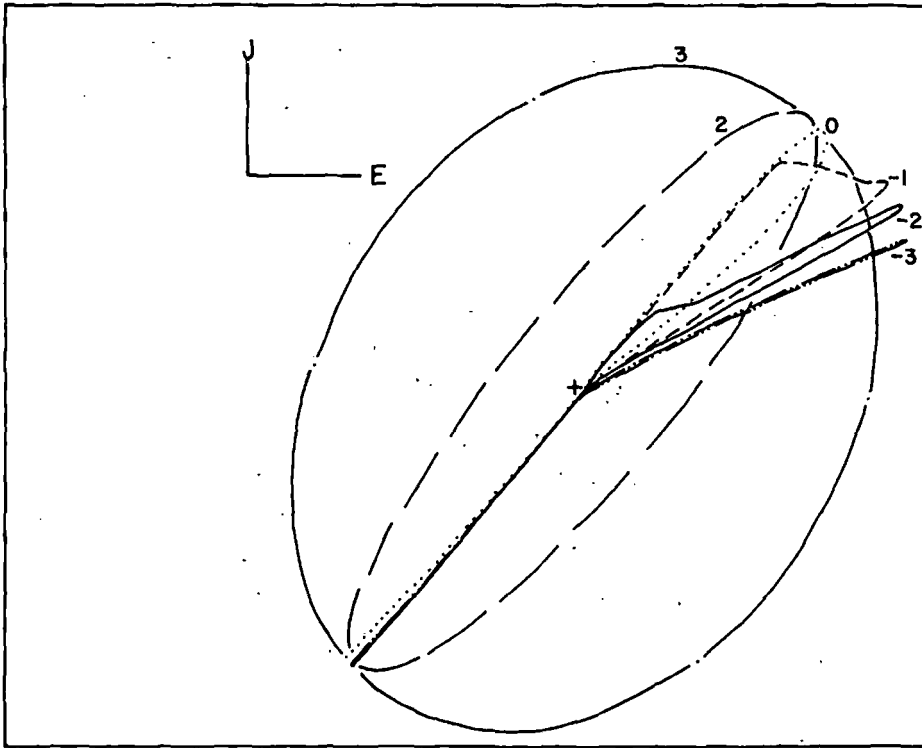


FIGURE 3: The frequency dependence of the Lissajous patterns for a cation exchange resin as a function of frequency. The numbers next to each curve are the logarithm of the frequency to base ten. The 1 Hz and 10 Hz patterns overlap and are nearly identical. The patterns are essentially linear above 10 Hz.

approaching a linear system response. The specimen in Figure 2 has a highly altered surface and requires higher current densities for nonlinear behavior than the highly polished specimen of Figure 1.

The second important charge transfer process in natural materials that causes measurable nonlinear electrical behavior is due to ion exchange. Unfortunately, the process of ion exchange is itself very little understood and the electrochemistry of ion exchange is even less well known. The best discussions occur in Carroll (1959), Payne (1972), Dukhin and Shilov (1974), Dukhin (1974), Dukhin and Derjaguin (1974), Derjaguin and Dukhin (1974), Adamson (1976) and van Olphen (1977). Some attempts at models of the electrochemistry have been made by Armstrong (1969), Timmer and others (1970), and others.

The following examples illustrate the type of behavior that has been observed in a variety of clays and zeolites. For simplicity, the examples will be drawn from investigations performed on ion exchange resins. Essentially similar results have been obtained with a variety of clay minerals. Figure 3 illustrates the

electrical behavior of a cation exchange resin (Table 1) in a four-terminal sample holder as a function of frequency. The resins are very dynamic and exhibit considerable memory. The cations easily adsorb onto the surface, but reluctantly desorb. This causes the distinct nonlinear asymmetry shown in the figure. Also, at the higher frequencies the cations cannot respond to the driving force and the process becomes linear as it is diffusion limited. Due to the memory and diffusion coefficients, the frequency dependence of the transfer function is measurably different depending upon whether it is measured from low to high frequencies or from high to low frequencies.

TABLE 1

Both exchange resins are styrene divinylbenzene copolymer matrix beads, 16-50 mesh size, laboratory grade, with a working range of 0-14 pH, and are manufactured by J.T. Baker Company.

Designation	C-267 cation	ANGA-542 anion
Type	strong acid	strong base
Form (ionic form)	H	OH
Group	sulfonic functional	alkyl quaterbary amine
Total dry exchange capacity (meq/g)	4.0	3.2
Moisture content	45-55	60-70 percent
Working density (g/l)	400-500	300-500

Figure 4 illustrates the frequency dependence of the cation resin and an equilant anion resin (Table 1) measured from low to high frequency. Note that the cation resin has a much higher total-harmonic-distortion (THD) than the anion resin, has a larger phase angle, and has a stronger frequency dependence. Also, the three resistivities plotted represent the asymmetry of the system with the resistivity determined from the whole waveform (W), from just the positive half (P), and from just the negative half (N). The cation resin is considerably more asymmetrical than the anion resin.

Due to the generally smaller size of the cation, it is not surprising that it is more important than the anion in adsorption processes (see discussions in van Olphen, 1977). Also, most materials tend to have negative surface charges in excess and thus prefer to attract cations over anions. Thus, all other things being equal, it is fortunate that the cation exchange process is more nonlinear than the anion process as this allows the nonlinear effects to be used to acquire additional information about the material surface with which the ions are interacting.



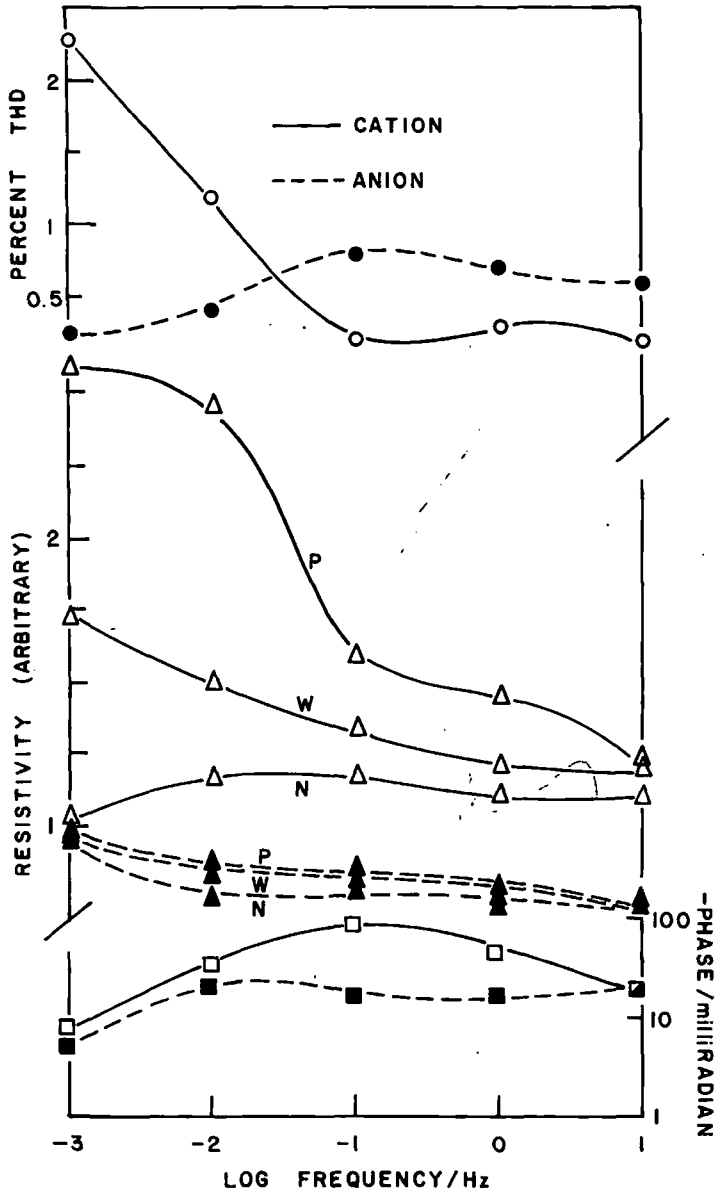


FIGURE 4: The frequency dependence of the total-harmonic-distortion (THD), the real part of the complex resistivity, and the phase angle of the cation exchange (solid lines with open symbols) and the anion exchange (dashed lines with closed symbols) resins of Table 1. P, W, and N on the resistivity plots indicate the use of only the positive half, the whole, or only the negative half of the waveforms (as in Figure 3) for the construction of the resistivity.

FIGURE 5: The Hilbert nonlinear effect as the deviation in percent of the real resistivity actually measured from that derived by the Hilbert transform from the actually measured imaginary resistivity. The dashed, solid, and dotted curves are the deviations for the following instrumentation: General Radio 1615 and Wayne-Kerr B-201 bridges together (dashed), General Radio 1621 and Wayne-Kerr B-201 bridges together (solid), and the U.S.G.S. Petrophysics Laboratory transfer function analyzer (dotted, Olhoeft, 1978). The triangles, crosses, and circles are data from real materials, respectively: an unaltered juvite in distilled water, very pure water (greater than 150,000 ohm-m), and a highly altered juvite in distilled water.

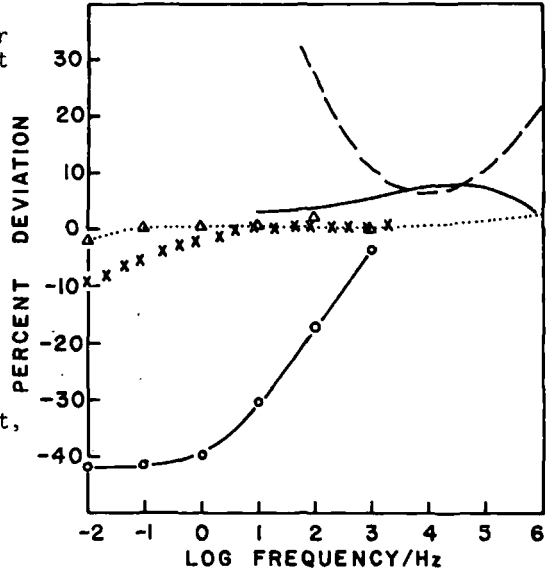


Figure 5 illustrates the final nonlinear example. This figure shows the percent deviation of a resistivity transfer function when the real and imaginary parts are tested with a Hilbert transform. A problem with the measurement of this type of nonlinearity lies in its occurrence in common laboratory measurement apparatus. Several examples are shown for commercial instruments as well as the instrument used to acquire the sample data illustrated (see Olhoeft, 1978).

The data in Figure 5 illustrating the nonlinear Hilbert response for real materials includes a juvite specimen saturated with distilled water (triangles), very pure water (crosses), and a highly altered specimen of juvite saturated with distilled water. This type of nonlinearity has been commonly observed in clays, zeolites, and other highly altered materials such as the altered juvite shown. The reason for the nonlinearity is not known, but it may be related to the cation exchange process as it is usually not observed in the materials where oxidation-reduction reactions dominate.

The Hilbert nonlinearity in water (crosses in Figure-5) has only been observed in water with DC resistivities above 150,000 ohm-m. There are other dielectric nonlinearities in water (Jones, 1975), but neither this nor the others are well understood.

There are many other examples of nonlinear electrical behavior than these given here, but these should suffice as an introduction. Other examples which may be found in the literature include nonlinear electrokinetic phenomena (Dukhin and Derjaguin, 1974), nonlinear dielectric phenomena (Kielich, 1972; Jones, 1975), ferroelectrics (Jona and Shirane, 1962; Burfoot, 1967), and others.

## APPLICATIONS

Several applications of nonlinear electrical properties are already in use as standard electroanalytical techniques (see texts referenced above), but several other interesting applications are worth mentioning. The first is the study of reactions versus frequency as a way to measure and study the kinetics of reactions. This has been done in the past, but very infrequently. Second is the study of chemical processes under high temperature and pressure conditions in which it is difficult to access the reaction products for analysis but it is relatively easy to insert wires and electrodes to monitor electrical properties. Third, through the use of borehole logging, it should be possible to exploit the electrical nonlinearities to measure ground water and mineral chemistry in situ.

There are other applications, but the first two are primarily laboratory tools to expand the general knowledge of chemistry, particularly of kinetics (Bernasconi, 1976). The last application is of the greatest interest, however, in a variety of current problems. Among these are the problem of determining geochemical parameters to design solution mining procedures for uranium and other scarce minerals, the problem of monitoring ground water chemistry for leaks around nuclear waste repositories, the problem of measuring the buildup of clays and other alteration products which may clog pore structures in geothermal systems, and a variety of problems in the study of permafrost.

Permafrost is particularly interesting because the colloidal clay particles have electrochemical double layers which may be thicker than the average dimension of the clay particle. Such thick double layers help depress the freezing point of water and harbor large amounts of unfrozen water in the permafrost. Electrical measurement techniques may exploit the current channeling capacity of this unfrozen water to utilize the nonlinear response of the cation exchange process to map and detect the presence of clay minerals. This is particularly important in the exploration for sulfide minerals in permafrost where the clay response may be very similar to various standard geophysical instruments, but easily distinguishable between the clays and sulfides through the nonlinear techniques.

In general, the more information upon which to base a decision or course of action, the better. Nonlinear electrical properties provide a considerable amount of information that may not be otherwise available. Rather than being limited to traditional measurements of electrical properties which provide only amplitude and phase versus frequency, nonlinear electrical measurements can also provide amplitude, phase, asymmetry, total harmonic distortion, Hilbert distortion, and a variety of other parameters versus frequency and current density.

## ACKNOWLEDGEMENTS

In addition to U.S.G.S. Geothermal and Uranium Program funding, this research has been partly funded by support from the Department of Energy Division of Geothermal Energy and the National Aeronautics and Space Administration Planetary Geology Program.

The use of trade or manufacturer's names in this report does not imply recommendation or endorsement by the U.S. Geological Survey.

## REFERENCES

- Adamson, A.W., 1976, *Physical Chemistry of Surfaces*, 3rd ed., New York: Wiley, 698p.
- Antropov, L.I., 1977, *Theoretical Electrochemistry*, Moscow: Mir Publishers, 596p.
- Armstrong, R.D., 1969, Relaxation times for adsorption coupled with a homogeneous reaction in solution, *J. Electroanal. Chem.*, 22, 49-53.
- Arvia, A.J. and Marchiano, S.L., 1971, Transport phenomena in electrochemical kinetics, pp. 159-241 in *Modern Aspects of Electrochemistry*, no. 6, J.O'M. Bockris and B.E. Conway, eds., New York: Plenum.
- Bernasconi, C.F., 1976, *Relaxation Kinetics*, New York: Academic Press, 288p.
- Biegler, T., Rand, D.A.J., and Woods, R., 1977, Oxygen reduction on sulfide minerals, pp. 291-302 in *Trends in Electrochemistry*, J.O'M. Bockris, D.A.J. Rand, and B.J. Welch, eds., New York: Plenum.
- Bockris, J.O'M. and Reddy, A.K.N., 1970, *Modern Electrochemistry*, 2 vols. New York: Plenum, 1432p.
- Burfoot, J.C., 1967, *Ferroelectrics: An Introduction to the Physical Principles*, London: Van Nostrand, 261p.
- Carroll, D., 1959, Ion exchange in clays and other minerals, *Bull. Geol. Soc. Am.*, 70, 749-780.
- Cooper, G.R. and McGillem, C.D., 1967, *Methods of Signal and System Analysis*, New York: Holt Rinehart and Winston, 432p.
- Derjaguin, B.V. and Dukhin, S.S., 1974, Nonequilibrium double layer and electrokinetic phenomena, pp. 273-336 in *Surface and Colloid Science*, vol. 7, E. Matijevic, ed., New York: Wiley.
- Dukhin, S.S., 1974, Development of notions as to the mechanism of electrokinetic phenomena and the structure of the colloid micelle, pp. 1-48 in *Surface and Colloid Science*, vol. 7, E. Matijevic, ed., New York: Wiley.
- Dukhin, S.S. and Derjaguin, B.V., 1974, Equilibrium double layer and electrokinetic phenomena, pp. 49-272 in *Surface and Colloid Science*, vol. 7, E. Matijevic, ed., New York: Wiley.
- Dukhin, S.S. and Shilov, V.N., 1974, *Dielectric Phenomena and the Double Layer in Disperse Systems and Polyelectrolytes*, New York: Halsted, 192p.
- Fleet, B. and Jee, R.D., 1973, *Electroanalytical chemistry: voltammetry*, pp. 210-237 in *Electrochemistry*, vol. 3, Specialist Periodical Report, G.J. Hills, Sr. Rptr., London: The Chemical Society.
- Fuller, B.D. and Ward, S.H., 1970, Linear system description of the electrical parameters of rocks, *IEEE Trans. Geosci. Electronics*, GE-8, pp. 7-18.
- Galus, Z., 1976, *Fundamentals of Electrochemical Analysis*, Chichester: Ellis Horwood, 520p.

- Hall, S.H., 1975, A method of measuring rock electrode kinetics, *J. Electroanal. Chem.*, 59, 323-333.
- Jona, F. and Shirane, G., 1962, *Ferroelectric Crystals*, Oxford: Pergamon, 402p.
- Jones, G.P., 1975, Nonlinear dielectric effects, pp.198-248 in *Dielectric and Related Molecular Processes*, vol.2, *Specialist Periodical Reports*, M.Davies, Sr. Rptr., London: The Chemical Society.
- Keller, G.V., 1959, Analysis of some electrical transient measurements on igneous, sedimentary, and metamorphic rocks, in *Overvoltage Research and Applications*, J.R.Wait, ed., London: Pergamon.
- Keller, G.V. and Frischknecht, F.C., 1966, *Electrical Methods in Geophysical Prospecting*, New York: Pergamon, 517p.
- Kielich, S., 1972, General molecular theory and electric field effects in isotropic dielectrics, pp. 192-387 in *Dielectric and Related Molecular Processes*, vol.1, *Specialist Periodical Reports*, M.Davies, Sr.Rptr., London: The Chemical Society.
- Klein, J.D. and Shuey, R.T., 1978a, Nonlinear impedance of mineral-electrolyte interfaces, Part I: pyrite, *Geophysics*, 43, 1222-1234.
- Klein, J.D. and Shuey, R.T., 1978b, Nonlinear impedance of mineral-electrolyte interfaces, Part II: galena, chalcopyrite, and graphite, *Geophysics*, 43, 1235-1249.
- Landau, L.D. and Lifshitz, E.M., 1960, *Electrodynamics of Continuous Media*, London: Pergamon, 417p.
- Mathews, D.B. and Bockris, J.O'M., 1971, The mechanism of charge transfer from metal electrodes to ions in solution, pp. 242-328 in *Modern Aspects of Electrochemistry*, no. 6, J.O'M. Bockris and B.E. Conway, eds., New York: Plenum.
- Milazzo, G. and Caroli, S., 1978, *Tables of Standard Electrode Potentials*, New York: Wiley, 421p.
- Nurnberg, H.W., ed., 1974, *Electroanalytical Chemistry*, New York: Wiley, 609p.
- Olhoeft, G.R., 1976, Electrical properties of rocks, pp. 261-278 in *The Physics and Chemistry of Minerals and Rocks*, R.G.J. Strens, ed., New York: Wiley.
- Olhoeft, G.R., 1978, Electrical properties, a chapter in *Initial Report of the Petrophysics Laboratory*, K.Watson, ed., U.S.Geological Survey Circular, in press.
- Olhoeft, G.R., Elliot, C., Fuller, B.D., Keller, G.V., Scott, W.J., and Strangway, D.W., 1978, Proposed Standards for the Presentation of Electrical and Electromagnetic Data, Interim Report of the Electrical Standards Subcommittee of the Mining Committee, Tulsa: Society of Exploration Geophysicists, 14p.
- Payne, R., 1972, The study of the ionic double layer and adsorption phenomena, pp. 43-140 in *Techniques of Electrochemistry*, vol.1, E.Yeager and A.J. Salkind, eds., New York: Wiley-Interscience.
- Peters, E., 1977, Electrochemistry of sulfide minerals, pp.267-290 in *Trends in Electrochemistry*, J.O'M.Bockris, D.A.J.Rand, and B.J.Welch, eds., New York: Plenum.
- Scott, P.D. and Nicol, M.J., 1977, The kinetics and mechanisms of the non-oxidative dissolution of metal sulfides, pp. 291-302 in *Trends in Electrochemistry*, J.O'M. Bockris, D.A.J.Rand, and B.J.Welch, eds., New York: Plenum.
- Shuey, R.T. and Johnson, M., 1973, On the phenomenology of electrical relaxation in rocks, *Geophysics*, 38, 37-48.
- Sneddon, I.N., 1972, *The Use of Integral Transforms*, New York: McGraw-Hill, 539p.
- Sluyters-Rehbach, M. and Sluyters, J.H., 1970, Sine wave methods in the study of electrode processes, pp.1-128 in *Electroanalytical Chemistry*, vol.4, A.J.Bard, ed., New York: Marcel Dekker.

Timmer, B., Sluyters-Rehbach, M., and Sluyters, J.H., 1970, Influence of non-specific adsorption of reactants on the electrode interface, *J. Electroanal. Chem.*, 24, 287-303.

van Olphen, H., 1977, *An Introduction to Clay Colloid Chemistry*, New York: Wiley, 318p

#### APPENDIX

This appendix is included to introduce the terminology of electrical properties as used by the exploration geophysicist based upon Olhoeft and others (1978). Unless otherwise specified, these terms are defined for systems which are causal, linear, time-invariant, dynamic, and isotropic. The systems may be either lumped-parameter (ordinary differential equation) or distributed-parameter (partial differential equation), and they may be either discrete time (difference equation) or continuous time (differential equation). For definitions of these specifying terms, see Cooper and McGillem (1967). Included with the definitions are the units in the SI system (shown in brackets).

Definitions of electrical properties logically begin with Ohm's Law

$$J = \sigma E \quad (1)$$

where  $J$  = free charge current density [Amp/m<sup>2</sup>]

$E$  = electrical field strength [Volt/m]

and  $\sigma$  = electrical conductivity [Siemen/m].

This is equivalently presented as

$$E = \rho J \quad (2)$$

where  $\rho = \sigma^{-1}$  = electrical conductivity [Ohm-m]. Up to this point, resistivity and conductivity are defined including only free charge transport.

In the general case, the following linear relationship also applies

$$D = \epsilon E \quad (3)$$

where  $\epsilon$  = dielectric permittivity [Farad/m]

and  $D$  = dielectric displacement = electric flux density [Coulomb/m].

Combining equations (1) and (3) through Maxwell's equation

$$\nabla \times H = J + \partial D / \partial t = J_T \quad (4)$$

where  $H$  = magnetic field strength [Amp/m],

yields a total current density,  $J_T$ , which includes both free carrier conduction and dielectric displacement terms

$$J_T = \sigma E + \epsilon \partial E / \partial t. \quad (5)$$

Since, in the general case, both the conductivity and the dielectric permittivity may be independently complex (Fuller and Ward, 1970), the total resistivity and the total conductivity may be defined through the relation

$$(\rho_T^i - i\rho_T^u)^{-1} = \sigma_T^i + i\sigma_T^u = (\sigma' + i\sigma'') + i\omega (\epsilon' - i\epsilon'') \quad (6)$$

with a loss tangent,  $\tan\delta$ , and a phase angle,  $\phi$ , defined

$$\tan\delta = \cot\phi = \rho_T^i / \rho_T^u = \sigma_T^i / \sigma_T^u \quad (7)$$

with the unsubscripted  $\sigma$  and  $\epsilon$  from equation (5).

Most instruments fall into two classes: they either measure electrical parameters by measuring voltage and current (related to E and J by the geometry of the system), or they measure equivalent series or parallel admittance or impedance by substitution against standards. In the latter case, the effective capacitance and conductance measured become the effective dielectric permittivity of  $(\epsilon' + \sigma''/\omega)$  from equation (6), and the loss tangent of equation (7).

Those instruments that measure voltage and current usually measure the total current, yielding a typical measurement of the form

$$E = E_0 \sin(\omega t + \phi_e) \quad (8)$$

$$J_T = J_0 \sin(\omega t + \phi_j)$$

where  $E_0$  = amplitude of E

$J_0$  = amplitude of  $J_T$

t = time [sec]

$\omega$  = circular frequency [rad/sec] =  $2\pi f$  (where f is frequency in Hertz)

$\phi_e$  = arbitrary phase offset relative to some time zero for E

and  $\phi_j$  = arbitrary phase offset relative to the same timebase as for E.

In terms of these equations (8), the total resistivity is given as

$$|\rho_T| = (\rho_T'^2 + \rho_T''^2)^{1/2} = E_0/J_0 = \text{resistivity magnitude [Ohm-m]} \quad (9)$$

$$\angle \rho_T = \phi = \text{arccot}(\rho_T'/\rho_T'') = \phi_e - \phi_j = \text{phase angle [radians]} \quad (10)$$

$$\rho_T' = (E_0/J_0) \cos\phi \quad \text{and} \quad \rho_T'' = (E_0/J_0) \sin\phi \quad (11)$$

The complex total conductivity may be obtained from equation (6). The loss tangent and phase angle of equation (7) are identical with the definition in equation (10).

The definitions up to this point have been formulated for steady state sinusoidal excitations. However, the definitions are equally valid whatever the form of the excitation and response, provided that only the fundamental frequency is employed in determining the resistivity and phase angle at that frequency from the measured E and  $J_T$ . Harmonics may be similarly used only if the system is demonstrably linear.

Further introduction and discussion of these parameters may be found in Keller (1959), Fuller and Ward (1970), Shuey and Johnson (1973), Cooper and McGillem (1967), and Olhoeft and others (1978).

DISCUSSIONG.R. OLHOEFT

Davies - I have not grasped what is the basis of the curve for the frequency-dependence of the conductivity of water ? Is it, perhaps, based on the Eigen-school studies of proton-jumping times in the medium.

Again, is it necessary to invoke the presence of liquid water in your permafrost specimens ? Is there reasonably direct evidence for the fluidity of this component .

Finally, I have not understood which non-linear effect in water is very sensitive to impurities such as dissolved carbon dioxide. The dielectric changes with high field ( $\Delta\epsilon/E^2$ ) are not sensitive to electrolyte until the conductivity exceeds  $10^2$  times that of "equilibrium" atmospheric water.

Olhoeft - The frequency dependence shown for the conductivity of water is experimental and not based upon any school. The presence of liquid water in permafrost has been demonstrated and known for several years. Basically, the water in between grains begins freezing from the center of the intergranular space towards the grain walls. The freezing rate is very slow (thousands of years) and the freezing process tends to exclude impurities from the ice, thus increasing the concentration of impurities in the remaining water. Between this process and the similar effects due to the electrical fields of the double layer at the water/grain interface, the remaining free water has a freezing point which is continually being depressed. Thus at any given temperature below  $0^\circ\text{C}$  there remains a small amount of unfrozen water. These processes and the resulting properties of the material have been reviewed by Anderson and Morgenstern (1973) and Anderson et al. (1973). The nonlinear behavior in water that is sensitive to the presence of impurities is the deviation of the frequency dependence of the transfer function (resistivity) from behavior that is consistent with the Hilbert transform (Kramers-Kronig transform) relating the real and imaginary parts to each other. Water with resistivities of 100,000 ohm-m does not (both at 20 kV/cm electric field). This is still under investigation.

Anderson, D.M. and Morgenstern, N.R., 1973, Physics, chemistry, and mechanics of frozen ground : a review, pp. 257-288 in : Permafrost - North American Contribution to the Second International Conference, Washington, D.C. : National Academy of Science.

Anderson, D.M. Tice, A.R., and McKim, H.L., 1973, The unfrozen water content and the apparent specific heat capacity of frozen soils, pp. 189-294 in : Permafrost - North American Contribution to the Second International Conference, Washington, D.C. : National Academy of Sciences.