Electrical conductivity of MHD coal slags to 2025 K
by David John Westpfahl

A thesis submitted in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE in Physics
Montana State University

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Signature David J. Westpfahl Jr

Date August 14, 1978

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Approved:

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ABSTRACT

The electrical conductivity of MHD coal slags must be known to design efficient open-cycle, coal-fired, MHD generators. In this work, the effect of slag composition on electrical conductivity is examined, with attention to the role of iron in slags. Electronic and ionic conductivity mechanisms are examined. The present theories of conductivity in slags and glasses are reviewed, and the equation $\ln \sigma = -A - B/T$ is derived. A system for measuring the AC conductivity of slags at 120 Hz, 1000 Hz, and 10,000 Hz is described in detail. Data up to 2025°K are presented for six slags. The data are interpreted considering the compositions of the slags and the above equation.

CHAPTER I

INTRODUCTION

As oil becomes scarce, and its price rises, new sources of inexpensive energy are sought. In recent years, researchers in universities, private corporations, and the government have turned their efforts to this problem.

Coal has been suggested as an easily available resource which could supply energy for many years. Coal reserves in the U.S. are estimated at between 390 billion metric tons and 1486 billion metric tons.[1] If consumption is limited to the present rate, which is not likely, coal could provide energy for at least 680 years, and possibly as long as 2872 years,[2] a very comfortable amount of time. If the consumption continues to grow at the present rate of 11 percent per year,[3] which is likely, U.S. coal will last only 39 to 52 years.[4] This is a short period, but could be extended by limiting consumption and by efficient use of this natural resource.

One promising way of using coal more efficiently is magnetohydrodynamic conversion (MHD). In an MHD generator, the electrically charged gases produced by burning coal (or other fuels) move by expanding through a nozzle or channel. Surrounding the channel is a magnet which produces a strong field. The force exerted by the magnetic field on the moving charged particles directs them to the side of the channel separating the positive and negative charges. Current is collected by electrodes placed in the channel walls.[5] Such a generator is simple--it has no moving parts.

When coal is burned in an MHD generator, the channel walls become coated with a layer of slag. This changes the performance of the generator by increasing the voltage loss at the electrode walls and reducing the resistivity of the insulators between the electrodes.[6] The magnitude of these effects depends upon the thickness of the slag layer and its electrical conductivity. Rosa[7] has analyzed this in detail, and emphasized the importance of knowing the electrical conductivity of slag at the temperatures found in MHD generator channels.

The conductivity of the slag must fall within certain limits if the generator is to function properly. It must conduct well enough so current may pass through the slag from the hot gases to the electrodes. At the same time it must conduct poorly enough so it does not allow shorting between electrodes.

The conductivity of a slag depends upon its chemical composition. Slags are composed of the inorganic oxides remaining after the coal is burned. The composition of the slag, then, depends upon the amount of inorganic material in the coal and the amount of inorganic material added to the coal before burning. This is different for different coals.

Coal from the large deposits in Montana will be used to fuel MHD generators. The purpose of this work is to examine the electrical conductivity of slags from Montana coal ash and other common MHD slags. Chemical composition is examined, especially the effect of iron oxide in slag. Iron oxide is an important contributor to the electrical conductivity, yet one which is often ignored.

Other investigators, especially Pollina and Larsen,[8,9] have examined the conductivity of various slags to 1450°C. It was decided to expand on their work by developing equipment capable of measuring the conductivity of slags (and other materials) to 1750°C. Temperatures between 1450°C and 1750°C are predicted for coal-fired MHD generators.

CHAPTER II

BACKGROUND

Coal slag does not have a definite chemical composition or physical structure. This makes studies of coal slag difficult, and the literature on crystalline solids is only occasionally helpful.

Luckily, most coal slags resemble certain glasses and glassy slags produced in steelmaking. These have been studied experimentally and theoretically for several years.

The main constituent of coal slag, SiO_2, tends to form extended, three-dimensional, non-periodic arrays, or networks, when found in the glassy state.[10] Because of this, SiO_2 is called a "network former". Other common network formers are B_2O_3 and P_2O_5.[11]

As the network forms, the silicon and oxygen atoms tend to align to form SiO_4 tetrahedra joined at their corners.[12] The extra oxygen atoms are provided by compounds such as Na_2O, K_2O, CaO, and BaO, which are known as "network modifiers". As the network is formed, the metallic cations in the network modifiers occupy holes in the network and can have a large effect on the physical properties of the glass.

Other oxides fall between these two cases; they may form networks or modify them. These are called "intermediate oxides". Some common ones are N_2O_3, Fe_2O_3, FeO, MgO, and ZnO.[13]

The structure of glass and the roles of these three types of oxides is described thoroughly by Owen[14] and Stevels.[15]

When the electrical conductivity of a slag (or a glass) is measured, a voltage is applied across a sample of the material causing a current to flow. This current may be carried by the movement of ions or electrons. In a slag with little or no transition metal oxide content, the current is carried by monovalent cations.[16] If sodium ions are present, even as few as several parts per million, they will carry most of the charge.[17] Should sodium ions not be present, the main charge carriers would be lithium, potassium, or hydrogen ions.[18]

These ions carry the charge by jumping from one hole in the network to another.[19] The voltage across the sample causes the ions to jump in a preferential direction, giving rise to the current. The small alkali ions, such as Li^+ and Na^+, seem to jump through the network more easily then the larger alkali ions, such as K^+.[20]

If modifier ions such as Ca^{2+}, Ba^{2+}, or Pb^{2+} are present, they, too, may fill the holes in the network. This can block some of the holes so Na^+ ions can no longer move through them,[21] reducing the conductivity.

The role of alumina in slags is uncertain. Al_2O_3 is not a network former, but the Al^{3+} ion may replace the Si^{4+} ion in the network, thus extending it.[22] This has been observed to increase the mobility of hydrogen ions,[23] increasing their contribution to the conductivity.

Sometimes an ion may become trapped in the network and prevented from carrying current. Thus, not all Na^+ ions are able to contribute to the conductivity.[24] Martin and Derge[25] have found a similar restriction on Ca^{2+} and Fe^{2+} ions.

More exotic ions may also carry current. The SiO_4^{4-} ion has been observed to migrate, contributing to the conductivity and forming SiO_2 at the anode.[26,27] This process has been observed in coal slag.[28]

The nature of the conductivity is changed if iron oxides are present in the slag. Many experimenters have shown that iron-containing slags and glasses show greatly enhanced conductivity due to an electronic contribution.[29-34] Trap and Stevels[35] have a list of methods used to determine whether a sample conducts by ionic processes or electronic ones.

Iron is multivalent in slags; it appears as Fe^{2+} and Fe^{3+}. Current is carried when electrons jump from the Fe^{2+} ions to the Fe^{3+} ions.[36] Trap and Stevels[37] have shown that at a given temperature the conductivity of an iron-containing sample is strongly dependent upon the ratio $f = Fe^{3+}/Fe^{2+}$ and upon the total iron content. They go on to explain that f is dependent upon the atmosphere surrounding the sample. Schuhmann and Ensio,[38] and Turkdogan[39] explain how oxygen in a furnace atmosphere affects f in iron-containing silicate slags. In measuring the conductivity of a slag, then, it is important to specify the iron content of the slag and the partial pressure of oxygen in the furnace atmosphere.

The ratio f may also depend upon the presence of platinum. Baak and Hornyak,[40] and Larson and Chipman[41] show that the reaction between iron and platinum changes the Fe^{3+}/Fe^{2+} equilibrium and the iron activity. They point out that platinum electrodes or crucibles may change f, giving a change in the measured conductivity.

Trap and Stevels[42] examine the relation between f and the conductivity. They find iron-containing glasses show strong electronic conductivity for $1.3 < f < 4.6$. The maximum in the conductivity occurs near $f = 2$.

Some iron-containing slags show a large ionic conductivity. This may happen at very high temperatures when the slag is molten and the alkali ions in the slag are highly mobile.[43] It may also happen as very low iron concentrations[44] if the iron ions are not close enough for the electron hopping mechanism to occur.

Recently, some work has been done on the electron band structure of glasses. This work is well summarized by Owen,[45] Mott,[46] and Davis.[47] Mott[48] also has written a general review of the theory of conduction in non-crystalline solids.

Studying the temperature dependence of conductivity in slags is an important part of MHD research.[49] The review papers previously mentioned and others,[50,51,52] cover the experimental results of slag and glass conductivity measurements in detail. So far few satisfactory theoretical studies have appeared on the electrical conductivity of a substance so complex as slag. Some simple models, however, do explain the important aspects of slag conductivity and provide helpful physical insight to experimenters.

Examine the electrical conductivity of a slag following the work of Owen.[53] Assume the network in the glass sets up potential wells through which the charge carriers must move. The structure of the network is aperiodic and there are several different ions in the network. The potential wells are not identical, and may resemble those in Figure 1. For simplicity, assume the wells are identical and periodic, as in Figure 2. Let the wells be of depth Q, separated by a distance λ.

At any temperature the charge carriers (ions) will oscillate in their wells. Let the frequency of this motion be b. Assume that the charge carriers have a Boltzmann distribution of energy, and they move along the X-axis. The probability that an ion will move to the left or right is

$$p = b\ e^{-Q/kT}.$$

When an electric field is applied to the slag the potential wells change shape, as in Figure 3. The left side of each well seems higher by the amount $\frac{1}{2}\, qE\, \lambda$, where E is the field strength and q is the charge on the ion. Similarly, the right side of each well seems lower by the same amount. This decreases the probability of a jump to the left to

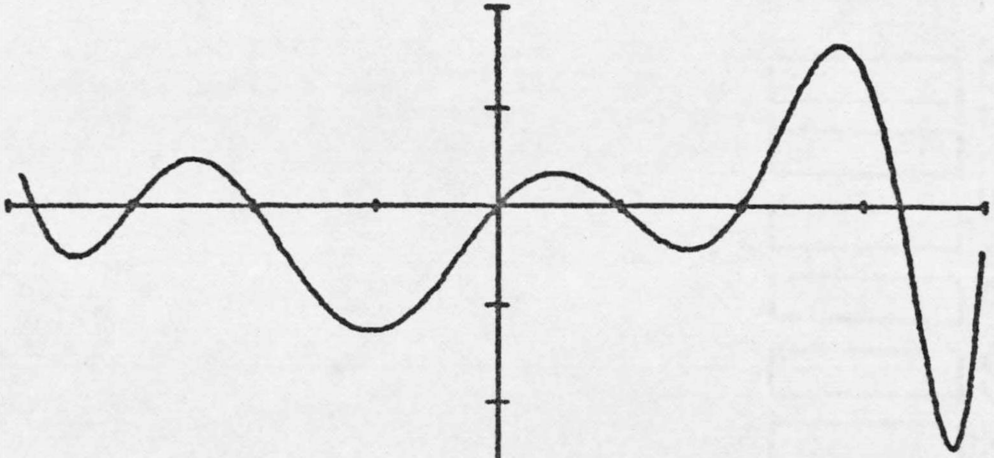

FIGURE 1. POTENTIAL WELLS IN A SLAG

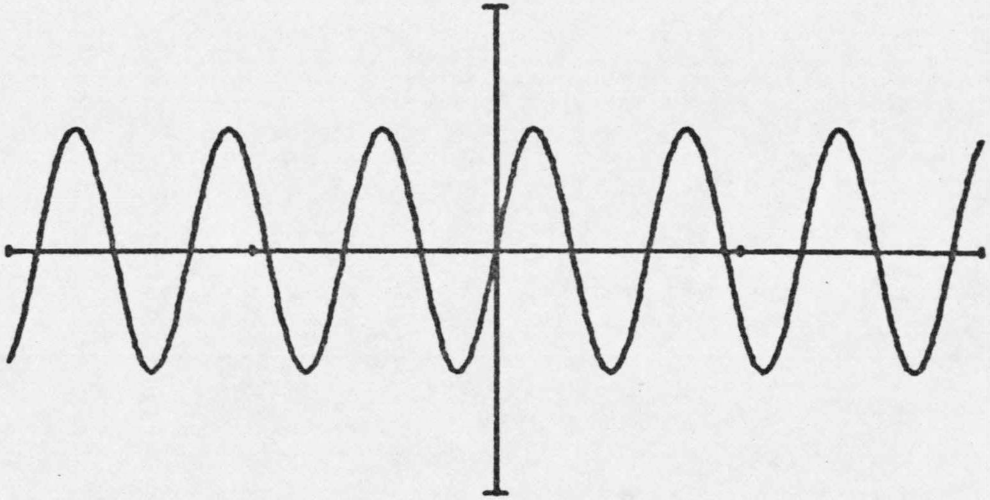

FIGURE 2. SIMPLIFIED, IDEAL POTENTIAL WELLS

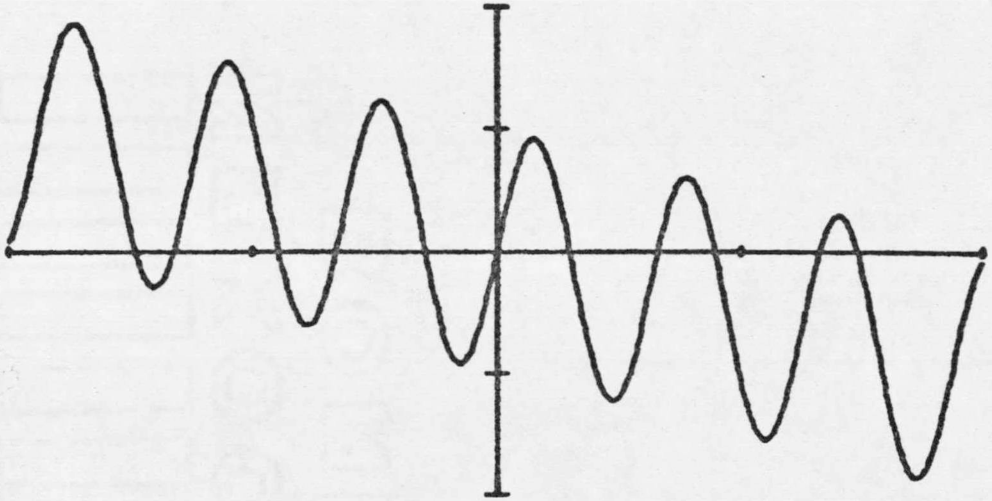

FIGURE 3. POTENTIAL WELLS IN AN ELECTRIC FIELD

$$p_\ell = \frac{1}{2}\, b\, e^{-(Q+\frac{1}{2}qE\lambda)/kT}$$

and increases the probability of a jump to the right to

$$p_r = \frac{1}{2}\, b\, e^{-(Q - \frac{1}{2}\, q\, E\, \lambda)/kT}.$$

Jumps to the right become more probable than jumps to the left, so current is carried. The main velocity of the ion drift is

$$\begin{aligned} \overline{\mu} &= \lambda(p_r - p_\ell) \\ &= \frac{1}{2}\, \lambda\, p(e^{qE\lambda/2kT} - e^{-qE\lambda/2kT}) \\ &= \lambda p \sinh \frac{qE\lambda}{2kT}. \end{aligned}$$

If $\frac{1}{2}qE\lambda << kT$, which holds for fields less than 10 V/cm at room temperatures and above, then

$$\overline{\mu} = \lambda p \sinh \frac{qE\lambda}{2kT} \simeq \frac{qE\lambda^2 p}{2kT} .$$

The current density due to this drift is

$$j = n\, q\, \overline{\mu} ,$$

where n is the number of mobile ions per cubic centimeter. This gives

$$\begin{aligned} j &= \frac{nq^2 E\lambda^2 p}{2kT} \\ &= \frac{nq^2 E\lambda^2 b}{2kT}\, e^{-Q/kT} . \end{aligned}$$

The conductivity, σ, is given by j/E, so

$$\sigma = \frac{nq^2\lambda^2 b}{2kT} e^{-Q/kT}$$

and

$$\ln \sigma = \ln \frac{nq^2\lambda^2 b}{2kT} - \frac{Q}{kT} = -A - \frac{B}{T} .$$

Many authors call QN (N is Avagadro's number) the activation energy. Trap and Stevels[54] have measured Q for several glasses and find $0.6 < Q < 1.1$ eV for $100°C < T < 300°C$. They point out that Q is a "rough average" of the actual potential barriers. It often shows a temperature dependence.

The quantity A is examined by Stevels[55] and Trap and Stevels.[56] They find that it is related to the probability of the jumps between wells. It has been measured, and generally falls in the range $-6 < A < 4$ for $100°C < T < 300°C$. They note that for the ionic conductors which were examined, A is usually in the range $1 \leq A < 4$, while for electronic conductors $-6 < A \leq 0$. This has been proposed as a method of distinguishing ionic conductors from electronic conductors.

In many experimental studies, ln σ is plotted versus $10^4/T°K$ or $10^3/T°K$. The theory shows why this is reasonable.

CHAPTER III

EXPERIMENTAL

The main purpose of the experimental work was to obtain electrical conductivities of slags up to 1750°C. An Astro 1000A Series furnace was used to provide these high temperatures. The furnace had a standard alumina muffle tube which separated the graphite heating elements from the slag samples. This prevented the inert atmosphere required by the heating elements from mixing with the oxygen-containing atmosphere used to study the slags.

Four important pieces of apparatus were added to the furnace: a temperature drive, a closed cooling system, a sample holder/electrode assembly, and a gas system for delivering controlled atmospheres to the sample. These are described below. Their development took a large part of the available research time.

The temperature drive used an accurately-regulated power supply and a clock-driven potentiometer to produce a small voltage. This small voltage was connected in series with the furnace's temperature control thermocouple which was connected to the temperature control apparatus of the furnace. The voltage coming from the potentiometer could be selected so its sum with the thermocouple voltage met the preset voltage requirement of the temperature controller. The clock-drive on the potentiometer could then be turned on. This would change the potentiometer's output voltage so the temperature controller would read a voltage different than the preset value. The temperature controller would then increase or decrease the power to the furnace. Thus, the furnace temperature could be raised or lowered as desired.

The Astro furnace needs a cooling system so that the elements which heat the furnace's working zone (to 1750°C or above) do not also melt the external structural members. The furnace's transformer and power leads must also be cooled. Usually cold tap water is used to cool the furnace. Unfortunately, local tap water is high in particulates, especially in spring and early summer when melt-water from the mountains carries soil and other matter into the reservoirs. These particles quickly clog laboratory filters and lodge in the small passages of the furnace's water jacket. Within 24 hours, filters become blocked, and the furnace is no longer properly cooled. In order to avoid these problems a closed cooling system was devised. It is shown schematically in Figure 4.

A Sears model 390.25310 three-quarter horsepower jet pump is mounted on top of a 30 gallon reservoir. The pump moves clean water (to which has been added some algicide) from the reservoir through the system. The water is sent to cool the furnace, then on to a heat exchanger. The heat exchanger cools the water which has just come from the furnace. This is done by running the warm water (from the furnace) through the core of the heat exchanger while cool tap water is run through the outer jacket of the heat exchanger. The tap water moves quickly enough and

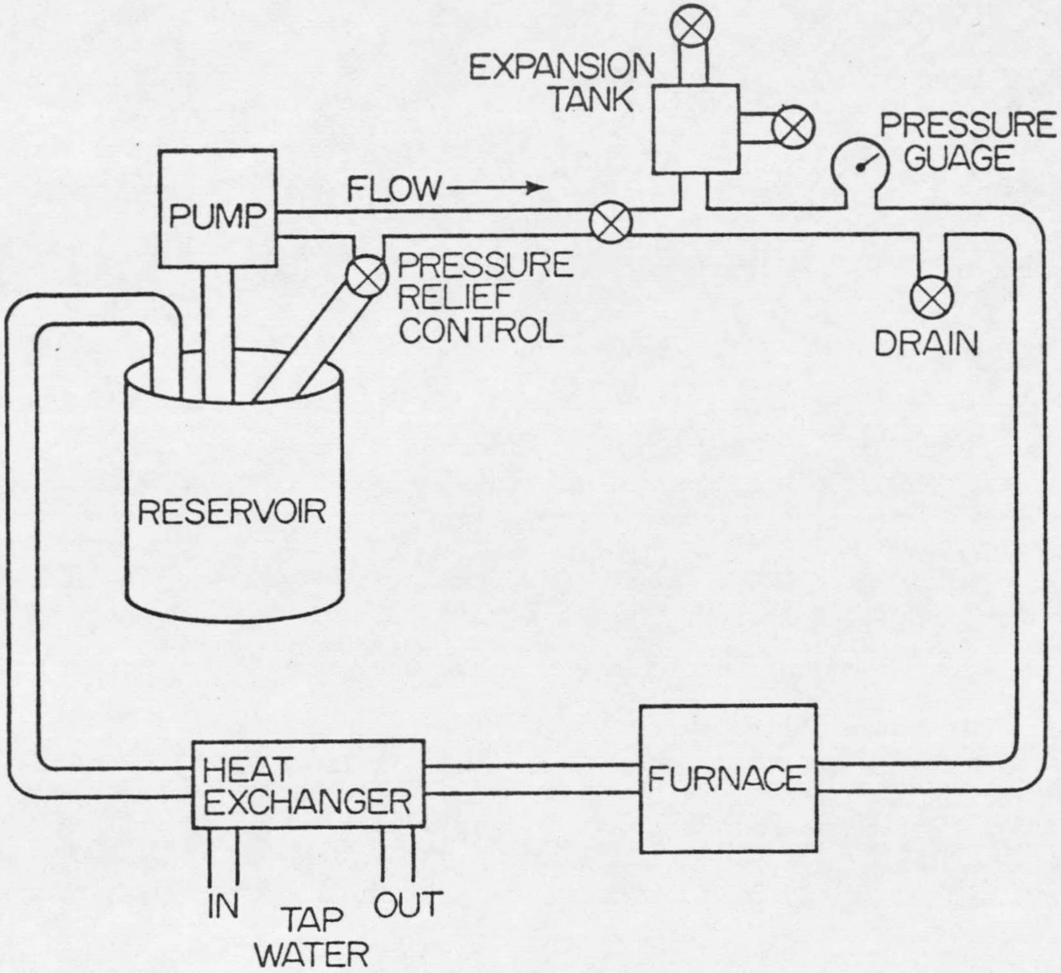

FIGURE 4 - SCHEMATIC REPRESENTATION OF THE FURNACE COOLING SYSTEM

the jacket of the heat exchanger is large enough that the particles in the tap water do not clog the heat exchanger. After leaving the heat exchanger, the water is returned to the reservoir. The tap water which leaves the heat exchanger is wasted during the winter, but during the summer it is used to water the lawn outside the laboratory.

The system contains a pressure relief control so the pump does not overdrive the system. There is a pressure gauge in the system which shows when the system is working properly. An expansion tank prevents quick changes of pressure in the lines. Several drains and cutoffs allow the lines to be emptied for repair.

The pump is connected to a relay so if the power goes off for longer than 15 seconds the pump will stay off. Should the power go off the furnace would quickly boil away the water sitting in its water jacket. If the pump were to come back on it would pump water into a hot water jacket, possibly causing an explosion.

A sample holder must be strong enough to avoid sagging at 1750°C. The original sample holder was too delicate, and fell apart under its own weight. Its sturdy replacement is shown in Figure 5. The main body parts (A, B, C, and D in the figure) are cylinders 3.8 cm (1.5") in diameter and 4.1 cm (1.625") long, made of Norton AN599 firebrick. In the center of the assembly, parts B and C, is a hollow area to accept a platinum crucible holding the slag. Holes .64 cm (.25") in diameter approach the hollow area axially from both ends. These allow alumina

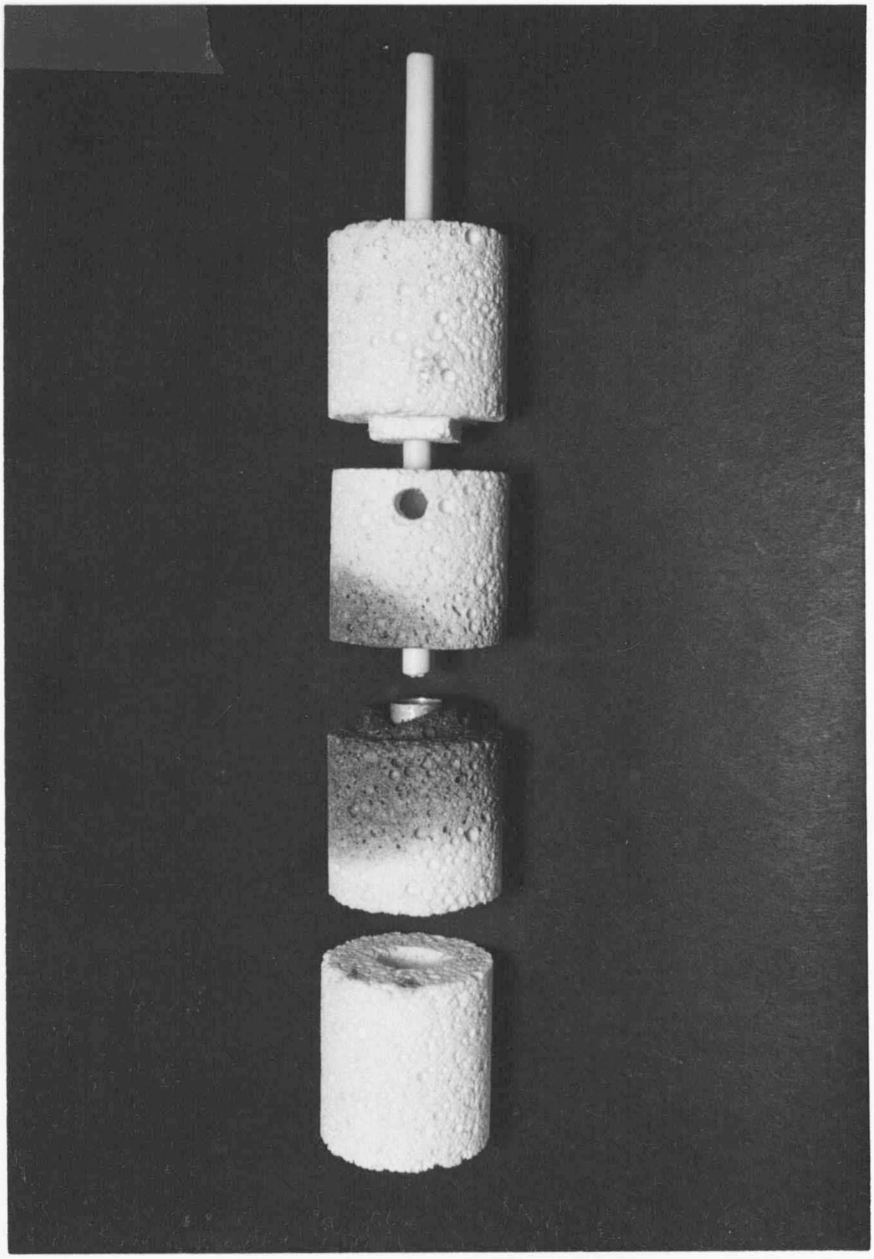

FIGURE 5. THE SAMPLE HOLDER

Part A is at the bottom, and part D is at the top. A crucible is visible in part B. The stains on parts B and C are from spilled slag.

tubes containing platinum electrodes and type B thermocouples access to the sample. The same tubes may carry a type K thermocouple (for accurate measurement of temperatures below 500°C) and the gas mixture used to control the atmosphere surrounding the sample. The entire sample rests on top of an alumina baffle inside the furnace, and is centered in the hottest part of the furnace.

At high temperatures, the bottom electrode forms a diffusion bond with the platinum crucible, giving excellent electrical contact and making the crucible one of the electrodes in contact with the slag. The top electrode is lowered into the molten slag to a depth of .49 cm using a threaded collar and bushing. They are shown in Figure 6, and are designed so the outer bushing turns, but the electrode does not. This keeps the electrode centered in the crucible to ensure accurate repeatable measurements.

In order to investigate the dependence of conductivity on oxygen content of the atmosphere, an atmosphere control system was assembled. It is shown schematically in Figure 7. The figure does not show the many shutoff values and fittings in the system.

There are two ways the oxygen in the atmosphere is controlled. One is by using mixtures of air and argon; the other is using mixtures of CO and CO_2. The air-argon method is used for oxygen partial pressures of 10^{-1} atmosphere to 10^{-4} atmosphere. The CO-CO_2 method may be used for

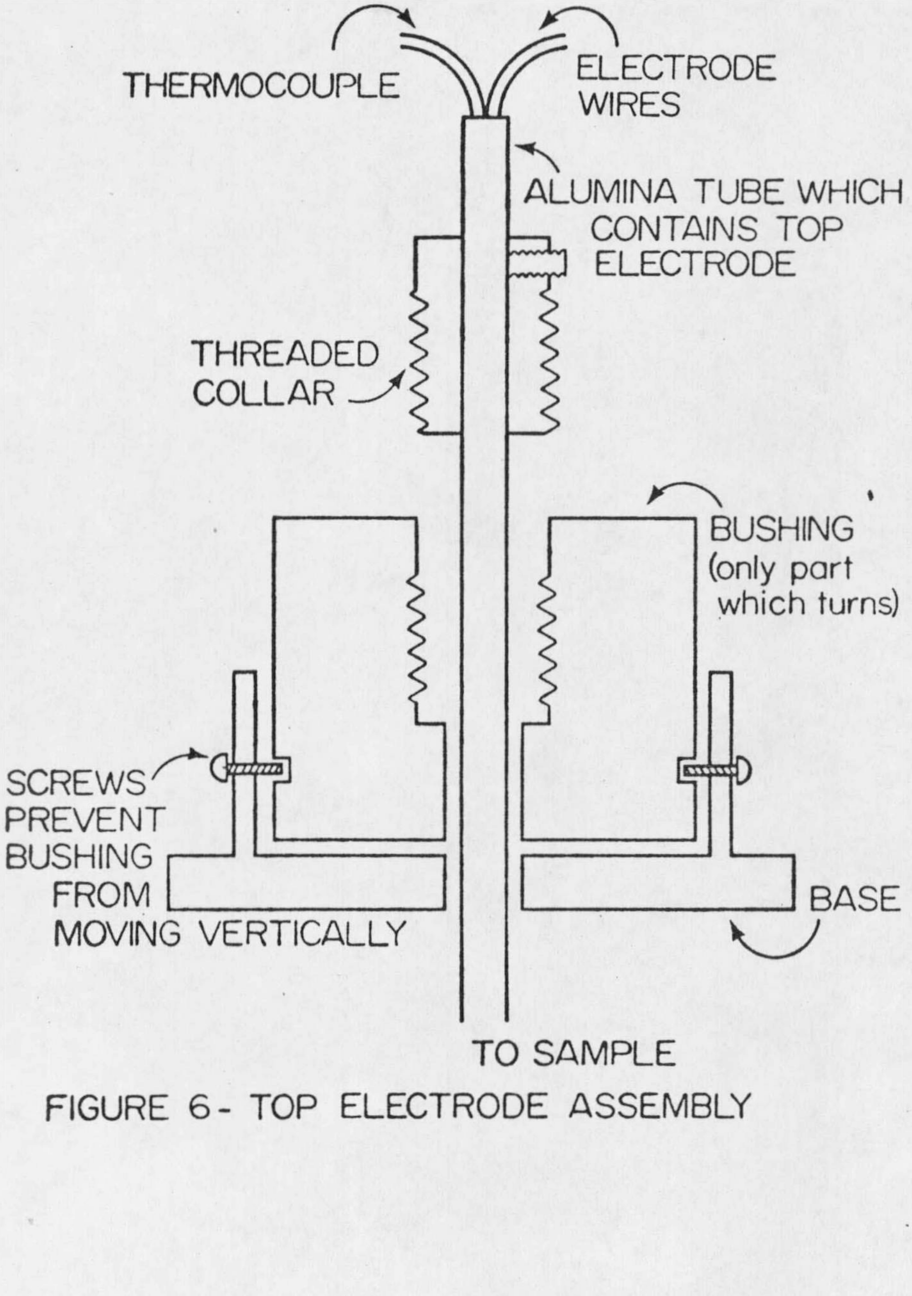

FIGURE 6- TOP ELECTRODE ASSEMBLY

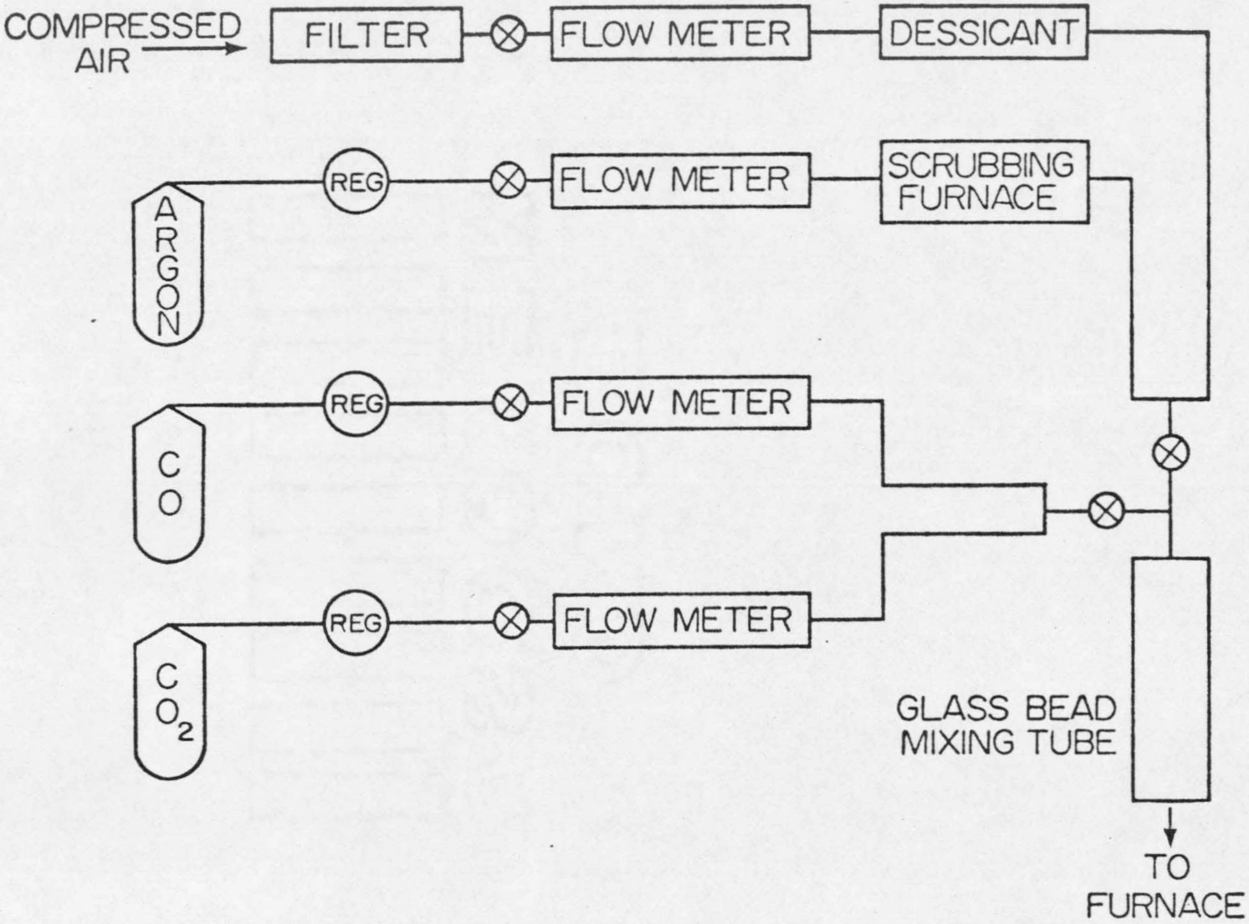

FIGURE 7- SCHEMATIC REPRESENTATION OF THE ATMOSPHERE CONTROL SYSTEM

oxygen partial pressures of 10^{-5} atmosphere to 10^{-8} atmosphere.

When in use, each gas goes directly to its own calibrated flowmeter which delivers the required amount of gas. When using the $CO-CO_2$ method, both gases then go immediately to the mixing tube, which is 30 cm long and 1 cm in diameter. It is filled with glass beads which cause turbulence, thereby mixing the gases.

Air and argon are cleaned before going to the mixing tube. This is done by passing the air through a desiccant, $CaSO_4$, to remove any water. The argon may be passed through a scrubbing furnace to remove oxygen.

From the mixing tube the gases go to the furnace. The gases pass up into the sample holder emerging just below the sample, thereby keeping the atmosphere near the sample constantly replenished. They pass out through the vents in part C of the sample holder, and from there travel out through the top of the furnace. The flow rate is slow enough for the gas to be at thermal equilibrium with the sample.

A description of how data were collected may be helpful in order to show how the various pieces of apparatus work together.

First, samples of slag were prepared by heating bottom ash (obtained from a local power plant) mixed with any necessary iron oxide or potassium oxide, in an alumina crucible. Each sample was heated to 1450°C for one to 24 hours. The samples were cooled quickly to produce a black, glassy slag.

The cooled sample was removed from the crucible and broken into small pieces no larger than 2 mm in diameter. These pieces were used to fill the platinum crucible which goes in the furnace. At least 2.5 grams, but no more than 2.9 grams, were necessary to fill the crucible.

Once the crucible was full the sample holder and electrodes were assembled. The crucible was placed in its well in firm contact with the lower electrode. The upper electrode was put into the furnace and lowered until it was about 1 cm above the crucible. At this point the cooling system and controlled atmosphere were turned on and the furnace was slowly heated to 1750°C.

Once the furnace was hot the top electrode was lowered 0.49 cm into the slag. The bridge was then used to measure R, C, and tan δ at 120, 1000, and 10,000 Hz. The temperature was allowed to drop to the next lower value, the sample was allowed at least 45 minutes to reach thermal equilibirum, R, C, and tan δ were measured again, the temperature was dropped again, and the process repeated until the lowest desired temperature was reached.

The atmosphere was then changed and the furnace set to reheat to 1750°C. Data points were taken, and the entire process repeated as necessary.

When all necessary data were taken the furnace was allowed to cool to room temperature, then turned off. The sample was removed through the top of the furnace and the top electrode was cut. The sample was saved for inspection.

Sometimes the atmosphere to the sample had to be changed between data points. The sample needed time to come into equilibrium with the new atmosphere. At least one hour was necessary at 1500°C, more time at lower temperatures. Whenever possible, the sample was allowed to reach equilibrium overnight.

After a sample was removed from the furnace and thoroughly inspected, the slag had to be removed from the crucible. This was done by soaking the crucibles in hydrofluoric acid. The acid was replaced every two or three days. It would dissolve all of the slag in about 6 days.

Occasionally the slag had to be dissolved using fused potassium bisulfate. The crucible would be left in the fused salt for about one hour, then removed and cooled to room temperature. A few minutes in boiling water would remove the leftover salt from the crucible. The HF treatment could then proceed.

At first, data points were taken in temperature increments of 50°C. When the conductivity was plotted against $10^4/T°K$, this method produced graphs with too many data points in the high-temperature region and too few in the low-temperature region. A new series of temperatures was chosen giving an even spacing of points on the $10^4/T°K$ graphs.

In order to measure R, C, and tan δ at the various temperatures, a Hewlett-Packard 4262A digital meter was used in the two-lead mode.

This meter can measure R, C, and tan δ to 0.3 percent accuracy. Measurements may be performed at 120 Hz, 1000 Hz, or 10,000 Hz. The range of the meter is 1 mΩ to 19.99 MΩ in resistance, 0.01 pF to 19.9 mF in capacitance, and 0.001 to 19.9 in dissipation.

Temperatures were measured by connecting the type B thermocouples to an Omega 400 thermocouple reader and the type K thermocouples to a Fluke 2100 A digital thermometer.

CHAPTER IV

MEANING OF MEASUREMENTS

An experimenter may measure either AC conductivity or DC conductivity and he may choose from several measuring techniques. The common techniques will be examined here; less common techniques are described in detail elsewhere.[57]

Measurements of DC conductivity may be performed by the two-electrode method or the four-electrode method. The two-electrode method uses two leads attached to the sample. A known constant current may be applied across the sample while the voltage necessary to maintain the current measured, or a known voltage may be applied and the current measured. In our laboratory the first method is used. In either case, the resistance is easily calculated, since $R = V/I$. To find the conductivity, the geometry of the sample must be known. If the sample is a cylinder with the electrodes on the ends $R = \rho \frac{\ell}{A}$, ℓ = length of cylinder, A = area of ends, so

$$\sigma = \frac{1}{\rho} = \frac{\ell}{AR} = \frac{\ell I}{AV} .$$

A problem with the two-electrode technique is that the sample often becomes polarized--the applied voltage causes a charge separation. This decreases the current flow (or equivalently, increases the voltage) causing the measured resistance to be falsely high so the conductivity is falsely low.

This problem may be avoided by using the four-electrode method. In this case, four electrodes are placed colinearly in the sample. The outer two electrodes are used to apply a constant current. The inner two electrodes are used to measure the voltage drop over the distance ℓ. The resistance is

$$R = \frac{V}{I} = \rho \frac{\ell}{A} , \text{ so}$$

$$\sigma = \frac{\ell}{RA} = \frac{I\ell}{VA} ,$$

where A is the cross-sectional area of the sample.

Most authors find the four-electrode method gives better sensitivity and reproducibility than the two-electrode method.[58-61] This is because the charge build-up, which causes polarization in the two-electrode method, is localized near the current electrodes. The voltage electrodes are not affected by the polarized region because they are outside it. Thus, the conductivity of the unpolarized sample is measured.

In practice, when DC conductivity is being measured, the current is turned on and a measurement is taken, then the current is reversed and another measurement is taken, then the current is turned off. This minimizes the effects of polarization and increases the reliability of the data.

The two-electrode technique is nearly always used for measuring AC conductivity. This is because the alternating current applied to the sample automatically causes the polarization to reverse, keeping the polarization effect to a minimum. The applied current is known, the resulting voltage is measured, and the resistance is calculated. The conductivity may be computed if the geometry of the sample is known. This is done by the same method followed in the DC case. Some more complex examples will be worked later in this chapter.

Actually, measuring the AC conductivity does not give complete information about the behavior of the slag. This is because the sample and electrodes act as a capacitor--the electrodes are the plates and the slag sample acts as an imperfect dielectric. This may be clarified by examining a capacitor, following the analysis of Holloway.[62]

The charge on a capacitor is given by

$$Q = CV.$$

For an ideal capacitor C is constant, so

$$\frac{dQ}{dt} = I = C\,\frac{dV}{dt}\ .$$

Let $V = V_o \sin \omega t$. Then

$$I = CV_o\ \omega \text{ COS } \omega t = V_o\ \omega\ C \sin\ (\omega t + \pi/2).$$

This shows that the current leads the voltage by π/2.

When a real dielectric is placed in the capacitor there will be a component of the current which is in phase with the voltage. This is because the dielectric allows some resistive current leakage between the plates, and because the dielectric takes a finite amount of time to polarize, which changes the electric fields in the capacitor (this will be clarified shortly). The total current is not $\pi/2$ out of phase, but some angle $(\pi/2 - \delta)$ out of phase. If

$$V = V_o \sin \omega t,$$

then

$$I = I_o \sin [\omega t + (\frac{\pi}{2} - \delta)] = I_o \cos (\omega t - \delta)$$

$$= (I_o \cos \delta) \cos \omega t + (I_o \sin \delta) \sin \omega t.$$

Now it is easy to see that the first term is $\pi/2$ out of phase with the voltage while the second is in phase with the voltage. The capacitor is still charged and discharged by the out-of-phase component, whose amplitude is related to C by

$$I_o \cos \delta = V_o \omega C ,$$

so

$$I_o = \frac{V_o \omega C}{\cos \delta} .$$

The in-phase component will dissipate energy according to

$$P = VI = V_o \sin \omega t \, I_o \sin \delta \sin \omega t$$

$$= V_o I_o \sin \delta \sin^2 \omega t .$$

Averaging over one period gives

$$\overline{P} = \frac{1}{2} V_o I_o \sin \delta ,$$

where δ is known as the loss angle. This expression may be rewritten

$$\overline{P} = \frac{1}{2} V_o \frac{V_o \omega C}{\cos \delta} \sin \delta$$

$$= \frac{1}{2} V_o^2 \omega C \tan \delta ,$$

with tan δ called the dissipation factor.

This system is seen to be equivalent to a capacitor with a large resistor R, in parallel. The energy dissipation takes place in the resistor, so

$$\frac{1}{2} \frac{V_o^2}{R} = \frac{1}{2} V_o^2 \omega C \tan \delta$$

$$R = \frac{1}{\omega C \tan \delta}$$

or, equivalently,

$$\tan \delta = \frac{1}{\omega c R} .$$

In order to get all the information about the slag R, C, and tan δ must be measured.

How does tan δ relate to the physical properties of the material? Again, examine a capacitor, this time following Owen.[63]

A vacuum-filled capacitor with charges $+\sigma$ and $-\sigma$ on its plates has an internal electric field

$$E = 4\pi\sigma .$$

If the capacitor is filled with a dielectric while the charges remain the same, the field becomes

$$E = \frac{4\pi\sigma}{\varepsilon_S} ,$$

where ε_S is the static dielectric constant. The change in the field may be attributed to a reduction in the charge, σ, by

$$P = \sigma(1 - \frac{1}{\varepsilon_S}) = \frac{\varepsilon_S - 1}{\varepsilon_S} \sigma .$$

P is the polarization of the dielectric. It is the result of displacement of bound charges in the atoms or molecules of the dielectric. This displacement does not happen instantaneously because the particles have some inertia and because they feel forces from nearby particles.

In order to separate the effects of the charge on the plates from the effects of the bound charges in the dielectric a new field, the electric displacement, is defined. It is labeled D, and

$$D = 4\pi\sigma .$$

In vacuum $D = E$, but in a dielectric

$$D = \varepsilon_S E = E + 4\pi P .$$

In an AC field, the time lag in P causes a phase difference between D and E which may be written as

$$E = E_o\, e^{i\omega t} ,$$

$$D = D_o\, e^{i(\omega t - \delta)} ,$$

where δ is the phase difference and ω is the applied frequency. Since

$$D = \varepsilon E,\ \varepsilon = \frac{D}{E} = \frac{D_o}{E_o} e^{-i\delta} = \varepsilon_S e^{-i\delta}$$

$$= \varepsilon_S \cos \delta - i\varepsilon_S \sin \delta ,$$

if $\varepsilon = \varepsilon' - i\varepsilon''$, then

$$\varepsilon' = \varepsilon_S \cos \delta,$$

$$\varepsilon'' = \varepsilon_S \sin \delta, \text{ and}$$

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'} .$$

This shows that the dissipation factor is due to the imaginary part of the dielectric constant.

The imaginary part of the dielectric constant should not be surprising. It has a simple physical interpretation revealed by examining Maxwell's equations.[64]

Ampere's Law says

$$\nabla \times H = \frac{4\pi}{C} J + \frac{1}{C}\frac{\partial D}{\partial t} .$$

For a medium which obeys Ohm's Law,

$$J = \sigma E, \quad \sigma = \text{electrical conductivity.}$$

Let the medium have a real dielectric constant ε_o, so $D = \varepsilon_o E$. Suppose $E = E_o e^{-i\omega t}$, where ω is the frequency of the electric field. Then

$$\begin{aligned} \nabla \times H &= \frac{4\pi\sigma}{C} E + \frac{\varepsilon_o}{C}\frac{\partial E}{\partial t} \\ &= \frac{4\pi\sigma}{C} E + \frac{\varepsilon_o}{C}(-i\omega) E \\ &= \frac{-i\omega}{C}\left(\varepsilon_o + \frac{4\pi i\sigma}{\omega}\right) E \\ &= \frac{-i\omega}{C}\varepsilon E , \end{aligned}$$

so $\varepsilon' = \varepsilon_o$, and

$$\varepsilon'' = \frac{4\pi\sigma}{\omega} .$$

The imaginary part of the dielectric constant, then, comes about because the slag has a non-zero conductivity.

To summarize, the slag in the conductivity cell acts as a dielectric with a complex dielectric constant, $\varepsilon = \varepsilon' - i\varepsilon''$. This produces a "leaky" capacitor described by the loss factor, tan δ, which gives rise to dielectric loss within the sample,

$$\overline{P} = \frac{1}{2} V_o^2 \omega C \tan \delta.$$

If the dielectric constant did not have an imaginary part, the slag would be a perfect insulator. This would mean coal-fired MHD generators could not work.

There are some other problems associated with both AC and DC electrical conductivity measurements. One important one is contact resistance. The electrodes must be in firm contact with the sample over a well-known area. In our laboratory, proper contact is assured by using the crucible as one electrode and inserting the other electrode to a known depth in the molten slag. Liquid slag "wets" the electrodes well and assures good contact after the slag solidifies.

Another problem, especially in DC work, is electrolysis of the sample. The current used to measure the conductivity may electrolyze elements or molecules in the sample. Thus, O_2 gas may be given off, and SiO_2 may form a glassy deposit around the anode.[65] This not only changes the composition of the sample, but may have a high resistance deposit near one of the electrodes.[66] Other experimenters note an evaporation of potassium from the sample[67] causing a depletion of these mobile ions.

A final problem is that of surface conduction. At times, there is less resistance between the electrodes along the surface of the sample than through the sample. The result is falsely low values for the resistance, so falsely high values for the conductivity. This problem may be eliminated for solid samples by using a three-electrode or five-electrode measuring technique.[68] Molten samples present a problem, for it is difficult to position the necessary guard rings accurately to use three-electrode or five-electrode techniques. To some extent, a proper design of the conductivity cell, one which has short distances between the electrodes through the bulk of the sample yet long ones across the surface, will minimize surface effects.

CHAPTER V

DATA REDUCTION

When data gathering was finished, the experimenter had a table of resistances of slags at various temperatures. These resistances were used to calculate conductivities by examining the geometry of the sample and its electrodes. Three methods were tried.

The first method was to assume the crucible had a simple shape and calculate the expected resistance. Actually, the crucible has tapered sides and looks like a thimble. Its diameter is 1.2 cm at the top and 1.0 cm at the bottom. It is 1.5 cm deep but usually filled to only .8 cm, The electrode is a cylinder of diameter .05 cm, and is inserted to a depth of .49 cm in the center of the sample. The sample with the crucible and electrode may be approximated by a cylinder or a hemisphere.

Resistance is defined as

$$R = \frac{V}{I} \qquad V = \text{voltage, } I = \text{current}$$

where $\quad I = \int j \cdot ds \qquad V = -\int E \cdot d\ell$

j is the current density, $j = \sigma E$, σ is the desired conductivity. This means

$$R = \frac{-\int E \cdot d\ell}{\int j \cdot ds} .$$

First, approximate the sample by a cylinder with a cylindrical electrode at the center. Gauss's Law gives the electric field between two cylinders as

$$E = \frac{q}{2\pi r} ,$$

where q is the charge on the inner cylinder (the charge is used as a computational device, it will drop out later). The voltage becomes

$$V = - \int_a^b \frac{q}{2\pi rh}\, dr = \frac{-q}{2\pi h} \int_a^b \frac{dr}{r} = - \frac{q}{2\pi h} \ln \frac{b}{a}$$

where b is the radius of the outer cylinder, and a the radius of the inner cylinder.

The current becomes

$$I = \int j \cdot ds = \int \sigma E \cdot ds = \frac{\sigma q}{2\pi h} \int \frac{ds}{r} = \frac{\sigma q}{2\pi h} \frac{2\pi rh}{r} = \sigma q \ .$$

This means

$$R = \frac{\frac{q}{2\pi h} \ln \frac{b}{a}}{\sigma q} = \frac{1}{2\pi h\sigma} \ln \frac{b}{a}$$

so $$\sigma = \frac{1}{2\pi hR} \ln \frac{b}{a} \ .$$

For our crucible, b = $\sim$.55 cm (since the crucible is not full to the top), a = .05 cm, h = .49 cm, so

$$\sigma = \frac{1}{2\pi(.49)R} \ln \frac{.55}{.05}$$

$$= \frac{.779}{R} \ .$$

The sample may also be approximated by a hemisphere with a concentric hemispherical electrode. Gauss's Law gives the field as

$$E = \frac{q}{2\pi r^2} \text{ , so}$$

$$V = \frac{-q}{2\pi} \int_a^b \frac{dr}{r^2} = \frac{q}{2\pi} \left(\frac{1}{b} - \frac{1}{a}\right) ,$$

where a is the radius of the electrode and b is the radius of the sample. The current becomes

$$I = \int \sigma E ds = \frac{\sigma q}{2\pi} \int \frac{ds}{r^2} = \frac{\sigma q}{2\pi} \frac{2\pi r^2}{r^2} = \sigma q .$$

This gives

$$R = \frac{\frac{q}{2\pi} \left(\frac{1}{b} - \frac{1}{a}\right)}{\sigma q} = \frac{1}{\sigma 2\pi} \left(\frac{1}{b} - \frac{1}{a}\right) ,$$

so $\sigma = \frac{1}{2\pi R} \left(\frac{1}{a} - \frac{1}{b}\right)$.

In this case, a = .05, b $\sim$ .55, so

$$\sigma = \frac{2.89}{R} .$$

The crucible is neither a cylinder nor a hemisphere, but something in between. The exact geometry is difficult to treat theoretically, so an experimental technique was used.

The crucible was filled to various depths with a potassium chloride solution of known conductivity, prepared according to the method of

Jones and Bradshaw.[69] The resistance of the known solution was measured at 120 Hz, 1000 Hz, and 10,000 Hz. It was found that near 2-1/2 turns of our standard screw the resistance was insensitive to small changes in electrode immersion depth. This corresponds to a depth of .49 cm. This depth was chosen as the standard immersion depth.

Following the conductivity cell calibration procedures of Jones and Bradshaw,[70] and Chiu and Fuoss,[71] it was found that

$$\sigma = \frac{.83}{R}$$

whenever the crucible was filled to a depth of .4 cm or more.

One final method was used to check the conductivity calculations. Some of the slags in this study had been studied by Pollina and Larsen.[72] Their values of σ were compared with the present values of R. It was found that $\sigma = \frac{.769}{R}$, though for some individual slags $\sigma = \frac{.625}{R}$ or $\sigma = \frac{.71}{R}$ proved more accurate.

A method evolved for calculating the final conductivities. If Pollina and Larsen had found the conductivity of a slag then its σ was computed by normalization to their data. If they had not studied a slag, then the formula $\sigma = \frac{.8}{R}$ was used because it well approximated the three formulas from KCl calibration, normalization to the other data, and the theoretical consideration of the cylinder.

CHAPTER VI

SOURCES OF ERROR

The possibility of errors in the conductivity measurements was investigated. Both systematic errors and reproducibility errors were considered.

To check for reproducibility errors the conductivity of one slag, Rosebud ash with 15 percent Fe_2O_3 added, was measured twice in an air atmosphere. Figure 8 shows the results. Even with the expanded scales in the figure the conductivities are indistinguishable. The reproducibility errors seem to be small, certainly less than ten percent of the measured conductivity, except near the phase transition at $\frac{10^4}{T} = 7.2$, where the error may be as high as 20 percent of the conductivity.

Systematic errors are more difficult to investigate. The conductivities in this paper agree with those of Pollina and Larsen. The values are very close above 1000°K, though at lower temperatures they may be different by one-half an order of magnitude. This could be due to the different thermal histories of the samples. Trap and Stevels[73] point out that this often happens.

Other sources of systematic error may be present. At times samples have changed composition at high temperatures. This may happen by electrolysis or evaporation. It may also be possible that the chemical analysis is not always accurate. This would mean correct data could be misinterpreted.

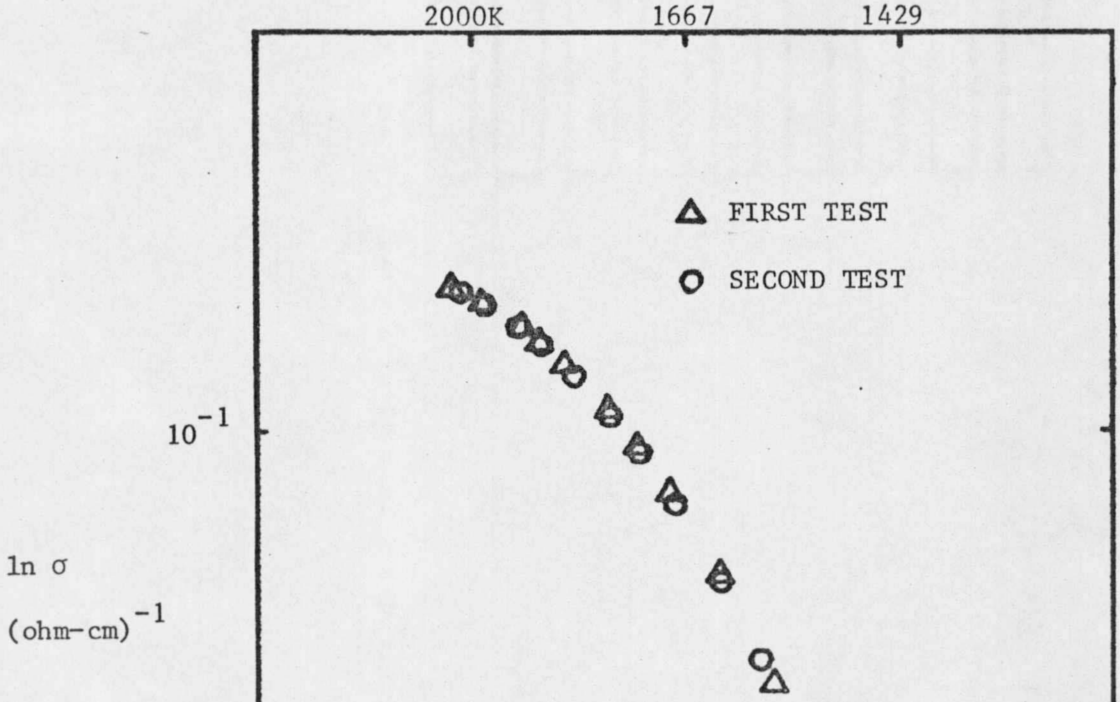

FIGURE 8. REPRODUCIBILITY CHECK USING ROSEBUD WITH 15% Fe_2O_3 ADDED

As pointed out earlier, the platinum crucibles and electrodes may be changing the Fe^{3+}/Fe^{2+} ratio, changing the electronic contribution to the conductivity. This problem will be investigated in the future using careful chemical analysis.

Another possible source of systematic error is leaks in the atmosphere control system. The tubes and connections are examined regularly and at present no leak problems have occurred.

Two more sources of error should be mentioned. The meters used to measure resistance and temperature must be accurate if the data are to be accurate. The Hewlett-Packard digital RC meter has been tested with standard resistors and found to be working at factory specifications. The three thermocouples used to monitor the temperature of the samples have been tested and found accurate to ± 2°K. So far these devices have not contributed significant errors to the measurements.

CHAPTER VII

DATA AND DISCUSSION

Six coal slags were selected for study--natural Montana Rosebud, natural Montana Rosebud with potassium seed added, natural Montana Rosebud with 15 percent iron oxide added, natural Montana Rosebud with 20 percent iron oxide added, Illinois #6 with potassium seed added, and New Hampshire with potassium seed added. The compositions of these slags are shown in Table 1. All the slags were measured at 120 Hz, 1000 Hz, and 10,000 Hz using the atmospheres listed in Table 2. This table also shows which slags were studied previously.

The natural Rosebud slag is made by heating ash produced by burning coal from the Rosebud seam. This ash was obtained from Montana Power Company's Corette Plant in Billings, Montana. The ash samples are homogenized before heating to assure uniform composition of the resulting slags.

The conductivities of the slags usually showed little frequency dependence. Comparison with the data of Pollina and Larsen show that their DC data and the present 120 Hz AC data are indistinguishable with two exceptions. The 1000 Hz and 10,000 Hz conductivities presented here are slightly higher than the 120 Hz conductivities, but still close to the DC values.

The two exceptions are illustrated in Figure 9 and Figure 10. Figure 9 shows the AC and DC conductivities of Rosebud with 20 percent

TABLE 1. Compositions of the Slags

Slag Oxide	Natural Rosebud	Rosebud Plus K_2O	Illinois #6	Rosebud Plus 15% Fe_2O_3	Seeded New Hampshire	Rosebud Plus 20% Fe_2O_3
SiO_2	41.6%	36.7	45	38.1	33.3	33.9
Al_2O_3	26.6%	23.4	20	24.3	18.7	20.6
CaO	19.6%	17.3	--	18.0	4.8	18.9
MgO	6.2%	5.5	--	5.6	1.1	4.9
Fe_2O_3	4.5%	5.0	11.3	17.2	19.6	23.7
K_2O	0.5%	11.8	12.6	0.5	15.1	0.4
Na_2O	0.5%	0.4	--	0.5	1.3	0.4

TABLE 2. Atmospheres Used With Each Slag

Slag	Atmospheres Used P_{O_2}	Studied by Pollina and Larsen?
Natural Rosebud	0.17 (air)	Yes
Rosebud plus K_2O	0.17	Yes
Illinois #6	0.17	No
Rosebud plus 15% Fe_2O_3	0.17, 10^{-4}, 10^{-6}	Yes
Seeded New Hampshire	0.17, 10^{-3}	Yes
Rosebud plus 20% Fe_2O_3	0.17, 10^{-4}	No

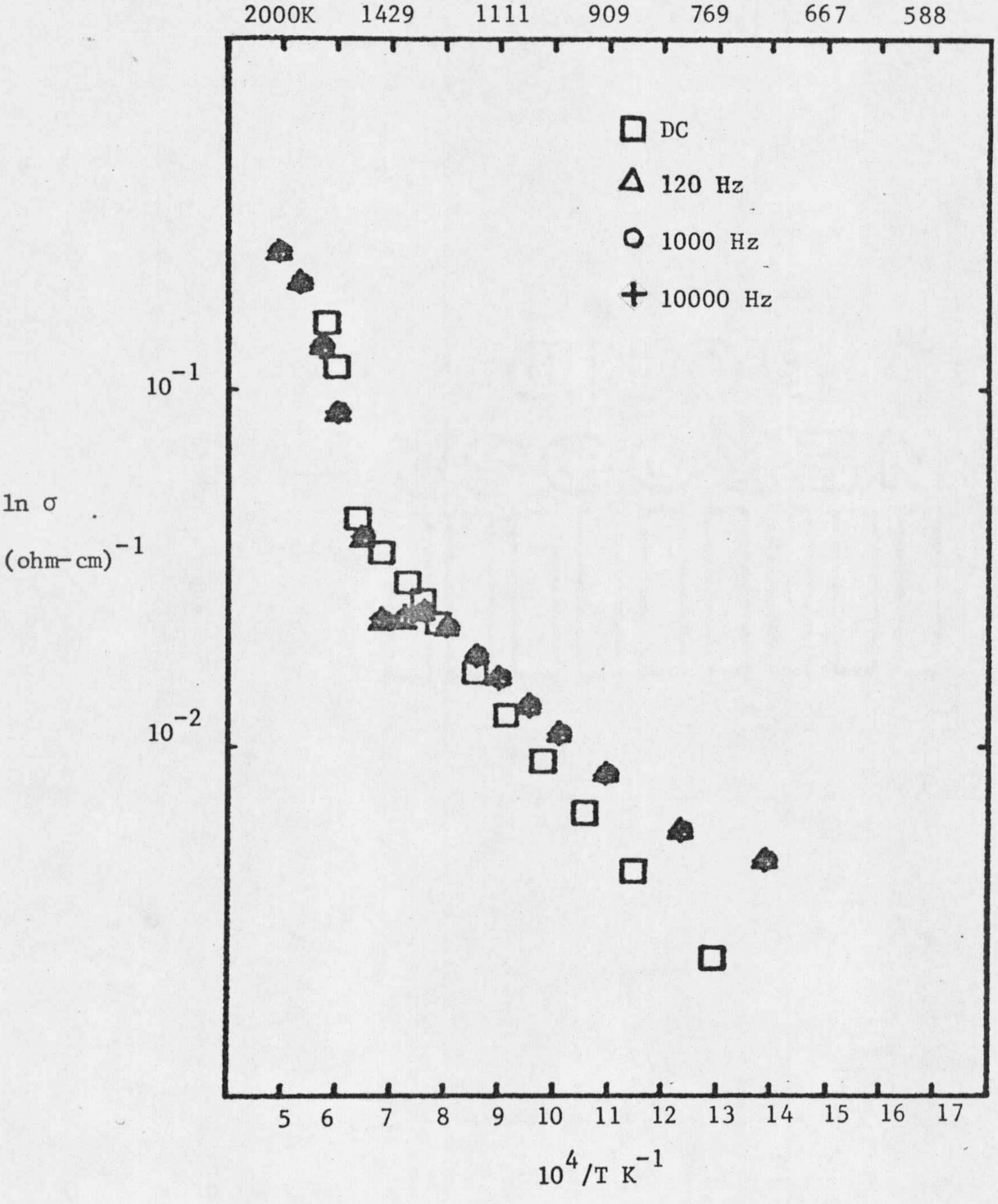

FIGURE 9. AC AND DC CONDUCTIVITIES OF ROSEBUD WITH 20% Fe_2O_3 ADDED

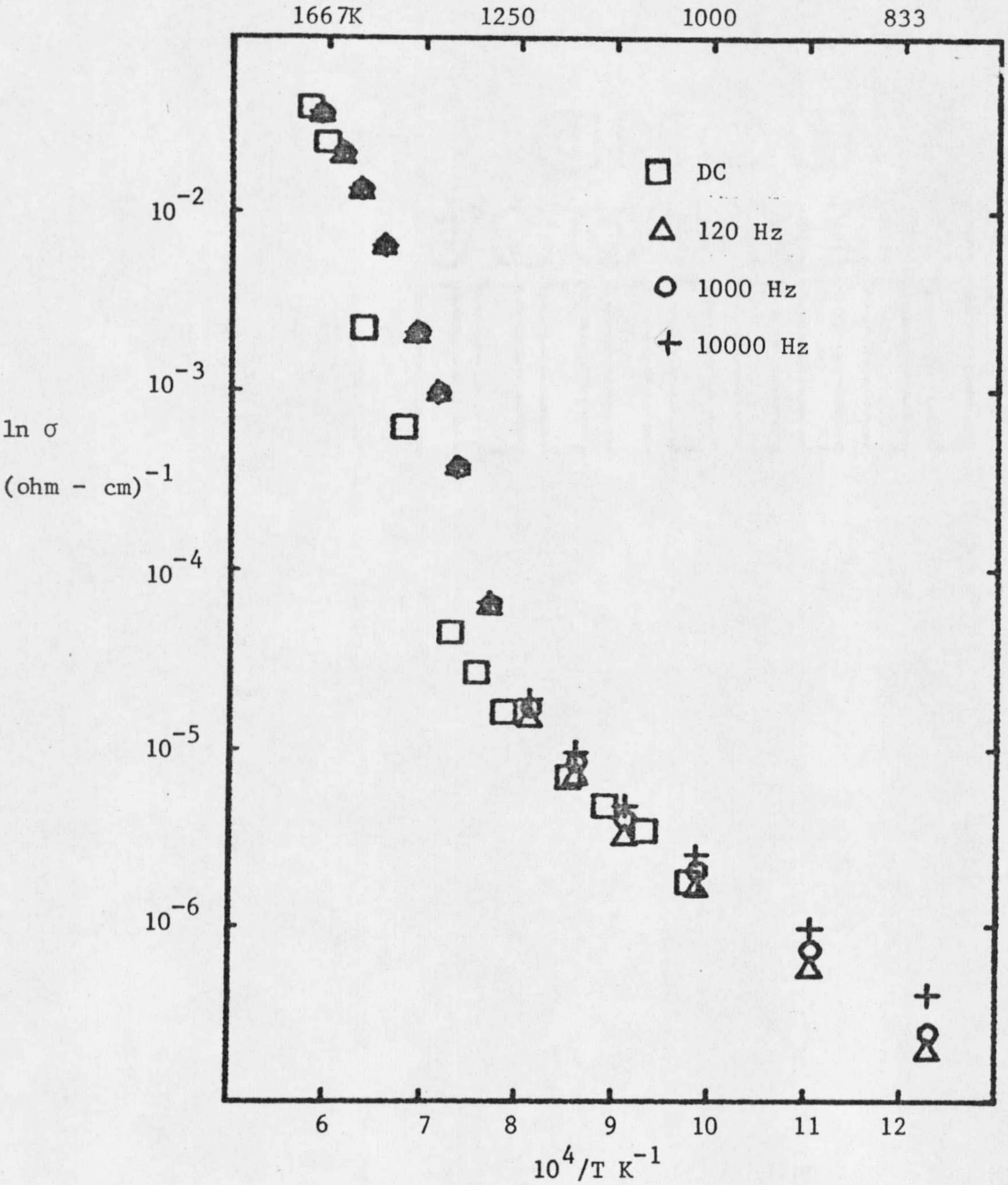

FIGURE 10. LOW-TEMPERATURE CONDUCTIVITY OF NATURAL ROSEBUD

iron added. Near $10^4/T = 7\ K^{-1}$ there is frequency dependence of the conductivity thought to be associated with the phase transition at that temperature.[74] The AC conductivities are all very close, but the DC conductivity is somewhat different. So far no good explanation has been found for this behavior, though it shows up in all of the samples with known DC conductivity.

The low-temperature conductivities of natural Rosebud slag are shown in Figure 10. In this case, the AC values are frequency-dependent near $10^4/T = 10\ K^{-1}$, but the DC value and the 120 Hz value remain close. This is the region in which the slag first seems to be a solid rather than a viscous liquid.[75] Other slags, including Illinois #6 and Rosebud with seed, show the same low-temperature frequency dependence. Figure 10 also shows the separation of the AC and DC conductivities near the phase transition at $10^4/T = 7.2\ K^{-1}$.

The phase transitions in natural Rosebud slag have been studied previously.[76] The transition at $10^4/T \sim 6.1\ K^{-1}$ is associated with the crystallization of anorthite from the liquid slags. The transition at $10^4/T \sim 7.2\ K^{-1}$ is associated with the crystallization of other materials.

In order to simplify the graphs, only the 120 Hz conductivity will be plotted to represent the AC data, except when low temperatures are examined. Figures 9 and 10 justify this procedure.

The slags showed little atmosphere dependence of the conductivity. Figure 11 shows the 120 Hz conductivity of Rosebud slag with 20 percent iron oxide added for $PO_2=0.17$ atm. (air) and $PO_2 = 10^{-4}$ atm. The two curves are similar; they separate near the point $10^4/T = 7\ K^{-1}$, then rejoin, then separate again at low temperatures. This behavior is typical of all the slags examined though most others show less atmosphere dependence, and only New Hampshire, with seed added, shows as much as Rosebud with 20 percent iron added. The conductivities differ by less than one-half an order of magnitude, about the same as the difference found by Pollina and Larsen for the same slags in the same atmospheres.

The atmosphere dependence of the conductivity in these slags may be related to their high iron content. It was mentioned earlier that the ratio f changes with the oxygen content of the atmosphere, and that a change in f can change the electronic component of the conductivity. High iron slags often show electronic conductivity at low temperatures ($10^4/T > 8\ K^{-1}$) so the atmosphere dependence at low temperatures is not surprising.

Figure 12 gives the conductivity at 120 Hz in air for all six slags. This figure has two striking features--all the slags have similar conductivity for $10^4/T \leq 6.5\ K^{-1}$ ($T > 1540°K$), yet they separate quickly below that point, and the conductivity of each slag falls along a nearly straight line. These features can be roughly explained, or at least

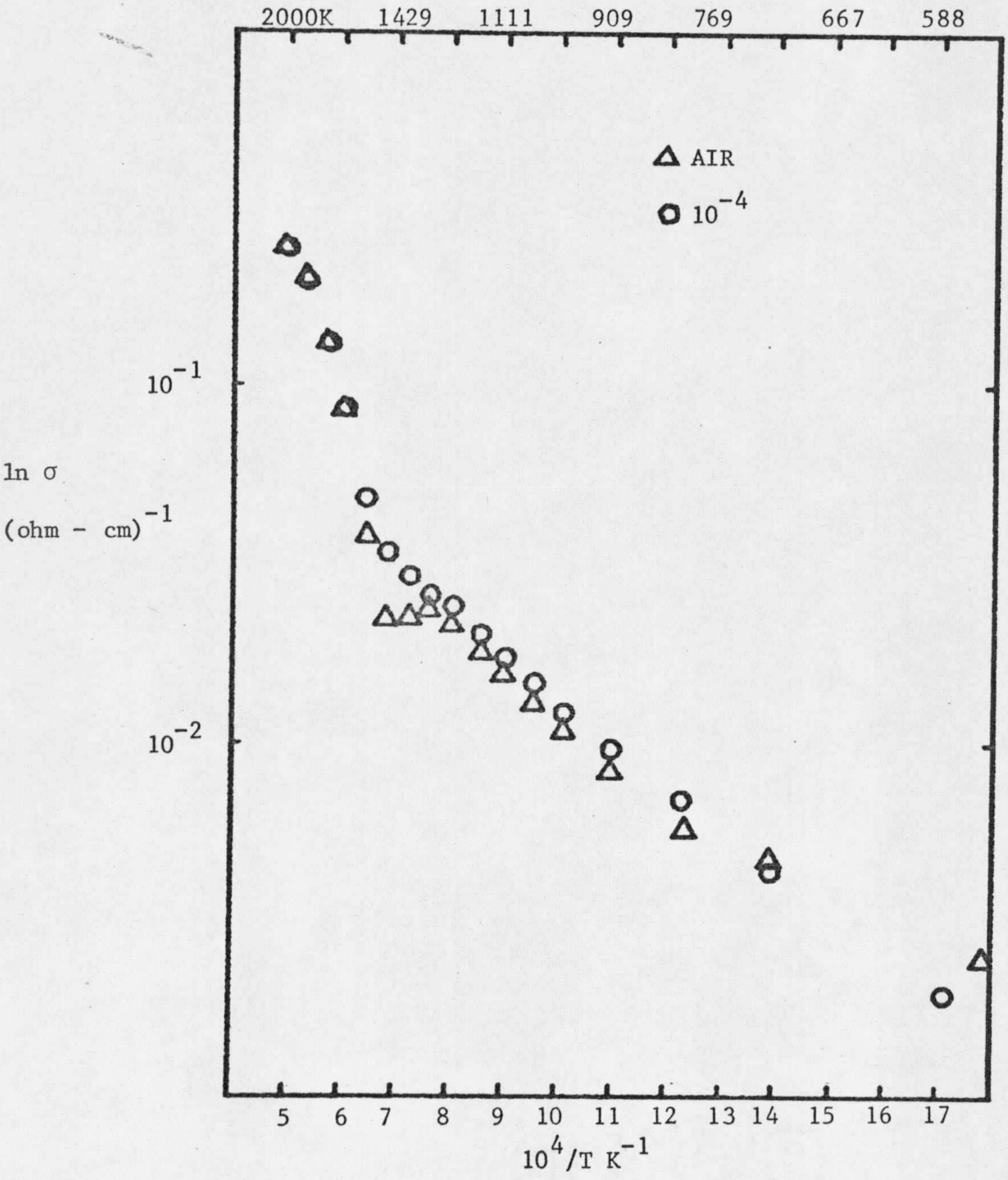

FIGURE 11. ATMOSPHERE DEPENDENCE OF ROSEBUD WITH 20% Fe_2O_3 ADDED

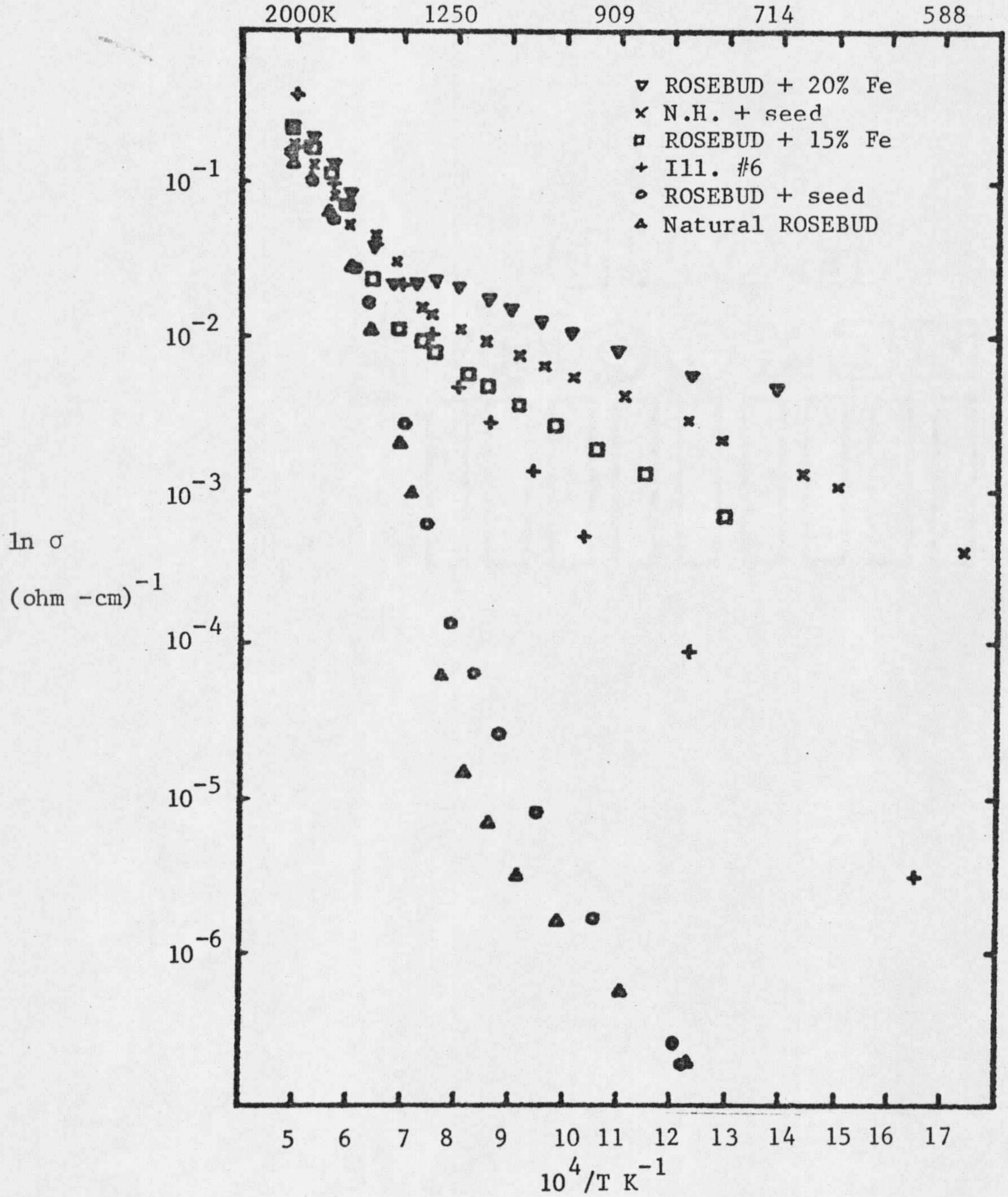

FIGURE 12. 120 Hz CONDUCTIVITY IN AIR FOR ALL SIX SLAGS

understood, using the concepts mentioned in Chapter II.

The similarity of the conductivities when $10^4/T < 6.5\ K^{-1}$ indicates that all the slags probably have the same conductivity mechanism in that region. At these high temperatures, the glass network has broken down, so almost all the ions are mobile and contributing to the conductivity. The iron ions are no longer organized by the network into centers for electronic motion. Instead, the iron ions themselves move and contribute to the ionic conductivity along with the other ions. Since the slags are mostly SiO_2 and Al_2O_3, and often contain Na_2O and K_2O, the ionic complexes involving Si and Al, and the Na^+ and K^+ ions may dominate the conductivity, leaving a less obvious dependence of the conductivity on iron concentration. This may also explain the lack of atmosphere dependence of the conductivity at these temperatures as shown in Figure 11. This atmosphere insensitivity at high temperature is shown in more detail in Figure 13; this time the slag is Rosebud with 15 percent iron added.

At lower temperatures, the network is well formed in the slag. Each slag has a different composition, so the shapes and spacings of the potential wells through which the current carriers move are different for each slag. This gives different values of the activation energy and different porbabilities that a current-carrying ion will jump between wells. That is, the values of A and B in the equation

$$\ln \sigma = -A - \frac{B}{T}$$

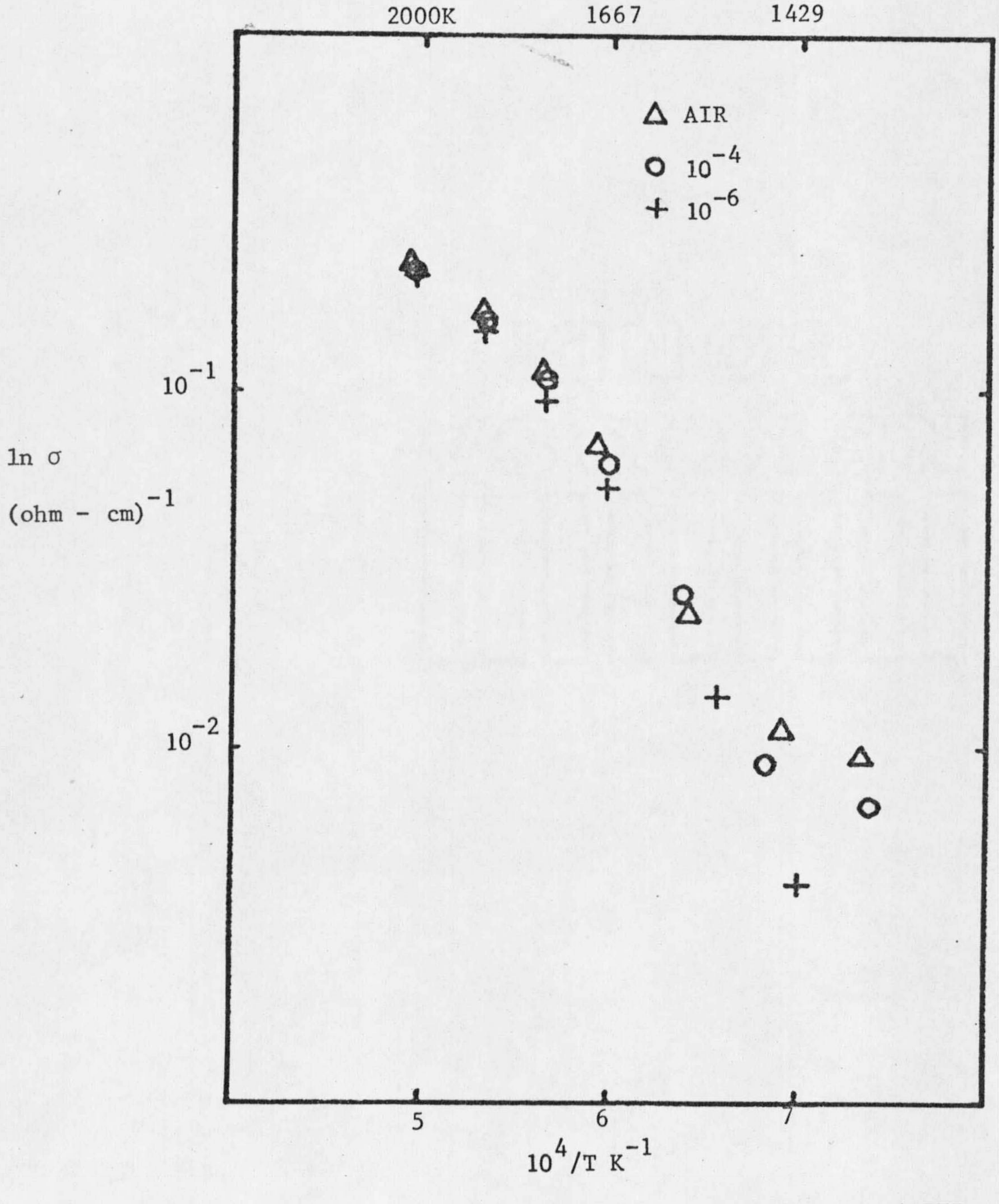

FIGURE 13. ATMOSPHERE DEPENDENCE OF ROSEBUD WITH 15% Fe_2O_3 ADDED

may be different for each slag, resulting in different conductivities.

The data points for each slag fall in nearly straight lines because A and B are nearly independent of temperature. Plotting ln σ versus 1/T should give a straight line with negative slope, as is the case. The data do not fall exactly on a straight line because A and B do have some temperature dependence and because phase changes or crystallization may be taking place in the slag.

At $10^4/T = 6.5\ K^{-1}$, the conductivity does not have a discontinuity; instead there is a smooth transition from the disorganized high-temperature region to the more organized low-temperature region. This is because the network of a glassy slag does not have a specific temperature at which it breaks down, but a range in temperature over which the breakdown occurs. For these slags the range seems to start at about $10^4/T = 7$ (1429°K) and end at about $10^4/T = 6$ (1667°K). This is the region in which crystallization takes place and strongly alters the nature of the glassy state. Thermal diffusivity measurements show no appreciable crystallization occurring below $10^4/T = 7.9\ K^{-1}$.[77]

It is interesting to compare the conductivities and compositions of the slags to see how the additions of various oxides change the conductivity. For this comparison, Figure 12 and Table 1 are important. Natural Rosebud slag will be used as a standard reference.

First, notice how the addition of iron oxide improves the conductivity of the slag. The Rosebud slag with 20 percent iron oxide added has consistently high conductivity; at 800°K its conductivity is four and one-half orders of magnitude higher than the conductivity of natural Rosebud slag. Rosebud slag with 15 percent iron oxide added is a good conductor too, and is almost four orders of magnitude above natural Rosebud slag.

The New Hampshire slag with potassium seed is an excellent conductor as well. It has more iron oxide than the Rosebud slag with 15 percent iron oxide added (17.6 percent versus 17.1 percent) but it has so much potassium that its conductivity is consistently higher, though not as high as the conductivity of Rosebud slag with 20 percent iron added (23.7 percent total iron oxide).

Examining the other slags, the conductivity of Rosebud slag with potassium seed added is low and generally similar to the conductivity of natural Rosebud slag. This may be because the K_2O content of the seeded slag is moderate, only 11.8 percent, while the CaO content is high, 17.3 percent. Calcium ions may be present in sufficient numbers to block the potassium ions from carrying current. Pollina and Larsen[78] have found that Rosebud slags enriched to 30 percent K_2O have high conductivities nearly matching those of Rosebud slag with 15 percent iron oxide added.

The conductivity of Illinois #6 with potassium seed added is more difficult to explain. This slag has a moderate amount of Fe_2O_3, 11.3 percent, and a moderate amount of K_2O, 12.6 percent. Apparently there is not enough iron or potassium to give this slag a conductivity as high as some of the others, though its conductivity is still almost three orders of magnitude higher than that of natural Rosebud slag.

After examining these slags it is tempting to say that the effect of iron and potassium oxides is additive, that is, the increase of the conductivity from adding potassium is independent of the increase from adding iron. As a first approximation this may be true, but more detailed examination shows that the statement should be made with caution.

Adding iron oxide reduces the percentage of potassium oxide in the slag, which may decrease the contribution to the conductivity from potassium. At the same time the percentage of blocking oxides, such as CaO, is reduced. This may increase the contribution of the potassium by reducing the blocking effect (this effect was described in Chapter II). Then, too, the addition of iron oxide decreases the percentage of SiO_2 and Al_2O_3, causing changes in the network on which the slag is based. This may have a large effect on the size and separation of the holes in the network and the separation of Fe^{2+} and Fe^{3+} ions. These sizes and separations determine the conductivity of the slag.

A complete model of slag conductivity would be very complex and difficult to quantify. For the present, it is encouraging to find that adequate explanations of slag conductivity can be made from simple considerations of composition and charge-carrier movement.

CHAPTER VIII

SUMMARY AND CONCLUSIONS

This work is part of a study of the electrical conductivity of coal slags to 2025°K involving systematic variation of chemical compositions and furnace atmospheres. The experimental part of this work involved building a new sample holder and electrode assembly, described in Chapter III.

Examination of the literature and theory of glasses and slags showed that a glassy slag is made of a network formed by SiO_4 tetrahedra and often supplemented by Al_2O_3. Network modifiers such as Na_2O and K_2O are responsible for most of the ionic conductivity, though other modifiers such as CaO may block this process. The presence of Fe^{2+} and Fe^{3+}, whose ratio depends on temperature, pressure, and chemical composition, provides a mechanism for electronic conductivity—electrons may hop from the Fe^{2+} to the Fe^{3+} ions. All this may be synthesized into a simple theory of the temperature dependence of the conductivity, with the result

$$\ln \sigma = - A - \frac{B}{T} .$$

A and B may be related to the composition and structure of the slag, or computed from electrical conductivity data.

Measuring only the AC resistance of a slag does not give complete information about the slag's behavior. Careful experimentation demands that the capacitance and loss factor be measured too. This reveals that slag acts as a dielectric with a complex dielectric constant.

Theoretical and experimental examination of the conductivity cell provided a method for computing a slag's conductivity from its measured resistance. The data, plotted in the previous chapter, show the effects of iron oxide and potassium oxide on slag conductivity. All the slags studied appear to share a common conductivity mechanism at high temperatures, but at low temperatures differences appear which may be understood by applying the equation

$$\ln \sigma = - A - \frac{B}{T} .$$

It has been seen that the electrical conductivity of Rosebud slags (and other slags) can be increased by the addition of oxides. This information will be used by the designers of MHD electrodes to choose the proper seeded slags for efficient use of MHD generators.

Knowing the conductivity of iron-containing slags may be important, for several researchers have proposed using iron-containing electrodes in MHD generators.[79] High-iron slags may be more compatible with these electrodes than low-iron slags. It is also possible that some iron may be transferred from the electrodes to the slag. This would change the conductivity of the slag and may result in extra factors to be considered in electrode design.

Some more specific conclusions can be drawn. The apparatus has worked remarkably well--still, several spare parts for the sample holder and electrodes should be kept on hand. The Norton AN599 firebrick used for the sample holder is easy to shape, durable, and absorbs spilled slag well, protecting the furnace from corrosion.

The top electrode was easy to lower into the slag to the required depth, but some fiduciary marks would be helpful for counting the turns of the bushing. Closer tolerances between the bushing and its mounting would make it easier to center the electrode in the crucible.

Much has been said about ionic and electronic conductivity and how they may be enhanced. It is often said that adding potassium oxide increases the ionic conductivity and adding iron oxide increases the electronic conductivity, but no experiments have been performed to prove this is true. Still, work of other investigators outlined in Chapter II and the graphs and tables in the previous chapter support these conclusions. Adding moderate amounts of iron oxide to a slag, 15 percent for instance, has a large effect on the conductivity, while adding as much as 25 percent potassium oxide does not increase the conductivity as much. It is unlikely that the iron ions themselves move in the glassy state, yet the small potassium ions are known to move easily through glass networks. The two oxides seem to participate in different processes, that is, electronic and ionic ones.

The atmosphere dependence of the conductivities is similar to that found by Pollina and Larsen. This indicates that the atmosphere control system works well, and that the platinum crucible and electrodes do not significantly interfere with the ratio f = Fe^{3+}/Fe^{2+}. This lack of interference may be because the crucibles and electrodes are only 60 percent platinum and 40 percent rhodium. The properties of this alloy may be different from those of the pure metal. In any case, the apparatus will be used for more thorough studies of the relationship between oxygen content of the atmosphere and conductivity.

Finally, even though the "theory" of slag conductivity is just a loose association of rules of thumb and oversimple equations, it is useful for explaining and understanding the electrical conductivity of real slags. Slags are difficult to study because they have no fixed composition or specific structure, but perhaps the present interest in slags and glasses will lead to a more satisfying theory.

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Westpfahl, David John
Electrical conductivity of MHD coal slags to 2025°K

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