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

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 In ς = - 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.

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Date August 14, 1978

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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

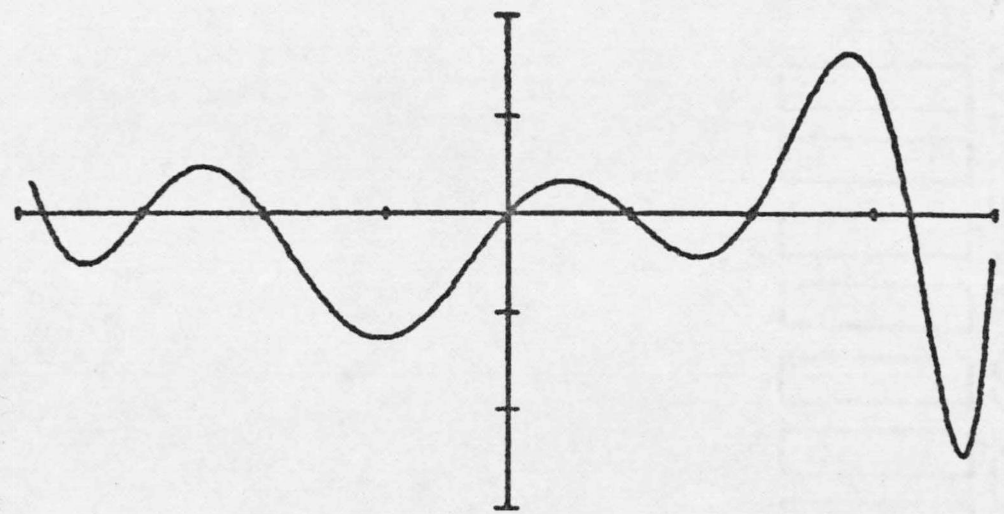

FIGURE 1. POTENTIAL WELLS IN A SLAG

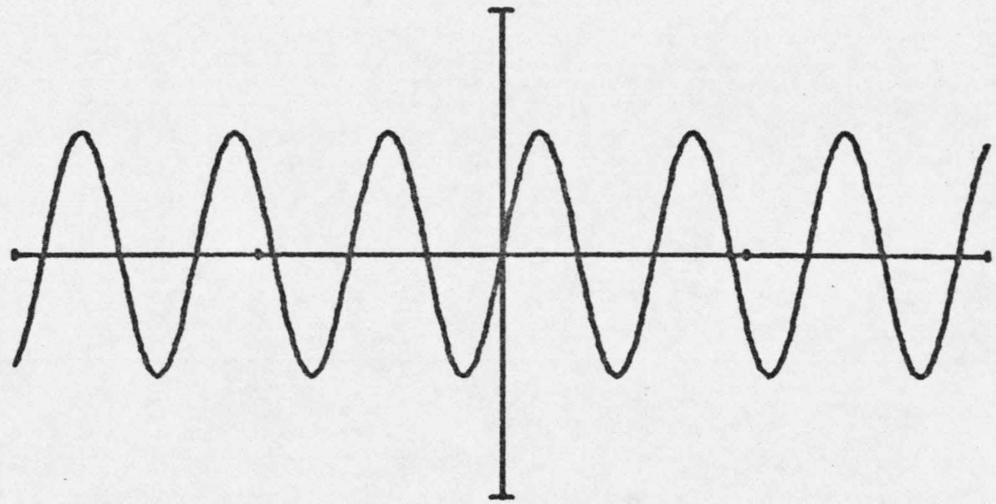

FIGURE 2. SIMPLIFIED, IDEAL POTENTIAL WELLS