



Thermionic emission from synthetic coal slags and MHD electrode materials
by Mark Lowell Wilson

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

Montana State University

© Copyright by Mark Lowell Wilson (1978)

Abstract:

The effective work functions for several synthetic coal slags and lanthanum chromite based ceramics were obtained using thermionic techniques. The effective work functions of the low silica coal slags that contained potassium were found to be about 3 eV at low temperatures, and about 4 eV at higher temperatures. The effective work functions for the high silica coal slags that contained potassium were found to be close to the effective work function of the slag which contained no potassium. X—ray fluorescence studies showed that substantial amounts of potassium had been lost from the high silica coal slags in their initial heating. The effective work functions for the Sr and Mg-Al doped ceramics were determined to be 3.28 eV and 3.13 eV respectively.

N378
W693

THERMIONIC EMISSION FROM SYNTHETIC COAL
SLAGS AND MHD ELECTRODE MATERIALS

by

MARK LOWELL WILSON

A thesis submitted in partial fulfillment
of the requirements for the degree

of

MASTER OF SCIENCE

in

Physics

Approved:

James R. Anderson
Chairperson, Graduate Committee

[Signature]
Head, Major Department

Henry L. Parsons
Graduate Dean

MONTANA STATE UNIVERSITY
Bozeman, Montana

August, 1978

STATEMENT OF PERMISSION TO COPY

In presenting this thesis in partial fulfillment of the requirements for an advanced degree at Montana State University, I agree that the Library shall make it freely available for inspection. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by my major professor, or, in his absence, by the Director of Libraries. It is understood that any copying or publication of this thesis for financial gain shall not be allowed without my written permission.

Signature

Mark L. Wilson

Date

August 3, 1978

ACKNOWLEDGMENTS

The author is grateful for the financial support of Montana State University (1976-1978). He is very grateful to Dr. James Anderson for his advice and encouragement in the accomplishment of this work. He wishes to thank Dr. Walter Anderson and Dr. Gerald Lapeyre for their help and guidance.

A special thanks must be given to his wife, Susan, for providing much of the motivation the author has needed. Finally, the author wishes to thank his mother Margaret L. Cutler for her support and Diane Stovall for typing the manuscript.

TABLE OF CONTENTS

<u>CHAPTER</u>		<u>PAGE</u>
I	Introduction	1
II	Theory	6
III	Experimental Techniques	20
IV	Experimental Results	40
V	Discussion and Conclusions	69
	Literature Cited	72

LIST OF TABLES

TABLE		PAGE
1	Composition of slags and ceramics	25
2	Potassium loss from high silica slags	49
3	Temperature dependence coefficients for high silica slags	62
4	Potassium content and loss from K510 after heating (20% K_2O before heating)	64

LIST OF FIGURES

FIGURE		PAGE
1	Conceptual diagram of a MHD channel	2
2	Potential energy diagram near the surface of an emitter . .	12
3	An ideal I-V curve	15
4	Thermionic current collection system	22
5	Richardson plots for high silica slags	29
6	Typical X-ray fluorescence spectrum	32
7	Typical Auger spectrum	36
8	Typical mass spectrometer spectrum	38
9	Effective work function vs. potassium content for	42
	high silica slags	
10	X-ray fluorescence calibration curves for high silica . .	45
	slags	
11	X-ray fluorescence calibration curves for low silica . . .	47
	slags	
12	Effective work function vs. temperature for K488	52
13	Effective work function vs. temperature for K492	54
14	Effective work function vs. temperature for K494	56
15	Effective work function vs. temperature for K510	58
16	Effective work function vs. temperature for K539	60
17	Richardson plot of Mg and Al doped lanthanum chromite . .	65
18	Richardson plot of Sr doped lanthanum chromite	67

ABSTRACT

The effective work functions for several synthetic coal slags and lanthanum chromite based ceramics were obtained using thermionic techniques. The effective work functions of the low silica coal slags that contained potassium were found to be about 3 eV at low temperatures, and about 4 eV at higher temperatures. The effective work functions for the high silica coal slags that contained potassium were found to be close to the effective work function of the slag which contained no potassium. X-ray fluorescence studies showed that substantial amounts of potassium had been lost from the high silica coal slags in their initial heating. The effective work functions for the Sr and Mg-Al doped ceramics were determined to be 3.28 eV and 3.13 eV respectively.

I. INTRODUCTION

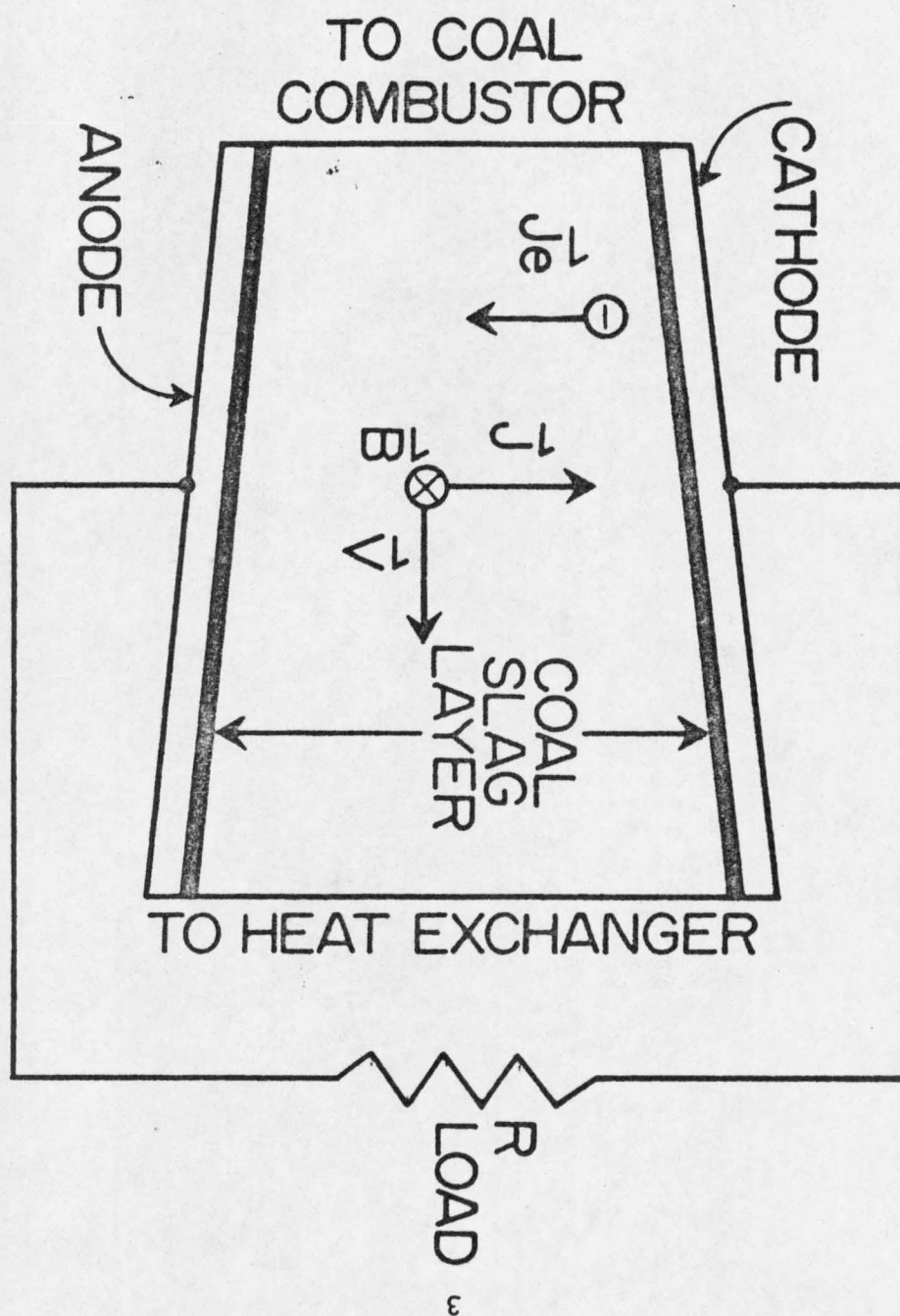
Magnetohydrodynamics (MHD) is the science of the interaction between a magnetic field and a flowing ionized gas. There is currently much optimism that MHD will be useful in the production of electricity from fossil fuels, particularly coal. An MHD channel has the potential of producing electricity with a greater efficiency than conventional power plants because of the higher temperature at which it operates (up to 3000°C). In an open-cycle MHD generator, the gases evolved from the combustion of the fuel are directed to flow at a high velocity through a duct or channel which contains a strong magnetic field oriented perpendicular to the direction of the gas flow. These gases are made conductive by seeding with a small amount of potassium, usually in the form K_2CO_3 , which is thermally ionized at the high temperature of the gas. An electromotive force is generated by the flow of this conducting gas through the applied magnetic field according to Faraday's law of magnetic induction. In a conventional generator, a coil of a conductor like copper rotates in a magnetic field which also induces an electromotive force according to Faraday's law.

Figure 1 shows a conceptual diagram of an MHD channel, and the geometry of the current flow induced by the electromotive force. Theoretically, the direction of the current flow is mutually perpendicular to both the magnetic field and the direction of the gas flow. This current flows through an external load resistance and does useful work.

1000 1000 1000 1000 1000 1000 1000 1000 1000 1000
1000 1000 1000 1000 1000 1000 1000 1000 1000 1000
1000 1000 1000 1000 1000 1000 1000 1000 1000 1000

FIGURE 1

Conceptual diagram of a coal fired MHD channel. The direction of the gas flow ($\vec{V}$), magnetic field ($\vec{B}$), and the induced current density ($\vec{J}$) are shown.



In order to close the current loop, electrons must be emitted from the cathode, pass through the ionized combustion gases and enter the anode. The electrons may be emitted from the cathode in two ways: 1) uniformly over the cathode surface by thermionic emission (the thermionic or diffuse mode) or if the thermionic emission is insufficient to supply the current, then 2) the electric fields generated are sufficient to strike arcs and the electrons leave the cathode in a small number of localized arcs (the arc mode). In the arc mode, enormous current densities, which can exceed 10^3 amp/cm^2 , cause localized ohmic heating which tends to destroy the electrodes. To prevent destructive arcing, it is preferable to operate in the diffuse mode if possible. This would require that the thermionic emission from the cathode must be sufficient to supply the necessary current.

The evident importance of thermionic emission in an MHD generator provides the motivation for the present investigation. It is the goal of this research to determine the thermionic emission properties of various cathode materials under consideration for a coal fired MHD generator, namely coal slag and certain refractory ceramics. The coal which is burned inevitably contains small amounts of impurities consisting of minerals that are common in the earth's crust. These minerals consist of oxides and silicates of aluminum, iron, magnesium, and other elements. Such materials, termed "slag" are liquified and

vaporized in the combustor, become entailed in the combustion and coat the inside of the channel, including the cathode surface. At the cathode, the electrons must now be emitted from the slag layer, so that it is the thermionic emission properties of the slag that controls the flow of electrons into the plasma. Alternatively, the channel walls may be allowed to become so hot ($\sim 2100^{\circ}\text{K}$) that the slag does not stick. In this case, only refractory ceramics can withstand both the high temperature and the corrosive chemical environment. So it is the thermionic emission properties of these ceramics that are at issue.

Historically, it has been difficult to obtain reproducible results from the thermionic studies due to the many factors that influence it. Most of the early thermionic work was done on bare metals like tungsten and tantalum which were used to construct electron tubes. Later, when vacuum techniques improved, thermionic studies of atomic films and semiconductors became possible. However, dirty emitters like coal slag have never been studied to any great degree. This is the first comprehensive study of thermionic emission from coal slags.

II. THEORY

It is the purpose of this section to examine the fundamental laws and physical quantities that influence thermionic emission.

A. The Richardson-Dushman Equation¹

Thermionic emission refers to the escape of electrons from a hot surface. If all of the electrons emitted are collected, the saturation current density J is related to the temperature T and the work function Φ of the emitter by the Richardson-Dushman equation

$$J = A_0 T^2 \exp(-\Phi/kT) \text{ amps/cm}^2$$

where

$$A_0 = 4\pi me k^2 h^{-3} = 120 \text{ amp/K}^2 \text{ - cm}^2. \quad (1)$$

This equation can be derived by assuming the potential energy of an electron due to its interactions with the ions and electrons in the emitter can be approximated by a square well of depth E_0 . This well will be partially filled by electrons up to the fermi level E_f . For an electron to escape from the emitter, it must have a sufficient kinetic energy to take it from the emitter to infinity. If the emitter is considered to be a semi-infinite plane with its normal parallel to the $\hat{x}$ direction, then only the x component of the escaping electrons kinetic energy contributes to the electrons' ability to leave the emitter. Thus the condition for an electron to leave the emitter is

$$\frac{p_x^2}{2m} > \Phi + E_F$$

or

$$p_{xc} = [2m(\Phi + E_F)]^{1/2} = (2mE_0)^{1/2} \quad (2)$$

where p_{xc} is defined by equation 2 and is the critical x momentum.

In general, the current density of electrons that flow through an arbitrary surface with momenta between $\vec{p}$ and $\vec{p} + d\vec{p}$ is proportional to the product of their momentum and the density of electrons with this momentum $n(\vec{p})$. The total current density that flows through this surface is

$$\vec{J} = \frac{e}{m} \int_{\text{All } \vec{p}} \vec{p} n(\vec{p}) d\vec{p}$$

Thus the current density that flows in the x direction is

$$J_x = \frac{e}{m} \int_{\text{All } \vec{p}} p_x n(\vec{p}) d\vec{p} \quad (3)$$

From Fermi-Dirac Statistics, the density of electrons with momenta between $\vec{p}$ and $\vec{p} + d\vec{p}$ is

$$n(\vec{p}) = f(\vec{p}) D(\vec{p})$$

where $f(\vec{p})$ is the fermi function

$$f(\vec{p}) = \left[1 + \exp \left(\frac{E - E_F}{kT} \right) \right]^{-1} \quad (4)$$

and

$$E = \frac{p_x^2 + p_y^2 + p_z^2}{2m}.$$

The quantity $D(\vec{p})d\vec{p}$ is the density of traveling wave states

$$D(\vec{p})d\vec{p} = \frac{2}{h^3} dp_x dp_y dp_z. \quad (5)$$

From equations 3, 4, and 5, the current density in the x direction is

$$J_x = \frac{2e}{mh^3} \int_{-\infty}^{\infty} dp_y \int_{-\infty}^{\infty} dp_z \int_{p_{xc}}^{\infty} \frac{p_x dp_x}{e^{(E-E_F)/kT} + 1} \quad (6)$$

For $(\frac{p^2}{2m} - E_F) > 5 kT$, the Fermi function can be approximated as

$$f(\vec{p}) \cong \exp \left[-\left(\frac{p^2}{2m} - E_F \right) / kT \right] = \exp \left[-\frac{(E-E_F)}{kT} \right]$$

For typical emitter temperatures (less than 2000°C) this is a valid form for the Fermi function. Under the change of variables

$$\theta = \frac{p_x^2 - 2mE_F}{2mkT}$$

equation (6) becomes

$$J_x = \frac{2ekT}{h^3} \int_{-\infty}^{\infty} dp_y \exp\left(\frac{-p_y^2}{2mkT}\right) \int_{-\infty}^{\infty} dp_z \exp\left(\frac{-p_z^2}{2mkT}\right) \int_{\Phi/kT}^{\infty} e^{-\theta} d\theta \quad (7)$$

Using the integral relation

$$\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}$$

equation (7) becomes

$$J = \left(\frac{4\pi m e k^2}{h^3} \right) T^2 e^{-\Phi/kT} \equiv A_0 T^2 e^{-\Phi/kT}$$

which is the Richardson-Dushman equation.

If an escaping electron comes too close to an ion in the emitter, it can be backscattered back into the emitter. This reduces the thermionic current emitted. In general, a qualitative description of this process can be very difficult. It is customary to define the quantity $\bar{r}$ as the fraction of electrons incident on the emitter-vacuum interface that are reflected back into the emitter. Then equation (1) takes the form

$$J = A_0 (1 - \bar{r}) T^2 e^{-\Phi/kT} \quad (8)$$

Typically, $\bar{r}$ is small compared to 1 ($\sim .05$) so the reflection of electrons can usually be neglected.

If the work function has a temperature dependence of the form

$$\Phi = \Phi_0 + \alpha T$$

then equation (8) is further modified to become

$$J = A_0 (1 - \bar{r}) e^{-\alpha/k} T^2 e^{-\Phi/kT} \quad (9)$$

Further modification of equation (9) occurs if the effective mass of the escaping electron m^* is assumed to be different from the mass of a free electron. So the Richardson-Dushman equation in its most general form under the above assumptions is

$$J = A_0 T^2 e^{-\Phi/kT} \left[\left(\frac{m^*}{m} \right) e^{-\alpha/k} (1-\bar{r}) \right] \quad (10)$$

There is no easy way to determine the effect of each factor that modified equation (1) into equation (10). Experimentalists usually determine the effective work function ϕ by assuming the quantities in the brackets of equation (10) are collectively equal to unity. If equation (10) is reduced to a form

$$J = (A_0 T^2 e^{-\Phi/kT})^\gamma$$

where $\gamma > 0$, then the difference between the thermionic work function and the effective work function is $\Phi - \phi = \Phi - \phi = -kT \ln \gamma$. If $\gamma = .5$, then

$$\Phi - \phi = 0.69 kT$$

which is a small change for usual thermionic temperatures ($< 2000^\circ \text{K}$).

It should be noted that the derivation of the Richardson-Dushman equation given in this chapter was done for a metal. Equation (1) also governs thermionic emission from insulators and semiconductors. This can be proven by considering a model independent statistical

mechanical derivation of the Richardson-Dushman equation such as that done by Herring and Nichols².

B. The Image Potential

Recall that the definition of the thermionic work function is the amount of energy required to remove an electron from the fermi level to the vacuum level. If an external force is applied to the escaping electron, it can force this electron out of or into the emitter depending upon the direction of the force. Thus this external force can add to or subtract from the thermionic work function.

A good example of such an external force is the attraction between an escaping electron and its image charge in the emitter. The potential energy of an escaping electron due to its attraction to its image charge in the emitter is (in MKS units)

$$U = \frac{-e^2}{16\pi\epsilon_0 x} \quad (11)$$

For a non-metal with a dielectric constant K, this energy is

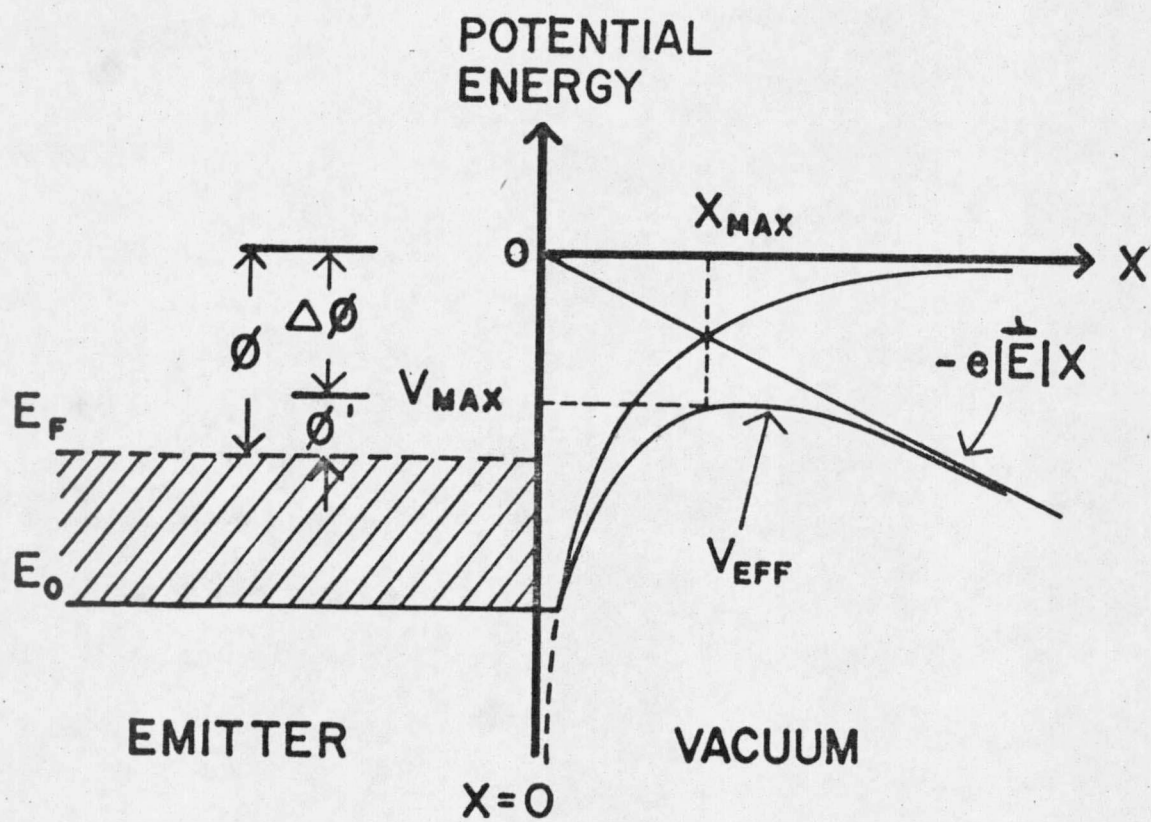
$$U = \frac{-e^2}{16\pi\epsilon_0 x} \left[\frac{K-1}{K+1} \right] \quad (12)$$

Equations (11) and (12) are only valid for relatively large distances. As the value of x goes to zero, the potential energy given by equations (11) or (12) approaches the bottom of the square well $-E_0$ as Figure 2 illustrates.

The first of these is the fact that the
 the first of these is the fact that the
 the first of these is the fact that the
 the first of these is the fact that the

FIGURE 2

Electron potential energy diagram near the surface of an emitter. V_{eff} is the sum of the image charge potential energy and the potential energy of the applied electric field. The new work function Φ' is $\Delta\Phi$ lower than the original work function Φ .



C. The Child-Langmuir Law

Although the Richardson-Dushman equation describes the flux of electrons flowing out from the surface of the emitter, the presence of these electrons sets up an electric field which will tend to drive the electrons back into the surface. Thus the measured emission current will be less than that given by the Richardson-Dushman equation unless a large enough external electric field is applied to overcome the space charge field. These conditions are known, respectively, as space charge limited and saturated. Figure 3 shows the net emission current as a function of the applied voltage. In the space charge limited region on the left, the current goes as $V^{3/2}$ according to the Child-Langmuir law of space charge limited emission. The region of the curve on the right would be perfectly flat except for a slight electric field induced work function lowering- the Schottkey effect.

The Child-Langmuir law can be derived by considering the effect of an electric field on the emitted electrons. If an electric field is established between the emitter and collector, the thermionically emitted electrons gain a kinetic energy

$$\frac{mv^2}{2} = eV \quad (13)$$

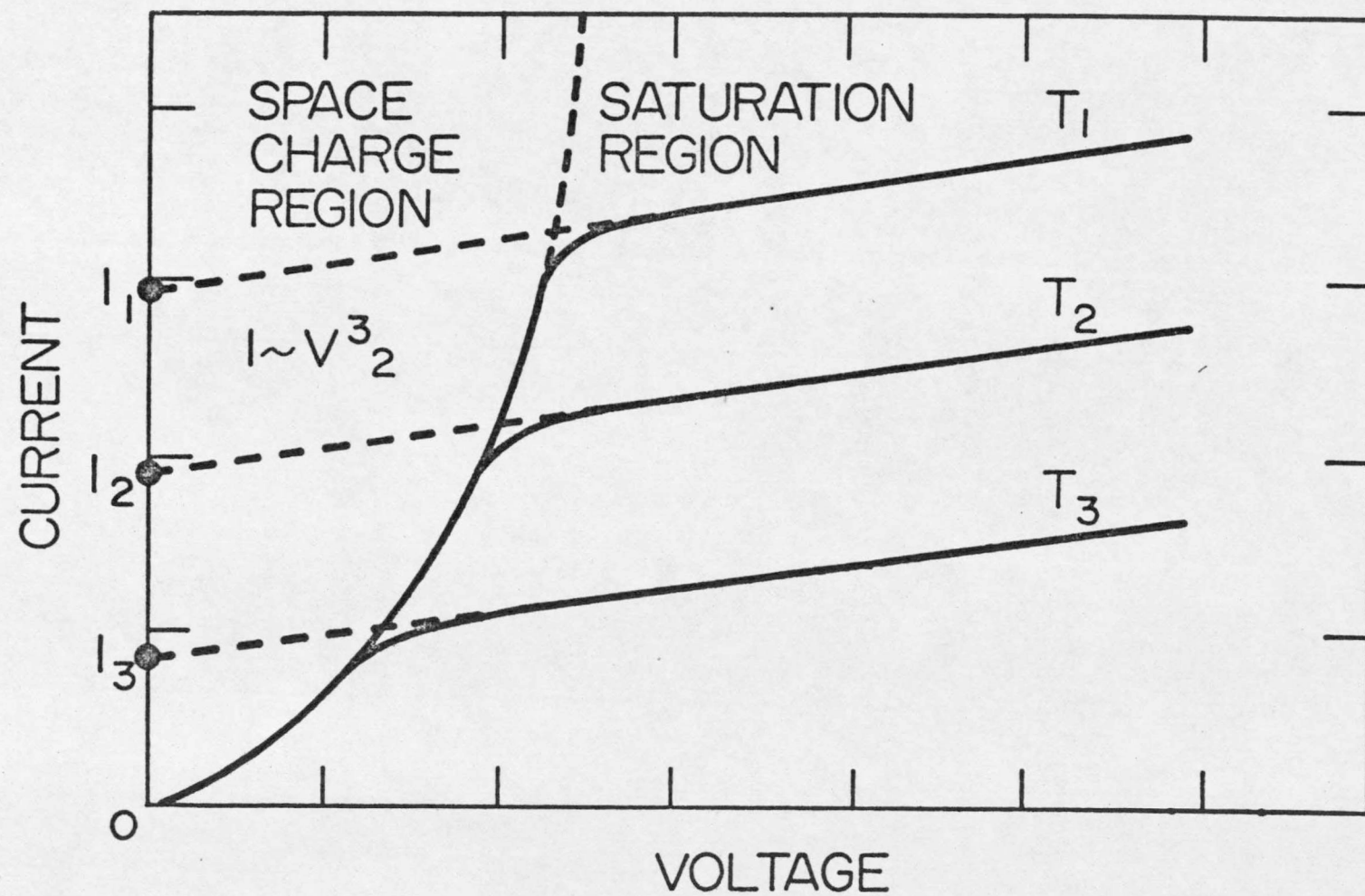
where v is the velocity of an electron after it has traveled through

Summary

The purpose of this study was to determine the effect of the use of a computer program on the learning of the basic concepts of the theory of sets. The study was conducted with a group of 30 students in a high school. The results of the study showed that the use of the computer program had a positive effect on the learning of the basic concepts of the theory of sets. The students who used the computer program showed a higher level of understanding and a higher level of achievement than the students who did not use the computer program.

FIGURE 3

An idealized I-V curve. The current on the left is space charge limited, while the current on the right is voltage saturated. The slight voltage dependence in the saturation region is due to the Schottkey effect. ($T_1 > T_2 > T_3$).



a potential difference V volts. Here it is assumed that the electrons are emitted with no kinetic energy. This is in fact a fairly good approximation since 90% of the thermionically emitted electrons have kinetic energies less than 0.5 eV. To determine how the current density J varies with the applied potential V , it is necessary to solve the one dimensional Poisson equation

$$\frac{d^2V}{dx^2} = \frac{\rho}{\epsilon_0} \quad (14)$$

where ρ is the space charge density. The velocity given by equation (13) can be related to the space charge density by the relation

$$J = -\rho v \quad (15)$$

Here J is the current density. Note that ρ has the dimensions of charge per unit volume. Solving equation (15) for ρ and substituting the value of v given by equation (13), and equation (14), becomes

$$\frac{d^2V}{dx^2} = \left(\frac{J}{\epsilon_0} \sqrt{\frac{m}{2e}} \right) V^{-1/2} \quad (16)$$

For simplicity, define $V = 0$ at $x = 0$ and $V = V_0$ at $x = d$. Here the cathode or emitter is located at $x = 0$. Using an integrating factor, solutions to equation (16) are easily found to be of the form

$$J = \frac{4\epsilon_0}{9} \sqrt{\frac{2e}{m}} \frac{V_0^{3/2}}{d^2} \quad (17)$$

This is the Child-Langmuir law³. A boundary condition that has been used to obtain equation (17) is that

$$\left. \frac{dV}{dx} \right|_{x=0} = E \Big|_{x=0} = 0 .$$

This boundary condition states that in the space charge limited region, the current density collected at the anode is in equilibrium when the applied electric field cancels the space charge field at the cathode. If the applied electric field is suddenly increased, the instantaneous electric field will be non-zero at the cathode surface. This forces electrons to flow out of the cathode until the electric field induced by the space charge again cancels the applied field. As the electric field between the emitter and collector increases, the space charge current density will approach the saturation current density given by equation (1). As the field increases still further, the current density saturates and is no longer space charge limited.

D. The Schottkey Effect⁴

As the applied field increases still further, the current density increases because the electric field lowers the amount of kinetic energy that escaping electrons must have to escape to infinity. That is the electric field lowers the work function. The energy associated with an electric field $\vec{E}$ is

$$U = -e |\vec{E}| x$$

When this energy is added to the energy of the image charge, a potential maximum occurs at $X_{\max}$ which is lower than the vacuum level. Figure 2 illustrates how the electric field potential energy and the image charge energy add up to an effective potential energy V_{eff} which has a maximum $V_{\max}$ located at $X_{\max}$. This lowers the original work function Φ by an amount $\Delta\Phi$. Thus the new work function is $\Phi' = \Phi - \Delta\Phi$.

The amount that the work function is lowered can be calculated by setting the first derivative of V_{eff} equal to zero. This yields that the change in work function is

$$\Delta\Phi = \frac{-e}{2} \sqrt{\frac{e|\vec{E}|}{\pi\epsilon_0}} \quad (18)$$

For non-metals with a dielectric constant K

$$\Delta\Phi = \frac{-e}{2} \sqrt{\frac{e|\vec{E}|}{\pi\epsilon_0} \left[\frac{K-1}{K+1} \right]^{1/2}}$$

Thus $\Delta\Phi$ is proportional to $|\vec{E}|^{1/2}$. This is commonly referred to as the Schottkey effect.

E. Surface Effects on the Work Function

If atoms are absorbed at the surface of the emitter as ions, such that there are N ions per unit area, their dipole moments with their image charges in the emitter set up an electric field

$$\vec{E} = \frac{eN}{\epsilon_0} \hat{n}$$

where $\hat{n}$ is the normal unit vector which is defined as $\hat{x}$ for the case of a semi-infinite emitter. Alternatively the absorbed atoms may not be ionized but only distorted into a dipole on account of their bonding to the surface. If each absorbed atom has a dipole moment M associated with it, the change in the work function is

$$\Delta \phi = \frac{NM}{\epsilon_0} \quad (19)$$

If the atoms are absorbed as singly charged positive ions, a distance d away from the emitter, the work function is lowered by an amount

$$\Delta \phi = N \left(\frac{2ed}{\epsilon_0} \right).$$

The work function is lowered by 1 eV if ions are one Angstrom away from their image charge, and there are 0.55×10^{18} dipoles/meter², which corresponds to about 13.5 Å between individual ions on the surface. This will increase the thermionic current density by a factor of $\exp(\Delta\phi/kT)$. For $\Delta\phi = 1$ eV and a temperature of 1800°K, the current density is increased by a factor of 630. Thus a small decrease in the work function causes a big increase in the current density.

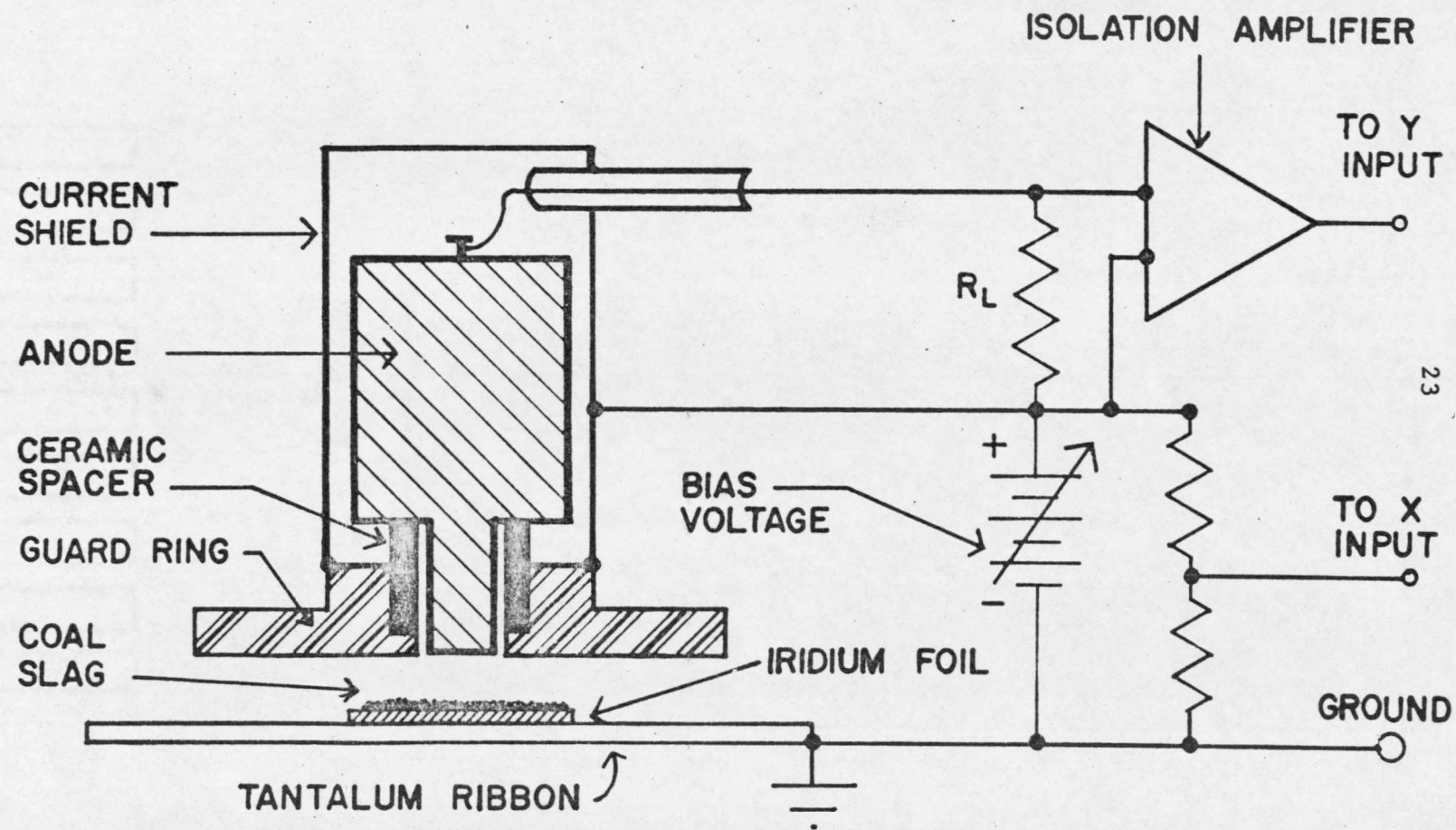
III. EXPERIMENTAL TECHNIQUES

The current collection structure used in these thermionic studies was chosen to have a planar diode geometry for simplicity. This structure consisted of a massive anode surrounded by an annular guard ring which ensured that only electrons emitted from the material being studied were collected by the anode. The anode is massive to keep neutral atoms that boil off the emitter from thermally ionizing on the anode. If positive ions were present on the anode, they would be accelerated back toward the emitter giving erroneous currents. Furthermore, these ions could produce secondary electrons at the cathode when they impact. These electrons would then be attracted toward the anode and would give even more erroneous currents. Figure 4 illustrates the structure of the anode — guard ring assembly used for these studies. Other current collection techniques, employing Faraday cups and suppression grids were also used in this research. These were used in an attempt to suppress secondary electrons and to isolate the anode from the hot cathode. However, the system shown in Figure 4 was found to give the best results.

Two lanthanum chromite based ceramics, and fourteen synthetic coal slags were obtained from the National Bureau of Standards MHD materials group. Two different series of coal slags were used for this research. One series contained slags with relatively low amounts of silica while the other series contained higher amounts. Both series contained known amounts of potassium oxide that varied from

FIGURE 4

Measurement geometry of the anode-guard ring assembly and
the measurement electronics.



0% to 30% by weight. Table 1 contains the percentage by weight of the individual components that make up both series of slags. The composition of the two lanthanum chromite ceramics is also listed in Table 1.

The coal slag specimens were pulverized into a fine powder to ensure uniformity and to make it easier to obtain a uniform slag layer at lower temperatures. This pulverized coal slag was placed on a thin square of iridium foil which was spot welded to a grounded tantalum ribbon. The iridium foil was used to isolate the slag from the tantalum ribbon. This was necessary because the slag reacted with the tantalum and quickly destroyed it.

The coal slag powder was heated in a vacuum of 10^{-7} torr to well over 1700°K by passing a high current through the tantalum ribbon. This vacuum was produced by a six inch oil diffusion pump with a cold trap. The main reason for the vacuum is to provide a long mean free path for the emitted electrons. This ensures that the current is not limited by diffusion through the atmosphere. Also, the vacuum minimizes the oxidation and heat loss of the tantalum ribbon, and reduces the chance that oxygen atoms could be absorbed on the slag's surface changing its work function.

The two lanthanum chromite based ceramics were machined into thin disks, placed on the tantalum ribbon, and heated in the same manner as the slags. No iridium foil was necessary for these

TABLE 1

High Silica Series (% by Weight)

Slag #	SiO ₂	Al ₂ O ₃	Fe ₃ O ₄	CaO	MgO	K ₂ O
K517	60.00	25.00	10.00	3.00	2.00	0
K520	57.00	23.75	9.50	2.85	1.90	5.00
K524	54.00	22.50	9.00	2.70	1.80	10.00
K527	51.00	21.25	8.50	2.55	1.70	15.00
K531	48.00	20.00	8.00	2.40	1.60	20.00
K533	45.00	18.75	7.50	2.25	1.50	25.00
K536	42.00	17.50	7.00	2.10	1.40	30.00

Low Silica Series (% by Weight)

Slag #	SiO ₂	Al ₂ O ₃	Fe ₃ O ₄	CaO	MgO	K ₂ O
K488	40.00	15.00	15.00	20.00	10.00	0
K492	38.00	14.25	14.25	19.00	9.50	5.00
K494	36.00	13.50	13.50	18.00	9.00	10.00
K509	34.00	12.75	12.75	17.00	8.50	15.00
K510	32.00	12.00	12.00	16.00	8.00	20.00
K512	30.00	11.25	11.25	15.00	7.50	25.00
K539	28.00	10.50	10.50	14.00	7.00	30.00

Ceramics

La_{.95} Mg_{.05} Al_{.25} Cr_{.75} O₃La_{.84} Sr_{.16} CrO₃

materials because they never melted or reacted with the tantalum, although the portion of these ceramics that was in direct contact with the tantalum ribbon did bond tightly to the surface. These ceramics were heated to about 1600°K in a vacuum of 10^{-7} torr for about one minute, to evaporate impurities from the surface.

The thermionic current collected from the slags and ceramics was converted into a voltage signal by passing this current through a load resistor. An isolation amplifier was employed to monitor this voltage signal, while providing protection to the chart recorder from the high voltages applied to the guard ring assembly. This high voltage was supplied by a KEPCO OPS-2000 operational power supply which is ramped up or down in voltage by a ramp generator. The voltage applied to the guard ring assembly was usually less than 700 volts. This voltage was monitored by the X-axis of an X-Y recorder after it was passed through a 1000 to 1 voltage divider. The voltage signal monitoring the thermionic current was input into the Y-axis. With this equipment, graphs documenting the thermionic current as a function of voltage were obtained. These graphs are commonly called I-V curves and are similar to those in Figure 3.

The temperature of the slags and ceramics was determined using an optical pyrometer. The temperature observed by the pyrometer was corrected to take into account the spectral emissivity ϵ , which was determined experimentally to be approximately 0.7. This value was

obtained by comparing the apparent temperature of the slags and ceramics to the apparent temperature of the tantalum ribbon which has a known value of ε^5 . Usually this correction added about 30°C to all of the apparent temperatures measured by the pyrometer. An additional 20°C was added to offset the absorption effects of the optical feed-through in the vacuum chamber.

Since the temperature and anode area are known, the effective work function can be obtained using equation (1). The factors that appear in the brackets in equation (10) which modify equation (1) to take into account reflections and temperature dependencies are assumed to collectively equal unity. Thus the work function obtained by this technique is the effective work function which was described earlier in this work.

If the results of a thermionic study are plotted as

$$\ln\left(\frac{J}{T^2}\right) \text{ vs } \frac{1}{T}$$

the results should be a straight line. From equation (1)

$$\ln\left(\frac{J}{T^2}\right) = \ln A - \left(\frac{\phi}{k}\right) \frac{1}{T}$$

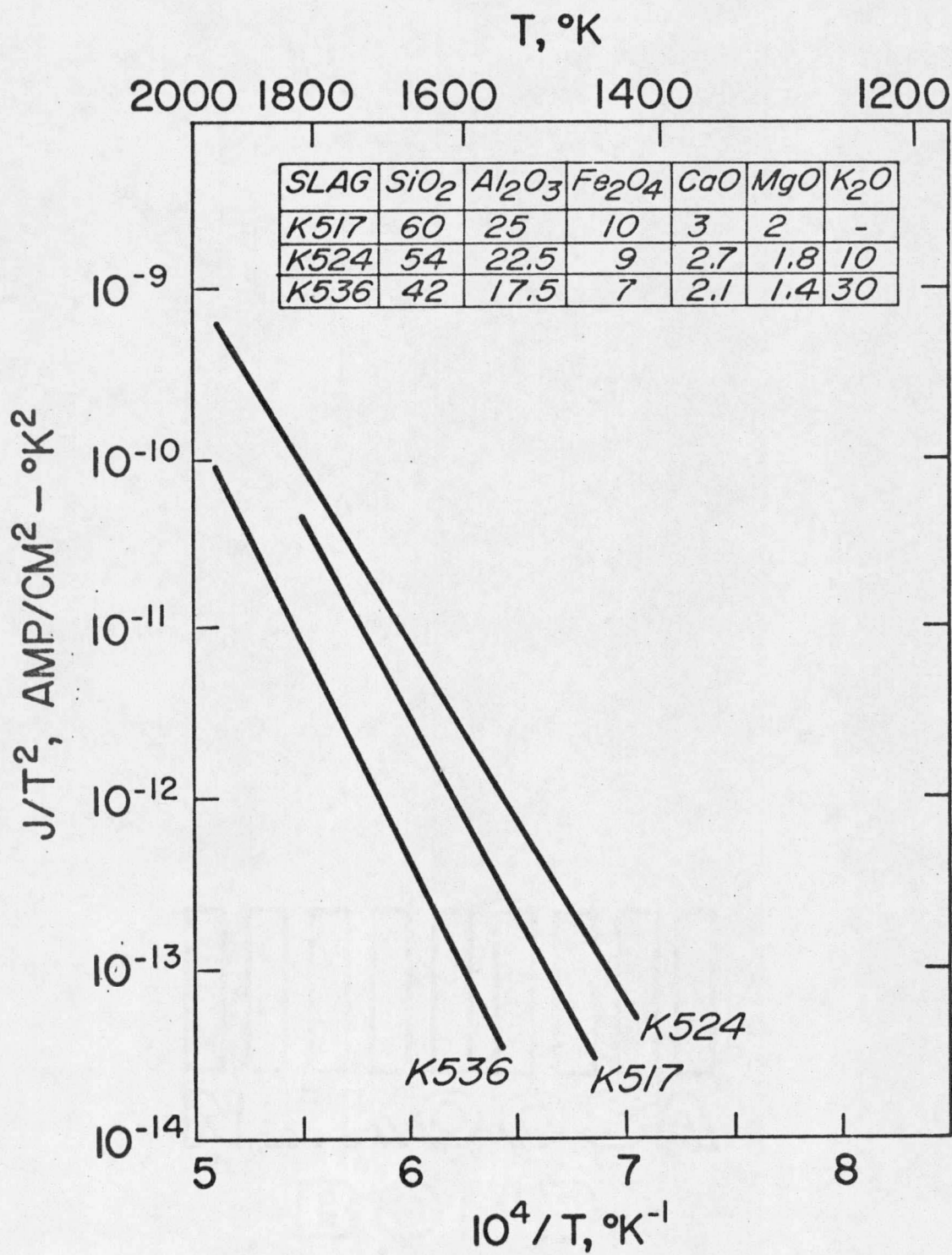
so the slope of the straight line gives the Richardson work function and the intercept at $T^{-1} = 0$ is $\ln A$. This type of plot is often referred to as a Richardson plot, and is one way the results of

thermionic studies can be presented. In general, because of the variation of the work function with temperature or other factors, the value of A obtained from the $T^{-1} = 0$ intercept of a Richardson plot will not be $120 \text{ amp/}^\circ\text{K}^2\text{-cm}^2$, and the Richardson work function will be different from the effective work function. Figure 5 shows Richardson plots for three high silica coal slags. Each of these lines is the average over several samples. The data points have been omitted for sake of clarity. The effective work functions for this research were obtained by averaging the effective work function at a given temperature for each data point of a particular slag. This technique yielded more reproducible data and better results than determining the Richardson work function from the slope of a Richardson plot. Also, this technique is more convenient since only one parameter need be specified (ϕ) rather than two (ϕ and A).

As the potassium doped slags used in this research are heated, potassium which has a low vapor pressure evaporates out of the slags and condenses on the vacuum chamber walls. As the potassium concentration of these slags drops, the amount of potassium ions on the surface will also change, thus changing the work function. To determine the extent of the potassium losses in these slags, an X-ray fluorescence study was undertaken. With this technique, an approximate measure of the potassium loss in the first few microns of the surface can be obtained.

FIGURE 5

Richardson plots of the high silica slags listed. Each line represents the average over several samples.

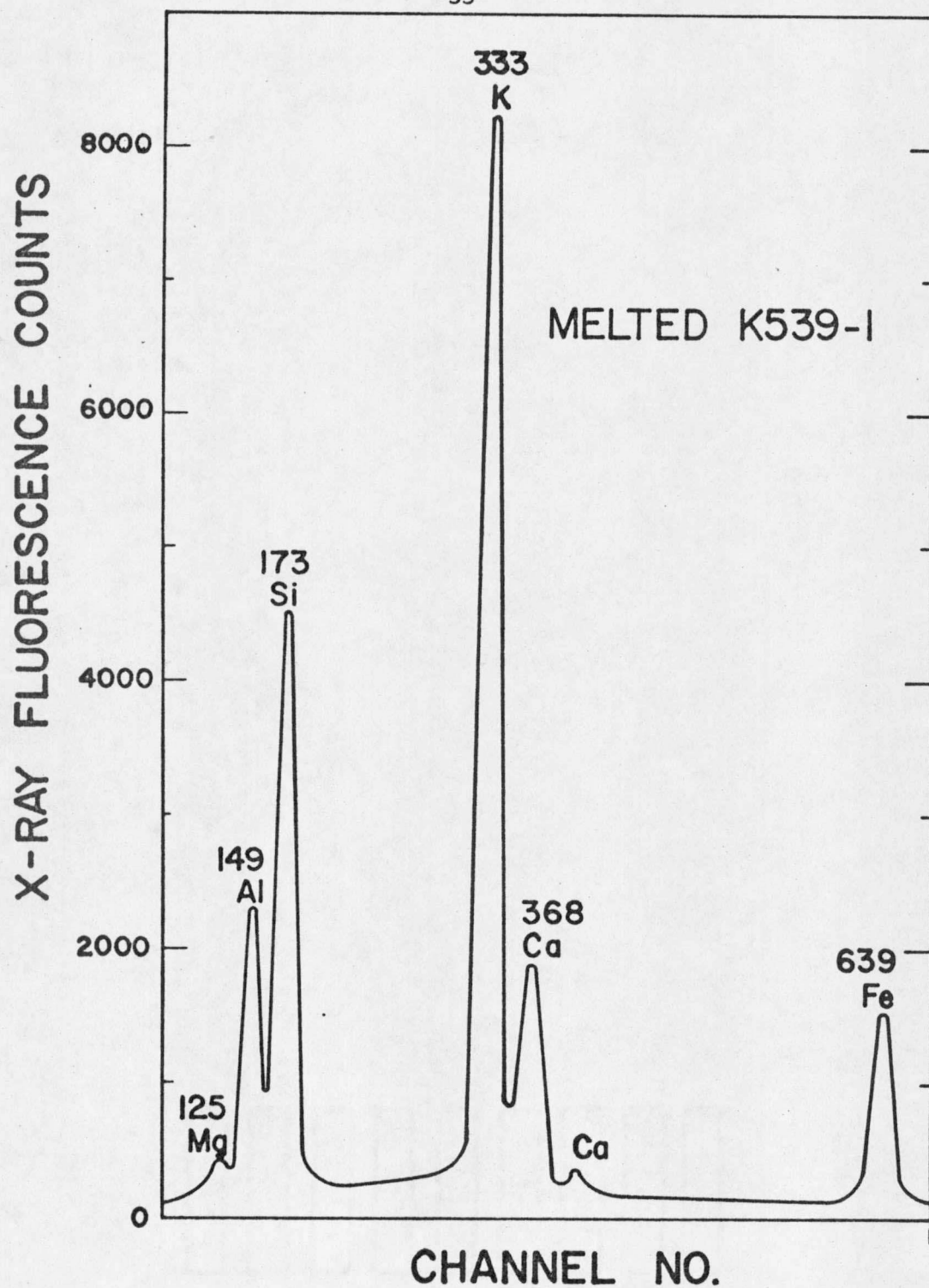


The X-ray fluorescence method consists of measuring the energies of the X-rays emitted from the atoms of a sample after excitation of the atoms by an impinging beam of 25 KeV electrons. Since each element emits its characteristic X-rays, the identities of the atoms in the first micron or so of the surface can be ascertained. The X-ray energies are measured with a lithium diffused silicon detector. The output was recorded with a pulse height analyzer. A typical spectrum of X-rays evolved from these coal slags is shown in Figure 6. A ratio of the peak number of counts of the potassium $K\alpha$ 1 line (3.33 KeV) to the peak number of counts of the silicon $K\alpha$ 1 line (1.73 KeV) was constructed for this research. The silicon was assumed to be a stable species which does not evaporate out of the slag in any appreciable amount at the temperatures used for this research. By comparing this K/Si ratio of X-ray fluorescence peaks, relative changes in the potassium concentration can be monitored.

Since the work function of a surface depends on the chemical nature of the first monolayer, Auger electron spectroscopy was used to determine the elemental identity of the surface atoms and, in particular, to determine if potassium was absent or present. Auger spectroscopy is, in principle, analogous to the X-ray fluorescence method. There are two important differences between them. These are: 1) The detected particles are electrons emitted from the atom by the radiationless Auger process after excitation by a beam of

FIGURE 6

An X-ray fluorescence spectrum obtained for K539 (30% K_2O).



3 KeV electrons. The kinetic energies of the electrons are characteristic of the emitting atom and the energy spectrum serves to identify the atoms present. 2) The mean free path of the Auger electrons is only a few Angstroms, so the defected electrons that still retain their characteristic energy must necessarily have been emitted from atoms within a few Angstroms of the surface. The X-ray mean free path is on the order of a micron so that in that method one measures an average composition over that depth. A retardation field analyzer (PHI 15-120) was used to measure the electron energy and lock-in techniques were used to separate the Auger electron signal from the large background of secondary electrons. The experimental techniques employed in this study are similar to those used by D. F. Stein *et al.*⁶ and P. W. Palmbert *et al.*⁷

The relative concentrations of an N-component system can be obtained from Auger electron spectroscopy using the relation

$$C_n = \frac{K_n/S_n}{K_1/S_1 + \dots + K_n/S_n} \quad (20)$$

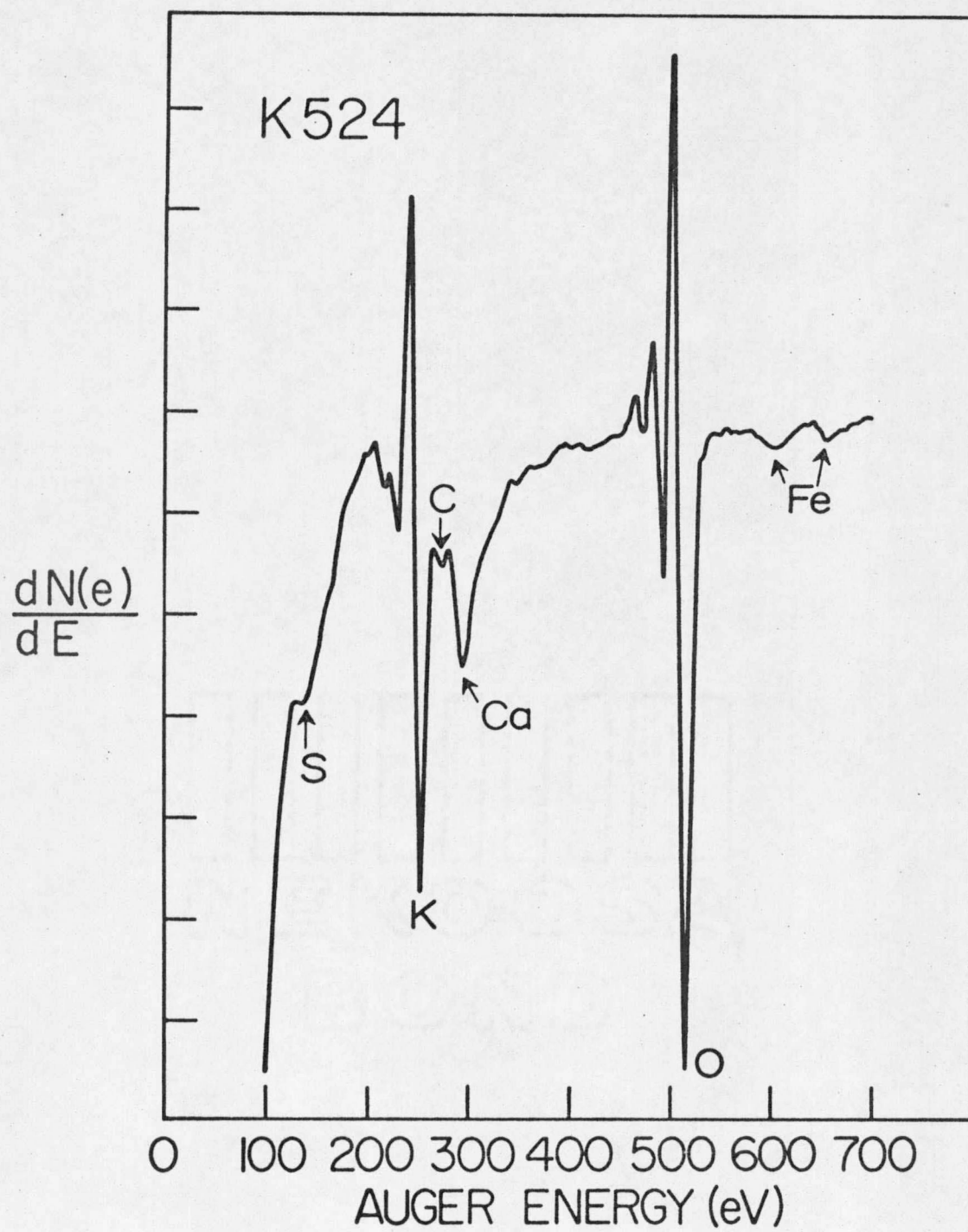
where K_n is the peak to peak amplitude of the Auger signal and S_n is the relative sensitivity of the n^{th} component of the slag compared to a silver standard. These relative sensitivities are tabulated⁸ and are in general very complicated functions of density, and beam

voltage as well as atomic number. Figure 7 illustrates a typical Auger spectrum obtained in this research.

A Balzers QMC101 quadrupole mass spectrometer was also used in this research to study the ions evolved from the hot coal slag. The only ions that were observable were K^{39} and K^{41} . Figure 8 is a spectrum obtained from K524 at about $1300^{\circ}K$. This slag contained 10% potassium oxide by weight before heating. The ratio of the K^{41} and K^{39} ion flux amplitudes as anticipated is the same as the ratio of the natural abundances of these isotopes⁹.

FIGURE 7

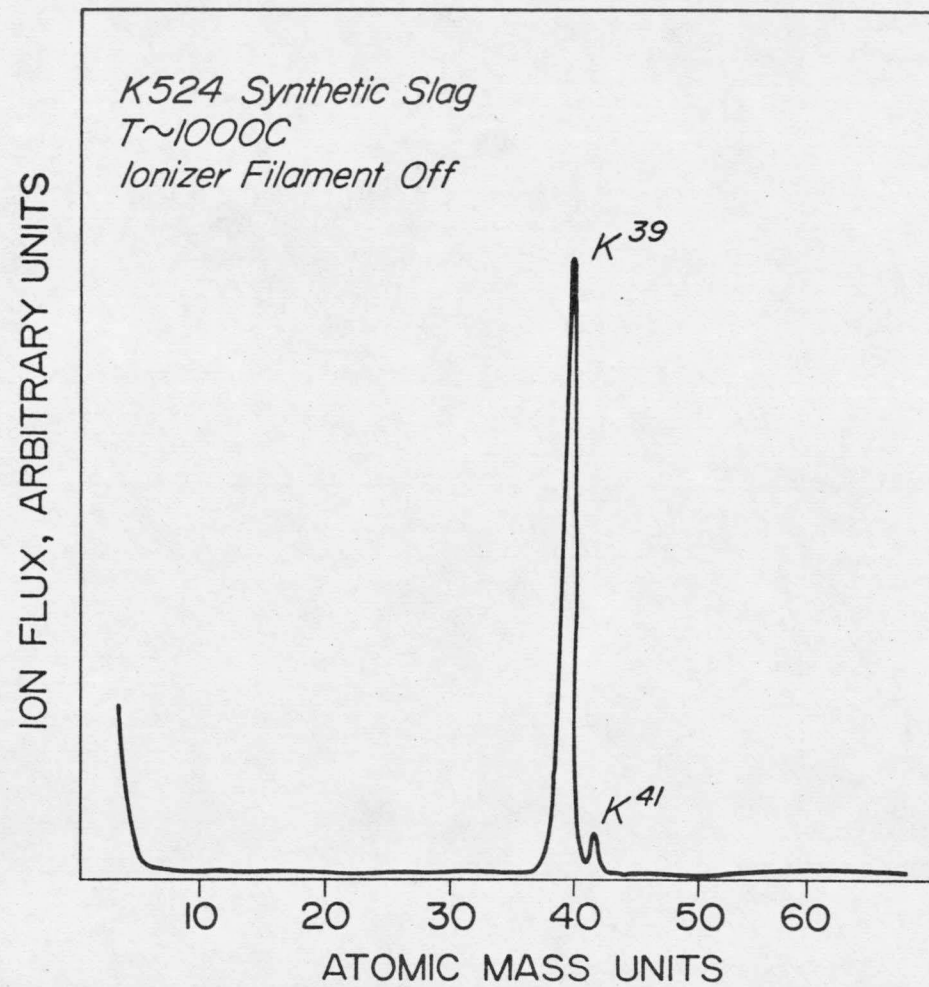
An Auger spectrum obtained from K524 (10% K_2O).



[illegible]

FIGURE 8

Mass spectrometer spectrum obtained with a quadrupole mass spectrometer from K524 (10% K_2O). The ionization filament was off so no neutral atoms were detected.



IV. EXPERIMENTAL RESULTS

The thermionic current collection system shown in Figure 4 was used initially to obtain the effective work function of two polycrystalline metals to test its reliability. These metals were tantalum and platinum. The emitting surface of these metals was cleaned of gross impurities by bringing these metals up to a high temperature in a vacuum of 10^{-7} torr. for about a minute. An effective work function of 4.23 eV was obtained for tantalum which has an accepted value of 4.19 eV¹⁰. This measurement has less than one percent error, and indicates that the current collection system is working quite well. An effective work function of 4.86 eV was obtained for platinum which has an accepted value of 5.32 eV¹⁰. This measurement has 8.7% error. Since platinum has a lower melting point than tantalum, it could not be flashed at a sufficiently high temperature to remove all the contaminants present on its surface. These impurities probably caused the erroneous work function measurement. Historically it has been difficult to measure the work function of platinum because of these impurities. The accepted value for the work function of platinum was obtained from a freshly sputtered layer of platinum¹¹. Those thermionic studies were done before any impurities had a chance to settle back on the surface.

Once the current collection assembly was proven reliable, thermionic studies on the high silica slags were begun. The high silica content in these slags made their melting points occur at

high temperatures. Powderized specimens of these slags were heated initially to over 1800°K in order to melt the powder into a uniform slag layer. Upon melting, the temperature of these slags was dropped to about 1000°K . It was hoped that the high temperatures needed to melt these slags would not cause substantial amounts of the potassium to evaporate out of these slags and condense on the vacuum chamber walls. If in fact the potassium did leave these slag samples, this would most likely affect the concentration of potassium on the surface, which would be reflected in a higher work function. Thermionic studies were done on K517, K524, K531, K533 and K536 which initially contained 0%, 10%, 20%, 25% and 30% potassium oxide by weight, respectively. Richardson plots for K517, K524, and K536 are shown in Figure 5. It is strange that the current density is lowest for the slag that initially had the highest potassium content. The effective work function vs. potassium oxide content before heating is shown in Figure 9. The effective work function for all four slag samples that contained potassium are surprisingly close to the work function of K517 which contained no potassium. It would seem that these slag might have lost substantial amounts of potassium in the initial melting operation.

To determine if in fact this potassium was leaving and to what extent, an X-ray fluorescence study of the melted and unmelted high silica series was undertaken. The X-ray fluorescence studies on the

THESE ARE THE RESULTS OF THE RESEARCH

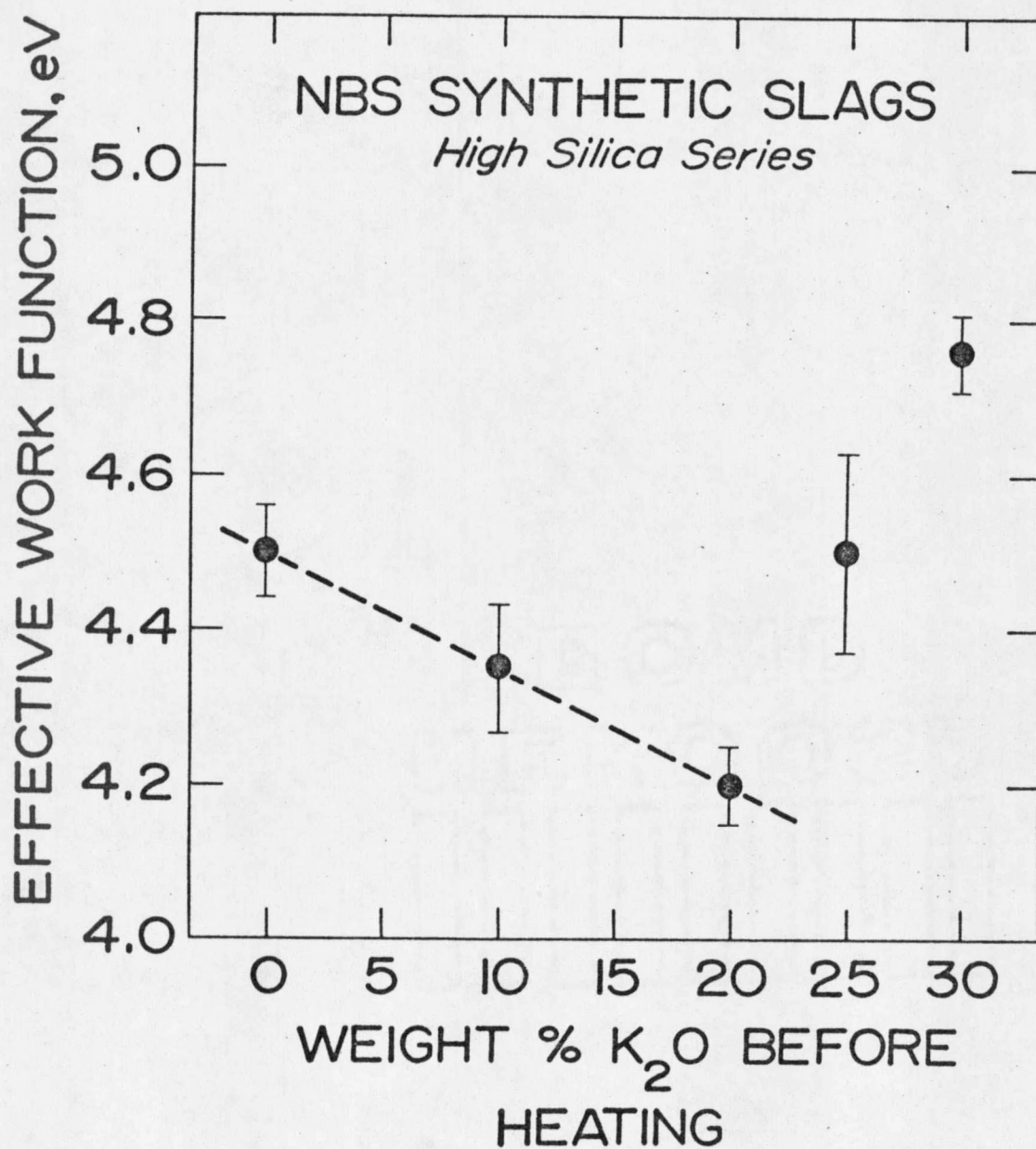
CONDUCTED BY THE RESEARCHERS

ON THE SUBJECT OF THE RESEARCH

ON THE SUBJECT OF THE RESEARCH

FIGURE 9

A plot of the effective work function vs. potassium content. The dotted line represents a downward trend which was anticipated. The data points for 25% and 30% K_2O , which do not follow this trend, may be higher due to potassium loss.



unmelted high and low silica series slags yielded a calibration curve which could be used to determine the percent potassium oxide left in a slag sample after heating, from the K/Si ratio which was defined earlier. Figures 10 and 11 contain the results of the unmelted X-ray fluorescence studies. In general, calibration curves of this sort can be a high order polynomial due to density, backscattering, and fluorescence yield corrections. Both a first and second order fit is made to the data displayed in Figures 10 and 11. The K/Si ratios for some of the melted high silica slags used in the thermionic studies were determined. Table 2 lists the K/Si ratio, the original potassium oxide content, and the potassium oxide left after heating. From Table 2, it is apparent that these melted high silica slags have lost from 43% to 65% of their original potassium oxide content.

The amount of potassium on the surface of K524 can be determined using equation (20). Since the potassium and oxygen peaks are substantially larger than the calcium and iron peaks, a good approximation of the amount of potassium on the surface can be obtained by considering this slag as a two component system: potassium and oxygen. Thus for $N = 2$, equation (2) states that

$$C_k \approx \frac{K_k/S_k}{K_k/S_k + K_0/S_0}$$

and

$$C_0 \approx \frac{K_0/S_0}{K_k/S_k + K_0/S_0}$$

FIGURE 10

An X-ray fluorescence calibration curve which can be used to determine the amount of K_2O left in a high silica coal slag sample after heating. The dotted and solid lines represent a first and second order least squares fit to the data, respectively..

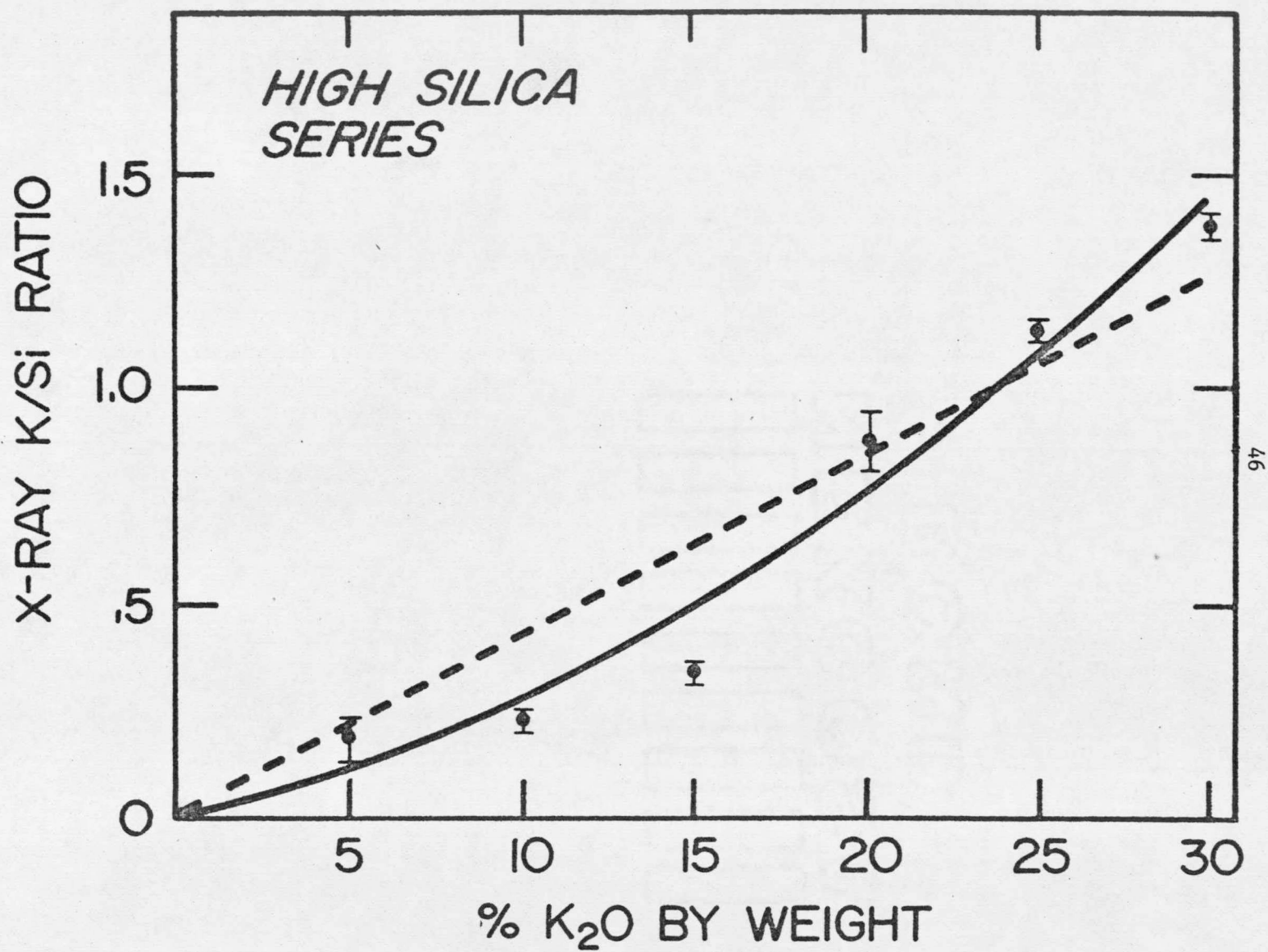


FIGURE 11

An X-ray fluorescence calibration curve which can be used to determine the amount of K_2O left in a low silica coal slag after heating. The dotted and solid lines represent a first and second order least squares fit to the data, respectively.

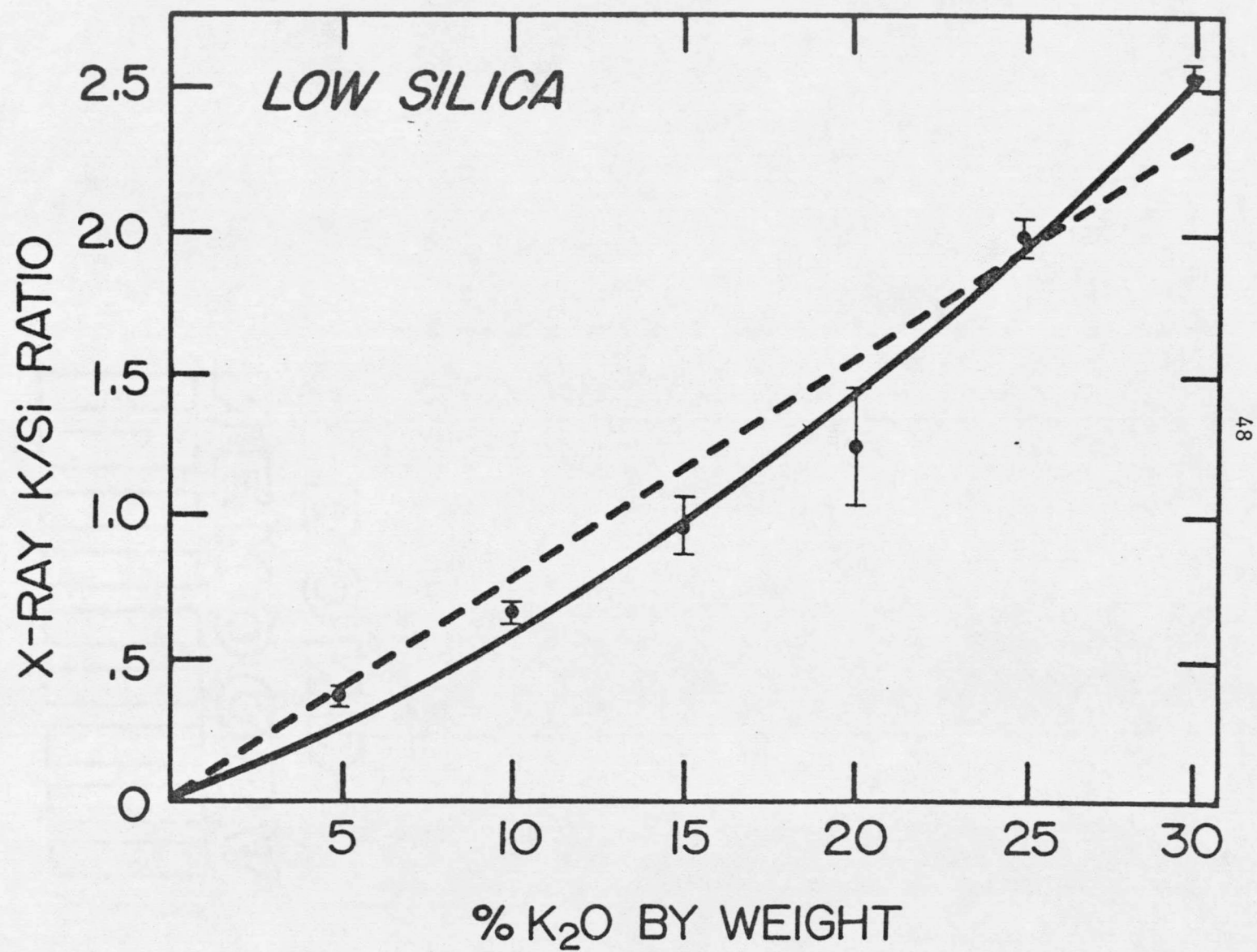


TABLE 2

Slag #	K/Si ratio	% K ₂ O before	% K ₂ O after	% change
524-2	.148 ± .003	10%	3.5%	35%
524-3	.197 ± .008	10%	4.5%	45%
531-1	.459 ± .192	20%	11.5%	58%
533-1	.518 ± .139	25%	13.0%	52%

The values of K_k and K_0 can be obtained from Figure 7 to be $K_k = 10.6$ and $K_0 = 15.4$. The relative sensitivities S_k and S_0 are⁷ $S_k = .8$ and $S_0 = .5$. This yields the result that $C_k = .301$ and $C_0 = .699$, or roughly 30% of the atoms on the surface are potassium, while about 70% of these atoms are oxygen. Since all of the components of these synthetic slags are metallic oxides, oxygen is the largest component of these slags. This indicates that there was a substantial amount of potassium on the surface at this time. No time dependent studies were undertaken to determine how the potassium on the surface changed with time and temperature.

The low silica series of slags melted at lower temperatures than the high silica series due to the decreased silica concentration. Powderized samples of these slags were heated to about 1600°K in order to melt the powder into a uniform layer. Immediately after all the powder had melted into the slag layer, the slags temperature was dropped to about 1000°K . Recalling the substantial potassium loss observed for the high silica slags, much more caution was shown to the maximum temperature of the low silica thermionic studies. It was hoped that potassium loss could be minimized by reducing the maximum temperature of these slags. Numerous thermionic studies were done on K488, K492, K494, K510 and K539 which contain 0%, 5%, 10%, 20% and 30% potassium oxide by weight, respectively. The data obtained from these studies is plotted in Figures 12 through 16 as the effective

work function vs. the temperature of the slag to better describe the temperature dependence of the work function. In all of these figures, the work function increases approximately linearly with increasing temperature. A first order least squares fit was done on this data. The slope of these lines appear in Table 3 along with the work function at 1300°K. The nearly vertical lines that appear on Figures 13, 14, and 16 connect different values of the work function for the same slag sample. The lower point in each case was the value of ϕ obtained immediately after the slag's temperature was raised to the temperature shown. The upper points are the equilibrium values for the effective work function after the slag's new temperature had been established for several minutes. All other data points that appear on these figures are equilibrium values of ϕ . This change of the effective work function at fixed temperatures can be attributed to potassium loss from the surface of the slag.

An X-ray fluorescence study similar to those done for the high silica slags, was done on a low silica slag. In this study, several samples of K510 (20% K_2O before heating) were each heated to successively higher temperatures. A K/Si ratio was determined for each slag sample and the potassium oxide content after heating was obtained using the calibration curve shown in Figure 11. The percentage potassium loss was calculated by the relation

FIGURE 12

The temperature dependence of the effective work function of
K488 (0% K_2O).

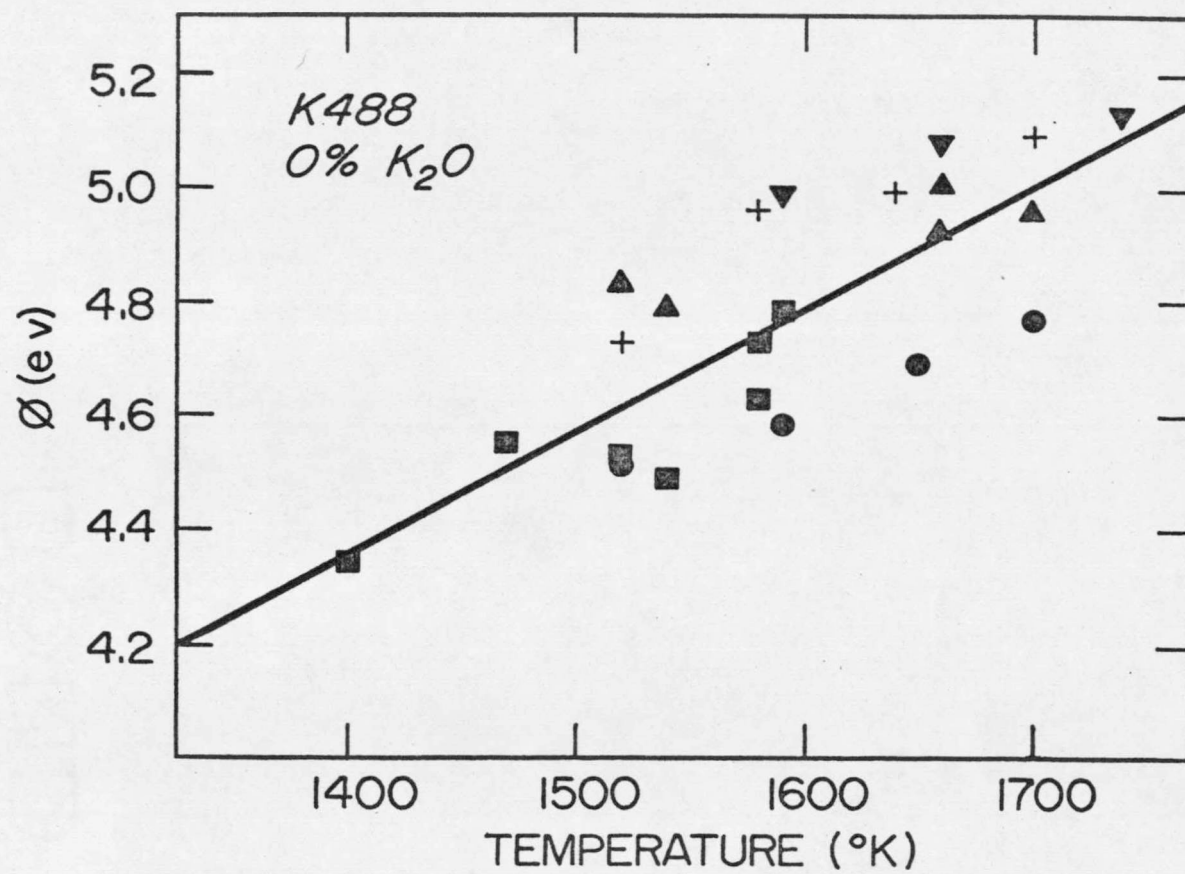


FIGURE 13

The temperature dependence of the effective work function of K492 (5% K_2O). The vertical line illustrates the difference between the equilibrium value and the initial value of the effective work function at the temperature shown.

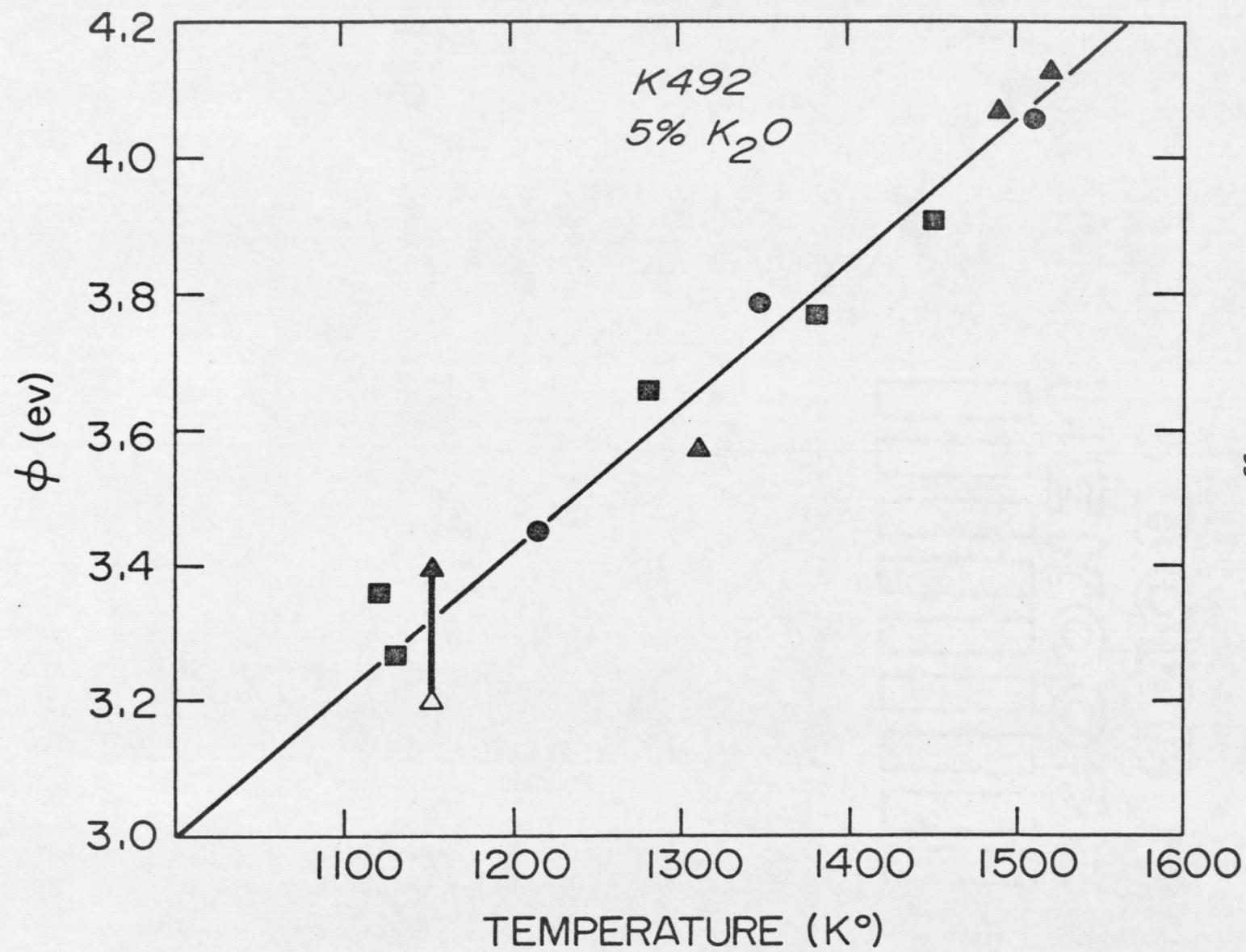


FIGURE 14

The temperature dependence of the work function of K494 (10% K_2O). The vertical lines illustrate the difference between the equilibrium value and the initial value of the effective work function at the temperatures shown.

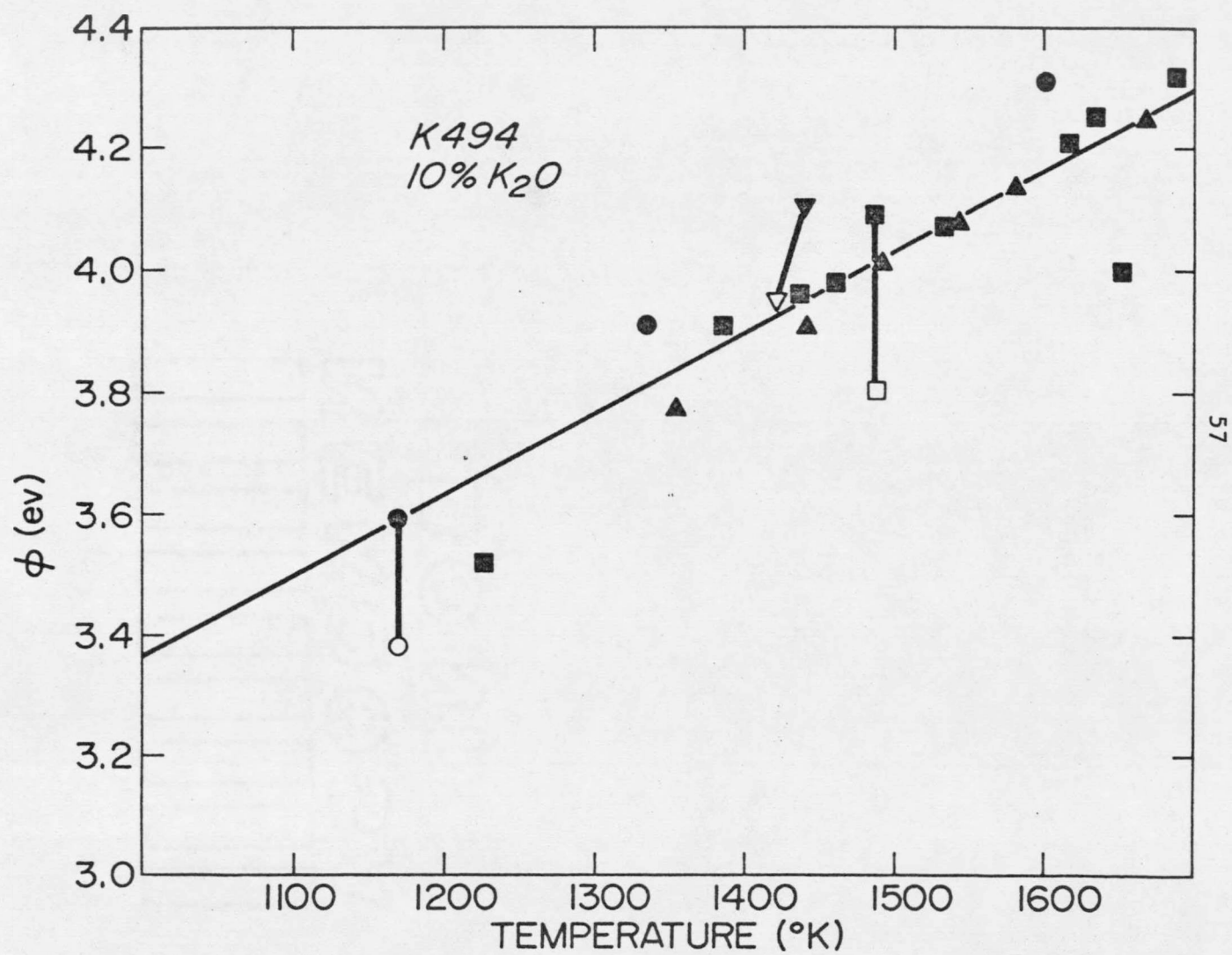


FIGURE 15

The temperature dependence of the effective work function
of K510 (20% K_2O).

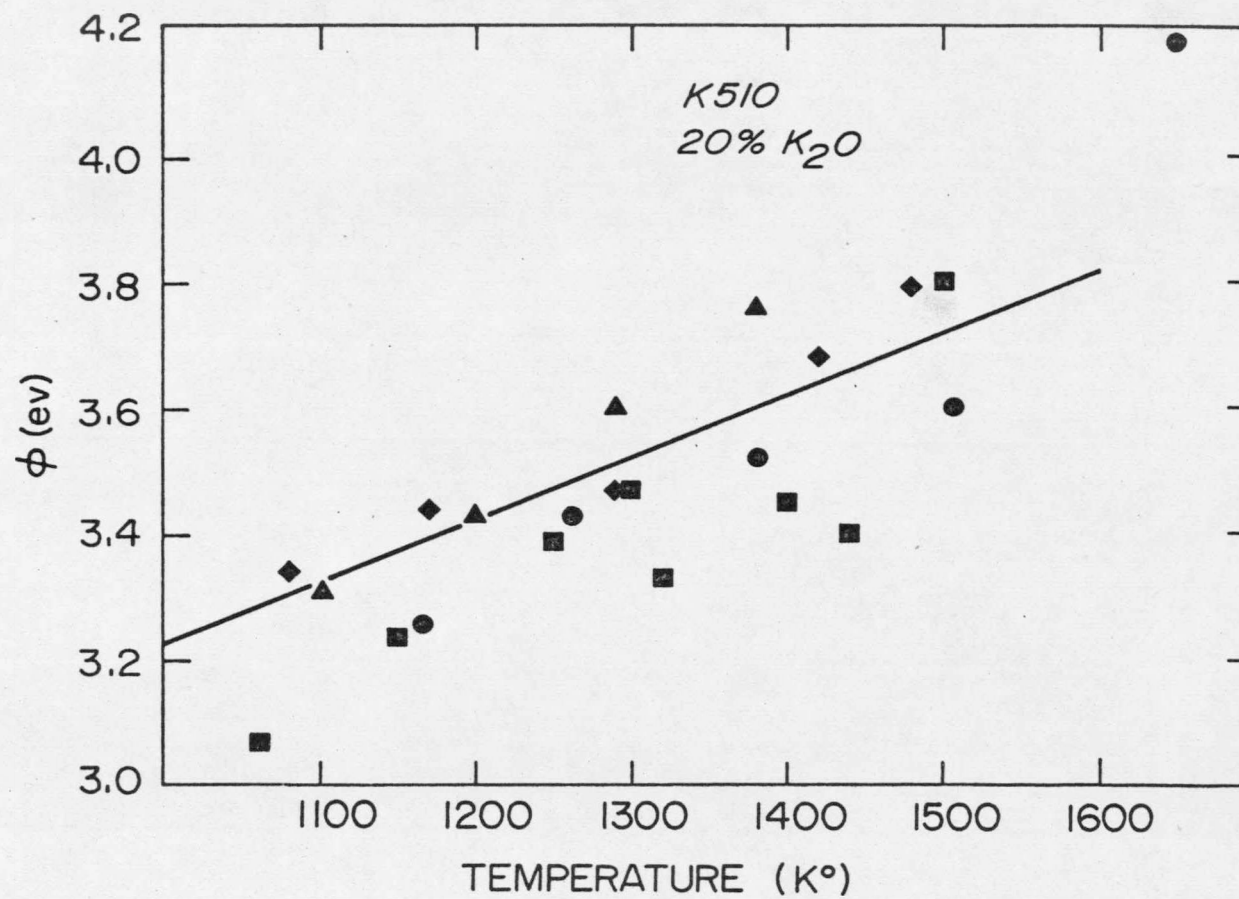


FIGURE 16

The temperature dependence of the work function of K539 (30% K₂O). The vertical lines illustrate the difference between the equilibrium value and initial value of the effective work function at the temperatures shown.

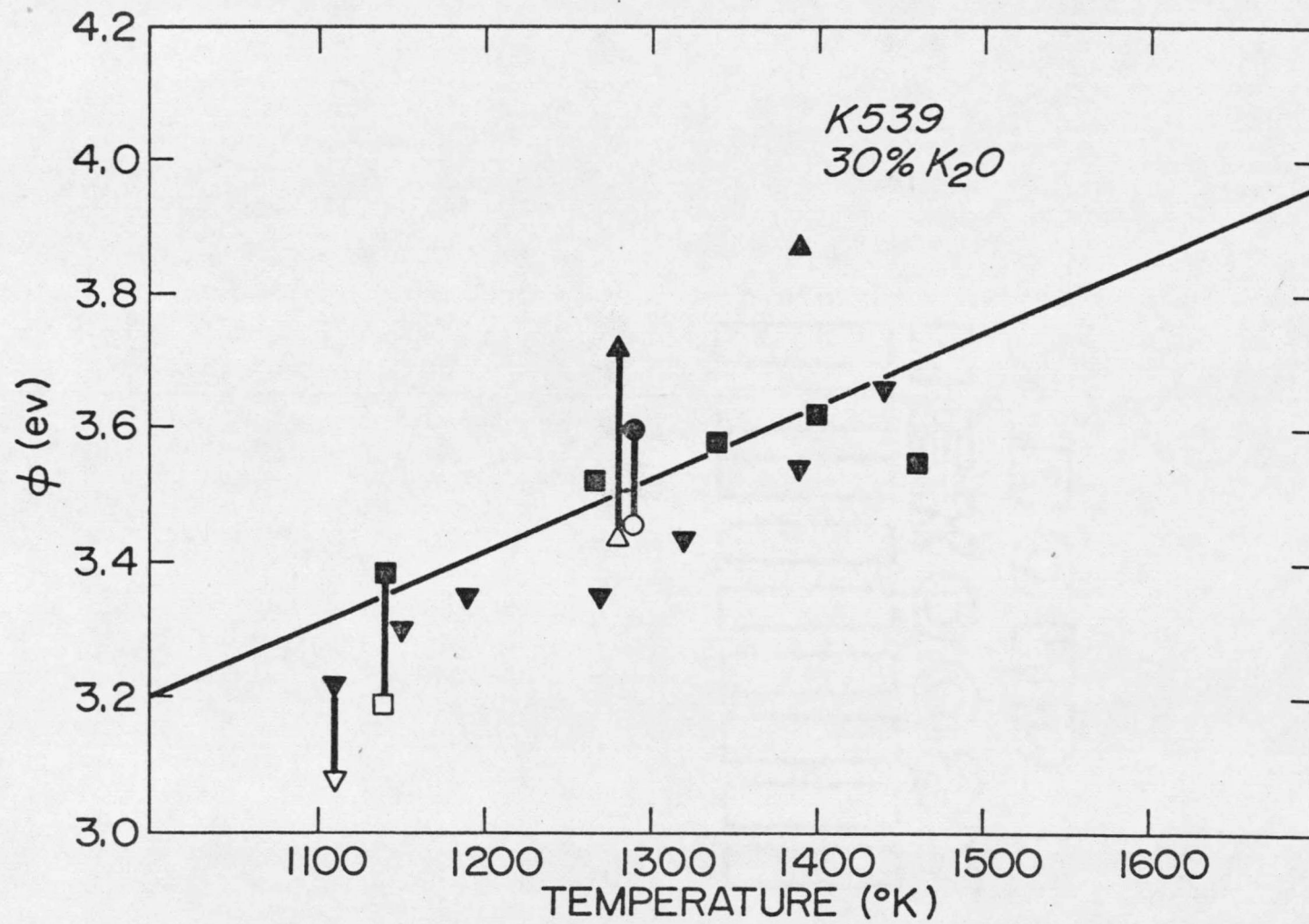


TABLE 3

Slag #	% K ₂ O by Weight	Slope (10^{-3} ev/°K)	ϕ @ 1300°K
K488	0	2.04	4.20
K492	5	2.17	3.64
K494	10	1.34	3.76
K510	20	0.99	3.52
K539	30	1.08	3.52

$$\% K_2O \text{ loss} = \left(\frac{\% K_2O \text{ before} - \% K_2O \text{ after}}{\% K_2O \text{ before}} \right) 100\%$$

Table 4 contains the results of this study. At lower temperatures ($\sim 1100^\circ K$) small amounts of potassium were lost while at higher temperatures ($\sim 1700^\circ K$) most of the potassium in these samples had evaporated out.

Thermionic studies were also done on two possible MHD ceramic electrode materials. These samples were $La_{.95}Mg_{.05}Al_{.25}Cr_{.75}O_3$ and $La_{.84}Sr_{.16}CrO_3$. The results of the thermionic studies on these lanthanum chromite based ceramics appear in Figures 17 and 18 as Richardson plots. An effective work function of $3.13 \pm .04$ eV was obtained for the magnesium and aluminum doped lanthanum chromite sample. An effective work function of $3.28 \pm .08$ eV was obtained for the strontium doped lanthanum chromite sample. For each sample the data points of three different runs appears along with the Richardson plots shown in Figures 17 and 18.

TABLE 4

Potassium content and loss from K510 after heating

(20% K_2O before heating)

Maximum Temperature ($^{\circ}K$)	K/Si Ratio	% K_2O after heating	% K_2O loss
1120 $^{\circ}$ K	1.30 $\pm$.11	17.4 %	13%
1180 $^{\circ}$ K	1.09 $\pm$.11	14.8%	26%
1530 $^{\circ}$ K	0.86 $\pm$.06	12.0%	40%
1610 $^{\circ}$ K	0.63 $\pm$.01	9.1%	55%
1680 $^{\circ}$ K	0.19 $\pm$.09	3.7%	82%

FIGURE 17

A Richardson plot for $\text{La}_{.95}\text{Mg}_{.05}\text{Al}_{.25}\text{Cr}_{.75}\text{O}_3$.

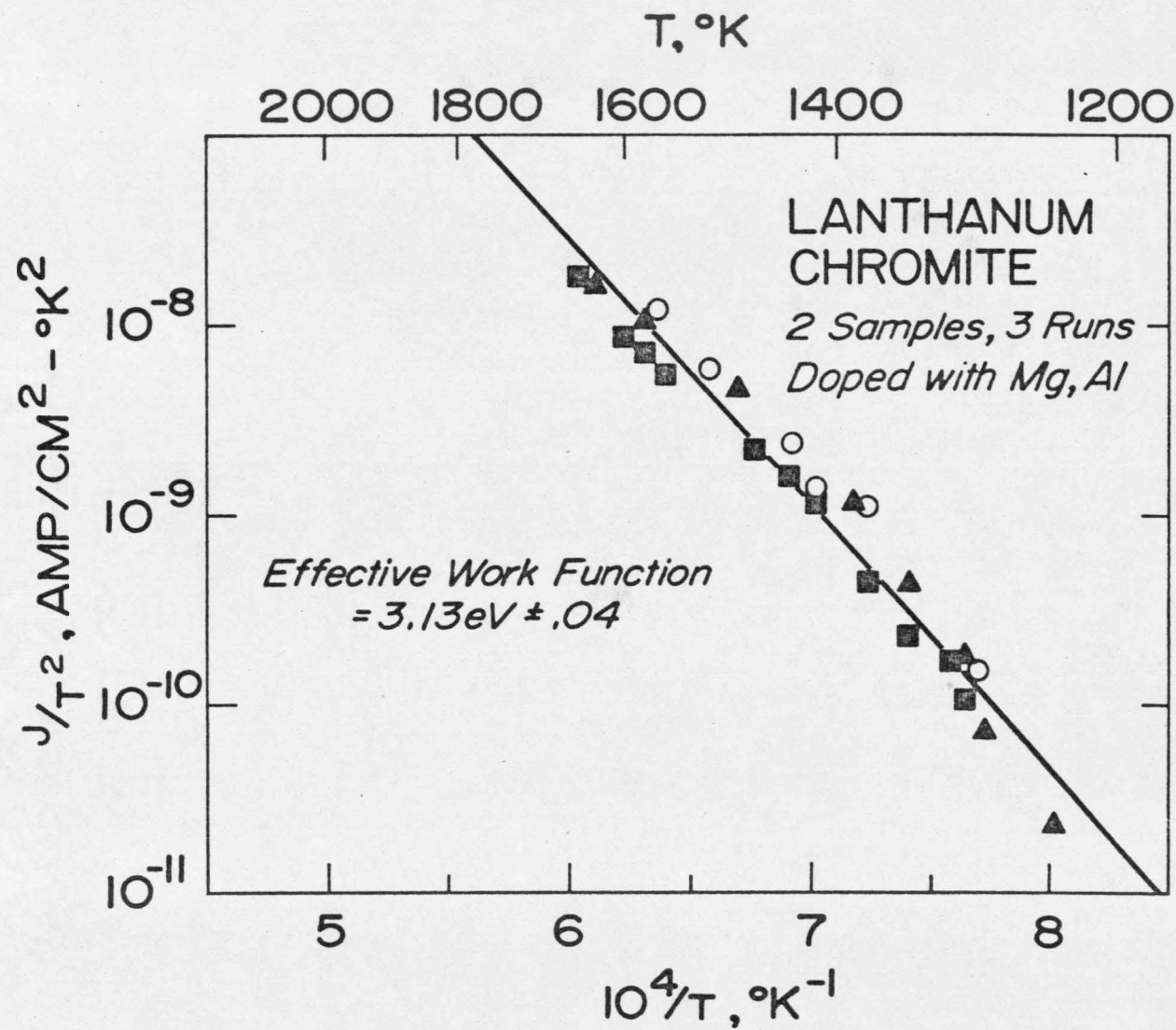
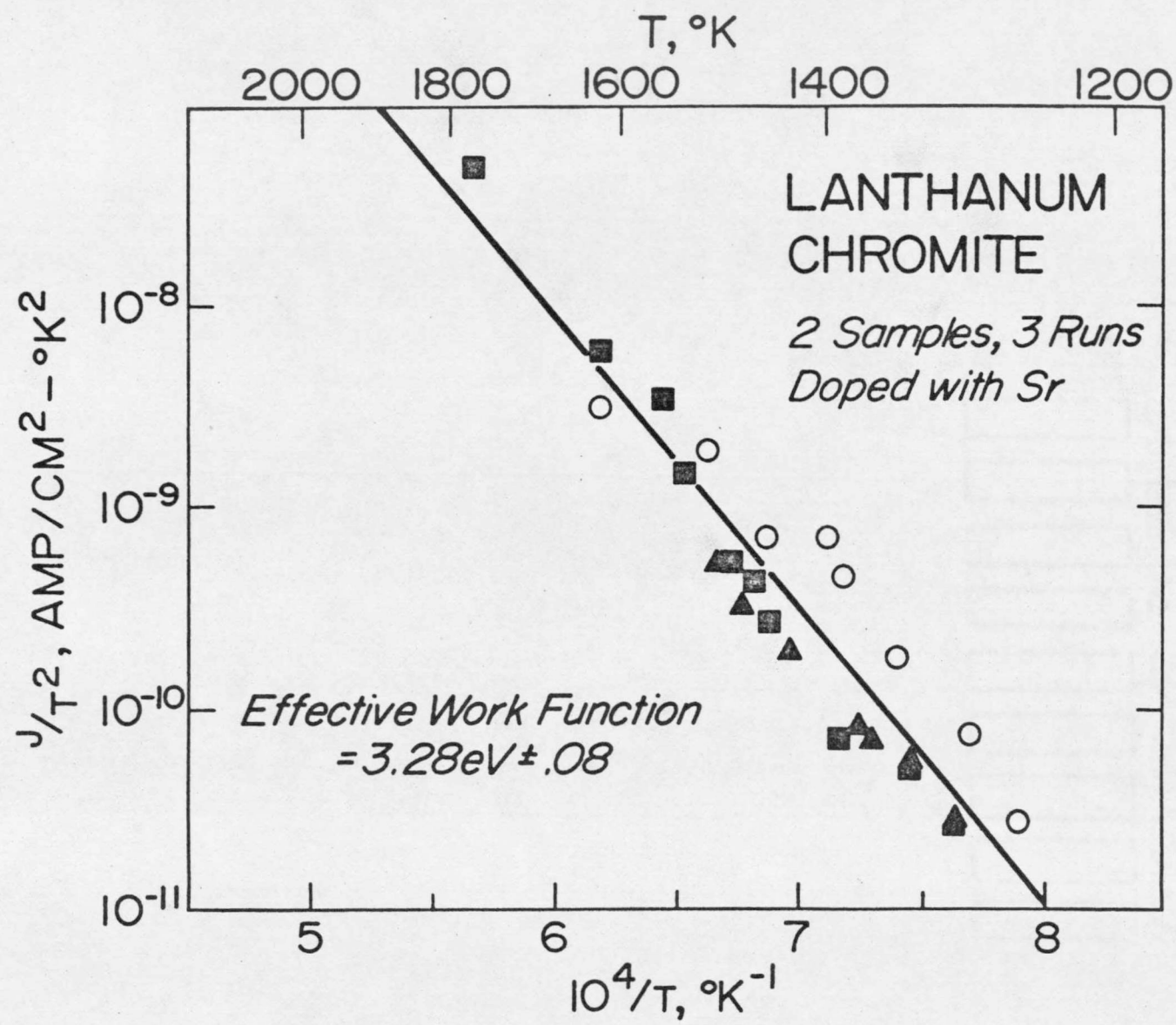


FIGURE 18

A Richardson plot for $\text{La}_{.84}\text{Sr}_{.16}\text{CrO}_3$.



V. DISCUSSION AND CONCLUSIONS

Using thermionic techniques, the effective work functions for several synthetic coal slags and lanthanum chromite based ceramics were determined in this research. Materials such as these will probably be used as the cathode material used to supply the current demand in a coal fired MHD generator. The minimum current density necessary for economical operation of an MHD channel is one amp per square centimeter. If the temperature of the cathode is 2000°K , a work function lower than 3.44 eV would be required to emit this current density.

Effective work functions of $3.28 \pm .08$ eV and $3.13 \pm .04$ eV were obtained for $\text{La}_{.84}\text{Sr}_{.16}\text{CrO}_3$ and $\text{La}_{.95}\text{Mg}_{.05}\text{Al}_{.25}\text{Cr}_{.75}\text{O}_3$. These values were obtained from clean surfaces. In a MHD generator, these cathodes would be in contact with a dense potassium seeded plasma. The electric field induced by the flow of the conducting combustion gases through the magnetic field forces electrons toward the anode while it forces potassium ions toward the cathode. As these ions build up, they reduce the thermionic work function of these ceramics and increase their current density. The potassium concentration will reach an equilibrium value when the diffusion of potassium out of these ceramics is balanced by the absorption of potassium from the plasma. If the work function of these lanthanum chromite ceramics

were reduced 1 eV by the potassium on their surfaces, the current densities would increase by a factor of 331 at 2000° K, to about 860 amps/cm² and 2050 amps/cm² for La_{.84}Sr_{.16}CrO₃, and La_{.95}Mg_{.05}Al_{.25}Cr_{.75}O₃ respectively. These current densities are extremely high and are far beyond what is needed for economical operation. By limiting the current demand from the load resistance on the channel, ohmic heating of the electrodes can be reduced and their lifetime extended. Unfortunately, the temperature of these electrodes cannot be reduced to further lengthen their lifetime because a coal slag layer would form over them.

If a slag layer has covered the cathode, then its thermionic properties are important. As with the ceramic electrodes, the equilibrium potassium concentration on the surface of this slag layer will increase its thermionic current density. It would be advantageous to be able to determine the effective work function with an equilibrium potassium concentration. However, the measurements of the effective work functions for the synthetic coal slags in this research were made under non-equilibrium conditions. That is, the potassium contained by these slags was leaving the samples while none was entering.

The effective work functions for the potassium doped low silica coal slags varied from between 3 eV and 4 eV. The lower values measured here were at lower temperatures. The X-ray fluorescence

studies that were undertaken to monitor the potassium loss from these slags indicates that very little potassium is lost at lower temperatures (less than 1300°K) while substantial losses occur at higher temperatures. This study indicates that the lower values obtained for the effective work function of the potassium doped low silica slags may be more representative of the actual work function than the higher values. This indicates that the current densities necessary for MHD power generation in a slagging environment may be obtainable.

In this research, evidence of work function lowering by absorption of ions, and potassium loss by diffusion has been observed. Also a work function temperature dependence has been observed which might be due to the potassium loss. This experimentation should be regarded as a preliminary investigation of the thermionic emission of these MHD materials. Studying thermionic emission in an equilibrium system such as was done by J. Koester¹² will give more realistic data to use in the design of a real coal fired MHD channel.

LITERATURE CITED

1. Sproull, R. L. Modern Physics.
2. Herring and Nichols, Rev. of Mod. Phy. April 1949, Vol 21, #2.
3. Langmuir, Irving. Phy. Rev. 21, 419(1923).
4. Van der Ziel, A. Solid State Physical Electronics, pp. 110.
5. Rosebury, Handbook of Electron Tubes and Vacuum Technology.
6. Stein, D. F. Jour. of Metals, Feb. 1971, p. 39.
7. Palmberg, P. w. Jour. of App. Phy. 39,2425 (1968).
8. PHI Handbook of Auger Electron Spectroscopy.
9. 51st CRC Handbook of Chem. and Phy. Table B-255.
10. 51st CRC Handbook of Chem. and Phy. Table E-87.
11. Whitney, L. V. Phy. Rev. 50, 1154 (1936).
12. Koester, J. K. Ph. D. thesis, California Inst. of Tech. (1970)
#70-24,302.

MONTANA STATE UNIVERSITY LIBRARIES

3 1762 10022701 4

W693

W693

cop.2

Wilson, M. L.

Thermionic emission
from synthetic coal
slags ...

DATE	ISSUED TO
	R. Collins ^E [unclear]
	- R
	334 L.
Sept 9	R. f. [redacted] 1378 [unclear] [unclear]