

EPA-650/2-74-074

July 1974

Environmental Protection Technology Series

**INFLUENCE
OF FLY ASH
COMPOSITIONAL FACTORS
ON ELECTRICAL
VOLUME RESISTIVITY**



Office of Research and Development
U.S. Environmental Protection Agency
Washington, DC 20460

INFLUENCE OF FLY ASH COMPOSITIONAL FACTORS ON ELECTRICAL VOLUME RESISTIVITY

by

R. E. Bickelhaupt

**Southern Research Institute
2000 Ninth Avenue South
Birmingham, Alabama 35205**

**Contract No. 68-02-0284
ROAP No. 21ADJ-029
Program Element No. 1AB012**

EPA Project Officer: L. E. Sparks

**Control Systems Laboratory
National Environmental Research Center
Research Triangle Park, North Carolina 27711**

Prepared for

**OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460**

July 1974

This report has been reviewed by the Environmental Protection Agency and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

ABSTRACT

Twenty-eight fly ash samples were characterized, chemically analyzed, and fabricated into sintered-disc resistivity specimens. These ashes represented a broad spectrum of ash compositions produced by burning coal in commercial power station boilers. Resistivity and transference experiments were performed in the temperature range in which volume conduction prevails.

The results confirmed the conclusions of an earlier investigation: 1) the volume conduction mechanism for fly ash is ionic and 2) the charge carriers are the alkali metal ions, principally sodium. It was learned that increasing iron concentration caused a decrease in resistivity for a given level of sodium and lithium. No evidence of biased data or electronic conduction was found. It was rationalized that in a manner analogous to that for glass the iron affected the structure of the predominant glassy phase of the ash thereby inducing the participation of a greater percentage of the available alkali metal carrier ions.

From these data, empirical equations were developed to predict the volume resistivity of fly ash as a function of ash chemistry, temperature and porosity.

This report was submitted in partial fulfillment of Contract No. 68-02-0284 by Southern Research Institute under the sponsorship of the Environmental Protection Agency. Work was completed as of July 1974.

TABLE OF CONTENTS

	<u>Page</u>
Abstract	iii
List of Figures	vi
List of Tables	vii
 <u>Sections</u>	
I Conclusions	1
II Recommendations	2
III Introduction	3
IV Scope	4
V Experimental Procedures	5
VI Results and Discussion	10
VII Prediction of Volume Resistivity	31
VIII Summary	37
IX References	39

LIST OF FIGURES

<u>No.</u>		<u>Page</u>
1	Alumina Resistivity Apparatus	7
2	Typical as Measured Resistivity versus Reciprocal Absolute Temperature for Three Ashes	13
3	Resistivity versus Atomic Percentage Lithium plus Sodium at $1000/T(^{\circ}K) = 1.6$ and 40% Porosity	18
4	Resistivity versus Atomic Percentage Iron at $1000/T(^{\circ}K) = 1.6$, 40% Porosity and 0.4 a/o Lithium plus Sodium	20
5	Gravimetric Data for Transference Experiments	24
6	Relative Effectiveness of Lithium and Sodium as Charge Carriers as a Function of Iron Concentration	27
7	Correlation Between as Determined and Predicted Resistivities	36

LIST OF TABLES

<u>No.</u>		<u>Page</u>
1	Chemical Analyses of Fly Ashes	12
2	Resistivity, Porosity, Atomic Concentration	15
3	Transference Experiments, Chemical Analyses of Specimens in Weight Percent	26

SECTION I

CONCLUSIONS

Electrical volume conduction takes place through a continuous matrix of glassy particles which make up at least 75 weight percent of the ash.

An ionic mechanism controls the conduction process. The alkali metal ions are the charge carriers, and because of the relatively high concentration and mobility, sodium is the principal participant.

The presence of iron attenuates the resistivity of fly ash having a given level of alkali metal ion concentration. The iron concentration does not reduce resistivity by either a direct ionic or electronic contribution to the conduction process. It is believed that the iron in solution in the glassy ash affects a structural modification that permits the migration of a greater number of the total alkali metal ions available.

In a regular and reproducible manner, the volume resistivity can be related to: the atomic percent of lithium and sodium, the atomic percent of iron, the temperature, and the porosity of the fly ash specimen. An expression has been developed to yield a reasonable prediction of volume resistivity in terms of these parameters.

SECTION II

RECOMMENDATIONS

The concluded research suggests that compounds containing sodium or iron might be useful as coal additions to attenuate high resistivity. Field experience with this approach would be beneficial.

Since the role of iron is imperfectly understood, additional laboratory work might be undertaken with respect to its use as a conditioning agent.

The expressions developed to predict volume resistivity from the chemical analysis of ash, temperature and porosity should be evaluated against high temperature field data as well as laboratory data acquired with various techniques of resistivity measurement. Laboratory work should be undertaken to evaluate the ability to predict resistivity for laboratory ashed coals.

Research similar to that reported herein should be conducted in the temperature range in which surface conduction is operable. An understanding of the surface mechanism could lead to the prediction of surface resistivity as a function of certain measurable parameters and explain the role of conditioning agents.

SECTION III

INTRODUCTION

The purpose of this research was to define the compositional factors that influence the electrical resistivity of fly ash. This information was desired to attempt to predict resistivity from fly ash and/or coal compositions. At the start of the program, it was planned to accomplish the above purpose with respect to the entire normal temperature range (125°C to 450°C) for the operation of electrostatic precipitators. The complex nature of the research and the limitations of the contract forced the scope to be limited to the high temperature region in which the resistivity of the ash is controlled by a volume conduction process and is not influenced by environmental characteristics such as water vapor and SO₃.

Early in 1972, research¹ conducted for Calgary Power, Ltd. of Calgary, Alberta, Canada was completed that showed the pronounced influence of certain alkali metal ions on the resistivity of two ashes that were almost identical in composition with the exception of the amount of sodium. This work was then expanded to include other ashes of generally similar composition coming from coals of the Western part of the United States. This research was recently published,² and is summarized below.

Above 250°C the volume conduction process in fly ash is controlled by an ionic mechanism. The quantity of electricity passed is proportional to a mass transfer, and lithium and sodium ions were found to migrate. The limited migration of potassium was also detected. Resistivity decreased about two orders of magnitude for a one order of magnitude increase in the combined concentration of lithium and sodium.

The research reported herein concerns an attempt to examine the compositional factors that influence volume resistivity for a broader spectrum of ash composition. In addition to qualitatively defining these factors, it was desired to develop an expression with which one could predict resistivity from the chemical analyses of ashes.

SECTION IV

SCOPE

Approximately twenty-five fly ashes produced commercially from Eastern and Western coals were utilized. From this group, representative ashes were selected for characterization regarding particle size, helium pycnometer density, optical microscopy, and X-ray diffraction. All ashes were chemically analyzed for the major constituent elements and were fabricated into sintered-disc specimens for resistivity determinations between 200 and 450°C. Transference experiments were conducted for certain ashes selected on the basis of the resistivity-chemistry behavior.

SECTION V

EXPERIMENTAL PROCEDURES

RESISTIVITY: SPECIMENS AND PROCEDURES

Electrical resistivity was determined by measuring current flow under known dc potential for self-supporting discs of fly ash. Although this type of specimen is unusual with regard to fly ash resistivity measurements, it is commonly used in work pertaining to other types of insulator materials. For the experiments to be conducted in this research, the self-supporting disc specimen was desirable. The specimens, experimental equipment, and procedures followed were generally similar to that suggested for this type of measurement by ASTM.³

Specimen Preparation

A known quantity of dry fly ash was mixed with 3% of polyvinyl alcohol (duPont's Elvanol Grade 70-05 used as 10% solids in distilled water) and sufficient distilled water to produce a paste. After thorough blending, the mixture was dried to about 4% moisture and rubbed through a 20-mesh screen. The resultant granulation was pressed into discs 3.2 cm in diameter and about 4 mm thick. Double-acting pressing was used with a 2270 kg load.

The discs were dried overnight at 110°C and sintered in air for two hours at temperatures selected to produce a given range of specimen porosity. Although the discs were weak, sufficient strength was secured so that the specimens could be handled and measured and would support themselves in the resistivity apparatus.

Physical measurements and microscopic analysis of the disc specimens showed that undue densification did not occur. The specimens were essentially assemblages of spherical particles having a porosity of 31 to 47%. Comparative chemical analyses were made for "as received" ash and respective sintered discs. No alteration in overall chemistry could be detected due to specimen preparation.

Using a gold alloy paste, Engelhard #9696, electrodes 1.9 cm in diameter were painted on opposite faces of the disc at the center. The electrodes were fired at 900°C for 30 to 40 minutes in air.

Resistivity Apparatus

A specimen holder was built exclusively from 99.5% alumina and was used to position the fly ash disc between contactors and leads under about 1 kg of load. A specimen holder similar to that used in this work is shown in Figure 1.

The assembled holder was inserted into a vertical, platinum-resistor tube furnace having a uniform temperature zone ($\pm 3^\circ\text{C}$) 8 cm in length. The holder was aligned vertically so that the specimen was at the center of this zone, and horizontally so that the apparatus did not contact the furnace. The leads, insulated with 99.5 alumina, were directed out the top and bottom of the furnace to the electrical terminals.

Specimen temperature was determined using a chromel-alumel thermocouple located 3 mm from the positive face of the specimen and 1 cm from the center of the specimen. The thermocouple output was measured using a Rubicon Model 2745 potentiometer with cold junction correction.

In addition to the specimen and related leads, the test circuit contained a dc voltage source, Keithley Model 240A high voltage supply, and a current measuring device, Keithley Model 610 electrometer.

Test Procedure

With the specimen holder in place, the power to the furnace was started. The furnace was allowed to heat and thermally equilibrate overnight at about 430°C. The dc potential (200 volts) was connected to the specimen and time recorded. The combination of the noble metal electrodes and direct current applied voltage resulted in a condition of electrode polarization. Electrometer readings decreased with time after the initiation of the applied voltage. It was

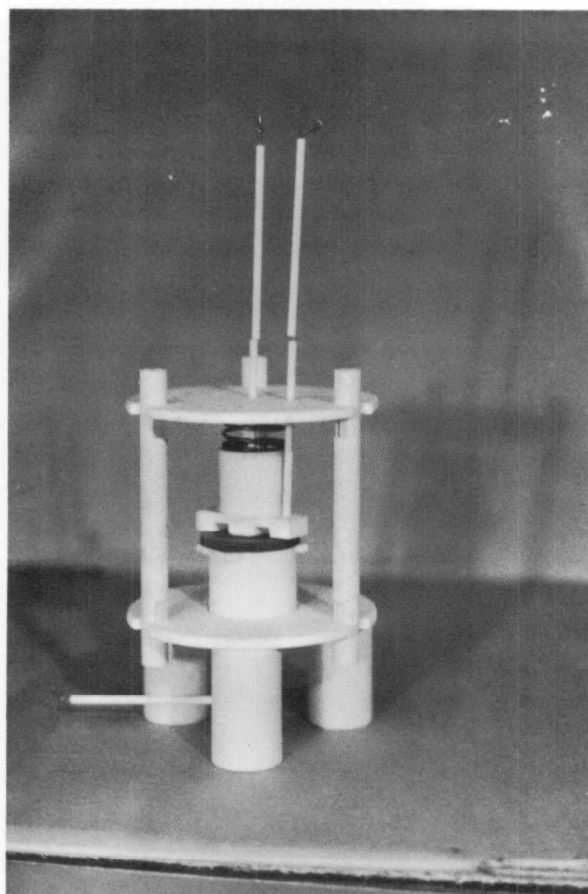


Figure 1. Alumina resistivity test apparatus

found that after 30 minutes, the rate of decrease in current was negligible with reference to the time required to obtain the resistivity data. Within the objectives of this research, this procedure was acceptable. After the 30 minute period, the power to the furnace winding was turned off, and the specimen temperature and current readings were simultaneously taken at about 30°C intervals as the temperature decreased. The test was conducted in a normal laboratory environment containing nominally 1% water by volume.

Resistance was calculated from:

$$R = V/I \quad (1)$$

where

R = resistance, Ω ,
V = dc voltage, volts, and
I = measured current, amperes.

Resistivity was calculated from:

$$\rho = R \times A/l \quad (2)$$

where

ρ = resistivity, Ω -cm,
R = resistance, Ω
A = area of electrodes, cm^2 , and
l = specimen thickness, cm.

Resistivity was plotted versus reciprocal absolute temperature.

TRANSFERENCE MEASUREMENTS

The principles and techniques used in making transference measurements are reviewed in the literature, for example by Kingery.⁴ An unsophisticated approach to this measurement was used because of the complex chemistry of fly ash. In violation of experimental boundary conditions for a transference experiment, blocking electrodes were used. The blocking electrodes, noble metals in this case, are incapable of accepting or introducing charge carriers to support ionic conduction. Therefore, one cannot obtain unequivocal quantitative data regarding the conduction mechanism.

Three disc specimens were positioned in axial alignment with disc faces contiguous. Electrodes were affixed only on those faces in contact with the positive and negative contactors and leads. After the furnace had equilibrated at about 600°C, the dc voltage (1000 volts/cm) was applied and the current-time relationship was recorded for approximately 200 hr.

The current-time plot was graphically integrated and converted to coulombs of electricity. This measured quantity of electricity, the measured weight change of the specimens, and pre- and post-test chemical analyses were used to illustrate a mass transfer and to qualitatively identify the charge carriers.

SECTION VI

RESULTS AND DISCUSSION

ASH CHARACTERIZATION

Several ashes representing both Eastern and Western coals were subjected to a characterization study. Optical and electron microscopy revealed that the ash particles were mainly spherical in shape over the entire size spectrum for all the ashes examined. Each ash possessed a wide variation in color and light transmission. Density measured by helium pycnometer on dried "as received" ashes varied from 2.2 to 2.7 grams/cc. It was noted that the ashes having the greater amounts of iron and/or calcium present possessed the higher densities; however, it should also be stated that unburned carbon and cenospheres greatly affect the density value. The mass-mean-diameter of the ashes varied from 7 to 20 microns. No particular significance is attached to these size data since the sample history was not known in all cases.

The ashes were also examined by microprobe analysis and X-ray diffraction. The microprobe analyses showed that, within a given particle and among particles of a given ash, chemical heterogeneity may exist. X-ray diffraction patterns for the Western ashes revealed the presence of the crystalline compounds: quartz, mullite, and a calcium silicate. Calcium sulfate was also found in certain ashes. The Eastern ashes contained: quartz, mullite, an iron oxide, and an iron-alumina-silicate. Although the various compounds produced a large number of diffraction lines, it was noted that the line intensities were quite low. Furthermore, a pair of halos at the low two theta position, usually an indication of amorphous material in an X-ray diffraction pattern, were observed. A quantitative analysis⁵ was made on two ashes to determine the amount of silica present. Silica was the most prominent crystalline compound in these ashes. Less than four percent silica was determined. From the observations, it was concluded that the ashes contained unburned carbon, minor amounts of several crystalline compounds, and large percentages of glassy solids.

The above statements of characterization are in contrast with the observations of certain European investigators.⁶ It has been observed that a European ash may microscopically display crystalline morphology and reveal a high percentage of crystalline compounds by X-ray diffraction. It is believed that this condition is caused by a combination of low boiler temperature and the use of coals producing very high percentages of ash.

All the ashes used in this research were chemically analyzed for the major elements. These data expressed in weight percent as oxides are shown in Table 1. Ashes 1 through 15 come from Western coals, while ashes 16 through 28 come from Eastern coals. Excluding one or two unusual ashes, the comparison between chemical analyses for Western and Eastern ashes may be summarized as follows: 1) The sodium oxide concentration of Western ashes ranges from less than that of a typical Eastern ash to six times as much, 2) Eastern ashes contain more lithium and potassium oxide than the Western ashes, and 3) The combined concentration of MgO plus CaO plus Fe₂O₃ is about 10 to 30 percent for all ashes. About 60 to 80% of this total is MgO plus CaO for Western ashes, while the large percentage is Fe₂O₃ for Eastern ashes.

RESISTIVITY DATA

Resistivity data were obtained in the temperature range of 200 to 450°C for the twenty-eight ashes shown in Table 1. Typical data are shown graphically in Figure 2 with resistivity plotted on a log scale ordinate versus the reciprocal of absolute temperature. For a given temperature, a wide range in resistivity was encountered (about 3 orders of magnitude) for all the ashes studied.

The linear curves indicate the data can be interpreted in terms on an Arrhenius equation, in logarithmic form,

$$\log \rho = \log \rho_0 + [(\theta/k) \log e] (1/T) \quad (3)$$

where

- ρ = resistivity
- ρ_0 = a complex material parameter
- θ = experimental activation energy
- k = Boltzmann's constant
- T = absolute temperature.

Table 1. CHEMICAL ANALYSES OF FLY ASHES

ASH NUMBER	EXPRESSED IN WEIGHT PERCENT AS OXIDES											
	<u>Li₂O</u>	<u>Na₂O</u>	<u>K₂O</u>	<u>MgO</u>	<u>CaO</u>	<u>Fe₂O₃</u>	<u>Al₂O₃</u>	<u>SiO₂</u>	<u>TiO₂</u>	<u>P₂O₅</u>	<u>SO₃[*]</u>	<u>LOI</u>
1	0.04	0.09	0.30	5.40	21.50	4.30	22.80	40.15	1.30	0.34	1.70	0.33
2	0.01	0.24	0.89	3.30	23.50	5.53	21.20	40.50	2.13	0.54	1.83	0.20
3	0.01	0.25	0.89	1.88	11.10	3.71	23.60	55.60	1.56	0.14	0.32	0.74
4	0.01	0.34	0.77	1.60	11.60	3.60	25.30	56.80	0.83	0.17	0.17	0.60
5	0.01	0.32	0.90	1.80	12.70	3.90	25.80	55.00	0.89	0.17	0.32	0.65
6	0.01	0.53	1.10	1.70	12.20	4.20	25.10	55.10	0.83	0.18	0.24	0.60
7	0.02	1.30	0.72	2.50	8.60	4.65	18.20	59.00	2.20	0.19	1.05	0.45
8	0.02	1.07	0.70	2.23	8.30	4.66	17.70	61.00	1.53	0.16	0.77	0.50
9	0.02	1.77	1.13	1.93	6.36	4.61	24.60	53.70	1.49	1.06	0.79	1.49
10	0.01	3.10	0.80	0.90	10.40	3.40	28.20	52.00	0.88	0.18	0.26	0.45
11	0.01	2.10	1.00	0.99	12.30	4.60	26.50	52.00	0.93	0.21	0.36	0.40
12	0.01	2.40	1.00	0.93	13.60	4.80	26.20	49.20	0.93	0.24	0.46	0.45
13	0.02	0.38	2.36	2.59	11.41	6.03	19.64	55.29	0.95	0.60	0.58	0.35
14	0.01	1.47	0.68	1.73	7.33	5.33	23.10	53.10	4.17	0.90	1.11	0.44
15	0.01	1.84	0.20	12.75	31.00	11.20	14.80	22.00	0.60	0.39	4.80	0.41
16	0.05	0.48	2.75	0.88	0.87	5.50	27.80	50.45	1.85	0.23	0.70	7.70
17	0.04	0.49	3.12	1.09	2.48	13.24	26.40	50.70	1.62	0.28	0.57	1.00
18	0.05	0.32	2.30	0.98	4.60	23.70	21.20	42.70	1.40	0.34	0.69	5.50
19	0.02	0.23	2.80	0.86	2.20	23.00	21.00	47.70	1.80	0.52	1.30	2.10
20	0.02	0.51	2.80	0.93	0.26	17.90	21.90	51.00	1.40	0.33	0.96	1.80
21	0.01	0.35	2.36	1.66	3.72	16.10	17.80	43.30	1.27	0.36	0.64	10.30
22	0.04	0.33	3.88	1.57	0.77	10.01	27.50	51.40	1.79	0.32	0.37	1.50
23	0.03	0.38	3.34	1.29	1.04	9.70	25.90	49.90	1.98	0.32	0.42	4.40
24	0.07	0.40	3.10	1.20	1.40	8.80	29.00	52.40	1.70	0.40	0.29	3.20
25	0.05	0.16	2.60	0.93	0.87	8.40	31.00	55.10	2.30	0.36	0.23	1.40
26	0.04	0.51	3.80	1.30	0.68	4.90	30.20	53.00	2.00	0.17	0.36	2.50
27	0.05	1.55	2.80	1.15	2.50	3.85	25.00	56.75	1.55	0.28	1.12	1.70
28	0.06	0.42	3.70	1.30	1.10	9.90	30.30	52.40	1.70	0.51	0.45	1.30

*Total Sulfur

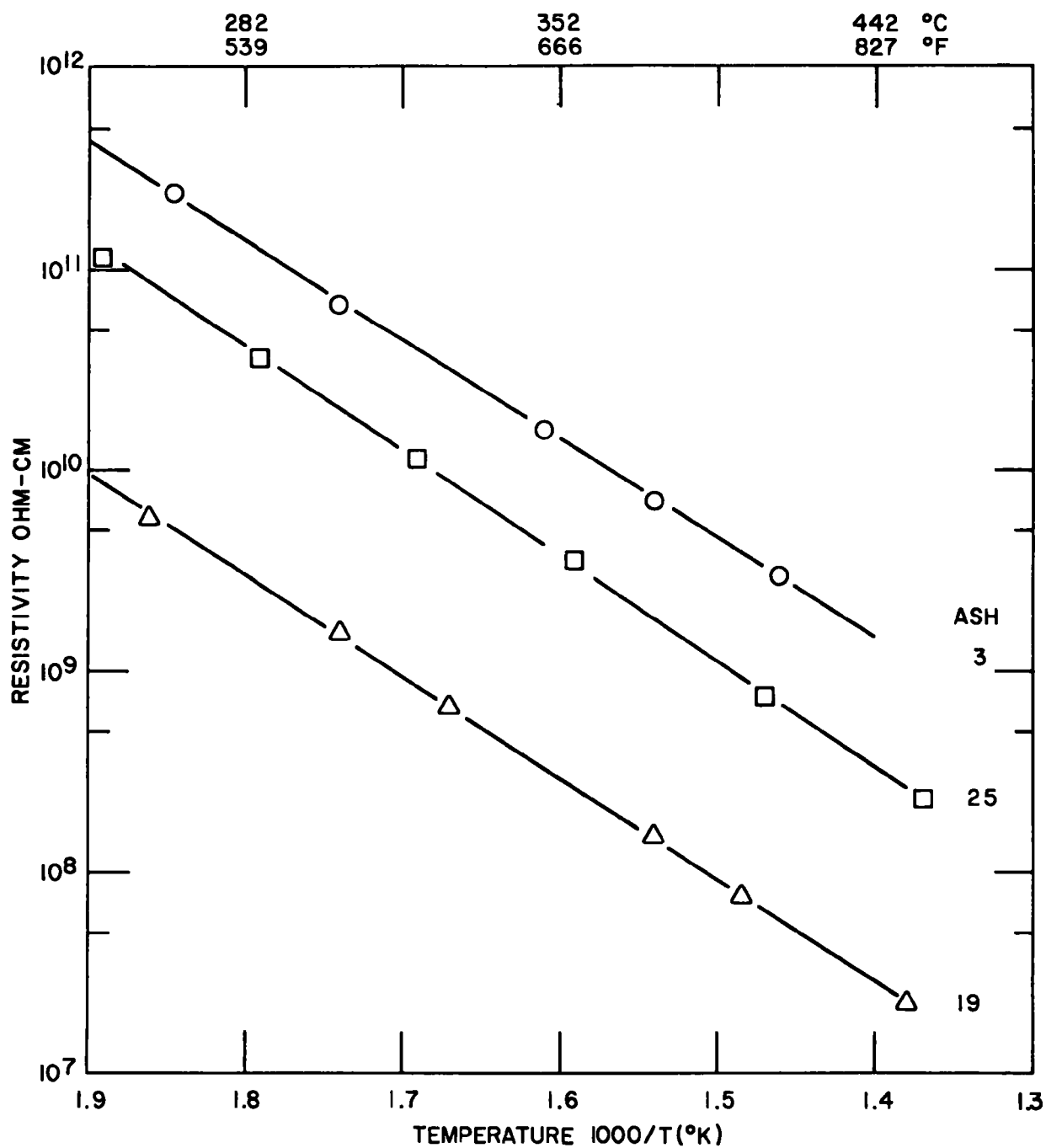


Figure 1. Typical measured resistivity versus reciprocal absolute temperature for three ashes

The experimental activation energy (θ) is proportional to the slope of the curves and was found to be between 1.0 and 1.1 eV for all the ashes. This suggests that a similar conduction mechanism prevails for each ash. An average value of 1.03 eV will be used later in the report to establish the equation for predicting resistivity from ash chemistry and temperature. To develop the relationship between resistivity and certain chemical parameters, the resistivity at the reciprocal temperature of $1000/T = 1.6$ was used. These data (as measured) for all the ashes studied appear in column two of Table 2.

Intuitively, one would expect the volume conduction process to be influenced by the amount of specimen porosity. This was found to be true. When resistivity was determined for several ashes fabricated to two levels of porosity, the higher porosity produced greater resistivity. Dalmon and Tidy⁷ also experienced this relationship.

An empirical expression was developed to correct the resistivity values acquired in this research to a constant porosity. Using the initial approximation of the curves relating resistivity to the concentrations of lithium plus sodium and iron (shown in final form later in the report), the as-measured resistivity value for each ash was normalized to a constant concentration of lithium, sodium and iron. The normalized resistivity value for each ash was then plotted against the porosity of the respective ash specimen. The percent specimen porosity was calculated from the measured bulk volume and the determined helium pycnometer volume as follows:

$$\%P = \frac{V_{\text{bulk}} - V_{\text{He Pyc}}}{V_{\text{bulk}}} \times 100. \quad (4)$$

The plot of normalized resistivity data versus porosity was subjected to a linear regression analysis. The following relationship was generated:

$$\log \rho_c = \log \rho_m + S (P_c - P_m) \quad (5)$$

where

$$\begin{aligned} \rho_c &= \text{resistivity corrected to porosity } P_c \\ \rho_m &= \text{resistivity measured at porosity } P_m \\ S &= \Delta \log \rho / \Delta \%P = 0.04 \end{aligned}$$

Table 2. RESISTIVITY, POROSITY, ATOMIC CONCENTRATIONS

Ash Number	Resistivity ohm-cm As Measured at $1000/T(^{\circ}K)=1.6$	% Porosity	Resistivity ohm-cm at $1000/T(^{\circ}K)=1.6$ and Porosity=40%	Atomic Concentration		Resistivity ohm-cm at $1000/T(^{\circ}K)=1.6$ Porosity=40% Li+Na=0.4 a/o
				Li+Na	Fe	
1	7.7×10^{10}	47	4.1×10^{10}	0.13	0.71	-
2	3.4×10^{10}	42	2.8×10^{10}	0.19	0.94	-
3	1.5×10^{10}	36	2.2×10^{10}	0.20	0.64	-
4	8.5×10^9	39	9.3×10^9	0.26	0.60	-
5	5.7×10^9	37	7.5×10^9	0.25	0.65	-
6	4.5×10^9	33	8.6×10^9	0.40	0.71	-
7	6.5×10^8	39	7.1×10^8	0.98	0.79	-
8	1.4×10^9	39	1.5×10^9	0.81	0.79	-
9	9.0×10^8	46	5.2×10^8	1.39	0.82	-
10	1.0×10^8	34	1.7×10^8	2.28	0.58	-
11	2.5×10^8	32	5.2×10^8	1.56	0.79	-
12	4.1×10^8	35	6.5×10^8	1.81	0.84	-
13	2.0×10^9	40	2.0×10^9	0.31	1.02	-
14	5.3×10^8	39	5.8×10^8	1.13	0.94	-
15	2.4×10^8	50	9.6×10^7	1.29	1.81	8.0×10^8
16	1.9×10^9	42	1.7×10^9	0.49	1.10	2.5×10^9
17	2.4×10^8	34	4.2×10^8	0.46	2.50	5.4×10^8
18	3.0×10^8	44	2.1×10^8	0.37	4.81	1.8×10^8
19	2.9×10^8	36	3.8×10^8	0.27	4.49	1.9×10^8
20	1.5×10^8	33	2.9×10^8	0.47	3.51	3.9×10^8
21	2.0×10^8	31	4.6×10^8	0.34	3.47	3.4×10^8
22	6.0×10^8	40	6.0×10^8	0.34	1.91	4.4×10^8
23	5.8×10^8	40	5.8×10^8	0.37	1.91	5.0×10^8
24	1.0×10^9	42	8.3×10^8	0.45	1.66	1.05×10^9
25	3.8×10^9	42	3.2×10^9	0.25	1.54	1.3×10^9
26	1.9×10^9	40	1.9×10^9	0.43	0.93	2.3×10^9
27	3.6×10^8	37	4.8×10^8	1.29	0.70	4.2×10^9
28	5.8×10^8	36	8.4×10^8	0.45	1.82	1.1×10^9

Although the positive slope of the normalized resistivity vs percent porosity data was obvious, the twenty eight data points presented considerable scatter. For confidence limits of 95%, the slope, S , was 0.04 ± 0.02 . Since the porosity correction factor is somewhat uncertain and since the average porosity for all resistivity specimens was about 40%, the as-measured resistivity data were corrected to a porosity level of 40% for subsequent use. The porosity values and the resistivity data corrected to 40% appear in columns 3 and 4 respectively in Table 2.

The chemical concentrations used to show the relationship between resistivity and ash chemistry are given in atomic percent in columns 5 and 6 of Table 2. These values were arrived at in the following manner. The weight percent chemical analyses shown in Table 1 were normalized to total 100% excluding the loss on ignition. The weight percentages were then converted to molecular percentages from which the atomic concentration of lithium, sodium, and iron were calculated.

In summary, Table 2 shows for each of the twenty eight ashes studied: the as-measured resistivity at $1000/T(^{\circ}K) = 1.6$, the porosity of the resistivity specimen, the resistivity corrected to 40% porosity, and the atomic percentages of lithium plus sodium and iron in the specimen. The last column in Table 2 will be referred to later.

RESISTIVITY-ASH CHEMISTRY CORRELATION

In reference 2 it was proposed that the volume conduction mechanism is ionic and that the alkali metals, principally sodium, are the charge carriers. This was substantiated by direct evidence of the proportionality between mass transfer and the quantity of electricity conducted and by the chemical identification of the migrating elements. For fly ashes of limited compositional range, it was shown that resistivity was inversely proportional to the concentration of lithium and sodium. The above points as well as other aspects of the conduction process were discussed in detail in the subject reference and will not be reiterated.

The research reported herein was designed to verify the initial results, expand the scope to include a greater number of ashes so that a wide range of ash composition might be evaluated, and develop an expression capable of a reasonable prediction of volume resistivity based on ash chemistry, temperature, and ash layer porosity. To satisfy the objectives, 28 ashes were acquired. The ashes were produced mainly from bituminous and sub-bituminous coals but also from lignite, anthracite and coal prepared for metallurgical use. It is believed that the ash compositional ranges are sufficiently broad for the effort. The resistivity data were presented in Table 2.

These data were initially examined by testing the inverse proportionality between resistivity and the combined concentrations of lithium and sodium. This was done by plotting on a log-log scale the resistivity of the 28 ashes taken at $1000/T(^{\circ}\text{K}) = 1.6$ ($\sim 350^{\circ}\text{C}$ or 665°F) and corrected to 40% porosity versus the atomic percentage of lithium plus sodium. Figure 3 illustrates the result. The ash designation numbers that are underlined are Eastern ashes while the remainder are Western. Viewing the data points showing the spread in resistivity at 0.4 atomic percent lithium plus sodium or the spread in concentration at a resistivity of 5×10^8 ohm-cm, one would doubt that a correlation exists. It was obvious that some factor in addition to the lithium-sodium concentration was affecting the results. To verify the earlier results from reference 2, a linear regression analysis was made between resistivity and lithium-sodium concentration for those Western ashes containing <1.0 atomic percent iron. This level of iron was chosen from the earlier work. The curve constructed in Figure 3 with a slope of -1.84 is the result of the regression analysis. The coefficient of correlation between the calculated curve and the data points used was 0.98, and the slope was within 5% of that previously determined with similar ashes.

With the correlation between resistivity and lithium-sodium concentration verified for a select group of ashes, the problem became one of explaining the observation that about half the ashes examined did not conform. Although the concentrations of other elements were considered, inspection of the resistivity and chemical analysis data suggested that the iron concentration affected resistivity.

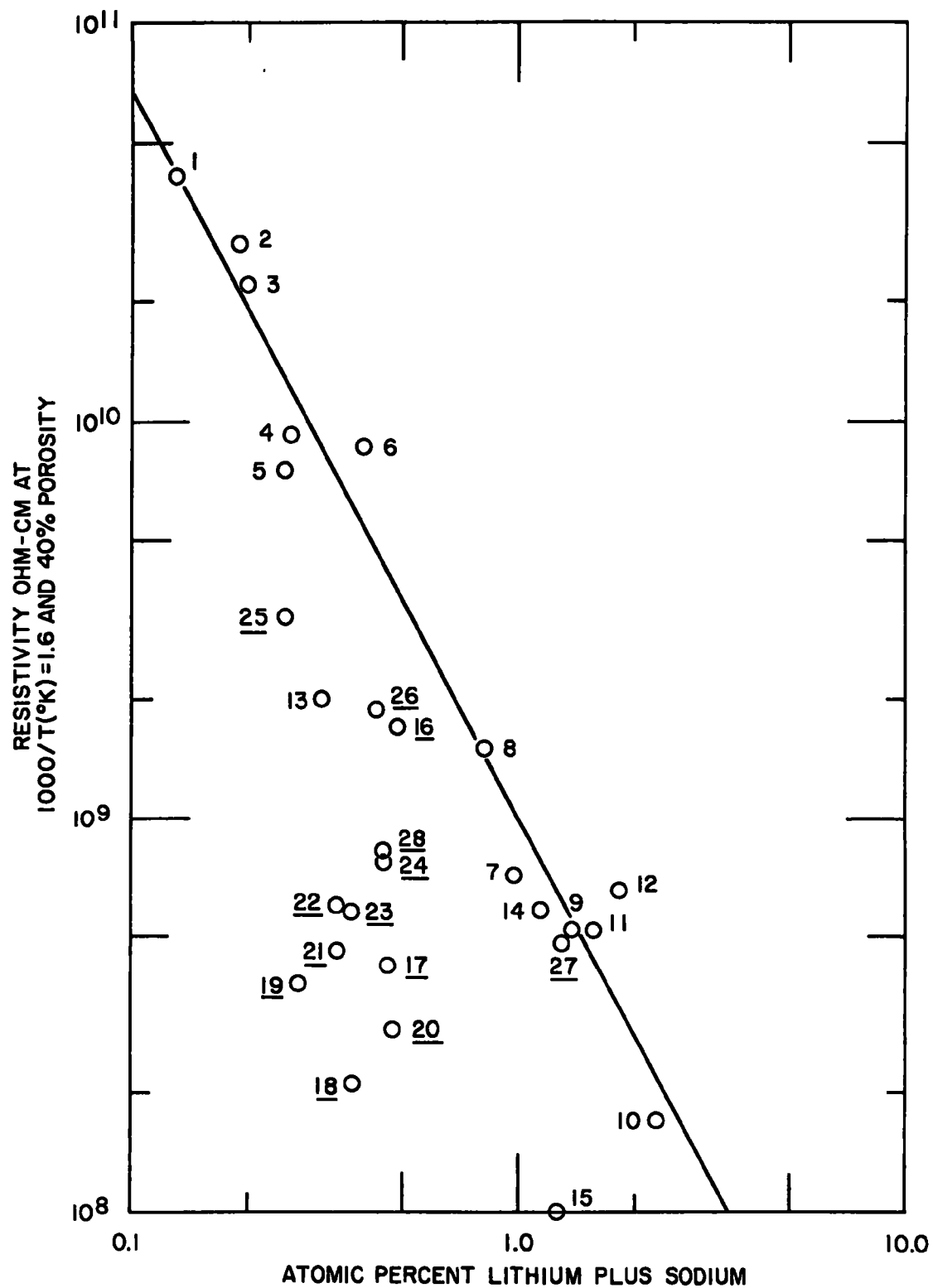


Figure 3. Resistivity versus atomic percentage lithium plus sodium at $1000/T(^{\circ}\text{K}) = 1.6$ and 40% porosity

The effect of iron was evaluated by normalizing the resistivity values to a constant amount of lithium and sodium for all Eastern ashes and the Western ash having an iron concentration >1.0 atomic percent. Resistivity values normalized to 0.4 atomic percent sodium plus lithium were obtained by drawing a line through the specific data point parallel to the constructed curve in Figure 3 and reading the resistivity at the point where this line intersected the 0.4% ordinate. Resistivity data acquired in this manner are tabulated in the last column in Table 2.

Figure 4 shows the resistivity data normalized to a constant lithium-sodium concentration plotted against the iron concentration on a log-log scale. The data point marked (*) represents the average resistivity and iron concentration for the Western ashes having <1.0 atomic percent iron. Again, the Eastern ash numbers are underlined and the Western is not.

A linear regression analysis of all data points in Figure 4 with the exception of numbers 22 and 23 produced the curve shown. This curve has a slope of -1.65 and a coefficient of correlation with the data points used of 0.99 . No definite explanation can be given for the two points that lie significantly below the constructed curve. It should be noted that there are many opportunities to introduce errors: 1) during the selection of ash samples and the fabrication of specimens, 2) in the measurement of weight percent chemical analyses, resistivity and porosity, and 3) during the subsequent manipulation of these data. On the other hand, it is conceivable that these points would become part of a band of data if a very large number of ashes were examined.

From Figure 4 it becomes apparent that the volume resistivity of fly ash is also inversely proportional to the iron concentration. The slopes of the curves in Figures 3 and 4 suggest that resistivity is only slightly less sensitive to iron concentration than it is to lithium-sodium concentration. Figure 4 empirically explains the scatter of data shown in Figure 3.

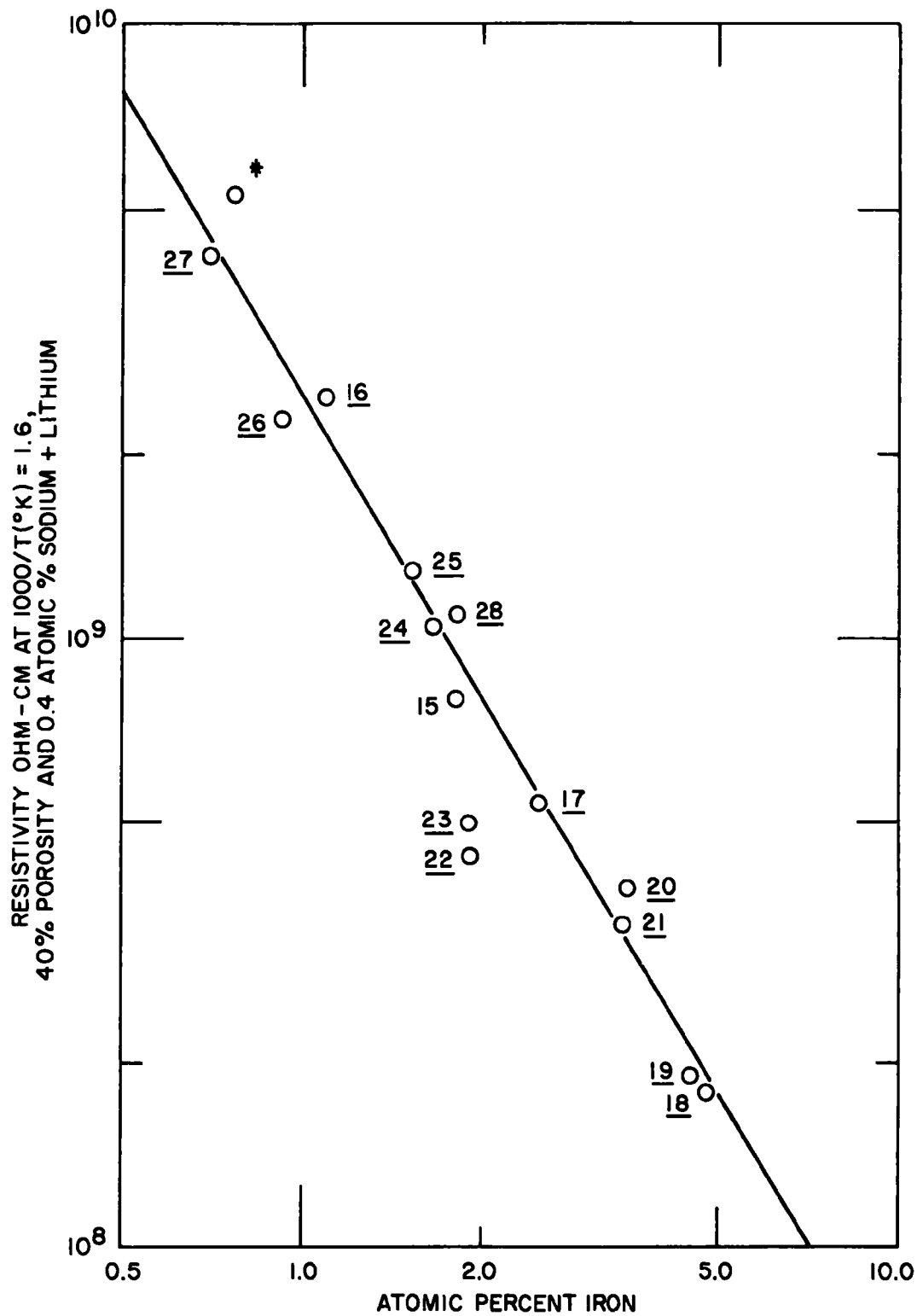


Figure 4. Resistivity versus atomic percentage iron at $1000/T(^{\circ}K) = 1.6$, 40% porosity and 0.4 a/o lithium plus sodium

In summarizing the resistivity data, one finds that the 28 ashes have the same resistivity value plus or minus 25% when temperature, porosity, and concentrations of iron, lithium and sodium are constants. Inspection of the resistivity and chemical analysis data does not suggest an additional factor to justify the variation of $\pm 25\%$ in resistivity. It is possible that this variation is due to the unknown physical and chemical inequities associated with the inherent character of the material being studied and possible inadvertent experimental error.

Previously it has been stated that the role of lithium and sodium in the volume conduction of fly ash was one of supplying mobile charge carriers to the glassy portion of the ash. One therefore would expect the resistivity to be inversely proportional to the concentration of these elements. Now it has been observed that iron concentration has a similar relationship to resistivity. Both from the fundamental viewpoint as well as the pragmatic with the respect to ash conditioning, it was desirable to explore the role of iron.

ROLE OF IRON

Background

Several investigators have mentioned the effect of iron with regard to fly ash resistivity. Shale *et al*⁸ experienced little difference in resistivity between two ashes having significantly different levels of iron. However, in this comparison, the ash having the lower iron content contained about twice as much Na_2O as the other ash. This coupled with the absence of information regarding lithium content and specimen porosity makes comment impossible.

A regression analysis⁹ of ash resistivity versus iron concentration for 38 low-sulfur Western coals, suggested that resistivity increases with increased iron concentration. The coefficient of correlation for these data was too low to consider the data meaningful. Without normalization of data for other parameters of influence, the effect of iron can be masked.

Dalmon and Raask¹⁰ observed a decrease in resistivity of accessory coal minerals that contained iron and sodium and were subjected to fusion at high temperatures. These authors also found that resistivity could be significantly lowered by coating the particles with an iron salt followed by oxidation at an elevated temperature. Utilizing synthetic coal slags, Frederikse and Hosler¹¹ showed a large decrease in resistivity with increase in iron content at a given elevated temperature and oxygen partial pressure. They attribute the lower resistivity of these slags to electronic conduction.

In general, iron content is held to a minimum in commercial glasses and other ceramics designed to have electrical insulative properties since this element decreases resistivity. Little work has been done with reference to small quantities of iron in glass since the element also has a great effect on optical character. Morey¹² mentions some early research that showed an initial increase followed by a dramatic decrease in surface resistivity as the iron content was increased in a simple sodium silicate glass. Considerable literature^{13,14,15} is available showing the effect of iron in producing semiconducting glasses. The low resistivity is associated with electronic conduction. These glasses however, are oxide glasses containing no silica, chalcogenide glasses or inverted silicate glasses that are unlike the glass one would probably find in fly ash.

From the foregoing, it would seem there is mixed evidence regarding the effect of iron on fly ash resistivity. With respect to silicate glasses, the decrease in resistivity with increase in or introduction of iron is associated with electronic conduction in invert glasses.

Observations And Experimentation

Several hypotheses were advanced that could explain the relationship illustrated in Figure 4. First, higher iron concentration reduces the fusion temperature of an ash and therefore, for a sintered-disc type resistivity specimen, could promote enhanced particle to particle bonding. Second, with sufficient concentration and in a particular state of oxidation, the iron could add an electronic component to the conduction process thereby

lowering resistivity. Third, the iron may affect the amorphous phase of the fly ash so that the effective concentration, the mobility, or the type of alkali metal serving as a charge carrier was affected. The following observations and experiments are discussed in an attempt to clarify the role of iron in the volume conduction process for fly ash.

Transference Experiments -

Transference experiments were conducted on four ashes (Nos. 19, 20, 22 and 26) to evaluate certain facets of the aforementioned hypotheses. These ashes contained a relatively uniform concentration of alkali metals and represented the total range of iron concentration encountered in this work. The experimental conditions and the character of the materials investigated precludes the extraction of unequivocal data. These limitations were discussed in reference 2. The data are used only for the qualitative understanding of the conduction process.

Gravimetric data for the transference experiments are shown in Figure 5. In this figure, the mass transferred out of the ash disc adjacent to the positive electrode toward the negative electrode is plotted against the quantity of electricity passed during the experiment. The lines labeled with the names of alkali metals represent Faraday's Law. For example, if conduction were entirely ionic and potassium were the only charge carrier, one would expect a weight loss of about 50 mg for the passage of 120 coulombs of electricity.

The open circles represent the experimental data points. The data for ashes 3 and 10 were acquired at an earlier date for ashes of the lowest iron level. Figure 5 strongly suggests that the electricity passed is accountable for by a mass transfer and that sodium is the principal charge carrier. The only other way in which the data points could occur near the sodium line would be due to some fortuitous situation whereby charge carriers both heavier and lighter than sodium ions participated to yield an average weight change equivalent to that of sodium.

The above is not meant to imply that sodium was the exclusive carrier. The migration of lithium was obvious; however, quantitatively this represents a small contribution. Also, the migration of potassium can be detected with the support of microprobe analysis; however, it too amounts to a small

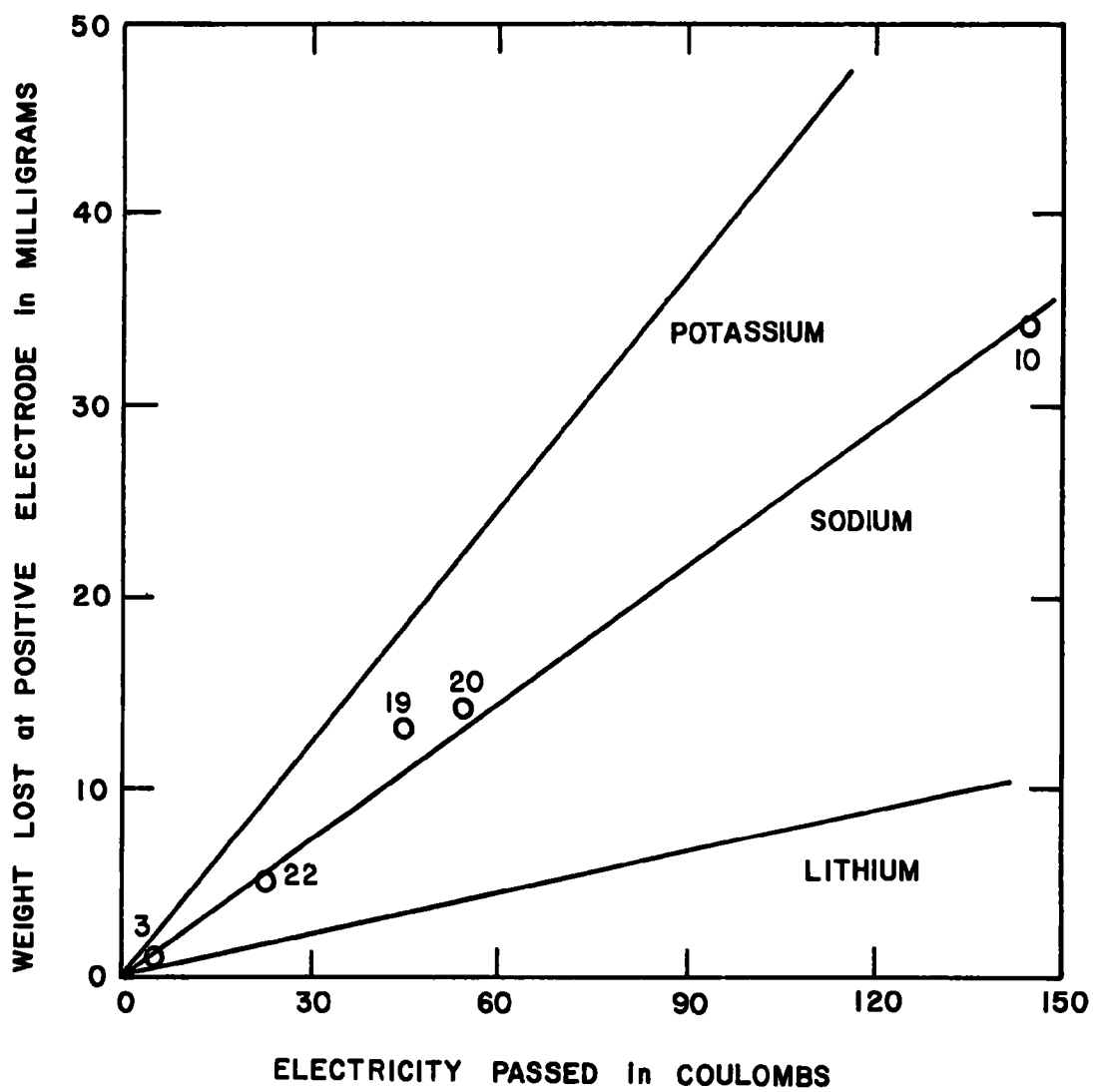


Figure 5. Gravimetric data for transference experiments

quantitative contribution. Since the amount of potassium migrating is extremely small in comparison to the relatively large concentration of this element in the ash, it is excluded from resistivity-ash chemistry correlations.

In Table 3, the results of the chemical analyses for the transference experiments are given. The data show a trend similar to that experienced previously for transference tests on low iron specimens and that these data compliment or support the gravimetric data expressed in Figure 5. For ashes containing from 5 to 22% weight percent iron, only the migration of sodium and lithium from the positive to the negative electrode can be unquestionably observed. The small variations in potassium and iron concentrations in Table 3 are thought to be within the data error for the technique of analysis and the selection of random samples. From this information, it was indicated that the iron does not act as an ionic carrier, and its presence in increased amounts does not induce an increased participation by potassium.

In carefully examining the data in Table 3, it was observed that the percentage of lithium and sodium that had migrated, relative to the amounts initially present, increased with increasing iron concentration. An empirical parameter was devised to demonstrate this point. For a constant amount of electricity passed in each test, the percent increase in sodium and lithium content at the negative electrode over that contained initially by the ash was computed as "relative effectiveness". When this parameter was plotted against the iron concentrations of the four ashes studied, the result shown in Figure 6 was obtained. The increase in the relative effectiveness parameter with increasing iron concentration suggests that the role of iron is indirect in that it seemingly enhances the participation of lithium and sodium in the conduction process.

Although the small deviations in experimental activation energies would not suggest it, it is possible that the iron concentration affects the mobility of the alkali metal ions. However, it is quite possible that the iron concentration could influence the number of mobile charge carriers. Although the total concentration of a particular ion species is used to graphically display

TABLE 3. TRANSFERENCE EXPERIMENTS, CHEMICAL ANALYSES OF SPECIMENS IN WEIGHT PERCENT

<u>ASH</u>	<u>OXIDE</u>	<u>DISC CONTIGUOUS TO POSITIVE ELECTRODE</u>	<u>BASELINE COMPOSITION</u>	<u>DISC CONTIGUOUS TO NEGATIVE ELECTRODE</u>
19	Li ₂ O	0.013	0.019	0.027
	Na ₂ O	-----	0.29	0.53
	K ₂ O	2.9	3.1	3.2
	Fe ₂ O ₃	21.1	21.6	21.0
20	Li ₂ O	-----	0.024	0.041
	Na ₂ O	-----	0.45	0.80
	K ₂ O	-----	2.9	2.9
	Fe ₂ O ₃	-----	16.8	16.6
22	Li ₂ O	0.03	0.04	0.05
	Na ₂ O	0.29	0.39	0.48
	K ₂ O	3.8	4.1	4.0
	Fe ₂ O ₃	10.0	10.2	10.2
26	Li ₂ O	0.030	0.04	0.049
	Na ₂ O	0.40	0.48	0.56
	K ₂ O	3.9	3.9	4.0
	Fe ₂ O ₃	4.8	4.9	4.9

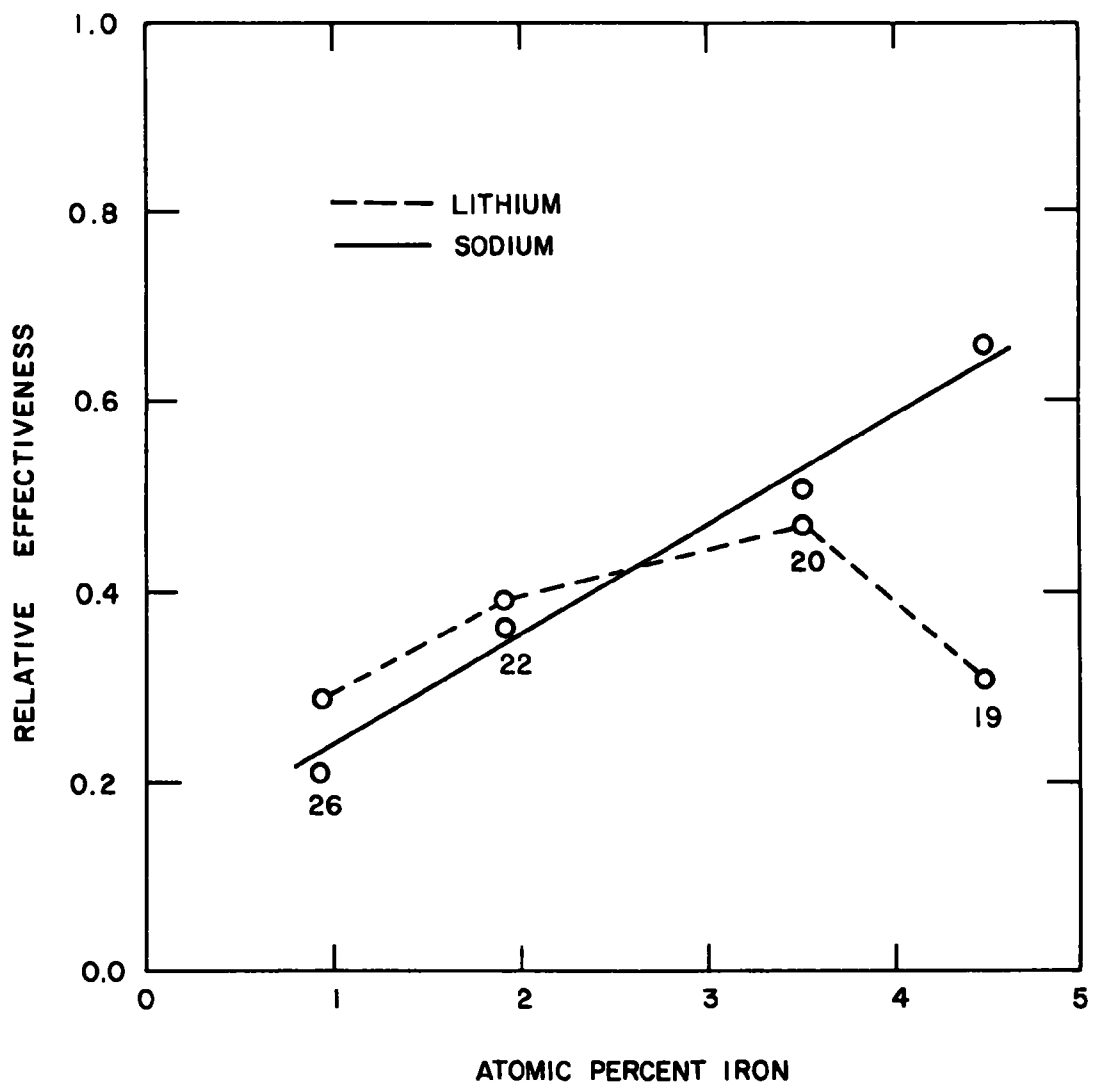


Figure 6. Relative effectiveness of lithium and sodium as charge carriers as a function of iron concentration

data, it is highly probable that not every ion of the given type is free to migrate. It can be suggested that the role of iron is to alter the amorphous ash structure allowing the participation of a greater percentage of the total available alkali metal ions or to enhance their mobility.

Miscellaneous Observations And Ancillary Experiments -

Although the transference experiments suggest that the role of iron is not related to an electronic contribution to the conduction process, this point was additionally considered. In the course of this research, as well as in previous efforts, it has been observed that within the estimated experimental error the experimental activation energy for conduction has varied little among ashes. If the high iron ashes imparted an electronic contribution to the total conduction process, one might expect a change in activation energy. Also, it has been noted that the current decreases with time for a given voltage potential using blocking electrodes. If there were an electronic conduction mechanism, the polarization effect should not be apparent.

Two additional experiments were run regarding the potential electronic contribution of iron. In one case, ash 22 was repeatedly passed through a magnetic separator prior to fabricating a resistivity specimen. The iron concentration was reduced by 50% without significantly altering the resistivity. It is believed that the iron removed was that fraction which most likely would have provided an electronic contribution, while that which remained was principally involved in the glassy portion of the ash. The observation that the removal of the magnetic fraction did not increase the resistivity indicates the absence of electronic conduction. Solid electrolyte experiments¹⁶ were conducted on sintered specimens of ashes 10 and 19 using a calcium stabilized zirconia as a standard. Both ashes produced sufficient emf so that the consideration of an electronic contribution to the overall conduction process for the ashes could be dismissed.

Intuitively, one might suggest that ashes containing high iron concentrations develop better particle to particle contacts thereby lowering the resistivity of sintered disc specimens. The following observations are submitted to clarify this thought:

a) The previously described experiment involving the magnetic removal of iron prior to specimen fabrication did not alter the resistivity.

b) If superior particle contact played an important role, one would neither anticipate the excellent correlation between resistivity and ash chemistry at all levels of iron nor the interpretation available from the transference experiments.

c) Superior particle contact should be reflected by variations in experimental activation energies for conduction. Little difference in activation energy was noted among the ashes utilized. When low, medium and high iron ashes were intentionally sintered to produce specimen shrinkage and increase particle bonding, the resistivity and experimental activation energies were dramatically reduced.

d) Two ashes having high and low iron concentrations were used to measure resistivity in the temperature range of 200 to 450°C utilizing the ASME, PTC 28 apparatus. These tests employing loose, as-received ash produced resistivity values almost identical to their respective sintered disc counterparts when the sintered disc data were corrected to the same porosities as the PTC 28 specimens.

The preceding observations indicate the sinterability of the various ashes does not bias the resistivity data when specimens are prepared at a high level of porosity without specimen shrinkage.

Summary

An unequivocal interpretation of the role of iron in the fly ash conduction process is not available. However, it is reasonably certain that the pronounced influence of the iron concentration shown in Figure 4 is neither related to an electronic contribution to the conduction process nor is it an aberration due to the particle to particle bonding in the sintered disc resistivity specimen. The evidence obtained indicates that the presence of increased iron concentration does not alter the previously identified mechanism for volume conduction, i.e., the ionic migration of the alkali metals. It is conceivable that the iron concentration associated with the principal fraction of the ash, the glassy phase, alters the structure of the glass so that either a greater number of the total alkali metal ions present are capable of migration or the ions move at an increased velocity. Although no direct proof of this rationalization is available, the concept is compatible with: 1) only obvious evidence of lithium and sodium migration has been found, 2) no electronic component to the conduction process has been shown, and 3) very little variation in conduction activation has been observed.

SECTION VII

PREDICTION OF VOLUME RESISTIVITY

GENERAL

One of the primary goals of this research was to obtain sufficient understanding of the volume conduction process so that an attempt could be made to predict volume resistivity from the chemical analysis of an ash. It has been observed that the volume resistivity of an ash is a function of the lithium-sodium concentration, the iron concentration, the temperature and the porosity of the ash layer. Since only a small unknown fraction of the total potassium present participates as carriers, it is impossible to include this element. When the resistivities for 28 ashes were normalized so the four parameters above were constant, the total range of resistivity was reduced from about 3 orders of magnitude to about one-half order of magnitude. Inspection of the data did not suggest additional approaches with which the data might be interpreted. The resultant half order of magnitude range of resistivities could be related to accumulated errors, an undetected chemical effect, the percentage of glassy phase in the individual ashes, etc.

In this prediction of volume resistivity the effect of water vapor, SO_3 , etc., has not been considered. It is believed that these agents are not of influence at temperatures above 250°C where volume conduction is most important. Also, the type of specimens used in this research precluded the consideration of the influence of unburned carbon. However for ashes containing less than 8% unburned carbon, Shale⁸ has indicated little effect on resistivity for this constituent. Almost all the ashes used in the current work in the as-received condition contained less than 5% unburned carbon.

CALCULATION OF RESISTIVITY

Effect Of Chemical Concentrations

The effect of lithium plus sodium on resistivity at a given temperature and porosity was shown in Figure 3. The effect of iron on resistivity at a given temperature,

porosity and lithium-sodium concentration was given in Figure 4. Both sets of data correlated well with a linear interpretation of a log-log plot. Since Figure 4 represents the variation of resistivity with iron for a constant level of sodium plus lithium, the equation for this line can be substituted for the value of resistivity in Figure 3 at the 0.4 atomic percent lithium-sodium ordinate and an equation developed yielding resistivity in terms of both concentration variables.

The general expression relating resistivity to iron concentration in Figure 4 is:

$$\log \rho(\text{Fe}) = \log \rho_0(\text{Fe}) - b(\log a/o \text{ Fe}) \quad (6)$$

With a known line slope (b) and an assumed value for ρ which defines the iron concentration in atomic percent (a/o), one can calculate $\log \rho_0(\text{Fe})$, the intercept.

For:

$$\begin{aligned} \rho &= 10^9 \text{ (assumed)} \\ \log \rho &= 9.0000 \\ b &= -1.65 \text{ (from Figure 4)} \\ a/o \text{ Fe} &= 1.75 \text{ a/o (from Figure 4 at } \rho = 10^9) \\ \log a/o \text{ Fe} &= 0.2430 \end{aligned}$$

substituted into equation (6), $\log \rho_0(\text{Fe})$ is calculated to be 9.4010, and equation (6) can be rewritten as:

$$\log \rho(\text{Fe}) = 9.4010 - 1.65 (\log a/o \text{ Fe}) \quad (7)$$

Equation (7) is the specific expression for the line in Figure 4 and also defines the resistivity values in Figure 3 along the 0.4 a/o lithium-sodium ordinate for all iron concentrations.

The general expression relating resistivity to lithium-sodium concentration in Figure 3 is

$$\log \rho_{(\text{Li-Na})} = \log \rho_0(\text{Li-Na}) - b(\log a/o \text{ Li-Na}) \quad (8)$$

Using the value of $\log \rho_{(\text{Fe})}$ defined in equation (7) at a lithium-sodium concentration of 0.4 a/o and the known value of (b) taken from Figure 3, one can calculate $\log \rho_0(\text{Li-Na})$ for equation (8) in terms of the iron concentration.

For:

$$\begin{aligned} \log \rho_{(\text{Li-Na})} &= 9.4010 - 1.65 (\log a/o \text{ Fe}) \\ &\quad \text{(equation 7)} \\ b &= -1.84 \text{ (from figure 3)} \\ a/o \text{ Li-Na} &= 0.4 \text{ a/o} \\ \log a/o \text{ Li-Na} &= -0.3979 \end{aligned}$$

substituted into equation (8), $\log \rho_0(\text{Li-Na})$ is calculated to be $8.6689 - 1.65 (\log a/o \text{ Fe})$, and equation (8) can be rewritten as

$$\log \rho_{(\text{Li-Na,Fe})} = [8.6689 - 1.65 (\log a/o \text{ Fe})] - 1.84 (\log a/o \text{ Li-Na}) \quad (9)$$

Equation (9) expresses resistivity in terms of the two critical concentration parameters obtainable from the chemical analysis of fly ash. The value of resistivity calculated from equation (9) is restricted to an ash layer porosity of 40% and a temperature of 625°K.

Effect of Temperature

In Figure 2, the linearity of the plot of $\log \rho$ versus $1/T$ indicates the resistivity-temperature relationship can be expressed with an Arrhenius equation. In logarithmic form,

$$\log \rho = \log \rho_0 + [(\theta/k) \log e] (1/T) \quad (3)$$

Using the value of $\log \rho$ at 625°K and 40% porosity given in equation (9), one can calculate $\log \rho_0$ in equation (3) and arrive at an expression for resistivity in terms of temperature and chemical concentrations for an ash layer of 40% porosity.

Given:

$$\begin{aligned}\log \rho &= 8.6689 - 1.65(\log a/o \text{ iron}) - 1.84(\log a/o \\ &\quad \text{lithium-sodium}), \text{ from equation (9)} \\ \theta &= 1.03 \text{ eV, average experimental} \\ &\quad \text{activation energy} \\ \text{eV} &= 1.602 \times 10^{-12} \text{ erg} \\ k &= 1.380 \times 10^{-16} \text{ erg } ^\circ\text{K}^{-1}, \text{ Boltzmann's constant} \\ \log e &= 0.4343\end{aligned}$$

$$[(\theta/k) \log e] = 5.193 \times 10^3 \text{ } ^\circ\text{K, calculated from above}$$

$$[(\theta/k) \log e] (1/T) = 8.3088, \text{ for } T = 625^\circ\text{K}$$

Substituting in equation (3) for $T = 625^\circ\text{K}$,

$$\log \rho_0 = 8.6689 - 1.65(\log a/o \text{ Fe}) - 1.84(\log a/o \text{ Li+Na}) - 8.3088$$

Rewriting equation (3) incorporating this value of $\log \rho_0$ yields an expression for $\log \rho$ for all applicable values of temperature and determined values of chemical concentrations at a porosity of 40%,

$$\begin{aligned}\log \rho_{(\text{Fe, Li-Na, T})} &= [8.6689 - 1.65(\log a/o \text{ Fe}) - 1.84(\log a/o \\ &\quad \text{Li+Na}) - 8.3088] + 5.193 \times 10^3 \text{ } ^\circ\text{K} \times \\ &\quad (1/T) \text{ } ^\circ\text{K}^{-1}\end{aligned} \quad (10)$$

Effect Of Porosity

Equation (10) defines the resistivity in terms of temperature, iron concentration, and lithium-sodium concentration for one value of ash porosity, 40%. Previously in this report, an empirical relationship was given relating volume

resistivity to percent porosity, equation (5). This equation can be used to determine $\log \rho_{(\text{Fe, Li-Na, T})}$, equation (10), for porosities other than 40%.

COMMENTS

The foregoing expressions represent an initial attempt to predict volume resistivity as a function of ash chemistry, temperature and porosity. A particular type of test specimen was used and twenty-eight fly ashes were examined to acquire the necessary data. The critical parameters controlling volume resistivity have been reasonably well documented with respect to the magnitude and mechanism of the effect.

Predicted resistivity values have agreed well with experimentally determined values for ashes coming into this laboratory. As-measured resistivity data have been plotted against predicted values for the temperature parameter of $1000/T(^{\circ}\text{K}) = 1.6$. In predicting the resistivity, the measured porosity of the individual ash specimens was utilized. The good correlation between predicted and measured volume resistivity data can be seen in Figure 7. The individual data points of maximum departure from the curve are less than one half order of magnitude removed.

Whether predicted volume resistivity values will duplicate or at least correlate with field measurements or laboratory measurements utilizing other experimental techniques remains to be shown. Many factors can contribute to variations in resistivity values resulting from the different techniques, locations and conditions of measurement. No opportunity to evaluate predicted resistivity against high temperature field measurements has been available. In this laboratory, surface resistivity has been determined for a number of fly ashes up to a temperature of 250°C using the ASTM, PTC 28 resistivity apparatus. It has been observed that in most cases the predicted volume resistivity data serves well in extending the surface resistivity data to higher temperatures. This evaluation of the method for resistivity prediction is being continued.

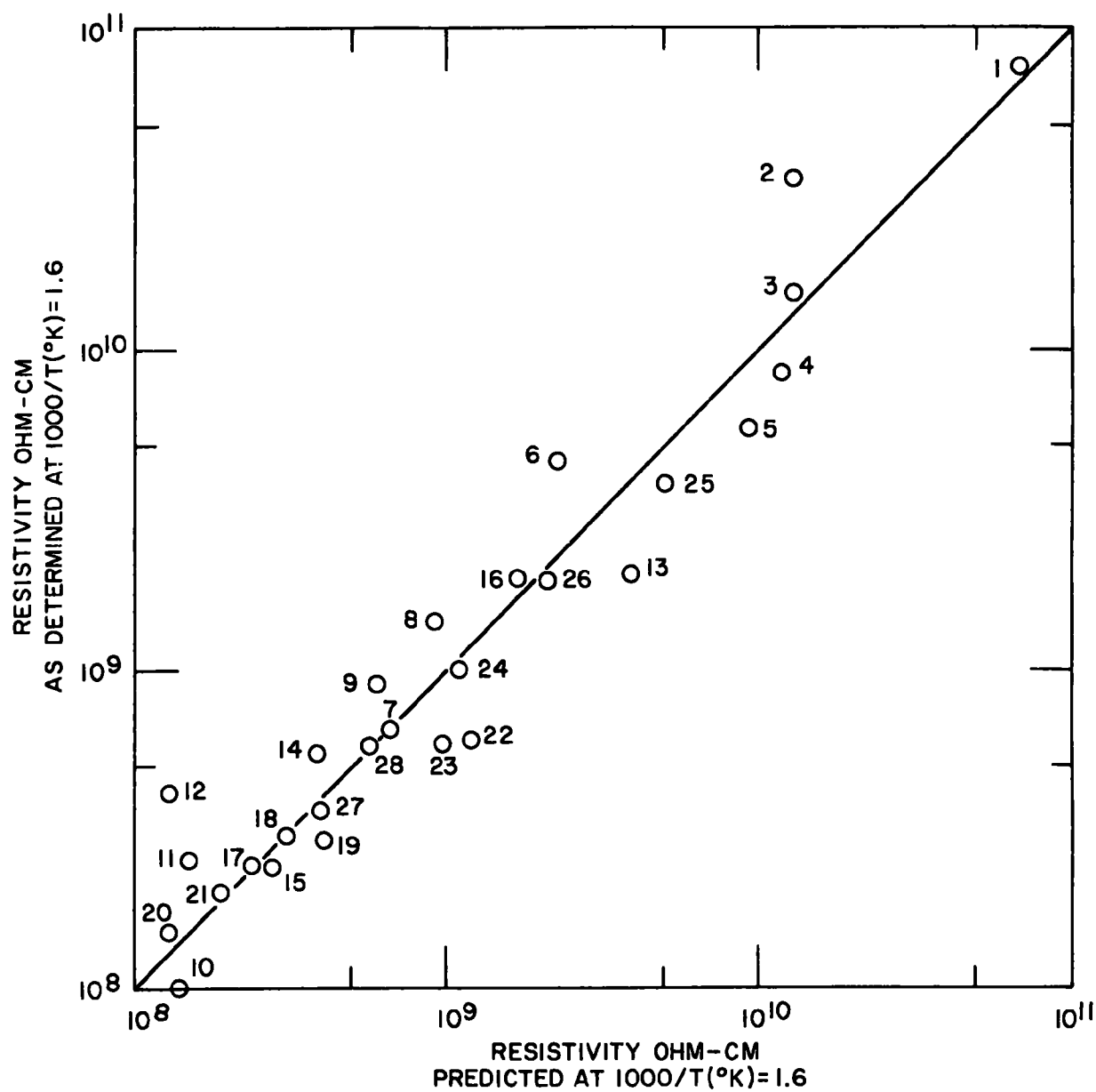


Figure 7. Correlation between as determined and predicted resistivities

SECTION VIII

SUMMARY

From characterizations of ashes for this research and previous work, it was estimated that an average ash is made up of 0-10% unburned carbon, 5-15% crystalline compounds, and 75-95% amorphous material. The amorphous material appears to be a heterogeneous glass that forms a continuous matrix in an ash layer. It probably forms by the volatilization and/or fusion of auxiliary minerals present in the coal at the peak boiler temperature and is retained as a glass due to rapid cooling. The particles are primarily spherical in shape and vary in diameter from 100 microns to submicron size. The ashes have a helium pycnometer density of 2.0 to 3.0 grams/cc. When placed into an ASTM, PTC 28 electrode, a porosity of 50 to 75% usually occurs.

The writer previously suggested that volume conduction takes place due to an ionic mechanism in which charge carriers migrate through the continuous matrix of glassy particles. It was shown in this earlier work and confirmed in this research that the principal charge carriers are the alkali metal ions, mainly sodium. It has been observed that the amount of electricity conducted is proportional to a mass transfer, and the migration of sodium and lithium has been chemically and visually demonstrated. Graphically it has been illustrated that the volume resistivity of fly ash is inversely proportional to the concentration of these elements for ashes of limited compositional range.

The objective of developing an empirical expression with which resistivity could be predicted from chemical analyses of ash required a broad spectrum of ash composition to be evaluated. It was observed that resistivity was disproportionately low for a given lithium-sodium concentration when ashes having high iron content were examined. A good linear correlation was established between resistivity and the atomic percentage of iron present in the ash for a specific level of lithium and sodium. From this information, an expression was developed to predict volume resistivity as a function of the

combined lithium and sodium concentrations and the iron concentration for a given temperature and ash layer porosity in the temperature range where volume conduction occurs. Additional expressions were given to account for changes in resistivity with temperature and porosity. These predictive expressions are considered initial approximations that are in need of substantiation with field tests and laboratory experiments utilizing other techniques.

An effort was made to determine the mechanism by which the iron concentration influenced resistivity. Unequivocal proof was not attained. Several items of circumstantial evidence indicate that the data were not distorted by superior bonding of particulates when preparing sintered-disc resistivity specimens containing above minimum iron concentration. No observations and no specific experiments produced data to indicate an electronic contribution to the conduction process due to the presence of elevated iron content. Transference experiments showed that at all levels of iron only sodium and lithium had significantly migrated. As the iron content among ashes increased, a disproportionate percentage of lithium and sodium was transferred based on the initial concentrations of these elements in their respective ashes for a constant quantity of electricity passed. This observation suggests that the iron present in the glassy phase alters the structure of the glass to permit the migration of a greater percentage of the total number of alkali metal ions available. Since the experimental activation energy did not vary significantly among all experiments with respect to the estimated error, it was considered not likely that the iron affected the carrier mobility.

It is generally noted in glass technology that compositional changes altering structure have a pronounced effect on properties. It is conceivable that this phenomenon occurs in fly ash. One might visualize the structural modification being a physical or chemical change that is particularly sensitive to an electric field.

SECTION IX

REFERENCES

1. R. E. Bickelhaupt and G. B. Nichols, "Investigation of the Volume Electrical Resistivity of Fly Ash from the Sundance and Wabamun Power Stations", Final Report A1231-2865-I from Southern Research Institute to Calgary Power, Ltd., Calgary, Alberta, Canada, June 30, 1972.
2. R. E. Bickelhaupt, "Electrical Volume Conduction in Fly Ash", APCA Journal 24 (3) 251-255 (1974).
3. "Tentative Method of Test for D-C Volume Resistivity of Glass", Designation C657-70T, Part 13, American Society for Testing Materials, Philadelphia, April 1972.
4. W. D. Kingery, Property Measurements at High Temperatures, Chapter 13, John Wiley & Sons, Inc., New York, 1959.
5. B. D. Cullity, Elements of X-ray Diffraction, Chapter 14, pp 396-398, Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1959.
6. "Studies into the Effects of Coal Ash Composition on Electrostatic Precipitation Performance", progress report covering period of September 1971 to May 1972, prepared for Environmental Protection Agency, Contract 02-513-4. University of Belgrade, Belgrade, Yugoslavia, May 1972.
7. J. Dalmon and D. Tidy, "A Comparison of Chemical Additives as Aids to the Electrostatic Precipitation of Fly Ash", Atmospheric Environment 6 (10) 721-734 (1972).
8. C. C. Shale, J. H. Holden, and G. E. Fasching, "Electrical Resistivity of Fly Ash at Temperatures to 1500°F", R17041, Bureau of Mines, U.S. Department of the Interior, 1968.
9. S. J. Selle, P. H. Tufte, and G. H. Gronhøvd, "A Study of the Electrical Resistivity of Fly Ashes from Low-sulfur Western Coals Using Various Methods", Paper 72-107 presented at the 65th Annual Meeting of the Air Pollution Control Association, Miami Beach, Florida (1972).

10. J. Dalmon and E. Raask, "Resistivity of Particulate Coal Minerals", J. Inst. Fuel 46 (4) 201-205 (1972).
11. H. P. R. Frederikse and W. R. Hosler, "Electrical Conductivity of Coal Slag", J. Am. Cer. S. 56 (8) 418-419 (1973).
12. G. W. Morey, The Properties of Glass, Chapter 20, Reinhold Publishing Corporation, New York (1938).
13. H. J. L. Trap and J. M. Stevels, "Ionic and Electronic Conductivity of Some New Types of Glass-like Materials", Physics and Chemistry of Glasses 4 (5) 193-205 (1963).
14. Robert H. Doremus, Glass Sciences, Chapter 10, John Wiley & Sons, New York (1973).
15. J. D. Mackenzie, "Semiconducting Oxide Glasses: General Principle for Preparation", J. Am. Cer. S. 47 (5) 211-214 (1964).
16. Kalevi Kiukkola and Carl Wagner, "Measurements on Galvanic Cells Involving Solid Electrolytes", J. Electrochemical Soc. 104 (6) 379-387 (1957).

TECHNICAL REPORT DATA <i>(Please read Instructions on the reverse before completing)</i>		
1. REPORT NO. EPA-650/2-74-074	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE Influence of Fly Ash Compositional Factors on Electrical Volume Resistivity	5. REPORT DATE July 1974	6. PERFORMING ORGANIZATION CODE
	8. PERFORMING ORGANIZATION REPORT NO. SORI-EAS-74-247 2938-F	
7. AUTHOR(S) R. E. Bickelhaupt	10. PROGRAM ELEMENT NO. LAB012; ROAP 21ADJ-029	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Southern Research Institute 2000 Ninth Avenue South Birmingham, Alabama 35205	11. CONTRACT/GRANT NO. 68-02-0284	
	13. TYPE OF REPORT AND PERIOD COVERED Final; Through July 1974	
12. SPONSORING AGENCY NAME AND ADDRESS EPA; Office of Research and Development NERC-RTP, Control Systems Laboratory Research Triangle Park, NC 27711	14. SPONSORING AGENCY CODE	
	15. SUPPLEMENTARY NOTES	
16. ABSTRACT <p>The report gives results of a study during which 28 fly ash samples -- representing a broad spectrum of ash compositions produced by burning coal in commercial power station boilers--were characterized, chemically analyzed, and fabricated into sintered-disc resistivity specimens. Resistivity and transference experiments were performed in the temperature range in which volume conduction prevails. Results confirmed conclusions of an earlier investigation; the volume conduction mechanism for fly ash is ionic; and the charge carriers are the alkali metal ions, principally sodium. Increasing iron concentration caused a resistivity decrease for a given level of sodium and lithium. No evidence of biased data or electronic conduction was found. It was rationalized that, in a manner analagous to that for glass, the iron affected the structure of the predominant glassy phase of the ash, thereby inducing the participation of a greater percentage of the available alkali metal carrier ions. From these data, empirical equations were developed to predict the volume resistivity of fly ash as a function of ash chemistry, temperature, and porosity.</p>		
17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution Fly Ash Chemical Analysis Coal Combustion Products Boilers	Air Pollution Control Stationary Sources Characterization Resistivity Volume Conduction	13B 21B 07D 21D 13A
18. DISTRIBUTION STATEMENT Unlimited	19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES 49
	20. SECURITY CLASS (This page) Unclassified	22. PRICE