

$G(s) = G_1(s)G_2(s) \dots G_5(s)$. Taking logs of both sides of this equation, differentiating with respect to s , and multiplying by -1 , we get

$$-\frac{1}{G(s)} \frac{dG(s)}{ds} = -\sum_{i=1}^5 \frac{1}{G_i(s)} \frac{dG_i(s)}{ds} \quad (\text{B23})$$

or from Equation (B22)

$$\tau = \tau_1 + \tau_2 + \tau_3 + \tau_4 + \tau_5 \quad (\text{B24})$$

Substituting for τ , τ_3 , and τ_5 from Equations (B16) to (B18) and solving the resulting equation for M_0 yield

$$M_0 = M_0' - (\tau_1 + \tau_2 + \tau_4 + \tau_a) \quad (\text{B7})$$

which is the desired result. [The time lag τ_4 has been re-labeled τ_3 in Equation (6) to avoid an unexplained omission in the sequence of subscripts shown in this equation.]

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Improving Efficiency of Electrostatic Precipitation by Physicochemical Modification of the Electrical Resistivity of Flyash

Theory and experiment show that lowered resistivity of fly ash, frequently caused by adding conditioning agents to flue gas to improve efficiency of electrostatic precipitation, is caused by capillary condensation of liquid at the contact points of ash particles, thereby providing additional pathways for flow of electrical current.

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SCOPE

The efficiency of electrostatic precipitation is adversely affected by high electrical resistivity of the layer of fly ash or dust situated on the collecting electrode. Such deleterious effects are associated with high voltage which builds up in the ash layer and causes dielectric breakdown by ionization of the gas within the interstices of the particle layer (so called sparking or back corona). It has been known (White, 1970) for some time that the electrical conductivity of the ash layer is sensitive to the composition of the flue gas, and such phenomena have been used to improve ash collection during electrostatic precipitation by increasing the moisture content of the flue gas and also by adding small quantities of so-called conditioning agents, such as sulfur trioxide, sulfamic acid, and ammonia, thereby simultaneously improving the performance of the precipitator and increasing the electrical conductivity of the fly ash. In spite of the widespread use (White, 1970) of such conditioning agents, especially in electric power plants burning low sulfur

coal, which produces fly ash of lower electrical conductivity (vis a vis higher sulfur coal), the phenomenon and mechanism of such conditioning remain poorly understood beyond the general rationale that they are associated with gas sorption phenomena and attendant ionic conduction either within the ash particles, at their surfaces, or at both locations. The present paper reports experiments relating the electrical resistivity of fly ash to gas sorption phenomena. In particular, a simple model has been developed which, for the first time, explains the rather extraordinary influence of temperature, gas moisture content, and concentration of conditioning agent upon the electrical resistivity of the fly ash. In this approach, the fly ash layer is represented by a well-ordered cubic array of monodisperse, spherical particles, wherein capillary condensation of water and conditioning agent occurs in the narrow crevices at the points of contact between the particles. Increased conductivity results from the added conduction path provided by the capillary condensed liquid. The conditioning agent actually enhances the extent of capillary condensation and thus the conductivity.

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CONCLUSIONS AND SIGNIFICANCE

The action of conditioning agents such as sulfur trioxide and water, which when added to the flue gas improve the efficiency of electrostatic precipitation by lowering the electrical resistance of the dust layer on a collecting electrode, may now be understood in terms of their ability to promote capillary condensation in the crevices formed at the points of contact of the collected particles. The capillary condensed liquid provides an additional electrically conductive path, the resistance of

which may be further lowered by the dissolution of ions from the solid or from the gas. The quantitative physicochemical description of such phenomena now provides an explanation of the dependence of fly ash resistivity on temperature, moisture content, and concentration of conditioning agent (such as sulfur trioxide) in the flue gas as well as offering a framework for correlating related experimental observations in terms of a single adjustable parameter.

It has been generally found that the electrical resistivity of the fly ash should lie below about $10^{11} \Omega\text{cm}$ in order to achieve normal and efficient collection by electrostatic precipitation. Recent relevant data have been reported by Bickelhaupt (1975*a, b*) referencing many earlier experimental results, which bring evidence for the ionic nature of electrical conductivity in flyash and which demonstrate a correlation between the conductivity and the chemical composition of the ash. Such a conductivity mechanism may be related to that observed in glass (Doremus, 1973; Tallan, 1974). Recently, Coughlin and Kanowski (1975) have shown how the sulfur trioxide/sulfur dioxide ratio in flue gas can be increased by inducing catalytic oxidation of the sulfur dioxide, thereby increasing the conductivity of the ash in contact with the gas.

A review of the literature indicates that the extensive experimental data reported for fly ash resistivity under different conditions of temperature and flue gas concentration stands in marked contrast to the absence of a quantitative physicochemical framework for the interpretation and correlation of such information.

The aim of the present paper is to develop such a framework in terms of a simplified theoretical model for electrical conduction of fly ash layers under the influence of conditioning agents in the flue gas. Although the development rests on simplified approximations, it provides a useful correlation and at least a preliminary explanation of many conditioning phenomena.

THEORETICAL MODEL

Examination of typical fly ash samples under the electron microscope (Neff, 1976) reveals approximate spherical shape but much surface roughness involving craters and fissures. In the simplified approach developed below, it is assumed that the layer of ash particles is an ordered array of smooth, uniform spheres packed as shown in Figure 1. Surface roughness, deviation from sphericity, and polydispersity will eventually be accounted for by a single adjustable parameter which will be introduced at a later stage.

It is presumed that the resistance of a layer of dry particles resides at the points of contact between individual particles. This viewpoint is in accord with the fact that the electrical conductivity of glasses of similar composition is about two orders of magnitude higher than that of a fly ash layer, thereby suggesting that the higher resistivity of the fly ash is associated with its particulate nature and presumably located at the interparticle contacts.

Since the ionic nature of conductivity in fly ash layers has been shown by Bickelhaupt (1975*a, b*), it is reasonable to assume that the ionic current carriers encounter major resistance at such interparticle contacts. In fact, such a contact between two perfect spheres is, by definition, a geometrical point, and the resistivity to electric

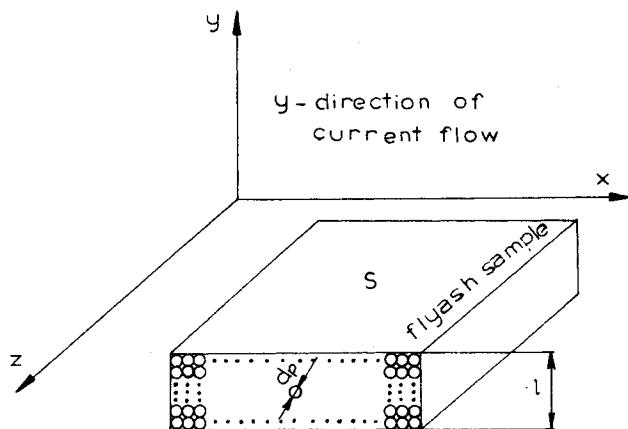


Fig. 1. Idealized array of uniform, spherical fly ash particles packed in a layer.

conduction at such a contact should, in principle, be essentially infinite.

The high but finite resistance of an actual fly ash layer may be attributed to roughness and deviation of the particles from perfect sphericity. The resistivity of a dry fly ash layer of thickness l and cross section S is determined experimentally by measuring the current I corresponding to the voltage drop U according to

$$\rho = \frac{1}{\kappa} = \frac{S}{l} \cdot \frac{U}{I} = \frac{S}{l} \cdot R \quad (1)$$

It is generally known that the resistivity of a fly ash layer is lowered by moisture in the environment, and moisture itself may be thought of as a conditioning agent. Measurements to be reported elsewhere (Ditl and Coughlin, 1976) indicate that an adsorbed amount of water even smaller than that corresponding to a monolayer causes a significant decrease in fly ash resistivity. The same measurements also indicate that in spite of the small number of capillaries inside the individual fly ash particles, there is evidence for capillary condensation at the points of contact between particles. Capillary condensation associated with fly ash particles has been suggested previously by Coughlin (1974). Although some condensation will occur within pores and fissures in the particles, that portion associated with increased electrical conductivity occurs in the locales of the points of contact, namely, in the ringlike crevices surrounding the points of contact between particles. The total resistance R_B of one point of contact with associated capillary condensed liquid is then written as the superposition of two resistances R_{BV} and R_{BS} connected in parallel:

$$\frac{1}{R_B} = \frac{1}{R_{BV}} + \frac{1}{R_{BS}} \quad (2)$$

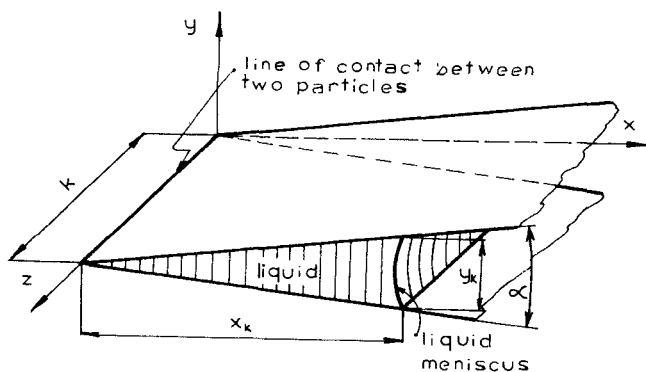


Fig. 2. Geometrical properties of capillary condensed liquid at a point of contact between spherical particles.

According to the geometrical configuration of Figure 1, with the electric field parallel to the y direction, only the points of contact along the y direction contribute to the resistivity, and there is no current flow in either the x or the z direction. The number of resistive contacts in a single chain of particles in the y direction is $n_y = (l_y - d_p)/d_p$, or for $l_y \gg d_p$, one can write approximately

$$n_y \approx \frac{l_y}{d_p} \quad (3)$$

The number of chains of particles (that is, parallel current paths) within a cross-sectional area S is

$$n_x \approx \frac{S}{d_p^2} \quad (4)$$

Since the resistance of one such current path is $n_y R_B$, the resistance of n_x such paths in parallel is

$$R = \frac{n_y}{n_x} R_B \quad (5)$$

Combining Equations (2), (3), (4) and (5), we get

$$\frac{1}{R} = \frac{S}{l} \cdot \frac{1}{d_p} \left(\frac{1}{R_{BV}} + \frac{1}{R_{BS}} \right) \quad (6)$$

where the y subscript has now been dropped from the l . Equation (6) may be rewritten as a resistivity

$$\frac{1}{\rho} = \frac{1}{R} \cdot \frac{l}{S} = \frac{1}{d_p R_{BV}} + \frac{1}{d_p R_{BS}} = \frac{1}{\rho_V} + \frac{1}{d_p R_{BS}}$$

or as a conductivity

$$\kappa = \frac{1}{\rho} = \kappa_V + \frac{1}{d_p R_{BS}} \quad (7)$$

Determination of the resistance R_{BS} of the capillary condensed liquid at the contact points requires information as to resistivity of the capillary condensed liquid and geometry and size parameters of the ringlike volume of liquid condensed at the contact point. The parameter d_p may be thought of as an effective diameter for a layer of polydisperse, nonspherical, rough particles.

Because a rigorous description of the current flow through a ring of capillary condensed liquid at a contact point involves the solution of a complex, three-dimensional problem, and because there is no known way to choose a regular geometrical model to describe contact points between polydisperse particles of significant surface roughness, the development here is based on a simplified wedge shaped pore at a contact point as shown in Figure 2. Accordingly, the current flow in the y direction through the liquid condensed in the pore is presumed to be governed by a resistance which can be expressed as

$$\frac{1}{R_{BS}} = \int \frac{1}{\rho_S} d\left(\frac{S}{y}\right) = \frac{K}{\rho_S} \int_{x_{\min}}^{x_K} \frac{dx}{x \tan \alpha} \quad (8)$$

$$\frac{1}{R_{BS}} = \frac{K}{\rho_S \tan \alpha} \ln \left(\frac{x_K}{x_{\min}} \right) \quad (9)$$

or

$$\frac{1}{R_{BS}} = \frac{K}{\rho_S \tan \alpha} \ln \left(\frac{y_K}{y_{\min}} \right) \quad (10)$$

where x_{\min} and the corresponding value of y_{\min} may be thought of as determined by the molecular size of the condensate. The values of y_K and y_{\min} can be expressed by the Kelvin equation applied to the meniscus (by neglecting the influence of curvature on y_K and by assuming zero contact angle) under the conditions shown in Figure 2

$$-\ln(p_K/p_o) = \frac{v\sigma}{RT} \cdot \frac{1}{y_K} \quad (11)$$

or the condition of minimal condensate at the contact point:

$$-\ln(p/p_o)_{\min} = \frac{v\sigma}{RT} \frac{1}{y_{\min}} \quad (12)$$

By using the Kelvin equation, the expression for R_{BS} becomes

$$\frac{1}{R_{BS}} = \frac{K}{\rho_S \tan \alpha} \ln \left[\frac{\ln(p/p_o)_{\min}}{\ln(p_K/p_o)} \right] \quad (13)$$

Combination with Equation (7) gives

$$\kappa = \frac{1}{\rho} = \kappa_V + \frac{K}{d_p \tan \alpha} \cdot \frac{1}{\rho_S} \cdot \ln \left\{ \frac{\ln(p/p_o)_{\min}}{\ln(p_K/p_o)} \right\} \quad (14)$$

In the foregoing development, it should be recognized that when y_{\min} is on the order of molecular dimensions, the Kelvin equation does not apply; thus it is best and most practical to suppose that y_{\min} and the value of $(p/p_o)_{\min}$ correspond to conditions of humidity in the laboratory environment where the resistivity of dry or unconditioned fly ash is measured. The terms y_K and (p_K/p_o) correspond to the normal partial pressure of the moisture in the environment of the electrostatic precipitator, with p_o in the denominator the normal vapor pressure of the liquid at the temperature of the electrostatic precipitator. In the term $(p/p_o)_{\min}$ p refers to the vapor pressure in the laboratory environment at which ash resistivity is measured and p_o to the normal vapor pressure at the laboratory temperature. Ideally, the laboratory experiments will be carried out under near dry conditions.

Equation (14) may be rewritten as

$$\kappa = \kappa_V + \kappa_S \cdot \phi \quad (15)$$

with

$$\phi \equiv \ln \left\{ \frac{\ln(p/p_o)_{\min}}{\ln(p_K/p_o)} \right\} \quad \text{and} \quad \kappa_S \equiv K / (d_p \cdot \rho_S \cdot \tan \alpha) \quad (15a), (15b)$$

κ_S is now an effective conductivity of the condensed liquid and may be thought of as an adjustable parameter which contains all of the uncertainties and nonidealities due to polydispersity, surface roughness, shape factors, nonuniform electric fields at particle surfaces, and other deviations from ideality. From the foregoing it is clear that in the layer of polydisperse fly ash, κ_V will depend on T (fly ash chemistry), d_p (roughness of the particle surface), porosity, extent of polydispersity, and the intensity of the electric field (kilovolts per centimeter) in the event Ohm's law is not satisfied.

κ_S will depend on T (particle diameter, roughness of the particle surface, shape factor, nonuniformity of electric field at particle surface), fly ash chemistry, chemical and electrochemical behavior of the solid-liquid interphase, conductivity of the capillary condensed liquid, and the intensity of the electric field when Ohm's law is not satisfied.

EXPERIMENTAL

Fly ash resistivity was measured according to Equation (1) by using the point-plane apparatus as shown schematically in Figure 3. High voltage from a Spellman power supply model 20 PN 30 was applied to the needle electrode, and the current flow through the fly ash layer was measured by a Keithley Electrometer 610C connected to the bottom electrode disk. This apparatus was used for measurements in the temperature range 20° to 220°C with the environmental gas moisture content less than about $c^v = 9\%$. Fly ash from the Portland PA power plant of the Metropolitan Edison Company was used in all resistivity experiments. The composition of this ash, as determined by chemical analysis, was 39 wt. % silica, 26% ferric oxide, 22.5% aluminum oxide, 1.0% calcium oxide, 0.63% magnesium oxide, 0.77% sulfur trioxide, 1.57% potassium oxide, 0.50% sodium oxide, and 0.09% phosphoric anhydride. The BET surface area of the fly ash determined by sorption of argon was 1.62 m²/g (based on 13.8Å² for the argon molecule) or 1.88 m²/g (based on 16.0Å² for the argon molecule). The mean particle diameter of the poly-disperse ash was about 15 to 25 μm as measured by sieving.

RESULTS AND DISCUSSION

The experiments provided data to test the theoretical model presented above. Typical experimentally obtained resistivity data are plotted in Figure 4 as log ρ vs. the reciprocal absolute temperature with moisture content c^v as a parameter; similarly shaped curves have been reported by Bickelhaupt (1975a) as well as by other authors. Also plotted in Figure 4, for comparison with the measured data, are theoretical predictions based on Equation (4). The values of κ_V and $(p/p_o)_{min}$ were determined from resistivity measurements made on dry ash ($c^v = 0$), whereas κ_S was adjusted to provide the best fit of the equations to the actual resistivities measured under conditions of nonzero moisture content as described in more detail below. It was found that a good fit could be obtained simply by using the maximum value of experimentally measured resistivity, as shown in Figure 4. Even at the locations of the maxima in resistivity, it was found that the capillary condensed amounts were small. Values of κ_S given in Table 1 were calculated by using Equation (15) in the form $\kappa_S = [1/\rho_{max} - 1/\rho(t_{max})]/\phi$. The determination of ϕ is discussed below. It should be noted that the conductivities κ_S of Table 1 are about four orders of magnitude smaller than what would be expected for liquid water. Aside from the effects of shape, polydispersity, surface roughness, and other deviations from the ideality implicit in the foregoing theoretical development, there are reasons to expect the electrical properties of capillary condensed water to deviate markedly from those of liquid water. For example, Zettlemoyer and McCafferty (1973) found that adsorbed water on oxide surfaces displayed the characteristic relaxation frequency of a hydrogen bonded, icelike solid (seven decades lower than

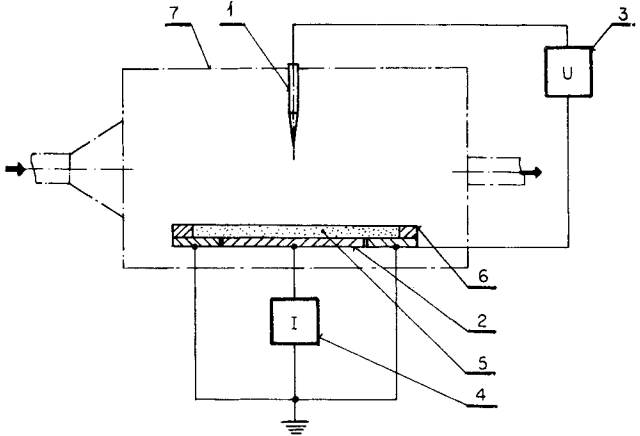


Fig. 3. Schematic diagram of apparatus: 1. needle cathode, 2. grounded anode, 3. high voltage power supply, 4. electrometer, 5. fly ash sample, 6. teflon (quartz) ring, 7. body of apparatus.

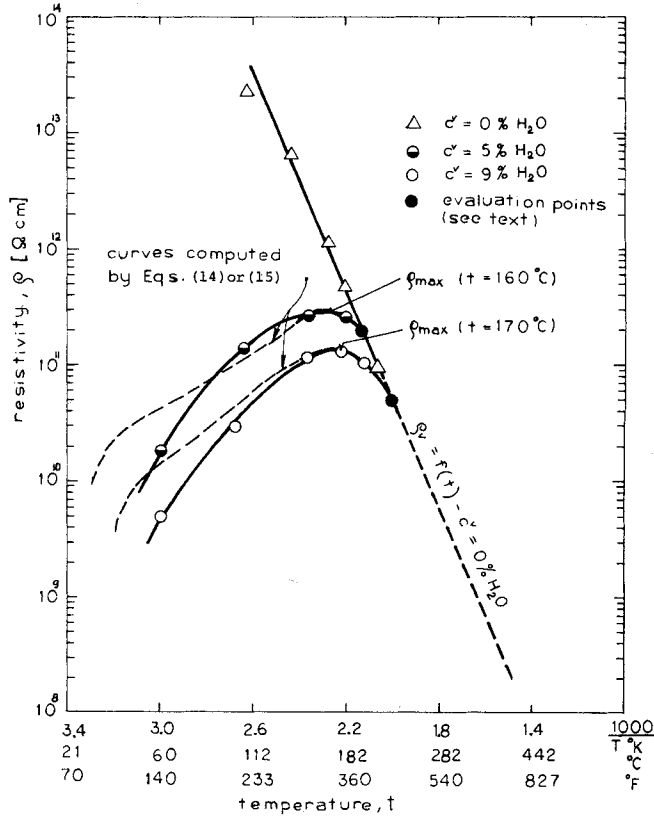


Fig. 4. Measured fly ash resistivity as a function of reciprocal absolute temperature. Solid curves are the prediction of the theoretical model [Equations (14) and (15)]. System: water-air-fly ash.

that of liquid water) even at 25°C and a thickness of about three layers. This is evidence that the sorbed water under such conditions has developed stronger hydrogen bonding than in the liquid, with the molecular rotational motion restricted to some extent as in ice. Furthermore, our measurements (Dittl and Coughlin, 1976) of water desorption from fly ash indicate that a portion of the water is irreversibly sorbed and not desorbed even at relative pressures near zero (experiments with flowing dry air). Yet another reason not to expect the value of κ_S to

TABLE 1. VALUES OF κ_S COMPUTED FROM EXPERIMENTAL DATA

c^v % H ₂ O	$t(\rho_{max})$ [°C]	ρ_{max} [Ω cm]	$\rho_V(t_{\rho_{max}})$ [Ω cm]	$\phi(t_{\rho_{max}})$ [1]	κ_S [Ω ⁻¹ cm ⁻¹]
5	160	$2.8 \cdot 10^{11}$	$1.2 \cdot 10^{12}$	0.172	$1.60 \cdot 10^{-11}$
9	170	$1.3 \cdot 10^{11}$	$6 \cdot 10^{11}$	0.249	$2.42 \cdot 10^{-11}$

TABLE 2. VALUES OF FACTOR ϕ COMPUTED BY EQUATION (15a)
[$\ln(p_k/p_o)_{\min} = -5.727$, $c^v = 5$, 9% H₂O]

c^v	5% H ₂ O	9% H ₂ O	
$t(\rho = \rho_v)$ [°C]	200	230	
$\lg(p_k/p_o)_{\min}$	-5.727	-5.727	
p_k/p_o	t	t	ϕ
(1)	(°C)	(°C)	(1)
	200	230	0
0.04	190.5	220	0.036
0.05	180.5	208	0.078
0.01	152	173	0.218
0.02	128	148	0.381
0.04	106.5	124	0.576
0.06	95	112	0.713
0.08	87	103	0.821
0.1	82	98	0.910
0.2	65	79	1.27
0.4	50.5	63	1.83
0.6	42.5	54	2.42
0.8	37	48	3.25
0.99	33	44	6.35
1.0	32.5	42.5	

conform to that of liquid water is the fact that the foregoing development has neglected the resistivity ρ_b of the ash particles themselves vis a vis their points of contact. If such a resistivity term is included in the development, Equation (15) becomes

$$\frac{1}{\rho - \rho_b} = \frac{1}{\rho_v - \rho_b} + \kappa_S \phi \quad (16)$$

The difficulties inherent in measuring ρ_b for a single fly ash particle require no discussion.

The values of $(p/p_o)_{\min}$ were determined from the experimental data as plotted in Figure 4 by using Equation (15) which tells us that $\phi = 0$ where $\rho = \rho_v$ or $\kappa = \kappa_v$; this condition is satisfied where the curves for a humid air environment join the straight line for the dry environment in Figure 4. These points where $\phi = 0$ must be satisfied are labeled [•] evaluation points on the graph. At these points, $\phi = 0$ or $(p/p_o)_{\min} = (p_k/p_o)$, so $(p/p_o)_{\min}$ is evaluated from $p_k = c^v p_{\text{tot}}$ at the humidity of the evaluation point [•] and from p_o at the temperature of the evaluation point (from steam tables). Calculated values of $\ln(p/p_o)_{\min}$ are given in Table 2 which also contains the corresponding values (p_k/p_o) , t , and ϕ calculated for the two different water concentrations $c^v = 5$ and 9% water. The values of t in Table 2 were taken from steam tables at saturation pressures computed from $p_o = c^v p_{\text{tot}} / (p_k/p_o)$. From $\ln(p/p_o)_{\min}$, κ_S and κ_v , the dependence of resistivity on temperature can be predicted from Equation (15).

It should be mentioned that in plotting the theoretical curves in Figure 4 according to Equations (14) or (15), the values of κ_S obtained as an adjustable parameter at the maximum points should contain a contribution from the equivalent ionic conductivity of the liquid. Since it is generally recognized that the conditionability of fly ash is favorably influenced by its sodium content (White, 1974), it appears reasonable to presume that Na⁺ ions may be present in and contribute to the conductivity of the capillary condensed liquid. Nevertheless, it was found that when the values of κ_S obtained from the maximum points of Figure 4 were corrected for temperature dependence of equivalent conductivity by using the data given in the Handbook of Chemistry and Physics (1972-1973), the conformity of the theoretical curves with the data in Figure 4 was less satisfactory than if the temperature correction was neglected. The smooth curves of

TABLE 3. RESISTIVITY VS. TEMPERATURE COMPUTED
ACCORDING TO EQUATION (15) FOR $c^v = 9\%$ H₂O AND
 $\kappa_S = 2.42 \cdot 10^{-11} \Omega^{-1} \text{cm}^{-2}$

t (°C)	ρ_v [Ω cm]	ϕ	ρ (Ω cm)
44	Negligible	6.35	$6.5 \cdot 10^9$
48	Negligible	3.25	$1.2 \cdot 10^{10}$
63	Negligible	1.83	$2.3 \cdot 10^{10}$
98	$9 \cdot 10^{13}$	0.910	$4.5 \cdot 10^{10}$
112	$3.3 \cdot 10^{13}$	0.713	$5.8 \cdot 10^{10}$
124	$1.8 \cdot 10^{13}$	0.576	$7.1 \cdot 10^{10}$
148	$3.8 \cdot 10^{12}$	0.381	$1.1 \cdot 10^{10}$
173	$7 \cdot 10^{11}$	0.218	$1.49 \cdot 10^{11}$
208	$1.5 \cdot 10^{11}$	0.078	$1.17 \cdot 10^{11}$
220	$7 \cdot 10^{10}$	0.036	$6.96 \cdot 10^{10}$

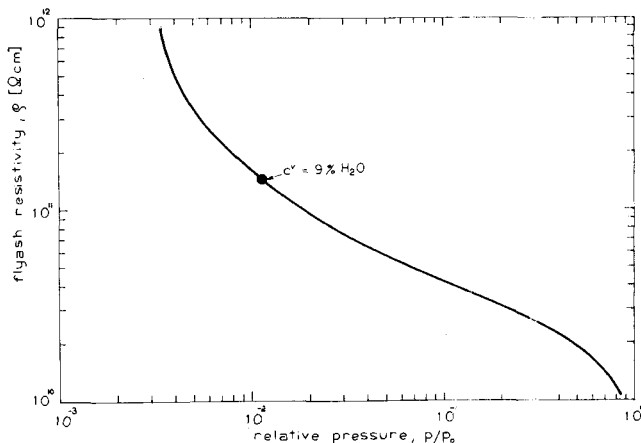


Fig. 5. Fly ash resistivity vs. relative vapor pressure of water. $t = 170^\circ\text{C}$, $\rho_v = 9.10^{11} \Omega\text{cm}$, $\kappa_S (170^\circ\text{C}) = 2.42 \cdot 10^{-11} \Omega\text{cm}$. System: water-air-fly ash.

Figure 4 were then drawn with such corrections ignored. The results of calculations by Equations (14) or (15) for prediction of fly ash resistivity vs. temperature for the constant moisture concentration $c^v = 9\%$ are tabulated in Table 3 as well as plotted in Figure 4. In general, the agreement between experimental data and the predictions of theory is best at higher temperatures. The deviations at lower temperatures are not unexpected in view of the fact that the amount of liquid condensed grows rapidly as the saturation pressure p_o is approached, under which conditions the influence of nonuniform contact geometry may become more pronounced. Moreover, as the saturation p_o is approached, adsorbed multilayers may be expected to build up on the surface of the particles, and such multilayers can provide additional conduction paths not considered herein.

Figure 5 shows the effect of p_k/p_o on resistivity at a constant temperature as computed from Equation (15) at 170°C and $\kappa_S = 2.42 \cdot 10^{-11} \Omega^{-1} \text{cm}^{-1}$.

The model, as plotted in Figure 5, predicts a resistivity drop of two orders of magnitude due to capillary condensation of water. The resistivity drop caused by the presence of 9% water in the air is also shown in this figure. This value of water concentration is commonly employed for electrostatic precipitation. It can be clearly seen from Figure 5 that beyond about 9% moisture, further addition of water to the gas will have smaller effects on resistivity, as inherent in the curvature of the function.

In the practice of electrostatic precipitation, other conditioning agents besides water are often employed for decreasing fly ash resistivity; experience has taught, however, that some minimum moisture content is required in order to achieve the increased conditioning due to the

combined effect of sulfur trioxide and water vapor. For a given constant water concentration ($c^v = \text{const.}$), the presence of sulfur trioxide (sulfuric acid) strongly influences the dew point in the system and enhances capillary condensation. Müller (1959) has published a diagram which permits determination of the sulfur trioxide partial pressure which is required to attain dew point conditions for different temperatures and moisture contents in the vapor (c^v). Because the scale of Müller's graphs does not permit accurate evaluation, his results were recalculated and are shown plotted in Figure 6, which shows the dependence of dew point temperature on sulfuric acid concentration for three different constant moisture contents of the gas. Figure 6 covers the usual range of conditions of interest in electrostatic precipitators for moisture contents of 5, 7, and 10%.

Figures 5 and 6 provide a plausible physical explanation of the experimentally observed fact that the presence of sulfur trioxide in flue gas, at concentrations lower than saturation, can cause a significant drop in the resistivity of the fly ash. It can be seen that values of $(p/p_o)_{\text{H}_2\text{SO}_4} > 0.5$ can provide conditions for capillary condensation and thereby cause a significant decrease in the fly ash resistivity without significantly affecting the dew point. Some influence of $(p/p_o)_{\text{H}_2\text{SO}_4}$ on the κ_s value can also be expected owing to the increased conductivity provided by the presence of sulfuric acid in the capillary condensed liquid at the points of contact of the ash particles.

The absence of chemical reaction between the ash and the acid in this system was discussed by Dittl and Coughlin (1976). It should be added that the effect of the well-known conditioning agent ammonia is not yet entirely clear. Although it is probable that ammonia can influence capillary condensation and alter the conductivity of capillary condensed liquid, it is thought that ammonia may also influence the particle charging process in precipitators (Dismukes, 1975).

The present model also explains the decrease in efficiency of conditioned precipitators observed experimentally when cyclones are located upstream of electrostatic precipitators. The cyclones separate the larger particles, thereby increasing the size uniformity of the fly ash particles and also decreasing the ratio of conduction pathways n_y/n_x according to Equations (4) and (5). Therefore, one can expect an increase in fly ash resistivity if the size of the ash particles is decreased.

As a final note, it should be mentioned that an equation of the precise form of Equation (15) can be derived under the assumption of capillary condensation within the pendular rings at the contact points of smooth, uniform spheres and by using the rigorous description of the phenomenon developed by Melrose (1966). The result produced from such a development relies on the approximation $d_p \gg x_k$ and leads to a value of effective liquid conductivity which does not contain shape factors; namely

$$\kappa_s = \frac{\pi}{2} \cdot \frac{1}{\rho_s}$$

In view of the great deviations of the sites of contact on a fly ash layer from those in a system of smooth uniform spheres, it does not appear worthwhile to elaborate the development based on the latter geometry.

ACKNOWLEDGMENT

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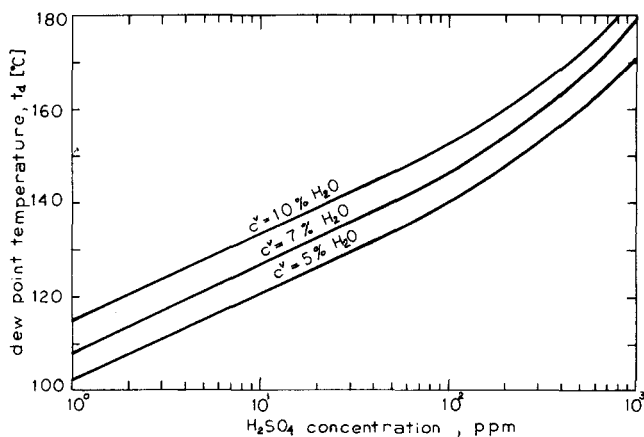


Fig. 6. Dew point temperature vs. sulfuric acid concentration for three different moisture contents, $c^v = 5, 7$, and 10%.

NOTATION

- c^v = absolute volumetric concentration of water in the air or flue gas, % water
- d_p = particle diameter, m
- I = current flow, A
- K = length of contact between two particles
- l = thickness of fly ash layer, m
- n_x = number of interparticle contacts in x direction (Figure 1)
- n_y = number of interparticle contacts in y direction (Figure 1)
- p_k = vapor pressure of capillary condensed or adsorbed compound, N/m²
- p_o = saturated vapor pressure of capillary condensed or adsorbed compound, N/m²
- p_{tot} = total pressure in apparatus, N/m²
- R = resistance, Ω ; gas constant, $R = 8.31432 \text{ kJ } ^\circ\text{K}^{-1} \text{ kmole}^{-1}$
- R_B = total resistance of one interparticle contact, Ω
- R_{BV} = resistance of one dry contact, Ω
- R_{BS} = resistance of the liquid formed by capillary condensation in crevice at one interparticle contact, Ω
- S = cross-section area within fly ash perpendicular to the direction of current flow, m²
- t = temperature, $^\circ\text{C}$
- t_d = temperature of the dew point, $^\circ\text{C}$
- T = temperature, $^\circ\text{K}$
- v = molar volume, m³/kmole
- U = voltage, V
- $x, x_k, x_{\text{min}}, y, y_k, y_{\text{min}}$ = length parameters depicted in Figure 2

Greek Letters

- κ = total electrical conductivity of fly ash, $\Omega^{-1}\text{m}^{-1}$ or $\Omega^{-1}\text{cm}^{-1}$, $\kappa = 1/\rho$
- κ_v = electrical conductivity due to dry contact points, $\Omega^{-1}\text{m}^{-1}$ or $\Omega^{-1}\text{cm}^{-1}$, $\kappa_v = 1/\rho_v$
- κ_s = effective electrical conductivity of capillary condensed liquid in ringlike crevices at contact points, $\Omega^{-1}\text{m}^{-1}$ or $\Omega^{-1}\text{cm}^{-1}$, $\kappa_s = 1/\rho_s$
- κ_{min} = minimal value of κ as it is depicted in Figure 4, $\Omega^{-1}\text{m}^{-1}$, $\Omega^{-1}\text{cm}^{-1}$, $\kappa_{\text{min}} = 1/\rho_{\text{max}}$
- ρ = resistivity, Ωm , Ωcm
- ρ_v = resistivity due to dry point contacts, Ωm , Ωcm
- ρ_s = effective resistivity of capillary condensed liquid in interparticle crevices at contact points, Ωm , Ωcm
- σ = surface tension, N/m
- θ = contact angle
- Ω = symbol for unit of electrical resistivity, ohm
- ρ_b = resistivity of the internal material within a single fly ash particle

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Flows of Nonlinear Fluids Through Porous Media

The conventional "cylindrical tube" model of porous media is shown to be inapplicable to flows of nonlinear fluids. A more precise geometric description of the converging-diverging pore geometry appears to enable accurate pressure drop-flow rate descriptions but requires further development.

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SCOPE

The understanding of flows through porous media represents an interesting challenge in chemical reactor design and in some polymer engineering and separational processes. Further, it may play a primary role in formulating optimum strategies for management of underground reservoirs, as in petroleum production and in the exploitation and control of aquifers. Consequently, an extensive literature has been developed on this subject. The two major features of this literature may be described as follows.

Analyses of non-Newtonian fluid flows through porous media under laminar flow conditions have almost universally been developed by coupling a specific model of the pore structure of the medium with a specific model of the rheological properties of the fluid being employed in the flow process. Most commonly the pore structure is modeled by means of the cylindrical equivalent capillary, a cylindrical duct of length and diameter such that it exhibits the same resistance to flow as the actual interstices in the real porous medium. Thoughtful and clear descriptions of this modeling are presented in the paper by Ergun (1952), the book by Bird, Stewart, and Lightfoot (1960), in the research papers of Christopher and Middleman (1965) and of Gaitonde and Middleman (1967), and in the comprehensive article of Savins (1969). This latter paper shows how a particular rheological model of the viscosity function of the fluid may be replaced with

a generalized analysis similar to that employed in laminar and turbulent flows of non-Newtonian fluids through tubes.

Separately, there has been a growing awareness of the fact that the actual pores in a granular bed are, of course, not isolated circular cylinders of constant cross-sectional area; they are interconnected and noncircular, and the changes in cross-sectional area to which a fluid element is exposed as it moves through the bed may occur rapidly and be of large magnitude. An early attempt to apply some of these considerations to the flow of viscoelastic fluids was published by Marshall and Metzner (1967); the subject of the flow of Newtonian fluids through pores of complex geometry has recently been extended substantially, and its current status is presented in a series of papers by Dullien (1975), Payatakes, Tien, and Turien (1973a, b, c), Dullien and Azzam (1973a, b), and Batra, Fulford, and Dullien (1970). At the present time, therefore, a designer may choose between analyses which consider either nonlinear fluid properties or some of the complexities of real pore geometries, but generally not both.

It is shown in the present work that, conceptually, the cylindrical capillary model of the pore structure must be a grossly inadequate representation for use when flows of nonlinear fluids are to be described and that this inadequacy may lead to order-of-magnitude errors in pressure drop-flow rate predictions. As a step toward resolution of this problem, a more realistic model of the pore structure is introduced and applied to flows of nonlinear but purely viscous fluids through porous media.

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