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MEASUREMENT AND PREDICTION OF THE RESISTIVITY OF ASH/SORBENT MIXTURES PRODUCED BY SULFUR OXIDE CONTROL PROCESSES

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The report describes the development of (1) a modified procedure for obtaining consistent and reproducible laboratory resistivity values for mixtures of coal fly ash and partially spent sorbent, and (2) an approach for predicting resistivity based on the chemical composition of the sample and the resistivities of the key compounds in the sample that are derived from the sorbent. Furnace and cold-side sorbent injection technologies for reducing the emission of sulfur oxides from electric generating plants firing medium- to high-sulfur coal are under development for retrofit applications. The particulate resulting from injecting this sorbent will be a mixture of coal fly ash and partially spent sorbent. The presence of this sorbent causes the resistivity of the mixture to be significantly higher than that of the fly ash alone. Since higher resistivity dusts are more difficult to collect in an electrostatic precipitator (ESP), accurate knowledge of the resistivity of the mixture is needed to determine if the ESP will operate within an acceptable efficiency range.				
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ABSTRACT

Furnace and cold-side sorbent injection technologies for reducing the emission of sulfur oxides from electric generating plants firing medium- to high-sulfur coal are under development for retrofit applications. The particulate resulting from injecting this sorbent material will be a mixture of coal fly ash and partially spent sorbent. The presence of this sorbent material causes the resistivity of the mixture to be significantly higher than that of the fly ash alone. And since higher resistivity dusts are more difficult to collect in an electrostatic precipitator, accurate knowledge of the resistivity of the mixture is needed to determine if the precipitator will operate within an acceptable efficiency range. This report describes the development of a modified procedure for obtaining consistent and reproducible laboratory resistivity values for these mixtures, as well as development of an approach for predicting the resistivity based on the chemical composition of the sample and the resistivities of the key compounds in the sample that are derived from the sorbent.

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SUMMARY

Injection of a sorbent material such as limestone or hydrated lime, either into a furnace or the combustion flue gas downstream of the furnace, will result in a particulate which is a mixture of coal fly ash and partially spent sorbent material. It was found that the partially spent sorbent material contained in these mixtures necessitated modifications to the procedure normally used for measuring the resistivity of ordinary fly ash. Application of the IEEE Standard 548-1984 procedure for measuring resistivity of fly ash to measuring resistivity of an ash/sorbent mixture resulted in inconsistent values of resistivity and an overall lack of repeatability, as well as large discrepancies between values measured using the ascending and descending temperature methods. This behavior was traced to large changes in the nature of the as-collected sample caused by heating to 450°C, as specified by the Standard. In particular, it was found that calcium hydroxide in the as-collected sample decomposed at about 300°C, accompanied by large changes in the surface area of the sample. Then in order to preserve the nature of the as-collected sample, it should not be exposed to temperatures above 250°C during resistivity measurements. Even with this stipulation, resistivity measurements made using ascending temperatures did not show good repeatability: the first test on a sample gave resistivity values which were lower than those obtained on subsequent tests at identical conditions. In contrast, resistivity measurements made using descending temperatures showed excellent repeatability and consistency. Therefore, resistivity measurements of ash/sorbent mixtures should be made in the descending temperature mode beginning at 250°C.

Multiple regression analyses of the resistivity data showed very strong correlations between the resistivities of the ash/sorbent mixtures and the resistivities of the calcium compounds found in the mixtures. In fact, the resistivity of the mixture appeared to be primarily determined by the resistivity of one or more of these calcium compounds. Based on these correlations, considerable work was done to develop a method for predicting the resistivity of an ash/sorbent mixture from its chemical composition. However, these efforts were not generally successful. One evident source of difficulty was the insufficient chemical analysis of the several calcium compounds in the sample (consisting of both the residue of the original sorbent and the products of reaction in the flue gas). Another possible source of difficulty was the omission of any resistivity effect due to components of the fly ash or products of reaction between the ash and the sorbent. Poor correlation was obtained between the chemical compositions and resistivities of the mixtures. But, for samples of sorbent only, exposed to SO_x in the absence of fly ash, more satisfactory agreement between chemical composition and resistivity was obtained in following the same approach. It thus seems that this approach should be successful for predicting the resistivities of ash/sorbent mixtures provided that an accurate method of determining the chemical composition of the mixtures can be developed.

INTRODUCTION

Furnace and cold-side sorbent injection technologies are under development for retrofit applications at electric generating plants firing medium- to high-sulfur coal. Both coal fly ash and sorbent material are expected to be collected in an existing electrostatic precipitator (ESP). In most candidate sites for retrofit installations, the existing ESP is quite small (SCA generally less than 300 ft²/1000 acfm or 60 m²/[m³/s]) since it was designed to collect low-resistivity fly ash. The presence of the sorbent causes the resistivity of the mixture to be significantly higher than that of the fly ash alone. And since the resistivity of the particulate influences the collection efficiency of the dust (higher resistivity dusts being more difficult to collect), it is important to be able to accurately measure the resistivity of the mixture to determine if the precipitator will operate within an acceptable efficiency range.

DEVELOPMENT OF RESISTIVITY MEASUREMENT PROCEDURE

A total of 40 ash/sorbent samples produced from burning pulverized coal and injecting sorbent material at various locations were used in this study. Eighteen of these samples involved injection of the sorbent into the flue gas downstream of the regenerative air heater. The other 22 samples were obtained from the LIMB program where the sorbent material is injected into the burner. Most of the work was performed with E-SOX dust, which is the residue from a process in which a slurry of $Ca(OH)_2$ is injected downstream from the air heater. The remainder of the work, with LIMB dust from furnace injection of limestone or $Ca(OH)_2$ and with HALT dust from low-temperature injection of dry $Ca(OH)_2$, was performed to determine whether the results with E-SOX samples might extend to the other types of materials.

Two additional samples that were studied were residues of slurries of $Ca(OH)_2$ that had been injected into a gas stream containing SO_2 but not containing fly ash. These samples came from a reactor operated by Babcock & Wilcox. The SO_2 concentration ranged from 1500 to 2500 ppm. The slurry injected produced Ca/S mole ratios of 0.6 to 1.3 and lowered the gas temperature to the range of 22 to 33°C from saturation.

Many of the samples mentioned above were subjected to a battery of tests designed to characterize them as completely as possible. These tests included chemical analysis, particle size analysis, density, thermogravimetric analysis (TGA), scanning electron microscope (SEM) photography, mercury porosimetry, and surface area measurements. Because the important qualitative features of the data were the same for all of the samples, the results reported here will focus on the sample generated by burning Pittsburgh coal and spraying a slurry of Longview hydrated lime into the a humidifying chamber in the Southern Research pilot-scale combustor, with an entering flue gas temperature of about 150°C. This sample is designated the "E-SOX sample" because one type of cool-side lime slurry injection process is the EPA E-SOX process.

SAMPLE CHARACTERIZATION

Moisture Adsorption

Because some calcium compounds, especially the hydroxide, have a distinct affinity for water vapor, it was necessary to test the E-SOX sample for adsorption of moisture to see if the material remained in its as- collected state long enough to permit routine laboratory tests on a sample. Any interaction of the E-SOX sample with moisture from the flue gas during its collection cannot be easily controlled in the field and was not investigated for this work. As a simple test for the adsorption of water, the specific surface area was measured according to the theory of Brunauer, Emmett, and Teller (1) (referred to here as the "BET area") for (a) a sample exposed to room air (relative humidity of about 60%), and (b) a sample continuously exposed to the flue gas conditions at which it was collected (67°C and 11% humidity by volume). Water wetting the surface of the particles would decrease the roughness of the surface and cause a corresponding decrease in the specific surface area. The results are shown in Figure 1. Although the changes are quite small, a slight decrease in the BET area of the sample exposed to room air can be seen, indicating adsorption of moisture. This was confirmed by noting that the sample gained weight during the 8 days of exposure. However, the weight gain was only 0.03 g for a 100 g sample, corresponding to about 1.7×10^{-3} moles of water. The sample maintained at flue gas conditions showed a very slight increase in BET area, indicating a possible small loss of adsorbed water. Due to the need for keeping its temperature elevated, it was not possible to confirm this by measuring the weight of the sample. Therefore, the data of Figure 1 indicate that, for reasonably short time delays (a few days) between acquiring the sample and transporting it to the laboratory, the change in BET area of the sample due to exposure to atmospheric humidity will be small.

Chemical Composition

Results of chemical analysis of the E-SOX type sample were as follows:

Chemical	Weight
Compound	Percent
Li ₂ 0	0.02
Na ₂ 0	0.19
K20	0.87
MgO	1.0
CaO	32.4
Fe ₂ O ₃	13.1
A1203	11.6
SiO	24.9
TiO ₂	0.5
P ₂ 0 ₅	0.12
SO3	13.5
LOI	11.1

where LOI is the loss-on-ignition when the sample was heated to 750°C. The presence of the sorbent material in this sample is reflected in the relatively



Figure 1. BET area of the E-SOX sample as a function of time of exposure to humidity. Circles are for exposure to ambient temperature and humidity; squares are for exposure to flue gas conditions (67°C and 11% water by volume).

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large amount of calcium present, conventionally reported as CaO. Analysis of the amount of carbon, hydrogen, and nitrogen (CHN) in this sample yielded the following (also in weight percent):

Results of thermogravimetric analysis (TGA), which measures the change in weight of a sample as it is heated, are shown in Figure 2. The initial decrease in the weight of the sample is due to driving off adsorbed moisture. The weight loss which occurs between about 300 and 450°C has been identified as decomposition of calcium hydroxide in the sample.

TGA is normally performed on samples in a nitrogen atmosphere in order to eliminate any effects caused by chemical reactions between the atmospheric gas and the surface of the sample. But since heating of the samples in our experiments takes place in an atmosphere of air, it was necessary to see if any differences were obtained when the weight loss occurred in air. The result for the E-SOX sample in air are shown in Figure 3. Comparison of Figures 2 and 3 shows that only small differences in weight loss were seen when TGA was run in the two different atmospheres.

Particle Morphology and Size Distribution

Figure 4 shows a typical area of the E-SOX sample, at a magnification of 500X, using a scanning electron microscope (SEM). Several spherical, amorphous particles typical of coal fly ash are present. The clusters of many small spheres sticking together, which can be seen in some areas of the photograph, are also seen in SEM photos of fly ash which contain relatively large (e.g., > 20% by weight) amounts of GaO. In addition, several clusters of crystalline material, which are probably composed mostly of sorbent matter, are evident. The spherical and crystalline particles appear to be dispersed uniformly in the photograph.

The results of Bahco particle size classification of the E-SOX sample are shown in Figure 5. The data in this figure have been corrected for the density of the sample, 2.35 g/cm³. The straight line indicates the result of linear, least-squares analysis of the data. The mass-median-diameter (mmd) obtained from this analysis was 6.3 μ m. However, the data appear to show a slight bimodal behavior, with a transition point somewhere around 5 μ m. Then characterization of the sample by a single mode (6.3 μ m) may not be rigorously correct, but the departure from unimodal behavior is so small that the computed mmd is probably sufficient for our purposes. The measured porosity (ratio of the volume of voids within the sample to the total volume occupied by the sample) was 77%, which is at the high end of the range of porosities typically observed for fly ashes (40 to 80%).



Figure 2. Thermogravimetric analysis (TGA) of the E-SOX sample from 50 to 450°C in a nitrogen atmosphere.



Figure 3. Thermogravimetric analysis (TGA) of the E-SOX sample from 50 to 450°C in air.

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Figure 4. Scanning electron microscope (SEM) photograph of particles in the E-SOX sample at a magnification of 500X.



Figure 5. Bahco particle size classification of the E-SOX sample. Straight line is a linear, least-squares fit to the data.

IEEE RESISTIVITY TESTS

The E-SOX sample was subjected to a resistivity test according to IEEE Standard 548-1984 (designed for testing fly ash only) at 9.6% water vapor by volume. This test calls for measuring the resistivity of a sample, in increments of about 30°C, beginning at 95°C and increasing to a temperature of about 215°C, and then at temperatures near 315 and 425°C (the "ascending temperature phase"). Next, the material is maintained at 460°C overnight in dry air, followed by resistivity measurements at about 30°C increments as the temperature decreases from 450 to 85°C (the "descending temperature phase"). The results of this test are shown in Figure 6. For most of the temperature range, the resistivity measured in the ascending phase is higher than that measured in the descending phase for a given temperature. However, this relationship was reversed for other samples. In the low temperature limit, the resistivity measured in the descending mode is three orders of magnitude less than that measured in the ascending mode. This discrepancy is intolerable since various sorbent injection processes will likely need to operate in this low temperature region.

Often, it is necessary to perform multiple resistivity measurements on a single sample at different atmospheric conditions. So, the next step in this work was to examine the effect of "cycling" the E-SOX sample in the descending temperature mode for measuring resistivity — i.e., using a single sample to measure resistivity at increasing humidity levels. The results are shown in Figure 7. In general, the data are similar to that typically seen with fly ash and no sorbent addition: coincident data in the volume conduction region (above about 250°C) and decreasing resistivity with increasing humidity levels in the surface conduction region (below about 180°C). For a truly dry atmosphere with ideal electrical conditions, the resistivity would be a straight line, since only the volume conduction mode would be active. However, the curvature in the dry data at low temperatures is typical of "real" conditions and is attributed to the presence of a trace amount of moisture (measured to be 0.21 volume percent) and leakage currents within the electrical connections and through the ambient air at these very high resistivities. The lack of coincidence between the dry and humid data in the volume conduction region is not uncommon with fly ashes and is not considered important here.

Between each test shown in Figure 7, a fresh sample was put in the environmental chamber to compare with the results for the cycled samples. Figures 8, 9, and 10 show the differences in resistivity measured for the fresh sample (circles) and the samples which have been cycled for each humidity level. For example, the sample labeled E-SOX 1 in Figure 10 was the fresh sample used in the dry atmosphere test and remained in the environmental chamber during the humidified atmosphere tests. Thus, it had been cycled a total of four times at the end of the 15% moisture (by volume) test. In general, the resistivity of the fresh sample was always higher than that of the cycled samples. Sometimes this difference was as much as an order of magnitude for a given temperature. Figure 11 shows the resistivity data for all fresh samples at the indicated humidity levels. Comparison with Figure 7 shows that, except for the dry air data (which was obtained only on a fresh sample), the resistivities of the fresh samples were slightly higher than those of the cycled samples.



Figure 6. Resistivity of the E-SOX sample obtained according to the IEEE Standard 548-1984 for resistivity measurements of fly ash.



Figure 7. Resistivity for a single E-SOX sample obtained at successively higher humidity levels.



Figure 8. Comparison of resistivity data for a fresh E-SOX sample (E-SOX 2) and a sample tested once previously (E-SOX 1).



Figure 9. Comparison of resistivity data for a fresh E-SOX sample (E-SOX 3) and samples tested once and twice previously (E-SOX 1) and E-SOX 2, respectively).



Figure 10. Comparison of resistivity data for a fresh E-SOX sample (E-SOX 4) and samples tested once, twice, and three times previously (E-SOX 1, E-SOX 2, and E-SOX 3, respectively).



Figure 11. Resistivity of E-SOX sample for various humidity levels. Data for each humidity level were taken using a fresh sample.

ANNEALING EFFECTS

The effect of temperature on the surface area of the E-SOX sample is shown in Figure 12. For this test, the sample was maintained in an atmosphere of dry air (measured water concentration of 0.21% by volume) at a temperature of 50°C. After 24 hours, a portion of the sample was removed for BET analysis. The temperature was then raised in increments of 50°C (to a maximum of 450°C) and the procedure repeated. A steady increase in the surface area with temperature up to 400°C was observed. Then when the sample was heated to 450°C for 24 hours, the surface area dropped sharply to a value which was a factor of 3 lower than the initial value.

Using the same procedure described in the preceding paragraph, the test was repeated in a humidified atmosphere (10.4 volume percent water). Also included in this test was a LIMB type sample (EPA Demo coal plus Tennessee Luttrel limestone injection) for comparison. The results are shown in Figure 13. Again, the E-SOX sample increased in surface area with increasing temperature, but only up to 350° C instead of 400° C like its counterpart in dry air. Then at temperatures of 400 and 450° C the surface area again dropped sharply. The reason for the 50° C discrepancy in the temperature at which the BET area decreases between the dry and humid data is not clear, but this temperature range corresponds to the area where the decomposition of Ca(OH)₂ begins in the TGA results of Figure 8. Thus, this discrepancy is probably due to interaction between the sample and atmospheric humidity. The surface area of the LIMB type sample showed the same general behavior, but in a much less dramatic fashion.

Additional investigations were made of the effect of annealing the E-SOX sample at 450°C. Because of the large change in the BET area, it was hoped that differences between the annealed and as-collected sample could be seen in the SEM photographs. However, the annealed sample was indistinguishable from the as-collected sample shown in Figure 10, even up to a magnification of lOkX. Bahco particle size classification of the annealed sample showed that the mmd increased from 6.3 μ m for the as-collected sample to 7.7 μ m for the annealed sample. Pursuing this further, the BET area of the size fractions collected in the Bahco machine were measured:

BAHCO MODE (µm)	BET AREA ORIGINAL SAMPLE	(m ² /g) ANNEALED SAMPLE	% CHANGE
1.6	7.0	4.7	33
2.5	6.1	2.9	52
4.7	5.6	2.0	64
8.3	5.5	1.8	67
11.6	5.2	1.4	73
· 19.0	5.4	1.2	78
24.1	6.2	1.2	81
26.9	6.1	0.9	85
remainder	9.4	1.7	82

where "original" refers to the as-collected sample. Although the surface area changed across the entire range of sizes, the percent change increased as the



Figure 12. BET area of the E-SOX sample as a function of annealing temperature in dry air.



Figure 13. BET area as a function of annealing temperature in an atmosphere containing 10.4% humidity by volume.

particle size increased. The density also increases from a value of 2.35 g/cm³ for the as-collected material to 2.51 g/cm³ for an annealed sample, while the porosity stayed relatively constant (77 and 74%, respectively).

Examination of the pore structure of the E-SOX sample before and after annealing, using a mercury porosimeter, is also of interest. Since mercury has a high surface tension, it does not readily wet most surfaces and must be forced, by pressure, to enter a small pore. The relationship between the applied pressure and the corresponding diameter of the pore which mercury will intrude was first derived by Washburn (2) and can be written as

$$Pd = -4\gamma \cos\theta \tag{1}$$

where P is the applied pressure; d is the pore diameter; γ is the surface tension of mercury (taken to be 480 dynes/cm); and θ is the contact angle between mercury and the wall of the pore (taken to be 140°). Note that equation (1) is derived for a capillary process, so cylindrical geometry is assumed. If P is measured in psia, then solving equation (1) for d gives

$$d = 213.4/P \text{ (micrometers)}$$
(2)

The results of the porosimeter measurements on the E-SOX sample are shown in Figure 14. In general, the distribution of pores was shifted toward larger diameters in the annealed sample compared to the distribution for an as-collected sample.

The surface area of the sample, S, can be obtained from the mercury intrusion data of Figure 14 by relating the total surface area to the pressure-volume work required to force mercury into the sample:

$$dW = -P \, dV = \gamma \cos\theta \, dS \tag{3}$$

where W is the work and V the volume of mercury. The total surface area is obtained by integration of equation (3) over the range of pressures used in the porosimeter:

$$S = \frac{1}{\gamma \cos \theta} \int P dV$$
 (4)

The value of the integral can be obtained directly from the pressure-volume data of Figure 14. The resulting surface areas of the as-collected and annealed samples are shown in Figure 15. These areas are in favorable agreement with the BET surface areas.



Figure 14. Volume-vs-diameter data from mercury porosimetry measurements of as-collected and annealed (450°C) E-SOX samples.



Figure 15. Area-vs-diameter data from mercury porosimetry measurements of as-collected and annealed (450°C) E-SOX samples.

Based on the TGA and BET area results, the differences in the resistivity obtained with the ascending and descending temperature techniques must be due to the decomposition of $Ca(OH)_2$ and the accompanying change in the surface area above 350°C. Therefore, the IEEE procedure for measuring resistivity produces fundamental changes in the nature of the ash/sorbent sample.

One explanation for the difference in resistivities of fresh and cycled samples may be that the process of decomposing the $Ca(OH)_2$, is incomplete after a single annealing of the sample at 450°C, but is completed during the second annealing. To test this hypothesis, TGA was run twice for several samples to see if any additional weight loss occurred during the second heating to 450°C. Examples of the results of these second runs for the E-SOX sample are shown in Figures 16 and 17. The small increase in weight at the beginning of the second runs has been attributed by the operators of the instrument to a slight buoyancy of the weighing pan in the TGA due to thermal convection currents. This effect would be obscured by the weight loss due to adsorbed moisture during the initial runs. For every sample tested, the weight change for these second runs was less than 1% so the above hypothesis does not seem very credible. However, it cannot be positively ruled out.

A second possibility is that the change in surface area is incomplete after a single annealing. This was confirmed during chemical analysis and BET measurements of the samples used for the data of Figure 7:

	E-SOX 1	E-SOX 2	E-SOX 3	
Chemical	(0,5,10,	(5,10,15	(10,15	E-SOX 4
Compound	15% H ₂ O)	% Η ₂ Ο)	ቄ H ₂ O)	(15% H ₂ O)
LizO	0,02	0.02	0.02	0.02
NazO	0.18	0.19	0.19	0.18
K ₂ 0	0.79	0.80	0.80	0.80
MgO	1.00	1.00	1.00	1.00
CaO	32.40	32.30	32.30	32.30
Fe_2O_3	13.40	13.40	13.20	13.20
A1 ₂ 0 ₃	11.90	11.90	11.90	11.80
SiO ₂	25.00	25.10	24.60	25.00
TiO_2	0.58	0,50	0.58	0.58
$P_2 O_5$	0.12	0.13	0.13	0.13
S 0 ₃	13.20	12.80	13.20	12.90
LOI	13.50	13.50	13.80	13.70
BET, m ² /g	1.80	1.80	1.90	3.00

Although no significant difference in the chemical composition of the samples could be seen, there was a 40% change in the BET area between the sample annealed only once (E-SOX 4) and the cycled samples.

MODIFIED RESISTIVITY TESTS

The preceding results indicate that, in order to evoid the large changes in BET area and the decomposition of $Ca(OH)_2$ induced by annealing the E-SOX sample at 450°C, it will be necessary to limit the upper temperature at which resistivity is measured. From the data of Figures 8, 12, and 13, restricting



Figure 16. TGA of E-SOX sample: second run in nitrogen.



Figure 17. TGA of E-SOX sample: second run in air.

the maximum temperature to 250°C should avoid such changes in the nature of the E-SOX sample. Thus, a series of resistivity measurements using a maximum temperature of 250°C were made to investigate the reliability and reproducibility of such a procedure.

The resistivity of the E-SOX sample measured in dry air in the ascending temperature mode is shown in Figure 18. The test was performed on the same sample three times. Note that the resistivity of the fresh sample (circles) was lower than that measured in the two subsequent tests, but the second and third test data showed excellent reproducibility. The reason for this discrepancy is probably due to the presence of adsorbed moisture which is gradually driven from the surface of the sample as the temperature is increased and would not be indicative of the resistivity of the sample in the flue gas of a precipitator. Figure 19 shows the resistivity of the E-SOX sample, again using the ascending temperature mode, as a function of atmospheric humidity. The dry data were acquired first, followed in order by the 5, 10, and 15% water data. Because the first (dry) data set gives resistivity values lower than subsequent tests, the dry and 5% water data are unusually close together. However, the data for the humidified samples should be representative of the sample. Heating is always done with the sample in dry air, although water vapor may be added when the resistivity values are measured at descending temperatures.

The tests described in the preceding paragraph were repeated for the descending temperature mode, starting at 250°C. The results for an E-SOX sample in dry air are shown in Figure 20. Except for some scatter at the lowest temperatures, the reproducibility is excellent, with no discrepancies seen between fresh and cycled samples. The data for humidified samples are shown in Figure 21. Differences in resistivity between the dry and 5% moisture data are much larger here than in the case for ascending temperature data. Comparison of Figures 18 and 20 shows that the resistivity of the E-SOX sample in dry air is greater when measured in the descending temperature mode than that measured with ascending temperatures, due to adsorbed moisture already being driven from the sample before the dry data were obtained in the descending mode. Figures 19 and 21 show that, up to about 150°C, the resistivities measured with ascending and descending temperatures agree well. Above 150°C, however, the resistivity measured with descending temperatures tends to be slightly higher than that measured with ascending temperatures. Therefore, resistivity measured in the descending temperature mode (beginning at 250°C) agrees well with the corresponding results from the ascending temperature mode, but avoids the problem of low values associated with the first test using the ascending temperature method. Resistivity measurements made in the descending temperature mode (beginning at 250°C) are then to be preferred for ash/sorbent mixtures because this method produces the most reliable and repeatable measurements.

The same heating procedure is deemed necessary for samples of LIMB dust as well as for samples of E-SOX dust. This conclusion was reached because the LIMB samples also showed evidence by TGA that the thermal decomposition of $Ca(OH)_2$ occurred in them at temperatures above 250°C, even though the evidence of changes in BET surface area was weak (Figure 13).



Figure 18. Resistivity of E-SOX sample taken in the ascending temperature mode in dry air to a maximum temperature of 250°C.



Figure 19. Resistivity of E-SOX sample taken in the ascending temperature mode at various humidity levels to a maximum temperature of 250°C.



Figure 20. Resistivity of E-SOX sample taken in the descending temperature mode in dry air, beginning at 250°C.



Figure 21. Resistivity of E-SOX sample taken in the descending temperature mode at various humidity levels, beginning at 250°C.

DEVELOPING A PREDICTION TECHNIQUE

Knowledge of the resistivity of the ash/sorbent mixture resulting from use of the E-SOX or other sorbent injection process is important in predicting the collection efficiency and, consequently, the economic and technical feasibility of applying the process on a given precipitator. To facilitate planning and to hold down costs, it would be helpful to be able to predict the resistivity of an ash/sorbent mixture in a manner similar to the computer model developed by Bickelhaupt for fly ash (3,4). However, applying the Bickelhaupt computer model (Model II, reference 4) to the samples used in this work yields predicted values of resistivity which are consistently lower than the measured values. Figure 22 shows an example of the failure of the computer model to predict the resistivity of the E-SOX sample. Thus, it is obvious that either the Bickelhaupt model must be modified, or a new computer model must be written for predicting the resistivity of ash/sorbent mixtures.

It must be understood that the expected value of a satisfactory model for predicting resistivity will be in estimating trends or relative values in laboratory data, not in predicting the values with absolute accuracy. Moreover, it will be apparent that the model may be substantially less successful in predicting the resistivity values that prevail in a flue gas duct than in predicting the resistivity values that occur under laboratory conditions. No laboratory procedure can be expected to duplicate all of the dynamic physical and chemical processes involved in the injection of a sorbent and the subsequent reaction of the sorbent with SO₂.

ELECTRICAL CONDUCTION MECHANISM

When unloading the test cells used for making the measurements shown in Figures 7 through 10, it was noted that some of the E-SOX sample was sticking to the negative electrode in each cell. Further, the amount of sample sticking to the electrode increased with the number of times the sample had been cycled. This stuck material was carefully removed from each cell and combined to obtain enough material for chemical analysis. The results were as follows:

Chemical Compound	As-Collected Sample	"Stuck" to Neg. Elect.	Percent Difference
 Li ₂ 0	0.02	0.01	50
Na ₂ 0	0.19	0.26	37
K₂Õ	0.87	0.87	0
MgO	1.0	1.0	0
CaO	32.4	34.4	6
Fe_20_3	13.1	13.0	1
A1203	11.6	11.7	1
Si0 ₂	24.9	25.0	0
TiO ₂	0.50	0.52	4
P205	0.12	0.02	83
ร0ิ _จ	13.5	12.5	7
LOI	11.1	10.6	5



Figure 22. Comparison of measured resistivity values and those predicted by the Bickelhaupt computer model (Model II, Reference 4) for an E-SOX sample in an atmosphere containing 15% water vapor by volume.

The results of the analysis are in weight percent and were performed on the samples after ignition at 750°C. Differences of less than 10% should be viewed with skepticism since they are within experimental error. In addition, the 50% difference for Li_20 may not be meaningful since it results from calculations on very small numbers. The 37% increase in the amount of Na₂O would appear to indicate a migration of sodium ions to the negative electrode. Although this evidence is limited, it is consistent with the results of Bickelhaupt (5,6), which show that sodium ions are the dominant charge carriers in coal fly ash. Migration of phosphorous away from the negative electrode has no ready explanation.

A more thorough search for correlations between the resistivity of an ash/sorbent mixture and its chemical composition was made. The first step in this search was to identify the charge carrying species through a "charge transference" experiment: applying voltage across a sample for a long period of time so that the mobile charge carriers can move through the sample away from the electrode of like charge and toward the electrode of opposite charge. To accomplish this, 0.5 cm thick ash/sorbent samples were loaded between parallel plate electrodes, one of which had a 0.102 mm recess. This recess allowed us to obtain a thin layer of the material adjacent to the electrode for chemical analysis. Two samples of each species were used, one with positive polarity on the recessed electrode and the other with negative polarity. In this way, we could look for an ion which showed an increase in concentration at one electrode and a corresponding decrease at the other electrode, as compared to its concentration in the bulk. The samples were then placed in an environmental chamber at a temperature of 60°C in an atmosphere containing 11% water vapor by volume. Then an electric field of 2 kV/cm was continuously applied across the samples for a period of 1 month. At the end of that time, the portions of the samples within the recesses were removed for chemical analysis.

In order to increase the chances of getting useful information from such a test, five LIMB samples were used in this transference experiment, in addition to the single E-SOX sample. Unfortunately, the results of chemical analysis of the samples from the recesses did not show any consistent pattern of ion migration. The three LIMB samples produced by injecting limestone did show a migration of the alkali metal ions (Li, Na, K), similar to what would be expected for fly ash only. However, the E-SOX sample and the two LIMB samples obtained by injecting hydrated lime did not show any evidence of ion migration. This was disappointing because the evidence from the cycling experiments discussed above indicated a possible sodium ion migration. However, the careful analysis of the charge transference results did not confirm this, even with the use of duplicate samples. Since the amount of charge transferred in each test was on the order of 40 coulombs, it cannot be argued that the migration of an ionic species was too small to be detected. Instead, it must be assumed that the charge carriers were not included in the compounds tested for in the usual chemical analysis.

Correlation of Resistivity with Ionic Species

Because the charge transference experiments did not immediately identify the charge carriers in an ash/sorbent mixture, an exhaustive search was made for a correlation between the measured resistivity of the samples and all reasonable combinations of the amount of alkali and alkaline earth ions in the sample in order to uncover more subtle relationships. In general, no correlations were found. Since the two LIMB samples with limestone injection showed a migration of sodium in the charge transference experiment, it would be expected that they would show a correlation with the atomic concentration of sodium (or sodium plus lithium). The two data points available appeared to show this to be the case. However, the small number of data points are insufficient to draw such a conclusion with any confidence.

Ideas from Glass Research

Since fly ash is composed of predominantly amorphous material, some researchers have found that many of the concepts developed to explain electrical conduction in glass can also be applied successfully to fly ash. Scanning electron microscope photographs of ash/sorbent mixtures also show a large amount of amorphous material, so there is reason to believe that some of the results from research on glasses may apply to these mixtures also.

The ionic conductivity of virtually all oxide glasses is due to the motion of monovalent cations (7). For the majority of these glasses, the conducting ion is sodium, although lithium and potassium ions can also contribute to the conductivity. However, there are various "alkali-free" silicate glasses whose conduction mechanism is uncertain. These glasses contain small amounts of alkali ions, but these ions do not carry appreciable current in the glass.

Since the ash/sorbent samples have such large amounts of calcium in them and no consistent motion of alkali ions was detected in the transference experiments, the results for alkali-free glasses with high calcium content are of special interest here. Within this group of glasses, the amount of alkali metal ions appears to have no influence on their electrical conductivity. For example, the conductivity of calcium silicate glass was found to be insensitive to sodium concentration up to 1.26 mole Na₂O (8). Two possibilities for the charge carrying species of these glasses have been suggested in the literature: (a) oxygen ions, and (b) hydrogen ions. In calcium aluminum silicate glasses, oxygen ion diffusion is apparently too low to account for their conductivity (9), although there is some dispute on this issue (10). Other studies have shown that the conductivity of lead silicate (11), calcium silicate (12,13), and barium aluminum borate (14) glasses was affected by the presence of OH groups, indicating that hydrogen ions are the charge carriers in these glasses. It is known that the mobility of hydrogen ions in most silicate glasses is several orders of magnitude lower than the mobility of sodium ions (15). But the presence of alumina groups tends to make the hydrogen ions less tightly bound in silicate glasses (15), so aluminosilicate glasses may well have relatively high hydrogen ion mobilities. These studies suggest that hydrogen ions are the charge carriers in these glasses, although electronic conduction cannot be completely ruled out. If these results can be extended to ash/sorbent mixtures, then it may be that hydrogen ions are the charge carriers in these mixtures as well. However, this work did not address that issue.

Resistivity of Calcium Compounds

Since the primary difference between an ash/sorbent mixture and the fly ash alone is the large amount of calcium in the mixture, an investigation of the resistivity of calcium-based compounds expected to be found in the mixtures was conducted to see if they were correlated with the resistivity of the mixtures. The resistivities of calcium hydroxide, calcium sulfite, calcium sulfate, and calcium carbonate are shown in Figure 23. The data were taken in an atmosphere containing 15% water vapor by volume. Calcium sulfite has the highest resistivity of the four compounds. The resistivity of calcium sulfate is about an order of magnitude lower for most of the temperature range. Magnitudes of the calcium hydroxide and carbonate curves are much lower than those of the sulfite or sulfate. Note that the peak resistivity values for the ash/sorbent mixtures ranged from 1×10^{12} to 1×10^{14} ohm-cm, so the data of Figure 23 seem to bracket the data for the mixtures.

Figure 24 compares the resistivity of the E-SOX sample with that of the two calcium compounds shown to be dominant in the sample. The shape of the E-SOX data is very much like that of the calcium hydroxide, but its magnitude is nearer that of the calcium sulfite. Similar data for four LIMB samples are shown in Figure 25. The resistivities of the two samples with limestone injection (101 and 119) are comparable to the calcium hydroxide resistivity; the resistivities of the two samples with hydrated lime injection show very good agreement with the calcium sulfate resistivity. The data in these two figures suggest that the E-SOX sample resistivity may be a combination of the resistivity of calcium hydroxide and sulfite, while the LIMB samples with hydrated lime injection have resistivities nearly identical to that of calcium sulfite. The resistivities of the other two LIMB samples are not as clear. They could be combinations of calcium carbonate, hydroxide, and sulfate.

The data in Figures 24 and 25 indicate the possibility that the resistivity of an ash/sorbent mixture is primarily determined by the resistivity of one or more calcium compounds in the mixture. This possibility was also indirectly indicated by other pieces of information from previous work: measurements made under Cooperative Agreement CR810284-01 indicated that the effective dielectric constant of high calcium content fly ash was independent of temperature, in contrast to results for more typical fly ash; inability of the Bickelhaupt computer model for fly ash resistivity to correctly predict the resistivity of ash/sorbent mixtures; and field data under this project which show the in-situ resistivity to be insensitive to the sorbent feed rate under many conditions. Therefore, an attempt was made to correlate the resistivity of an ash/sorbent sample with the resistivity of the sorbent compounds contained in the mixture.

SIMPLIFIED MODEL OF ASH/SORBENT MIXTURES

Scanning electron microscope photographs of ash/sorbent mixtures show that they consist of predominantly spherical particles and clusters of spheres. Although the precise dispersion of fly ash and sorbent particles throughout the mixture is not known, assume, for simplicity, that the layer consists of discrete particles of either fly ash or one of the sorbent compounds. In addition, assume that the resistivities of all fly ash particles are the same and those of all sorbent particles of a given compound are



Figure 23. Resistivities of calcium compounds expected to be present in ash/sorbent mixtures.



Figure 24. Comparison of the resistivities of an E-SOX sample, calcium hydroxide, and calcium sulfite.



Figure 25.

Comparison of the resistivities of 4 LIMB samples (17 and 18 with hydrated lime injection, 101 and 119 with limestone injection), calcium hydroxide, and calcium sulfate.

the same. Then a charge traversing the bulk of the sample through or along these resistive particles can be represented by an electrical circuit composed of resistors representing the fly ash and sorbent particles. Because the resistivities of the calcium compounds are so high (Figure 23) and no correlation between resistivity and chemical composition was found, the resistivity of the fly ash is expected to be negligible in comparison to that of the sorbent. Also, the results of multiple regression (discussed below) suggest that only two compounds are important for a given ash/sorbent mixture. Then by the usual method of adding resistors in series, we could write:

$$R = (n_1 R_1) + (n_2 R_2)$$
(5)

where R is the equivalent resistance of the entire circuit, and n_1 and n_2 are the number of calcium compounds of type 1 and type 2, respectively, in the path of the charge.

Although the sample will be highly inhomogeneous on the local level, we would expect that, on the average, a charge would encounter the same number of resistors of type 1 and the same number of resistors of type 2 during any complete traverse of the sample. Therefore, the relative number of each type of resistor would be the important parameters in determining the contribution of each species to R, and we could rewrite equation (5) as:

 $R' = (a_1R_1) + (a_2R_2)$ (6) where $R' = R/(n_1+n_2)$ $a_1 = n_1/(n_1+n_2)$ $a_2 = n_2/(n_1+n_2)$ $1 = a_1 + a_2$

Note that the resistance calculated from equation (6) will always be less than that of the larger resistor and greater than that of the smaller resistor. Moreover, if a_1 and a_2 are comparable and one resistance is much greater than the other, then the overall resistance will be essentially equal to this higher resistance. This is the type of relationship suggested by Figures 24 and 25.

Of course, the true nature of an ash/sorbent mixture will be much more complicated than that assumed here. But the development of equation (6) can be easily extended to the case where more than two calcium compounds contribute to the overall resistivity of the mixture. This simple picture is intended only as a starting point for trying to understand the resistivity of the ash/sorbent samples.

DETERMINING AMOUNTS OF CALCIUM COMPOUNDS IN MIXTURES

Determining the amounts of calcium sulfite, sulfate, hydroxide, and carbonate within an ash/sorbent mixture using available methods proved to be a difficult task. A serious handicap in this endeavor is the difficulty of physically separating the ash and sorbent fractions of a sample and thus avoiding the influence of the ash constituents on the calcium constituents to be determined in the sorbent fraction. The steps followed to achieve a reasonably satisfactory solution to the analytical problem are described in the following paragraphs.

The total calcium content of the sample was obtained by igniting the sample in air at 750°C, dissolving the residue in a combination of mineral acids, and then determining calcium by atomic absorption spectroscopy. The total amount of calcium thus found was assumed to represent the contribution of the sorbent alone. This was done in the absence of information of the amount of calcium in the ash component of the mixture. In a literal sense, the assumption that the ash made no contribution to the calcium content of the sample cannot be right; however, in a practical sense, the assumption is acceptable if the ash has a low calcium content or if the weight fraction of sorbent in the sample is high.

The sulfite, sulfate, and hydroxide constituents were determined by extracting a portion of the original, unignited sample with water and then following a set of analytical steps for the several anions associated with calcium. Sulfite was determined both by titration (with aqueous iodine) and by ion chromatography. Sulfate was determined by treating a portion of the sample extract with peroxide and then determining the total amount of sulfate then present by ion chromatography; the original quantity of sulfate was then calculated by subtracting from the total amount of sulfate the amount of sulfite determined previously (which was converted to sulfate by peroxide). Hydroxide was determined by titrating a portion of the extract with aqueous acid.

Any part of the calcium not associated with sulfite, sulfate, and hydroxide was assumed to be present as the carbonate. A possible error in this assumption, of course, is that calcium in the original fly ash was likely to be present as a silicate, rather than as the carbonate. Attributing all of the sulfate found to the sorbent is also a possible source of error since part of the sulfate may have occurred in the ash. In special circumstances, as mentioned later in this report, the amount of carbonate present was determined more directly by performing an elemental analysis of the sample and calculating the amount of carbonate that was equivalent to the amount of elemental carbon found.

MULTIPLE CORRELATION RESULTS

In accordance with the simplified model represented by equation (6), a search was made for correlations between the resistivity of the calcium compounds of Figure 23 and the various ash/sorbent mixtures using step-wise multiple regression. The regression coefficients (r^2) for this purely mathematical approach generally exceeded 0.97. For example, the resistivity of the E-SOX mixture could be expressed as the sum of the resistivities of calcium hydroxide and calcium sulfite according to the equation

$$\rho(\text{E-SOX}) = 1.80 \times 10^{12} + 24.62 \rho[\text{Ca}(0\text{H})_2] + 0.01 \rho(\text{CaSO}_3)$$
(7)

where ρ is the resistivity (in ohm-cm) and $r^2 = 0.98$. The comparison between the measured resistivity and that predicted by this equation is shown in Figure 26. Note that the constant term in the equation is an artifact of the regression process. Later modifications to the computer program which forced the additive constant to zero in the regression calculations showed that the correlation coefficient actually increased in general. For instance, the correlation of equation (7) becomes

$$\rho(E-SOX) = 26.56\rho[Ca(OH)_2]$$
(8)

with an r^2 of 0.99 when the additive term is set to zero.

It was unfortunate that the coefficients in equations (7) and (8) could not be directly related to the amounts of calcium hydroxide and calcium sulfite in the sample determined by the chemical analysis described above. The problem is almost certainly due to inaccuracies in the analytical procedure.

The correlation procedure gave somewhat better results when it was applied to two samples (referred to here as 821 and 901) that were derived by injection of a $Ca(OH)_2$ slurry into a gas stream containing SO_2 but not fly ash. The correlation equations for these two samples were

$$\rho(821) = 48.10\rho(CaCO_3) + 2.00\rho(CaSO_4)$$
(9)

and

 $\rho(901) = 11.35\rho(CaCO_3) + 0.51\rho(CaSO_4)$ (10)

with correlation coefficients (r2) of 0.97 and 0.99, respectively. Adjustment of these equations to the form of equation (6) produced the following:

$$\rho'(821) = 0.96\rho'(CaCO_3) + 0.04\rho'(CaSO_4)$$
(11)
$$\rho'(901) = 0.96\rho'(CaCO_3) + 0.04\rho'(CaSO_4)$$
(12)

The coefficients 0.96 and 0.04 in equations (11) and (12) are to be interpreted as the apparent weight fractions of $CaCO_3$ and $CaSO_4$, respectively, in both samples.

For comparison, the actual results of determinations of the four calcium compounds in these two samples are as follows:



Figure 26. Comparison of the measured resistivity of an E-SOX sample and that predicted from a combination of the resistivities of $Ca(OH)_2$ and $CaSO_3$ in an atmosphere containing 10% water vapor by volume.

	Weight pe	rcent in
Compound	Sample 821	Sample 901
Ca(OH) ₂	9.9	4.2
CaSO ₃	47	35
CaSO ₄	5.4	5.8
CaCO ₃	30	48

The above concentrations of $CaCO_3$ were calculated by difference, as already explained. Since such high concentrations of $CaCO_3$ in samples of this type seemed anomalous, $CaCO_3$ was redetermined on the basis of elemental carbon; essentially the same results were obtained — 30% for sample 821 and 42% for sample 901. If the calcium compounds are reported on the basis of just $CaCO_3$ and $CaSO_4$, the equivalent concentrations in sample 821 are as follows:

$$CaCO_3 = 100(30/[30 + 5.4]) = 85$$

 $CaSO_4 = 100(5.4/[30 + 5.4]) = 15$

Similarly, the values in sample 901 are $CaCO_3 = 89$ and $CaSO_4 = 11$. The comparison of the interpretations of sample compositions derived from the resistivity correlations and the experimental analyses gives the basis of an evaluation of the predictive model. This comparison is more favorable than that referred to earlier for samples of the E-SOX type but obviously is still not very satisfactory. Improved analytical information, it may be hoped, would provide a more satisfactory comparison in an absolute sense.

The fact that the method for determining the relative amounts of the four calcium compounds was relatively unsuccessful for those samples containing both ash and sorbent is not surprising. Interactions of the fly ash and sorbent materials would be expected to form a very complex mixture that would be difficult to analyze. In addition, the unavailability of the chemical composition of the fly ash made estimation of the amounts of calcium compounds within the mixtures very uncertain. However, the overall results of this work indicate that the approach of correlating the resistivity of these mixtures with the resistivities of the four calcium compounds will be successful, providing a more adequate analytical method for estimating the amount of these compounds within the mixture can be obtained.

Results of multiple correlation analysis of the resistivities of the three general classes of mixtures studied and the four sorbent compounds of interest can be summarized as follows:

- The resistivity of samples with sorbent injection in the downstream flue gas correlates directly with the resistivity of Ca(OH)₂, as indicated by equation (8).
- 2) The resistivities of the LIMB samples are a linear combination of the resistivities of $CaCO_3$ (largest coefficient) and $CaSO_4$. The data underlying this observation are not included in this report.

3) The resistivities of the samples derived from sorbent only are linear combinations of the resistivities of $CaCO_3$ and $CaSO_4$, as shown by equations (9) and (10). The fact that the larger of the two compositional coefficients is associated with $CaCO_3$ is anomalous, in that in samples of the type $CaCO_3$ is not usually an important constituent. The conclusions given here, therefore, may not apply to samples of more usual compositions that result from low temperature reactions of $Ca(OH)_2$ slurry with SO_2 , which consist mainly of $CaSO_3$ and $Ca(OH)_2$.

Although the results summarized above are true in general, it should be kept in mind that slight variations can be encountered with samples from individual sorbent injection processes. The relative importance of each of the four calcium compounds to the overall resistivity of the mixture will depend on the chemical interaction history of the sample.

CONCLUSIONS

Application of IEEE Standard 548-1984 (intended for measuring the resistivity of fly ash only) is not appropriate for use with fly ash/sorbent mixtures. This is due to decomposition of calcium hydroxide and large changes in the surface area of these samples which occur when they are heated above 300°C. In order to avoid the large changes in the sample caused by heating, the IEEE procedure should be modified to limit the upper temperature at which resistivity is measured to 250°C for these mixtures. And to obtain best repeatability of the resistivity measurements, the test should be conducted in the descending temperature mode. Measurements using this modified procedure produce consistent and repeatable values of resistivity for ash/sorbent mixtures.

Results of multiple regression analysis show that the resistivity of an ash/sorbent mixture is primarily determined by the resistivities of one or more calcium compounds within the sample. Indeed, the correlation coefficients (r^2) obtained for all samples generally exceeded 0.97. For a sample consisting of only sorbent exposed to SO_X , the agreement between the amounts of calcium compounds found within these samples by analysis and the amounts deduced from the resistivity coefficients is plausible if not quantitatively satisfying. For a sample containing both ash and sorbent, however, the agreement is unacceptable, presumably because of inadequate procedures for estimating the amounts of the calcium compounds in an ash/sorbent mixture.

If the obstacles to relating sample resistivity to both sample composition and resistivities of the individual calcium compounds could be overcome, the prediction of the resistivity of an ash/sorbent sample would likely proceed as follows: 1) the sample would be identified as to type based on origin (LIMB or E-SOX process, for example), 2) it would be analyzed for the different calcium compounds contained, and 3) the normalized concentration factors, as illustrated earlier in this report, would be used, along with resistivity values of the appropriate calcium compounds, in an equation that predicts resistivity for the given type of sample.

Efforts to improve the resistivity model are now continuing as part of the contract work for the Electric Power Research Institute under RP 1833-17.

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APPENDIX A.

QUALITY CONTROL EVALUATION REPORT

Quality Assurance Project Plan

The work described in this topical report was supported through Cooperative Agreement CR 812282. A Quality Assurance Project Plan (QAPP) was not originally required for this project. However, the measurement efforts for this work were performed in accordance with the QAPP for CR 811683, Task 1. This task concerned the development of a method for predicting the resistivity of an ash/sorbent mixture resulting from a dry, post furnace flue gas desulfurization process. The QAPP was submitted on June 1, 1985 and approved by EPA in January of 1986. All tasks of CR 811683 were designated as EPA QA Category III. Since CR 812282 involves measurement and sampling efforts with procedures identical to those addressed in the CR 811683 QAPP, it has been assumed that the same QA classification and QA procedures are applicable.

Management and Technical Systems Audits

On July 15, 1985, EPA conducted a Management Systems Audit (MSA) and a Technical Systems Audit (TSA) on project CR 811683. Based on the results of these audits, the program was rated as "Acceptable, with Qualifications". The major qualifications were that separate QAPPs be prepared for Tasks 3 and 4 and that Standard Operating Procedures (SOPs) be more thoroughly documented for certain measurement systems. SRI responded by upgrading existing SOPs, writing new SOPs, and by preparing and submitting separate QAPPs for Tasks 3 and 4. The resistivity, bulk chemical analysis, particle size distribution, and scanning electron microscopy measurements are covered under the approved QA plan for Task 1. Auxiliary measurements of specific surface area, particle density, and thermogravimetric analysis are covered under the separate QA plan for Task 4.

Evaluation of Measurement and Analytical Systems

All measurement and analytical systems were operated in accordance with the procedures given in the QAPP unless stated otherwise in the following paragraphs. The critical measurements which relate to this topical report are discussed below.

Resistivity. The electrical resistivity of ash/sorbent mixtures is the most important parameter addressed in this topical report. The different nature of these mixtures compared with the properties of fly ash alone required alterations of the standard laboratory measurement procedure (IEEE Standard 548-1984, descending temperature technique). This procedure was originally developed for fly ash from pulverized coal combustion. But by the middle of 1986, it had been determined that this method caused changes in the physical and chemical properties of ash/sorbent mixtures during the measurement, resulting in erratic and nonreproducible data. By the middle of 1987, it had been determined that consistent and reproducible data could be obtained by limiting the highest test temperature to 250°C instead of the value of 455°C which is normally used for fly ash. <u>Chemical Analysis</u>. The mineral content of an ash sample is normally determined after igniting it at 750°C. However, it was found that the physical and chemical nature of ash/sorbent mixtures was altered by exposing them to temperatures higher than 300°C. In particular, calcium hydroxide contained in the sample decomposed above 300°C. Then in order to determine the chemical composition and have it be representative of the sample, the standard chemical analysis was performed on an unignited sample.

In addition to the standard chemical analysis normally run on fly ash, auxiliary tests were performed to determine the amounts of calcium sulfate, calcium sulfite, calcium hydroxide, and calcium carbonate in the mixture. These four compounds occur in varying amounts in ash/sorbent mixtures and largely determine the resistivity of the sample. Free and hydrated water was determined from the weight loss of the sample at 110 and 300°C, respectively. The carbon and hydrogen in the sample were determined with an elemental analyzer in which a weighed quantity of sample is burned in an oxygen-rich system and the products of combustion are fixed in an absorption train after complete oxidation and purification for interfering substances (standard CHN measurement). SO_3 was determined by both titration and ion chromatography. The sulfate content was determined by measuring the soluble SO_4 (which determines both SO_3 and SO_4 as SO_4) and taking the value of SO_3 determined by titration, converting it to its equivalent SO_4 value, and subtracting it from the soluble SO_4 value.

The amount of $Ca(OH)_2$ in the mixture was determined directly from titration. However, in order to estimate the remaining calcium compounds of the sample and the fly ash to sorbent ratio, several assumptions were made: (a) the sulfur and calcium concentration of the fly ash is insignificant compared to the total sulfur and calcium present in the samples, (b) SO_3^{-2} , SO_4^{-2} , and OH^{-1} are all associated with calcium and any excess calcium is in the form of $CaCO_3$, and (c) the sorbent material was relatively pure so that the fly ash concentration can be approximated by a summation of those oxides other than calcium, magnesium, and sulfur. These assumptions were necessary because samples of the corresponding fly ashes were unavailable.

Sample Custody and Tracking

Sample custody and tracking requirements were met as specified in the QAPP. All samples were assigned unique SRI notebook numbers referring to the page and section in which they were described in the laboratory notebook. Sample containers were marked with the corresponding numbers and other appropriate identifying information.

Internal Audits, OC Checks, and Corrective Measures

An internal audit was performed by the SRI QA manager on CR 811683. The audit revealed no serious deficiencies in the internal QC checks and data reduction. However, recommendations were made to standardize the use of laboratory notebooks for recording data during field measurement activities. This replaced the use of loose-leaf binders and loose forms. In cases where the forms were desirable, they were attached in the notebook. This facilitated access to the data for subsequent QC checks.

Limitations of Use of Data

The most significant limitation on the use of these data is that they should not be applied outside the range of conditions studied. The unique electrical characteristics of ash/sorbent mixtures indicate resistivity data require careful interpretation. In particular, the resistivity characteristics obtained in this work should not be compared with that of samples of significantly different origin or with data obtained when the ash/sorbent sample was exposed to temperatures in excess of 250°C.

The Quality Assurance Review evaluation requires this Statement: "QA/QC requirements apply to this project. Data are NOT supported by QA/QC documentation."

It is not deemed feasible to incorporate the evaluation comments into the report.