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Use of Solid Waste for Chemical Stabilization: Adsorption Isotherms and ^{13}C Solid-State NMR Study of Hazardous Organic Compounds Sorbed on Coal Fly Ash

Topical Report

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SUMMARY

This report describes the adsorption properties of hazardous organic compounds on the Dave Johnston coal fly ash using adsorption isotherm and carbon-13 solid-state Nuclear Magnetic Resonance techniques. In addition, the Dave Johnston and Laramie River power plants coal fly ashes were characterized extensively in an effort to correlate the chemical and structural properties of coal fly ashes with their adsorption capacities for hazardous organic compounds. The report covers the research effort for Task 3.4.1, Use of Solid Waste for Chemical Stabilization, of the 1990-1991 and 1991-1992 Annual Project Plans under Cooperative Agreement DE-FC21-86MC11076.

The two fly ashes were characterized using elemental, X-ray, and solid-state silicon-29 NMR techniques and were found to differ significantly in their chemical and structural composition. The major differences by NMR in the two anhydrous coal fly ash materials are the concentration of the SiO_4^{-4} anions and the concentration of SiO_2. The Dave Johnston fly ash has a much higher concentration of quartz (SiO_2) than the Laramie River fly ash, whereas the Laramie River fly ash has a much higher concentration of monomeric silicate anions.

Solid-gas equilibrium adsorption isotherm studies of hydroaromatics and chlorobenzenes adsorbed on Dave Johnston coal fly ash indicate that the adsorption capacity of the coal fly ash is much less than the adsorption capacity of activated carbon by a factor greater than 3000. The comparison of the adsorption capacities for coal fly ash with activated carbon is based upon a solid-gas equilibrium and a solid-liquid equilibrium, respectively. Verification of these results is needed to confirm that the solid-gas adsorption isotherms can indeed be compared directly with solid-liquid equilibrium isotherms.

The solid-liquid equilibrium adsorption isotherms of pyridine, pentachlorophenol, naphthalene, and 1,1,2,2-tetrachloroethane on the Dave Johnston fly ash were determined and compared to the same compounds sorbed on activated carbon. The Dave Johnston fly ash appears to adsorb these organic compounds nearly as well as activated carbon. Thus, the Dave Johnston coal fly ash can be a good adsorbent for some types of compounds. Similar adsorption data are needed for the Laramie River coal fly ash which is known to have significantly different chemical properties.

Carbon-13 solid-state NMR was used to investigate directly the adsorption of hazardous organic compounds on coal fly ash. Spectra of pure compounds and of compounds mixed with fly ash were obtained using both single-pulse and cross-polarization techniques. To obtain the NMR spectra of hydroaromatic and polychlorophenol in the solid state requires that the nuclear spin relaxation times be known. In most cases the relaxation times were very long resulting in long experimental time to obtain a spectrum.

Using a jumbo probe, low concentrations of some hazardous organic compounds could be detected and, in one specific case of pentachlorophenol adsorbed onto fly ash, a change in the chemical shift of the phenolic carbon was noted. This change in chemical shift is assumed to be due to a strong interaction of pentachlorophenol and the active site on the coal fly ash.

The use of solid-state NMR to study directly the bonding interactions between the hazardous organic compounds and coal fly ashes needs additional study since nothing is known of the strength of these interactions.

INTRODUCTION

Fly ash is a by-product from the combustion of coal. The 1985 annual U.S. production was estimated to be about 1 x 10^8 metric tons. The utilization for fly ash during the 1980s remained stable at about 25% per year. Because of its pozzolanic properties, nearly 50% of the utilized fly ash is for cement and concrete products. The vast quantity of fly ash is not being used and its availability throughout the country and worldwide has initiated research for new uses for commercial and industrial applications.

Three areas of applicability for fly ash are: (1) as a stabilizing agent for soils, (2) as an additive to cements and concrete, and (3) as an adsorbent for organic pollutants. Because of its pozzolanic properties, the utilization of fly ash as a soil stabilizing agent would increase the strength and durability of pavement subgrade and dirt roads, and stabilize soil embankments. As an additive to cements, the coal fly ash could lower the cost and may increase the strength of the cement. The cementing potential appears to be related to the formation of various hydrated silicates and aluminates. However, the actual cementing mechanisms have yet to be identified. The inability to predict adequately the performance of ash-enhanced cement and concrete remains an impediment to its greater use.

Little is known of the organic adsorbent properties of fly ash. However, if known and favorable, the potential commercial application of the adsorptive characteristics of fly ash could include its use as an adsorbent sandwich for organics in combination with landfill or other dump site liners, in traps for organics in waste waters, in filters for organics in process air streams, and as a stabilizer for organic wastes in drums. Variables that may affect the adsorbability of the fly ash towards organics in water include temperature; solution pH; interactions between solute molecules and fly ash, and between solvent molecules and fly ash. Thus, there is an essential need to characterize each coal fly ash type to enable potential correlation between coal fly ash structural properties and the nature of the adsorption characteristics of coal fly ash for organic hazardous waste compounds.

The composition and properties of pulverized fly ash depend on the type of coal burned and the combustion process. Thus, fly ashes from different origins may have significantly different effects on the properties of concrete, the durability of pavement subgrade, the stability of soil embankment, and sorption of organic compounds of environmental interest. Eastern and western coal fly ashes differ significantly in their physical and chemical properties. Eastern coal fly ash alone has little or no cementitious value in the presence of water. Western coal fly ash, on the other hand, will become cementitious in the presence of moisture. The major minerals found in coal fly ash are α-quartz (SiO_2), mullite ($3Al_2O_3 \cdot 2SiO_2$), hematite (Fe_2O_3), magnetite (Fe_3O_4), lime (CaO), and gypsum ($CaSO_4 \cdot 2H_2O$) White and Case 1990). Very few techniques exist which can quantitatively differentiate the mineral composition, and the pozzolanic and adsorption properties of fly ashes. Little is known of the siliceous and aluminous material coordination state distribution in coal fly ashes. Most siliceous and aluminous materials in fly ash are amorphous and, thus are not detected and quantified by X-ray techniques. X-ray diffraction has been used to characterize crystalline minerals, but cannot be used to study minerals that are amorphous. Even with crystalline minerals, difficulties are encountered in ascertaining the general characteristics for fly ash material using X-ray diffraction (White and Case 1990).

Very few (if any) methods exist to differentiate between fly ashes with regard to concrete properties, as soil stabilizers, and as adsorbers of organic hazardous waste materials. It is possible, however, to chemically characterize solid materials by nuclear magnetic resonance (NMR) techniques. Solid-state NMR techniques are complementary to X-ray diffraction techniques, and, in addition, are ideally suited for both amorphous and crystalline materials.

The NMR techniques include multinuclear (^1H, ^{13}C, ^{27}Al, and ^{29}Si) single-pulse excitation with magic-angle spinning and cross-polarization with magic-angle spinning (SPE/MAS and CP/MAS, respectively), and hydrogen spin-lattice relaxation spectroscopy. These techniques have been used to study coal pyrolysis residue and coal minerals under combustion-related conditions. However, the NMR techniques have not been extensively applied to the study of coal fly ash.

Using newly developed analytical state-of-the-art NMR techniques, a means of characterizing the coal fly ash based upon its properties under a variety of physical and chemical conditions can be realized. It should be possible to screen coal fly ash based upon its molecular structure for its potential use. Also, newly developed characterization methods will allow direct correlation of coal fly ash chemical and structural data with

(1) the engineering performance data when coal fly ash is used in concrete and cements, (2) the road conditions when it is used as a soil stabilizer, and (3) the adsorption of organic waste materials.

The economic value of being able to fully characterize coal fly ash in terms of its chemical structure and performance as it relates to different applications such as enhancing concrete strength, road soil stabilization, and as an organic waste adsorbent cannot be overestimated. Not only will this waste by-product from coal combustion be more fully utilized in these and other applications, but it will eliminate the need for storing or disposing of many millions of tons of this material produced annually worldwide.

There is a considerable amount of information in the literature concerning adsorption of organic compounds on activated charcoal (Faust and Aly 1987), zeolites (Meiler and Wutscherk 1989; Deininger 1981), silicates (Parfitt and Rochester 1983), alumina (Dawson et al. 1982), and clays (Essington et al. 1992). Even though solid waste materials that arise from combustion processes, such as coal fly ash and spent oil shale, are composed principally of alkaline-earth and alkali metal oxides, silicates, and aluminosilicates (Essington and Spackman 1988; Rai et al. 1987; and Netzel 1992), relatively few studies have been conducted using spent oil shale and coal fly ash as adsorbents. In a review on fossil fuel combustion wastes, Rai et al. (1987) suggest that combustion wastes may have a high affinity for sorbing various types of organic compounds.

The potential for spent oil shale to reduce the inorganic and organic chemical concentrations in retort waters has also been suggested by Fox et al. (1980), George and Jackson (1985), and Boardman et al. (1985). Boardman et al. (1985) examined the adsorption of 2-hydroxynaphthalene, 1,2,3,4-tetrahydroquinoline, and 2,3,5-triethylphenol by several spent oil shale samples from the Green River Formation. The reduction in organic compound solution concentrations ranged from 21% to greater than 96%, depending on the organic compound type. Essington and Hart (1990) studied the adsorption of pyridine by combusted oil shales. They found that pyridine adsorption can be classified as L-type and that the adsorption isotherms followed both the Langmuir and Freundlich equations. However, it was concluded that the reduction in solution of the pyridine concentration does not sufficiently justify using spent oil shale as a stabilizing medium for hazardous organic compounds.

Sorini and Lane (1991) studied organic and inorganic hazardous waste stabilization using combusted oil shale. The five wastes selected were a separator sludge, creosote-contaminated soil, mixed metal oxide-hydroxide waste, metal-plating sludge, and smelter dust. They concluded that (1) the spent shales apparently stabilized the smelter dust and mixed metal oxide-hydroxide waste by reducing the mobility of cadmium, (2) the mixture of smelter dust with spent oil shale caused the waste to become alkaline which significantly reduced the mobility of cadmium, (3) the opposite behavior was detected for chromium in the mixtures involving the metal-plating sludge, and (4) the analysis of the leachates of the mixtures involving the separator sludge showed that the spent oil shales did not stabilize the sludge. Little information could be obtained from mixtures of creosote-contaminated soil with spent shale samples because of poor homogeneity. They further concluded that "real-world" organic wastes are too complex for initial evaluation of the ability of spent oil shale to stabilize organic compounds and that initial stabilization evaluations involving organic compounds should involve testing synthetic wastes containing a single class of organic compounds.

Little work is known of the use of coal fly ash to adsorb or stabilize organic waste materials. Recently, Lane (1992, unpublished data) has performed adsorption studies which show the affinity of certain coal fly ash samples for organic compounds. Sharma et al. (1989) discussed in detail the use of coal fly ash as a soil amendment. Their review dealt with adsorption and leaching of inorganic trace elements and the effects of fly ash on soil microorganisms, plant growth, and surface and groundwater. Because so little is known about the organic stabilization properties of coal fly ash, it is the purpose of this study to define the adsorption characteristics for coal fly ash and that the adsorption parameters for organic compounds be correlated with the coal fly ash chemical structural composition.

Adsorption Isotherms

Adsorption isotherms represent the equilibrium distribution of an adsorbate in solution and that adsorbed on a surface versus the concentration of adsorbate in solution. Experimentally determined adsorption isotherms are used to describe the adsorption capacity and, thus, the usefulness of an adsorbate. The shape of the adsorption isotherm gives information about the adsorption process and the extent of the surface coverage by the adsorbate.

Adsorption isotherms have been measured for many types of organic compounds using activated carbon as the adsorbent (Faust and Aly 1987 and literature cited therein). Bernardin (1985) reported that activated carbon made from lignite, wood, or coal having high ash contents have adsorptive capacities equal to or greater than those materials of lower ash contents. The mineral ash consists mainly of silica and insoluble silicates of aluminum, iron, magnesium, and calcium. These components are similar to those found in coal fly ash.

Adsorption isotherms were determined for pyridine on several types of spent oil shales (Essington and Hart 1990). They found that pyridine was poorly adsorbed. The dominant minerals in the Green River Formation oil shale are quartz, ankerite, calcite, dawsonite, and feldspars. The silicate and aluminosilicate minerals in spent oil shale are less than that found in coal fly ash and may be the reason for the low adsorption capacity of spent oil shale for pyridine.

For coal fly ash which contains numerous minerals, the effects of these minerals on the sorption of organic waste materials are not adequately known or understood. No adsorption isotherms of organic compounds on coal fly ash have been reported in the literature.

Solid-State NMR Study of Adsorbed Hazardous Organic Compounds

NMR techniques have been used extensively to characterize the adsorption of organic molecules onto various types of surfaces. The application of these techniques involves measuring the changes in nuclear relaxation times and chemical shift values when a molecule is adsorbed onto a surface. NMR has been used to follow changes in the nuclear properties of either the adsorbent or adsorbate. Changes in the NMR parameters for hydrogen, carbon, and nitrogen are most often measured for adsorbates, and changes in the silicon and aluminum NMR parameters are measured for adsorbents.

Derouane (1969) used ^{1}H NMR to study the adsorption of benzene, ethanol, ethylene glycol, and 2,2-dimethylbutane on alumina. Borovkov and Kazansky (1974) investigated methanol, ethanol, and propan-2-ol adsorbed on silica gels, aerosil, alumina, and aluminosilicates. The specific adsorption of these alcohols in the case of alumina was attributed to the interaction with Lewis acid sites. In several papers, studies of the ^{13}C NMR spectra of acetone adsorbed on silica gel have been reported (Gay 1974; Bernstein et al. 1981; Borovkov et al. 1982). Significant shifts to lower magnetic fields with respect to liquid acetone were observed for the C=O group of acetone molecules adsorbed on silica gel surfaces. Bernstein et al. (1982) using both ^{13}C and ^{15}N NMR studied the interaction of pyridine molecules with OH groups on a partially dehydroxylated silica gel surface. The bonds formed between the proton of the hydroxyl group and the lone-pair electrons of the nitrogen atom caused a strong ^{15}N NMR chemical shift to a higher field. Only small changes were observed for the ^{13}C NMR chemical shifts, indicating that no significant interaction occurs between the π-electrons of pyridine and the surface sites.

Few, if any, applications of NMR techniques to the study of the adsorption of hazardous organic compounds on silicates, aliminosilicates, and alumina have been reported, and even fewer techniques on coal fly ash have been reported.

The objectives of this study were threefold: (1) to characterize the silicate and aluminosilicates in anhydrous coal fly ashes by elemental analyses, X-ray mineral analysis, and solid-state silicon-29 (^{29}Si) NMR techniques, (2) to study the adsorption properties for selected organic compound types by determining the Freundlich adsorption isotherms, and (3) to study the sorption characteristics of fly ashes for organic compounds of environmental interest using solid-state carbon-13 (^{13}C) NMR techniques.

EXPERIMENTAL

Materials

The Dave Johnston coal fly ash was produced at the Dave Johnston Power Plant located near Glenrock, Wyoming, using a conventional pulverized coal process. The feed coal was mined near the plant which is in the Powder River Basin. The Laramie River coal fly ash was produced at the Laramie River Power Plant located near Wheatland, Wyoming, using a conventional fired unit containing a calcium-based sorbent for sulfur dioxide removal. The feed coal was also mined in the Powder River Basin of Wyoming.

The compounds, benzene, toluene, chlorobenzene, ethylbenzene, 1,2-Dichlorobenzene, 1,3-Dichlorobenzene, and 1,4-Dichlorobenzene, were purchased as a single solution containing 200 μL each in CH_3OH (Supelco Purgeable Aromatics Mixture 602-M). Pyridine, naphthalene, and tetrachloroethane were purchased as certified neat compounds from chemical manufacturers. Pentachlorophenol was purchased as a certified stock solution in methanol. Technical and analytical grades of pentachlorophenol were purchased from J.T. Baker Chemical Co.

Adsorption Isotherm Procedure

Solid-Gas Equilibrium

Headspace samples were taken using a Hewlett Packard Model 19395A Headspace Sampler. Samples were weighed into 20 mL headspace vials which were sealed, then placed in a sample tray held at 60°C (140°F). For the injection process, sample vials were pressurized for 10 s and a 1.0 mL sample was withdrawn and transferred by Helium carrier gas at 15 mL/min to a Hewlett Packard Model 5890 Gas Chromatograph (GC). The GC separation was performed on a DB-624 capillary column, 0.53 mm x 30 m, 3.0 μm film thickness. The following oven temperature program was used: initial temperature, 50°C (122°F); initial time, 1.0 min; temperature program rate, 4°C/min (7.2°F/min); final temperature 100°C (212°F); final time, 1.5 min. The injection port used was a packed injection port, fitted with a liner to accommodate the GC column, held at 150°C (302°F). Detection was accomplished by a photo ionization detector (HNU Model PI-52 operated at 150°C (302°F) with a 10.2 eV lamp).

Samples were prepared by weighing varying amounts of fly ash (0.1 g - 10 g) directly into the headspace vial. Varying amounts of the standard mixture containing methanol as the solvent (1.0 μL - 50 μL) were pipetted directly to the fly ash and the vials were immediately sealed.

Five standards were also prepared by pipetting varying amounts (1.0 μL - 50 μL) of the standard solution into the headspace vials, and immediately sealing them. Both samples and standards were placed in a box that was rotated end over end at ambient temperature for 72 hours. The vials were withdrawn and placed in the autosampler for 2 hours before the injection procedure was begun. Sample concentrations in 1 mL of headspace injected into the GC were determined by an external standards calculation based on the responses of the five-point initial calibration.

Solid-Liquid Equilibrium

Pyridine is the only one of the four compounds evaluated that is miscible with water, the other three exhibit minimal solubility in water. The preparation of aqueous solutions of these three compounds required the addition of methanol as a co-solvent. Methanol was limited to 1% of the total volume of the solution.

To determine the concentration ranges that were used, individual standard solutions were prepared and analyzed. UV spectra for each compound were obtained using a wavelength scan from 190 to 450 nm (Shimadzu Model UV-265 Spectrophotometer). For each compound, the wavelength of maximum adsorbance was chosen as the quantitation wavelength, and an appropriate concentration range to be studied was determined:

	λ, nm	[lower], μg/mL	[upper], μg/mL
Pyridine	255	0.250	100
Pentachlorophenol	302	1.00	400
Naphthalene	275	0.250	100
Tetrachloroethane	202	5.00	2000

Ten concentrations bracketed by the lower and upper concentrations, and one blank, were studied for each compound. For each compound, two sets of solutions were prepared.

The first set of solutions was designated the standard or control solutions consisting of the aqueous solutions of the organic compound. The second set of solutions was designated the sample solutions consisting of the aqueous solutions in contact with the fly ash.

Standard solutions were prepared in 50 mL screw-cap vials. Pyridine standards were prepared directly in water, at a final volume of 20.0 mL. The other organics were also prepared at a final volume of 20.0 mL, using 200 μL of standard prepared in methanol added to 19.8 mL of water. Sample solutions were prepared as above, and 4.0 g of fly ash was added to each solution.

Standard and sample vials were capped and rotated end over end on a mechanical rotator for 24 hours to assure complete mixing. The vials were then allowed to sit undisturbed for 4 hours so that the fly ash could settle to the bottom. The supernatant solution was withdrawn by pipette for analysis. The spectrophotometer was calibrated using the blank solution and ten standard solutions. Each compound exhibited linear response through these eleven points, so an average response factor was calculated and used for determining analyte concentration in the samples.

NMR Instrumentation and Conditions

^{13}C and ^{29}Si solid-state NMR measurements were made using a Chemagnetics CMX 100/200 solids NMR spectrometer. ^{13}C spectra were obtained at a ^{13}C frequency of 25 MHz using the techniques of single-pulse excitation with magic-angle spinning (SPE/MAS) and cross-polarization with magic-angle spinning (CP/MAS) and high-power ^{1}H decoupling. A 12.5-mm-diameter zirconia bullet spinner was used. Spinning rates were between 3.5 and 3.6 kHz. The ^{13}C spectra were externally referenced to liquid tetramethylsilane (TMS) based on the solid-state spectrum of hexamethylbenzene (HMB) as the secondary reference and assigning 17.21 ppm to the shift of the aliphatic carbons of HMB relative to liquid TMS (Hayashi and Hayamizu 1989).

^{29}Si SPE/MAS and CP/MAS NMR spectra with ^{1}H decoupling were obtained at a ^{29}Si frequency of 39.6 MHz. A 7.5-mm-diameter zirconia bullet spinner was used. Spinning rates were between 3.5 and 3.8 kHz. A 90° pulse width of 4.0 μs was used for all experiments. The pulse delays were 5 and 10 s and the number of acquisitions varied from 700 to 16,000. For the CP/MAS technique, the contact time was 3 ms. All ^{29}Si spectra were externally referenced to liquid TMS based on the solid-state spectrum of sodium 3-(trimethylsilyl)-propane-1-sulfonate (DSS) as the secondary reference and assigning 1.46 ppm to the shift of the silicon of DSS relative to liquid TMS (Hayashi and Hayamizu 1991).

RESULTS AND DISCUSSION

Coal Fly Ash Characterization

Elemental, Mineral, and Oxide Composition of Coal Fly Ash

To fully utilize coal fly ash as a component in cement, as a stabilizer for soil, and as an adsorber for organic waste materials, the chemical structural components of coal fly ash must be known.

The elemental and mineral composition of coal fly ash depends upon the parent coal and the operating conditions of the power plant. Nearly all existing naturally-occurring elements can be found in coal depending on the sensitivity of the method of analysis. Table 1 lists the concentration of some of the more abundant elements found in the coal fly ash from the Dave Johnston and Laramie River power plants and Table 2 lists the mineral composition from X-ray analysis. Of interest to this NMR study are the concentrations of the elements, carbon, calcium, silicon, aluminum, and iron. Carbon, silicon, and aluminum are more abundant in the coal fly ash from the Dave Johnston power plant than the Laramie River power plant coal fly ash (Table 1). However, the Laramie River coal fly ash contains more calcium and iron than the Dave Johnston coal fly ash. Hydrogen was not found in either of the coal fly ash samples indicating that the coal fly ash samples contained very little water and/or organic hydrogens. Table 3 lists the oxide composition of the two coal fly ashes.

^{29}Si NMR Investigation of Coal Fly Ashes

The ease by which the solid-state ^{29}Si and ^{27}Al NMR spectra can be obtained make this technique ideally suited for studying many types of silicate and aluminosilicate minerals (Englehardt and Michel 1987).

The use of ^{29}Si and/or ^{27}Al NMR to study of coal fly ash has not been reported. However, several papers discuss the use of ^{29}Si and ^{27}Al to study similar materials (Pradip et al. 1987; Parry-Jones et al. 1988; Groves and Rodgers 1989; Young 1988; Wilson et al. 1986; and Barnes et al. 1986).

Table 1. Elemental Composition of Coal Fly Ash[a]

	Coal Fly Ash Source	
Elements	Dave Johnston Power Plant	Laramie River Power Plant
Aluminum	12.3%	8.89%
Antimony	<19.6	<19.1
Barium	0.166%	0.606%
Beryllium	<0.198	<0.195
Bismuth	<194	<200
Boron	404	732
Cadmium	<1.96	<1.91
Calcium	12.4%	19.7%
Carbon	1.3%	0.3%
Chromium	98.3	53.0
Cobalt	24.9	34.6
Copper	128	175
Iron	2.51%	3.29%
Lead[b]	103	151
Lithium	35.7	28.9
Magnesium	1.97%	3.65%
Manganese[b]	288	373
Mercury	0.755	0.282
Molybdenum[b]	6.04	3.23
Nickel	42.2	48.8
Phosphorous	0.155%	0.282%
Potassium	<0.849%	<0.955%
Selenium	10.3	23.3
Silicon	23.3%	14.6%
Silver	1.75	2.04
Sodium	0.134%	0.778%
Strontium	0.123%	0.387%
Sulfur	0.3%	0.9%
Thorium[b]	25.9	33.3
Vanadium	222	163
Zinc	123	91.6

[a] All values in mg/kg unless noted: Unpublished WRI report to DOE

[b] These elements showed poor NBS SRM recoveries: Lead 65%, Manganese 64%, Molybdenum 67%, and Thorium 127%.

Table 2. Mineral and Chemical Composition of Coal Fly Ashes[a]

		Coal Fly Ash Source	
Mineral	Chemical Composition	Laramie River Power Plant	Dave Johnston Power Plant
Quartz	SiO_2	X	X
Periclase	MgO	X	X
Anhydrite	$CaSO_4$	X	
Merwinite	$Ca_3Mg(SiO_4)_2$	X	
Ferrite Spinel	$(Mg,Fe)(Fe,Al)_2O_4$	X	
Lime	CaO	X	X
Melilite	$(Ca,Na)_2(Mg,Al,Fe)(Si,Al)_2O_7$	X	
Brownmillerite	$Ca_4Al_2Fe_2O_{10}$	X	
Mullite	$Al_6Si_2O_{13}$	X	X
Hematite	Fe_2O_3	X	X
Sodalite	$Ca_2(Ca,Na)_6(Al,Si)_{12}O_{24}$	X	
	Ca_3SiO_5		
	Ca_2SiO_4		
	$Ca_3Al_2O_6$		

[a] Brown 1991

Table 3. Oxide Composition of Coal Fly Ash

	Coal Fly Ash Source[a]	
Oxide	Dave Johnston Power Plant, wt %	Laramie River Power Plant, wt %
CaO	13.6	23.7
SiO_2	38.8	26.8
Al_2O_3	36.3	28.9
MgO	2.6	5.2
Fe_2O_3	5.6	8.1
Na_2O	0.2	1.2
SrO	0.1	0.4
P_2O_5	0.6	1.1
SO_3	0.6	1.9
K_2O	1.6	2.0
BaO	0.2	0.6

[a] Calculated from elemental data in Table 1 and normalized to 100%

Notation and ^{29}Si NMR Chemical Shift Ranges for Silicates and Aluminosilicates. The Q^n and Q^n(mAl) notations are used to represent the anion structural units of silicates and aluminosilicates in both solution and solid states (Englehardt and Michel 1987). In this notation, Q represents the silicon atom bonded tetrahedrally to four oxygen atoms and the superscript, n, refers to the number of other SiO_4^{-4} attached to the SiO_4 tetrahedron being investigated. In the case of aluminosilicates, m represents the number of aluminum atoms bonded via the oxygen bridge to the silicon atom of the SiO_4 group under study.

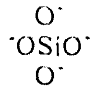
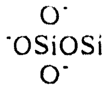
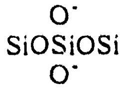
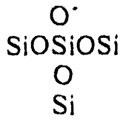
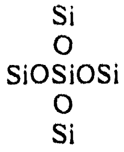
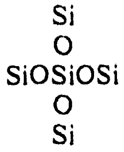
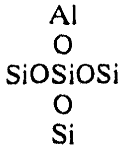
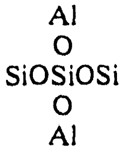
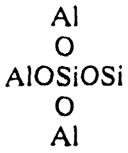
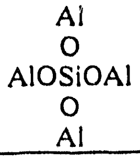
Schematic representations and some examples of the Q^n and Q^n(mAl) notation for silicates and aluminosilicates are shown in Table 4. Figure 1 gives the estimated ^{29}Si NMR chemical shift ranges for the various polymerized silicates and aluminosilicates.

Anhydrous Fly Ash. The ^{29}Si NMR spectra of the anhydrous coal fly ashes from the Dave Johnston and Laramie River power plants are shown in Figures 2a and 2b, respectively. The spectra are shown for the total sweep width of the experiment (300 to -450 ppm). The resonance between 0 and -150 ppm is the ^{29}Si signal. The other broad resonances (150, 30, -195, and -300 ppm) are due to spinning side bands of the center band. These side bands are the result of magnetic susceptibility broadening due to the high iron content (Oldfield et al. 1983).

The spinning side band intensities relative to the center band intensity are greater for the Laramie River coal fly ash than for the Dave Johnston coal fly ash. This is because of the higher Fe to Si ratio (0.226 versus 0.107) for the Laramie River fly ash. The high silicon content of the Dave Johnston coal fly ash (23.3 wt %) relative to the Laramie River (14.6 wt %) coal fly ash is reflected in the signal-to-noise ratio for both spectra. Six thousand scans were used to obtain the ^{29}Si spectrum of the Dave Johnston coal fly ash compared to twelve thousand scans for the ^{29}Si spectrum of the Laramie River coal fly ash.

Aside from the spinning side band intensities and the noise ratios, there are other noticeable differences in the ^{29}Si NMR spectra of the two coal fly ashes as a result of their mineral composition (Figures 2a and 2b; Table 2). Because of their complex mineral composition and high iron content, the ^{29}Si NMR spectra of the coal fly ashes are a broad envelope of resonances due to chemical shift dispersion and paramagnetic broadening. Therefore, it is not possible to assign any one resonance to a given mineral except for resonances that appear at either edge of the chemical shift range.

Table 4. Coordination State Notation and Structure of Silicates and Aluminosilicates

Notation	Structure	Name
Q^0	 $\begin{array}{c} O^- \\ {}^-OSiO^- \\ O^- \end{array}$	Monomer (Nesosilicates)
Q^1	 $\begin{array}{c} O^- \\ {}^-OSiOSi \\ O^- \end{array}$	End Group (Sorosilicates)
Q^2	 $\begin{array}{c} O^- \\ SiOSiOSi \\ O^- \end{array}$	Middle Group (Enosilicates)
Q^3	 $\begin{array}{c} O^- \\ SiOSiOSi \\ O \\ Si \end{array}$	Branching Group (Phyllosilicates)
Q^4	 $\begin{array}{c} Si \\ O \\ SiOSiOSi \\ O \\ Si \end{array}$	Cross-linking Group (Tectosilicates)
Q^4 (0Al)	 $\begin{array}{c} Si \\ O \\ SiOSiOSi \\ O \\ Si \end{array}$	
Q^4 (1Al)	 $\begin{array}{c} Al \\ O \\ SiOSiOSi \\ O \\ Si \end{array}$	
Q^4 (2Al)	 $\begin{array}{c} Al \\ O \\ SiOSiOSi \\ O \\ Al \end{array}$	
Q^4 (3Al)	 $\begin{array}{c} Al \\ O \\ AlOSiOSi \\ O \\ Al \end{array}$	
Q^4 (4Al)	 $\begin{array}{c} Al \\ O \\ AlOSiOAl \\ O \\ Al \end{array}$	

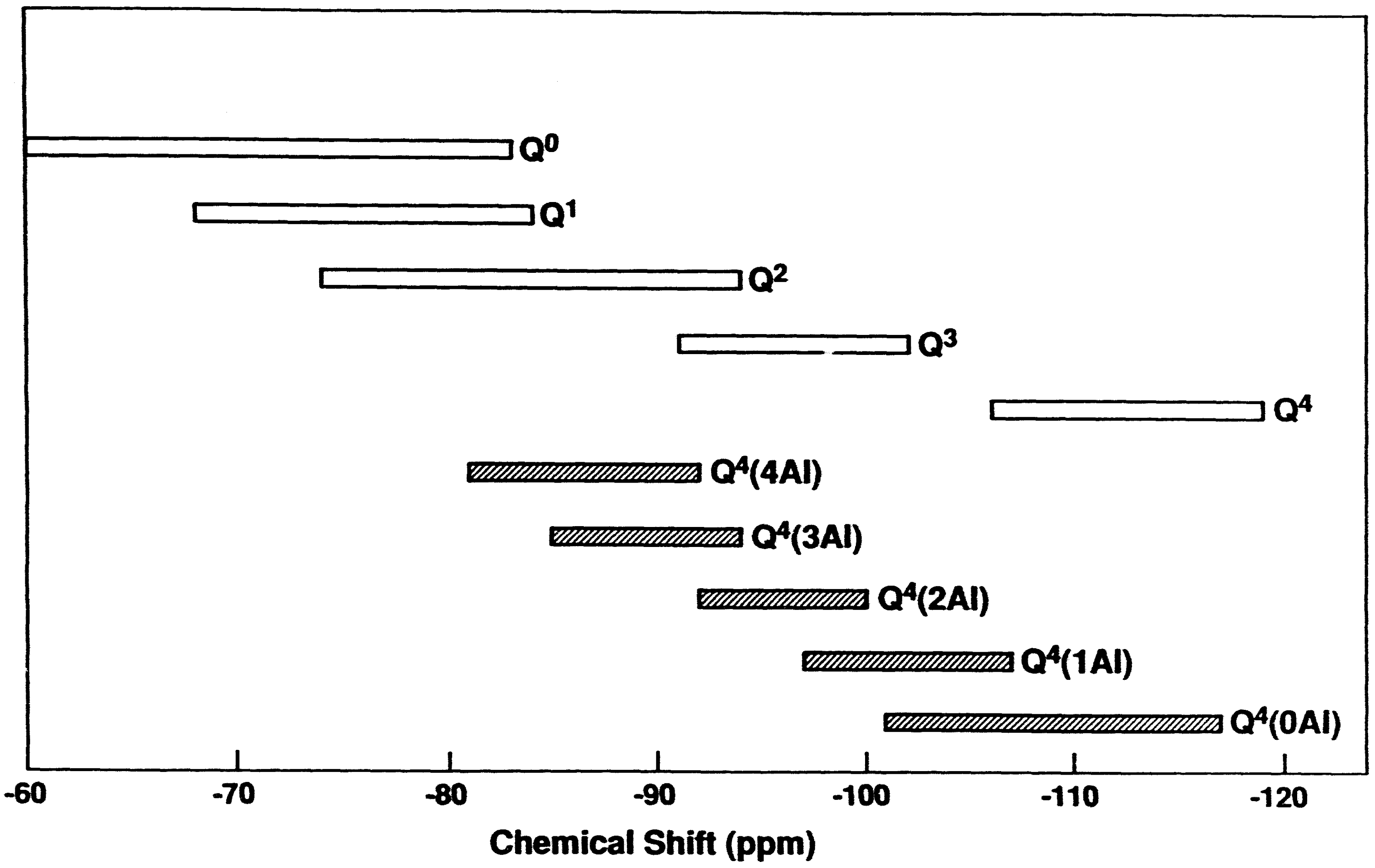


Figure 1. Approximate ^{29}Si Chemical Shift Ranges for Various Coordination States of Silicates and Aluminosilicates

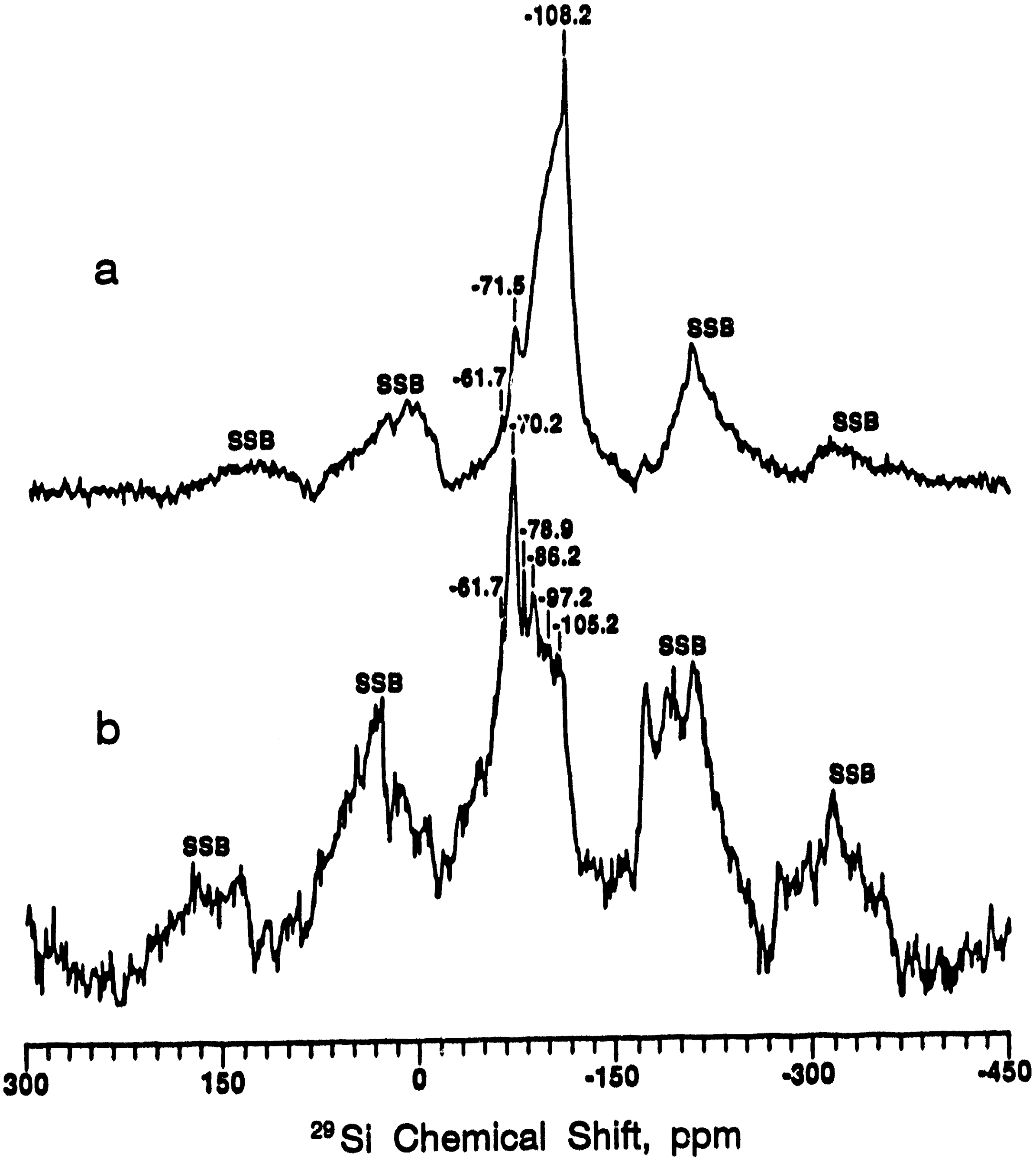


Figure 2. ^{29}Si NMR SPE/MAS Spectra of the Anhydrous Coal Fly Ashes from: (a) The Dave Johnston Power Plant, Pd = 10 s, Acq = 6480; (b) The Laramie River Power Plant, Pd = 5 s, Acq = 12,240

The major differences by NMR in the two anhydrous coal fly ash materials are the concentration of the SiO_4^{-4} anions (Q^0) at -70.2 and -71.5 ppm for the Laramie River and Dave Johnston coal fly ashes, respectively, and the concentration of SiO_2 (Quartz, Q^4) at -105.2 and -108.3 ppm, respectively. The Laramie River fly ash has a much higher concentration of monomeric silicate anion relative to the concentration of the fully polymerized quartz, whereas with the Dave Johnston fly ash, the concentration of the monomeric SiO_4^{-4} anion is much less than the concentration of quartz.

The most downfield signal at -61.7 ppm which appears in the spectra can be assigned to either of the minerals chondrodite [$(Mg_5(SiO_4)(OH,F)_2$], forsterite (Mg_2SiO_4), or olivine [$(Mg,Fe)_2SiO_4$]. These minerals appear to be the only minerals that have resonance signals in this region of the spectrum (Goberdhan 1988).

Because of the broad, featureless resonances in the region of -75 to -105 ppm, no other spectral assignments can be made for the anhydrous Dave Johnston coal fly ash. However, in this spectral region of the Laramie River coal fly ash, some well defined resonances and broad resonances are noted. The resonances at -78.9 and -86.2 ppm are assigned the coordination units of Q^1 (Si end group) and Q^2 (Si middle group), and Q^4(4Al) (Si cross-linking groups with 4Al), respectively. The broad resonances centered at -97.2 and -105.2 ppm are assigned the coordination units of Q^3 (Si branching group) and Q^4(1Al) (Si cross-linking group with 1Al), and Q^4 (Si cross-linking group) and Q^4(0Al) (Si cross-linking group with no aluminum), respectively.

To extract additional information from the ^{29}Si spectra of coal fly ash, a mathematical smoothing function was used to reduce the spectral noise level and to define more precisely the major silicate and/or aluminosilicate components. With the major components defined, a curve-fitting routine was used to determine the distribution and quantity of silicates and aluminosilicate species within the coal fly ash sample. Figures 3a and 3b show the expanded spectra of the anhydrous coal fly ashes. These spectra were deconvoluted and the relative area measured for the silicate and/or aluminosilicate anions. Table 5 lists the relative percent of anion types and the silicate coordination state assignment for each coal fly ash. The three resonances below -60 ppm (Figure 3b) are silicates and aluminosilicates which have not been reported by any other technique. Although the curve-fitting techniques determining the silicate species within a fly ash sample are semi-quantitative, they do provide concentration information that cannot be obtained by any other method.

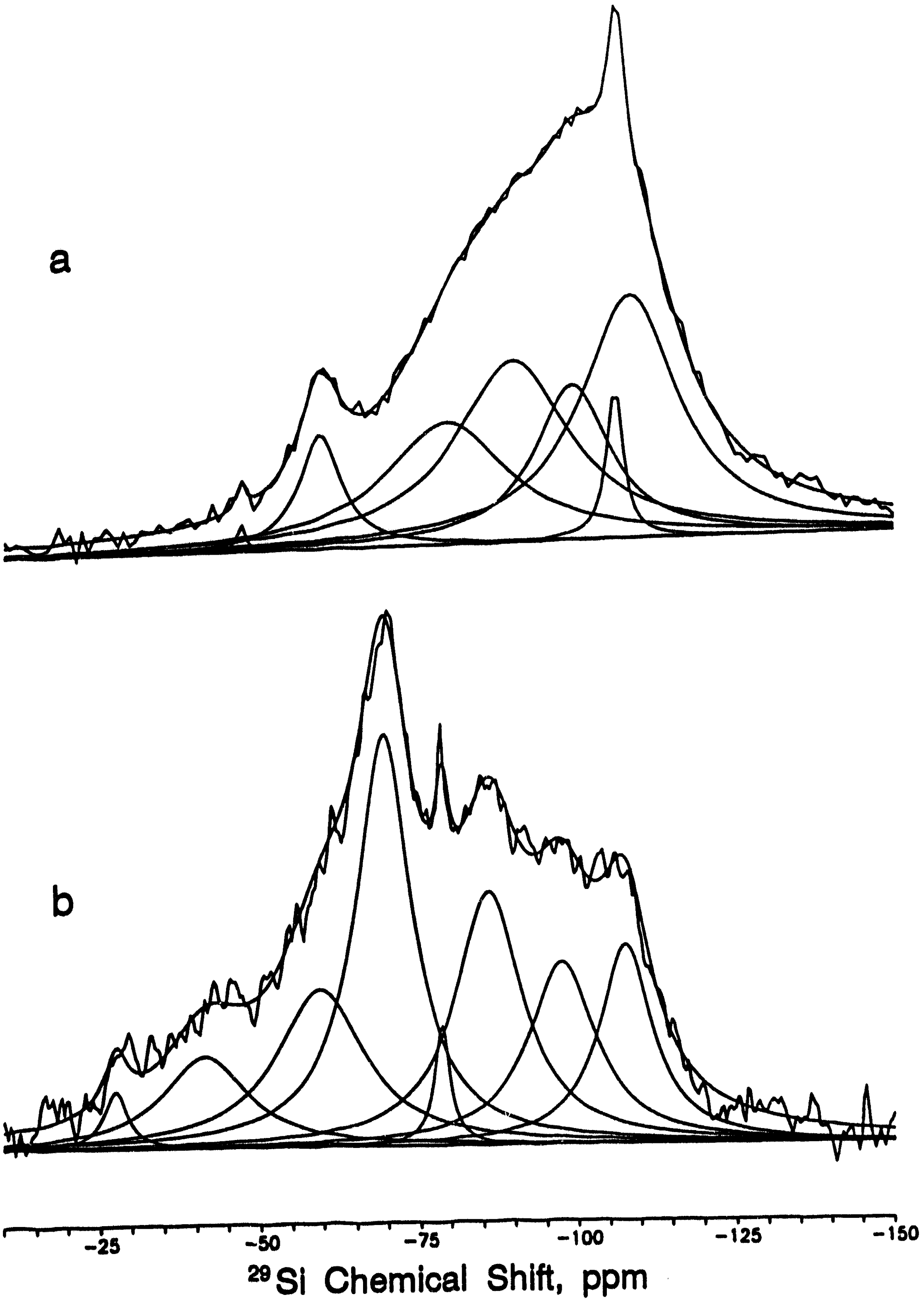


Figure 3. Deconvoluted ^{29}Si NMR Spectra of Coal Fly Ashes: (a) Dave Johnston Power Plant; (b) Laramie River Power Plant.

Table 5. Relative Percent of Silicate Anions in Dave Johnston and Laramie River Power Plants Coal Fly Ashes

	Dave Johnston Coal Fly Ash		Laramie River Coal Fly Ash	
Deconvoluted Peak No. Left-to-right	Silicate Coordination State	Relative Area %	Silicate Coordination State	Relative Area %
1	-	0.3	-	1.6
2	Q^0, Q^1	6.1	-	8.3
3	Q^2	23.8	-	15.2
4	Q^3	28.5	Q^0	26.8
5	Q^3	10.6	Q^1, Q^2	2.3
6	Q^4	4.2	Q^2	19.5
7	Q^4	26.5	Q^3	14.0
8			Q^4	12.4

Adsorption Isotherms of Hazardous Organic Compounds Sorbed on Coal Fly Ash

Several equilibrium models have been developed to describe adsorption data. The most common adsorption isotherm equations used for describing adsorption data are those derived by Langmuir (1915) and by Freundlich (1926).

The logarithmic expression for the Freundlich adsorption isotherm is given in equation 1.

$$\log (x/m) = \log K + (1/n)(\log C_e) \tag{1}$$

where x = the amount of adsorbate adsorbed, m = the weight of adsorbent, C_e = the adsorbate equilibrium concentration, and K and $1/n$ = constants characteristic of the system. The equation is widely used to describe the adsorption in aqueous systems. A plot of log q, where $q = x/m$, versus log C_e gives an intercept of log K and a slope of $1/n$. The value of K can be taken as a relative indicator of the adsorption capacity, while $1/n$ is indicative of the energy or intensity of the reaction (Weber 1972). A value of $1/n$ of ~ 1 indicates high adsorptive capacity at high equilibrium concentrations. For $1/n << 1$, the adsorptive capacity is only slightly reduced at the lower equilibrium concentrations.

Solid-Gas Equilibrium

The Freundlich adsorption isotherms were obtained for three aromatic hydrocarbons and several chlorobenzene compounds using the headspace analysis technique (Figures 4 and 5). In these experiments a dilute solution of all of the compounds in CH_3OH was applied directly to the Dave Johnston coal fly ash in a vial and allowed to equilibrate for 72 hours at ambient temperature. Because the amount of solution added to the fly ash was totally adsorbed, only a solid-gas equilibrium exists. The headspace above the fly ash contained the vapor phase of the organic compounds in equilibrium with the adsorbed compounds on the fly ash. Table 6 lists the Freundlich adsorption isotherm constants (K and 1/n) for the compounds adsorbed on the Dave Johnston coal fly ash and the same compounds adsorbed on activated carbon. The Freundlich adsorption isotherm constants for the organic compounds on activated carbon were obtained from the literature (Faust and Aly 1987 and literature cited therein). These constants represent a solid-liquid adsorption equilibrium. However, to a first approximation they can be compared to the solid-gas adsorption equilibrium because both equilibrium processes depend on monolayer coverage.

Table 6. Freundlich Adsorption Isotherm Constants for Organic Compounds on Dave Johnston Coal Fly Ash and Activated Carbon

	Coal Fly Ash			Activated Carbon[a]	
Compound	K (mg/Kg)	1/n	r^2 [b]	K (mg/Kg)	1/n
Benzene	3.94	0.2533	0.363	1×10^3	1.6
Toluene	9.38	0.0872	0.169	16.1×10^3	0.44
Ethylbenzene	10.04	0.3842	0.803	53×10^3	0.79
Chlorobenzene	15.67	0.2055	0.565	91×10^3	0.99
1,2-Dichlorobenzene	40.25	0.4595	0.754	129×10^3	0.43
1,3-Dichlorobenzene	140.80	1.1431	0.945	118×10^3	0.45
1,4-Dichlorobenzene	46.46	0.4922	0.727	121×10^3	0.47

[a] Ref. 10 in Faust and Aly

[b] Regression coefficient

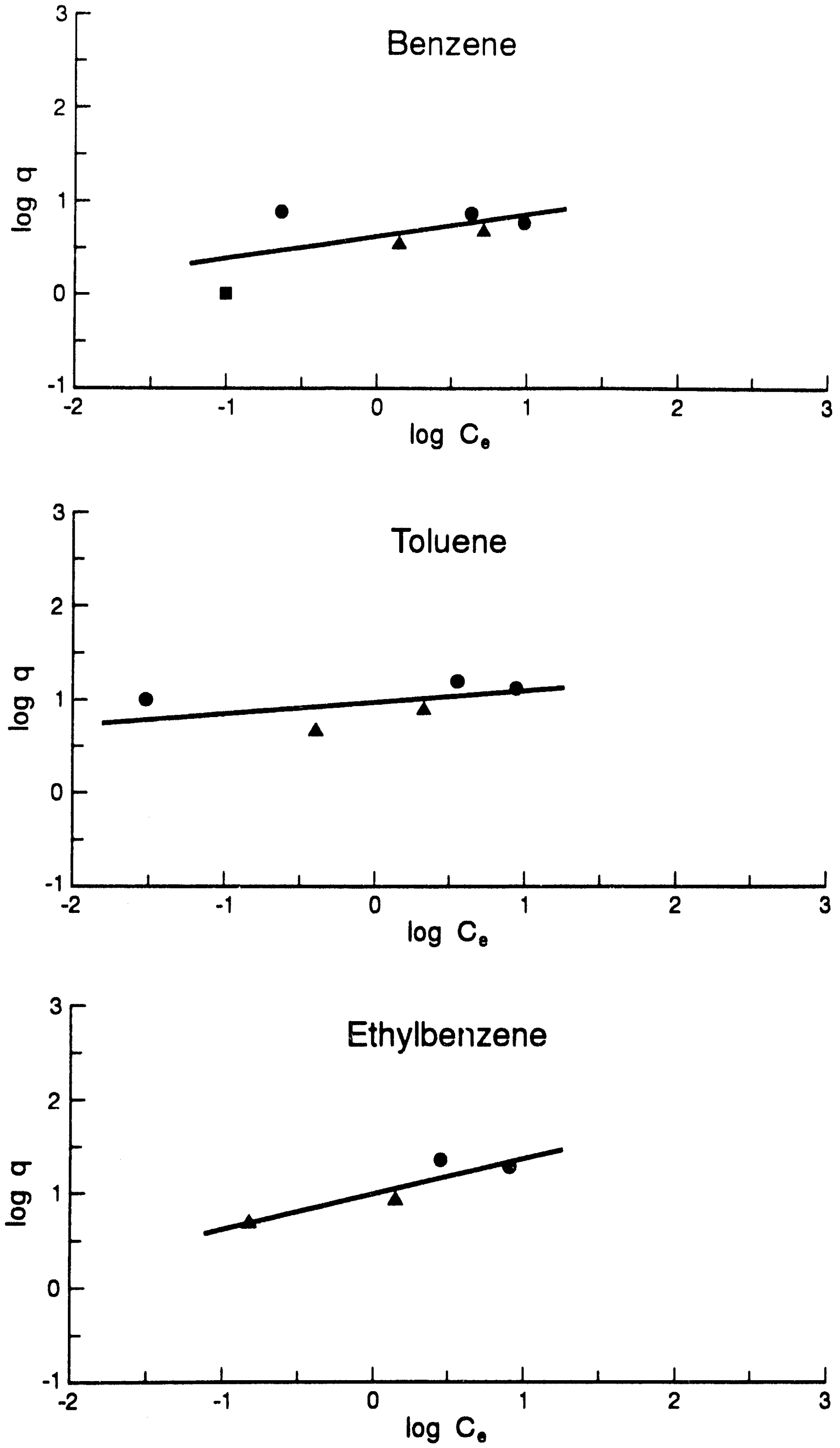


Figure 4. **Freundlich Adsorption Isotherms for Benzene, Toluene, and Ethylbenzene. (Adsorption Capacity, q, in mg/Kg; Equilibrium Concentration, C_e, in mg/L) Symbols ■, ●, and ▲ represent different experimental runs.**

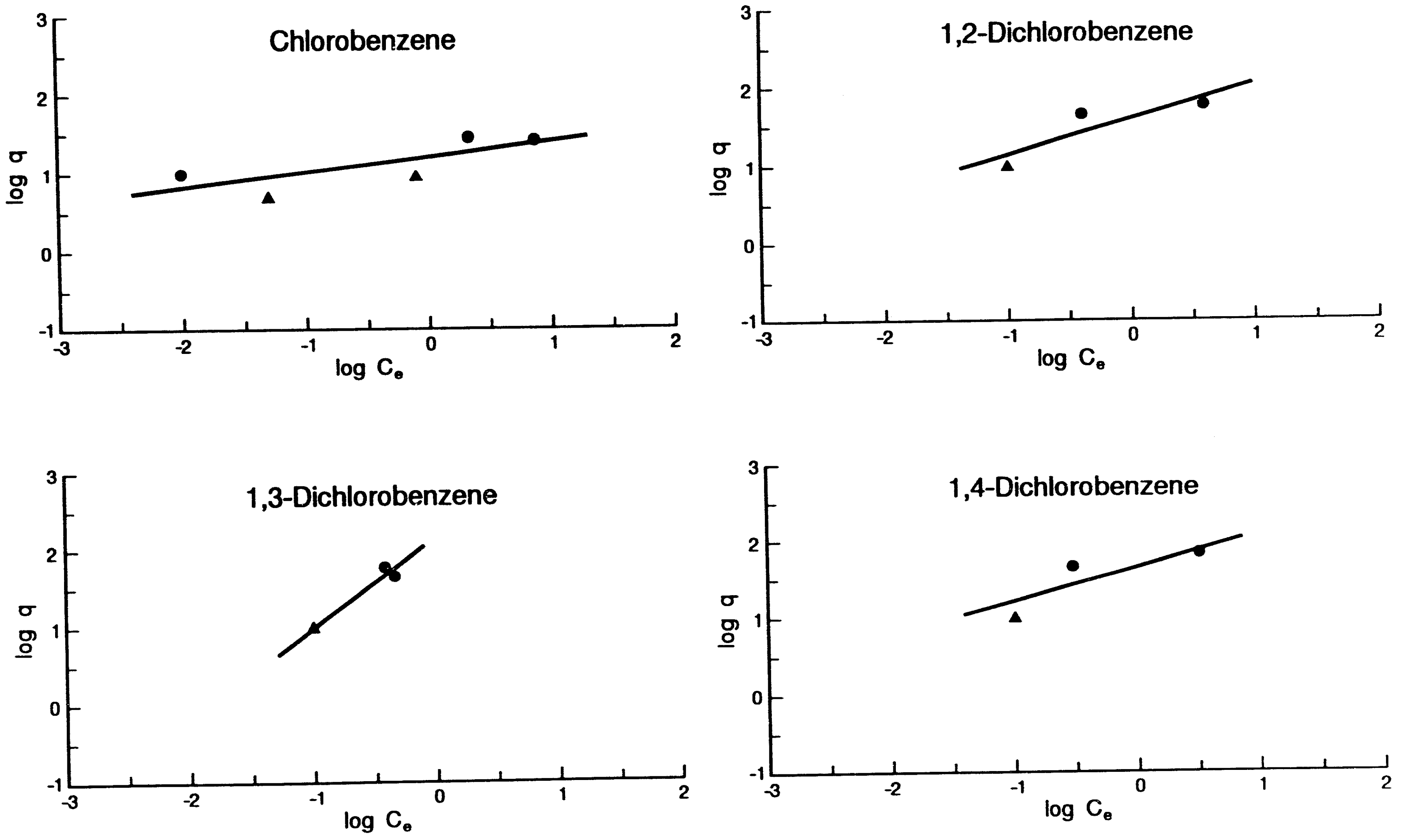


Figure 5. Freundlich Adsorption Isotherms for Chlorobenzene, 1,2-Dichlorobenzene 1,3-Dichlorobenzene and 1,4-Dichlorobenzene (Adsorption capacity, q, in mg/Kg; Equilibrium Concentration, Ce, in mg/L). Symbols ● and ▲ represent different experimental runs.

Table 7 shows the comparison of the adsorption capacity (q) of coal fly ash to that of activated carbon for the hydroaromatics and chlorobenzenes at an equilibrium concentration of 10 mg/L. The adsorption capacity was calculated using the respective Freundlich constants and the Freundlich adsorption isotherm equation. Table 7 shows that activated carbon adsorbs the compounds to a much greater degree than coal fly ash, as one would expect. In fact, activated carbon adsorbs the hydroaromatics and chlorobenzenes compared to the fly ash by a factor greater than 3000 at an assumed equilibrium concentration of 10 mg/L. Although 1,3-dichlorobenzene appears to be adsorbed on coal fly ash to a much greater extent than the other compounds, the higher value represents essentially two data points over a very narrow concentration range and thus the confidence level is low even though the regression coefficient is high (Table 6).

Table 7. Adsorption Capacities for Dave Johnston Coal Fly Ash and Activated Carbon at an Equilibrium Concentration of 10 mg/L

	Adsorption Capacity q (mg/Kg)	
Compound	Coal Fly Ash[a]	Activated Carbon[b]
Benzene	7	40×10^3
Toluene	11	72×10^3
Ethylbenzene	24	327×10^3
Chlorobenzene	25	889×10^3
1,2-Dichlorobenzene	116	347×10^3
1,3-Dichlorobenzene	1957	332×10^3
1,4-Dichlorobenzene	144	357×10^3

[a] Solid-gas equilibrium

[b] Solid-liquid equilibrium

It should be noted that the comparison of the adsorption capacities for coal fly ash with activated carbon are based upon a solid-gas equilibrium and solid-liquid equilibrium. Additional experiments are needed to confirm that the solid-gas adsorption isotherms can indeed be directly compared to the solid-liquid adsorption isotherms.

Solid-Liquid Equilibrium

The Freundlich adsorption isotherms were obtained for pyridine, pentachlorophenol, naphthalene, and 1,1,2,2-tetrachloroethane in aqueous solution in the presence of known amounts of Dave Johnston coal fly ash (Figure 6). In this figure the straight lines were drawn through the points that best represent the adsorption process. The data are a composite of several experimental runs (represented by different symbols) and the data points that appeared to be outliers were dropped in computing the Freundlich adsorption isotherm constants. Table 8 lists the adsorption constants for the four compounds adsorbed on coal fly ash and activated carbon as reported in the literature (Faust and Aly 1987 and literature reported therein).

Table 8. Freundlich Adsorption Isotherm Constants for Pyridine, Pentachlorophenol, Naphthalene, and Tetrachloroethane on Dave Johnston Coal Fly Ash and Activated Carbon

	Coal Fly Ash			Activated Carbon	
Compound	K (mg/Kg)	1/n	r^2 [a]	K (mg/Kg)	1/n
Pyridine	120	0.33	0.979	1220	0.2[b]
Pentachlorophenol	780	0.12	0.811	150×10^3	0.42[c]
Naphthalene	896	0.22	0.982	132×10^3	0.42[c]
Tetrachloroethane	2003	0.40	0.659	10.6×10^3	0.37[c]

[a] Regression coefficient

[b] Ref. 13 in Faust and Aly 1987

[c] Ref. 10 in Faust and Aly 1987

To compare the adsorption data, the adsorption capacity q, for the coal fly ash and activated carbon were calculated for each compound using the Freundlich constants and the Freundlich equation, and an equilibrium concentration of 10 mg/L. These data are reported in Table 9. The adsorption capacities for both the coal fly ash and the activated carbon are based upon a solid-liquid equilibrium in which only a monolayer adsorption is assumed possible because of the rapid motion of molecules in the liquid phase. This prevents a multilayer build-up of the adsorbed molecules at the surface of the fly ash and activated carbon.

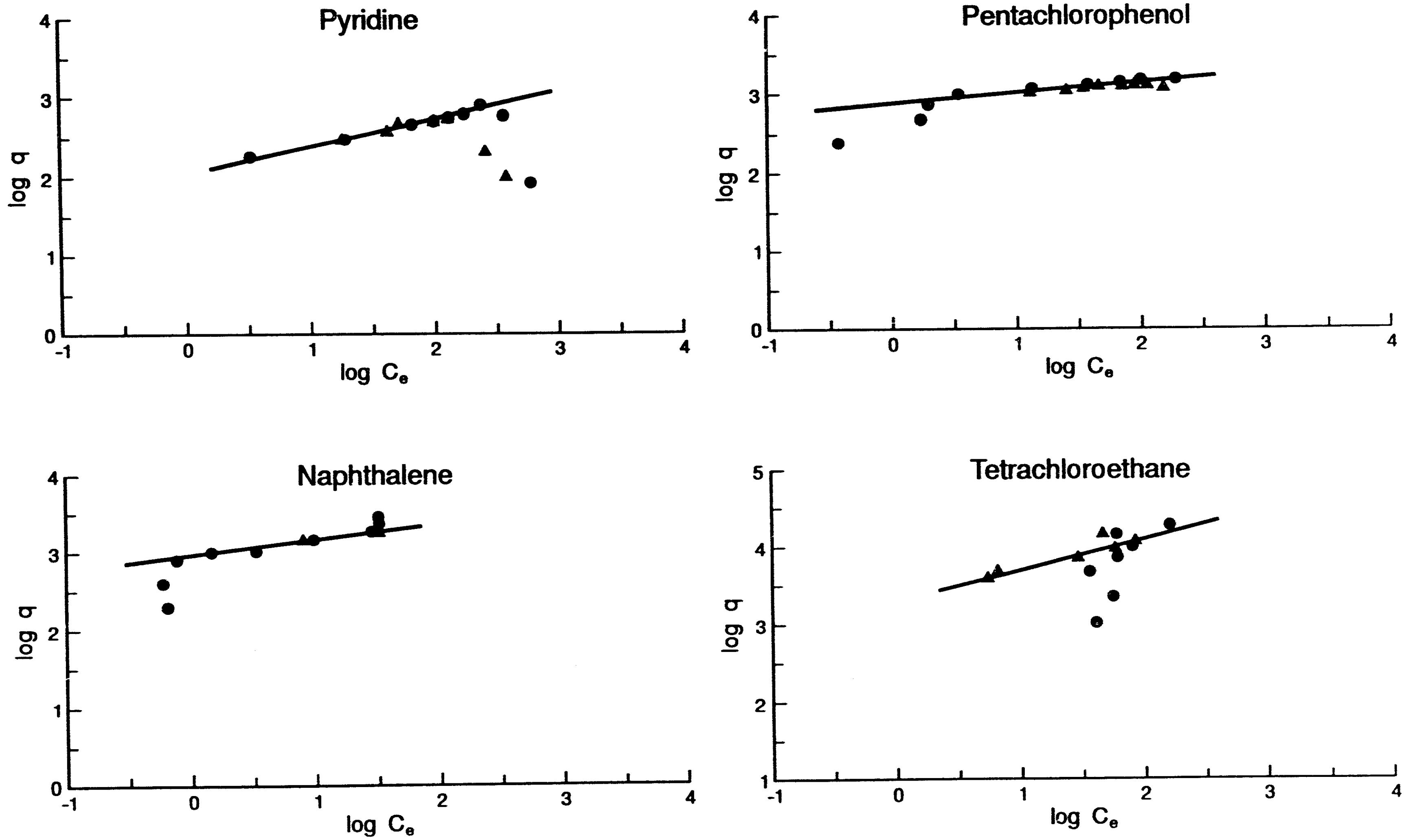


Figure 6. Freundlich Adsorption Isotherms for Pyridine, Pentachlorophenol, Naphthalene, and Tetrachloroethane (Adsorption Capacity, q, in mg/Kg; Equilibrium Concentration, Ce, in mg/L). Symbols ● and ▲ represent different experimental runs.

Table 9. Adsorption Capacity of Dave Johnston Coal Fly Ash and Activated Carbon at an Equilibrium Concentration of 10 mg/L for Pyridine, Pentachlorophenol, Naphthalene, and Tetrachloroethane

	Adsorption Capacity q (mg/Kg)	
Compound	Coal Fly Ash	Activated Carbon
Pyridine	0.25×10^3	1.934×10^3
Pentachlorophenol	1.04×10^3	395×10^3
Naphthalene	1.48×10^3	347×10^3
Tetrachloroethane	5.05×10^3	24.8×10^3

As shown in Table 9, the Dave Johnston coal fly ash appears to adsorb these organic compounds nearly as well as activated carbon. The coal fly ash adsorption capacity is a factor of about 300 less, relative to activated carbon. In fact, 1,1,2,2-tetrachloroethane is adsorbed on coal fly ash almost as well as it is on activated carbon (5×10^3 mg/Kg versus 25×10^3 mg/Kg). Thus, it appears that the Dave Johnston coal fly ash can be a good adsorber for some types of compounds.

The relationship of the adsorption properties of the Dave Johnston coal fly ash to its chemical composite cannot be made with any certainty at this time. Similar adsorption data are needed for the Laramie River coal fly ash, which is known to have significantly different chemical properties.

^{13}C Solid-State NMR Study of Hazardous Organic Compounds

Observing the ^{13}C NMR signal of a compound in the solid state can be more difficult than observing the ^{13}C NMR signal of the same compound in the liquid state. Major factors contributing to the difficulties are: (1) sample phase (amorphous versus crystalline), (2) long hydrogen and carbon spin-lattice relaxation times, (T_1^H and T_1^c), (3) short spin-lattice relaxation times in the rotating frame ($T_{1\rho}$), (4) long polarization-transfer time (T_{CH}), and (5) Hartmann-Holin matching conditions (Axelson 1985; Botto and Sanada 1993).

Before studying the adsorption of various types of hazardous organic compounds on coal fly ash, several experiments were conducted to determine the conditions necessary for observing the NMR signal of pure compounds in the solid state and to determine qualitatively the level of detection when using a jumbo NMR probe.

Aromatic Hydrocarbons and Polychlorophenols

Figures 7a and 7b show the ^{13}C solid-state NMR spectra of naphthalene using SPE/MAS and CP/MAS. In Figure 7a, the carbon resonances of naphthalene are barely discernable at 128 ppm using SPE/MAS with 780 scans, a pulse delay of 20 s and about 2.5 g of sample in a jumbo probe. However, using CP/MAS with a contact time of 2 ms and a pulse delay of 20 s, a spectrum was obtained after 500 scans. The difficulty in obtaining a spectrum of naphthalene with good signal-to-noise ratio in a short time is the inherent long spin-lattice relaxation times of the hydrogen and carbon atoms when the material is in its crystalline state. Figures 7c and 7d show the ^{13}C NMR SPE/MAS and CP/MAS spectra of naphthalene in which a 0.05 M solution of the relaxation agent chromium III Acetylacetonate (CrAcAc) in $CDCl_3$ was added and the mixture heated to remove the $CDCl_3$. The signal-to-noise of the SPE/MAS spectrum was not improved indicating that the Cr ion was not close to the site of the carbon atom; however, the signal-to-noise ratio of the CP/MAS spectrum did improve relative to the spectrum in Figure 7b. In addition, this spectrum was obtained in less time using a 5 s pulse delay instead of 20 s. Apparently, the Cr ion was in a position to reduce the hydrogen relaxation time permitting a more effective cross-polarization to occur.

Figures 8a and 8b clearly show the effect of increasing the pulse delay time from 1 to 30 s for the ^{13}C solid-state SPE/MAS spectra of 2,3-dimethylnaphthalene. In Figure 8a only the methyl resonance (~ 25 ppm) is detected at a pulse delay time of 1 s, indicating a short relaxation time for the methyl carbons relative to the aromatic carbons. At a pulse delay of 30 s, all aromatic carbons (~ 128 ppm) are now observed (Figure 8b). However, the aromatic carbon intensities are less than the methyl carbon intensity indicating the aromatic carbons have not fully relaxed to the ground state before the next pulse. The theoretical ratio of resonances should be 4:4:2:2 reading the resonance peaks from left to right. Figure 8c does show the theoretical ratio of the ^{13}C resonances for 2,3-dimethylnaphthalene. This spectrum was obtained using CP/MAS with a pulse delay of 1 s, a contact time of 3 ms and 500 scans. In this case the long relaxation time of carbon is not detrimental. The good spectrum in the short experiment time is due to hydrogen spin diffusion from the methyl group and the relatively short relaxation time of the hydrogen atoms.

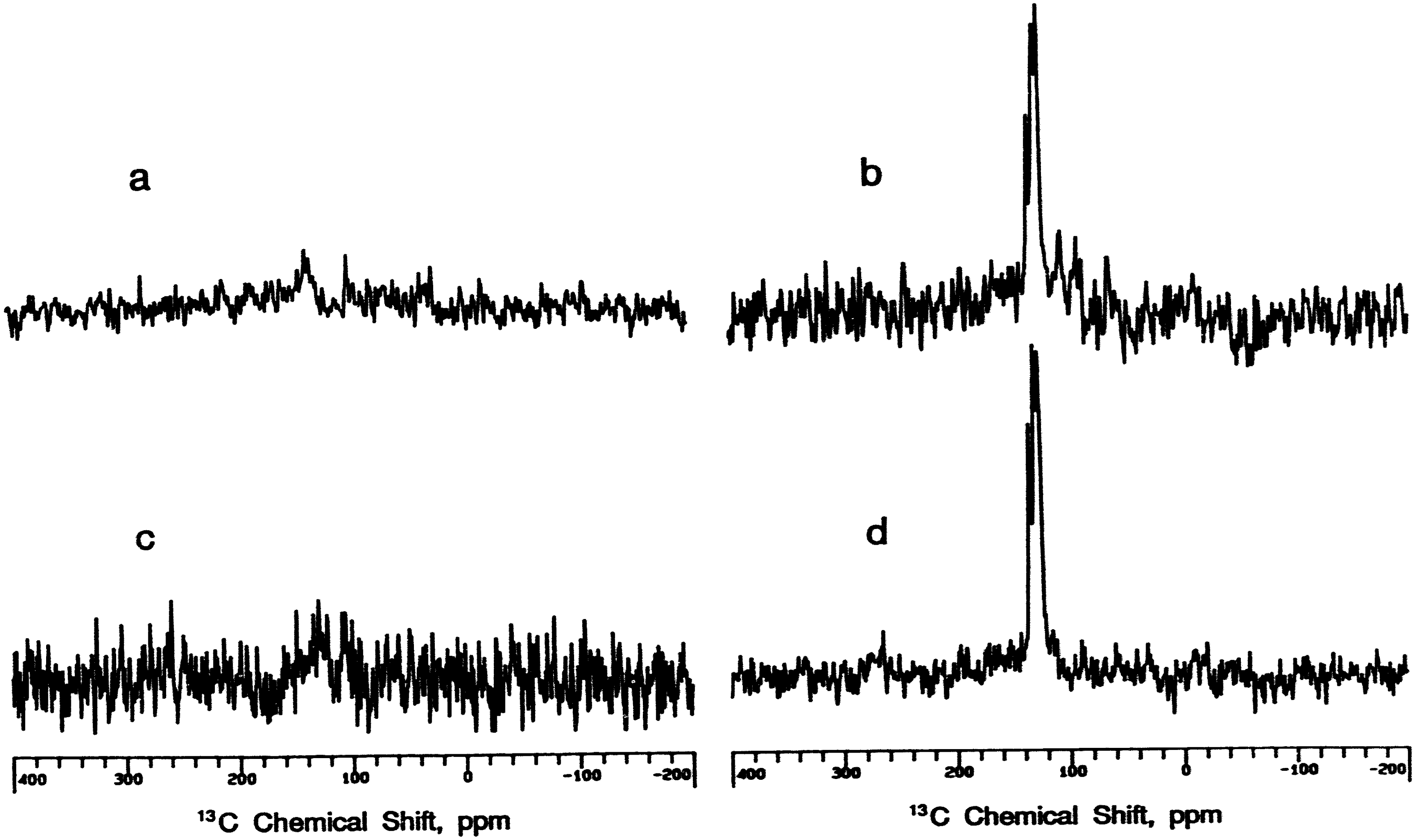


Figure 7. ^{13}C Solid-State NMR Spectra of Naphthalene: (a) SPE/MAS, Pd = 20 s, 780 scans; (b) CP/MAS, ct = 2 ms, Pd = 20 s, 500 scans; (c) SPE/MAS, with CrAcAc, Pd = 10 s, 500 scans; (d) CP/MAS, with CrAcAc, ct = 1 ms, Pd = 5 s, 500 scans

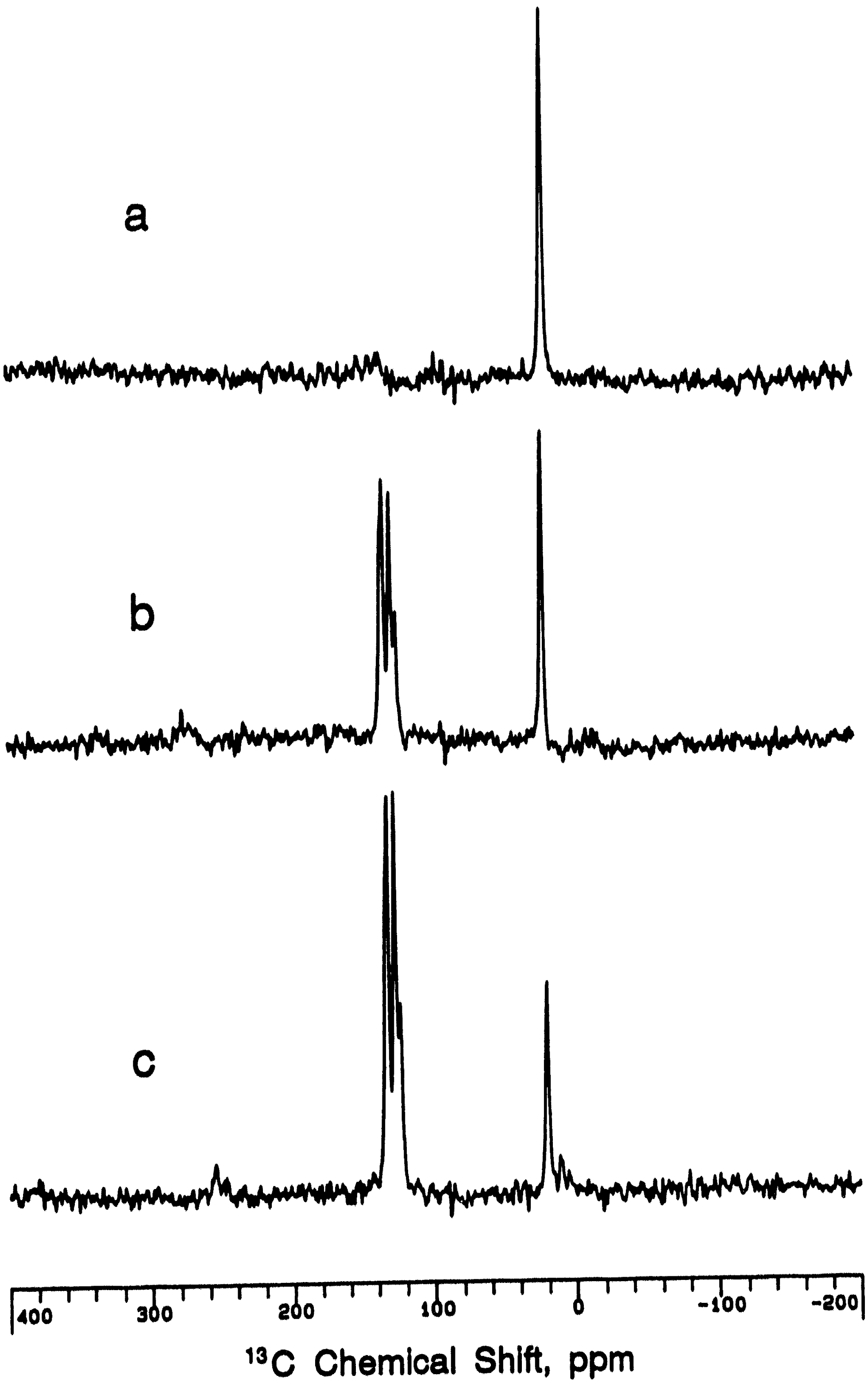


Figure 8. ^{13}C Solid-State NMR Spectra of 2,3-dimethylnaphthalene: (a) SPE/MAS, Pd = 1 s, 300 scans; (b) SPE/MAS, Pd = 30 s, 72 scans; (c) CP/MAS ct = 3 ms, Pd = 1 s, 600 scans

Figures 9a through 9j are the SPE/MAS and CP/MAS solid-state ^{13}C NMR spectra of phenol and polychlorophenols using ~ 2.5 g of sample in a jumbo probe. The SPE/MAS spectrum of solid phenol (Figure 9a) was obtained using a pulse delay of 20 s and 200 scans. The resonance signal at ~ 155 ppm is that of carbon with OH attached. The resonances signals at ~ 130, ~ 121, and ~ 115 ppm are due to carbons at the meta, para, and ortho position within the aromatic ring. The ^{13}C CP/MAS spectrum of phenol is shown in Figure 9b. The spectrum shows only two resonance signals - the phenolic carbon at ~ 155 ppm and the para carbon at ~ 121 ppm (contact time 500 μs and pulse delay time 20 s). Varying the contact time from 50 μs to 8 ms and the delay time from 1 to 60 s did not result in observing the resonance signals for either the ortho or meta carbons. The observed spectrum suggests that the phenol molecule is rotating rapidly in the solid state about the C_{2v} symmetry axis. Carbon and hydrogen atoms in the ipso and para positions remain relatively static and, thus, effective cross-polarization occurs between the hydrogen and carbon atoms resulting in the two signals observed. Low temperature studies will be required to slow the rotational motion of the phenol molecule so that the ortho and meta carbon resonances can be observed by CP/MAS.

The ^{13}C SPE/MAS spectra of 4-chlorophenol, 2,6-dichlorophenol and 2,4,6-trichlorophenol shown in Figures 9c, 9e, and 9g respectively, were obtained using a pulse delay of 120 s and 60 scans. The spectrum of pentachlorophenol (Figure 9i) was obtained with a pulse delay of 20 s and 200 scans. It is readily apparent that as the number of chlorine atoms increases, the spectral resolution decreases. In fact, for pentachlorophenol, the phenolic carbon is no longer evident in the spectrum. The long pulse delay time (120 s) was necessary because carbon atoms with chlorine attached have spin-lattice relaxation times up to 66 s (Freeman and Hill, 1971). For quantitative results the pulse delay should be greater than 300 s or 5 min between pulses.

The ^{13}C CP/MAS spectra of the polychlorophenols (Figures 9d, 9f, 9h, and 9j) were obtained using a contact time of 500 μs, a pulse delay of 120 s and approximately 500 scans. As the number of chlorine atoms increases, the signal-to-noise ratio and the resolution decrease. With an increase in the number of chlorine atoms, there is a corresponding decrease in the hydrogen atom and cross-polarization becomes ineffective.

From the above observations, it is apparent that any adsorption studies using solid-state ^{13}C NMR to directly observe the adsorbed chlorinated phenols should be carried out in the SPE/MAS mode.

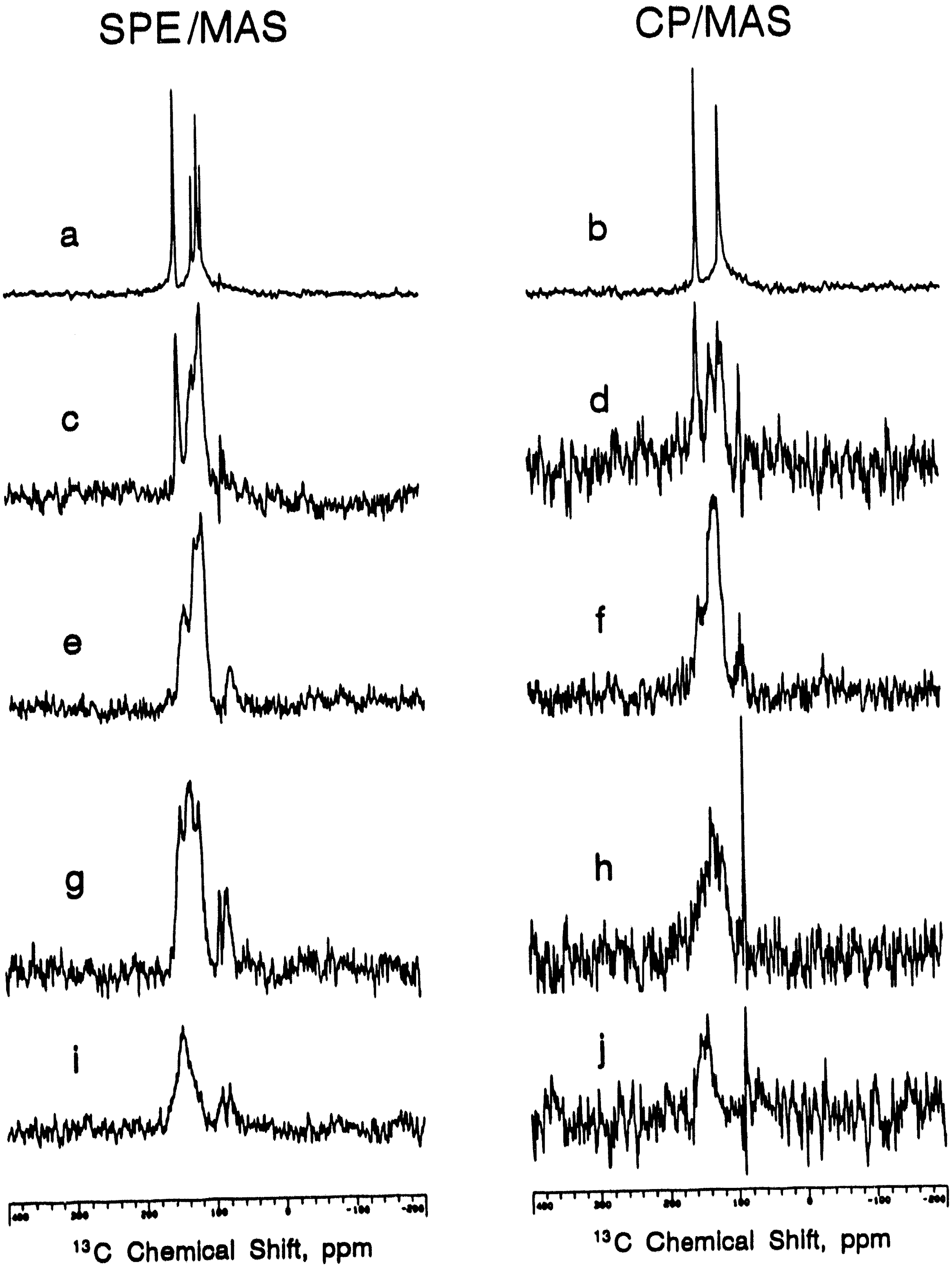


Figure 9. ^{13}C Solid-State NMR Spectra: (a, b) Phenol; (c, d) 4-chlorophenol; (e, f) 2,6-dichlorophenol; (g, h) 2,4,6-trichlorophenol; (i, j) pentachlorophenol

The purity of the starting material can affect the spectral resolution observed even if the material is highly chlorinated. In the case of pentachlorophenol, the spectral resolution for technical grade pentachlorophenol is better than the pure material. Figures 10a through 10d show the SPE/MAS and CP/MAS ^{13}C NMR spectra of technical and pure pentachlorophenol. The four carbon resonances (148, 131, 125, and 119 ppm) are clearly resolved in SPE/MAS spectrum of the technical grade pentachlorophenol (Figure 10a) and discernible in the CP/MAS spectrum (Figure 10b). High resolution ^{1}H NMR spectra of the technical and pure grades of pentachlorophenol showed little or no difference in composition. Attempts to obtain ^{13}C spectra of pure pentachlorophenol doped with CrAcAc were unsuccessful. Obviously, additional experiments are needed to ascertain the reason for the enhanced resolution in the ^{13}C NMR spectrum of technical grade pentachlorophenol.

Sorption of Organic Compounds

Silica Gel. Silica gel is a siliceous adsorbing material having two ^{29}Si NMR resonance signals at -101.3 and -110.5 ppm (Netzel 1991, unpublished data). These signals correspond to the Q^3 and Q^4 coordination states of the silicate anions. The Q^3 and Q^4 coordination states also account for 70% of the silicate anions in the Dave Johnston coal fly ash (see Table 5). Thus, silica gel was used as a model adsorbent to investigate the use of ^{13}C NMR to measure the adsorption capacity and bonding interactions of organic materials with the adsorbent.

Figure 11a is the ^{13}C CP/MAS spectrum of 2,3-dimethylnaphthalene (100 mg) physically mixed with silica gel (1 g). The spectrum was obtained using a jumbo probe, a pulse delay of 1 s, a contact time of 3 ms and 36,000 scans, whereas only 500 scans were necessary when the sample was neat (see Figure 8c). Methylene chloride was then added to the mixture of silica gel and 2,3-dimethylnaphthalene to ensure complete interaction of the two components. The methylene chloride was removed by evaporation and the ^{13}C CP/MAS NMR spectrum obtained on the intimately mixed mixture (Figure 11b) using the same conditions as for the physically mixed sample. The only signal observed is that due to sorbed methylene chloride at ~ 50 ppm. The broad signal centered at ~ 140 ppm is mainly the background signal from the probe. It may be argued that the small signal at ~ 20 ppm is due to the methyl resonances of 2,3-dimethylnaphthalene.

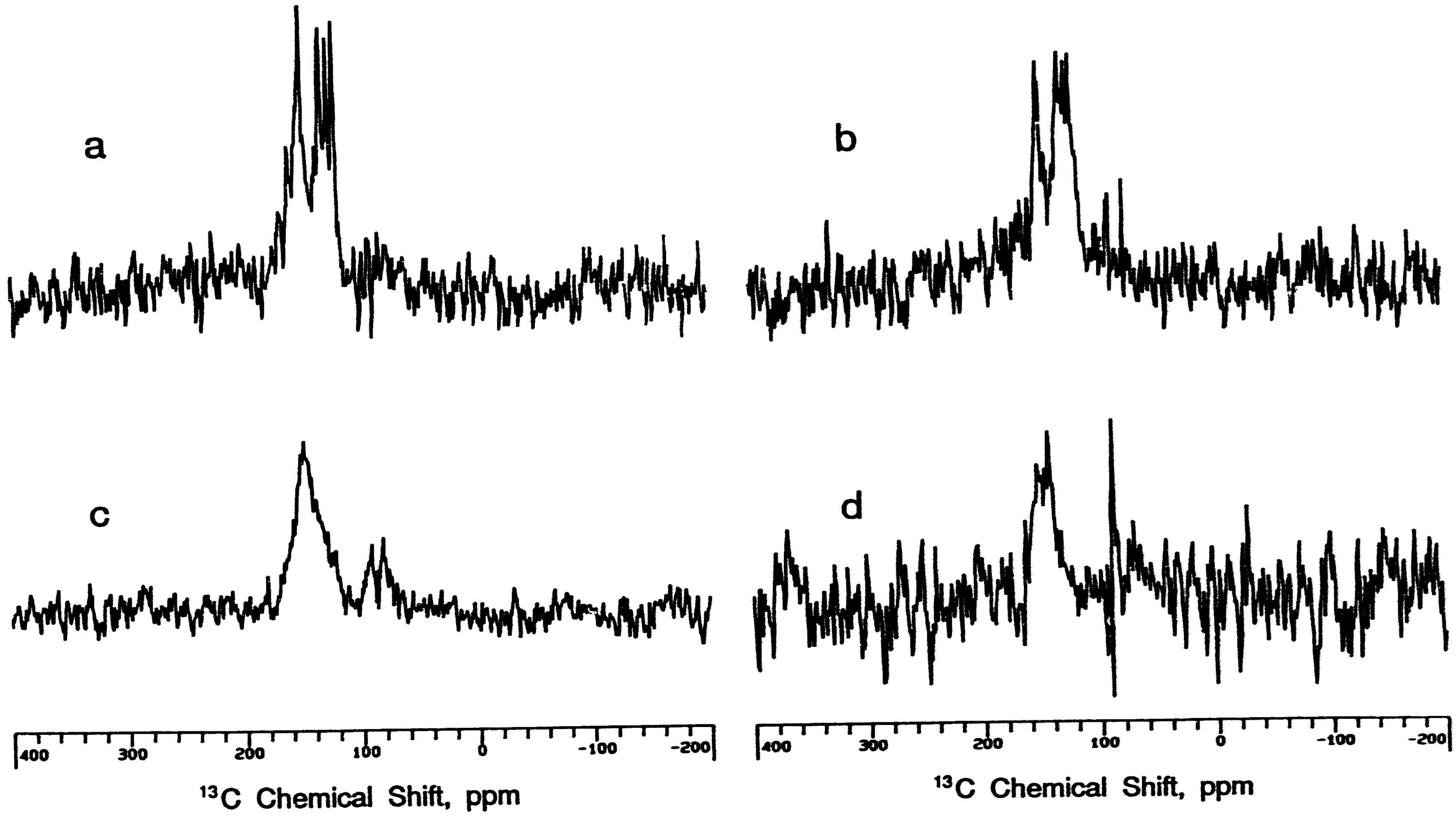


Figure 10. ^{13}C Solid-State NMR Spectra of Pentachlorophenol: (a) Technical Grade, SPE/MAS, Pd = 3 s, 3,000 scans; (b) Technical grade, CP/MAS, ct = 3 ms, Pd = 1 s, 3,000 scans; (c) Reagent Grade, SPE/MAS, Pd = 20 s, 200 scans, (d) Reagent Grade, CP/MAS, ct = 500 μs, Pd = 120 s, 480 scans

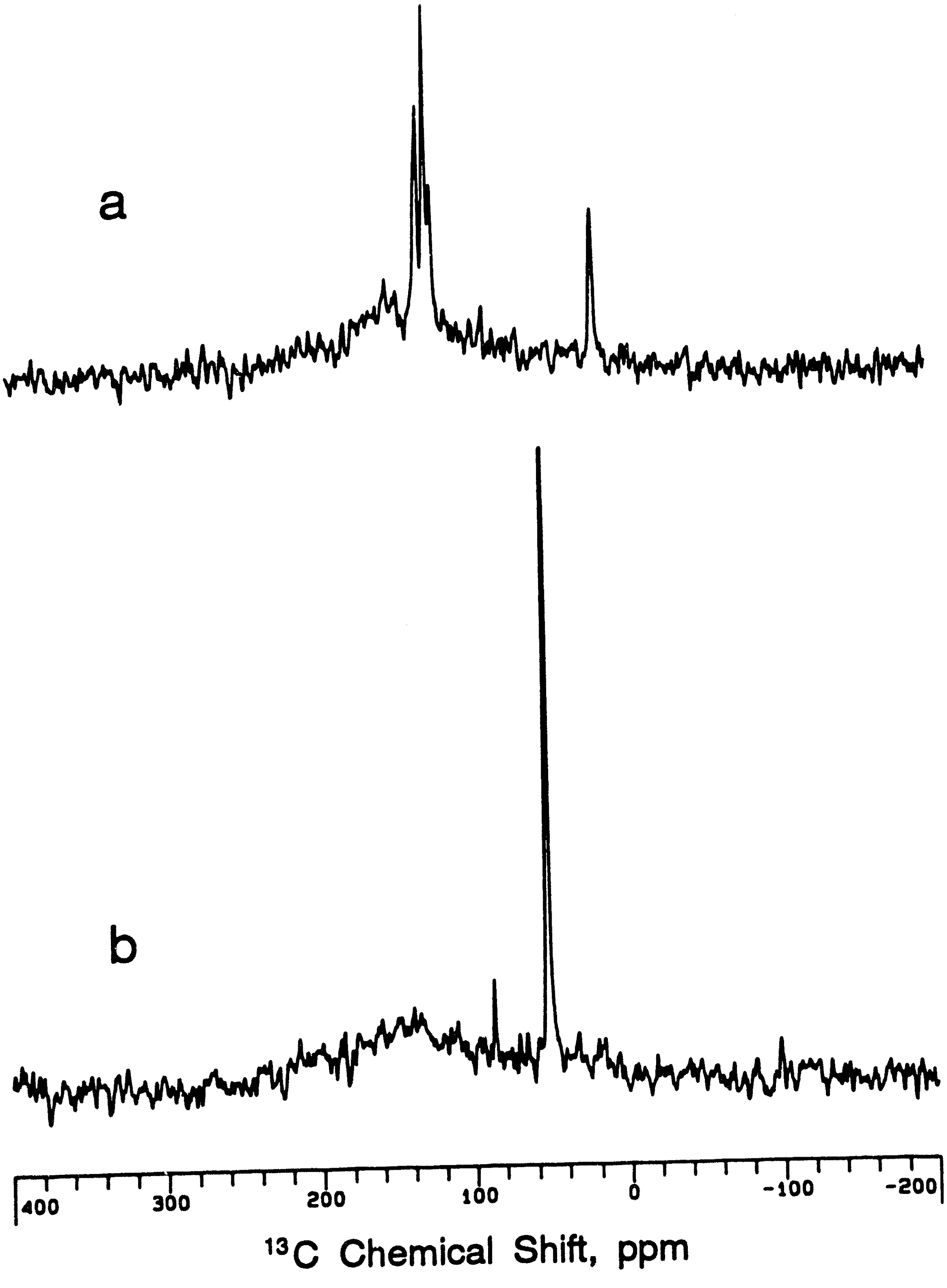


Figure 11. ^{13}C Solid-State NMR Spectra of 2,3-dimethylnaphthalene: (a) physically mixed with silica gel, CP/MAS, ct = 3 ms, Pd = 1 s, 36,000 scans; (b) CH_2Cl_2 solution on silica gel, CP/MAS, ct = 3 ms, Pd = 1 s, 36,000 scans

Either the NMR signal of 2.3-dimethylnaphthalene is broadened due to the adsorption onto silica gel or new instrumental parameters must be set to extract the signal from the noise. That is, the relaxation time of carbon and hydrocarbon are significantly different for the adsorbed molecule than the "free" molecule in the solid state. If this is the case, the contact time and pulse delay time must be adjusted accordingly. Nevertheless, it is apparent that little information can be obtained about the bonding interaction of 2,3-dimethylnaphthalene with silica gel.

Figure 12a and Figure 12b show the ^{13}C SPE/MAS and CP/MAS NMR spectra of 20 mg of pure pentachlorophenol sorbed on 1 g of silica gel. The pentachlorophenol was intimately mixed with silica gel using methylene chloride which was then evaporated. The only resonance signals that can readily be observed are due to sorbed methylene chloride (~ 50 ppm). The resonance peak at ~ 170 ppm in Figure 12b may be real. This resonance signal may be due to the ipso carbon having the OH group attached to it.

Coal Fly Ash. The coal fly ashes obtained from the Laramie River and Dave Johnston Power plants were exposed to pyridine vapor for 11 days. The ^{13}C CP/MAS NMR spectra of the ashes were obtained using a contact time of 5 ms, pulse delay time of 1 s and 65,000 (Figure 13a and Figure 13b). The spectra given in Figures 13a and 13b are the difference spectra in which the probe background signals were subtracted from the composite spectra. The pyridine does not appear to be sorbed on the Laramie River coal fly ash (Figure 13a) while the Dave Johnston fly ash does sorb pyridine, as determined by adsorption isotherm experiments, but the resonance signals are broadened over the range of 120-160 ppm (Figure 13b). In contrast, pyridine is readily adsorbed on silica gel as shown in Figure 13c. The silica gel was exposed to pyridine vapor for only a few hours and the spectrum was obtained in less than 3 hours.

Attempts were made to observe pentachlorophenol sorbed on Dave Johnston fly ash using ^{13}C NMR. Figures 14a and 14b show the SPE/MAS and CP/MAS spectra of 20 mg of technical grade pentachlorophenol physically mixed with 1 g of fly ash. Broad signals are observed in the chemical shift region for pentachlorophenol. Methylene chloride was added to the mixture of pentachlorophenol and fly ash, and then evaporated. Figure 14c shows the SPE/MAS ^{13}C NMR spectrum of the intimately mixed pentachlorophenol with the fly ash. A pulse delay of 20 s was used and 300 scans. The carbon resonances of pentachlorophenol are barely visible above the noise level at ~ 130 ppm. The ipso carbon, the carbon of most interest, was not observed.

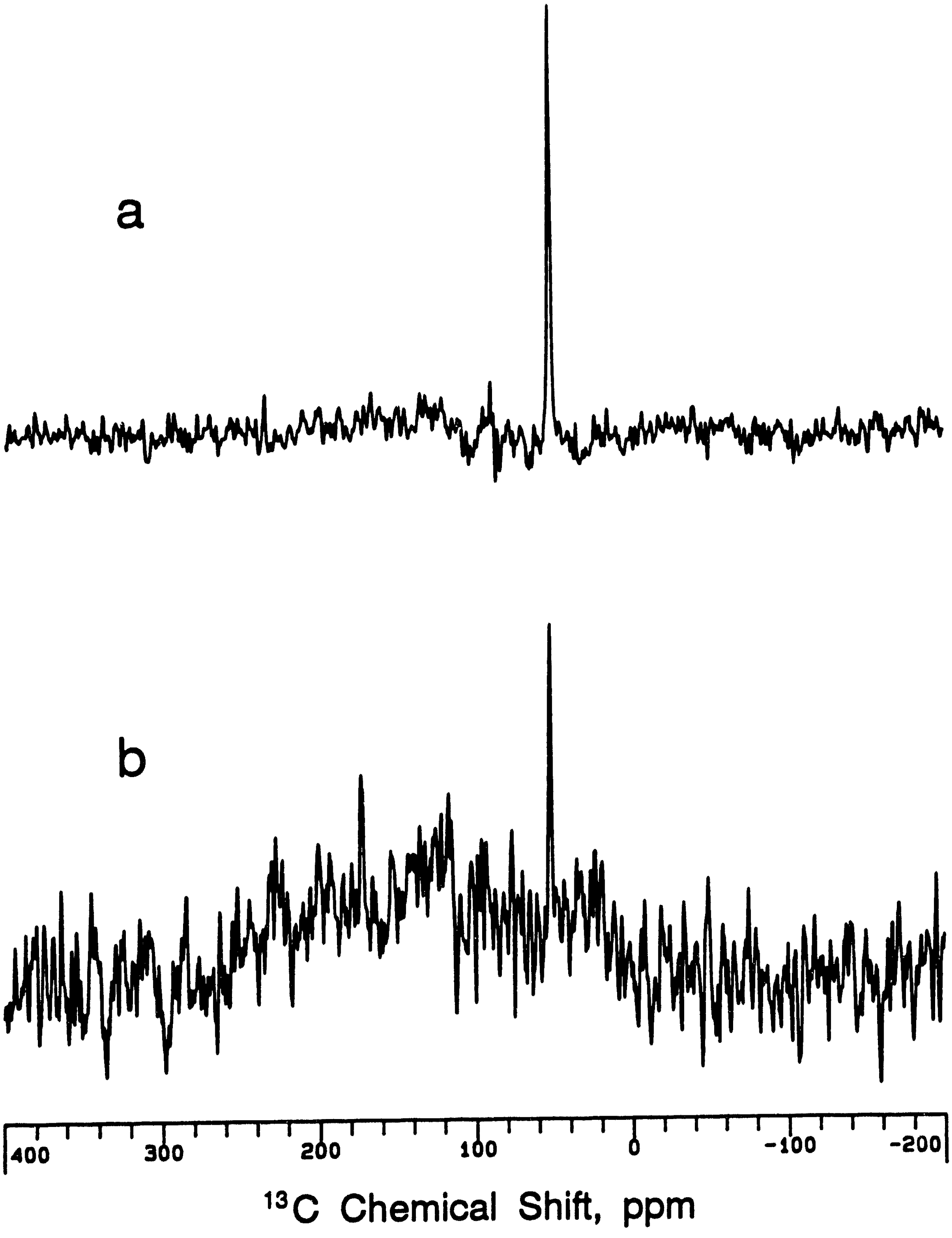


Figure 12. ^{13}C Solid-State NMR Spectra of Pentachlorophenol: (a) CH_2Cl_2 solution, on silica gel, SPE/MAS, Pd = 30 s, 1,800 scans; (b) CH_2Cl_2 solution on silica gel, CP/MAS, ct = 3 ms, Pd = 1 s, 10,800 scans

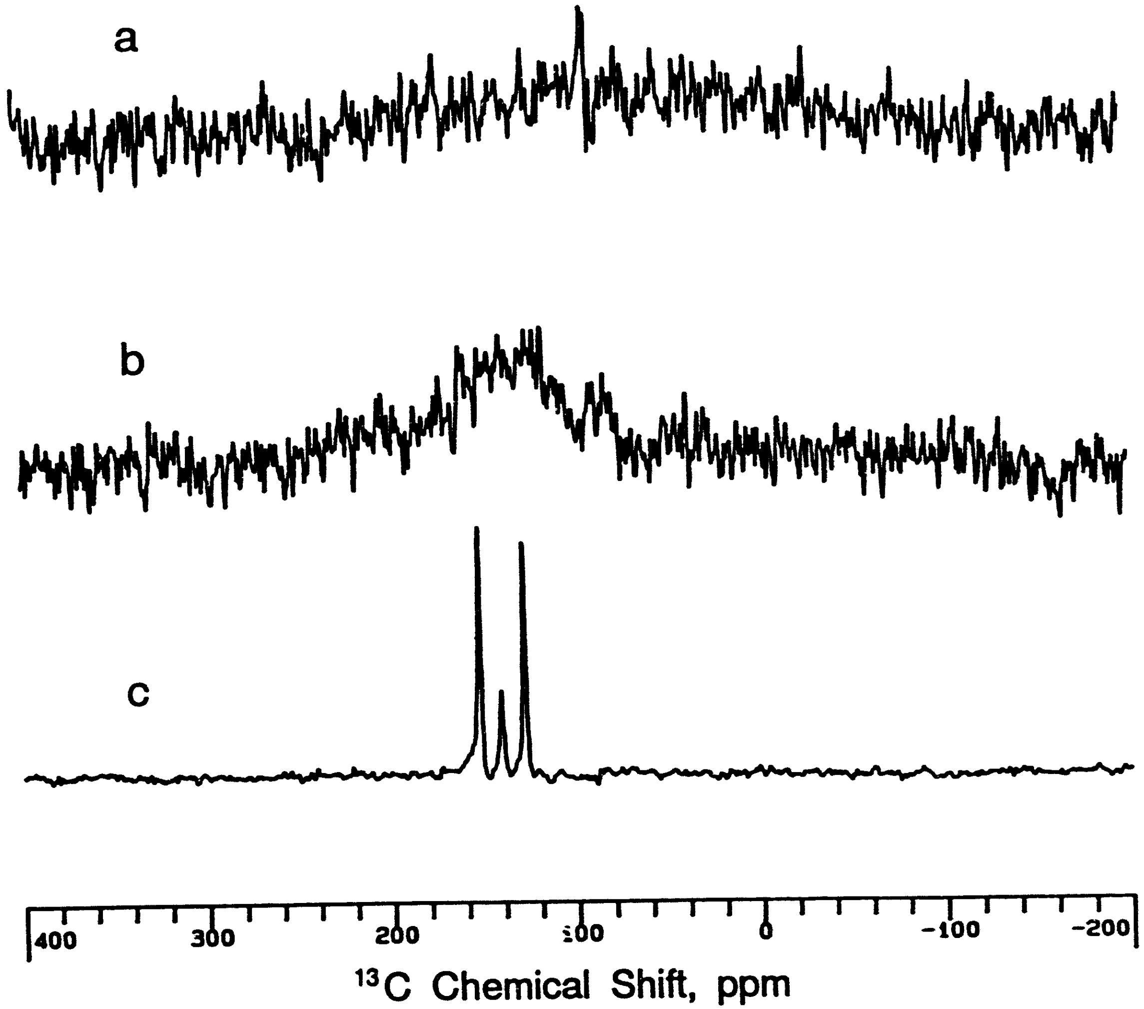


Figure 13. ^{13}C Solid-State NMR Spectra of Pyridine Adsorbed on: (a) Laramie River Coal Fly Ash, CP/MAS, ct = 5 ms, Pd = 1 s, 65,000 scans; (b) Dave Johnston Coal Fly Ash, CP/MAS, ct = 5 ms, Pd = 1 s, 65,000 scans; (c) Silica Gel, SPE/MAS, Pd = 10 s, 900 scans

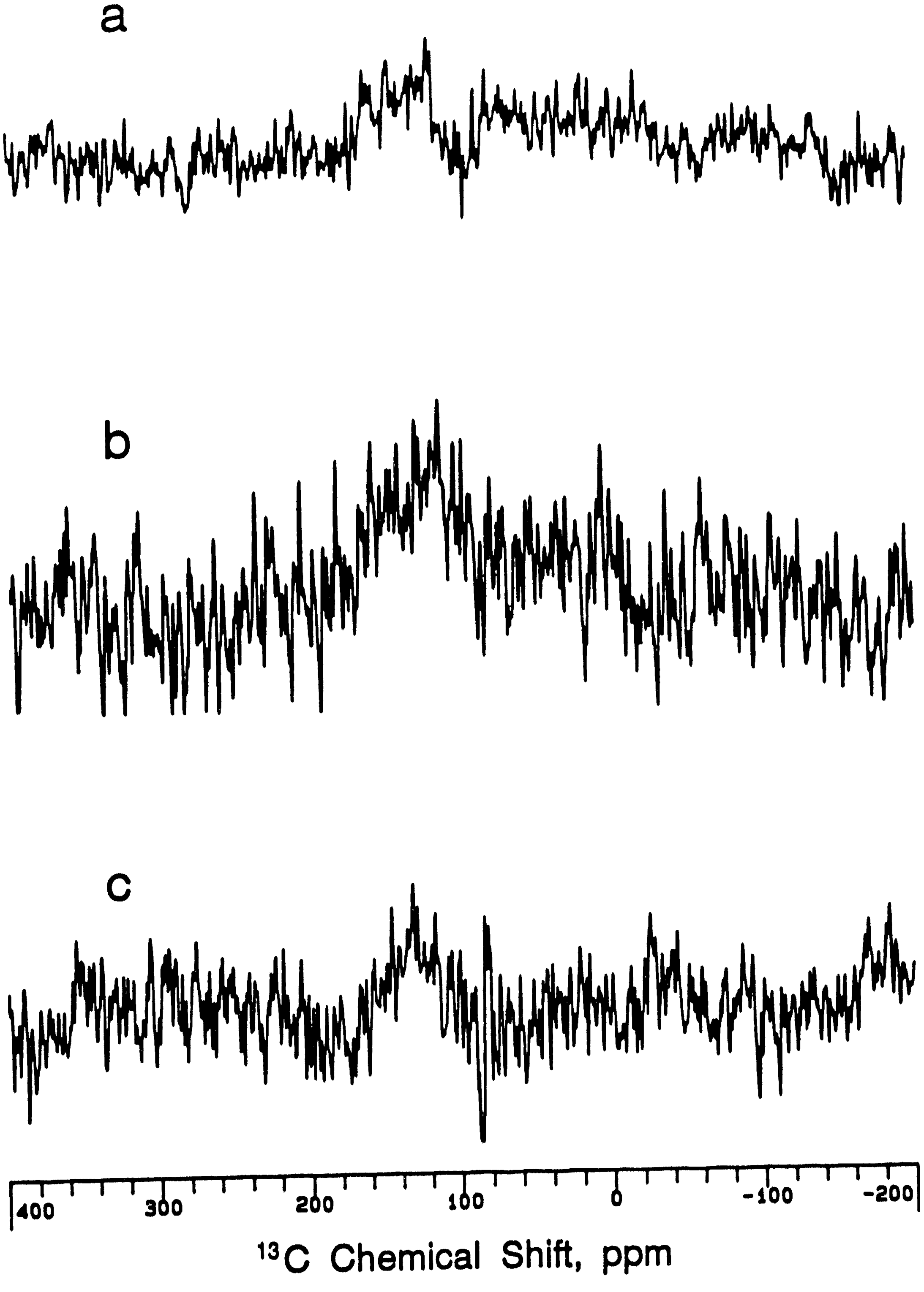


Figure 14. ^{13}C Solid-State NMR Spectra of Pentachlorophenol (a) physically mixed with Dave Johnston Coal Fly Ash, SPE/MAS, Pd = 3 s, 12,000 scans; (b) same, CP/MAS, ct = 3 ms, Pd = 1 s, 7,200 scans; (c) CH_2Cl_2 solution with Dave Johnston Coal Fly Ash, SPE/MAS, Pd = 20 s, 300 scans

In a related experiment, technical grade pentachlorophenol in methylene chloride was added to Tennessee Valley Authority (TVA) coal fly ash to give a concentration of 20 mg of pentachlorophenol per gram fly ash. Figure 15a shows the ^{13}C SPE/MAS spectrum of technical grade pentachlorophenol, coal fly ash with sorbed pentachlorophenol (Figure 15b), and the mixture leached with water (Figure 15c). In Figure 15b, the ipso carbon of pentachlorophenol sorbed on the fly ash had shifted to 169 ppm from 148 ppm for the pentachlorophenol alone. This shift is quite significant and suggests that there is a sstrong bonding interaction of pentachlorophenol and the TVA coal fly ash.

Figure 15c shows the ^{13}C SPE/MAS spectrum of the pentachlorophenol adsorbed on the fly ash after leaching with water. An enhancement of the carbon with the OH attached is observed at ~ 170 ppm. The CP/MAS spectrum of the same sample (Figure 15d) shows an enhanced aromatic carbon intensity but no ipso carbon resonance. These spectra suggest that water molecules may be near carbon sites providing rapid relaxation of the carbon-spin state and a source of hydrogens for cross-polarization of carbon to be effective.

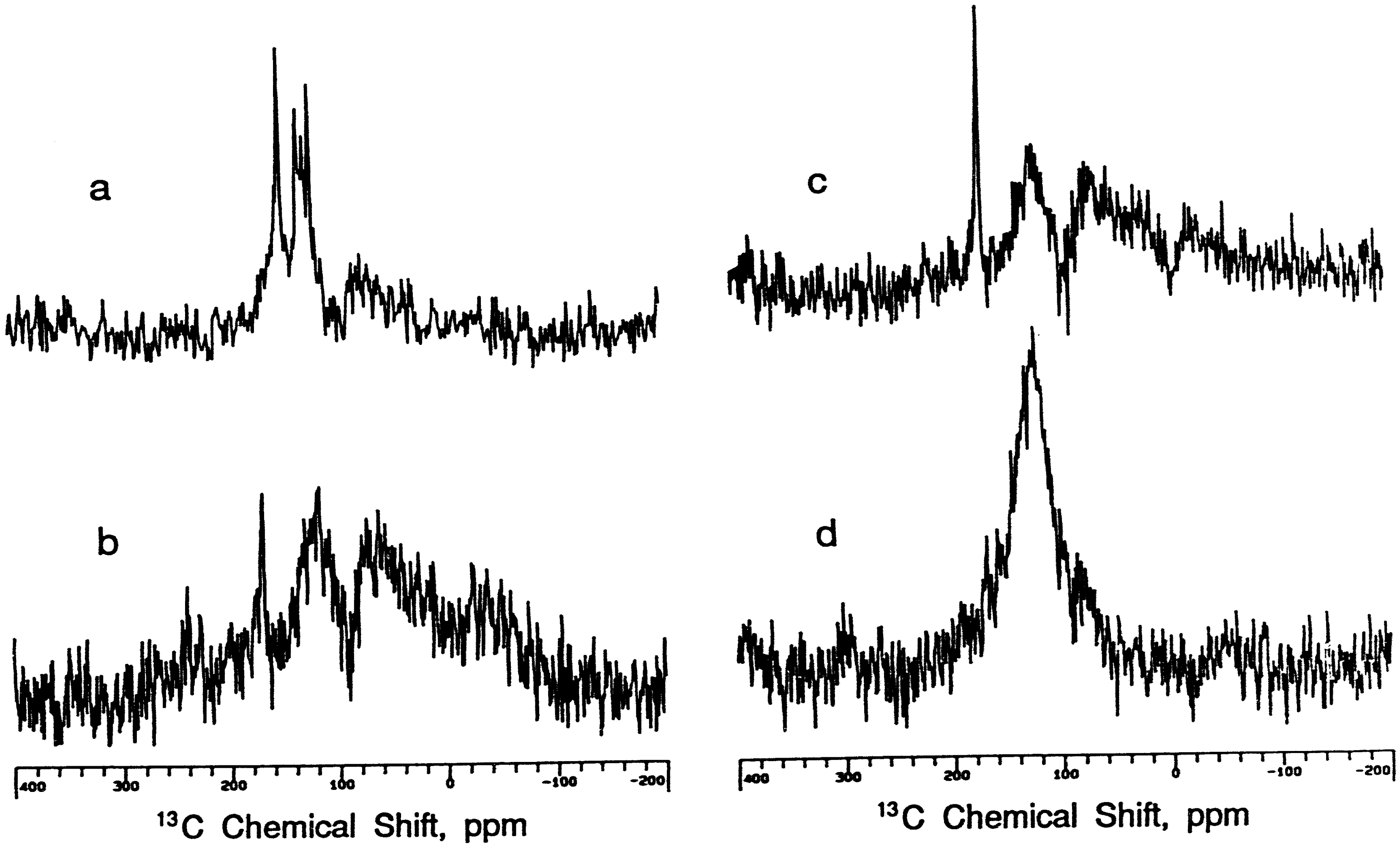


Figure 15. ^{13}C Solid-State NMR Spectra of Pentachlorophenol: (a) technical grade, SPE/MAS, Pd = 1 s, 43,000 scans; (b) adsorbed on TVA Coal Fly Ash, SPE/MAS, Pd = 1 s, 72,000 scans; (c) after leaching fly ash with water, SPE/MAS, Pd = 1 s, 72,000 scans; (d) after leaching fly ash with water, CP/MAS, ct = 5 ms, Pd = 1 s, 65,000 scans

CONCLUSIONS

Dave Johnston and Laramie River power plant coal fly ashes were characterized by elemental, X-ray, and ^{29}Si NMR analyses. These fly ashes differ significantly in their chemical and mineral composition. Although this study on adsorption isotherms and ^{13}C NMR spectra of adsorbed hazardous organic compounds was based on Dave Johnston coal fly ash, one experiment with the adsorption of pyridine on both types of ashes suggests that the Dave Johnston fly ash which contains a higher proportion of polysilicate anions, is a better adsorbent than the Laramie River fly ash. Many of the experiments carried out using the Dave Johnston fly ash need to be performed using the Laramie River fly ash. If this were to be done, it would be possible to correlate the chemical, mineral, and structural properties of the ashes with their adsorption capacity for hazardous organic compounds. This was outside the scope of the current project.

Adsorption isotherm studies of hydroaromatics and chlorobenzenes have shown that the Dave Johnston coal fly ash is less effective as an adsorbent than activated carbon by factors ranging from 3000 to 35,000. This conclusion was based upon comparisons of the solid-gas adsorption isotherm equilibrium for coal fly ash and the solid-liquid adsorption isotherm equilibrium. Additional investigation is needed to ascertain the degree of validity for comparing the adsorption isotherm data of two different phase equilibrium even though the adsorption process in both cases depends on the monolayer coverage model of the adsorbent.

Solid-liquid phase adsorption isotherm studies were conducted using pyridine, pentachlorophenol, naphthalene, and 1,1,2,2-tetrachloroethane in aqueous solution sorbed on Dave Johnston coal fly ash. The results were compared to the adsorption capacity of activated carbon. The adsorption capacity of the four compounds on the fly ash was found to be less than that reported for activated carbon. The difference in the adsorption capacity for pyridine and tetrachloroethane on fly ash and activated carbon was found to be less than a factor of 10. However, for pentachlorophenol and naphthalene, the factor was found to be between 200 and 400. Clearly, the Dave Johnston coal fly ash is a relatively good adsorber of organic hazardous compounds of the type studied, but not as effective as activated carbon.

Solid-state ^{13}C NMR studies were conducted in an effort to determine directly the adsorbed organic compounds on coal fly ash and to measure the strength of the bonding interaction between coal fly ash and the organic compound adsorbed. It is possible to observe the ^{13}C NMR resonances of the adsorbed compounds on fly ash with the use of: (1) a jumbo probe (~ 2.5 g of sample) and (2) a long pulse delay time (120 s or longer) to compensate for long relaxation times. The most successful experiments were those using single pulse excitation. However, such experiments take a considerable amount of time to perform. The resulting data, however, should be quantitative. ^{13}C cross-polarization experiments are most successful for those types of compounds having hydrogens. The experiments are less time consuming. However, the optimum contact time must be determined for each compound.

Because the fly ash contains considerable amounts of paramagnetic impurities, the observed resonances can be broadened and the chemical shift of the carbon resonance ill-defined. This will preclude any effort to determine bonding strength for some adsorbed species. It has been observed, however, that the ^{13}C chemical shift of the phenolic carbon in pentachlorophenol when adsorbed on coal fly ash, shifted downfield relative to its position in the "free" solid state. The magnitude of this shift should be directly related to the bonding strength.

Additional solid-state NMR experiments are needed to properly evaluate the technique as a means to study directly the adsorption properties of organic hazardous compounds.

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DISCLAIMER

Mention of specific brand names or models of equipment is for information only and does not imply endorsement of any particular brand.

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