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Multinuclear NMR Approach to Coal Fly Ash Characterization

Topical Report

Daniel A. Netzel

September 1991

Work Performed Under Contract No.: DE-FC21-86MC11076

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
University of Wyoming
Western Research Institute
Laramie, Wyoming

MASTER

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SUMMARY

This report describes the application of various nuclear magnetic resonance (NMR) techniques to study the hydration kinetics and mechanisms, the structural properties, and the adsorption characteristics of coal fly ash. Coal fly ash samples were obtained from the Dave Johnston and Laramie River electric power generating plants in Wyoming.

Hydrogen NMR relaxation times were measured as a function of time to observe the kinetics of hydration for the two coal fly ashes at different temperatures and water-to-cement ratios. The kinetic data for the hydrated coal fly ashes were compared to the hydration of portland cement. The mechanism used to describe the kinetic data for the hydration of portland cement was applied, with reservation, to describe the hydration of the coal fly ashes. The results showed that the coal fly ashes differ kinetically from that of portland cement and from each other. Consequently, both coal fly ashes were judged to be poorer cementitious materials than portland cement.

Silicon-29 NMR spectra were obtained for the anhydrous and hydrated coal fly ashes. Spectra of the anhydrous coal fly ashes show that the Dave Johnston coal fly ash contains more silicates in the higher coordination units than the Laramie River coal fly ash. The dominate specie in the Dave Johnston coal fly ash was quartz, whereas monomeric silicate anions were the dominate species in the Laramie River coal fly ash. The greater concentration of silicate anions of low coordination units in the Laramie River coal fly ash may account for its better cementitious properties relative to the Dave Johnston coal fly ash. Cross-polarization/magic angle spinning (CP/MAS) experiments were conducted on the hydrated coal fly ashes. Signals were not observed for the two coal fly ashes, indicating either that water was not in a rigid environment in close proximity to the silicon atoms within the silicate structure or that the signals could not be observed because of the high iron content in each coal fly ash.

Carbon-13 NMR CP/MAS spectra were obtained for the anhydrous coal fly ashes in an effort to determine the type of organic species that may be present, either adsorbed on the surface or entrained. A broad resonance peak was observed in the aromatic region of the spectrum for each coal fly ash and assigned to residual char. Elemental carbon is not detected by this method.

Of environmental interest is the adsorption properties of coal fly ash with its active surface sites. The carbon-13 NMR spectra were obtained for the anhydrous coal fly ashes after saturation with pyridine vapors. The carbon-13 signal due to pyridine could not be detected, indicating little or no adsorption of pyridine. If the surface of the coal fly ashes consist mainly of Brönsted acid sites, pyridine is not basic enough to be adsorbed onto the surface.

INTRODUCTION

Fly ash is a by-product from the combustion of coal. The 1985 annual United States production was estimated to be about 1×10^8 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 not being used and its availability throughout the country and worldwide has initiated research for new uses of fly ash for commercial and industrial applications.

Two new areas of applicability for fly ash are: (1) as a stabilizing agent for soils and (2) as an adsorbent for organics. 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. The cementing potential of coal fly ash appears to be related to the formation of various hydrated silicates and aluminates. However, the actual cementing mechanisms have yet to be identified.

Little is known of the 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. However, the inability to adequately predict the performance of ash-enhanced cement and concrete remains an impediment to its greater use.

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 have significantly different effects on the properties of concrete, the durability of pavement subgrade, and the stability of soil embankment. 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 properties of fly ashes. X-ray diffraction has been used to characterize crystalline minerals, but cannot be used to study minerals that are amorphous. Even with crystalline minerals using X-ray diffraction (White and Case 1990), difficulties are encountered in ascertaining the general characteristics for fly ash material.

It is possible, however, to chemically characterize solid materials and to investigate reactions in the solid state 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 single-pulse excitation and cross-polarization/magic angle spinning (SPE/MAS and CP/MAS, respectively), and hydrogen spin-lattice relaxation. These techniques have been used to study coal pyrolysis residue (Wilson et al. 1986), coal minerals under combustion-related conditions (Burchill et al. 1990 and Barnes et al. 1986), and the hydration of portland cement (Schreiner et al. 1985 and Al-Dulaÿan et al. 1990). However, the NMR techniques have not been extensively applied to the study of fly ashes (Kocuvan et al. 1979).

The primary objective of this investigation was to obtain preliminary NMR data on coal fly ashes. The secondary objectives of this study were threefold: (1) to investigate the hydration kinetics and mechanism of coal fly ashes using hydrogen-1 (^1H) NMR spin-lattice relaxation time spectroscopy, (2) to characterize the silicate and aluminosilicates in fly ashes from their silicon-29 (^{29}Si) NMR spectra, and (3) to identify the carbon-type composition and adsorption characteristics of the ashes using carbon-13 (^{13}C) NMR spectroscopy.

EXPERIMENTAL

Sample Source

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 mined in the Powder River Basin of Wyoming.

Portland Cement which was used to establish instrumental conditions and for modeling coal fly ash chemical behavior, was obtained from the Mountain Cement Co., Laramie, Wyoming. The cement was a low alkali Type I-II.

Sample Preparation and Reagents

The coal fly ash and portland cement samples were used as received for most experiments. The hydrated coal fly ash and portland cement samples used in the ^{29}Si study were the same samples used in the NMR relaxation studies of the hydration process. In experiments where the coal fly ash samples were dried, the drying was done at a temperature ranging from 110° to 120°C (230° to 248°F) for 24 hours and at barometric pressure between 580 and 590 mm of mercury.

In an attempt to remove iron from the coal fly ash samples, 6N HCl (J.T. Baker analyzed reagent) and 0.5 M oxalic acid (J.T. Baker analyzed reagent) were used. Silica gel (Grace Davison) used in the adsorption experiments was grade 62 and activated using a temperature of 265°C (509°F) for 15 hours (Hirsch et al. 1972). Pyridine (E.M. Science) for ^{13}C CP/MAS adsorption experiments was used as received.

Instrumentation

An IBM PC-20 spectrometer with a fixed magnetic field of 0.47 T and a frequency field of 20 MHz for hydrogens was used. The temperature of the magnet and probe assembly was held constant at 40° ± 0.01°C (104° ± 0.02°F). For room temperature (19°C (67°F)) experiments, the sample was inserted into the probe and the measurement of the spin-lattice relaxation time (T_1) was made in less than 5 minutes. Because of the amount of sample (0.5 g), it was assumed that temperature effects on T_1 were small. A 7.5-mm variable-temperature solid/liquid probe was used, but it was modified with a 1-cm Teflon™ spacer in the bottom of the probe assembly. This spacer was added to ensure that the sample was within the 20-mm coil height when it was placed in a 7.5-mm flat-bottom NMR tube. The spectrometer was operated in the phase-sensitive detector mode. The number of transients per pulse sequence to ensure a good signal-to-noise ratio was 36, and the delay time between pulse sequences was set at 1 s.

The NMR inversion-recovery (π-τ-$\pi/2$) technique and an interactive, nonlinear, three-parameter curve fit were used to calculate the spin-lattice relaxation times, T_1, by

$$M_\tau = M_\infty(1-\theta e^{-\tau/T_1})$$

where, M_τ is the magnetization intensity at a pulse delay of τ, τ is the pulse delay time between π and $\pi/2$ pulses, θ is the flip angle, and M_∞ is the magnetization intensity at infinite τ. It should be noted that with this technique, the observed magnetization is due to all hydrogen types present in the sample.

To validate the instrumental and operational conditions used to obtain T_1 values for the different coal fly ash samples, the T_1 value of water was determined. The T_1 value of deionized water at 40°C (104°F) has recently been reported by Schmidt et al. (1986) using a PC-20 spectrometer. Our value of 3.98 s compares favorably with their value of 3.84 ± 0.02 s.

^{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 (SPE) and cross-polarization (CP) with magic-angle spinning (MAS) and high-power ^1H decoupling. A 12.5-mm-diameter zirconia bullet spinner was used. Spinning rates were between 3.5 and 3.6 kHz. A total of 60,000-90,000 acquisitions (acq) were collected for the CP/MAS spectra. Other ^{13}C CP/MAS NMR parameters were a 90° pulse width of 6.5 µs, contact times (ct) of 1 ms and 5 ms, and a pulse delay (pd) of 1 s. For the SPE/MAS technique, a pulse delay of 10 s was used and 900 acquisitions were accumulated. 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

Elemental and Mineral Composition of Coal Fly Ash

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 natural 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. 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.

^{1}H NMR Relaxation Investigation of the Hydration of Coal Fly Ash

Portland cement was used as a model for studying the hydration of coal fly ash because: (1) the molecular structural changes that occur during the hydration have been studied extensively (Al-Dulaÿan et al. 1990; Barnes et al. 1985; Blinc et al. 1978; Clayden et al. 1984b; Groves and Rodger 1989; Lasic 1989; Parry-Jones et al. 1988; Parry-Jones et al. 1989; Schreiner et al. 1985), (2) its major component, tricalcium silicate has also been studied extensively (Clayden et al. 1984a; Lippmaa et al. 1982; Regourd 1987; Rodger et al. 1987; Rodger et al. 1988; Stade and Müller 1987), and (3) because the mechanism during the hardening of cement is generally understood (Blinc et al. 1978; MacTavish et al. 1985; Schreiner et al. 1985; Czermin 1980; Lea 1971; Stuble and Brown 1987). Portland cement is essentially a mixture of tricalcium (54%) and dicalcium (19%) silicates with small amounts of tri and tetracalcium aluminates (15%) (Schreiner et al. 1985). Table 3 lists the oxide composition of a typical portland cement (Schreiner et al. 1985) and the oxide composition of the two coal fly ashes. For pozzolanic materials, such as coal fly ash which contains numerous minerals (Table 2) and most of which alone are not pozzolanic in nature; the effects of these impurity minerals on the structural changes and hydration mechanism are not adequately known or understood.

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%
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%.

The hydration process for both portland cement and the two coal fly ash materials was followed by observing the changes in the water ^1H NMR spin-lattice relaxation times as a function of time, water-to-cement ratio (w/c), and temperature. Changes in the relaxation times are attributed to changes in the mobility of the water molecules during the hydration process. For highly mobile water molecules, ^1H relaxation times are long. For water molecules having some restricted motion, the ^1H relaxation times are short. However, for water molecules that are completely immobile, such as water of hydration in crystals, the ^1H spin-lattice relaxation is again very long (Schreiner et al. 1985).

Table 2. **Mineral and Chemical Composition of Portland Cement[a] and Coal Fly Ash[b]**

Mineral	Chemical Composition	Coal Fly Ash Source		Portland Cement, wt %
		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		6
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			54
	Ca_2SiO_4			19
	$Ca_3Al_2O_6$			9

[a] Schreiner et al. 1985

[b] Brown 1991

Table 3. Oxide Composition of Portland Cement and Coal Fly Ash

Oxide	Portland Cement[a], wt %	Coal Fly Ash Source[b] Dave Johnston Power Plant, wt %	Coal Fly Ash Source[b] Laramie River Power Plant, wt %
CaO	63.68	13.6	24.2
SiO_2	20.94	39.1	27.4
Al_2O_3	4.60	36.5	29.5
MgO	2.33	2.6	5.4
Fe_2O_3	2.05	5.6	8.2
Na_2O	0.52	0.2	1.2
TiO_2	0.17	-	-
SrO	0.14	0.1	0.4
P_2O_5	0.12	0.6	1.1
H_2O	0.00	-	-
SO_3	3.89	-	-
LOI[c]	1.05	-	-
Free CaO	0.60	-	-
K_2O	-	1.6	2.0
BaO	-	0.2	0.6

[a] Schreiner et al. 1985

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

[c] Loss on ignition

Portland Cement

Figure 1 shows the hydration of portland cement as a function of time and for w/c ratios of 0.4 and 0.6, and for temperatures of 24° and 40°C (75° and 104°F). The hydration process was followed for nearly 200 hours, after which changes in the relaxation times become very small. Near maximum strength for portland cement is reached after 28 days (672 hours) (Parry-Jones et al. 1989). At the near maximum strength of the cement, the water molecules which are not part of a rigid hydrate structure, are now much less mobile than initially and, thus, the ^1H relaxation time of water is very short.

Water at 40°C (104°F) has a ^1H spin-lattice relaxation time of about 4 s. When added to portland cement, the relaxation time drops rapidly to a value ranging from 20 to 40 ms depending on the water-to-cement ratio and temperature (Figure 1). For high values of the w/c ratio, water is less tightly bound than for systems in which the w/c ratio is smaller, resulting in a longer ^1H relaxation time. As might be expected, an increase in temperature from 24° to 40°C (75° to 104°F) accelerate the hydration process for portland cement and, thus, a shorter ^1H relaxation time is observed.

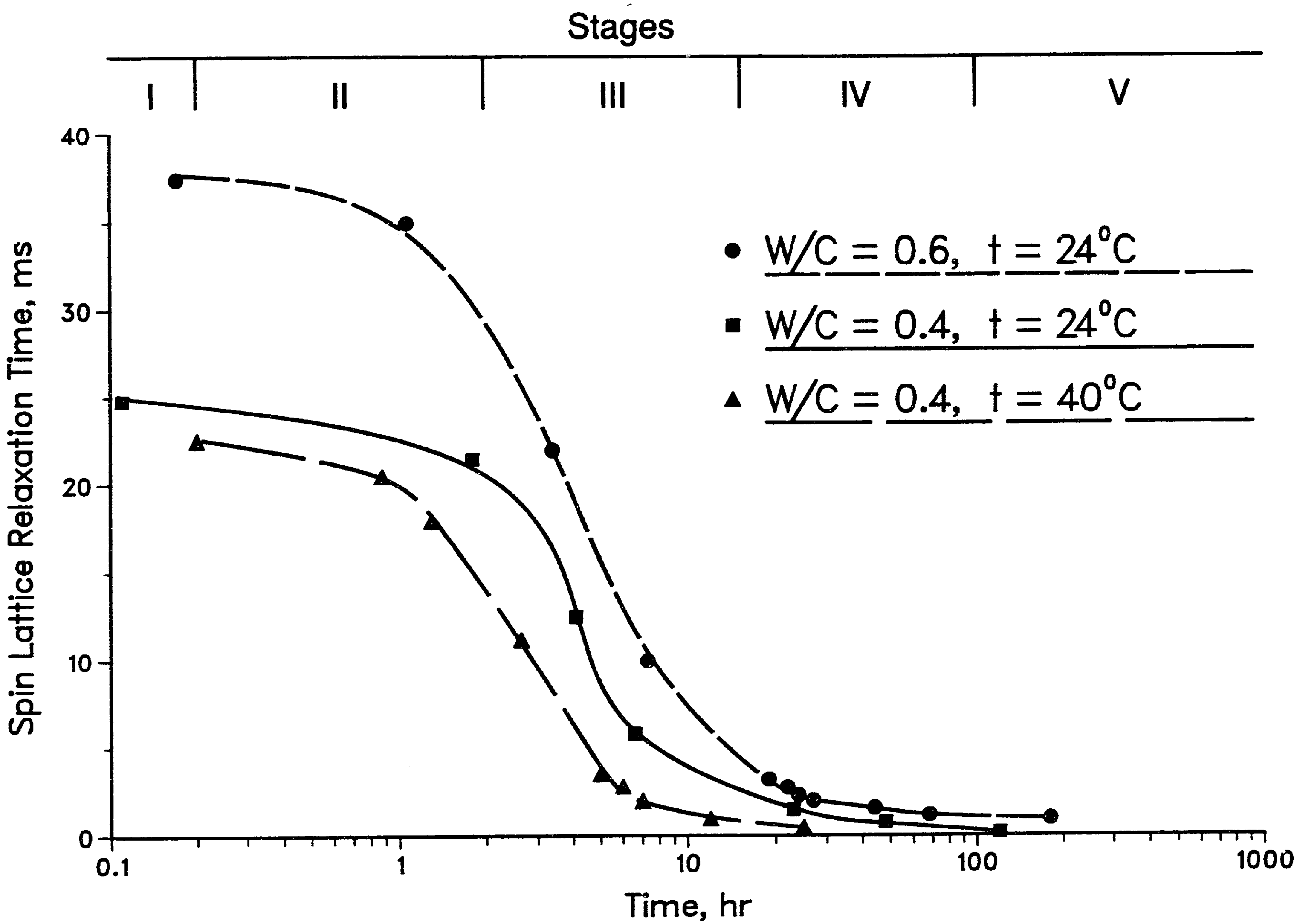

Figure 1. ^1H Spin-Lattice Relaxation Time Versus Time for the Hydration of Portland Cement

The molecular structural changes during hydration of portland cement occur in five well defined stages (Lasic 1989; Schreiner et al. 1985). Two theories, the delayed-nucleation theory (Young 1972) and the protective-layer theory (Double and Hellawell 1976), have been developed to explain the chemical reactivity during the various stages.

Stage I. 0.0 to 0.2 Hours. The initial reaction of water with cement is rapid and produces a gelatinous coating about the cement grains. This gelatinous coating acts as a semipermeable membrane allowing water and smaller ions to diffuse through it, while the larger silicate anions are prevented from leaving. The gel component (hydrated calcium silicate) is of variable composition that depends on the chemical composition of the cement and experimental conditions. The composition of the gel phase ultimately determines the extent of hardening of the cement. In this time domain there is a fast exchange between bonded water molecules near the solid surface and the free (or bulk) water. These highly mobile water molecules give rise to the long ^1H relaxation times initially observed.

Stage II. 0.2 to 2.0 Hours. This stage of hydration is represented by the relatively flat region (Figure 1), the dormant period, in which the ^1H relaxation time of water is not changing. However, the fast exchange of water between the gel and bulk phases becomes increasingly hindered by the continued formation of the gel structure. Toward the end of this stage of hydration, large concentrations of water molecules spend an appreciable amount of time very near the grain surface, resulting in a decrease in the relaxation time. The water within the gel coating continuously dissolves the cement grains.

According to the delayed-nucleation theory, the dormant period is the time needed for the Ca^{+2} ion to reach the supersaturation concentration level. The water phase within the gel structure must be supersaturated with Ca^{+2} ions in order for the crystallization of $Ca(OH)_2$ to begin. The protective-layer theory characterizes the end of the dormant period as the rupture of the gel membrane and the formation of tubular fibrils.

Stage III. 2.0 to 15 Hours. After 2 hours, the cement paste is still fluid and the water molecules are relatively mobile. However, during this stage crystallization of $Ca(OH)_2$ begins and the dissolution of tricalcium silicate increases, with eventual recrystallization into hydrated polymerized silicates. The concentration of mobile water decreases, resulting in an increase in bound water characterized by a shorter relaxation time. The fibrils from different grains eventually interlock and the cement paste begins to develop rigidity.

Stage IV. 15 to 100 Hours. The reactions that were occurring in Stage III come to near completion in Stage IV. Most of the water is now bound in three phases: (1) in a solid-like gel structure, (2) in micropores and interlayers of the silicate crystals, and (3) in silicate hydrates and $Ca(OH)_2$.

Stage V. 100 Hours and Beyond. Hydration of dicalcium silicate occurs at this stage. This reaction is much slower than the hydration of tricalcium silicate. In addition, structural changes continue to occur in the calcium silicate hydrate gel and recrystallization and polymerization of the silica continue to take place at a much slower rate.

Coal Fly Ash

Figure 2 shows the change in the ^1H spin-lattice relaxation time of water during the hydration of the Dave Johnston Power Plant coal fly ash. Also shown are the effects of the w/c ratio and temperature on the hydration process. The coal fly ash hydration process was observed over the four stages associated with the hydration of portland cement. With a w/c ratio (where w/c now represents the ratio of water to fly ash) of 0.6 at a temperature of 24°C (75°F), the dynamics of the hydration process for the fly ash appear to be similar in all stages to portland cement (Figure 1). However, at a w/c ratio of 0.4 and at temperatures of 24° and 40°C (75° and 104°F) the dynamics of the hydration process changes considerably from that of portland cement during Stage II through Stage IV.

The mobility of the water molecules as it relates to the initial change in the magnitude of the ^1H relaxation time after mixing fly ash with water (Stage I) suggests that a fluid gelatinous material may have formed, encapsulating the grains of the fly ash in a manner similar to that observed for the hydration of portland cement.

The dormant stage (Stage II) for the Dave Johnston coal fly ash (Figure 2, w/c = 0.4, t = 24°C) appears to last up to 20 hours when compared to portland cement, suggesting that it takes much longer to achieve supersaturation of Ca^{+2} ion. Stage III is also exceedingly slow, beginning at 20 hours and lasting to 50 hours after the initial mixing of the coal fly ash with water. If the mechanism for the hydration of fly ash follows that of portland cement, it is at this stage that $Ca(OH)_2$ begins to crystallize along with the possible formation of calcium silicate hydrate gel. These processes are proceeding at a much slower rate than observed for portland cement.

Stage IV may be similar to Stage IV of the hydration of portland cement, but begins at 50 hours rather than at 15 hours. This stage is an intermediate stage where the main reaction is becoming a diffusion-controlled hydration of the calcium silicates moieties.

The fact that Stage IV of the hydrated Dave Johnston coal fly ash has a ^1H relaxation time considerably longer than observed for hydrated portland cement in Stage IV suggests that the same level of hydration and crystallization has not been achieved for the fly ash. Visual examination of the hydrated coal fly ash product several hundred hours after mixing showed that the fly ash never hardened to the extent that portland cement had.

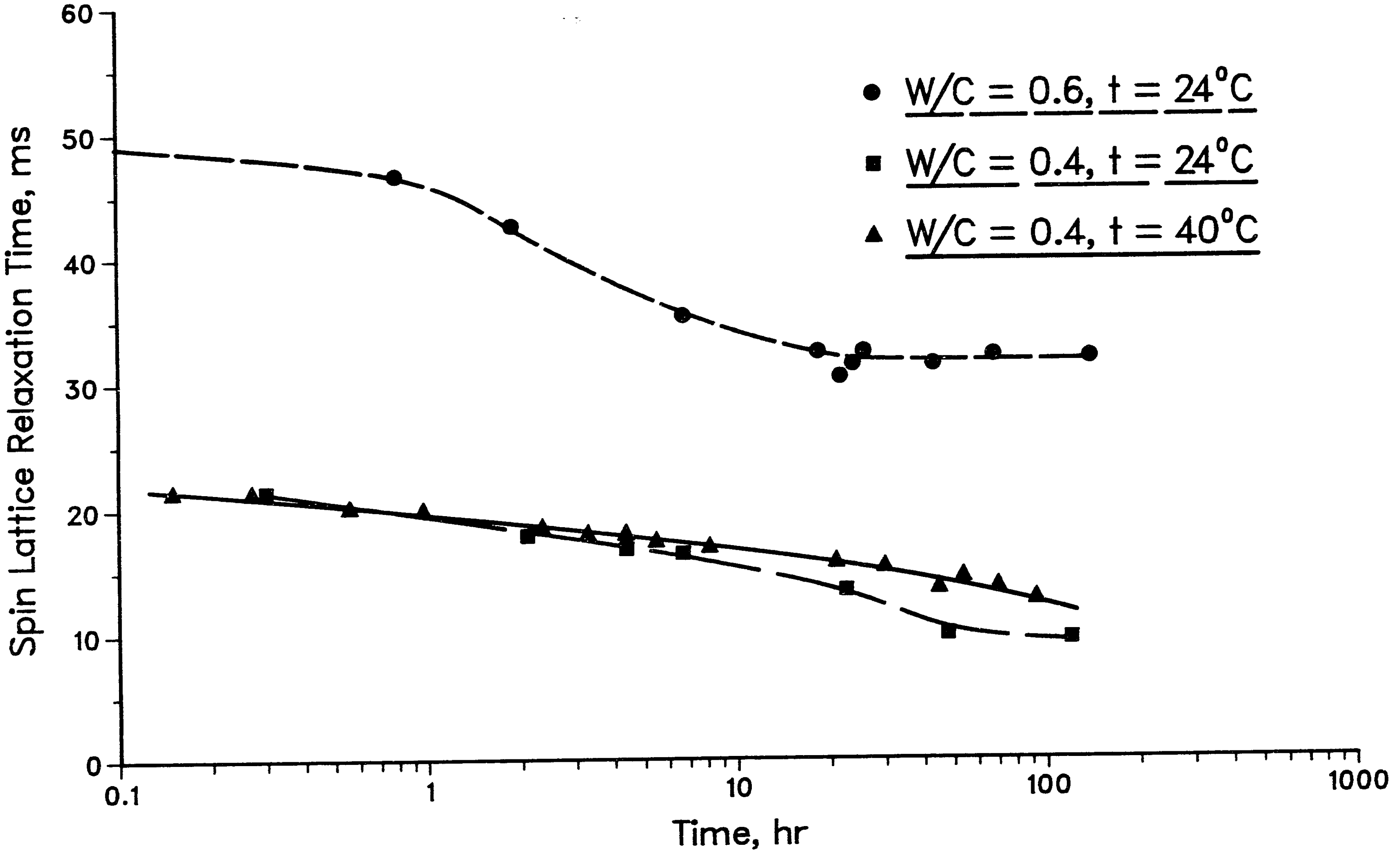

Figure 2. ^{1}H Spin-Lattice Relaxation Time versus Time for the Hydration of the Dave Johnston Power Plant Coal Fly Ash

Increasing the temperature to 40°C (104°F) for the water to fly ash ratio of 0.4 appears to prolong Stage II of the hydration process. A long dormant stage or incubation period (one or more weeks) is a known fact for reactions of coal fly ash in concrete (Fraay et al. 1989). It has been postulated that the fly ash behaves as a more or less inert material serving as a precipitation nucleus for $Ca(OH)_2$ and for calcium silicate hydrate gel originating from the cement hydration process.

Figure 3 shows the change in the ^1H spin-lattice relaxation time of water during the hydration of the Laramie River Power Plant coal fly ash for w/c ratios of 0.4 and 0.6 and at temperatures of 24° and 40°C (75° and 104°F) The hydration mechanism of this fly ash is considerably different from portland cement (Figure 1) and the Dave Johnston coal fly ash (Figure 2). Almost immediately after mixing, the ^1H relaxation time of water for the water to fly ash ratio of 0.6 and a temperature of 24°C (75°F) falls to a value near 20 ms. Both portland cement and the Dave Johnston coal fly ash immediately after mixing had spin-lattice relaxation time values near 50 ms. The rapid decrease observed for the water ^1H spin-lattice relaxation of the Laramie River coal fly ash may be due to the paramagnetic effect caused by the higher concentration of iron in the many different mineral components of this fly ash relative to the Dave Johnston coal fly ash. The Laramie River Power Plant coal fly ash appears to have the five stages of hydration in approximately the same time domain stages as discussed for the hydration of portland cement. This fly ash is known to set up fast and has some pozzolanic properties (Brown 1991).

By decreasing the Laramie River fly ash w/c ratio to 0.4 at a temperature of 24°C (75°F), the water ^1H relaxation time falls to approximately 7 ms within the first hour of mixing and remains almost constant over the next 100 hours. This behavior represents either an extremely long dormant period like that observed for fly ash in concrete (Fraay et al. 1989) or a rapid and near completion of the hydration process (Stages IV and V).

By increasing the temperature to 40°C (104°F) for a w/c ratio of 0.4, the ^1H relaxation time of water changes with a characteristic time domain function similar to but much less pronounced than that observed for portland cement. The fact that the relaxation time continues to decrease after 20 hours to a value of approximately 3 ms suggests that the hydration process for this fly ash at 24°C (75°F) is already in Stage IV. That is, the dormant stage for this fly ash is exceedingly short. This is confirmed by the fact that the hardening process was observed to be rapid (Brown 1991).

A comparison of the ^1H relaxation times and the hydration profile for the Dave Johnston and Laramie River power plants coal fly ashes and portland cement is given in Figure 4. The data suggest that the water ^1H relaxation time measurement may be a useful method for evaluating the potential cementation properties of different coal fly ashes.

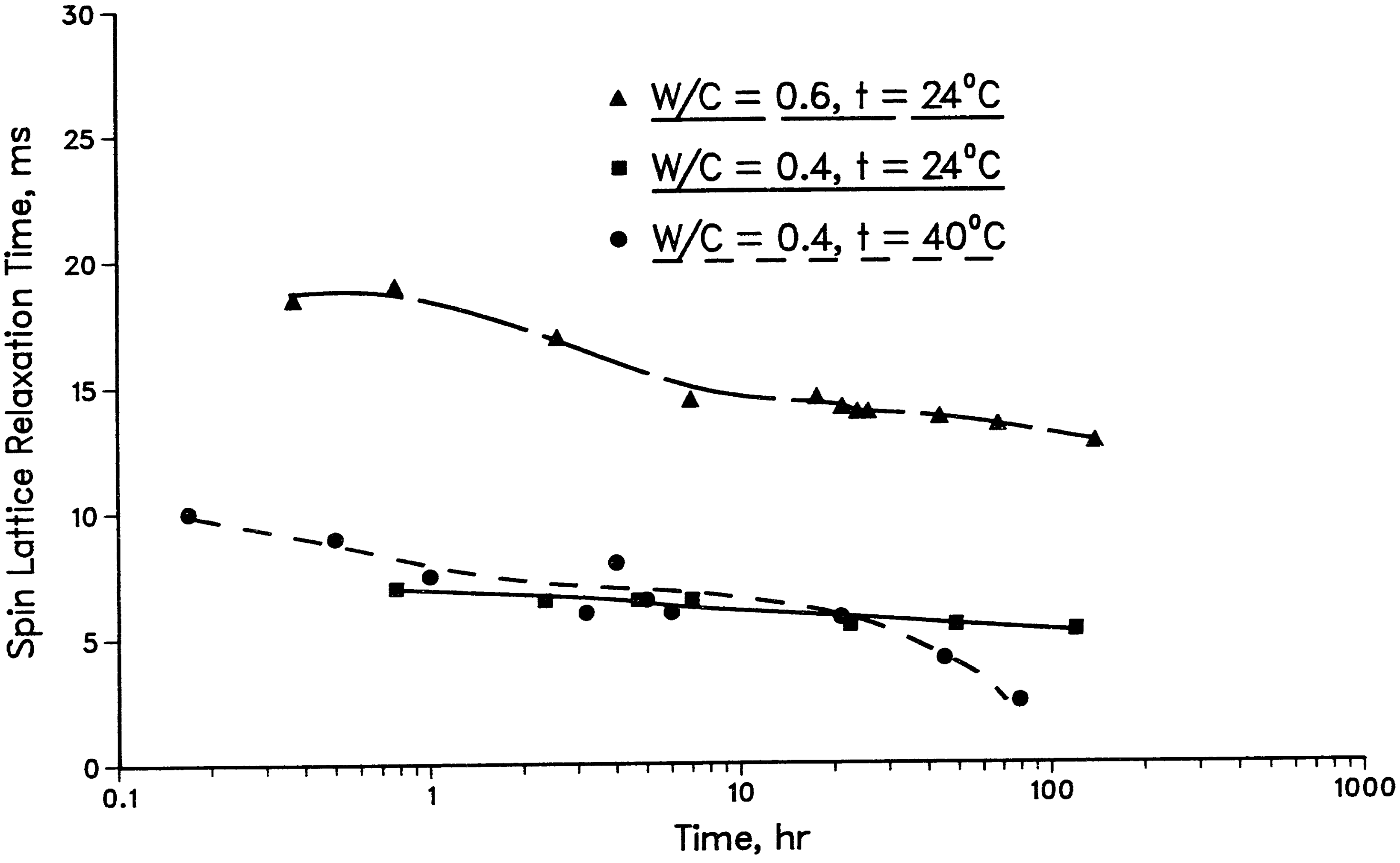

Figure 3. ^1H Spin-Lattice Relaxation Time versus Time for the Hydration of the Laramie River Power Plant Coal Fly Ash

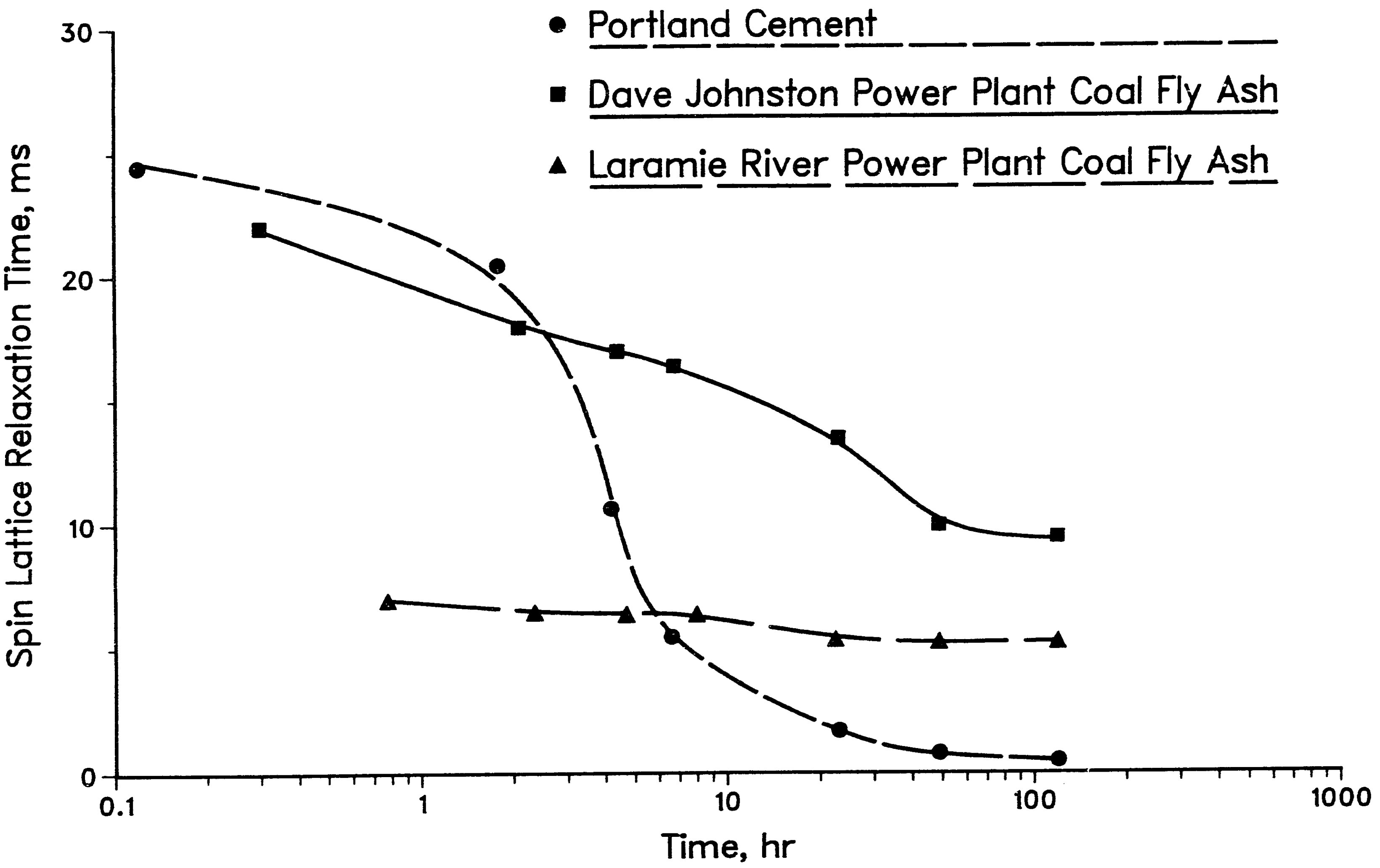

Figure 4. A Comparison of the Hydration Kinetics at w/c = 0.4 and t = 24°C for Portland Cement, Dave Johnston Power Plant Coal Fly Ash, and Laramie River Power Plant Fly Ash

^{29}Si NMR Investigation of the Hydration of Coal Fly Ash

The ease by which the solid-state ^{29}Si and ^{27}Al NMR spectra can be obtained make this technique ideally suitable for studying many types of silicate and aluminosilicate minerals (Englehardt and Michel 1987). ^{29}Si NMR has been extensively used to study the hydration mechanism of portland cement (Parry-Jones et al. 1989; Barnes et al. 1985; Al-Dulaÿan et al. 1990; Parry-Jones et al. 1988; Clayden et al. 1984b; and Groves and Rodger 1989) and tricalcium silicate (Rodgers et al. 1987; Lippmaa et al. 1982; and Clayden et al. 1984a). ^{27}Al NMR has also been used to a lesser extent to study the hydration mechanism of cement (Stade and Müller 1987; Luong et al. 1989; Greenslade and Williamson 1990).

The use of ^{29}Si and/or ^{27}Al NMR to study of coal fly ash is nonexistent. However, several papers discuss the use of ^{29}Si and ^{27}Al of 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).

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 5 gives the estimated ^{29}Si NMR chemical shift ranges for the various polymerized silicates and aluminosilicates.

Anhydrous and Hydrated Portland Cement

^{29}Si NMR measurements on portland cement were conducted to verify and optimize the instrumental parameters for observing the ^{29}Si resonance and to illustrate the effects of hydration on the ^{29}Si NMR signal. It was assumed that similar effects might be observed for the hydration of the two coal fly ashes used in this study.

The ^{29}Si NMR spectrum of anhydrous portland cement acquired using 244 single-pulse excitations is shown in Figure 6A. The resonance peak at -71.2 ppm from external reference TMS is due to the SiO_4^{-4} anions (Q^0) of di- and tricalcium silicate. Upon hydration, the intensity (concentration) of the monomeric anions decrease with the occurrence of two new resonances at -78.9 (Q^1) and -84.2 (Q^2) ppm due to the dimerization of the silicate anions (Figure 6B).

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

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

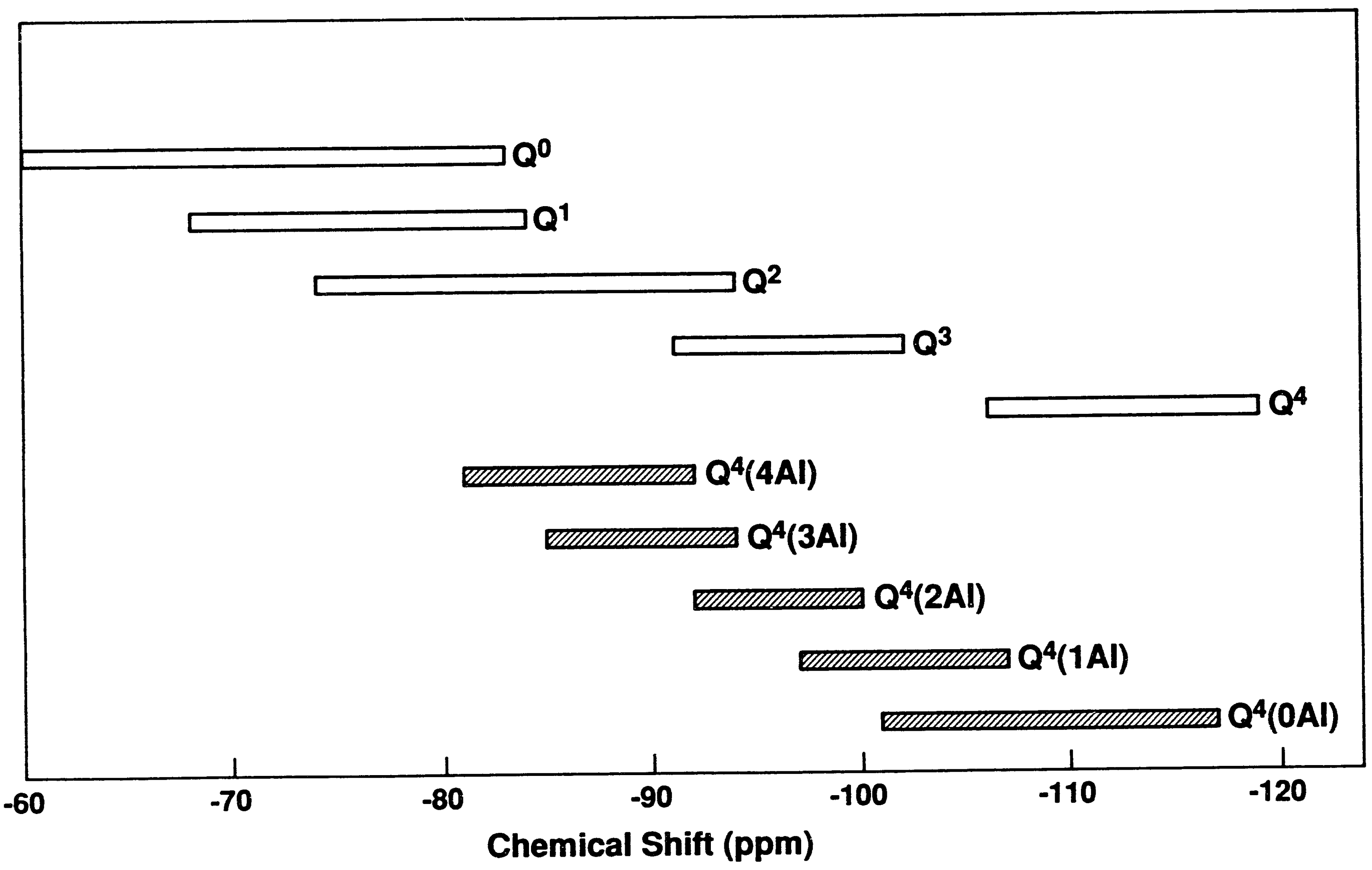

Figure 5. Approximate ^{29}Si Chemical Shift Ranges for Various Coordination States of Silicates and Aluminosilicates

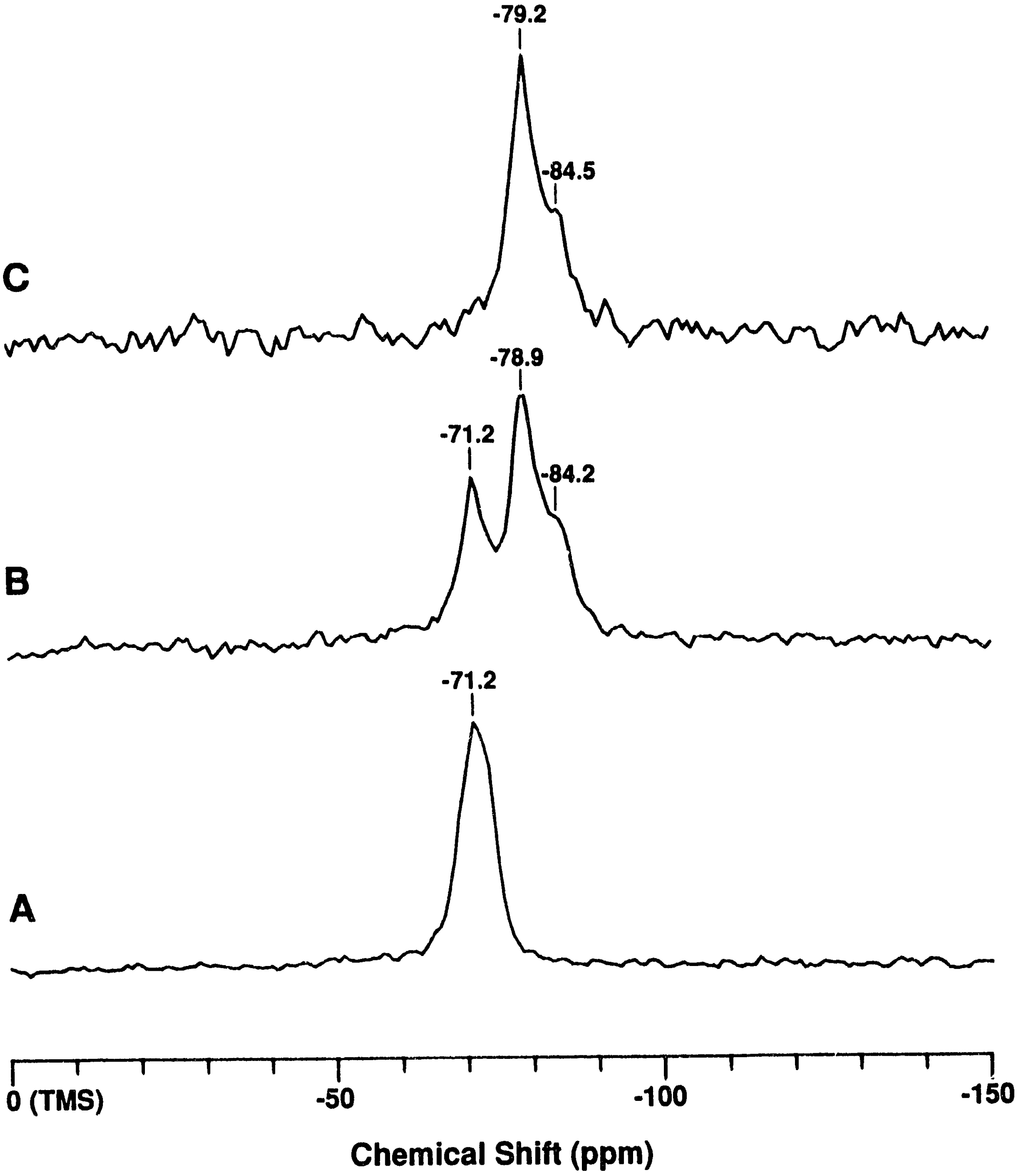

Figure 6. ^{29}Si NMR Spectra of: (A) Anhydrous Portland Cement, SPE/MAS, pd = 10 s, acq = 244; (B) Hydrated Portland Cement, SPE/MAS, pd = 5 s, acq = 720, w/c = 0.4, t = 24°C, 57 days into the Hydration Reaction; (C) Hydrated Portland Cement, CP/MAS, pd = 5 s, ct = 3 ms, acq = 3488, w/c = 0.4, t = 24°C, 68 days into the Hydration Reaction

By using the NMR technique of cross-polarization from ^{1}H to ^{29}Si, it can be shown that water is closely associated with the dimerized silicate anions. Figure 6C shows the ^{29}Si CP/MAS spectrum of the hydrated portland cement. The resonance signal corresponding to the monomeric silicate anions is not observed because ^{1}H from the water are not rigid enough to polarize the ^{29}Si atom. However, the ^{29}Si resonances due to the hydrated silicate dimers are clearly observed at -79.2 and -84.5 ppm, indicating that ^{1}H from the water molecules are in close proximity to the ^{29}Si atoms within the structure of the silicate anions.

Anhydrous and Hydrated Coal Fly Ash

The ^{29}Si NMR spectra of the anhydrous coal fly ashes from the Laramie River and Dave Johnston power plants are shown in Figure 7A and 7B, 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 (SSB) of the center band. These side bands are the result of magnetic susceptibility broadening (Oldfield et al. 1983) due to the high iron content.

The spinning side band intensities relative to the center band intensity are greater for the Laramie River (LR) coal fly ash than for the Dave Johnston (DJ) coal fly ash. This is because of the higher Fe to Si ratio (0.226 vs. 0.107) for the Laramie River fly ash. The high silicon content of the Dave Johnston (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 Dave Johnston ^{29}Si spectrum compared to 12,000 scans for 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 7A and 7B; 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, possibly, for resonances that appear at either edge of the chemical shift range. Chemical shift values shown in all the figures and listed in Table 5 are those of well defined resonance peaks and the center of the much less defined broad resonances.

The major difference 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

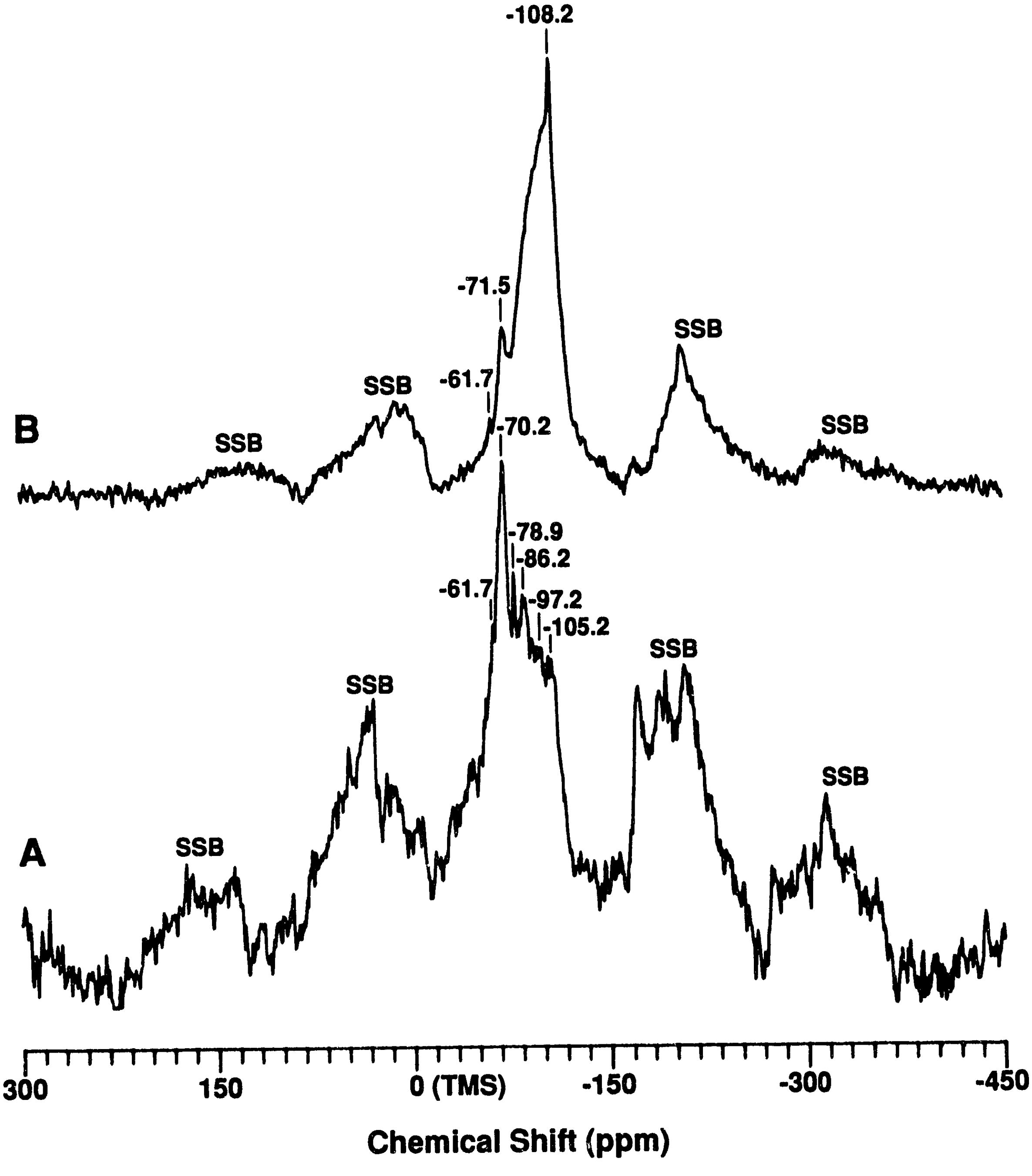

Figure 7. ^{29}Si NMR SPE/MAS Spectra of the Anhydrous Coal Fly Ashes from: (A) the Laramie River Power Plant, pd = 5 s, acq = 12,240; (B) the Dave Johnston Power Plant, pd = 10 s, acq = 6480

Table 5. ^{29}Si NMR Chemical Shifts and Coordination State Assignments for Portland Cement and Coal Fly Ash

Portland Cement		Dave Johnston Power Plant Coal Fly Ash			Laramie River Power Plant Coal Fly Ash				Silicate and Aluminosilicate Coordination State Assignment[b]
Anhydrous	Hydrated	Anhydrous	Hydrated	Acid Wash[a]	Anhydrous	Hydrated	Acid Wash[a]	Acid Wash[b]	
		-61.7	-61.7	-61.7	-61.7	-61.8	-62.2		Q^0
-71.2	-71.2	-71.1	-71.5		-70.2	-70.8	-72.8		Q^0, Q^1
	-78.9				-78.9	-77.0			Q^1
	-84.2		-88.3 BP[c]		-86.2 BP	-86.2 BP	-89.5		Q^2, Q^4(4Al)
			-99.6 BP	-102.2	-97.2 BP	-98.2 BP	-101.2	-103.2	Q^3, Q^4(1Al)
		-107.1	-108.3	-108.3	-105.2 BP	-106.6	-108.3	-109.9	Q^4, Q^4(0Al)

[a] 0.5 M Oxalic acid
[b] 6 N HCl
[c] BP = broad peak

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 all spectra, some to a greater extent than others, 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 from the spectrum of 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.

The single-pulse excitation ^{29}Si NMR spectra of the hydrated Dave Johnston and Laramie River coal fly ashes are shown in Figure 8. The spectra were obtained nearly 60 days after the initial mixing of the fly ash paste. The spectrum of hydrated portland cement is also shown for comparison in the figure.

The ^{29}Si spectra of the hydrated coal fly ashes are essentially the same as the spectra of the anhydrous materials (Figures 7A and 7B). That is, the number of observed resonances are the same with essentially the same chemical shifts (variation due to noise) and the same peak intensity ratios. No resonances are observed for the formation of hydrated silicates and/or aluminosilicates as observed for portland cement (-78.9 and -84.2 ppm). ^{29}Si cross-polarization experiments were conducted in an effort to detect any hydrated components in the hydrated coal fly ashes. No CP/MAS resonances were observed for either of the coal fly ashes under several different instrumental conditions. It is concluded that either the hydration of the coal fly ashes have not formed any hydrated species of the type that occurs for portland cement, or that the high iron content prevented any observation of the signal. Any hydrated silicates or aluminosilicates may have water molecules loosely bound and at a greater distance from the silicon atom of the silicate anions and, therefore, not detected by ^{29}Si cross-polarization experiments.

Loosely bound water in the hydration of the coal fly ash is also supported by the ^{1}H relaxation studies described previously. The spin-lattice relaxation times of the water ^{1}H in the coal fly ash pastes never reached the lower limit as that observed for the hydration of portland cement (Figure 4), which is known to have strongly coordinated water molecules.

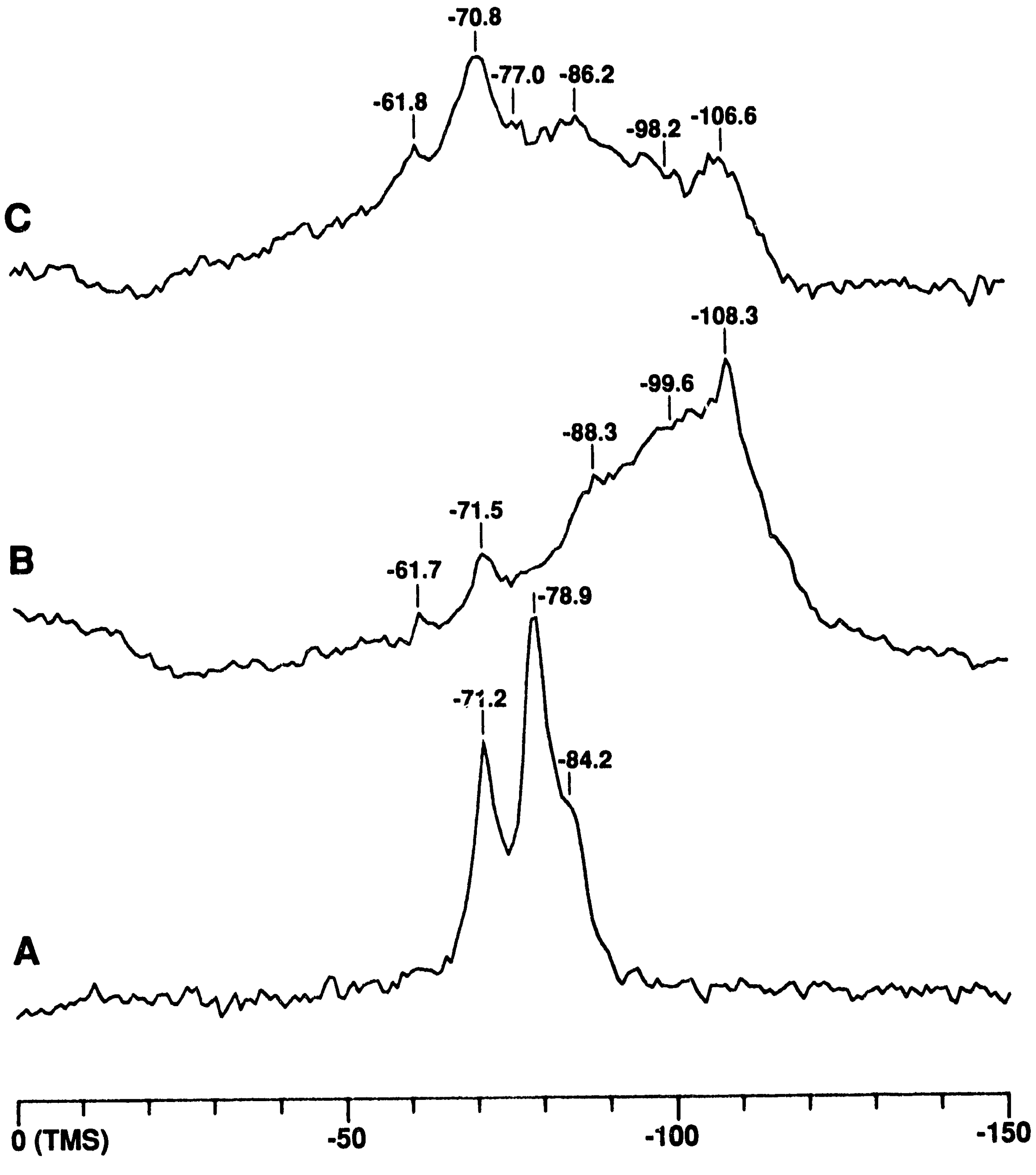

Figure 8. ^{29}Si NMR SPE/MAS Spectra of the Hydrated: (A) Portland Cement; (B) Dave Johnston Power Plant Coal Fly Ash, pd = 10 s, acq = 6480, w/c = 0.4, t = 24°C, 62 days into the Hydration Reaction; (C) Laramie River Power Plant Coal Fly Ash, pd = 5 s, acq = 15,840, w/c = 0.4, t = 24°C, 58 days into the Hydration Reaction

Treatment of Coal Fly Ash with Acids

The high iron content in the Dave Johnston and Laramie River power plants coal fly ashes is detrimental to many NMR experiments because of large spinning side bands and broadened signals with the loss of spectral resolution due to iron. In an effort to obtain better ^{29}Si spectra of the coal fly ashes the ashes were washed with 0.5 M oxalic and 6 N HCl acids to reduce or eliminate the iron contents. Figure 9A shows the ^{29}Si spectrum of the Dave Johnston coal fly ash after it was washed with 0.5 M oxalic acid. The acid treatment did reduce the SSB (not clearly shown in Figure 9A due to the expansion of the spectrum). Compared to the hydrated and anhydrous ^{29}Si spectra (Figures 9B and 9C) of the coal fly ash, the acid treatment may have either solubilized some of the silicate anion (Q^0) at -71.5 ppm and possibly anions of the type Q^1 and Q^2 or caused the anions to react with the formation of the more heavy branched Q^3 anions. The Mg containing silicate mineral at -61.7 ppm does not appear to be affected by the acid treatment.

The ^{29}Si spectrum of the Laramie River coal fly ash treated with 0.5 M oxalic acid is shown in Figure 10A. Because of the chemical shift range of the spectrum, the reduction of the spinning side band (not clearly shown) is due to the reduction of iron. The acid wash removed most of the silicate anion (Q^0) at -70.8 ppm. The anion species Q^2 and Q^3 are more clearly resolved in the spectrum relative to the hydrated and anhydrous spectra (Figures 10B and 10C). The Mg containing silicate mineral at -62.2 ppm is clearly resolved in the acid treated coal fly ash (Figure 10A).

Figure 11A shows the ^{29}Si spectrum of the Laramie River coal fly ash washed with 6 N HCl. The spinning side bands are completely eliminated because all of the iron has been removed. Not only has the iron been removed but also all silicate and aluminosilicate species having resonances downfield from -90 ppm have been removed. The silicate species at -103.2 (Q^3) is clearly resolved. The acid had no affect on the quartz mineral (Q^4) at -109.9 ppm. Treatment of the Dave Johnston coal fly ash with 6 N HCl completely destroyed the sample. Therefore, no attempts were made to record a spectrum.

^{13}C NMR Investigation of Coal Fly Ash

Residual Carbon

There has been relatively little effort in the investigation of the organic components in fly ash by NMR (Majid et al. 1989). Figures 12A and 12B show the ^{13}C CP/MAS spectra of the Dave Johnston and Laramie River power plant coal fly ashes, respectively. The signal-to-noise ratio for these spectra reflect the measured carbon content (1.3 wt % DJ and 0.3 wt % LR). Because these spectra were obtained by CP/MAS, the observed carbon signals are for those carbons that are in close proximity to hydrogen atoms. The spectra for the two coal fly ashes are featureless, having a broad resonance centered about the aromatic carbon region. This is to be expected, because any carbon remaining in the fly ash would most likely be unburnt carbon (not observed in NMR) (Shibaoka 1986) and aromatic carbon in various stages of char formation.

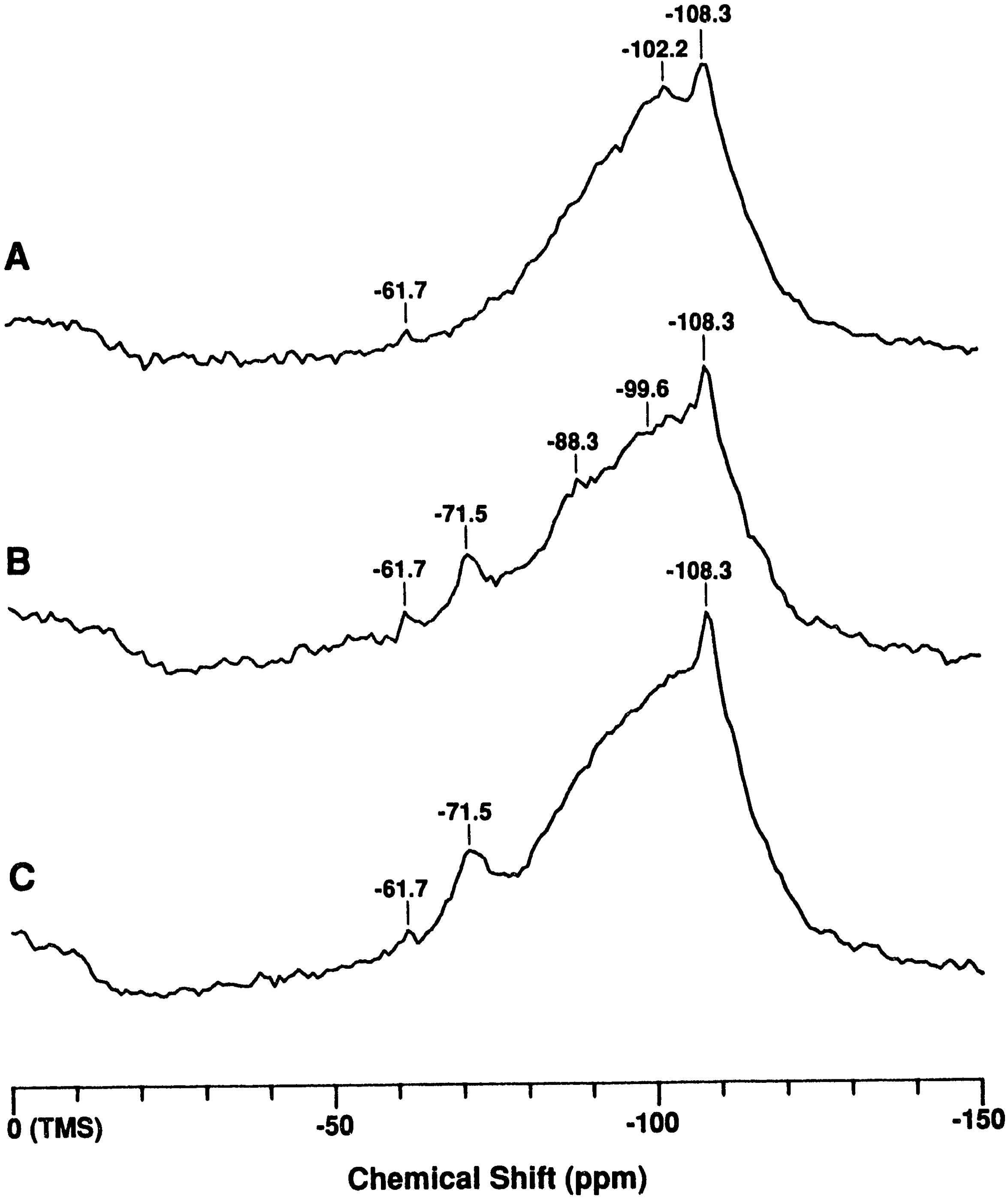

Figure 9. ^{29}Si NMR SPE/MAS Spectra of the Dave Johnston Power Plant Coal Fly Ash: (A) Washed with 0.5 M Oxalic Acid, pd = 10 s, acq = 6480; (B) Hydrated; (C) Anhydrous

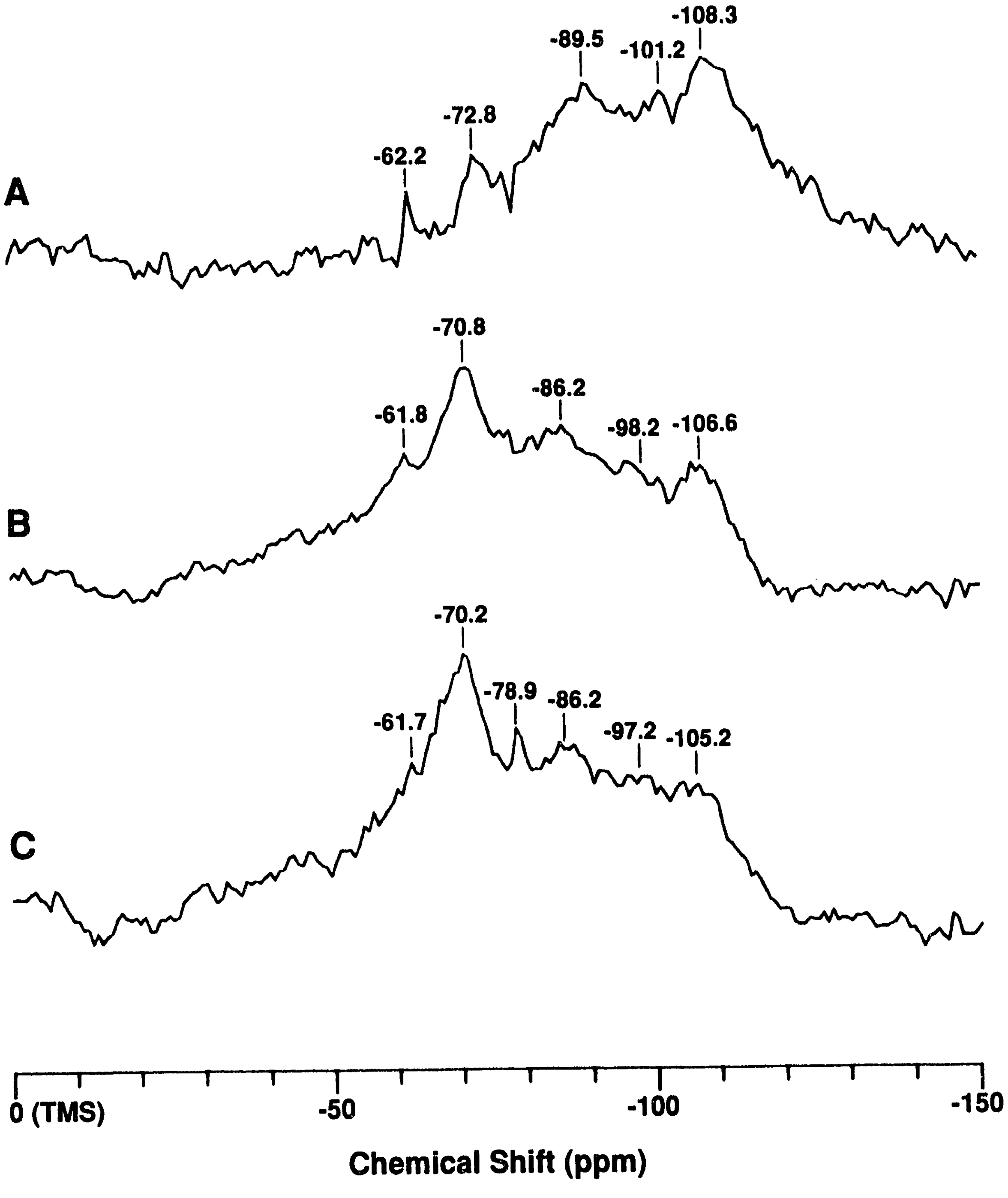

Figure 10. ^{29}Si NMR SPE/MAS Spectra of the Laramie River Power Plant Coal Fly Ash: (A) Washed with 0.5 M Oxalic Acid, pd = 10 s, acq = 6480; (B) Hydrated; (C) Anhydrous

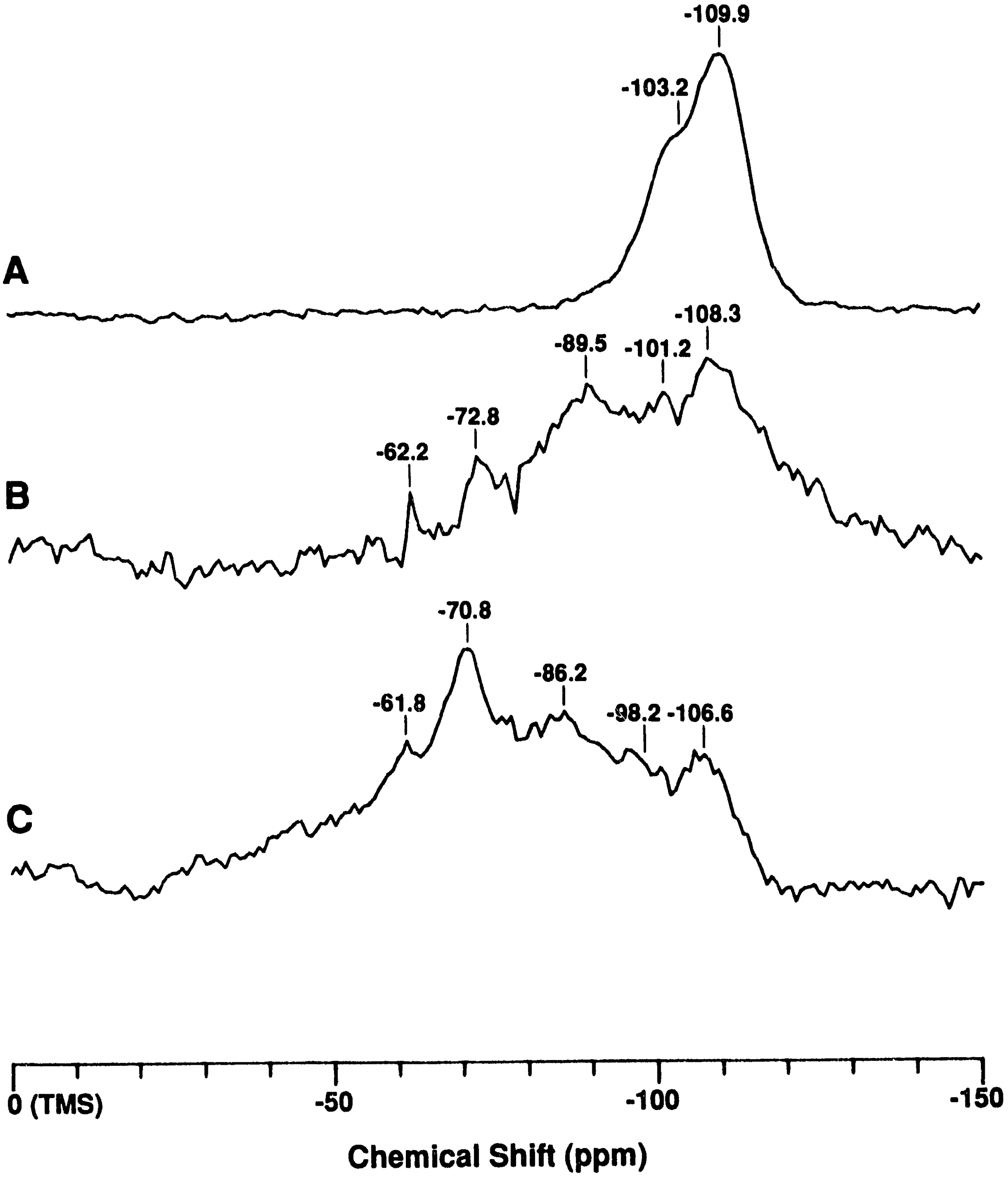

Figure 11. ^{29}Si NMR SPE/MAS Spectra of the Laramie River Power Plant Coal Fly Ash: (A) Washed with 6 N HCl; (B) Washed with 0.5 M Oxalic Acid; (B) Hydrated

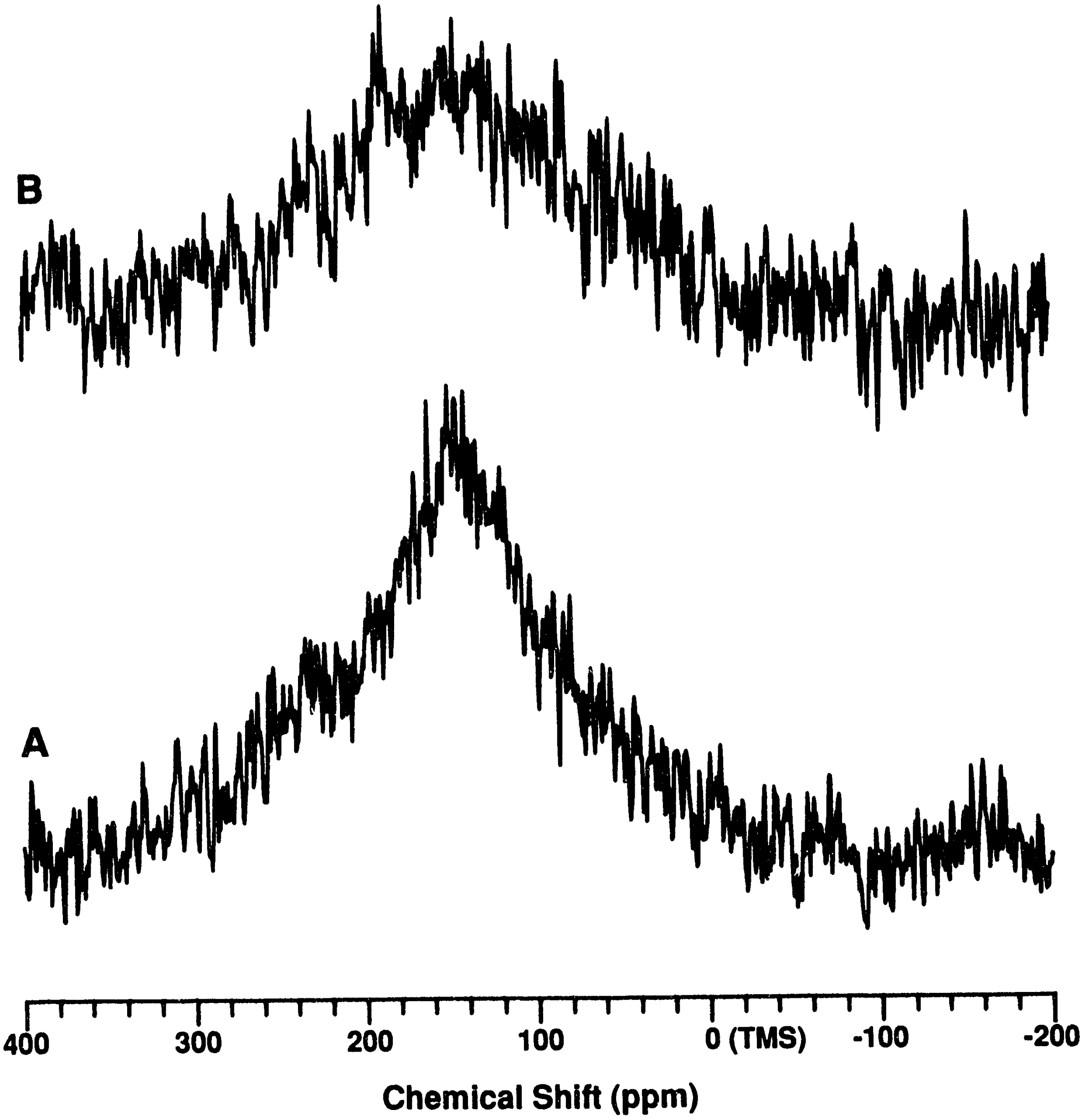

Figure 12. ^{13}C NMR CP/MAS Spectra of the Anhydrous Coal Fly Ashes: (A) Dave Johnston Power Plant, pd = 1 s, ct = 1 ms, acq = 79,200; (B) Laramie River Power Plant, pd = 1 s, ct = 1 ms, acq = 8640

Adsorption of Pyridine on Coal Fly Ash

Preliminary experiments were conducted to determine if coal fly ash readily adsorbs pyridine. The coal fly ash samples from the Dave Johnston and Laramie River power plants were subjected to pyridine vapor for one month. The ^{13}C CP/MAS spectra for the two coal fly ashes are shown in Figures 13A and 13B. The adsorption of pyridine onto the coal fly ashes was not observed. Any significant adsorption of the pyridine would give the spectrum shown in Figure 14. In this figure, silica gel was exposed to pyridine vapors for 16 hours. Similar results of pyridine adsorption onto silica-alumina were published by Maciel et al. (1983). Pyridine would not be adsorbed onto the surface of the fly ashes if their surfaces consisted mainly of Brönsted acid sites because pyridine is not basic enough (Clague and Alma 1989). Any Lewis acid sites on the surfaces of the fly ashes may have been preferentially occupied by water (Ripmeester 1983) even though the fly ashes were dried at 120°C for 15 hours before being exposed to pyridine vapors. In the investigation of aqueous solution adsorption of pyridine onto coal fly ashes, Lane (1991) found that very little adsorption occurs.

CONCLUSIONS

The ^{1}H spin-lattice relaxation studies of the hydration of the Dave Johnston and Laramie River power plant coal fly ashes have shown that the kinetics of hydration of the coal fly ashes differ considerably from that of portland cement and from each other.

The Dave Johnston coal fly ash remains in a dormant stage or induction period much longer than portland cement, whereas the Laramie River coal fly ash either has a very short dormant stage or a dormant stage exceeding 100 hours. A very short induction period is favored and is most likely based on reported observations. Neither coal fly ash achieves the same degree of hydration as found for portland cement. This is because of the extensive differences in chemical and mineral composition as determined by elemental analysis, X-ray spectroscopy, and ^{29}Si NMR spectroscopy.

The ^{29}Si NMR spectra of the coal fly ashes show major differences in the silicate and aluminosilicate anions content as well as the quartz content. In general, the Dave Johnston coal fly ash has more silicates in higher coordination units than the Laramie River coal fly ash. One of the reasons the Dave Johnston coal fly ash is a poor pozzolanic material may be because it has a high content of silicates in the higher coordination units and, thus, has limited sites for hydration and polymerization of the silicate anions. On the other hand, the Laramie River coal fly ash has a greater silicate anions content in the lower coordinate unit and, thus, more readily forms hydrated and polymerized silicate anions to give it some pozzolanic properties. However, CP/MAS experiments on the hydrated coal fly ashes have shown no indication of hydrate silicates or aluminosilicates. Acid washing of the coal fly ashes to remove the iron in an effort to improve the ^{29}Si NMR spectral resolution mostly transformed the coal fly ashes.

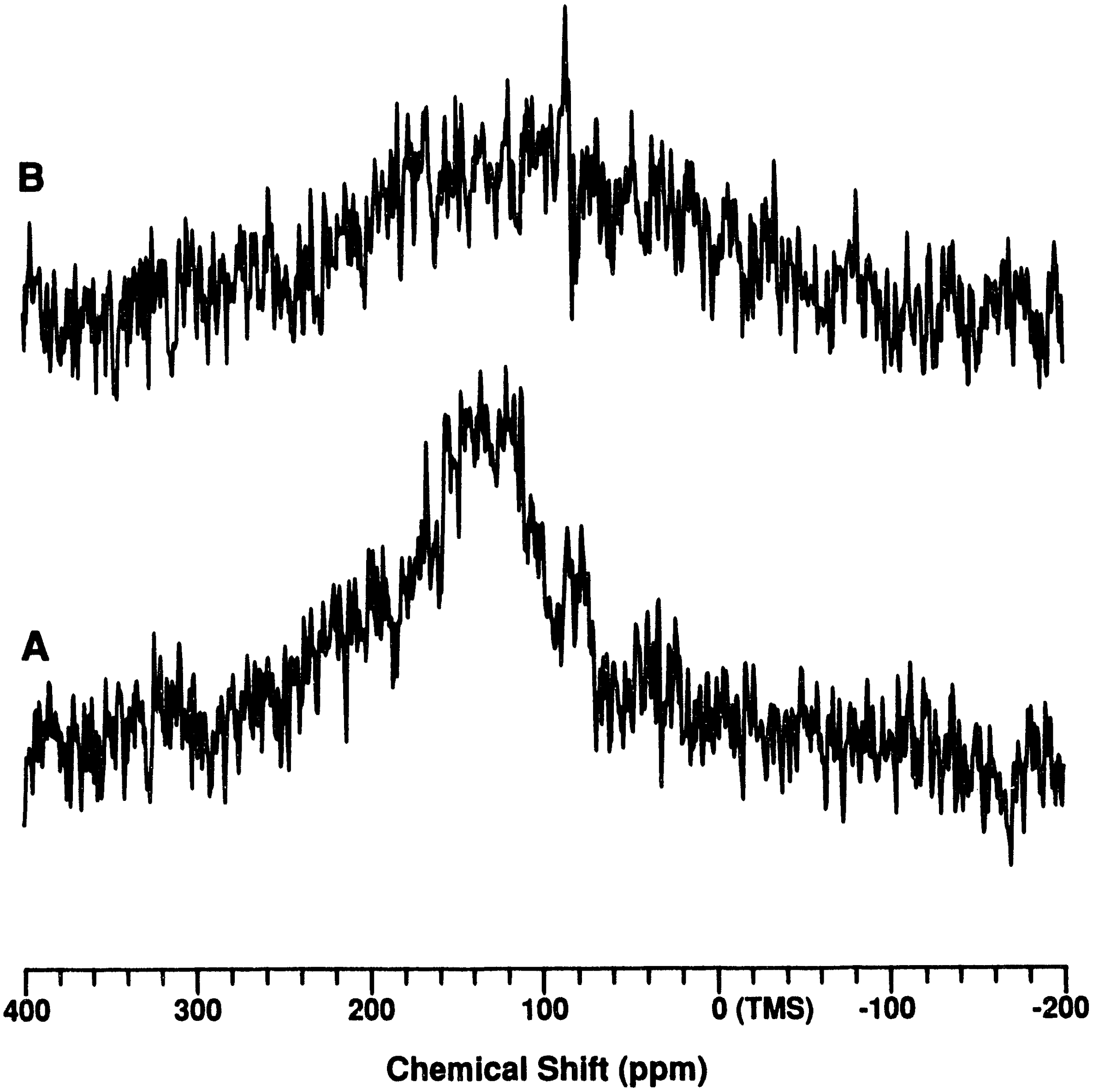

Figure 13. ^{13}C NMR CP/MAS Spectra of the Anhydrous Coal Fly Ashes Saturated with Pyridine Vapor: (A) Dave Johnston Power Plant, pd = 1 s, ct = 5 ms, acq = 64,800; (B) Laramie River Power Plant, pd = 1 s, ct = 5 ms, acq = 64,800

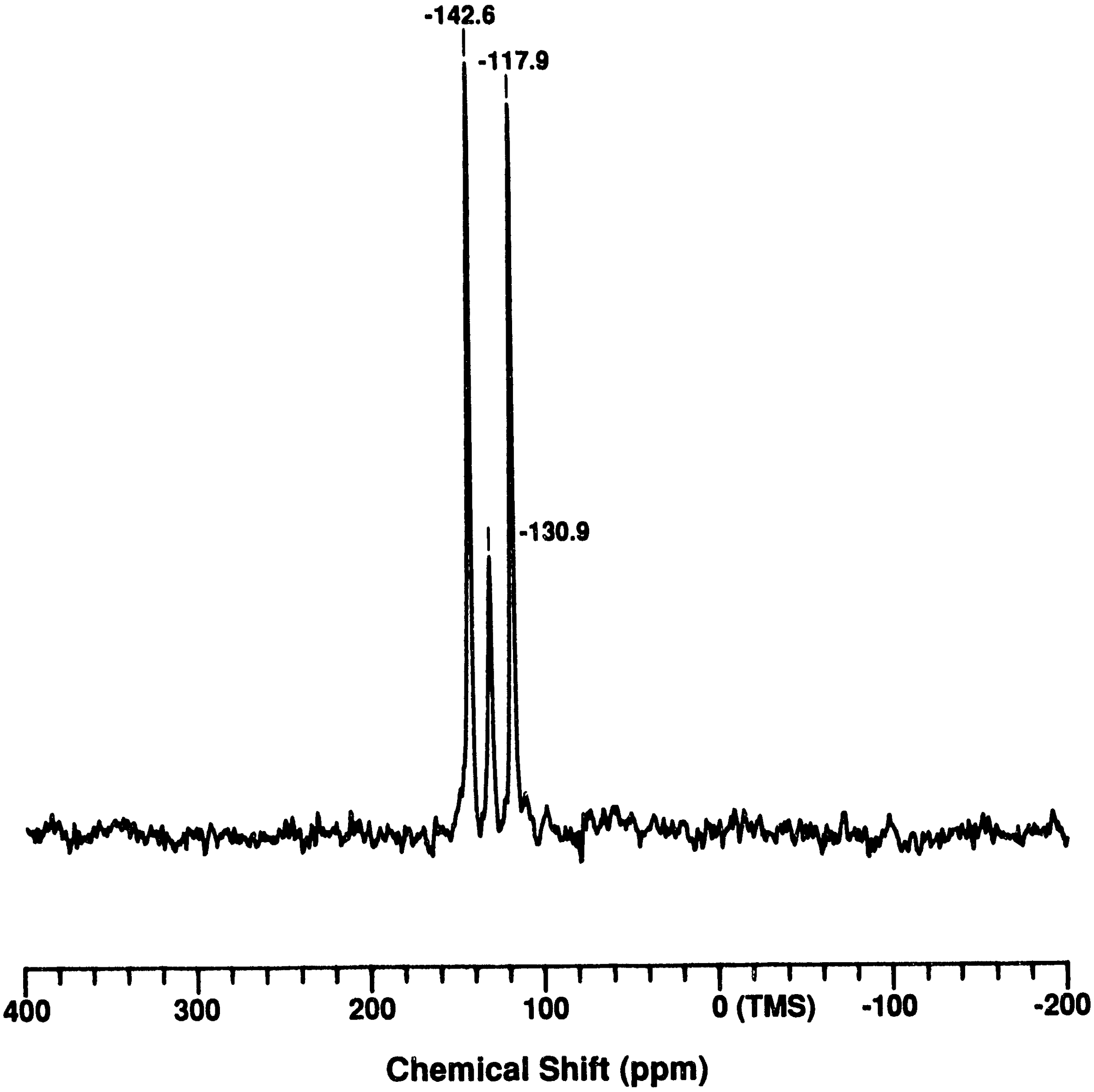

Figure 14. ^{13}C NMR SPE/MAS Spectrum of Silica Gel Saturated with Pyridine Vapor, pd = 10 s, acq = 900

The carbon-13 spectra of the two coal fly ashes show only aromatic and heteroaromatic type carbon. This carbon residue is possibly a char consisting of highly condensed aromatic rings. Preliminary carbon-13 NMR experiments involving the adsorption of pyridine vapors onto the coal fly ash surface have indicated that little, if any, pyridine is adsorbed; thus, the surfaces of the two coal fly ashes may consist mainly of Brönsted acid sites.

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DISCLAIMER

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