1994

Bituminous Fly Ash Release Potential Modeling and Remediation of Arsenic, Boron and Heavy Metals

Digital Object Identifier: https://doi.org/10.13023/kwrri.rr.189

V. P. Evangelou
University of Kentucky

Repository Citation

Evangelou, V. P., "Bituminous Fly Ash Release Potential Modeling and Remediation of Arsenic, Boron and Heavy Metals" (1994). *KWRRI Research Reports*. 19.
https://uknowledge.uky.edu/kwrri_reports/19

Research Report No. 189

Bituminous Fly Ash Release Potential Modeling and Remediation of Arsenic, Boron and Heavy Metals.

by

V.P. Evangelou
Principal Investigator

Project Number: G2021-04* (A-124)

Agreement Number: 14-08-0001-G2021

Period of Project: July, 1992 to June, 1994

Water Resources Research Institute
University of Kentucky
Lexington, KY

The work upon which this report is based was supported in part by funds provided by the United States Department of the Interior, Washington, D.C. as authorized by the Water Resources Research Act of P.L. 101-397.

DISCLAIMER

Abstract

In Kentucky, approximately 3 million tons of coal fly ash are produced annually at a disposal cost around $20 per ton. Moreover, disposal is becoming a major issue because of the ash's potential to contaminate surface and groundwater with arsenic, boron, heavy metals, etc. Knowledge on the chemistry of fly ash is essential in developing a methodology that can predict release rate(s) and concentration(s) of chemical constituents of environmental concern (pollutants). Currently, there is major concern in the state how to dispose of safely the fly ash generated from the combustion of coal by electrical generating plants. Safe disposal of fly ash with respect to surface and groundwater protection depends on having the know-how and technology to evaluate the potential of a given fly ash to release toxic pollutants and 2) having the know-how to do something about it, assuming that a given fly ash is shown to have the potential to pollute. Kentucky is in major need of the above technologies because a major portion of its electrical needs comes from coal-fired electricity generating plants. The results of this study showed that Kentucky fly ashes were made of three types of solids: 1) chemically water stable solids (SiO, FeO, AlO), 2) chemically water reactive solids (SO_4, BO_3,), and 3) metal-oxides (CaO, K_2O,) unstable at the pH range of natural water. The selected fly ashes varied from acidic to alkaline because of the chemical make-up of the source coal. Physical appearance of the samples tested varied depending on coal type and furnace. All fly ash samples were mainly composed of glass-like porous beads that varied in chemical composition with respect to Al/Si/Fe ratio and varied in pH from extremely low (pH near 3) to near pH 11. Alkaline fly ash samples were associated with high boron levels and exhibited extremely low potential pH buffering capacity. Potentiometric titrations revealed a fly ash PZC_{pH} somewhere around 4.6 which was approximately midway between the PZC_{pH} of iron-oxides and SiO_2. Also, these data revealed that fly ash surfaces exhibited an apparent pH-dependent positive charge. A positive charge of approximately 40 $cmol_c\ kg^{-1}$, and a negative charge of approximately 40 $cmol_c\ kg^{-1}$ with intrinsic protonation and dissociation constants of $10^{6.2}$and $10^{-7.8}$, respectively). Little if any charge was exhibited between pH 4 to 8.5. Low pH buffering capacity, low pH dependent charge and relatively low PZC_{pH} appeared to make the fly ash samples tested extremely sensitive to pCO_2 with respect to pH and boron release. Increasing pCO_2 increased boron release but pCO_2 had no influence on nickel release. This suggested that nickel was most-likely strongly chemisorbed. Nickel and cadmium adsorption isotherms showed that adsorption maximum took place above pH 6. The acidic fly ash showed a greater metal adsorption potential than the alkaline fly ash. Because boron (the major pollutant detected in the fly-ash samples tested) is weakly held, one should avoid burying such "fresh" fly-ash in water permeable waste disposal sites.

Descriptors: Fly ash, Groundwater pollution, Arsenic, Boron, Heavy metals, Fate, Remediate.

Table of Contents

List of Tables

List of Figures

List of Photos

<u>Text</u>

CHAPTER I - Introduction

In Kentucky, coal fly ash disposal is a major environmental issue because of the fly ash potential to contaminate surface and groundwater with heavy metals, arsenic, boron, etc. This groundwater pollution potential by fly ash is requiring the federal government to regulate fly ash disposal. Effective regulation of fly ash disposal requires knowledge on its chemistry with respect to release rate(s) and concentration(s) of pollutants. Furthermore, considering that a given fly ash is determined to be a potential groundwater pollutant, new remediation technologies are needed to allow its safe disposal.

Generally, composition of butaminous fly ash varies depending on the chemical make-up (source) of coal. However, knowledge on the chemical composition of fly ash is not all that is needed for someone to predict potential release of toxic constituents to groundwater. Below, a description of the major components of butaminous fly ash and how these components could be related to release of arsenic (As) will be given. In general, fly ash is composed of three groups of solid components. The first group of solid components exhibit low water reactivity but possess surface electric charge (may adsorb metal cations, e.g., Cd, Ni, Pb, etc., or oxyanions, e.g., arsenate, borate, sulfate, etc. These solids, in butaminous coal fly ash, are made of SiO_2 (7-8%), Al_2O_3 (4-39%), Fe_2O_3 (2-44%), and TiO_2 (1-2%), (Terman, 1978; Adriano et al., 1980).

The surface electrical pH-dependent charge of the above solids is characterized by three pH regions. The first pH region involves an extremely narrow pH range (a few tenths of a pH unit) and in this range the positive charges on the surface of the oxide(s) equal the negative charges. Also, in this pH region the surface adsorbs both metal cations and oxyanions. This pH is known as the zero point of charge (ZPC_{pH}). Below the ZPC_{pH} oxides exhibit a net positive charge and prefer to adsorb oxyanions; above the ZPC_{pH} oxides exhibit a net negative charge and prefer to adsorb metal cations (Anderson and Malotky, 1979). In our own laboratory work (Harsin and Evangelou, 1989) we have shown that an iron-oxide synthesized in the laboratory exhibited a ZPC_{pH} in the pH range of 6.5 to 7. The ZPC_{pH} of Al_2O_3 is known to be around 9 and the ZPC_{pH} of SiO_2 is known to be around pH 2 (Stumm and Morgan, 1970). Moreover, when minerals are made of chemical mixtures ZPC_{pH} changes. For example, if instead of Fe_2O_3 we have a chemical mixture of Fe_2O_3 and SiO_2 ($Fe_{2-x}Si_xO_3$) the ZPC_{pH} of this oxide will need to be determined experimentally (Stumm and Morgan, 1970). This means that the pH at which these surfaces act as metal cation adsorbers or oxyanion absorbers is not known. Consequently, one does not know if and when pollutants will be released from such surfaces to water.

The second group of solid components of butaminous coal fly ash are those that are adsorbed onto the oxide surfaces. These components include heavy metals and oxyanions. According to Adriano et al. (1980) these heavy metals and oxyanions are mostly found adsorbed on to surfaces of oxides (discussed above) which are represented by the smallest of fly ash particles (largest surface area). The chemical behavior and release of heavy metals and oxyanions to water is highly interrelated to the surface electric properties of oxides described above.

The third group of solid components include highly water reactive components. Generally, this group of solids include oxides of Ca ($\simeq$15,000 ppm), Mg ($\simeq$16,000 ppm), K ($\simeq$23,000 ppm), Na ($\simeq$2,000 ppm), Ba($\simeq$1000 ppm) as well as gypsum ($CaSO_4 \cdot 2H_2O$) and sulfite (SO_3). The later upon exposure to water and O_2 oxidizes readily to SO_4.

When fresh fly ash is exposed to the open environment (H_2O and CO_2 gas) two chemical pathways can be hypothesized with respect to fate of heavy metals and oxyanions. If CO_2 gas is introduced to a fly ash slurry most metals will precipitate as metal carbonates and the oxyanions are expected to be adsorbed by the oxide surfaces, depending on ZPC_{pH}. Therefore, release of heavy metals to water is expected to be dependent greatly on the partial pressure of CO_2 (pCO_2). In the absence of excess pCO_2 a smaller fraction of the metals is expected to precipitate as carbonates and a larger fraction of heavy metals and oxyanions is expected to interact with each other and the surfaces of the oxides. If the oxide surfaces are physically blocked by the various precipitates or the total quantity of the oxides available for metal cation and/or oxyanion surface adsorption is low, then, both metal cations and oxyanions will be released to the water and may remain soluble or coprecipitate depending on types of minerals that can be formed, e.g. $Ba(AsO_4)_2$ a very insoluble mineral ($Ksp = 8.0 \times 10^{-51}$). Some butaminous coal fly ashes do not contain metal oxides such as CaO and are quite acidic. In such fly ashes, oxide-surface ZPC_{pH} and surface charge behavior with respect to pH would be a major controlling factor in metal and/or oxyanion release.

A great deal of research has been carried out on the chemical make-up of fly ash, and water soluble salts, heavy metals, and oxyanions (Adriano et al., 1980 and references there in. Terman, 1978; Phung et al., 1979; Roy and Griffin, 1982; Hodgson et al., 1982, 1984; Elseewi et al., 1980). Additionally, a great deal of research has been carried out on using fly ash as a soil amendment to improve soil physical properties and/or soil pH. Furthermore, research has been carried out on the availability of heavy metals and oxyanions of fly ash to agricultural plants (Adriano et al., 1982). Although a great deal of information is available on the use of fly ash as soil amendment, however, not all fly produced in Kentucky can be used for such purpose. In other words, demand for fly ash for such purpose is far shorter than the available fly ash supply. For that reason a big portion of the fly ash produced will have to be put in landfills. The physical-chemical properties of fly ash with respect to pollutant reactions must be known before effective disposal takes place.

Objectives

I. Characterize selected Kentucky fly ash samples physically with the aid of x-ray diffraction and electron microscopy.

II. Characterize selected Kentucky fly ash samples chemically with respect to the major elements and some trace elements.

III. Quantify the role of CO_2 partial pressure (pCO_2) on the chemical behavior of oxyanions and heavy metals with respect to precipitation and oxide surface adsorption by Kentucky fly ash samples.

IV. Quantify the surface chemistry of fly ash metal oxides with respect to heavy metal (cadmium, Cd; nickel, Ni) adsorption.

CHAPTER II - Research Procedures

In order to successfully accomplish the objectives, various samples of fly ash having as source various types of coals were selected. The purpose of this selection was to identify fly ash types of bituminous coal that are low to high in water reactive metal oxides (CaO, K_2O and Na_2O) and low to high in oxides of Al, Fe and Si. The purpose of this selection of fly ash samples was to allow us to investigate a) the role of water reactive metal oxides on generating metal carbonate precipitates as a function of partial pressure of carbon dioxide gas, b) the influence of metal carbonates on the solubility of heavy metals, c) the influence of carbonate formation on the surface properties on the heterogeneous metal oxides (Al_2O_3, Fe_2O_3, SiO), and d) surface adsorption of oxyanions, borate. XRD analysis was carried out employing Cu-K_a radiation.

Electron Photomicrographs

The surface status of the pyrite particles were examined using a field emission scanning electron microscope (FESEM) (Hitachi S-800)

Potentiometric Titrations

Treatment of fly ash prior to potentiometric titrations was carried out as follows:

1) Thirteen grams of fly ash were placed in a 250 ml centrifuge tube with 200 ml of 1 M HCl. The suspensions were shaken for 4 hours, centrifuged at 2000 rpm for 5 minutes, and the supernatant was discarded. The above procedure was repeated three times.

2) After discarding the supernatant from the third wash in step 1, 200 ml of 200 mmol L^{-1} NaCl solution was added, the suspension was shaken for 20 minutes, centrifuge at 2500 rpm for 10 minutes, and the supernatant was discarded. The above procedure was repeated five times.

3) After discarding the supernatant from the fifth wash in step 2, 200 ml of distilled-deionized water was added, the suspension was shaken for 20 minutes, centrifuge at 2000 rpm for 5 minutes, and the supernatant was discarded. The above procedure was repeated five times.

4) The sample was air dried and then used for potentiometric studies and metal adsorption isotherm studies.

Potentiometric titrations were carried out on normal (absence of any secondary treatment) fly ashes to evaluate pH buffer regions, and on acid washed/sodium saturated fly ashes to evaluate their surface charge properties. The potentiometric titrations were carried out employing an autotitrimeter (Radiometer Copenhagen Set) using a stop and go approach between titrant discharges. These titrant discharge intervals were determined experimentally and represented the time needed for the fly ash suspension to reach a chemical equilibrium state. Titrant discharge intervals varied between 15 seconds and 3 minutes, depending on fly ash source. These titrations were performed on both natural, untreated ash samples, as well as on treated samples. The stopping interval was established separately for each of the six ashes.

Compositional analyses of the fly ash samples were carried out by digestion with HF in a closed vessel, then added saturated boric acid to recover the silica.

were carried out on fly ashes to evaluate their pH buffering behavior. Titrations were carried out in a nitrogen atmosphere (simulating zero pCO_2) employing a stop and go approach with 3-minute intervals between discharges of titrant. Titrations using a CO_2 atmosphere were also performed.

Long-Term Water Equilibrations

Long-term water equilibrations were conducted using 50:950 fly ash:water suspensions by weight in 1000 ml plastic Erlenmeyer flasks under various (pCO_2) levels. Accompanied by vigorous stirring, half of the fly ash suspensions were bubbled for one hour per day with pure nitrogen gas (simulating zero pCO_2), and the other half of the fly ash suspensions were bubbled with pure carbon dioxide ($pCO_2 = 1$) . Conductivity, and pH of the suspensions were measured after each bubbling, and six samples were collected at intervals throughout the duration of the experiment. After a 45-day equilibration, all fly-ash suspensions were equilibrated with atmospheric air ($pCO_2 = 0.0003$) and sampled.

Adsorption Isotherms

Adsorption isotherms of nickel (Ni^{2+}) and cadmium (Cd^{2+}) were produced at pH values in the range of 3.2 to 9.5. For each pH value, a metal-fly ash isotherm was produced employing 0, 2, 6, 12, 24, and 36 ppm Ni or cadmium in the form of $NiSO_4$ or $CdSO_4$, respectively. All isotherms were run in duplicates. Solution/fly ash suspension pH adjustments were made as follows:

1. Prepare eight liters of 10 millimolar buffer solutions at the approximate six pH values listed above by mixing various volumes of acetic acid, sodium acetate, and sodium hydroxide.

2. Weigh 26 grams of treated fly ash into each of the six pH-adjusted solutions above.

3. Stir the ash thoroughly, and then adjust the pH of the buffer solution at a pre-determined pH listed above using NaOH. Check the pH after in 1 to 2 hours, and if necessary adjust again. When the pH did not change for 48 hours, the fly-ash was filtered, and the buffer was saved for introducing the heavy metals for the isotherm solutions.

4. Weigh 2 grams of the pH-adjusted, dried fly ash into 50 ml centrifuge tubes which have been labelled in duplicate for the appropriate nickel concentrations and pH. Quantity of adsorbed heavy metals was calculated by the difference in heavy metal concentration between original concentration minus final concentration.

Fly Ash Breakthrough Columns

1. Establish pore volumes for the relevant fly ashes using procedures from Methods of Soil Analysis, Part 1, A. Klute (ed.), 1986, pp 377-409, ASA. Porosity was determined to vary between 59-70%.

2. Using dry untreated fly ash, chromatographic columns 9.9 cm high and 1 cm inside diameter were filled up by avoiding major compaction. The weight of the fly ash to fill the column varied between 7.5-9 grams.

3. The columns were then flushed with either nitrogen or atmospheric air, using bottled gas to avoid contamination.

4. Using distilled-deionized water which had been bubbled with nitrogen or compressed air, the columns were leached at the rate of 0.43 ml min^{-1} for 120 pore volumes.

5. For the first 2 pore volumes, 5 fractions per pore volume were collected (approximately 2 min/fraction, depending on type of fly ash sample).

6. For the remaining pore volumes, 2 pore volumes were collected (approximately 20 minutes/2 pore volumes, depending on type of fly ash sample).

7. Each fraction was analyzed for boron and silica.

CHAPTER III - Data and Results

The fly ash samples evaluated in this study varied from acidic to alkaline because of the chemical make-up of the source coal (see Figure 1).

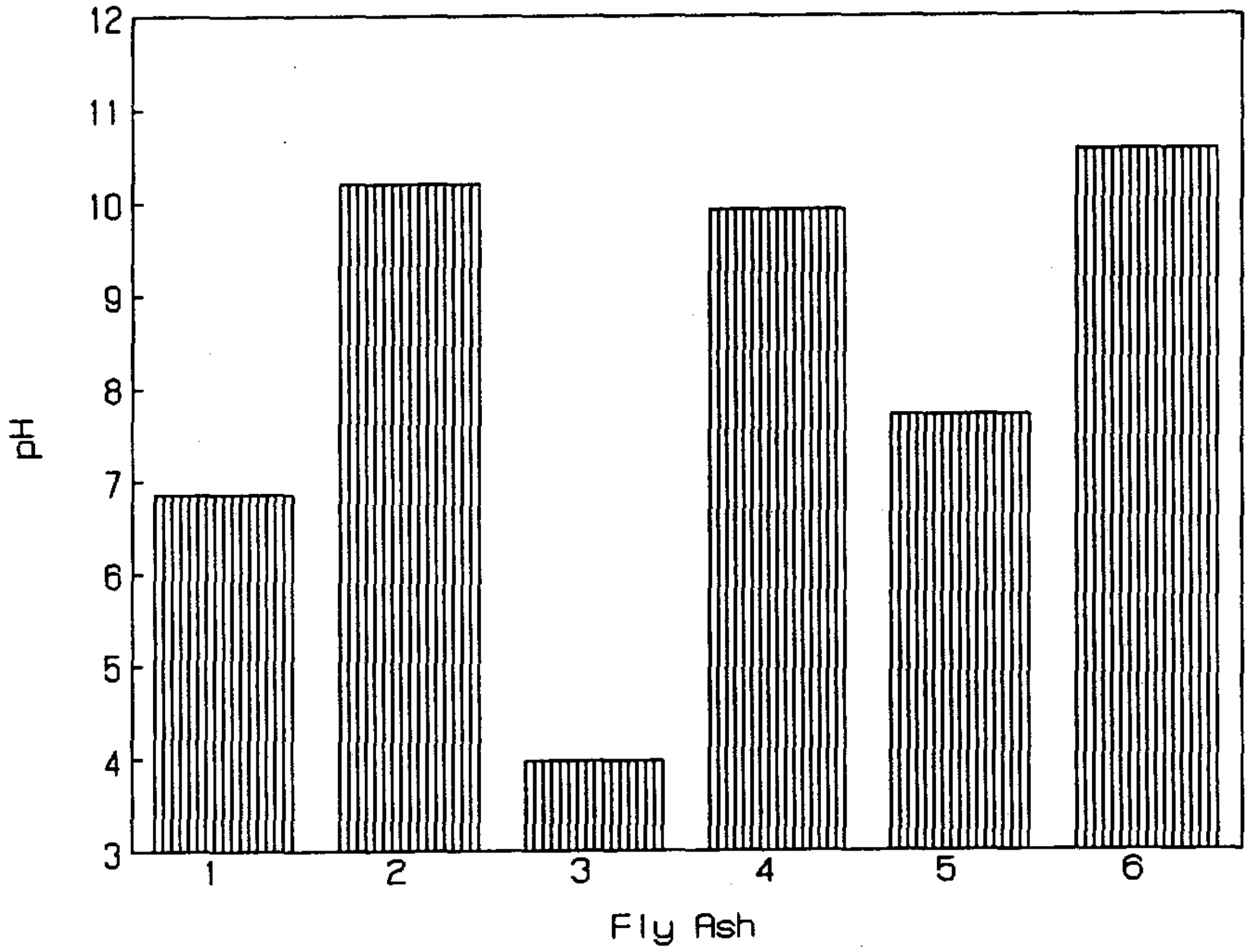

Figure 1. Initial pH values of various Kentucky fly ashes.

The x-ray diffractograms of the fly ashes gave information about the crystalline portion of the ash. This crystalline portion was made largely of iron oxides in the form of hematite (Fe_2O_3) or in the form of spinels, the most prominent one being magnetite (Fe_3O_4). Spinels are formed at 1100 ^{o}C and consist of a common formula AB_2X_4, where A is one or more divalent metals (Mg,Fe,Zn,Mn,Ni), B is one or more trivalent metals (Al,Fe,Cr,Mn,Ti), and X is oxygen. Magnetite has strong magnetic properties, but other members of the spinel group exhibit it as well but to a lesser degree.

Aluminum silicates were represented in all four ashes solely by mullite ($3Al_2O_3,2SiO_2$) which is formed at 1300 ^{o}C and largely represents the crystalline product of clays and feldspars. Temperature in a coal-fired burner vary from 1800-2400 ^{o}F (980-1200 ^{o}C) depending on the exact position within the burner. Temperatures may not have been consistently high enough to have formed mullite from all the existing Al and Si in the ash. Quarts is present in all four fly ashes and is from quartz found in the original coal, since temperatures in a coal burner are insufficiently high to melt quartz (> 1700 ^{o}C).

The diffractograms of all four samples showed similar major peaks, though the intensity of the peaks was much smaller in the acid, extremely fine-grained, high aluminum content ash. Two strong peaks were present in all four scans that did not seem to meet up with any minerals possible or likely to occur in a fly ash, such as alpha iron, calcium vanadate, or chromium oxide.

Chemical composition of two fly ash samples are given in Table 1.

Table 1. Chemical analyses of aqueous samples taken during the long-term water equilibration, and some elemental analyses of decomposed solid.

	Aqeous analysis for long-term equilibration samples								Elemental Analysis of solid	
	Ash 3				Ash 6				Ash 3	Ash 6
	N_2	CO_2	Atm	Av	N_2	CO_2	Atm	Av		
pH	3.6	3.8	3.9	3.8	11.4	6.0	7.1	8.2		
Conductivity (mmhos cm^{-1})	1.6	1.6	1.6	1.6	3.4	1.9	7.8	2.0		
	ppm				ppm					
Aluminum	*	*	-	*	*	*	-	*	12 %	6 %
Arsenic	-	-	-	-	-	-	-	-	39 ppm	67 ppm
Boron	2.0	2.2	2.0	2.1	2.3	12.8	8.0	7.7	34 ppm	227 ppm
Cadmium	*	*	-	*	*	*	-	*	7 ppm	10 ppm
Calcium	68	75	-	72	16	133	-	75		
Chloride	2.3	1.8	-	2.0	2.0	1.5	-	1.8		
Iron	-	-	-	-	-	-	-	-	15.8 %	16.3 %
Lead	*	*	-	*	*	*	-	*		
Nickel	0.8	0.8	0.8	0.8	0	0	0	0	242 ppm	123 ppm
Potassium	176	178	-	177	24	24	-	24		
Silicon	12.7	13.6	22.2	16.2	1.2	13.	7.9	7.4		
Sodium	18	16	-	17	6	6	6	6		
Sulfate	129	130	157	139	19	14	93	85		

- Not analyzed

* Values below detection limits

Electron photomicrographs

The following electron micrographs show the nature of these fly ash surfaces. Photos 1 and 2 show an overview of two Kentucky fly ashes at a 100X magnification. Note that fly ash 3 is much finer grained than fly ash 6. This seems to be due to the dynamics of the generating boiler in which they were formed. The same generator will create similarly-textured ashes from different types of coal. The basic spherical shape shown in photos 3 and 4 indicated that particles were formed in uncrowded freefall conditions which will produce spheres of any melted material. Cooling will freeze the spherical shape. Vesicular particles on photo 2 are most likely an agglutination of spherical particles which were broken later.

Whereas magnetite was abundant in both ashes, (a fact established from the mineral's magnetic behavior), it was not visible as free particles. When seen under high magnification they protruded from spherical particles as shown in photo 4. We hypothesize that magnetite crystals formed at very high temperatures and were incorporated into the spherical glassy particles during cooling. Some of the larger spheres were broken and filled with other spheres within (photo 6). One of the broken spheres (photo 7) shows gypsum crystals growing on its inner surface (photo 8).

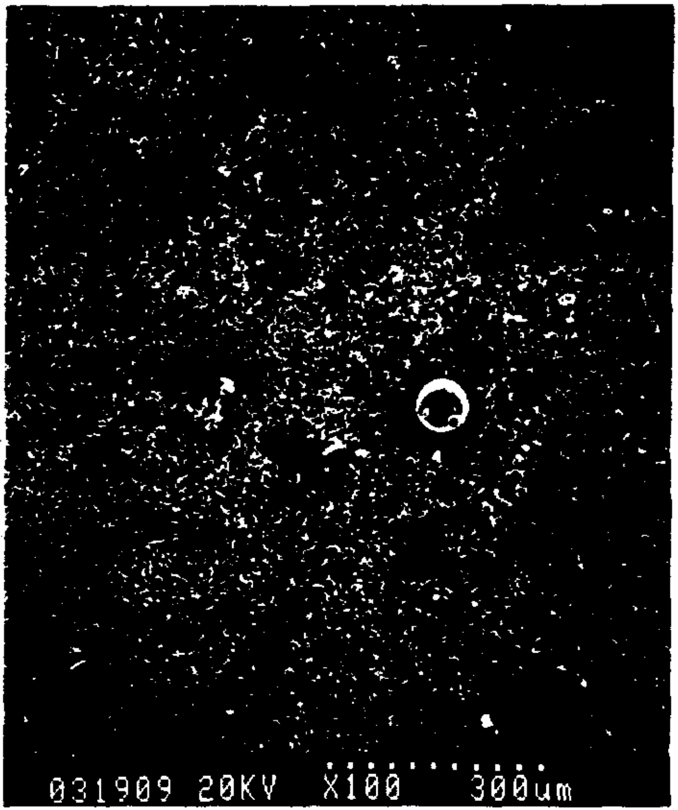

Photo 1. Overview of fly ash 3 (acid).

Photo 2. Overview of fly ash 6 (alkaline).

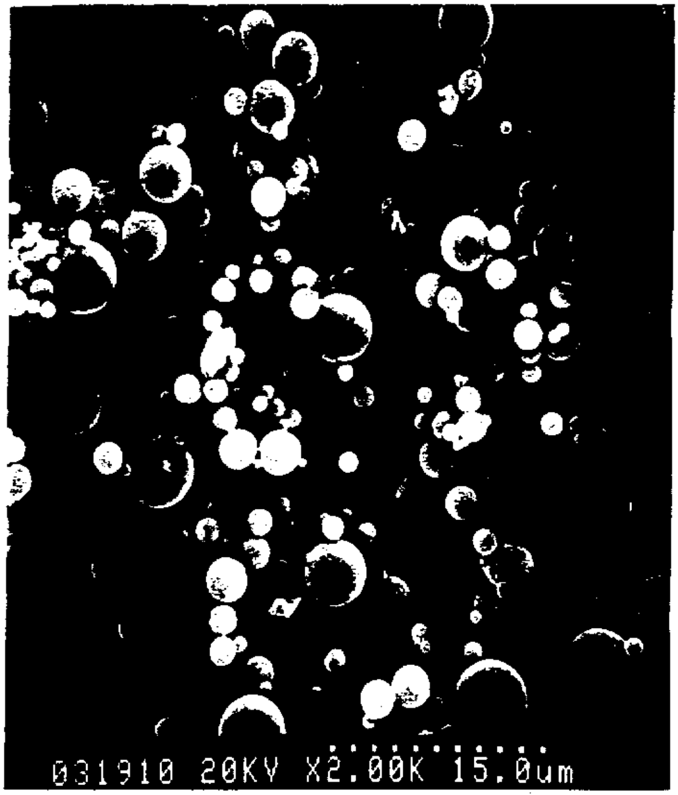

Photo 3. Detail of fly ash 3 (acid).

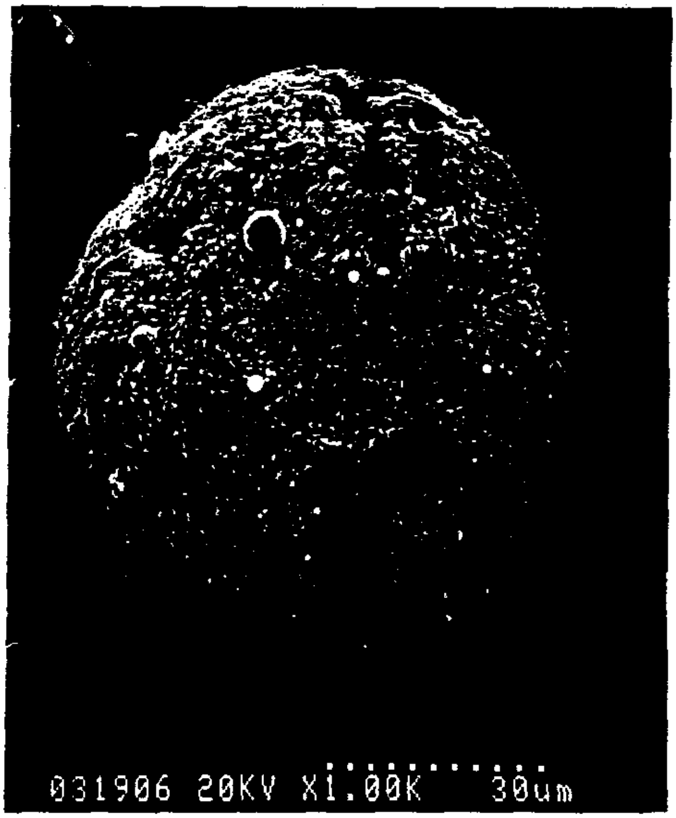

Photo 4. Detail of fly ash 6 (alkaline).

Photo 5. Detail of the magnetite on particle in photo 4 (alkaline fly ash).

Photo 6. Fly ash spheres within spheres (alkaline fly ash).

Photo 7. Broken fly ash sphere of fly ash 6 (alkaline).

Photo 8. Detail of gypsum crust on surface of broken particle in photo 7 (alkaline fly ash).

Potentiometric titrations

Titrations of two untreated fly ashes in a nitrogen background (Figure 2) shows the ashes to be unbuffered in the pH range around 7. Because of this lack of buffering in the presence of an unreactive gas, we hypothesized that pH would be controlled by carbon dioxide gas which is water reactive and plentiful in nature, especially where microbiological activity is present. In Figure 3, note that the moment CO_2 was bubbled into the water-fly ash suspension, pH fell almost instantly below 6. Because CO_2 is the predominant reactive gas in natural soil and some water systems, we believe that this sudden drop in pH, shown in Figure 3, has large implications on the release of metals from the ash to the water. See the EQUILIBRATION section for long-term tests of the effect of pCO_2.

Figure 4 demonstrates the "salt effect" on the fly ash potentiometric titrations. It reveals a PZC_{pH} of approximately 4.6 which is approximately halfway between the PZC_{pH} of FeOOH and the PZC_{pH} of SiO_2.

Figure 5 demonstrates protonation and dissociation intrinsic constants for one of the fly ash samples. They are in the range of intrinsic constants of As/Fe/Si-oxides reported in the literature. The potentiometric titrations shown in the Figure 6 reveal that in the case of fly-ash an approximate pK_a in the vicinity of 10 is shown which is indicative of CO_3^{2-} protonation. Note also however, that in the case of the fly-ash no equal-length titration plateau was obtained in the pH range of 6.2 indicative of HCO_3^-protonation (note a very small pH buffer plateau at near pH 6). This suggested that the plateau at pH 10 was not solely due to CO_3^{2-}. On the other hand, when CO_2 was introduced, the fly-ash titrated briefly at pH 5 but mostly below pH 5. Again, this was not indicative of HCO_3^- protonation. Bicarbonate (HCO_3^-) titration behavior was demonstrated by the titration of NaOH plus CO_2 shown to titrate at around pH 6, as expected.

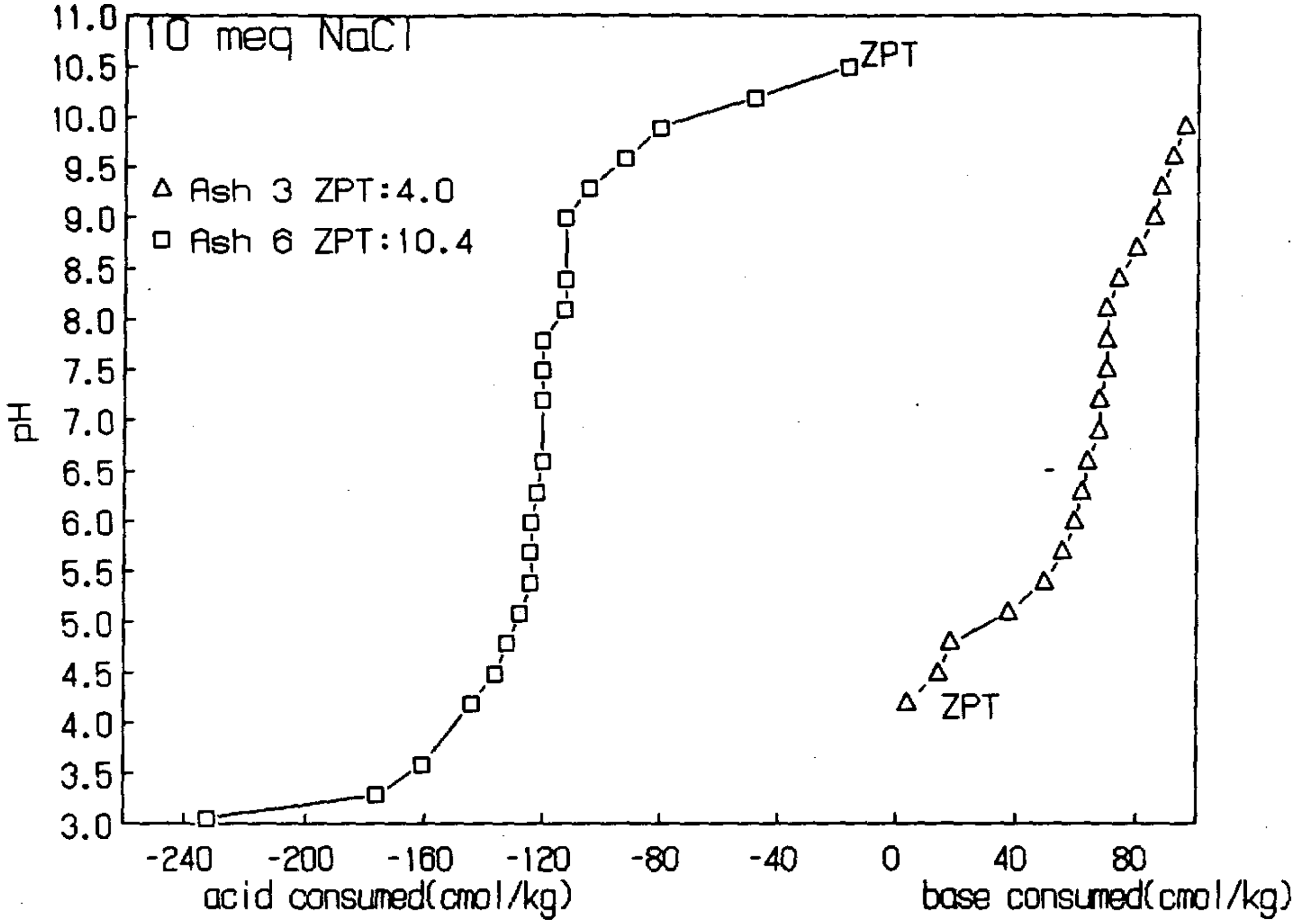

Figure 2. Titrations of two Kentucky fly ashes.

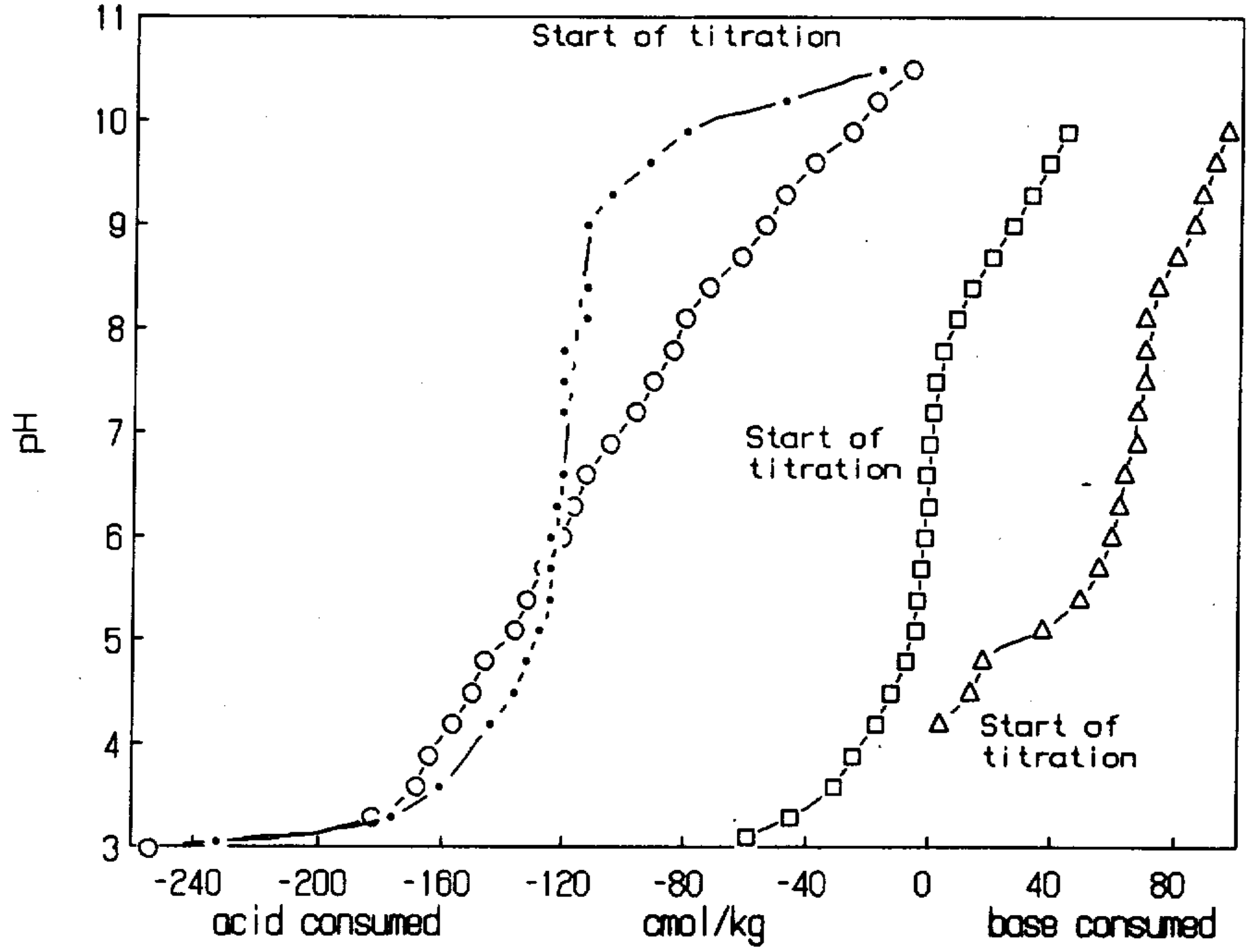

Figure 3. Titration of a fly ash in 1) nitrogen gas (N = unreactive gas) and in 2) carbon dioxide (CO_2 = reactive gas).

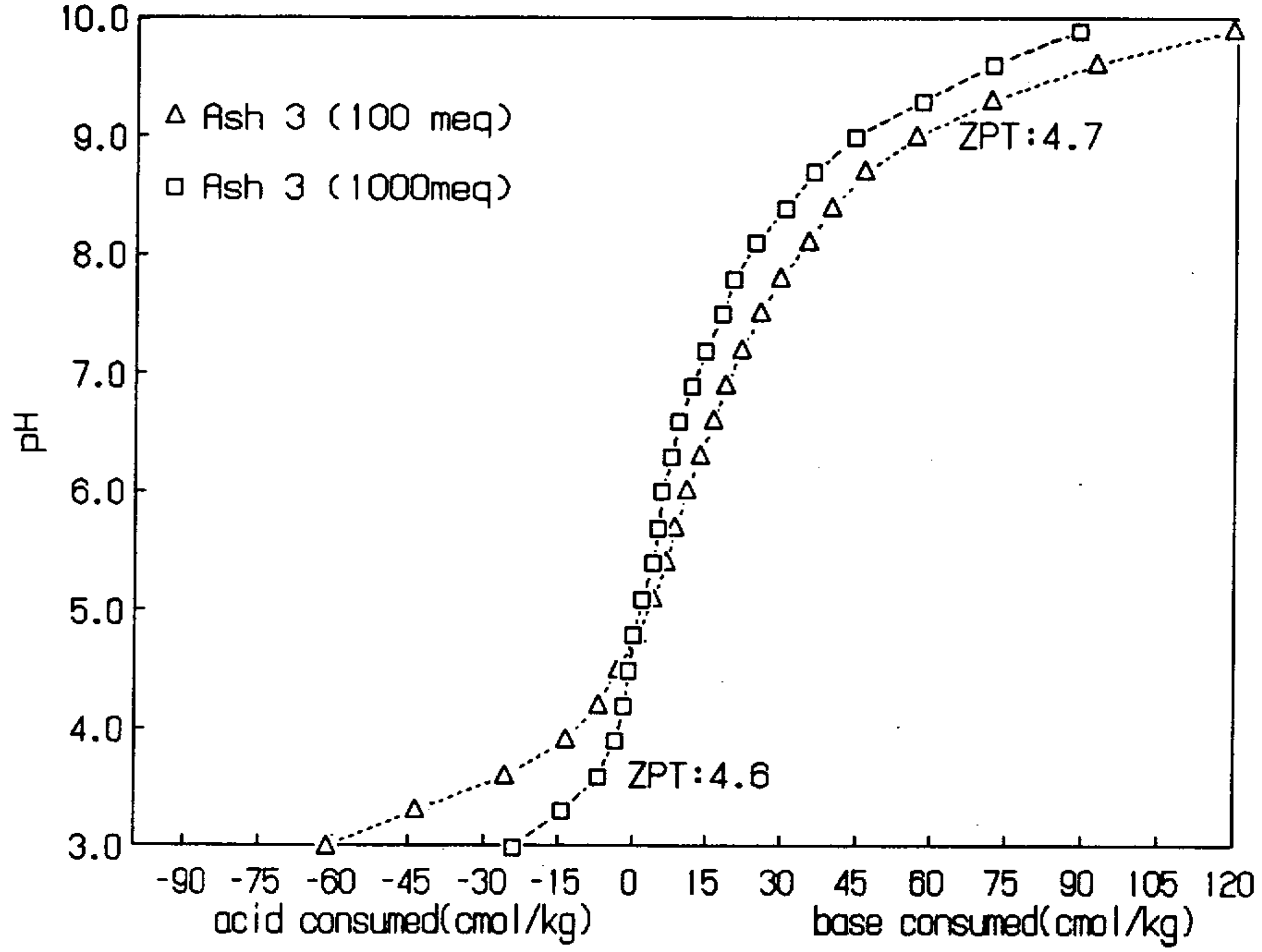

Figure 4. Potentiometric titration of fly ash demonstrating the "salt effect".

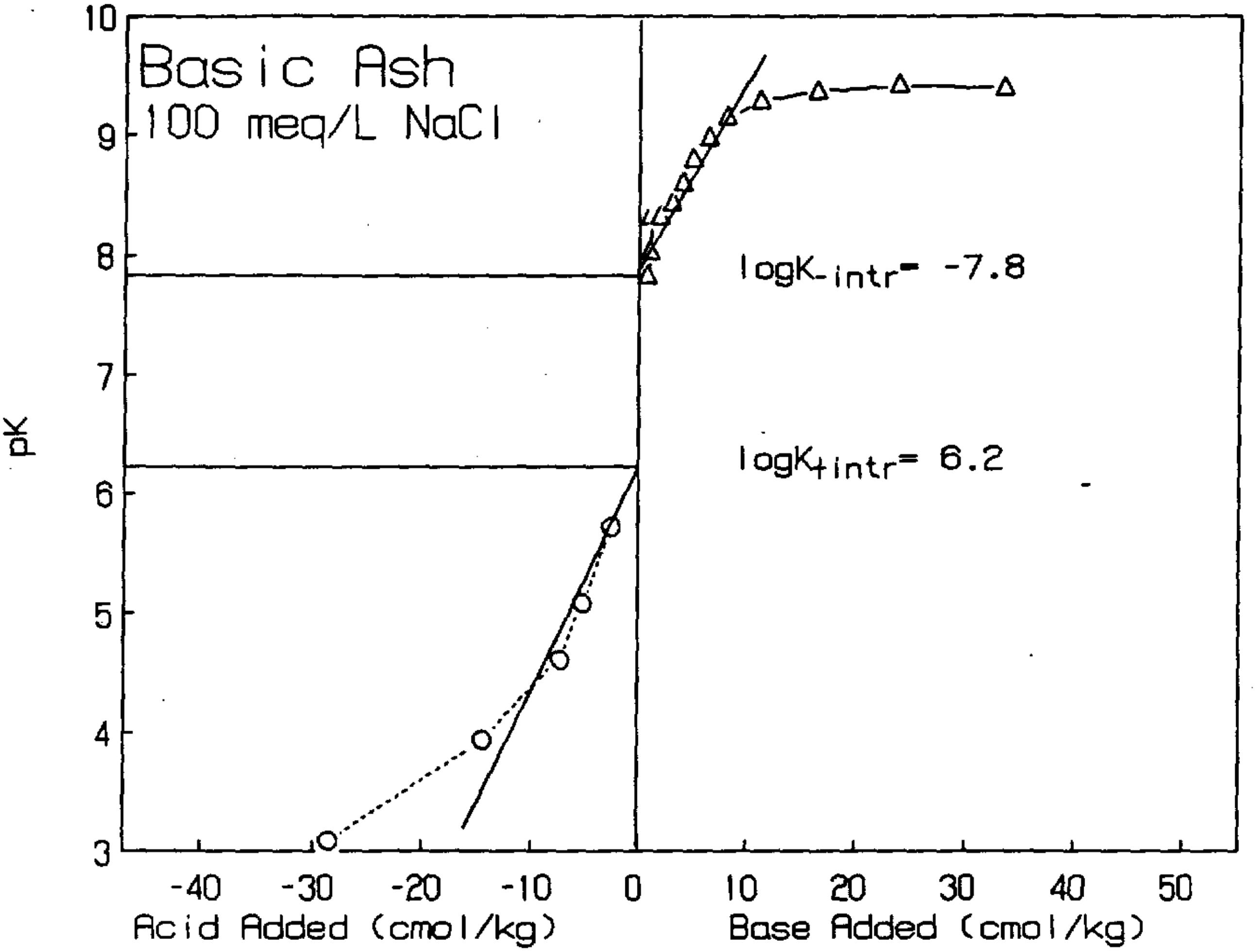

Figure 5. Protonation/deprotonation constants (K_{st}) of fly ash as determined by potentiometric titrations.

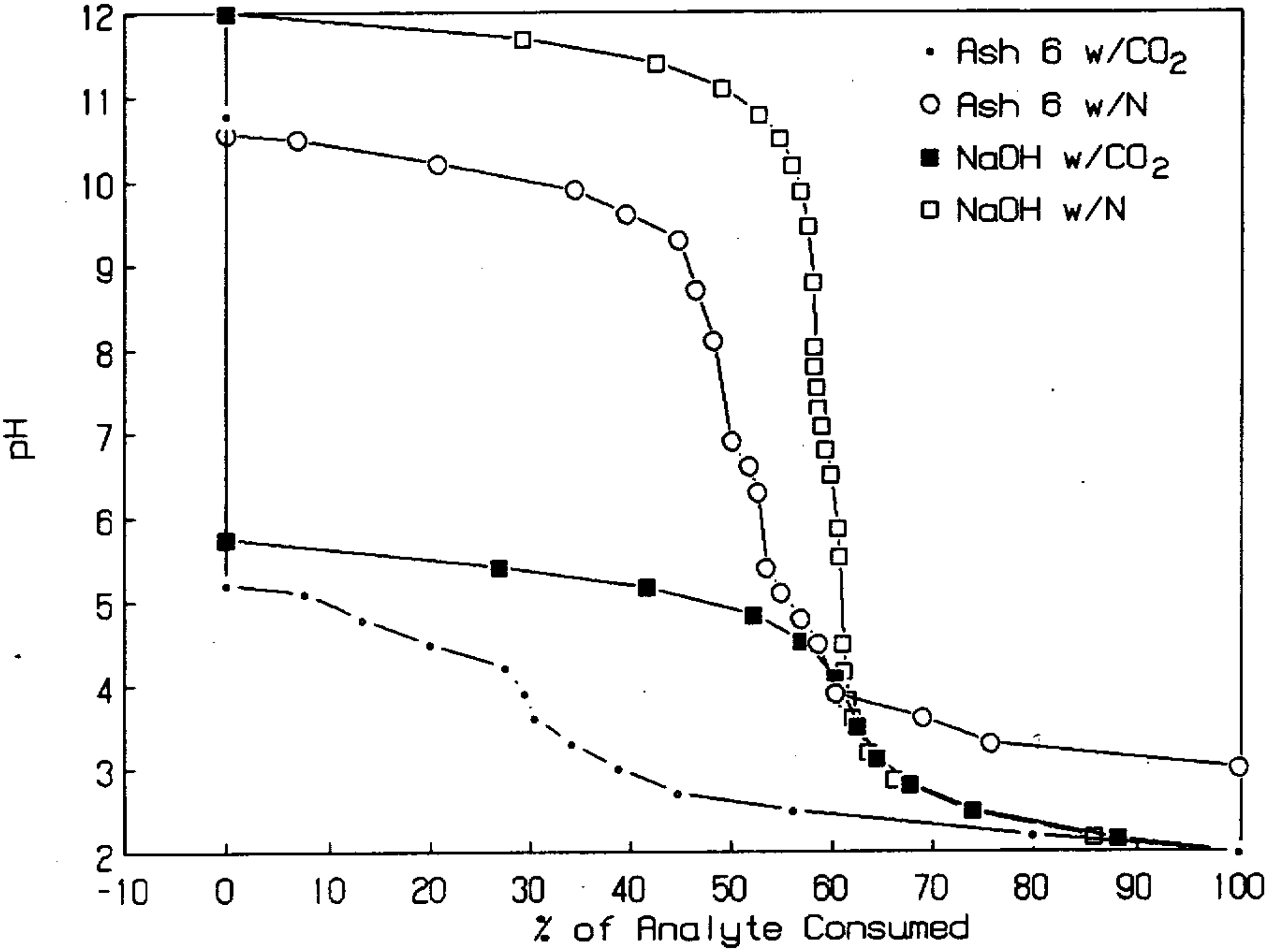

Figure 6. Potentiometric titrations of fly ash and NaOH with and without CO_2.

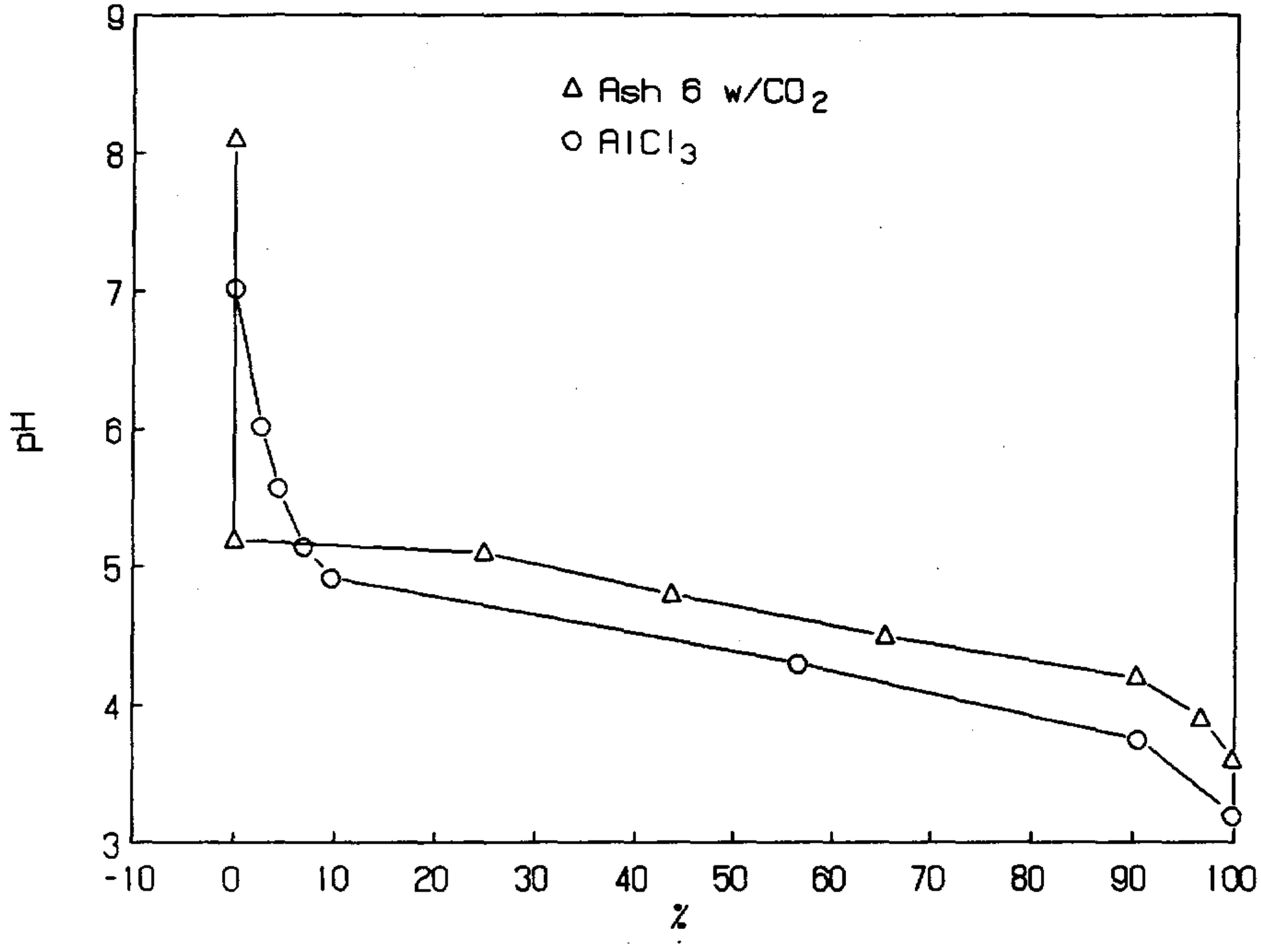

Figure 7. Potentiometric titration of fly ash and $AlCl_3$.

Long-term water equilibration

With regard to boron, of the two ashes in question, the ash which was originally high in pH released more boron (Figure 8) as the pH went down in response to pCO_2. The low pH ash did not respond to P_{CO_2} with respect to change in pH and boron release (Figure 9). With regard to nickel, neither the originally high nor low pH fly ash released nickel differently with respect to partial pressure of CO_2 (Figure 10).

Although the long-term equilibration experiment lasted for 62 days, the first sampling was only one hour after the start of the experiment, most of the release was complete by then (Figure 11).

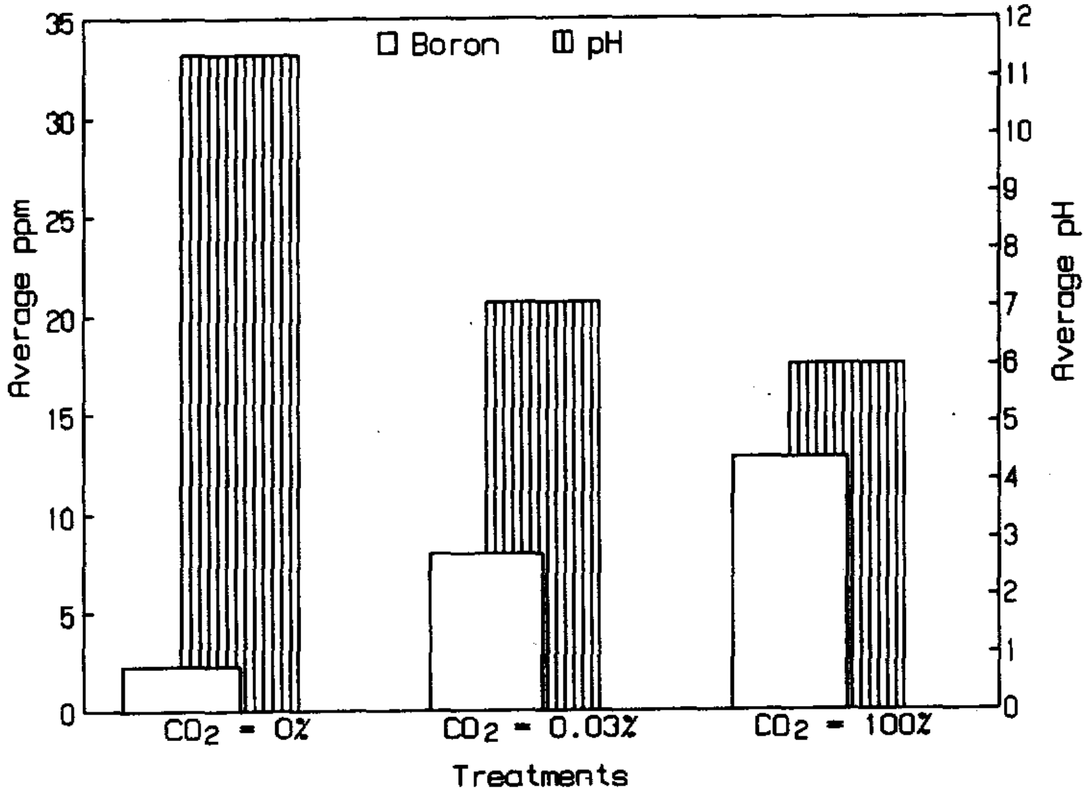

Figure 8. Boron release as a function of pH and P_{CO_2} for an initially high pH fly ash (Data for $CO_2 = 0\%$, and $CO_2 = 100\%$ are averages of six data points each. Value for $CO_2 = 0.03\%$ is from a single sampling).

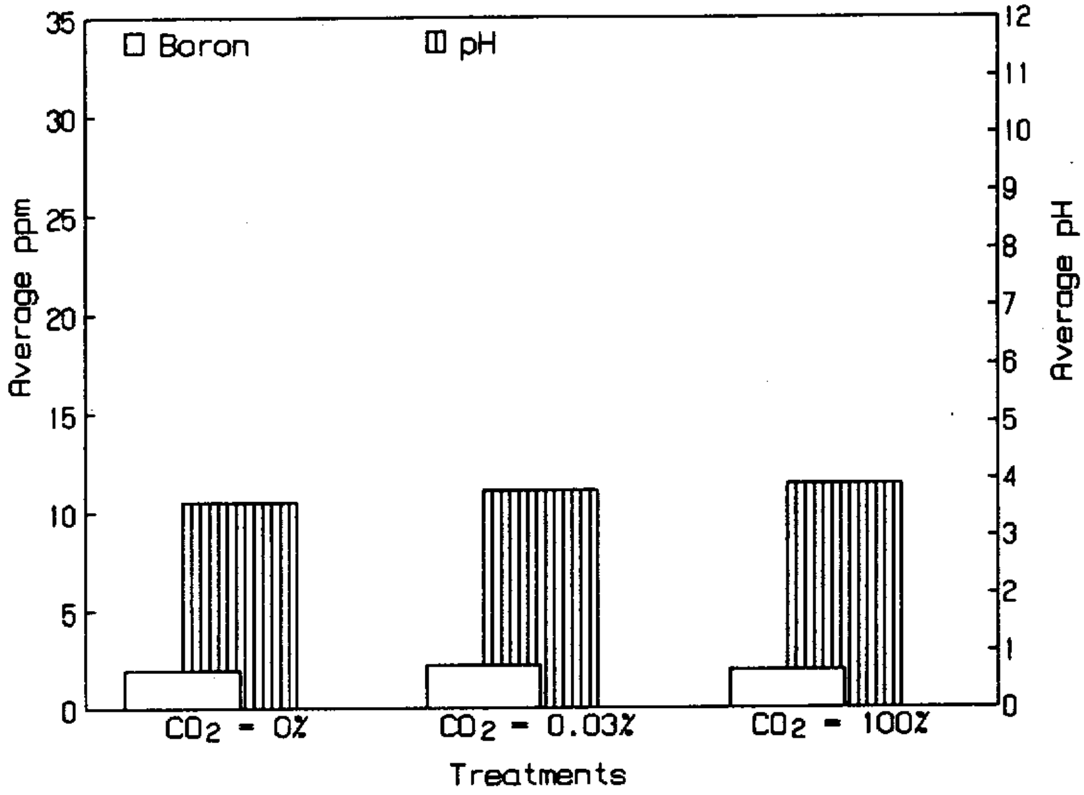

Figure 9. Boron release as a function of pH and partial pressure of CO_2 for an initially low pH fly ash(Data for $CO_2 = 0\%$, and $CO_2 = 100\%$ are averages of six data points each. Value for $CO_2 = 0.03\%$ is from a single sampling).

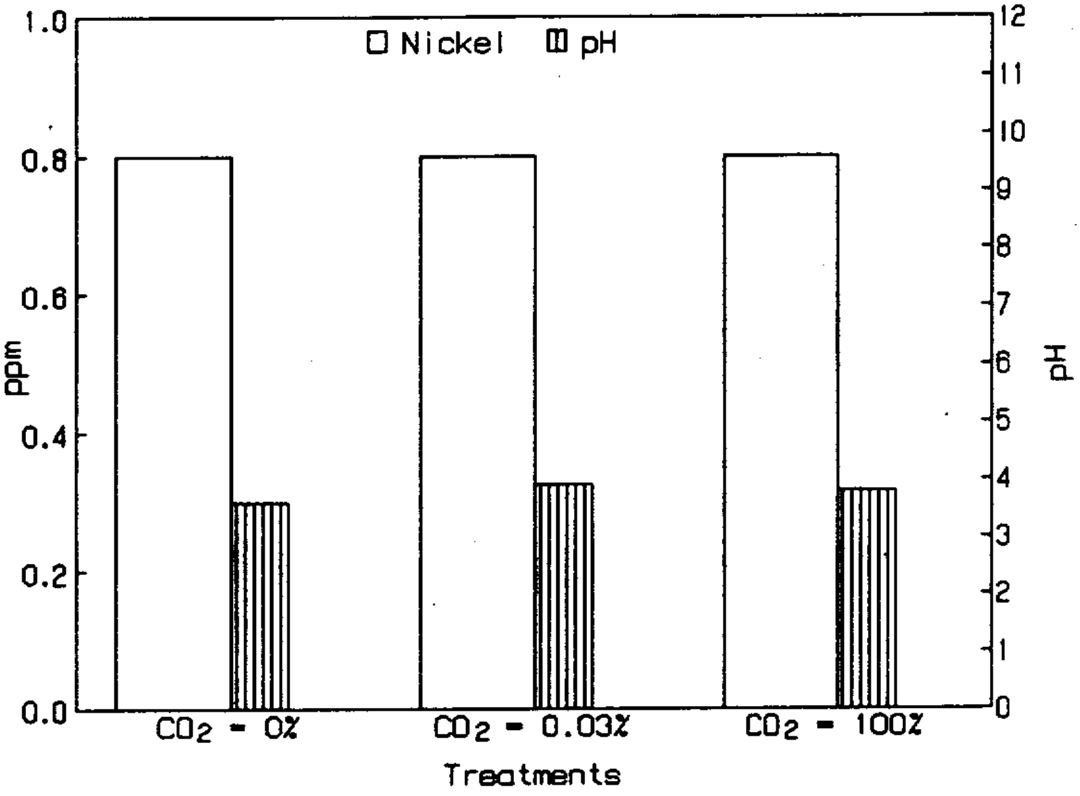

Figure 10. Nickel release as a function of pH and partial pressure of CO_2 for an initially high and an initially low pH fly ash (Data for CO_2 = 0%, and CO_2 = 100% are averages of six data points each. Value for CO_2 = 0.03% is from a single sampling).

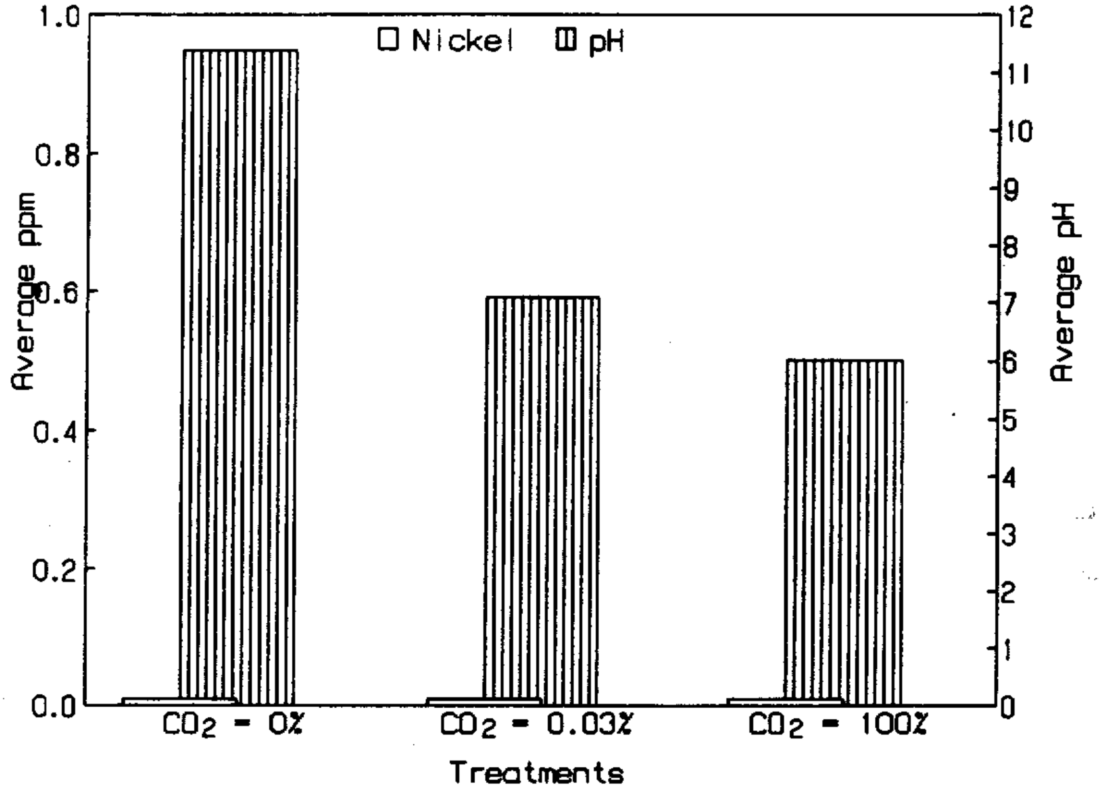

Figure 11. Nickel release with respect to time for an initially high and an initially low pH fly ash. (Data for CO_2 = 0%, and CO_2 = 100% are averages of six data points each. Value for CO_2 = 0.03% is from a single sampling).

Metal Adsoption Isotherms

The data in Figures 12 and 13 show the potential of the 'alkaline fly ash' and 'acid fly ash', respectively, to adsorb nickel. These two figures clearly show that the adsorption of nickel by fly ash is strongly pH depended as one would expect due to variable charge surfaces of the fly ash metal oxides. It is also quite clear from these data that the acid fly ash exhibits a greater potential for nickel adsorption at the two highest pH values tested. This behavior is clearly demonstrated in Figures 14 and 15. They show that in the case of the 'alkaline fly ash' adsorption maxima at pH 7 is only obtained for the 2 ppm nickel level (Figure 14). On the other hand, for the 'acid fly ash' adsorption maxima is attained nearly by all solution nickel concentrations tested (Figure 15).

The data in Figures 16 and 17 show the potential of the 'alkaline fly ash' and 'acid fly ash', respectively, to adsorb cadmium. These two figures clearly show that the adsorption of cadmium by fly ash is strongly pH depended as one would expect due to variable charge surfaces of the fly ash metal oxides. It is also quite clear from these data that the acid fly ash exhibits a greater potential for cadmium adsorption at the two highest pH values tested. This behavior is clearly demonstrated in Figures 18 and 19. They show that in the case of the 'alkaline fly ash' adsorption maxima at around pH 7 is only obtained for the 2 and 6 ppm cadmium levels (Figure 18). On the other hand, in the case of 'acid fly ash' cadmium adsorption maxima was attained nearly by all solution nickel concentrations tested (Figure 19).

These data clearly demonstrate that the acid fly ash exhibits greater potential to adsorb heavy metals as pH was increased. On the other hand, the alkaline fly ash exhibits greater potential to release heavy metals to water under weathering conditions.

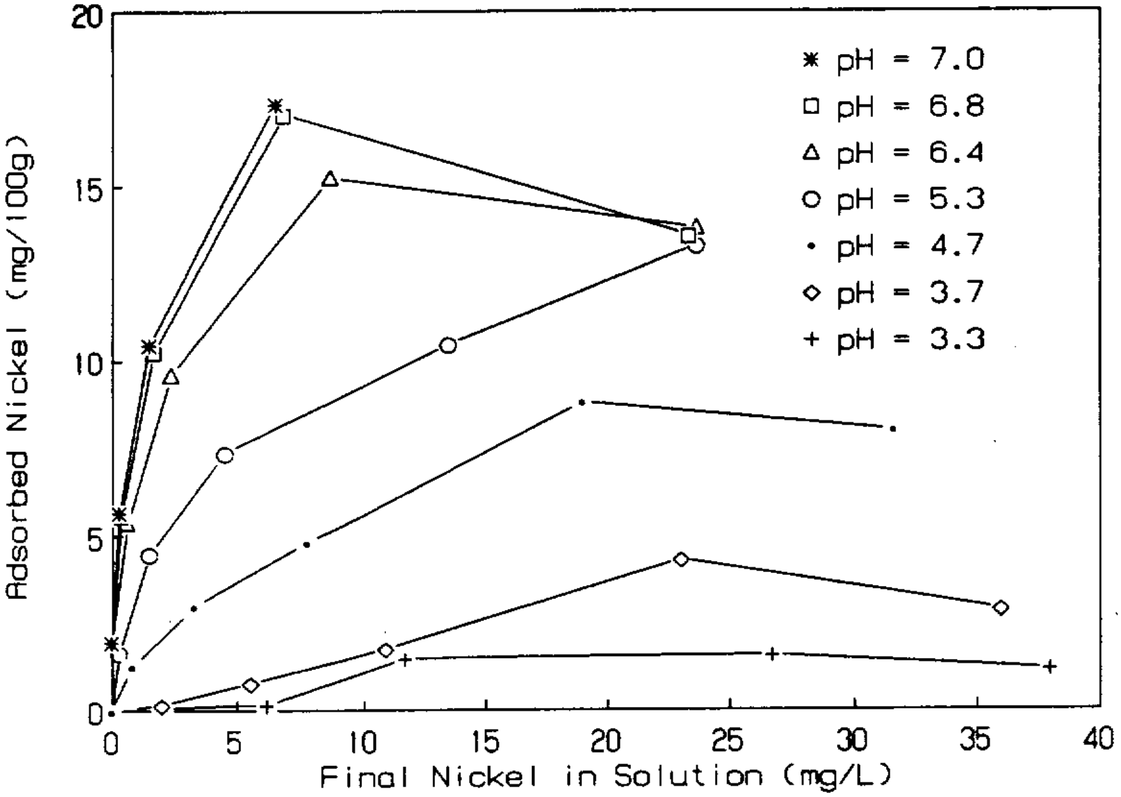

Figure 12. Relationship between adsorbed nickel by 'alkaline fly ash' and solution concentration of total nickel dissolved at equilibrium under various pH values.

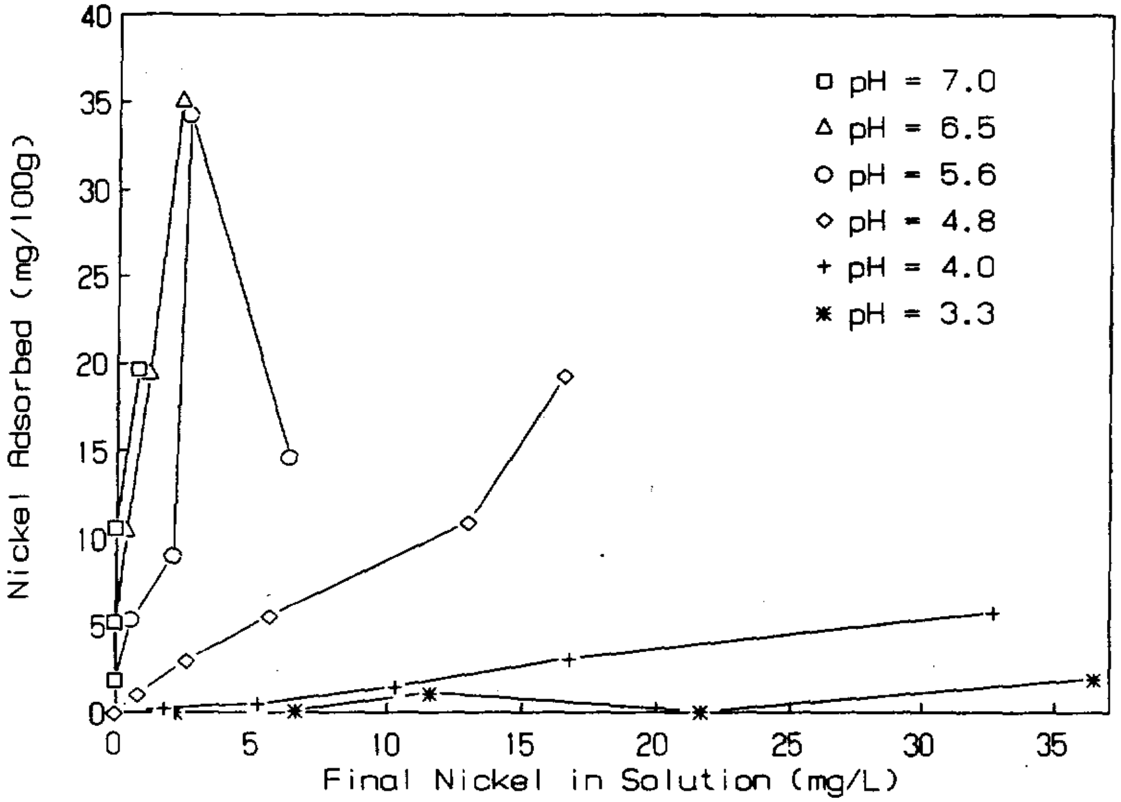

Figure 13. Relationship between adsorbed nickel by 'acid fly ash' and solution concentration of total nickel dissolved at equilibrium under various pH values.

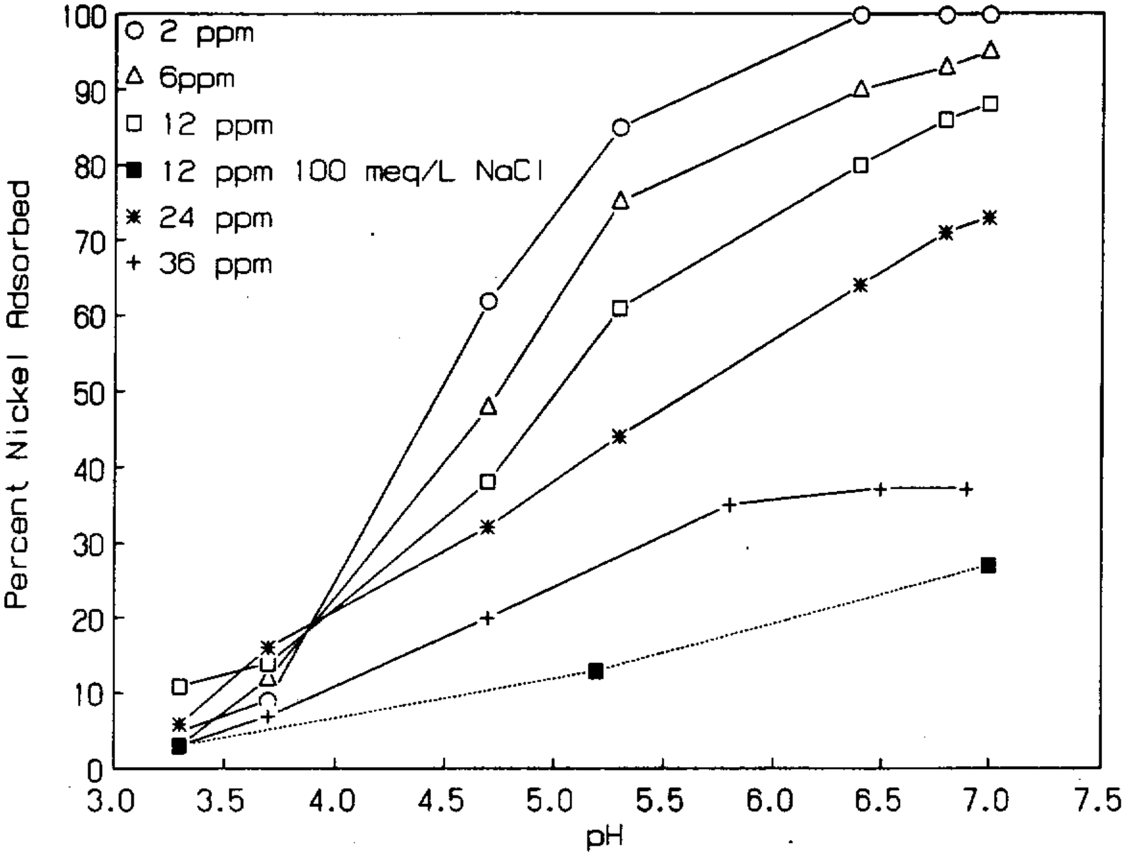

Figure 14. Relationship between percent adsorbed nickel relative to maximum adsorbed by the 'alkaline fly ash' and suspension pH. (Maximum adsorbed nickel was that obtained at the highest pH tested and at the highest total nickel solution concentration).

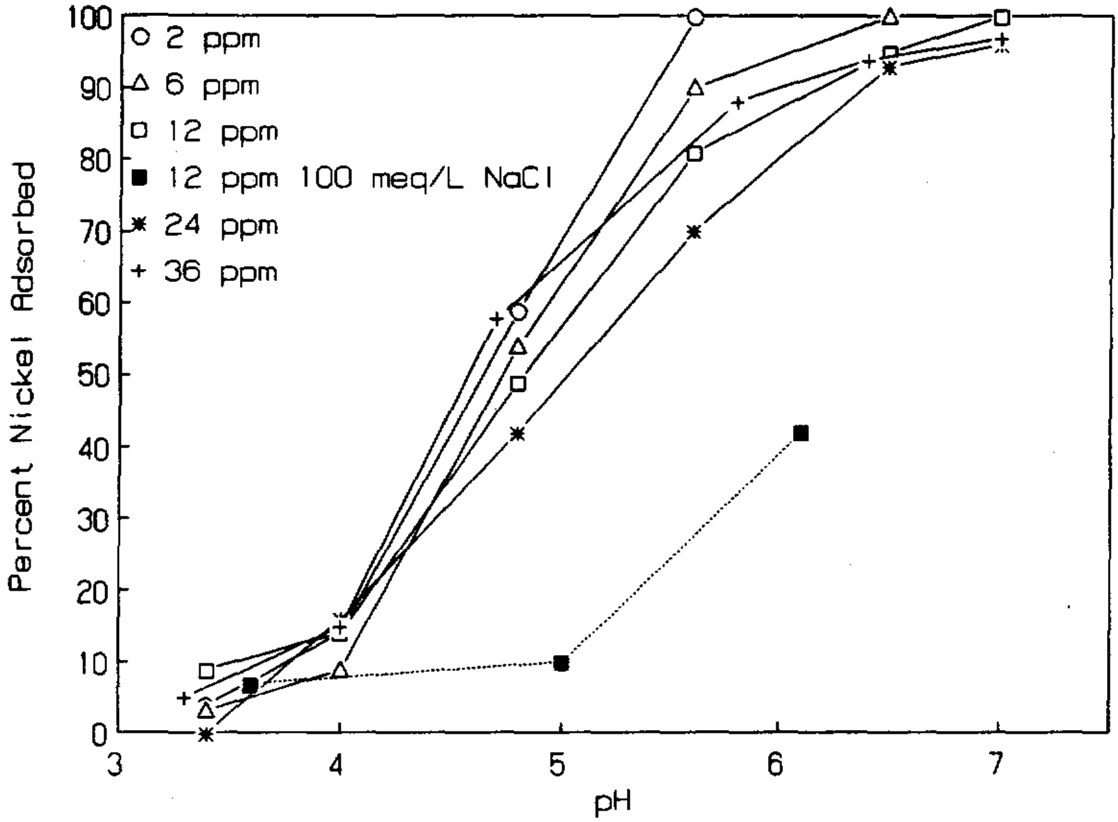

Figure 15. Relationship between percent adsorbed nickel relative to maximum adsorbed by the 'acid fly ash' and suspension pH. (Maximum adsorbed nickel was that obtained at the highest pH tested and at the highest total nickel solution concentration).

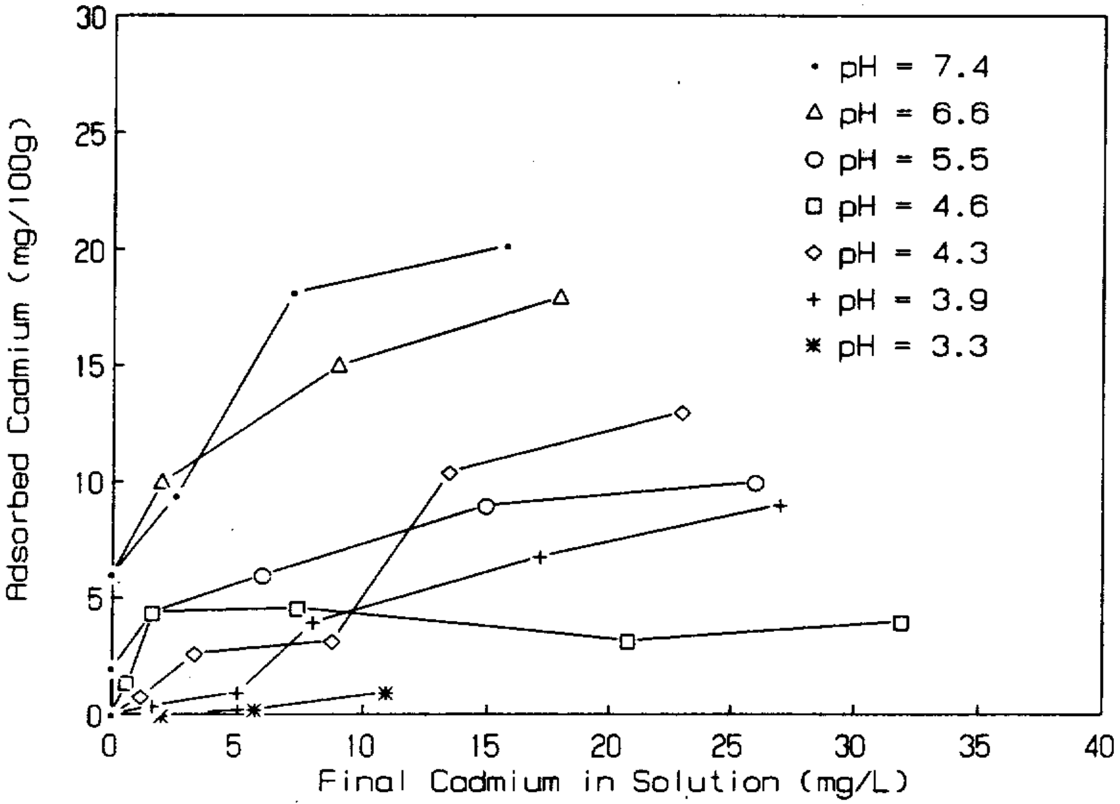

Figure 16. Relationship between adsorbed cadmium by 'alkaline fly ash' and solution concentration of total cadmium dissolved at equilibrium under various pH values.

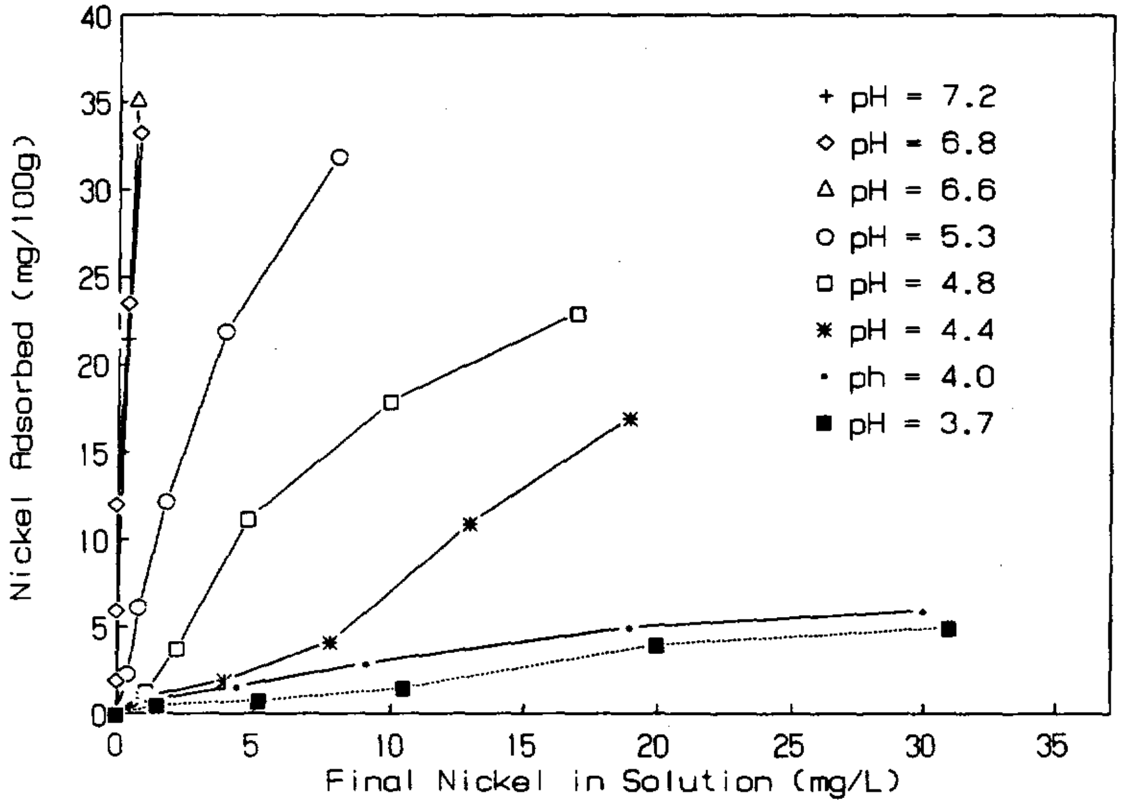

Figure 17. Relationship between adsorbed cadmium by 'acid fly ash' and solution concentration of total cadmium dissolved at equilibrium under various pH values.

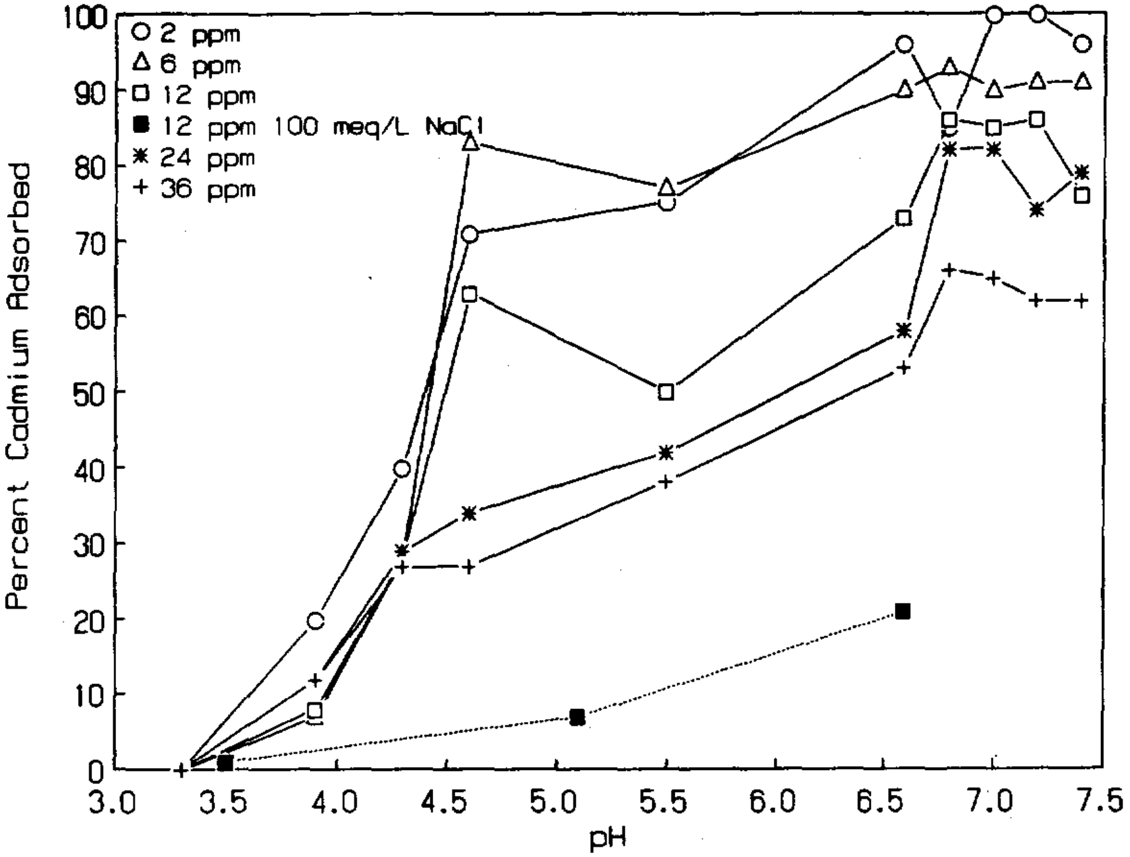

Figure 18. Relationship between percent adsorbed cadmium relative to maximum adsorbed by the 'alkaline fly ash' and suspension pH. (Maximum adsorbed cadmium was that obtained at the highest pH tested with the highest total cadmium solution concentration).

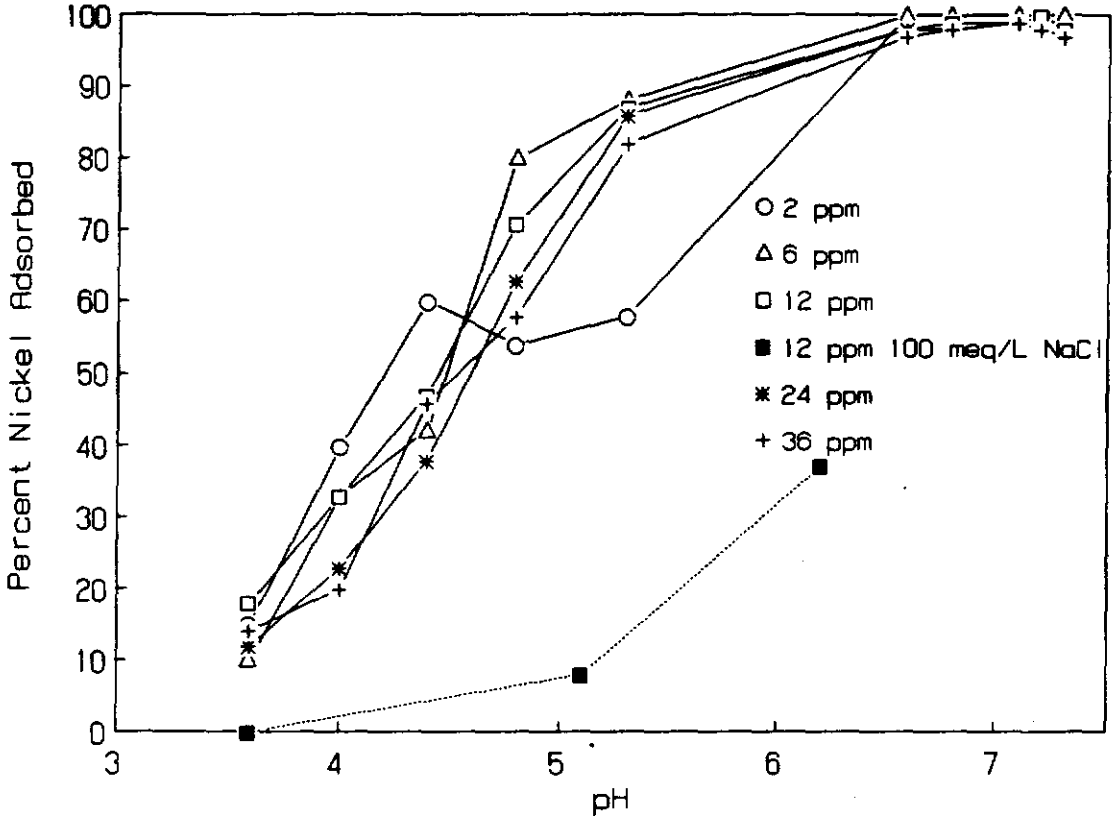

Figure 19. Relationship between percent adsorbed cadmium relative to maximum adsorbed by the 'acid fly ash' and suspension pH. (Maximum adsorbed cadmium was that obtained at the highest pH tested with the highest total cadmium solution concentration).

Fly Ash Breakthrough Columns

The results of the breakthrough column studies are shown in Figures 20 through 23. These data demonstrate that there is some gas influence on the release of boron and silica from the various fly ash samples tested. The data clearly show that the alkaline fly ash (KU6) released the most boron and silica. Furthermore, the data show that the air produced a small delay in the release of boron (compare Figure 20 with Figure 21). Some differences by gases were also observed in the case of silica release. However, these differences appear to be depended on fly ash sample.

Perhaps, the most important information to be gained from these breakthrough curves is the major differences between fly ash samples in constituent release. The data suggest that a careful evaluation of each fly ash should be carried out prior to disposal since each fly ash is chemically unique as far as pollutants are concerned.

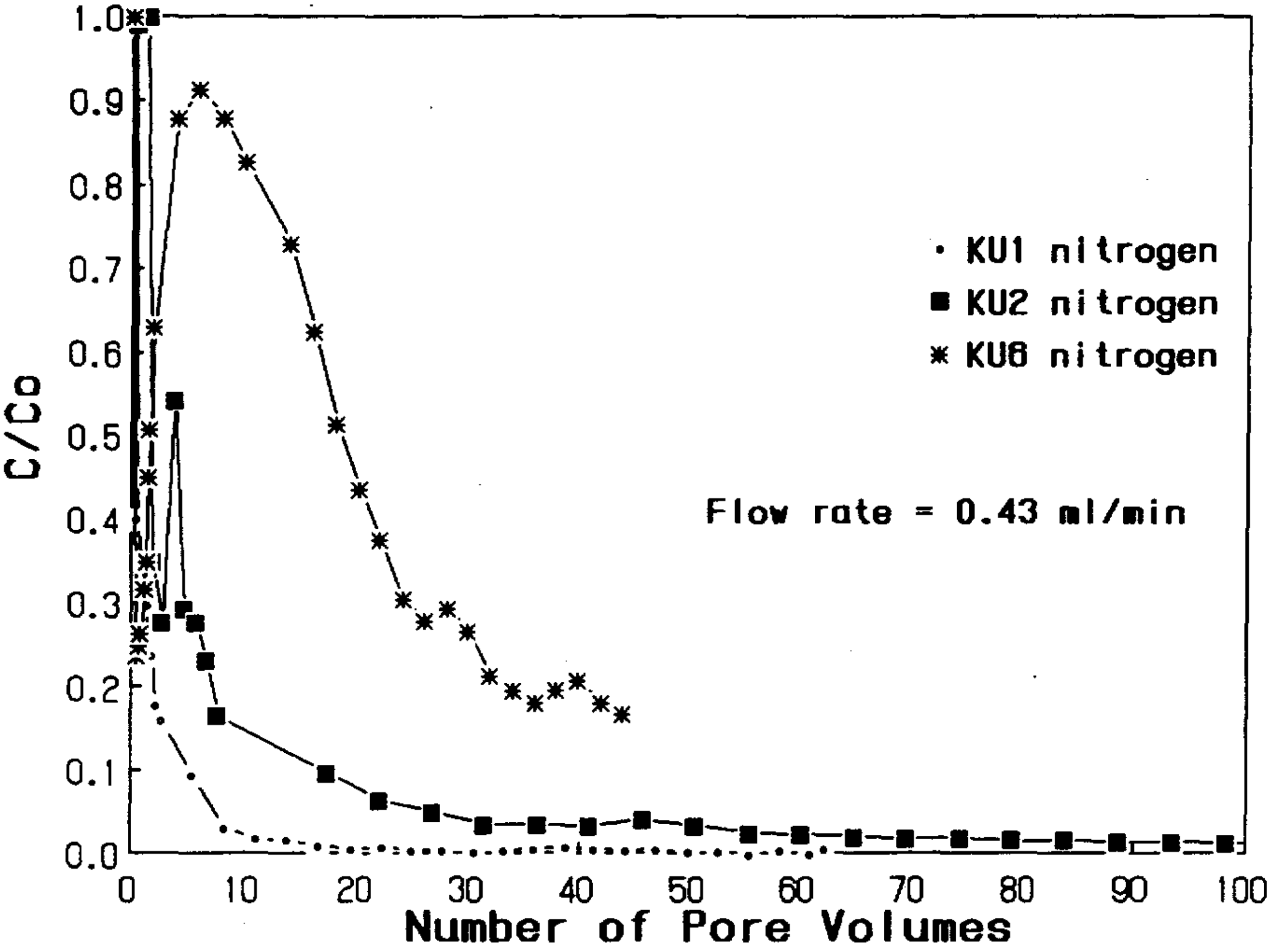

Figure 20. Breakthrough column data for boron in the presence of nitrogen gas.

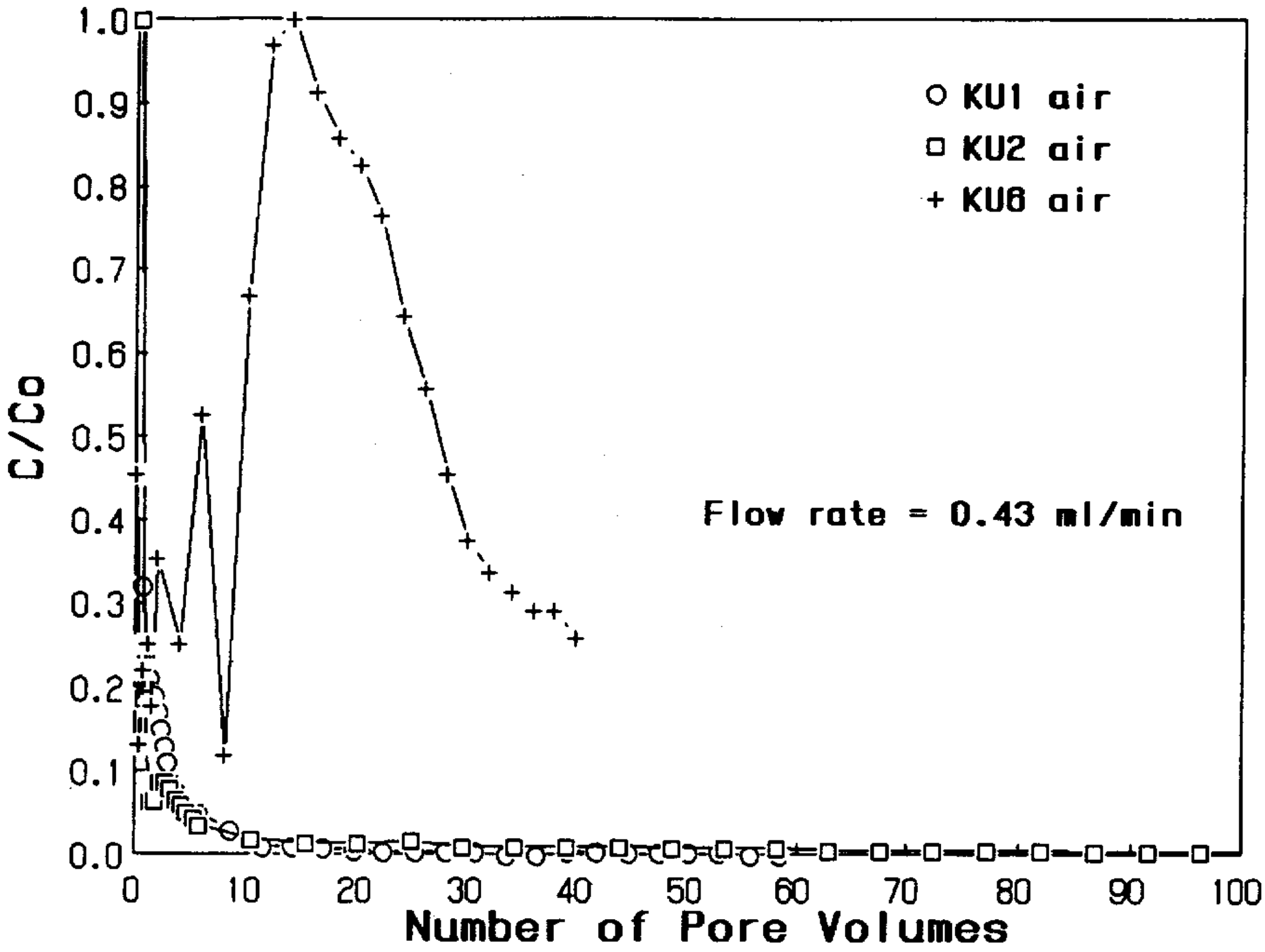

Figure 21. Breakthrough column data for boron in the presence of air with atmospheric composition.

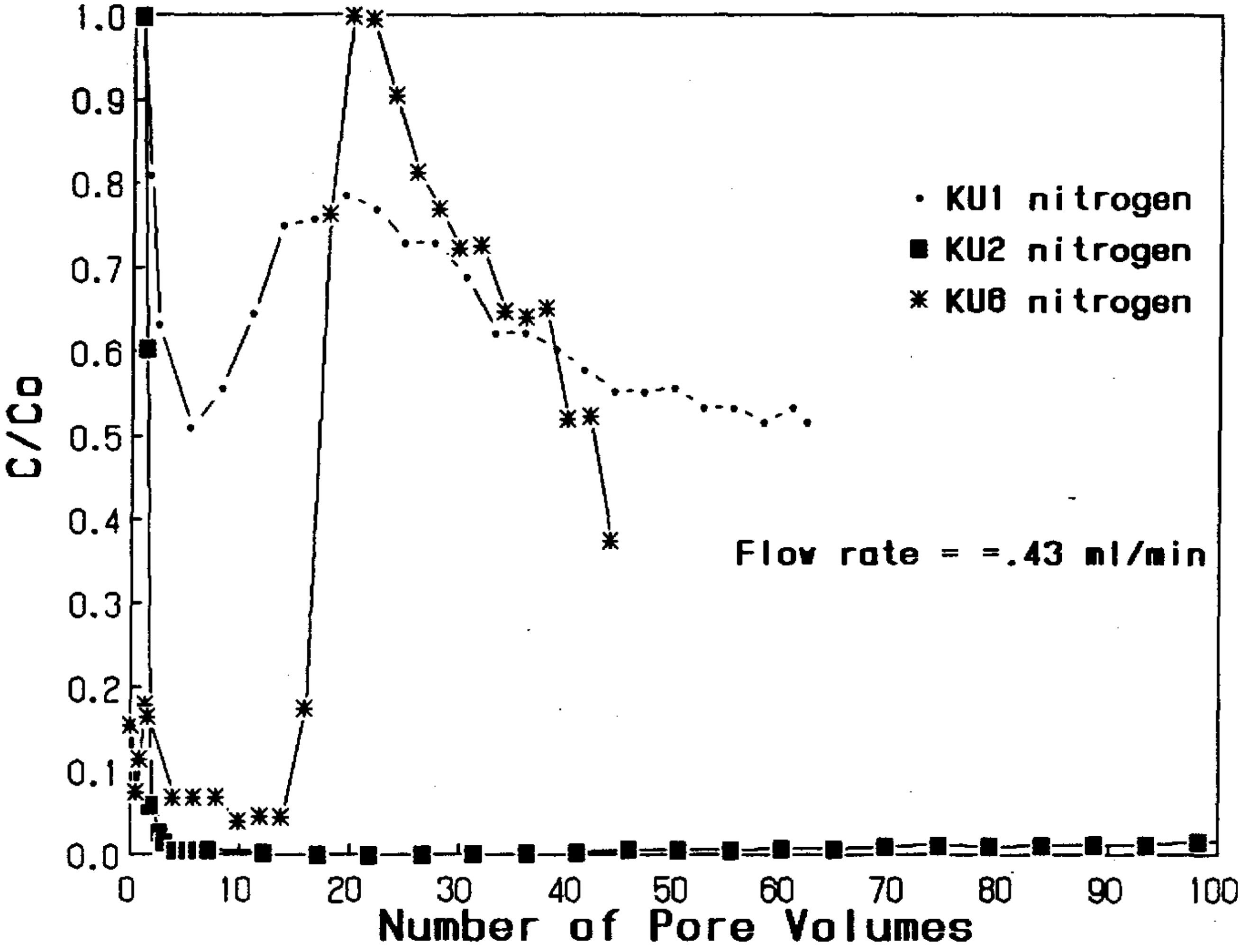

Figure 22. Breakthrough column data for silica in the presence of nitrogen gas.

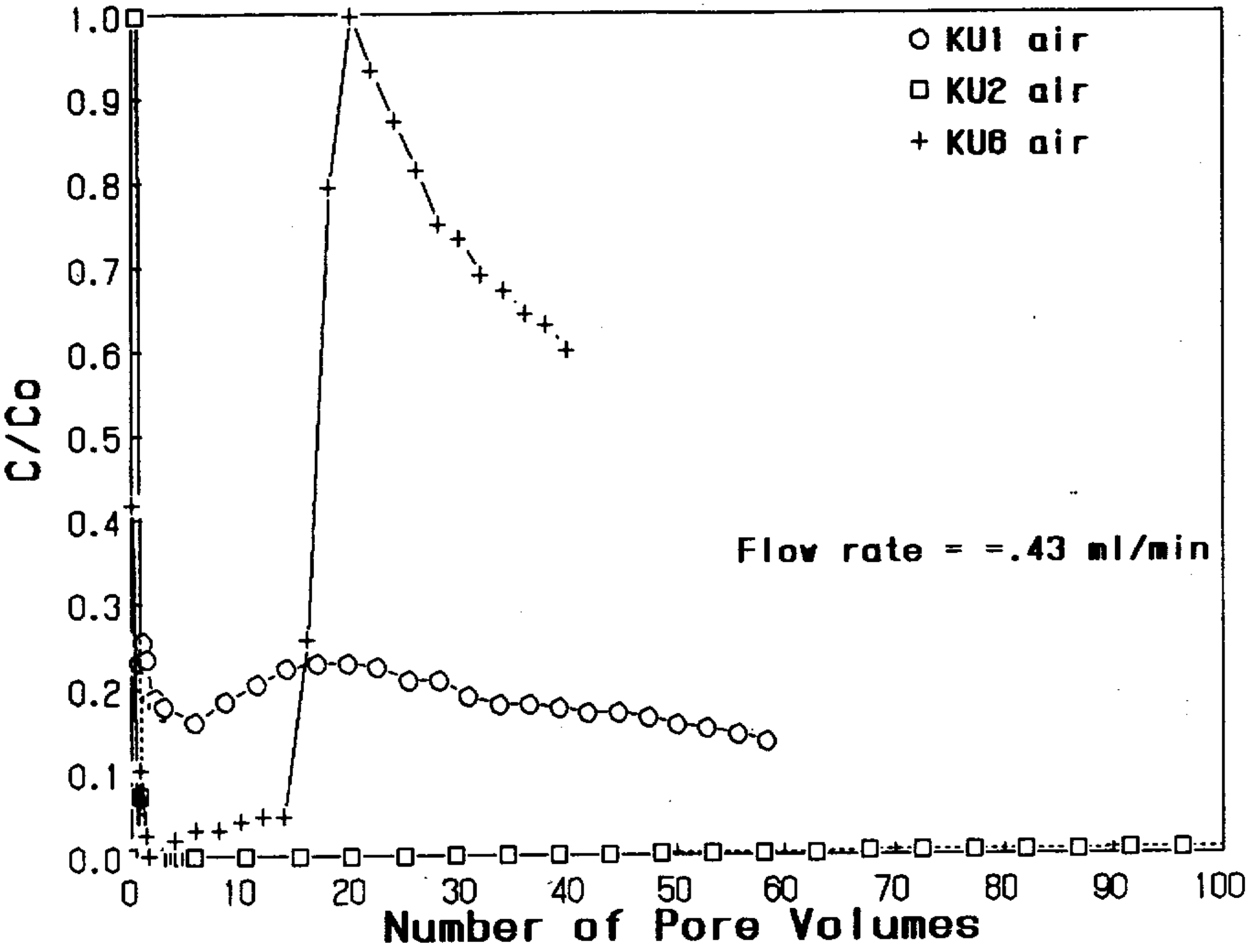

Figure 23. Breakthrough column data for silica in the presence of air with atmospheric composition.

CHAPTER IV - Conclusions

1. Fly-ash physical appearance of the samples tested varied depending on coal type and furnace.

2. Fly-ash composed of glass-like porous beads varied in chemical composition with respect to Al/Si/Fe ratio and varied in pH from extremely low (pH near 3) to near pH 11.

3. In our fly-ash sample selection we found out that the alkaline ones were associated with high boron levels.

4. Fresh Fly ash exhibited extremely low potential pH buffering capacity.

5. Potentiometric titrations of fly ash surfaces revealed a PZC_{pH} somewhere around 4.6 which was approximately midway between the PZC_{pH} of iron-oxides and SiO_2. Also, these data revealed that fly-ash surfaces exhibited an apparent pH-dependent positive charge (approximately 40 $cmol_c\ kg^{-1}$, and negative charge of approximately also 40 $cmol_c\ kg^{-1}$ with intrinsic protonation and dissociation constants of $10^{6.2}$and $10^{-7.8}$, respectively). Little if any charge was exhibited between pH 4 to 8.5.

6. Low pH buffering capacity, low pH dependent charge and relatively low PZC_{pH} appeared to make the fly ash samples tested extremely sensitive to pCO_2 with respect to lowering pH and releasing boron.

8. Increasing pCO_2 increased release of boron but it had no influence on Nickel release. This suggested that Nickel was most-likely strongly chemisorbed.

7. Because boron, the major pollutant detected in the fly-ash samples tested, is weakly held, one should avoid burying such "fresh" fly-ash samples for the purpose of protecting groundwater from boron. A more logical approach would be to allow the fly-ash to be washed by rainfall on the surface, allowing dilution of boron by major natural bodies of surface water, e.g. large rivers.

8. The acid fly ash appears to exhibit greater adsorption potential for heavy metals as pH was increased.

LITERATURE REVIEW

Adriano, D.C., A.L. Page, A.A. Elseewi, A.C. Chang and I. Straughan. 1980. Utilization and disposal of fly ash and other coal residues in terrestrial ecosystems: A review. J. Envir. Qual. 9:333-344.

Adriano, D.C., A.L. Page, A.A. Elseewi, and A.C. Chang. 1982. Cadmium availability to sundangrass grown on soils amended with sewage sludge and fly ash. J. Envir. Qual. 11:197-203.

Anderson, M.A., and D.T. Malotky. 1979. The adsorption of protolyzable anions on hydrous oxides at the isolectric pH. J. Colloid Interface Sci. 72:413-427.

Elseewi, A.A., A.L. Page and S.R. Grimm. 1980. Chemical characterization of fly ash aqueous systems. J. Environ. Qual. 9:424-428.

Harsin, A.E., and V.P. Evangelou. 1989. The electrochemical properties of soil minerals. Influence on physico-chemical stability. In "Weathering Its Products and Deposits." (ed.) S.S. Augustithis. Theophrastus Publications, S.A., Athens Greece. p. 1:197-229.

Hodgson, L., D. Dyer and D.A. Brown. 1982. Neutralization and dissolution of high-calcium fly ash. J. Environ. Qual. 11:93-98.

Phung, H.T., L.J. Lund, A.L. Page, and G.R. Bradford. 1979. Trace elements in fly ash and their release in water and treated soils. J. Environ. Qual. 8:171-175.

Roy, W.R. and R.A. Griffin. 1984. "Illinois Basin Coal Fly Ashes. 2. Equilibria relationships and qualitative modeling of ash-water reactions." Environ. Sci. Technol. 18:730-742.

Roy, W.R., and R.A. Griffin. 1982. A proposed classification system for coal fly ash in multidisciplinary research. J. Envir. Qual. 11:563-568.

Stumm, W., and J.J. Morgan. 1970. Aquatic Chemistry. John Wiley and Sons, Inc., New York, NY.

Terman, G.L. 1978. Solid wastes from coal-fired power plants - Use of disposal on agricultural lands. Natl. Fert. Devel. Center, Muscle Shoals, AL.