



Mobility of boron from coal ash in an aqueous system
by Anne Shirley Halligan

A thesis submitted in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE
in Chemistry

Montana State University

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Abstract:

An investigation of boron leachability and adsorption by coal ash under a variety of conditions was undertaken. Boron leachability was studied as a function of pH, time, ash type, particle size, and ash concentration. Total available boron, aluminum, and iron were determined. Ash retention of boron was calculated. The adsorption of boron by ash that was water conditioned and ash that was acid conditioned was studied. A re-leaching of adsorption samples was pursued to determine changes in the ash after adsorption had taken place.

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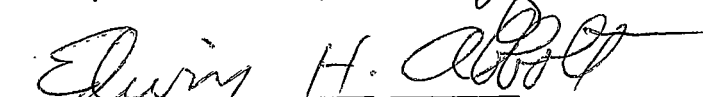
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ABSTRACT

An investigation of boron leachability and adsorption by coal ash under a variety of conditions was undertaken. Boron leachability was studied as a function of pH, time, ash type, particle size, and ash concentration. Total available boron, aluminum, and iron were determined. Ash retention of boron was calculated. The adsorption of boron by ash that was water conditioned and ash that was acid conditioned was studied. A releaching of adsorption samples was pursued to determine changes in the ash after adsorption had taken place.

INTRODUCTION

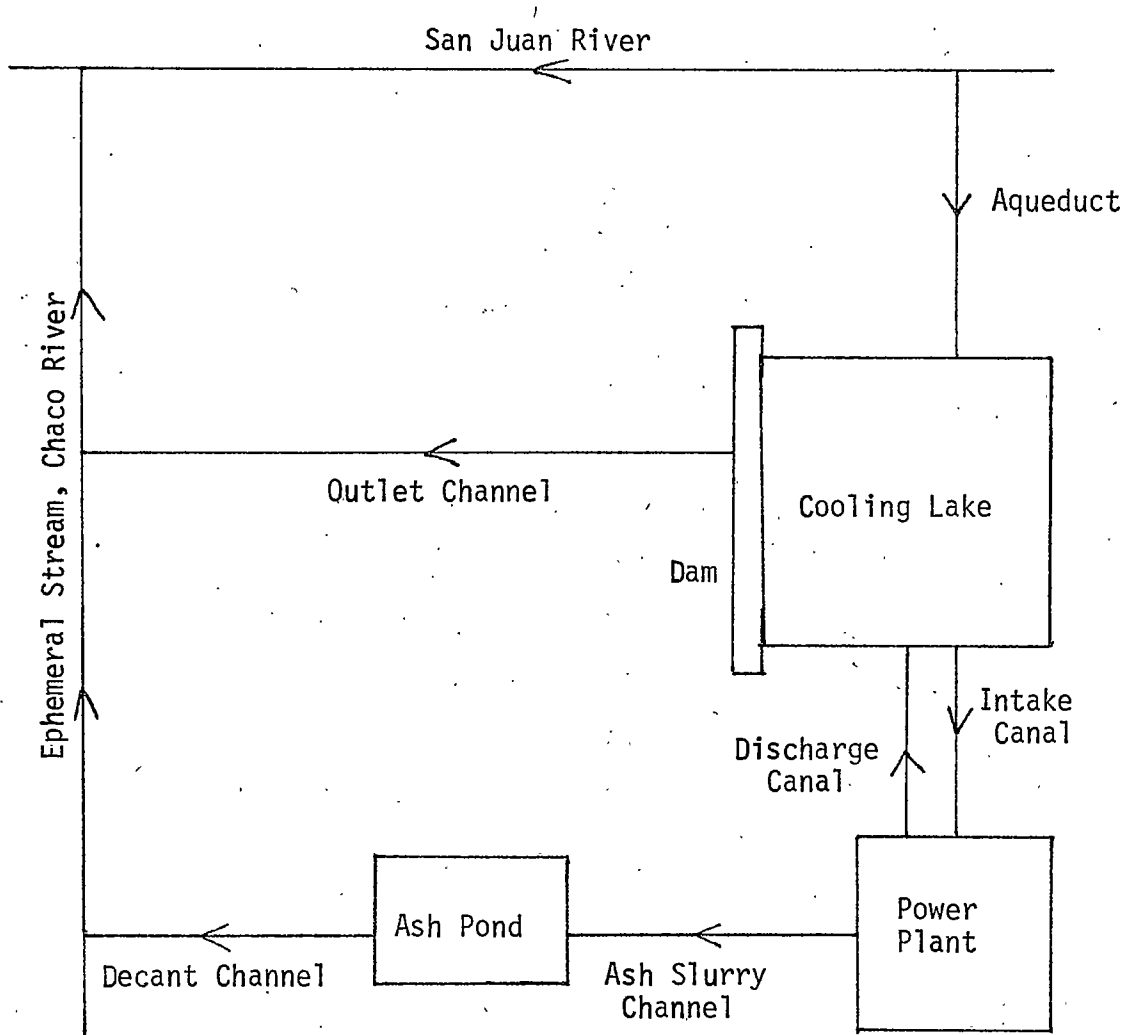
The combustion of coal as a fuel has become an important alternative power source in our modern society. Coal is among the fossil fuels which are readily available, convenient, and practical for use.

Coal combustion, like all other large scale industrial processes, does not come without its technical and environmental considerations. As a mined resource, coal has natural variability in its composition and its properties. For instance, not all coals burn consistently hot depending on when and where they were mined. The solid and gaseous wastes resulting from coal combustion present an increasing challenge in their disposal.

Solid coal wastes are commonly referred to as ash. Several methods of ash disposal are currently in use. One popular method involves sluicing in lagoons. In developing our understanding of the aqueous behavior of a sluicing pond, it is helpful to envision a schematic of a power plant operation. Figure 1 is a schematic originated by Dreesen (1) and it represents water flow at a power plant. The coal is burned in the plant to heat water to produce steam which drives the generators and produces electricity. The function of the cooling pond is to allow the superheated water to cool before returning to the river. The ash pond is involved in an entirely segregated cycle of water. Water is sprayed into the stacks. This procedure cleans the ash out of the stacks and keeps large amounts of particulate matter

Figure 1

Schematic of Water Flow at a Power Plant.
Dreesen and coworkers (1).



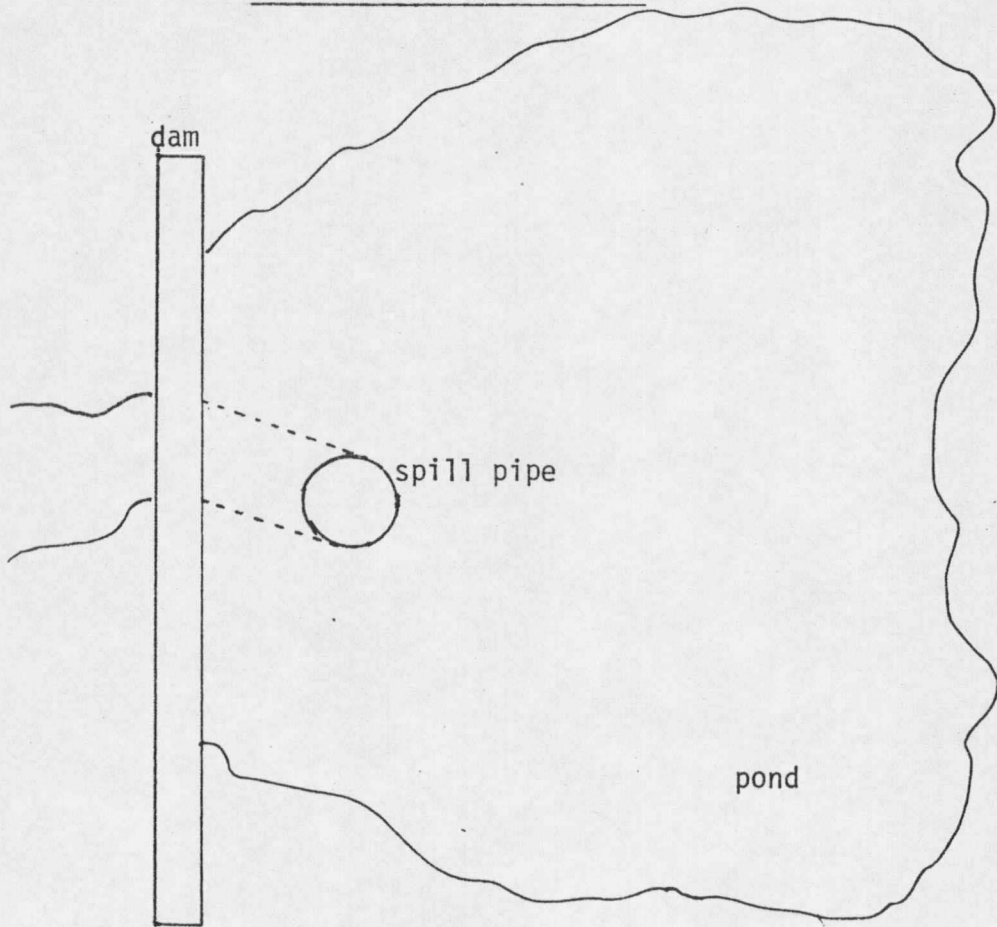
from escaping out of the stacks into the atmosphere and increasing air pollution. The slurry of water and ash is then channeled into the ash pond. The engineering of this pond is schematically shown in Figure 2. During the holding time in this pond, the solid particles in the slurry settle to the bottom and the aqueous portion is then allowed to spill back into the natural water system of the area.

Western coal often contains sizable quantities of alkali and alkaline earth oxides which upon contact with water provide basic solutions. Talbot and coworkers (2) studied the pH change of several suspended ash slurries with time. They looked at systems both open and closed to the atmosphere. They noted that in the open system there was a dramatic initial increase in pH, with hopper ash exhibiting the most change. After one week their slurries equilibrated at a pH of approximately 8.5. With the closed system they reported the same pH increase but it took several weeks to decline. Green and Manahan (3) dissolved ash in mineral acid, allowing the ash to equilibrate overnight and then back-titrated with NaOH. They reported the fly ash dissolved in discrete steps of increasing acidity, indicating the presence of specific fractions in the material. The authors also stated that scatter of data typified in their plots was due to sample inhomogeneity and uncertain pH readings in the fly ash suspensions. Compensation was made by taking large numbers of data points.

Generally, the nature of coal ash is nonvolatile, inorganic matter.

Figure 2

Schematic of an Ash Pond.



In 1977 Dreesen and coworkers (1) analyzed and found some components of ash, including such toxic elements as boron, arsenic, fluorine, molybdenum, and selenium, to be leached with water. They proved this by sampling the effluent waters of the Los Alamos, New Mexico power plant and comparing the results with samples of the influent waters. They found elevation of these elements in the effluents. For example, intake river water contained less than $0.1 \mu\text{g}/\text{ml}$ of boron but ash pond effluents contained $12.0 \mu\text{g}/\text{ml}$ and cooling lake effluents contained $0.95 \mu\text{g}/\text{ml}$ boron.

Analyses of ash content have been extensively reported and compared using a variety of analyses techniques (4-7). Ash and its parent coal vary greatly in exact content from sample to sample, but the major components can be summarized from the reports of analyses in the literature. The major component analyses condenses to: silica, calcium, aluminum, magnesium, iron, potassium, and sodium. Many trace analyses are also reported in these papers.

Other interesting interpretations of ash content have been added to the literature through the use of electron micrographs. By radiating at selected wavelengths the major component concentrations can be photographed (4,5).

In a unique study, Furr and others (7) grew cabbages in soil amended with seven percent coal ash from twenty-one coal burning power plants. They measured uptake of the toxic elements by the

cabbages. The concentrations in the cabbages of arsenic, boron, molybdenum, selenium, and strontium showed high correlation with those in the ash.

This study involves one trace component of coal ash, boron. Interest in boron comes from the fact that, although it is an essential trace nutrient for plants (8), it becomes toxic at concentrations greater than one part per million (9,10).

Boron is a rare element in the earth's crust and is most abundantly associated with fossil fuels such as oil and coal with geothermal waters (11). Boron is always found in trace amounts in natural water systems. Most natural waters contain less than one half of a part per million with slightly higher concentrations found in geothermal waters and waterways through coal rich areas (12).

Few authors have looked specifically at the relationship of boron leaching in aqueous systems. Cox and others (13) looked at boron released from coal ash. They determined total boron by dc-arc emission spectrometry. Over a sixty second span they measured boron released at pH 4.55 and pH 7.40. They reported fifty percent of total boron, which could be as high as 1900 ppm, was leached into water. They also reported the quantity of boron leached was independent of pH over the range of 6 to 8 but availability was greater in acid. Also in this paper, they suggest that thermal fixation of the boron into an insoluble chemical state could be obtained by treating the ash at

1200°C for thirty minutes.

Choi and Chen (14) reported the amount of boron leached from four common adsorbents; hydro Darco, Eiltrisorb, activated bauxite, and activated alumina, as a function of pH. For all but one adsorbent the amount of boron leached at 25 g/l increased as pH decreased below pH 6 with boron leached remaining approximately constant above pH 6.

Part of the variability in analyses of ash can be improved by fractionation of particle size. There is a relationship between the size of the ash particles and their elemental composition. Electron micrographs done by Smith (15) and Campbell (4) showed ash to be an amorphous, fragile material composed of many particle sizes, shapes, and densities. Two separate reports (16,17) group the ash into three mass-size distributions. Those elements associated with large particles ($>20.0 \mu\text{m}$) are depleted relative to the original coal composition; a second group of elements in the intermediate size fraction ($20.0\text{-}6.0 \mu\text{m}$) have similar concentrations in ash and parent coal; and a third fraction of small particles ($6.0\text{-}2.5 \mu\text{m}$) contain elements including boron, which have enriched concentrations in ash.

Another group (18) which studied size fractionation defined seventeen size fractions in ash ranging from $10 \mu\text{m}$ through submicron in size. Their results showed that volatile trace elements increased in concentration with decreasing particle size above one micron; but,

for submicron particles the concentration becomes independent of particle size. These are significant findings since small particles are most easily suspended in water and the enriched boron content is easily released.

The adsorption characteristics of boron onto soils has been extensively studied. In a series of papers, Harder (19-21) studied boron in sediments and associated it with the clay mineral, illite. His primary concern in these studies was of agricultural significance so pH and temperature were not monitored. He did however, note that boron uptake was rapid at first and then gradual after a few hours.

In 1964 Hingston (22), also interested in the study of natural sediments, investigated boron adsorption onto illite, kaolinite, and montmorillonite. He studied boron uptake as a function of pH over the range of 3.8 to 10.5 and as a function of concentration. He was the first to suggest that boron adsorption exhibited Langmuir behavior. Couch and Grim (23) also studying the clays; illite, kaolinite, and montmorillonite, determined that the initial boron concentrations and temperature had a direct relationship on boron uptake.

Metwally (24) studied boron adsorption onto freshly precipitated aluminum hydroxide as a function of pH. Sims and Bingham (25) followed this procedure but also reported an inverse relationship between boron uptake and aging of the precipitate. A similar paper by McPhail and others (26) confirmed Sims' results.

Concurrent with these studies, several investigators while looking at volcanic soils in Chile, Hawaii, and Mexico (27-29) correlated a high boron adsorption by these soils with high concentrations of aluminum in them.

In addition to aluminum hydroxide, freshly precipitated iron hydroxide was studied for boron adsorption by Metwally (24) and by Sims (25,30,31). Iron is also capable of participating in the adsorption of boron but has 200 times less capacity for adsorption than does aluminum.

Bingham and Page (32) reported that sulfur and phosphorous exhibited no influence upon the adsorption of boron by an allophanic soil.

Choi and Chen (14) reported that calcium (II) ions and magnesium (II) ions showed an effect on boron adsorption with some adsorbents.

An increase in the concentration of calcium (II) ions to a certain value resulted in a decrease in the removal of boron for all adsorbents studied. The value was dependent upon the adsorbent used. Little or no additional effect was found with further increase in the concentration of calcium (II) above the value. For example, Filtrasorb removed boron less efficiently in the presence of calcium (II) ions up to a concentration of 100 mg/l but showed no further influence with increasing calcium (II) concentration. Magnesium (II) ions effected boron removal only when Filtrasorb was the adsorbent. Silica has been suggested in several papers (2,29,32) to exhibit a competitive effect with boron for the adsorption sites. Theis and Wirth (33) suggested

that some species of manganese may play a role in the adsorption of boron.

Choi and Chen (14) examined the effects of pH upon leaching of boron from the adsorbents and conversely the pH effects upon adsorption of boron onto the adsorbents. They reported increasing boron leached below pH 6 and approximately constant amounts of boron leached for all adsorbents between pH 6 and 9. They reported the optimum pH for adsorption of boron was dependent upon the adsorbent present and upon the concentration of boron in solution. In the same paper, they reported that salinity effected removal efficiency of boron. Removal efficiency decreased sharply and the pH at which removal is most efficient, increased sharply with increasing salinity up to 8% for hydro Darco, 5% for Filtrasorb, 8% for activated bauxite, and 10% for activated alumina. Above these concentrations no further decrease in removal efficiency and increase in pH was noted.

All of the previous adsorption studies used soil or some well-characterized surface as the adsorbent. In this study the ash was examined as a participant in the adsorption process. The mobility of boron in an aqueous system has been shown to be influenced by: pH, temperature, type and amount of adsorbing solids, the shape and density of the ash, and other chemical species present.

STATEMENT OF THE PROBLEM AND RESEARCH OBJECTIVES

Boron is one of the toxic elements in coal ash which is readily leachable into an aqueous system. The determination of the mechanism of boron mobility in a natural system involves many factors. A mechanism has been suggested to involve the adsorption and desorption of boron species from solid surfaces. Many conditions can influence such a process and need to be studied specifically. What type of soil or ash are present and does total concentration of these effect the efficiency of the system? What is the species of boron involved and what is its solubility in water? What are the maximum limits of the adsorption and desorption? And it must be determined if the process is simple reversible or if some parameters such as pH, time, and temperature effect the forward and reverse sequences differently.

Boron adsorption and desorption from soils has been studied by many workers. Few people have looked at the role of boron from coal ash. In this study, investigations were undertaken to determine the influence of pH, time, and ash type upon boron leachability. The influence of particle size upon a variety of components was studied. Ash concentration was varied and was determined to have a significant effect upon the amount of boron released. The boron retained was calculated and total availability of boron was then experimentally determined. Based upon the enhanced leachability of a variety of

major components with acid, analyses of total availability of these components was made. Iron and aluminum were specifically studied.

Further investigation of retained boron lead to adsorption experiments. Adsorption was studied by water conditioned ash and acid conditioned ash. The effects of pH upon the process were also determined. Additionally, releaching of the adsorption samples was investigated to determine changes in the ash after adsorption had taken place.

EXPERIMENTAL SECTION

Ash samples were obtained from the Boundry Dam Power Station near Estevan, Saskatchewan, Canada, and from a test burn of coal to be used at the Poplar River Power Project in southern Saskatchewan. A description of the ash samples is presented in Table 1. The ash samples were passed through 100 mesh screen prior to leaching. Particles were manually fractionated with the use of concentric sieves. The sieve sizes were 100, 140, 200, and 325 mesh. The mesh sizes correspond to openings of 150 μm , 125 μm , 75 μm and 45 μm , respectively. All adsorption studies were done on ash which passed through the 325 mesh sieve.

Whenever possible all procedures were carried out in polypropylene or teflon containers to avoid any possibility of leaching boron from glassware, especially at extreme pH values or elevated temperatures.

The leaching studies involved mixing 50.0 ml of leachate water, distilled or natural, with the desired amount of ash. The solutions were kept in polypropylene beakers covered by watch glasses. This provided for exchange of carbon dioxide. Water lost by evaporation was replaced through the regular addition of doubly-distilled water. At the desired time interval, an aliquot of leachate solution was withdrawn and analyzed. A Parr, teflon-lined bomb was utilized to digest the ash samples when elevated temperatures and HF were used.

Table 1

Description of Ash Samples.

<u>Sample</u>	<u>Description</u>
A1	Bottom Ash--Poplar River
A2	Upper Ash--Poplar River
A3	Dust Ash--Poplar River
A4	Upper Ash, 5-day composite, Boundry Dam
A5	Bottom Ash, 5-day composite, Boundry Dam
A6	Composite: A1 (23.5%), A2 (4.7%), A3 (71.8%), Poplar River
A7	Composite: A4 (58%), A5 (42%), Boundry Dam

Adsorption experiments involved suspending the ash samples in solutions of known boron concentration and measuring the decrease in solution boron concentration after forty eight hours.

Ash was conditioned for the adsorption experiments by leaching 25 grams with three liters of doubly-distilled water. This was done in three consecutive liter portions for one and one half hours each. The ash was filtered and air dried. The acid conditioned ash prepared by the same procedure was mixed with one molar HCl or HNO₃ and immediately filtered and dried. Adsorption experiments were carried out in covered polypropylene bottles to minimize evaporation. Sodium borate was used as the standard boron reference. Adsorption experiments were allowed to equilibrate for two days before measurement. The adsorption experiments were done at fifty five grams of ash per liter and in 10 ml portions. The releachings of the adsorbent were in 5 ml portions.

Ash was succesively washed for a determination of total release of components to leachates. One gram of ash was subjected to washes in one liter of 1 M HNO₃, 1 M NaOH and doubly-distilled water. Samples were then shaken on a mechanical shaker for twenty four hours, centrifuged for twenty minutes at nine thousand rpms, and decanted. This procedure was repeated for a total of three washings. The nine leachates were analyzed separately.

Solution pH was adjusted with additions of variable concentrations

of NaOH or HNO_3 for the leaching experiments. For the adsorption experiments buffers were used. The buffers used were: Trizma base [Tris (hydroxymethyl) amino methane], phosphate buffer, ammonia buffer, and acetate buffer.

All reagent solutions were prepared using doubly-distilled water. Unless otherwise specified, all experimental solutions were also made with doubly-distilled water.

All natural water samples were filtered through 0.45 micron filters prior to use. The natural water obtained from the Boundry Dam Project had the following characteristics: pH = 8.25, specific conductance = 740 $\mu\text{mhos/cm}$, $\text{HCO}_3^- = 2.4 \text{ mg/l}$, $\text{SO}_4^{2-} = 210 \text{ mg/l}$, $\text{Cl}^- = 10.3 \text{ mg/l}$, $\text{Ca} = 4.4 \text{ mg/l}$, $\text{Mg} = 22.3 \text{ mg/l}$, $\text{K} = 11.2 \text{ mg/l}$, $\text{Na} = 92.2 \text{ mg/l}$, $\text{B} = 0.343 \text{ mg/l}$. The natural water obtained from the Poplar River had the following characteristics: pH = 8.30, specific conductance = 986 $\mu\text{mhos/cm}$, $\text{HCO}_3^- = 406 \text{ mg/l}$, $\text{SO}_4^{2-} = 189 \text{ mg/l}$, $\text{Cl}^- = 6.0 \text{ mg/l}$, $\text{Ca} = 33.0 \text{ mg/l}$, $\text{Mg} = 33.9 \text{ mg/l}$, $\text{K} = 9.8 \text{ mg/l}$, $\text{Na} = 140 \text{ mg/l}$, $\text{B} = 0.820 \text{ mg/l}$.

Boron concentrations were evaluated by the curcumin method utilizing drying at 75.0°C. The sensitivity of the adsorption experiments lead to an examination of nitrate interference. Nitrate was determined to yield erroneously high results which are significant when working in the lower limits of sensitivity of the curcumin method of boron analyses. Hydrochloric acid was utilized for all acid related portions of the adsorption experiments. Atomic adsorption spectrophotometry, with

appropriate radiation buffers, was used to determine sodium, potassium, calcium, magnesium, aluminum, cadmium, chromium, copper, manganese, lead, and iron. Bicarbonate was determined by HCl titration, and pH was monitored by a Radiometer M-26 pH meter using glass-SCE electrodes. Sulfate was determined by colorimetric titration (38) and chloride by iron-thiocyanate procedure. Table 2 contains a summary of these procedures. The standard curve for the boron analyses, curcumin method is presented in Figure 3.

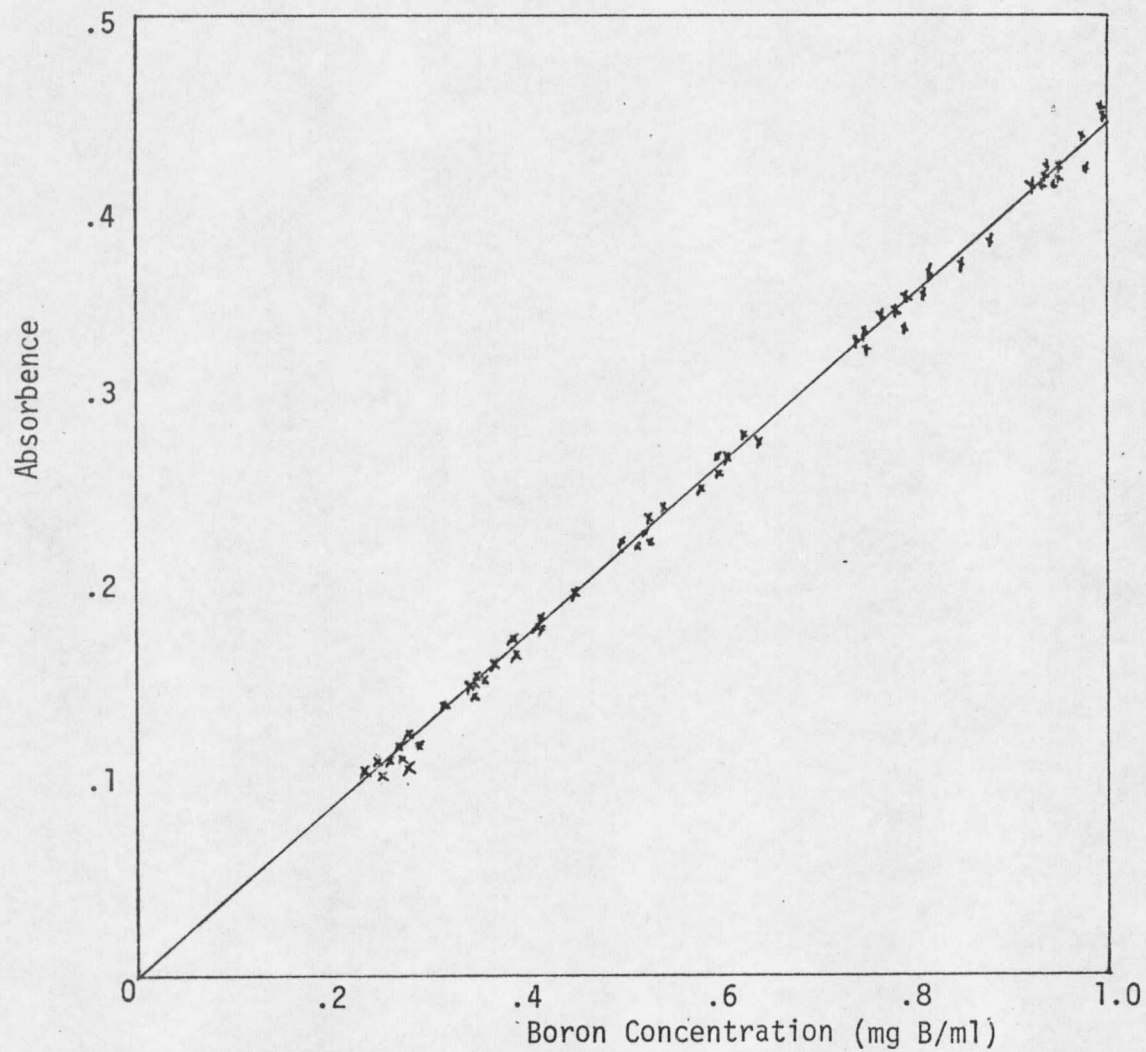
Table 2

Analytical Procedures.

Specific Conductance	Determined by standardized probe and corrected to 25°C.
pH	Measured by standardized electrodes, glass and SCE reference.
HCO ₃ , CO ₃ , OH	These are determined potentiometrically (pH) by titration with standard acid.
SO ₄	Titration with standard barium using nitrosulfazo III indicator for equivalence point detection.
Cl	Spectrophotometric using Hg(SCN) ₂ and Iron (III).
NO ₃	Brucinic sulfate and/or spectrophotometric method.
Na, K, Ca, Mg	Determined by atomic absorption spectrophotometry using appropriate radiation buffers.
SiO ₂	Spectrophotometric using molybdo-silicate procedure.
Boron	Curcumin method, spectrophotometric with color development at 75°C.
Al, Cd, Cr, Cu, Fe, Mn, Pb, Zn	Determined by atomic absorption spectrophotometry.

Figure 3

Standard Curve for Boron Analyses.
(over 12 different experiments).



RESULTS AND DISCUSSION

Ash Composition

Four ash samples were leached with doubly-distilled water to ascertain water leachable components. The results are summarized in Table 3. The major water leachable components of these ashes are sodium, potassium, calcium, magnesium, sulfate, carbonate, iron, and aluminum. The important water leachable trace metals are strontium, vanadium, boron, copper, and zinc. The data indicates that some ash components, including boron, are readily leachable into water. Component analyses of ash from different parent coals can not be compared directly because of the variability of mined natural resources. It is reasonable to note that the ash samples analyzed show major components similar to those reported by other authors (4-7).

Three samples of A2 were leached with reservoir water as shown in Table 4. In one sample the water was concentrated, in one sample the ash was heated. The analysis of the reservoir water is also included in Table 4. The heated ash composite was prepared from bottom ash that had been heated to 2000°F for ½ hour, and upper and dust ash that had been heated to 350°F for 1 hour. The concentrated reservoir water was prepared by slow evaporation of the reservoir water as received.

Four aliquots of leachate were withdrawn at 168 hour intervals for time analyses. It can be noted that time is a factor in the leachability of the components. Boron leached with reservoir water

TABLE 3

Chemical Analyses of Ash Leachate Solutions.

A1, A2, A3, A6, 1 g/l, open to atmosphere, 166 hours.

Major Component Leached from Fly Ash Samples.

<u>Sample</u>	<u>HCO₃⁻</u>	<u>CO₃⁼</u>	<u>SO₄⁼</u>	<u>Cl⁻</u>	<u>NO₃⁻</u>	<u>Na⁺</u>	<u>K⁺</u>	<u>Ca⁺⁺</u>	<u>Mg⁺⁺</u>
Values are mg/g Ash									
A2	42.31	3.44	5.49	<1.00	<1.00	.349	.204	12.33	1.54
A3	40.16	18.95	6.49	<1.00	<1.00	.602	.077	20.47	1.72
A1	25.49	2.19	2.50	<1.00	<1.00	.192	.127	7.11	1.68
A6	36.42	15.22	5.79	<1.00	<1.00	.508	.164	17.45	1.56

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Measured Parameters for Ash Leachates.

<u>Sample</u>	<u>pH</u>	<u>S.C. mmhos/cm</u>	<u>Σcation meq/l</u>	<u>Σanion meq/l</u>	<u>TDS mg/g</u>
1.0 gr Ash + 1000 gr H ₂ O, equilibration with atmosphere.					
A2	9.05	0.072	0.76	0.88	67.60
A3	9.78	0.109	1.19	1.17	90.50
A1	8.98	0.051	0.51	0.51	41.40
A6	9.72	0.098	1.03	1.02	79.10

Table 3 (continued)

Trace Metals Water Leached from Fly Ash Samples.

Values are $\mu\text{g/g}$.

<u>Sample</u>	<u>Cd</u>	<u>Cr</u>	<u>Cu</u>	<u>Fe</u>	<u>Mn</u>	<u>Ni</u>	<u>Pb</u>	<u>Zn</u>	<u>B</u>
A2	<5.1	<5.1	7.17	183.4	<5.1	<41	<41	<5.1	264
A3	<5.1	<5.1	<5.1	29.7	<5.1	<41	<41	<5.1	586
A1	<5.1	<5.1	<5.1	32.8	<5.1	<41	<41	7.2	215
A6	<5.1	<5.1	<5.1	24.6	<5.1	<41	<41	5.1	504

<u>Sample</u>	<u>As</u>	<u>Mo</u>	<u>Sr</u>	<u>Se</u>	<u>Zr</u>	<u>Sb</u>	<u>Co</u>	<u>Al</u>	<u>V</u>
A2	<41	<20.5	177.2	<41	<5.1	<41	<41	--	6.15
A3	<41	<20.5	339.1	<41	<5.1	<41	<41	--	7.17
A1	<41	<20.5	121.9	<41	<5.1	<41	<41	788.2	<5.1
A6	<41	<20.5	304.3	<41	<5.1	<41	<41	--	9.22

Table 4.

Successive Leaches with Reservoir Water.

A2, time separation 168 hours. Results in mg/l leached at 60 g/l, open to atmosphere.

<u>Sample</u>	<u>Wash</u>	<u>pH</u> *	<u>HCO₃</u>	<u>CO₃</u>	<u>Na</u>	<u>K</u>	<u>Ca</u>	<u>Mg</u>	<u>B</u>	<u>Cl</u>	<u>NO₃</u>	<u>SO₄</u>
A2 reservoir water	1	9.01	171	56	183	10.9	33.4	41.4	16.0	9.3	4.5	425
	2	9.10	331	71	158	17.7	19.0	59.2	4.8	8.8	3.2	238
	3	9.12	367	55	170	20.0	20.3	53.1	2.6	9.0	3.5	243
	4	8.97	380	48	167	20.2	20.8	52.3	1.9	5.6	2.2	222
A2- concentrated reservoir water	1	9.08	280	95	323	19.1	21.1	56.7	17.0	15.3	9.4	601
	2	9.22	499	125	299	34.4	15.4	88.1	5.6	14.7	6.9	437
	3	9.22	526	105	314	38.4	15.6	75.1	3.3	15.2	5.8	418
	4	9.19	538	98	320	39.0	14.0	73.0	2.6	15.2	3.3	437

* not in mg/l

Table 4 (continued)

<u>Sample</u>	<u>Wash</u>	<u>pH</u> [*]	<u>HCO₃</u>	<u>CO₃</u>	<u>Na</u>	<u>K</u>	<u>Ca</u>	<u>Mg</u>	<u>B</u>	<u>Cl</u>	<u>NO₃</u>	<u>SO₄</u>
A2-heated ash in reservoir water	1	8.85	203	30	160	10.7	23.1	33.0	10.0	12.3	2.7	338
	2	9.00	384	52	161	17.3	17.0	60.1	3.0	8.2	3.0	229
	3	9.03	393	47	165	26.5	17.4	55.1	1.9	8.2	3.4	245
	4	9.02	370	41	169	21.1	20.6	47.3	1.4	7.0	2.3	230
Reservoir water		8.30	406	-	140	9.8	33.0	33.9	.8	6.0	3.2	189
Concentrated Reservoir water		8.88	542	42.5	257	17.9	18.0	59.6	1.6	12.6	7.1	360

* not in mg/l

16 ml/l (0.30 mg/g) in the first 168 hours but had leached a total of 26 mg/l (0.47 mg/g) by 720 hours. The use of natural water assimilates the natural system at the power plant site.

Variation of pH with Time

The leaching of ash materials derived from western coals with distilled water or a natural water generally provides a basic solution. The pH of the distilled water solutions rapidly rises as the oxides dissolve, with subsequent decrease in pH due to absorption of carbon dioxide. This decrease in pH as a function of time is shown in Figure 4, curve a and Table 5. Long-term leaching studies using distilled water with the exclusion of carbon dioxide exhibit a much slower rate of pH decrease (2). When the leachate water has sizeable bicarbonate buffering capacity, curve b in Figure 4, the pH does not exhibit the rapid initial rise, but rather gradual approach to a steady-state pH value as bicarbonate is converted to carbonate. The leaching of ash with a water that contains bicarbonate alkalinity ($\text{pH} = 8.3$, $\text{HCO}_3^- = 6.7 \times 10^{-3} \text{M}$) will not obtain the high pH values observed for the distilled water leach (see Figure 4, curve b). However, at high concentrations of ash the buffer capacity of the water could be exhausted and result in higher steady state pH values.

Summation of sodium, potassium, magnesium, and calcium analyses values, in Table 3, provide an indication of basic material present

Figure 4

pH of Leachate Solutions with Time. Curve (a) 1 gr A6/liter distilled water;
curve (b) 60 gr A4/liter of Boundry Dam water.

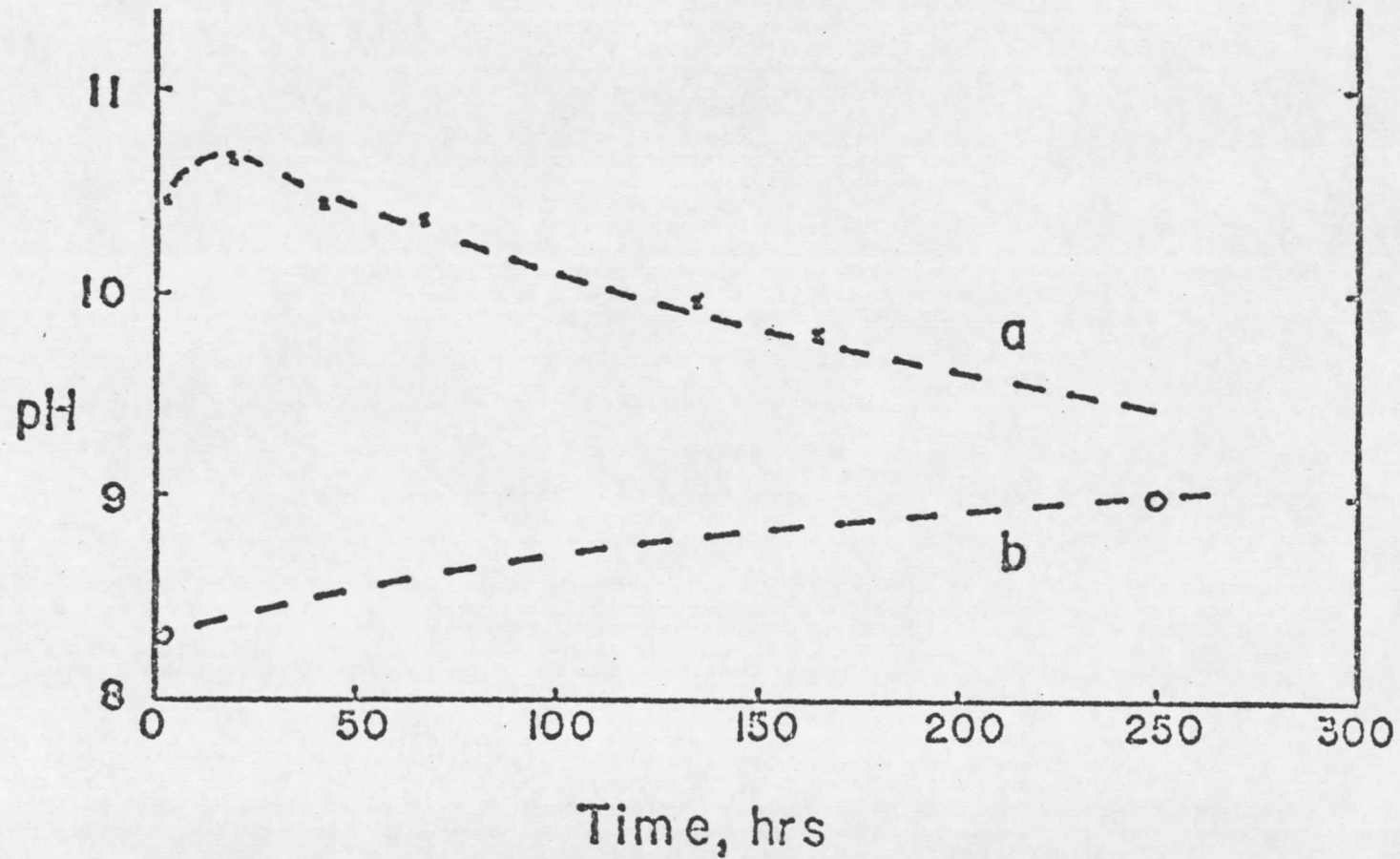


Table 5

pH of Ash Slurry with Time.

A6 and A4, doubly-distilled water leach, 1 g/l, natural water leach
60 mg/l.

<u>Time: hours</u>	<u>pH A6 with doubly- distilled water</u>	<u>pH A4 with natural water</u>
0	10.4	8.3
19	10.7	-
43	10.5	-
67	10.4	-
135	9.9	-
165	9.8	-
250	-	9.0

in the ash. The final pH values will be dependent upon the number of basic sites in the ash, with a larger number providing a higher steady state pH.

Release of Boron with Time

Several studies were undertaken to investigate the influence of contact time on the concentration of boron in the leachate solutions. The results are summarized in Figure 5 and Table 6. The amount of boron released exhibits a rapid initial increase, with the rate of release decreasing with time. For example, sample A4 releases 72 $\mu\text{g B/g}$ ash in 216 hours. After 720 hours the additional boron leached is only 36 $\mu\text{g B/g}$ ash.

Boron concentration exhibits a steady-state value after approximately thirty days. Boron leaching rates are characteristic of the ash type used. Therefore, leaching rate differences should be considered when comparing analyses of different ash types. To compare studies of the same ash but different leaching times, the leaching values can be calculated to standardize the time relationship.

It is interesting to note that the boron concentrations continue to change after the pH of the leachate solutions has approached its steady state value. In addition, the specific conductance remains essentially constant during this time span.

Figure 5

Release of Boron from Ash as a Function of Time. Curve (a) 60 g A6/liter of Poplar River water; curve (b) 55 g A4/liter of Boundry Dam water; curve (c) 55 g A5/liter of Boundry Dam water.

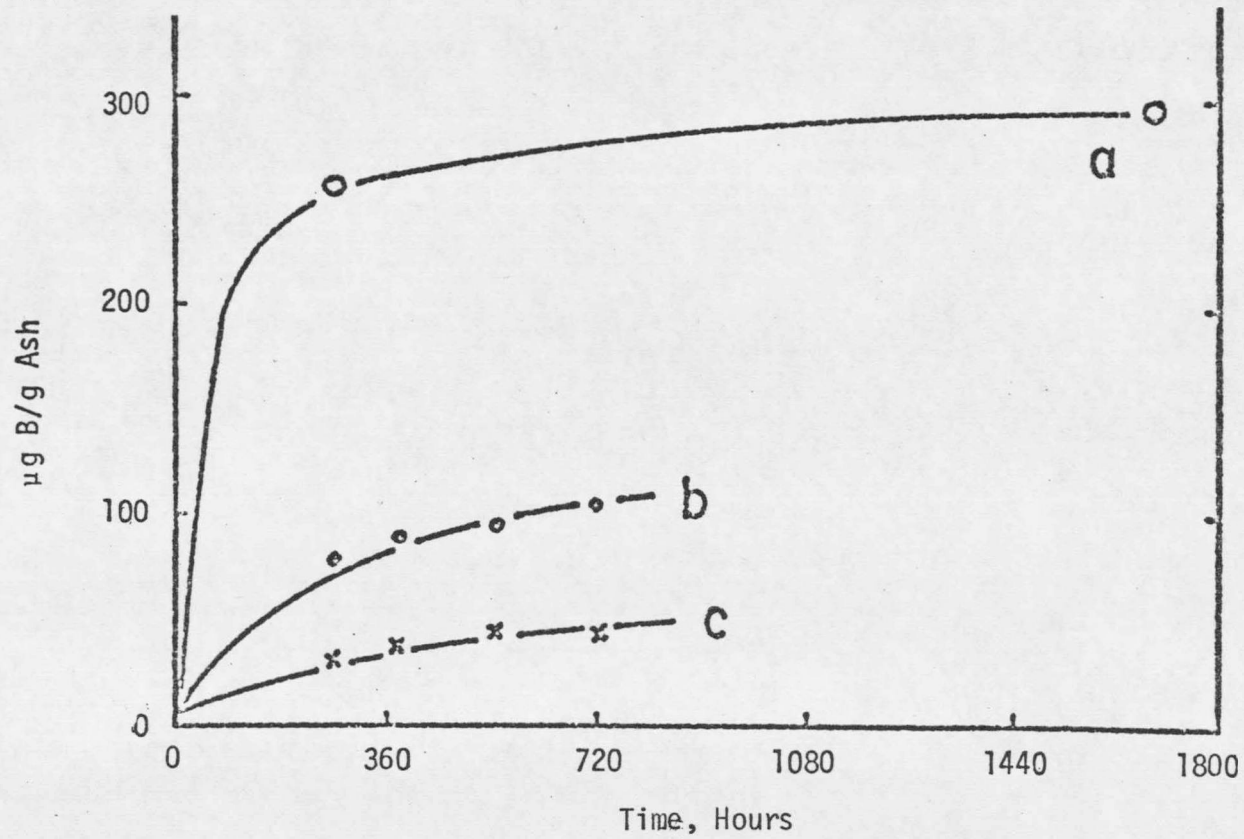


Table 6

Release of Boron with Time.

A6, A4, A5, 60 g/l, 55 g/l, 55 g/l, open to atmosphere, results in
 $\mu\text{g B/g}$ ash.

<u>Time: hours</u>	<u>a</u>	<u>b</u>	<u>c</u>
216	259	72	30
384	-	89	36
552	-	95	44
720	-	108	39
1680	294	-	-

Variation of Boron Leached with pH

Ash samples A4, A5, and A6 were leached with solutions of various hydrogen ion concentrations to determine the effects upon boron leachability. These leachings were done at ash concentrations of 1.0 gram per liter. In addition, sample A4 was studied over the same pH range and at an ash concentration of 5.5 grams per liter. The results of these studies are summarized in Figures 6 and 7 and Table 7.

The data indicates that boron leachability is influenced by hydrogen ion concentration and that boron is most readily leached into acid solutions. Sample A4 at 5.5 g/l leached 0.8 mg B/g at pH 2.5 and 0.4 mg B/g at pH 12.0.

Many elements exhibit enhanced release from solid materials under high and low pH conditions (33). Since boron forms anionic species, its leachability may be enhanced at higher pH values. Other studies indicate the boron leaching rate is greater in acid, but that the total amount leached was pH independent over the range of 6-9 (13,14).

Acid Leachable Components

The dissolution of the ash samples with a mixture of acids, HCl/HNO₃/HF, at 100°C, was utilized to provide an indication of the total available sodium, potassium, calcium, magnesium, and boron. The results are summarized in Table 8. The values for potassium, calcium, and

Figure 6

Release of Boron from Ash as a Function of pH, 1 g/l.

A4, A5, A6, open to atmosphere, time: 192 hours.

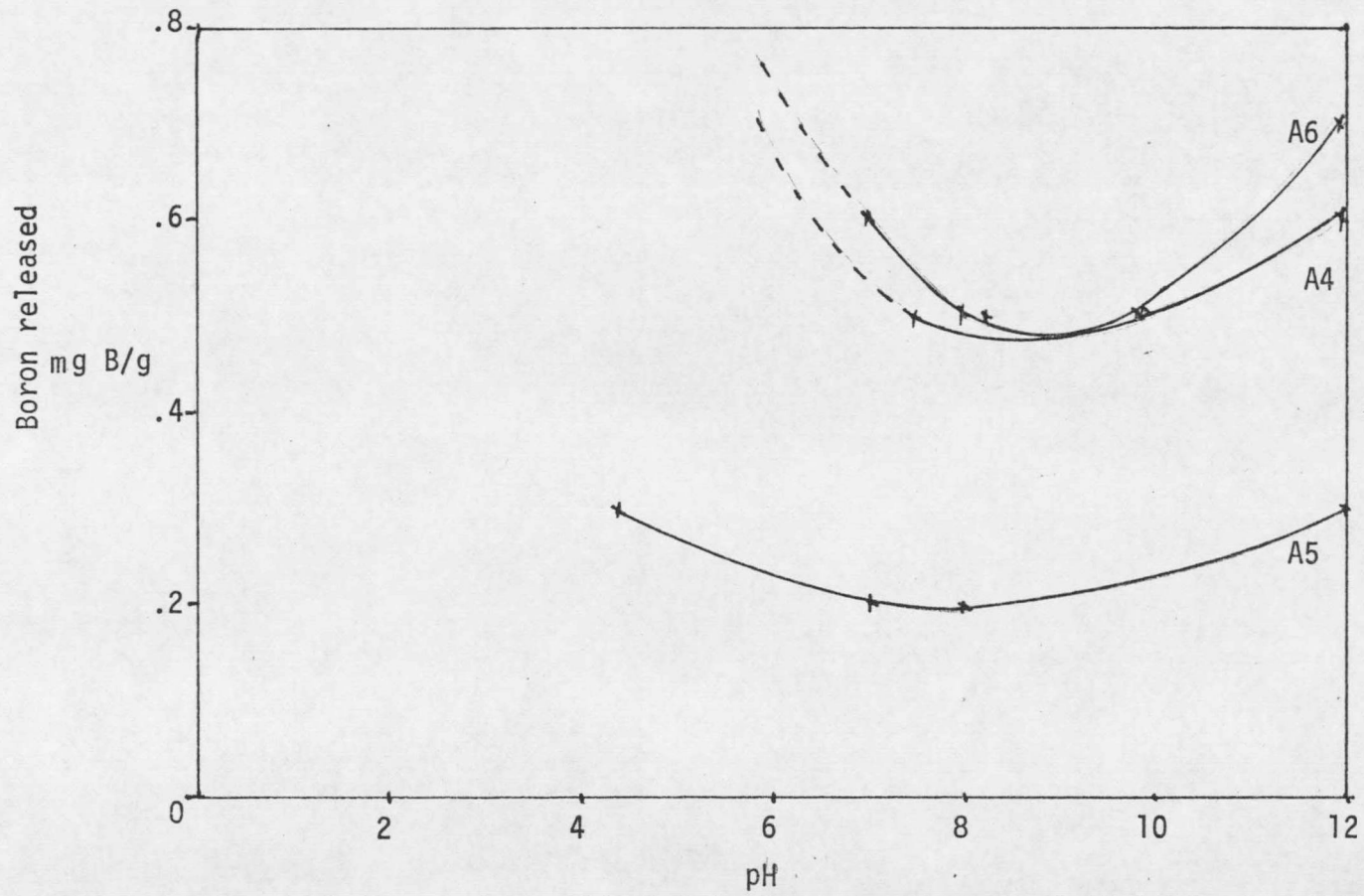


Figure 7

Release of Boron from Ash as a Function of pH, 5.5 g/l.

A4, open to atmosphere, time: 720 hours.

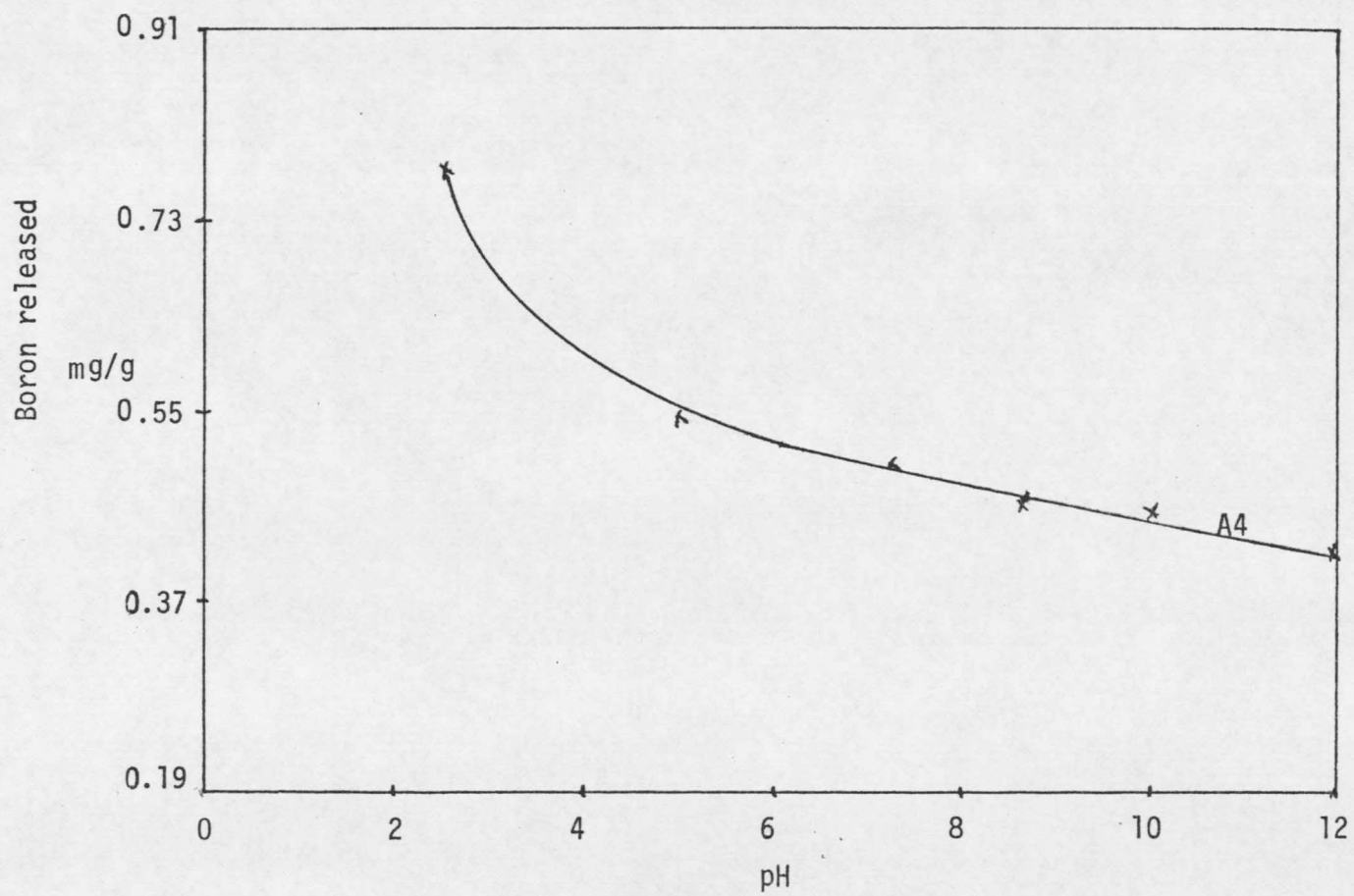


Table 7

Release of Boron as a Function of pH.

A4, A5, A6 1 g/l, A4 5.5 g/l, results in mg/g.

<u>pH</u>	<u>A4(1 g/l)</u>	<u>A5</u>	<u>A6</u>	<u>A4(5.5 g/l)</u>
2.6	-	-	-	.78
4.0	-	-	1.1	-
4.4	-	.3	-	-
5.0	1.7	-	-	.54
7.0	-	.2	.6	-
7.3	-	-	-	.49
7.5	.5	-	-	-
8.0	-	.2	.5	-
8.2	.5	-	-	-
8.7	-	-	-	.47
9.7	-	-	-	.45
9.8	.5	-	-	-
9.9	-	-	.5	-
10.0	-	.2	-	-
12.0	.6	.3	.7	.42

Table 8

Acid Leachable Components of Ash.

A1, A2, A3, A4, A5, results in mg/g.

<u>Sample</u>	<u>Na</u>	<u>K</u>	<u>Ca</u>	<u>Mg</u>	<u>B</u>
A1	39.9	8.7	49.4	16.9	0.68
A2	61.7±15.1	14.4±1.6	46.9±32.9	15.8±4.3	0.86±.51
A3	43.7	12.1	53.4	12.2	.67
A4	60.3	3.9	64.8	23.9	.57
A5	71.4	17.7	37.6	13.1	2.62

2 ml of aqua regia, plus 1 ml of 48.9% HF for 4 hours at 100°C,
50 mg of ash.

magnesium are comparable to those obtained by other investigators (3,7, 17). The sodium values are comparable or somewhat greater. The boron values are higher than those observed by Furr (7), Dreesen (1), Gladney (35) and von Lehmden (6), but comparable to those observed by Cox (3). The values of iron and aluminum, Table 9, are lower than those observed by other investigators (3,6,7,17,33). The data in Table 10 also indicate that 1 M HCl and 1 M HNO₃ are not as effective in leaching the iron and aluminum as the aqua regia-HF mixture at 100°C. For example, A4 released 0.5 mg B/g with 1 M HCl but only 0.2 mg B/g with 1 M HNO₃. Data presented in Table 11 indicates an increase in temperature to 150°C results in a loss of material, possibly through volatilization, and thus higher temperatures are not recommended. A4 released 0.6 mg B/g at 100°C in the Parr Bomb digest, but 0.4 mg B/g was observed when the temperature was raised to 150°C. The concentration of aluminum and iron in slightly basic solutions was less than 0.1 mg/g, which is in agreement with prediction based on the solubility of the respective hydroxides.

Ash Material Homogeneity

Five samples of A2 were leached to establish the homogeneity of the material. The results are summarized in Table 12. The standard deviations are sizable (59% for boron) and surprising since the material had passed through 100 mesh screen. Since there are reports

Table 9

Acid Leachable Iron and Aluminum.

A1, A2, A3, A4, A5, results in mg/g.

Sample	Element	Conditions			
		<u>1(a)</u>	<u>2(b)</u>	<u>3(c)</u>	<u>4(d)</u>
A1	Fe	10.0	8.3	29.4	29.0
	Al	22.5	29.3	94.5	17.1
A2	Fe	12.2	12.2	43.1	27.2
	Al	67.6	84.3	110.4	15.1
A3	Fe	8.0	10.1	32.5	24.5
	Al	18.1	31.9	57.3	<1.0
A4	Fe	13.9	14.2	20.0	21.5
	Al	84.3	83.9	92.3	4.2
A5	Fe	13.4	13.7	29.1	25.3
	Al	22.5	42.2	86.0	<1.0

(a) 1 M HCl, 1 g. ash/l, 25°C for 24 hours.

(b) 1 M HNO₃, 1 g ash/l, 25°C for 24 hours.

(c) 2 ml aqua regia plus 1 ml HF at 100°C for 4 hours, 50 mg ash.

(d) 2 ml aqua regia plus 1 ml HF at 150°C for 2 hours, 50 mg ash.

Table 10

Boron Leached with 1 M HCl and 1 M HNO₃.

A1, A2, A3, A4, A5, 1 g ash/l, 24 hours, results in mg/g.

<u>Sample</u>	<u>1 M HCl</u>	<u>1 M HNO₃</u>
A1	0.7	0.5
A2	1.0	0.2
A3	0.7	0.2
A4	0.5	0.2
A5	1.0	0.5

Table 11

Parr Bomb Acid Digestions.

A1, A2, A3, A4, A5, 0.050 g ash, 2 ml aqua regia, 1 ml HF brought to 50 ml with doubly-distilled water, results in mg/g.

100°C, 4 hours

<u>Sample</u>	<u>Na</u>	<u>K</u>	<u>Ca</u>	<u>Mg</u>	<u>10¹xB</u>
A1	40	9	49	17	7.4
A2	42	14	92	17	9.6
A3	44	12	53	12	7.4
A4	60	4	65	24	6.3
A5	71	18	38	13	8.6

150°C, 2 hours

<u>Sample</u>	<u>Na</u>	<u>K</u>	<u>Ca</u>	<u>Mg</u>	<u>B</u>
A1	60	8	45	12	1.1
A2	28	20	33	9	0.8
A3	27	9	38	11	0.4
A4	48	1	55	22	0.4
A5	32	1	29	15	0.9

Table 12

Determination of Ash Homogeneity.

Parr Bomb acid digest of 5 samples of A2, 0.50 g ash, 2 ml aqua regia, 1 ml HF, 100°C, 4 hours brought to 50 ml with doubly-distilled water, results in mg/g.

<u>Sample</u>	<u>Na</u>	<u>K</u>	<u>Ca</u>	<u>Mg</u>	<u>B</u>
A2-1	63	13	72	14	0.9
A2-2	77	14	23	17	0.4
A2-3	51	14	19	21	0.8
A2-4	75	17	29	9	0.4
A2-5	42	14	92	17	1.8
mean	61.7	14.4	46.9	15.8	0.86
standard deviation	15.1	1.6	32.9	4.3	0.51

(15,16,17,36) that composition varies with particle size, additional size fractionation was conducted. Three subsamples of A4 were separated, 75-100 μm , 45-75 μm , and less than 45 μm . These samples were leached with distilled water for 24 hours at 1 g ash/liter. The results are shown in Tables 13 and 14. Similarly, ashes A4, A5, and A6 were fractionated, 125-150 μm , 75-125 μm , 45-75 μm , and less than 45 μm . These samples were leached at the same conditions for 1176 hours. The results are presented in Table 15. These data indicate that a majority of the available boron comes from the smallest particles, A6 yields 0.5 mg/g from particles less than 0.45 μm but only 0.2 mg/g for particles 125-150 μm . Though not as pronounced, there is an increase in leached sodium, calcium, potassium, and magnesium as the particle size decreases. The standard deviations are considerably smaller than those shown in Table 12. Boron analyses of A4 particles, which were less than 45 μm , had a standard deviation of 1%. The use of small samples, 50 mg, and particle size variability is believed to be the main contributor to the larger standard deviations (shown in Table 8). The standard deviations for the analytical procedures are much less than the observed values. Except for the data in the particle size studies, all leaching experiments used ash that passed through 100 mesh screen ($\leq 150 \mu\text{m}$). This could cause sample inhomogeneity, but the samples are more representative of ash used in the sluicing process.

Table 13

Influence of Particle Size on the Availability of Boron, Sodium, Magnesium, and Calcium.

Triplicate samples of A4. 1 g ash/l, 24 hours, results in mg/g and standard deviation. (S.D.).

<u>Mesh Size</u>	<u>Leach no.</u>	<u>pH units</u>	<u>10¹x B/S.D.</u>	<u>Na/S.D.</u>	<u>Mg/S.D.</u>	<u>Ca/S.D.</u>
75-150 μm	1	7.5	7.4	0.99	0.34	6.08
	2	7.4	6.4	0.99	0.30	5.87
	3	7.5	8.2	0.90	0.29	5.75
			} .01	} .25	} .16	} .11
45-75 μm	1	8.0	1.0	1.09	0.53	8.32
	2	7.9	0.8	1.01	0.40	7.90
	3	7.7	1.1	0.91	0.40	7.71
			} .01	} .30	} .30	} .22
<45 μm	1	8.4	5.5	1.35	1.04	-
	2	8.3	5.5	1.31	0.95	-
	3	8.3	5.5	1.31	1.07	-
			} .00	} .17	} .12	

Table 14.

Influence of Particle Size on the Availability of
Boron, Sodium, Magnesium, and Calcium, Composite.

A4, 24 hour contact, 1 g/l.

<u>Size Increment</u>	<u>Percent of Total</u>	<u>Boron μg/g</u>	<u>Sodium mg/g</u>	<u>Magnesium mg/g</u>	<u>Calcium mg/g</u>	<u>pH</u>
75-100 μm	10.4	73±13	0.96±.08	0.31±.03	5.90±.23	7.5±0.0
45-75 μm	9.3	97±20	1.00±.13	0.44±.11	7.98±.45	7.9±0.2
<45 μm	80.3	548± 1	1.32±.04	1.02±.09	--	8.3±0.1

Table 15

Particle Size Study, 4 Size Separations.

Triplicates of A4, A5, A6, 1 g ash/l, leached in doubly-distilled water, 1176 hours, results in mg/g unless otherwise stated, standard deviation (S.D.).

Particle Size μm	Leach no.	pH units	S.C./S.D. $\mu\text{mhos/cm}$	Sample A4					
				Na/S.D.	Ca/S.D.	K/S.D.	Mg/S.D.	10^1B/S.D.	
125-150	1	8.0	75	1.05	7.4	1.26	1.5	2.9	.07
	2	8.0	70	1.25	7.3	0.77	1.5	1.5	
	3	7.7	87	2.37	8.6	0.94	1.7	1.7	
75-125	1	8.1	71	0.68	8.6	0.91	2.0	2.2	.05
	2	8.1	70	0.46	8.3	0.71	1.9	2.5	
	3	8.1	67	0.50	7.5	0.78	1.5	3.2	
45-75	1	8.8	90	0.36	11.9	1.11	2.3	3.0	.04
	2	8.8	89	0.29	12.0	0.44	2.8	2.8	
	3	8.8	93	0.45	10.5	0.75	2.8	2.2	
<45	1	8.5	178	0.93	27.0	0.79	5.0	5.9	.01
	2	8.5	178	0.73	23.1	1.28	5.0	5.6	
	3	8.5	175	0.68	7.5	1.57	4.0	5.8	
Sample A5									
125-150	1	7.9	59	1.56	7.8	1.87	0.9	1.2	0.0
	2	8.0	53	1.03	8.4	0.92	1.0	1.2	
	3	7.9	56	1.03	8.5	1.61	1.0	1.2	
75-125	1	8.0	58	0.98	8.8	0.53	1.2	1.2	.01
	2	8.0	61	0.98	9.8	0.38	1.2	1.2	
	3	8.0	58	0.90	8.7	0.59	1.2	1.4	
45-75	1	7.9	66	0.97	10.0	0.90	1.5	1.4	.01
	2	8.0	67	1.01	10.0	0.67	1.5	1.6	
	3	8.0	67	0.95	10.2	0.80	1.5	1.4	
<45	1	8.2	107	1.58	16.7	1.41	1.8	1.4	0.0
	2	8.1	107	1.48	16.0	0.42	1.9	1.4	
	3	8.2	106	1.49	16.9	0.97	1.9	1.4	
Sample A6									
125-150	1	7.9	54	0.15	6.5	1.30	1.5	1.8	.02
	2	7.9	52	0.02	7.0	0.86	1.5	1.7	
	3	7.9	54	0.05	6.0	0.70	1.6	2.2	
75-125	1	8.0	72	0.26	9.3	0.76	2.4	1.6	.02
	2	8.1	75	0.17	8.6	0.53	2.6	1.6	
	3	8.1	77	0.13	9.3	0.57	2.4	1.1	
45-75	1	8.3	119	0.20	16.1	0.64	4.3	1.4	.01
	2	8.2	105	0.22	12.3	0.18	3.8	1.5	
	3	8.3	113	0.17	12.8	0.43	4.1	1.7	
<45	1	8.5	161	0.52	21.2	0.45	5.5	5.2	.02
	2	8.4	166	0.65	20.7	0.25	5.8	4.9	
	3	8.5	165	0.48	20.6	0.46	5.8	4.8	

Table 16

Separation of Ash by Mesh Size.

A4, A5

<u>mesh</u>	opening size <u>μm</u>
100	150
120	125
200	75
325	45

Size, μm	<u>Upper Ash (A4)</u>	<u>Bottom Ash (A5)</u>
<100	4.82%	27.19%
<120	10.41%	50.97%
<200	9.33%	16.49%
<325	80.26%	32.25%

In the initial size separation shown in Table 16, sample A5 yielded 32.35% in the smallest fraction and sample A4 80.26% in the same size fraction.

Release of Boron at Different Ash to Water Ratios.

Table 17 summarizes the results of a leaching study at three concentrations, of five samples, leached in reservoir water for 768 hours. Table 18 summarizes a leaching study at six concentrations of samples A4, A5, and A6 in doubly-distilled water for 456 hours. The concentration of boron in the leachate solutions is dependent upon the ratio of ash to water. This dependence is shown in Figure 8 and in Table 19. The nonlinear behavior indicates incomplete release of boron when the ash-to-water ratio is increased. For example, A4 leaches 0.7 mg B/g ash at 1 g ash/l but leaches 0.1 mg B/g ash at a concentration of 100 g ash/l. Leached boron concentration is dependent upon ash type, with the largest amount being released from the upper ash.

Using the boron released in the 1 g/l solutions as an estimate of the total available boron, it is possible to calculate the amount of boron that is retained by the ash in the solutions where the ash-to-water ratio is higher. The data are presented in Table 20. The values in Table 20 are comparable to those reported by Choi and Chen (14). A plot of μg boron retained/g of ash as a function

Table 17

Influence of Ash Concentration on Leachability in Reservoir Water.

A1, A2, A3, A4, A5, 768 hours, results in mg/l unless otherwise stated.

Conc.	Sample	pH units	S.C. $\mu\text{mhos}/$ cm	HCO_3^-	$\text{CO}_3^{=}$	NO_3^-	$\text{SO}_4^{=}$	Na^+	K^+	Cl^-	Ca^{++}	Mg^{++}	B	B. mg/g
1 g/l	A1	8.7	751	198	18	4.4	183	74	13	13	44	25	0.5	0.5
	A2	8.7	746	221	12	8.7	195	79	11	10	48	24	0.5	0.5
	A3	8.7	777	234	15	3.9	186	76	11	10	55	24	0.7	0.7
	A4	8.7	801	247	14	4.6	195	79	10	10	56	26	0.7	0.7
	A5	8.7	744	212	8	3.5	188	76	12	11	43	22	0.4	0.4
25 g/l	A1	8.8	896	260	23	4.0	240	82	15	11	30	49	3.1	0.1
	A2	8.8	905	228	29	1.5	255	86	17	10	23	48	5.0	0.2
	A3	9.0	1015	239	50	3.1	300	89	12	12	29	62	8.5	0.3
	A4	8.8	839	158	26	2.0	267	89	12	11	71	18	7.9	0.3
	A5	8.7	830	263	16	1.4	215	84	13	9	34	32	1.7	0.1
100 g/l	A1	8.9	1141	205	50	6.1	379	101	13	14	25	73	12.8	0.1
	A2	9.1	957	-	-	1.4	339	116	15	11	62	11	11.0	0.1
	A3	9.3	991	131	7	2.5	354	123	12	11	78	4	15.3	0.2
	A4	9.5	892	14	95	2.0	280	123	1	10	55	3	12.8	0.1
	A5	8.8	942	246	22	1.3	267	116	11	12	21	37	0.4	0.0

Table 18

Release of Boron as a Function of Ash Concentration.

Triplicate of A4, A5, A6. 456 hours, doubly-distilled water leach.

		pH	S.C. mmhos/ cm	B $\mu\text{g/ml}$	B $\mu\text{g/g ash}$	Avg.
1 g/l	A4-1	8.4	1.54	0.49	489	
	-2	8.4	1.62	0.56	543	509
	-3	8.4	1.61	0.49	494	
	A5-1	7.9	.88	0.13	133	
	-2	8.0	.86	0.17	169	144
	-3	8.0	.86	0.13	131	
	A6-1	8.3	1.31	0.42	425	
	-2	8.4	1.34	0.43	418	433
	-3	8.4	1.31	0.46	457	
12.5 g/l	A4-1	8.7	3.07	4.4	348	
	-2	8.9	3.06	4.4	350	350
	-3	8.7	3.26	4.4	352	
	A5-1	8.6	2.23	0.83	66	
	-2	8.5	2.33	0.70	56	46
	-3	8.5	2.34	0.21	17	

Table 18 (continued)

		<u>pH</u>	<u>S.C.</u> <u>mmhos/</u> <u>cm</u>	<u>B μg/ml</u>	<u>B μg/g ash</u>	<u>Avg.</u>
	A6-1	8.8	3.08	3.6	285	
	-2	8.9	3.16	3.6	289	331
	-3	8.8	3.12	5.2	419	
25 g/l	A4-1	9.2	3.33	6.6	264	
	-2	9.1	3.21	6.2	249	265
	-3	9.0	3.54	7.0	281	
	A5-1	8.7	3.37	1.2	48	
	-2	8.7	3.38	1.3	50	48
	-3	8.7	3.28	1.2	46	
	A6-1	8.7	3.50	6.4	256	
	-2	8.8	3.55	6.3	252	253
	-3	8.8	3.72	6.3	251	
50 g/l	A4-1	9.5	4.26	7.1	141	
	-2	9.5	4.27	9.5	190	174
	-3	9.8	4.64	9.6	192	
	A5-1	8.8	3.72	2.1	43	
	-2	8.7	3.89	2.1	42	43
	-3	8.7	3.74	2.2	43	

Table 18 (continued)

		<u>pH</u>	<u>S.C.</u> <u>mmhos/</u> <u>cm</u>	<u>B μg/ml</u>	<u>B μg/g ash</u>	<u>Avg.</u>
	A6-1	8.2	4.15	8.4	169	
	-2	9.2	3.91	7.8	156	154
	-3	9.3	3.47	6.8	137	
75 g/l	A4-1	9.6	4.05	11.1	148	
	-2	10.2	4.22	11.2	150	153
	-3	10.0	4.22	12.1	162	
	A5-1	9.2	4.12	2.8	38	
	-2	8.8	4.11	2.7	36	38
	-3	8.8	4.21	2.9	39	
	A6-1	9.8	4.79	9.6	128	
	-2	9.8	4.65	9.5	127	130
	-3	9.8	5.00	10.2	136	
100 g/l	A4-1	10.3	4.35	13.0	129	
	-2	10.4	4.43	12.1	121	136
	-3	9.6	5.41	15.7	157	
	A5-1	8.9	4.08	3.1	31	
	-2	8.9	4.32	3.6	36	34
	-3	9.0	4.24	3.6	36	

Table 18 (continued)

	<u>pH</u>	<u>S.C.</u> <u>mmhos/</u> <u>cm</u>	<u>B μg/ml</u>	<u>B μg/g ash</u>	<u>Avg.</u>
A6-1	10.4	4.46	7.8	78	
-2	10.3	4.82	9.1	91	94
-3	9.8	5.21	11.4	114	

Figure 8

Release of Boron from Ash as a Function of Concentration.

time: 456 hours.

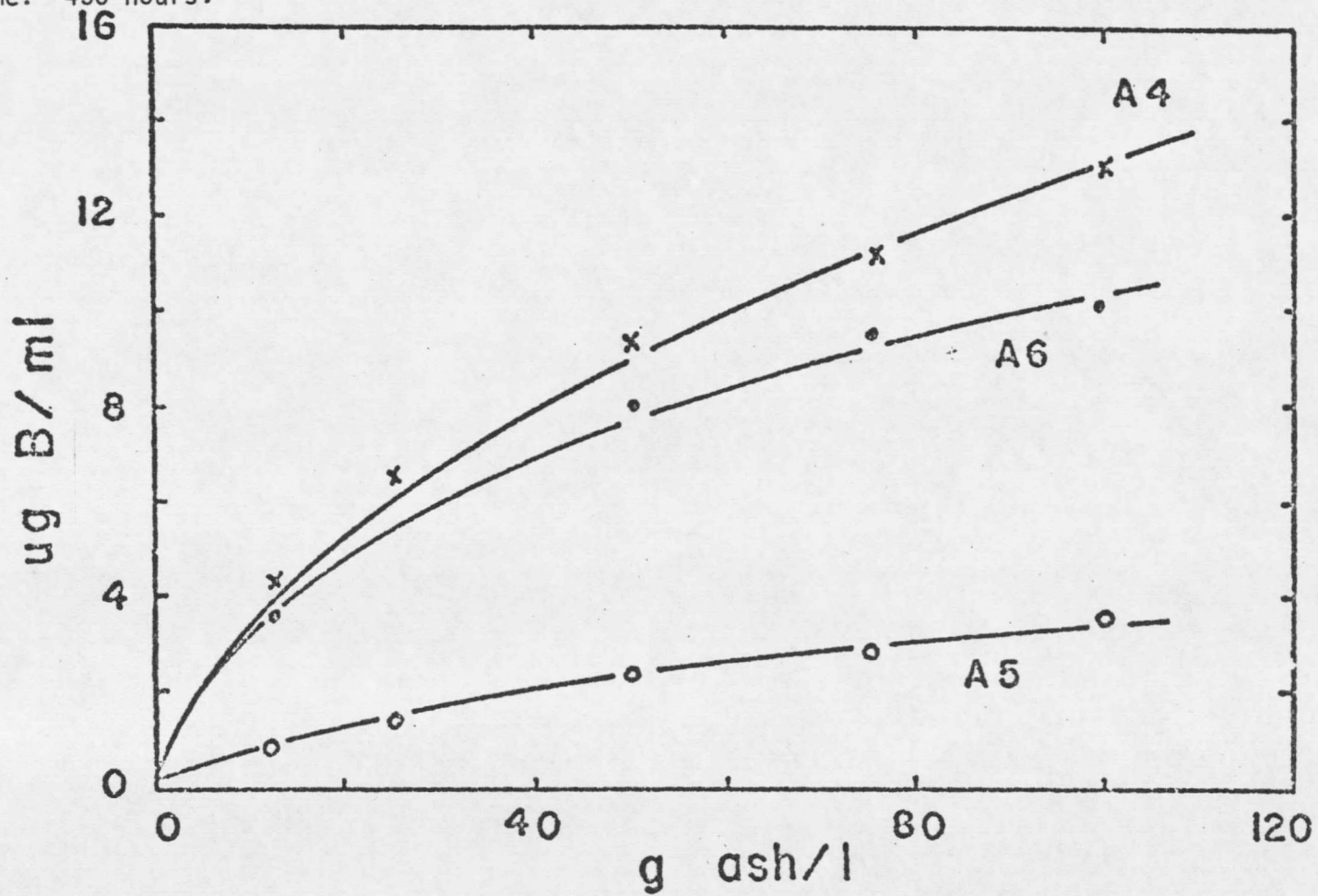


Table 19

Summary: Release of Boron as a Function of Ash Concentration.

A4, A5, A5, time: 456 hours, results in mg B/l and (mg/g).

<u>Concentration</u> g ash/l	<u>A4</u>	<u>A5</u>	<u>A6</u>
1.0	0.51 (0.51)	0.14 (0.14)	0.43 (0.43)
12.5	4.4 (0.35)	0.61 (0.05)	3.7 (0.30)
25.0	6.6 (0.26)	1.2 (0.05)	6.3 (0.25)
50.0	9.5 (0.19)	2.1 (0.04)	7.8 (0.16)
75.0	11.3 (0.15)	2.8 (0.04)	9.6 (0.13)
100.0	13.5 (0.14)	3.5 (0.04)	10.5 (0.11)

Table 20

Boron Released and Retained at Various Leaching Ratios.

A4, A5, A6, time: 456 hours.

<u>Ratio Ash/Water</u> ^(a)	<u>Boron Leached</u> ($\mu\text{g/ml}$)			<u>Boron Retained</u> ($\mu\text{g/g}$)		
	<u>(g/l)</u>	<u>A4</u>	<u>A5</u>	<u>A6</u>	<u>A4</u>	<u>A5</u>
1.0	0.5	0.1	0.4	--	--	--
12.5	4.4	0.8	4.1	158	83	102
25.0	6.6	1.2	6.3	244	96	180
50.0	9.5	2.1	7.7	318	102	279
75.0	11.5	2.8	9.8	355	107	303
100.0	13.6	3.4	9.4	373	110	339

(a) Total volume 50.0 ml

of $\mu\text{g B/ml}$ is shown in Figure 9. Sample A5, which is bottom ash, exhibits a maximum retention of $105 \mu\text{g B/g ash}$. Sluicing this ash at 55 g/l should provide leachate waters containing 1.9 mg B/l . The retention behavior for A4 and A6 is not as well defined, but the shape of the curve indicates Langmuir behavior, with a limiting value in excess of $400 \mu\text{g B/g}$. Correspondingly, the sluicing of these ash materials at 55 g/l would provide boron concentration in excess of those predicted for the bottom ash. The retention of boron by the ash material complicates the assessment of how much boron will be released to a natural water system over a given time span. These results indicate that the 1 mg/l agricultural limit may be exceeded. However, since not all of the boron is removed initially, there will be a dependence upon how rapidly water moves through the system.

The boron retained by the ash material is readily available, as evidenced by the following. The A4 ash from the 50 g/l , 75 g/l , and 100 g/l leaching experiments was isolated and re-leached at a ratio of 1 g/l . The total available boron was released from the ash and found in the leachate solutions. The results are shown in Table 21. There is good agreement between the boron released by these re-leachings and that expected from calculations. A4 ash when leached at 100 g ash/l released $136 \mu\text{g B/g ash}$ and released $498 \mu\text{g B/g ash}$ when resuspended at 1 g ash/l . A4 at 1 g ash/l leached $508 \mu\text{g B/g ash}$.

Figure 9

Boron Retained by Ash as a Function
of Boron Concentration.

A4, A5, A6, time: 456 hours.

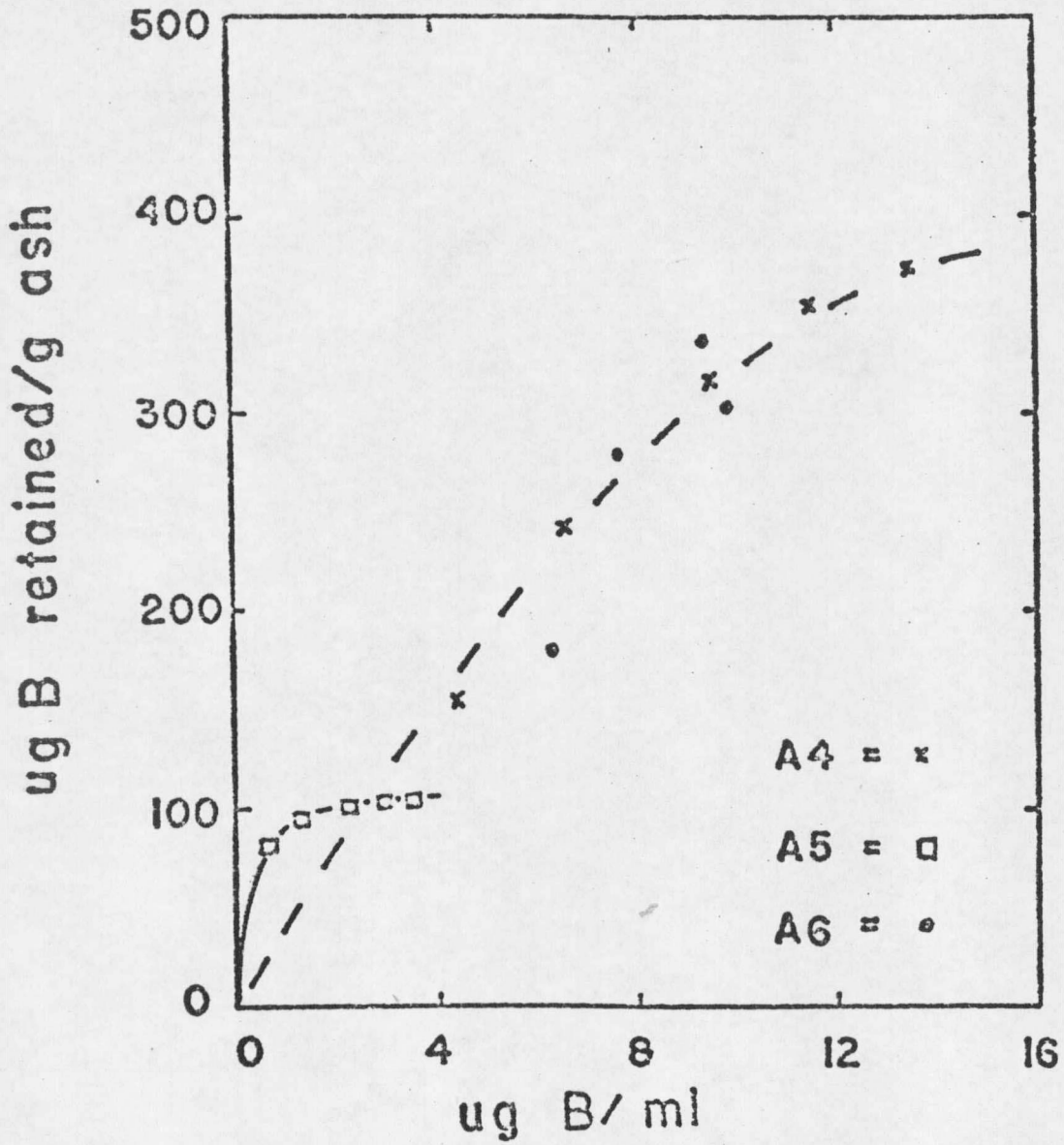


Table 21

Release of Retained Boron.

A4, 24 hours, doubly-distilled water.

<u>original concentration g ash/l</u>	<u>µg B/g ash when leached at 1 g/l</u>
1	508
50	523
75	460
100	498

Boron Adsorbed at Varying Solution Concentrations.

Ash that was conditioned by water washing was mixed with solutions containing varying concentrations of boron to determine adsorption, the results are shown in Figure 10 and Table 22. Many data points were collected to compensate for the scattering due to variability of the ash. The ash adsorbed boron with a Freundlich type behavior. Choi and Chen (14) have also reported Freundlich adsorption isotherms for boron adsorption onto solids. The amount of boron adsorption was dependent upon the concentration of boron in the solution. For example, sample A4 has the capacity to adsorb 36 mg B/g ash at 55 g ash/l and with 160 mg B/ l in solution. The amount adsorbed is a function of ash type, amount of ash in solution, and concentration of boron. The pH for these experiments was held at the 8.6-8.8 range. This is within the maximum adsorption pH range of 6-9 reported by others (14,25,30,31). Tris buffer at a concentration of 0.5 M was used to maintain pH. The effects of this buffer from 0.1 M to 1.0 M were studied, Inadequate buffering capacity was found below 0.5 M Tris and there were no buffer effects up to 1.0 M.

Adsorption of Boron by Acid Conditioned Ash.

The effects on boron adsorption by ash conditioned with acid were studied. A sample of A4 was washed with 1 M HNO_3 and another sample of A4 with 1 M HCl . The data in Table 23 and shown in

Figure 10

Adsorption of Boron by Water Conditioned Ash.

A4, 0.5 M Tris buffer, pH 8.6, 55 g ash/l.

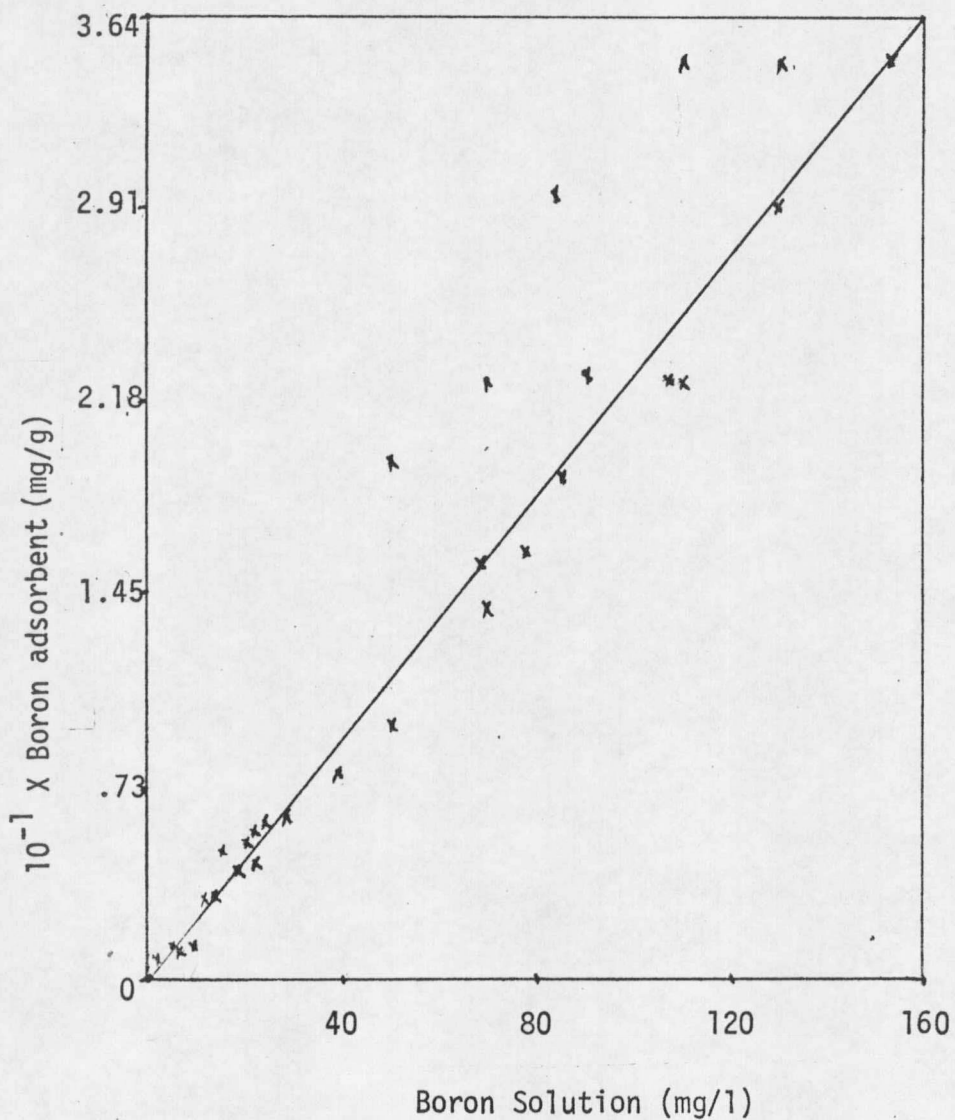


Table 22

Adsorption of Boron onto Water Conditioned Ash.

A4, pH 8.6, 55 g ash/l, 48 hour adsorption, results in mg/l and mg/g.

10^{-1} xB baseline mg/l	10^{-1} xB added to solution mg/l	10^{-1} xB change in baseline mg/l	10^{-1} xB in solution mg/l	10^{-1} xB adsorbed mg/l	10^{-1} xB adsorbed mg/g
0.2	0.0	0.1	0.3	-	-
0.2	0.0	0.1	0.4	-	-
0.2	0.4	0.1	0.7	-	-
0.3	0.8	0.1	1.0	0.2	0.4
0.2	1.1	0.1	1.3	0.1	0.2
0.2	1.2	0.1	1.3	0.2	0.4
0.2	1.2	0.1	1.3	0.2	0.4
0.2	1.5	0.1	1.7	0.1	0.2
0.2	1.6	0.1	1.6	0.3	0.5
0.2	2.0	0.1	2.1	0.2	0.4
0.3	2.0	0.1	2.0	0.4	0.7
0.2	2.4	0.1	2.3	0.4	0.7

Table 22 (continued)

$10^{-1} \times B$ baseline mg/l	$10^{-1} \times B$ added to solution mg/l	$10^{-1} \times B$ change in baseline mg/l	$10^{-1} \times B$ in solution mg/l	$10^{-1} \times B$ adsorbed mg/l	$10^{-1} \times B$ adsorbed mg/g
0.2	2.4	0.1	2.6	0.1	0.2
0.2	4.0	0.1	3.9	0.4	0.7
0.2	5.1	0.1	5.0	0.4	0.7
0.2	7.4	0.1	7.0	0.7	1.3
0.2	7.5	0.1	7.0	0.8	1.5
0.2	9.5	0.1	8.8	1.0	1.8
0.2	10.0	0.1	9.0	1.3	2.4
0.2	12.0	0.1	11.0	1.3	2.4
0.3	13.0	0.1	11.0	2.4	4.4
0.2	14.0	0.1	13.0	1.3	2.4
0.2	15.0	0.1	13.0	2.3	4.2

Table 23

Adsorption of Boron on Acid Washed Ash.

A4, pH 8.5, 55 g ash/l, 48 hours, results in mg/l and mg/g.

<u>10^{-1}xB added to solution mg/l</u>	<u>10^{-1}xB in solution mg/l</u>	<u>10^{-1}xB adsorbed mg/l</u>	<u>10^{-1}xB adsorbed mg/g</u>
1.9	1.9	0.2	0.4
5.9	4.9	1.1	2.0
8.0	6.8	1.3	2.4
9.9	8.3	1.7	3.1

Figure 11 indicates that adsorption by these ashes was more than onto water washed ash. Sample A4, when water conditioned, adsorbed 0.13 to 0.18 mg/g onto 55 g ash in a liter of 70 mg/l boron solution. When A4 was acid washed it adsorbed 0.24 mg/g under the same conditions. Perhaps this is due to its ability to "clean" the adsorption sites of interfering species.

The effects of solution pH on the adsorption of boron by ash A4 is shown in Figure 12 and in Table 24. The results show that the ash is less effective in adsorbing boron at pH 9.5 than at 8.6. Comparison of data in Tables 24 and 22 shows that in a 40 mg/l boron solution, A4 will adsorb 0.73 mg B/g at pH 8.6 and 0.36 mg/g at pH 9.5. Since the possible effect of ammonia buffer interference is undetermined, further interpretation cannot be made. The data correlates with the pH dependence of boron adsorption onto soils as reported by other authors (11,14,25,30,31) and suggests that ash may follow a similar pH dependence behavior.

Regeneration of Ash Surface.

The finding that an isotherm generated using acid-conditioned ash exhibits higher adsorption capacity than the water-conditioned ash suggests that the surfaces of these ashes may be similar and contain large amounts of iron and aluminum. Those samples which had been used to generate the isotherms (Figures 10 and 11) were released with

Figure 11

Adsorption of Boron by HCl Conditioned Ash.

A4, 55 g ash/l, pH 8.6.

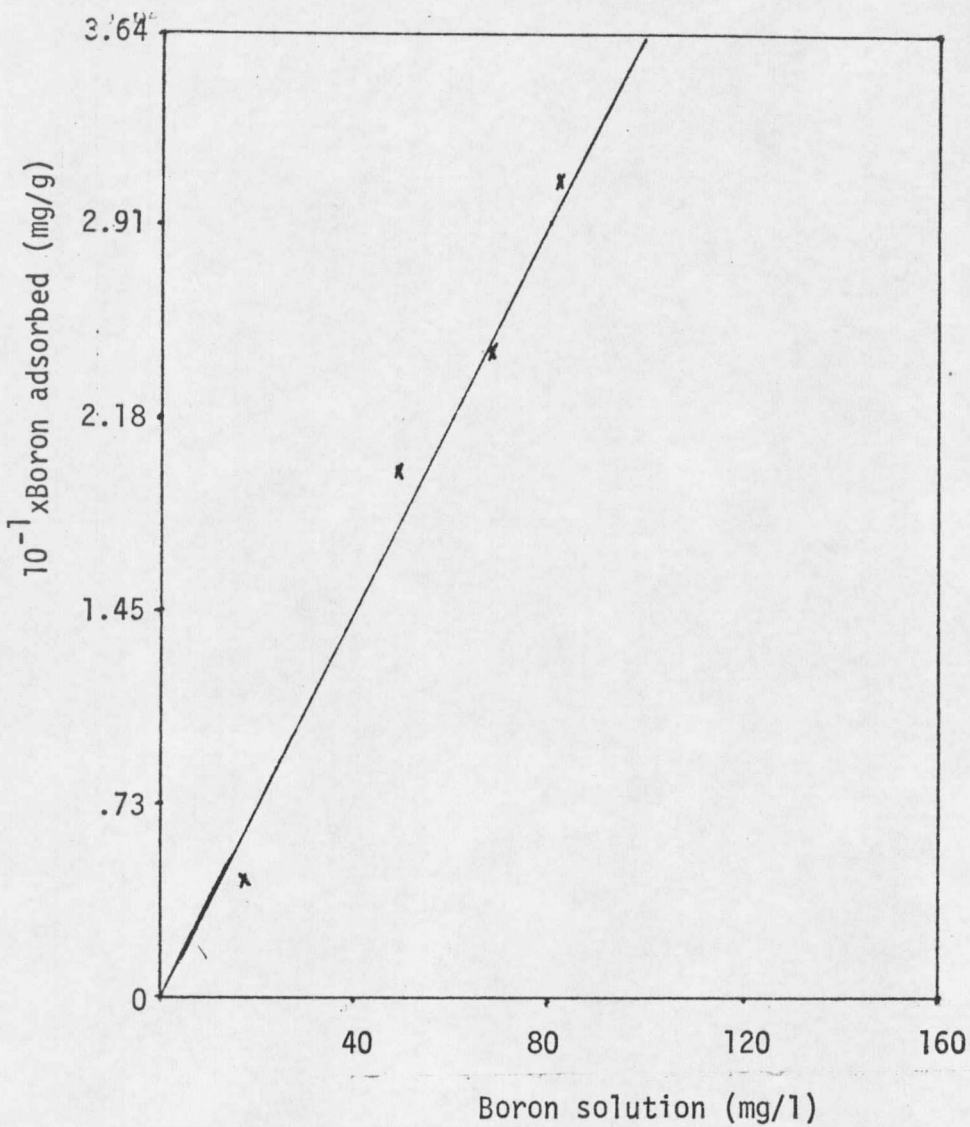


Figure 12

Adsorption of Boron as a Function of Solution Concentration.

A4, water conditioned ash, pH 9.5, 55 g ash/l, 0.5 M ammonia buffer.

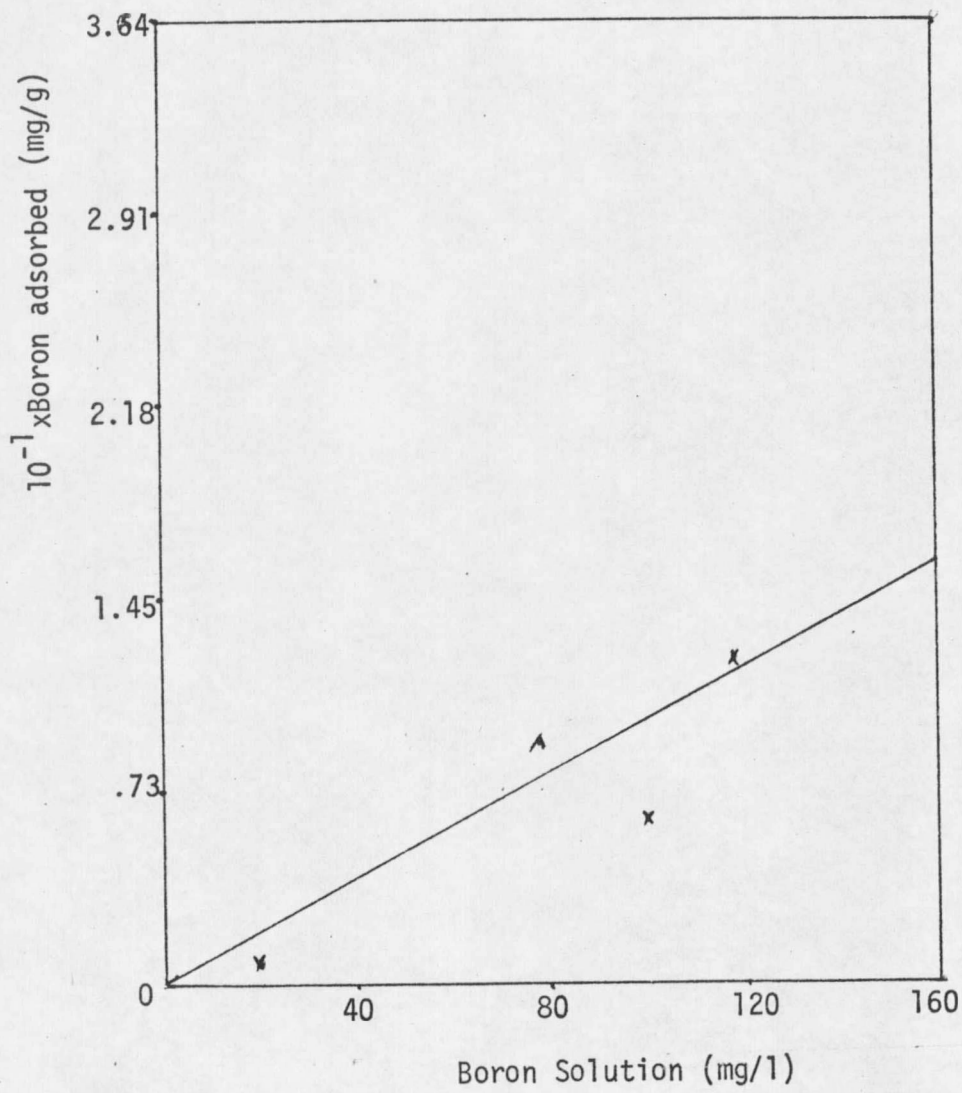


Table 24

Adsorption of Boron as a Function of Boron in Solution.

A4, 55 g/l, pH 9.5, water conditioned ash, results in mg B/ml and mg/g.

<u>10^{-2}xB in solution (mg/l)</u>	<u>B adsorbed (mg/l)</u>	<u>10^2xB adsorbed (mg/g)</u>
0.2	0.3	0.5
0.4	0.2	0.4
0.8	5.0	9.0
1.0	3.3	6.0
1.2	7.5	14.0

1 M HCl at 55 g ash/l. The leachates were analyzed for aluminum and iron and the results are shown in Table 25. Water conditioned ash samples of A4 yielded 13 to 15 mg Fe/g and 73 to 91 mg Al/g.

Acid conditioned A4 leached 8 to 9 mg Fe/g and 51 to 62 mg Al/g into the acid. Table 26 shows the results from an experiment in which samples A4, A5, and A6 were washed for three successive 24 hour periods at 1 g ash per liter with 1 M HCl, 1 M NaOH and doubly-distilled water. The conclusion of this experiment was that acid was effective in washing iron and aluminum from the surface of ash. Sample A4 released a total of 56 mg Al/g and 13 mg Fe/g into the 3 acid washes. A4 released undetectable amounts of iron and aluminum into the water and basic washes.

The combined results from these two experiments lead to the possible suggestion that there is regeneration of the ash surface. This could lead to an interpretation consistent with a sputtering-etching experiment run by Campbell and co-workers (37) which showed the relative concentrations of sodium, carbon, oxygen, and sulfur to decrease with layer depth but silica, aluminum, and iron to increase upon sputtering to a depth of approximately fifty angstroms.

Releachability of Boron

Table 25 suggests that boron released with acid from samples of A4 which had previously adsorbed boron (see Tables 22 and 23) is

Table 25

Acid Releaches of Adsorption Samples.A4, HNO₃ leach, 12 hours, water conditioned ash, mg/g.

<u>Sample</u>	<u>Fe</u>	<u>Al</u>	<u>B</u>
1	15	91	0.4
2	13	87	0.5
3	13	87	0.5
4	14	91	0.4

A4, HCl leach, one hour, acid conditioned ash.

<u>Sample</u>	<u>Fe</u>	<u>Al</u>	<u>10¹xB</u>
5	10	58	0.5
6	10	62	0.7
7	10	55	0.6
8	8	51	0.6
9	10	58	0.9

Table 25 (continued)

Sample Number		Boron initial treatment mg B/g	Boron adsorbed by sample mg B/g
1	doubly-distilled water concentration ash	0.9	0.4
2		1.4	0.2
3		1.8	0.3
4		2.4	0.4
5	HCl concentration ash	0.0	-
6		0.3	-
7		1.0	0.2
8		1.5	0.2
9		1.8	0.3

Table 26

Successive Washes with Acid (1 M HCl), Doubly-
Distilled Water and Base (1 M NaOH).

A4, A5, A6, 1 g ash/l, 24 hours, results in mg/g unless otherwise stated.

A4

	<u>wash no.</u>	<u>pH units</u>	<u>S.C. mmhos/cm</u>	<u>Fe</u>	<u>Al</u>	<u>Mg</u>	<u>B</u>
acid	1	4.2	23.9	0.5	17	9.6	0.6
	2	3.3	4.6	7.8	34	6.5	0.4
	3	2.3	6.3	4.4	5	2.9	0.4
doubly-distilled water	1	11.0	21.0	-	-	0.3	0.4
	2	9.8	6.9	-	-	0.8	0.1
	3	10.4	5.9	-	-	0.8	0.1
base	1	11.1	2.4	-	-	0.6	0.5
	2	10.8	1.0	-	-	0.9	0.2
	3	10.4	0.4	-	-	0.8	0.1

A5

acid	1	3.2	23.9	5.4	17	9.4	0.3
	2	2.2	8.9	1.7	-	2.3	0.5
	3	2.1	7.7	0.3	-	0.3	0.3

Table 26 (continued)

	<u>wash no.</u>	<u>pH units</u>	<u>S.C. mmhos/cm</u>	<u>Fe</u>	<u>Al</u>	<u>Mg</u>	<u>B</u>
doubly- distilled water	1	9.5	5.6	-	-	0.5	0.1
	2	10.3	4.6	-	-	0.4	0.1
	3	9.8	3.5	-	-	0.3	0.1
base	1	9.9	2.2	-	-	0.5	0.1
	2	10.1	1.0	-	-	0.4	0.1
	3	9.7	0.4	-	-	0.2	0.0
A6							
acid	1	4.2	21.7	1.3	17	14.6	0.1
	2	2.6	5.2	5.4	17	5.8	0.2
	3	2.0	6.6	1.5	-	1.7	0.2
doubly- distilled water	1	10.9	17.2	-	-	0.4	0.6
	2	10.3	7.3	-	-	0.9	0.2
	3	10.3	4.3	-	-	1.0	0.1
base	1	11.1	2.2	-	-	0.8	0.5
	2	10.7	0.9	-	-	1.0	0.2
	3	10.1	0.4	-	-	0.9	0.1

independent of the amount of boron they originally adsorbed. In Table 23, samples 1, 2, 3, and 4 of water conditioned A4 ash all released 0.4 to 0.5 mg B/g into the acid leach irregardless of how much boron the samples had originally adsorbed (0.2-0.4 mg B/g). The experiments were repeated for verification and yielded comparable results. All containers were checked for adsorption loss to walls; but the amounts found did not constitute the difference between that originally adsorbed by these samples and that releached from them. There are no similar experimental check of this type in the literature to indicate whether boron is releachable from other adsorbents.

SUMMARY AND CONCLUSIONS

This investigation was undertaken to determine the influence of certain factors upon the mobility of boron from coal ash to an aqueous system. The leachability of boron was determined to be a function of pH, time, and ash type. Upper ash taken from the stack, leached more boron than did bottom ash which resides in the furnace and sustains higher temperatures. Over time, boron leaches continually until a steady state is reached in approximately 920 hours. Leaching is rapid initially but drops off dramatically after 158 hours. Acid is most effective for leaching and there is a minimum leached in the pH range of 6-9.

The ash was specifically examined for aluminum, iron, and boron since these have demonstrated a relationship in the adsorption process (24,25). The ash samples contained significant amounts of these components.

A size fractionation of the ash into four segments, 150 microns to 45 microns, was made. The analyses showed that certain elements tend to associate with particular size fractions. Boron predominately associates with the smallest particles, less than forty five microns. The standard deviation of triplicate runs of each fragment indicated that improved homogeneity of analyses can be accomplished by size fractionation. Homogeneity is important for analysis comparison. In the natural system, particles of many sizes add to the complexity

of the system.

Slurries were prepared, varying ash concentrations from one gram of ash per liter to one hundred grams of ash per liter. Boron released from these slurries was analyzed and revealed an incomplete release of boron at high concentrations of ash. One gram of ash per liter was taken as an indication of total leachable boron. This was checked by re-leaching of ash samples used in the higher concentration studies at one gram per liter. Based upon these calculations of total available boron, the concentration of boron retained by the ash was assessed. The retained boron exhibits Langmuir adsorption behavior.

Adsorption of boron by ash was studied by first conditioning ash by a process which removed boron, then resuspending the ash in a standard solution of boron. Ash was shown to adsorb boron increasingly with increasing boron solution concentration in a Freundlich relationship. Acid conditioned ash showed enhanced boron adsorption. A study of the influence of pH upon adsorption by ash indicated that at pH 9.5 adsorption was less than at pH 8.6. These results are consistent with pH influence on boron adsorption by soils as reported by other authors (14,25,26,30,31). An acid re-leach of adsorption samples was analyzed for iron, aluminum, and boron. If the adsorption of boron was a simple surface layer coating, one would expect the boron to be easily re-leached. Experiments did not affirm this. Also noted, from

the acid releach, was that the surfaces of water conditioned ash and acid conditioned ash were similar and contained comparable amounts of iron and aluminum.

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