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FINAL REPORT

PROJECT No. I-97-80

**The Mineralogical and Chemical Forms of Boron,
Molybdenum and Selenium in Fly Ash and Their
Mobility and Interaction in Soils**

M. Gal, S.V. Mattigod

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Results - Body of Research Report

The results obtained by the Israeli and U.S. groups are reported separately in this final report.

The Israeli group report results of the study of soluble forms of B, Mo and Se in fly ash and the interaction of B with ash-amended soils. Part of the results are presented in the form of a paper ready to submit for publication entitled: "Boron release and adsorption by fly ash as affected by pH and particle size". Results of a physical study of the interaction of fly ash with soil are also reported.

The American results consist of two publications; 1) A report entitled "The separation and identification of compounds in fly ash", and 2) a summary of a pH.D. thesis entitled "Chemical Speciation of Selenium in Fly Ash".

ABSTRACT

A kinetic study of the dissolution and sorption of B, Mo and Se by fly ash was made. The findings showed that the pH of the fly ash - water suspensions determined the dissolution and adsorption of these 3 elements. It was shown that the presence of CaO on the fly ash surface was connected with the sorption of these 3 elements. Some solution species of the elements are given and some mechanisms for their sorption by fly ash are suggested.

Mobility of the elements were measured in columns of ash mixed with inert sand under different flow rates.

The interaction of B dissolved from the fly ash with 3 amended soils was studied. The dependence of the mobility of B on the solution pH of the ash-amended soils was clearly shown.

The effect of fly ash on the hydraulic conductivity (HC) of the three soils was studied in columns. Improvement to the HC of the loamy sand soil was small whereas fly ash prevented clay swelling and dispersion when distilled water was leached through an amended clay soil. The effect of ash on the infiltration rate (IR) of amended soils was only slight, but by adding 10% ash to a clay soil, its workability was improved considerably.

INTRODUCTION

Fly ash is a major solid residue produced from the combustion of coal in modern coal-fired power plants. Although the use of fly ash in soil as a plant nutrient (Rees and Sidrak, 1956; Martens, 1971) and as an improver of some soil physical properties (Chang et al., 1977) has been demonstrated, the extent of utilization has been negligible because of the release of elements injurious to plants (Hodgson and Holliday, 1966).

Greenhouse experiments have demonstrated that addition of fly ash to soil tends to increase boron levels as well as pH and soil salinity (Page et al., 1979). Boron is of special concern in soil because of the relatively small range between levels causing deficiency and toxicity symptoms in plants (Philipson, 1953). Plants grown on mixtures of ash and soil contained excessive levels of Mo and Se which would endanger animals feeding off these plants (Straughan et al., 1978; Tolle and Arthur, 1983). Therefore before ash can be used as a soil amendment, it is necessary to study the dissolution of B, Mo and Se from fly ash and the interaction of these elements in amended soils.

The effectiveness of ash as a soil amendment was measured by studying the hydraulic conductivity (HC) and infiltration rate (IR) of amended soils. The HC is a measure of flow of water through the soil profile and IR is a measure of the permeability of the soil surface. Powdered gypsum and phosphogypsum have been used to improve HC and IR respectively in soils (Shainberg et al., 1982; Kazman et al., 1983). They both dissolve calcium which has a beneficial effect on soils by

exchanging sodium and increasing electrolyte concentration (EC). Therefore since fly ash also contains soluble Ca (Elseewi et al., 1980), its effect on HC and IR was studied.

The work covered in this project was divided into five objectives:

(1) Study of the effect of time, pH, ash to water ratio and ash particle size on the dissolution of Ca, B, Mo and Se from fly ash.

(2) Study of the effect of pH, ash salinity, time and ash particle size on the sorption of B, Mo and Se by fly ash.

(3) Study of the effect of water flow rate on the mobility of Ca, B, Mo and Se in fly ash mixed with inert sand.

(4) Study of the effect of pH and soil texture on the interaction of Ca and B (dissolved from fly ash) with amended soils.

(5) Study of the effect of fly ash on: a) the hydraulic conductivity and b) the infiltration rate of amended calcareous smectitic soils of Israel with differing soil texture and exchangeable sodium percentage ESP.

Materials and Methods

The fly ash used was obtained from the Hadera M.D. Power Station (Hadera, Israel) and was derived from an English coal.

Total B and Mo in the ash were determined as described in the first year annual report.

B, Mo, Se, Ca and Mg dissolution from fly ash were studied in suspension by shaking 6g ash in 50 ml polypropylene centrifuge tubes containing 30 ml solution at various compositions. Distilled water was used for the systems at natural pH and the pH was adjusted by

adding 1.0 M HCl. At predetermined time intervals the fly ash suspensions were centrifuged, filtered through a Whatman No.42 paper and the filtrate analyzed for B, Mo, Se, Ca, Mg, Na, K, Cl, Al, Fe, electrical conductivity (EC) and pH. Methods and instruments used for these determinations are described in the first and second year annual report.

To study the effect of ash to water ratio on the dissolution of B and Mo from ash, less ash than before was added to 30 ml distilled water. Six different amounts of ash were used ranging from 0.187 g to 6.0 g per 30 ml distilled water.

To study the effect of ash particle size on the dissolution of B, Mo and Se from fly ash, particles were first separated into different size fractions (using a zig-zag air classifier) and then used as described above.

B, Mo and Se sorption by fly ash was studied in suspension by shaking fly ash in solution at a solution to solid ratio of 1-5 (as used for the dissolution study). The fly ash was washed prior to the sorption study to remove most of the B, Mo and Se which is associated initially with the solid phase. The ash was washed by sequential neutralization with dilute HCl at a suspension pH of about 6.5 until there was not further change in B, Mo, Se and Ca concentration from one washing to the next.

During washing 2.2% of the ash as Ca and 0.5% as Mg were the main elements extracted. The washed ash was dried at 40°C and solution of either NaCl or CaCl₂ was added at appropriate amounts to form a final solution having an ionic strength of 0.15 M. Suspension pH was

adjusted with NaOH, Ca(OH)_2 or HCl until there was no pH change after 24 hours of shaking. B, Mo and Se were then added to the suspensions making an initial concentration of 10.0, 2.0 and 0.10 mg per l, respectively, and the suspensions were shaken, centrifuged and filtered as detailed above.

To study the effect of Ca(OH)_2 and Mg(OH)_2 contained in the fly ash on the sorption of B and Se by fly ash, after washing, these hydroxides were added to the washed ash in the same amount as were washed out. Solutions of either NaCl or CaCl_2 were added to form a final solution having an ionic strength of 0.15 M and B and Se added at the same concentrations as above.

To study the effect of water flow rate on the mobility of B, Mo and Se, fly ash was mixed with inert sand and the mixture packed in columns, saturated and leached with distilled water at different flow rates adjusted using a peristaltic pump. The leachates were removed in a fraction collector and analyzed. Further details of the procedure are contained in the second year annual report.

Fly ash was added to two soils (a clay and a loamy sand shown in Table 1) at amounts ranging from 5 to 50% by weight of the soil. 500 ml of distilled water was added to 100g of each mixture in a one litre plastic bottle and the suspension shaken at a constant partial pressure of CO_2 maintained by bubbling through air. At predetermined time intervals, aliquots of suspension were transferred to centrifuge tubes, centrifuged, filtered and the filtrate analyzed for pH, OH, CO_3 , HCO_3 , Ca, Mg and B. OH, CO_3 and HCO_3 were determined by titration

with 0.01N H_2SO_4 (U.S.D.A., 1954) and analysis of the others is described in the first year annual report.

To make a comparison of the effect of a fly ash - soil mixture on B dissolution and sorption with fly ash alone, ash was added to inert sand in the same proportions as to soil and the same procedure used as above. The inert sand is a fine sand washed of its soluble components with dilute HCl and therefore does not interact with fly ash.

Amounts of fly ash varying from 5 to 20% were mixed with the three different soil types shown in Table 1 and the mixtures packed in 10 cm columns at a bulk density shown in Table 2. Each column was saturated with leaching solution of either distilled water, simulating the salt concentration of rain water or 0.01 N solution of sodium adsorption ratio (SAR) of 2, simulating tap water. Care was taken to ensure that the soil column was completely saturated with water and free of any air bubbles. CO_2 dissolved in the leaching solution was kept at a similar concentration in each column during the experiment by bubbling air through the leaching solution.

After saturation, the flow rate of water through the column was kept constant using a peristaltic pump at values shown in Table 2. The pore volume of the soil is defined as the volume of soil not occupied by solid particles and it can be calculated from the following equation:

$$\frac{(d_p - d_b) \times V_b}{d_p}$$

d_p is the density of soil particles = 2.65 g.cm^{-3} .

δ_b is the bulk density of the soil (Table 2).

V_b is the bulk volume of the soil.

In a water saturated soil, the hydraulic head is the height between the point at which water leaves the column and the point water reaches above the column in a manometer. The saturation hydraulic conductivity, K , was calculated using Darcy's equation.

$$\frac{dQ}{dt} = \frac{AK}{dx} \frac{dH}{dx}$$

where dQ/dt is the rate of flow of leachate in $\text{cm}^3 \cdot \text{h}^{-1}$.

A is the area of cross-section of the soil column in cm^2 .

dH is the hydraulic head in cm

and dx is the height of soil in the column.

The initial hydraulic conductivity HC_i was calculated at the first few PV of leaching and the relative hydraulic conductivity was calculated by dividing the HC during leaching by the HC_i .

The leachate was collected and measured for pH, electrical conductivity EC and concentrations of Ca and B.

To study the effect of salts dissolved from fly ash on the HC of the ash-amended soil, the addition of ash with most of its soluble salts removed (washed ash) to the soil was compared to the addition of untreated ash to the same soil. Washed ash was obtained in the same way as that used in the sorption study.

Although the sample of clay soil collected had an exchangeable sodium percentage (ESP) of 4.2, it is not uncommon for this soil to have a much higher ESP. To simulate a higher ESP, solutions of SAR 20

were leached through the ash-amended clay soil, thus raising the ESP of the soil to about 20. To prevent dispersion of the soil while raising its ESP, a solution of high salt concentration (0.5 N) of SAR 20 was initially leached, followed by successively lower concentrations (0.05 N and 0.01 N) of SAR 20, and finally with distilled water.

Due to the high concentration of salt solution initially leached through the column, no attempt was made to measure the dissolution of salt from the fly ash. Therefore a simpler leaching procedure than that previously described was used. Instead of measuring the hydraulic head, the water flow was measured by the volume of leachate collected in a fraction collector and the hydraulic head was kept constant using a Marriot bottle. Initial HC and relative HC were again calculated using Darcy's equation. All experiments were conducted in a room where the temperature was controlled at $23 \pm 2^{\circ}\text{C}$.

Cation and anion exchange capacities of the washed ash at two different suspension pHs of 6 and 10 were measured. The washed ash was first equilibrated with 1M NaCl and the pH adjusted with dilute NaOH. Excess NaCl solution was washed out with alcohol, and exchangeable Na and Cl removed, using 1M $\text{Ca}(\text{NO}_3)_2$ and analyzed in the $\text{Ca}(\text{NO}_3)_2$ solution extract.

A loam (loess) soil and a clay soil were sampled in this study. Some chemical and physical properties of these soils are presented in Table 1.

Layers of soil, 2 cm thick, were packed in 30 x 50 cm perforated metal boxes over 8 cm of coarse sand (3 replications). The boxes were

placed in a rainfall simulator (Morin et al., 1967) at a slope of 5% and subjected to a rainfall intensity of 34 mm/h. Distilled water was used to simulate rainwater and the amount added was equivalent to a depth of 56 mm. The volume of effluent was measured during the "rainstorm" and the infiltration rate (IR) was calculated.

Before rain simulation, the loam soil was treated in 3 ways and each treatment compared to a control. Either fly ash, phosphogypsum or pure sand were added on top of the soil at a rate equivalent to spreading 5 ton per ha.

The clay soil was mixed with 5, 7.5 or 10% fly ash or 10% ash washed of most of its soluble salt. After the "rainstorm", the amended soils were dried and another "rainstorm" applied. Comparison was made with a control and with phosphogypsum spread on top of the soil equivalent to 5 ton per ha.

To simulate the effect of several seasons on the clay soil mixed with 10% ash, a "rainstorm" was applied after 4 cycles of wetting and one weeks drying of the amended soil.

The results are given in Figs. 40-45 and all points are the average of 3 replicates.

RESULTS AND DISCUSSION

(1) The dissolution of Ca, B, Mo and Se from fly ash

The amount of Mo extracted from the fly ash by concentrated acid digestion was 13.5 ± 0.6 ug per g fly ash. The amount of B extracted from the ash by successive shakings in dilute HCl was 135 ± 15 ug per

g fly ash. Further details are given in the first year annual report.

The main salt dissolved in fly ash - distilled water extracts (pH 12.5) and fly ash - dilute HCl extracts (pH 7.0) was a calcium salt. Results of the element composition of fly ash - water extracts at these two pHs are enclosed (Hollis et al., 1986).

In suspensions of 6 g fly ash in 30 ml distilled water, Ca concentration reached a maximum in solution after shaking for one hour (Table 3). Ca^{2+} cations are countered by an equal concentration of OH^- anions after taking into account CaOH^+ ion pairs (Hollis et al., 1986). Therefore the source of Ca is CaO (identified by X-ray diffraction and EDXA in results enclosed by Mattigod) which hydrates in a fly ash - water extract to Ca(OH)_2 . After one hour the solution was supersaturated with respect to Ca^{2+} and OH^- ions and becomes undersaturated with time (Hollis et al., 1986). This may indicate that low soluble precipitates of Ca other than Ca(OH)_2 are present in the system.

B, Mo and Se all reached maximum solution concentrations within 24 hours shaking (Table 3) and then decreased to an equilibrium after about 4 days shaking of 0.07, 0.16 and 0.001 mg.L^{-1} respectively. This decrease is probably due to the sorption of solution species of these elements by fly ash and will be discussed in detail later.

As the pH of suspensions of 6 g ash in 30 ml solution was decreased from 12.5 to 6.0, the amount of Ca dissolved was increased from 23 mmol.L^{-1} to 110 mmol.L^{-1} (Fig. 1). The pH dependence of Ca dissolution suggests that its source in the ash is a basic salt of Ca

and probably the same source as at pH 12.5 which is CaO . Ca concentration in solution reached equilibrium within 24 hours shaking at all pHs except at the natural pH of a fly ash - water extract (12.5) suggesting that precipitation of low soluble Ca salts only takes place at this pH.

Above pH 8.5, less than 0.1 mmol.L^{-1} Mg was dissolved. As the pH was decreased below this value to 6.0, the amount of Mg dissolved was increased to 18 mmol.L^{-1} (Fig. 1). The source of soluble Mg is therefore also a basic salt which is probably MgO identified by Mattigod (results enclosed).

Phung et al. (1979) reported a large increase in the concentration of B dissolved from fly ash when the pH of an aqueous ash suspension was lowered from 12.3 to 6.0. Hollis et al. (1986 - results enclosed) showed that the extractability of B from fly ash was also pH dependent. At pH 12 less than 1% of the total extractable B was removed after 4 successive extractions. At pH 9 60% of the total extractable B was removed after 3 extractions, whereas at pH 6 100% was removed after 2 extractions.

Fig. 2 shows the concentration of Mo dissolved from 6 g fly ash in 30 ml solution at pHs ranging from 12.5 to 6.0. Maximum dissolution of Mo occurred between pH 8 and 10, and 60% of the total Mo was dissolved after 4 days shaking. The decrease in Mo in an ash-distilled water extract (pH > 12) after 24 hours shaking was also shown in Table 3.

In the same ash-water extracts as above, when the pH was reduced from 12.5 to 6.0 the amount of Se dissolved was increased from 0.001

mg.L⁻¹ to 0.10 mg.L⁻¹ (Fig. 3). At all pHs in the above range, Se concentration in solution decreased after shaking the aqueous ash suspension more than 24 hours and up to 4 days (Fig. 3).

By diluting the amount of ash to distilled water, more B was dissolved per unit weight of fly ash, whereas the amount of Mo dissolved remained the same. In a one to five ratio of ash to distilled water less than 1% of total extractable B was dissolved. Dissolution of the remainder is not only a function of reducing the pH but is also a function of increasing the surface area of fly ash in contact with solution by dilution. In the case of Mo, 30% of the total was already dissolved in a one to five ratio of ash to distilled water, and therefore not a great deal more was available for dissolution upon dilution of this ratio. Details of results are described in the first year annual report.

Ca, Mg, B, Mo and Se concentrations in neutralized fly ash-water extracts as a function of particle size are given in Table 4. Whereas, Ca and Mg were present in all particle size fractions, B and Mo were concentrated in the smaller size fractions and only a small amount was dissolved from particles >20 um in diameter. The contribution of the largest particles to B and Mo concentration in solution was very small even after crushing the particles to a size range smaller than 10 um (Table 4). Se was concentrated in both the small size fraction (3-8 um) and the large fraction (45-120 um) and only a small amount was dissolved from particles inbetween this size range (Table 4).

By knowing the fraction of each particle size range and its contribution of B, Mo and Se concentrations in solution after 24 h interaction, it is possible to calculate the total B, Mo and Se concentrations in solution of a bulk fly ash suspension. The calculated values are 14.4, 1.1 and 0.07 mg.L^{-1} for B, Mo and Se respectively, which are close to the experimental results (14.0, 1.2 and 0.05 mg.L^{-1} for B, Mo and Se respectively). Further details of results are described in the second year annual report.

(2) The sorption of B, Mo and Se by fly ash

Hollis et al. (1986 - results enclosed) described the effect of pH on B adsorption by washed ash at two different solution compositions ($\text{NaCl} + \text{NaOH}$ and $\text{CaCl}_2 + \text{Ca(OH)}_2$). Although the results indicated that the B adsorption at pH 7 was independent of solution composition (Ca^{2+} vs. Na^+), a great difference was observed in the alkaline range. B adsorption decreased with increasing pH in the $\text{NaCl} + \text{NaOH}$ system, whereas B adsorption increased in the $\text{CaCl}_2 + \text{Ca(OH)}_2$ system.

The behaviour of B adsorption in the $\text{NaCl} + \text{NaOH}$ system was explained by a ligand exchange mechanism and in the $\text{CaCl}_2 + \text{Ca(OH)}_2$ system two possibilities for the B interaction were put forward: 1) co-precipitation of B with Ca(OH)_2 or some other low soluble solid phase of Ca on to the fly ash surface; or 2) reaction of ion pairs containing B and Ca with the fly ash surface. The concentration of ion species of B in solution at the range of pH under study can be calculated using the first hydrolysis constant of boric acid, K_h ,

which is 5.8×10^{-10} at 20°C (Owen, 1934) and the association constant of $\text{CaB}(\text{OH})_4^+$ ion pairs, K , which is 0.015 at 25°C and an ionic strength of 0.16 (Keren and Bingham, 1985). Between pH 12 and 9 and Ca concentration 25 and 70 mmol.L^{-1} respectively, $\text{B}(\text{OH})_4^-$ ions and $\text{CaB}(\text{OH})_4^+$ ion pairs are at approximately equimolar concentrations in solution of a fly ash-water extract. Below pH 9 the predominant solution species is $\text{B}(\text{OH})_3$.

The main species of B available for adsorption are therefore $\text{B}(\text{OH})_4^-$ and $\text{CaB}(\text{OH})_4^+$ which are present above pH 9. Increasing the pH above 9 would decrease $\text{B}(\text{OH})_4^-$ adsorption due to competition with OH^- ions. Because the magnitude of free energy of desolution is much less for monovalent ion-pairs as compared to divalent free cations (Mattigod et al., 1985), affinity of fly ash for $\text{CaB}(\text{OH})_4^+$ ion pairs should be greater than for Ca^{2+} cations. Therefore adsorption of $\text{CaB}(\text{OH})_4^+$ by the fly ash is one possible mechanism for the decrease in B concentration in a fly ash-water extract above pH 9. The cation exchange capacity of the washed ash didn't change as the pH of the fly ash-water extract was increased, but its value of $3.0 \times 10^{-2} \text{ mol. Kg}^{-1}$ was high enough to make possible exchange of Ca^{2+} ions for $\text{CaB}(\text{OH})_4^+$ ions and cause the observed decrease in B concentration in solution.

Fig. 4 shows the rate of sorption of B by a suspension of washed ash and $\text{Ca}(\text{OH})_2$ in 0.05 M CaCl_2 solution. The same amount of $\text{Ca}(\text{OH})_2$ was added as that washed out of the fly ash. A large amount of the added B was sorbed by washed ash (bulk) within 4 hours (Fig. 4). Sorption continued slightly after this time. During the 4 days shaking of the ash suspension, the pH dropped slightly from 12.13 to

12.05 and the Ca concentration in solution decreased from 56 to 41 mmol.L⁻¹.

The rate of sorption of B by washed small ash particles (3-8 um diameter) (Fig. 4) shaken under the same conditions as described above, was the same as by the washed bulk ash. The rate of sorption of B by washed large ash particles (45-120 um diameter) was slower than by the washed bulk ash but continued fairly steadily over the 4 days of shaking (Fig. 4). This behaviour is to be expected from a surface reaction where the large ash particles have a much smaller surface area than the bulk fly ash particles.

The rate of precipitation of low soluble salts of Ca from solution of the washed ash suspensions described above was a function of particle ash size in a similar way to the rate of B sorptions by washed ash (Fig. 5). This supports a possible mechanism for the behaviour of B in a fly ash-water extract mentioned earlier, that B is co-precipitated with Ca(OH)₂ or some other low soluble solid phase of Ca onto the fly ash surface.

The sorption of Mo by fly ash shaken in distilled water at a pH above 12 has already been shown (Table 3). Fig. 6 shows the increase in sorption of Mo by washed ash when the pH in a fly ash - 0.05 M CaCl₂ solution extract was increased by adding Ca(OH)₂. At pH 12 about 80% of the added Mo was sorbed by the washed ash. No sorption of Mo by washed ash shaken in 0.15 M NaCl solution was observed even after increasing the pH up to 12 with NaOH solution. Neither was there any sorption of Mo by an aqueous suspension of Ca(OH)₂ in the

absence of fly ash. Therefore the behaviour of Mo sorption by fly ash is similar to the sorption of B by ash.

The main ion species in solution dissociated from molybdic acid above pH 6 is MoO_4^{2-} (Lindsay, 1979). In solution Ca^{2+} and MoO_4^{2-} ions associate to form CaMoO_4^0 ion pairs (First Year Annual Report). The constant (K) for this association calculated in ClO_4 medium is 5.7×10^3 . Ca^{2+} and MoO_4^{2-} ions also react to form the solid $\text{CaMoO}_4(c)$ with an equilibrium constant (K) for its formation of 8.7×10^7 . Therefore in the presence of Ca^{2+} ions, the main solution species of Mo above pH 6 are the ion pairs CaMoO_4^0 which have a maximum solution activity of 6.2 mg Mo.L^{-1} with respect to solid $\text{CaMoO}_4(c)$ and independent of pH above 6. It is difficult at this stage to attribute any mechanism to the interaction of Ca(OH)_2 -Mo with fly ash.

The sorption of Se by fly ash has already been shown over a wide pH range between 12.5 and 7.0 (Fig. 3). Fig. 7 shows the rate of sorption of added Se by washed ash and Ca(OH)_2 shaken in solutions of 0.05 M CaCl_2 in which sorption of added B had already been measured (Fig. 4). Within one hour shaking 99% of added Se had been sorbed by washed bulk ash. This fast reaction rate was probably due to the small initial amount of Se (0.50 mg.Kg^{-1} ash) which was added according to the amount washed out in preparing the fly ash for the sorption studies.

The rate of sorption of Se by washed large ash particles was slower than by washed bulk ash (Fig. 7). This behaviour is to be expected where like B, sorption of Se is a function of the surface area of the fly ash.

As with B and Mo sorption by washed ash, no sorption of Se by washed ash in the absence of Ca(OH)_2 or by Ca(OH)_2 in the absence of washed ash was observed. Neither was there any sorption of Se by washed ash when the pH of an ash-water extract was increased to 12 with NaOH solution.

Quinn (1985, summary of a Ph.D thesis enclosed) showed that in the presence of Ca ions, the main ion species of Se in solution are the ion pairs, CaSeO_3^0 and CaSeO_4^0 . Figs. 3 and 7 show values of Se determined by a selenium hydride generator attached to an atomic absorption spectrophotometer. This method specifically determines Se in its tetravalent form. Prior to this determination several samples were heated at 80°C for 10 minutes to reduce any hexavalent Se present in the sample to its tetravalent form (Perkin Elmer, 1981). The increase of Se in these samples was very small and therefore it was assumed that most of the Se present in solution of a fly ash - water extract was in an oxidation state of 4.

Although it is clear that Se and Ca(OH)_2 interact with fly ash, it is difficult at this stage to attribute any mechanism to this interaction.

(3) The mobility of Ca, B, Mo and Se in columns of fly ash mixed with inert sand and leached with distilled water

Hollis et al. (1986, results enclosed) showed that the main ions in solution of distilled water extracts of fly ash are Ca and OH. When fly ash (8% mixed with 92% inert sand) was leached with distilled water, one pore volume (PV) was enough for Ca and OH (calculated from pH) to reach maximum concentrations in the leachate (Figs. 8 and 9).

At the highest flow rate of 0.88 PV of leachate.h⁻¹, peak Ca concentration was actually higher than at the lower flow rates (Fig.8). This shows that dissolution of Ca from fly ash is fast and that probably precipitation of low soluble Ca salts caused the reduction in peak Ca concentration as the flow rate was reduced.

The concentration of ion species in the leachate can be calculated using the extended Debye Huckel equation (Stumm and Morgan, 1970) and the equilibrium constant for the formation of CaOH⁺ ion pairs given by Lindsay (1979). At the maximum salt concentration of the leachate (0.88 PV.h⁻¹ flow rate), 25 mmol.L⁻¹ free Ca²⁺ ions and 13 mmol.L⁻¹ CaOH⁺ ion pairs were approximately balanced (according to the electroneutrality of the leachate) by 66 mmol.L⁻¹ OH⁻ anions (calculated from the pH). At these concentrations, the ion activity product (IAP) of Ca and OH is $25 \times 10^{-6} \text{ M}^3$ which is considerably higher than the solubility product (K_{sp}) of Ca(OH)₂ of $6.3 \times 10^{-6} \text{ M}^3$ reported by Lindsay (1979). As to be expected, precipitation occurred in the leachate. However, a precipitate was observed even where the leachates were undersaturated with respect to Ca(OH)₂ and therefore other low soluble salts of Ca are also precipitated.

Total soluble Ca in fly ash was estimated by sequentially extracting the ash with dilute HCl at an ash-water suspension pH of about 6.5. 2.2% of the ash was extracted as soluble Ca. When ash was leached with distilled water at a flow rate of 0.88 PV.h⁻¹, by measuring the area under the leaching curve it was calculated that 4 PVs removed 40% of the total soluble Ca. The concentration of Ca in the leachate continued to decrease with a further 46 PVs of water from

5.0 to 0.5 mmol.L⁻¹ (Fig. 8) and 27% more of the total soluble Ca was removed from the fly ash. After 6 PVs of leachate the release of Ca was independent of flow rate (Fig. 8) indicating that at a certain volume of leaching solution, solid and solution forms of Ca were in equilibrium. The leachate pH after 50 PVs of distilled water was 11.0 (Fig. 9). This high pH prevents the remainder of the soluble Ca (33%) from dissolving since the solubility of the fly ash Ca salt is lower at pH 11 than pH 7 (Fig. 1).

Very little boron was leached out in the first 3 PVs of distilled water due to the sorption of B by the fly ash at the high leachate pH (above 12.4). When the pH was lowered below this value, a lot more B was leached out (Fig. 9), reaching a maximum concentration of 0.88 mg.L⁻¹ at 4 PVs of leachate and a flow rate of 0.88 PV.h⁻¹. Lowering the flow to 0.08 and 0.02 PV.h⁻¹ increased the volume of water necessary to leach B to a maximum concentration and decreased this maximum concentration of B to 0.70 and 0.65 mg.L⁻¹ respectively. Two reasons for this behaviour are: 1) the increased Ca leachate concentration and hence the increased pH when lowering the flow rate during 4 and 6 PVs of leachate (Fig. 8) which lowers B dissolution; and 2) the increased time of contact of leaching solution and fly ash at the lower flow rates which increases the amount of B sorbed (compare with Fig. 4). Further leaching of fly ash decreased the concentration of B in the Leachate to 0.2 mg.L⁻¹ after 50 PVs irrespective of the flow rate.

Total soluble B was estimated in the same way as Ca by sequentially extracting the ash with dilute HCl. It amounted to 120

ug B per g fly ash. By measuring the area under the leaching curve, it was calculated that 37% of the total soluble B was leached out in 50 PVs distilled water at a flow rate of 0.88 PV.h^{-1} . The final pH and the amount of B extracted in 50 PVs leachate didn't change when the flow rate was lowered. Therefore, extractability of B is independent of time of contact of solution with fly ash and the 63% of soluble B which was not leached out is due to the high leachate pH (above 11.0). The enclosed results of Hollis et al. (1986) show the pH dependence of B extractability which supports the above conclusion. More details of the leaching of B from fly ash are shown in the second year annual report.

Fig. 10 shows the concentration of Mo leached out of fly ash at different flow rates. One PV of distilled water was enough for Mo to reach maximum concentration of 1.0 mg.L^{-1} at a flow rate of 0.88 PV.h^{-1} . After 4 PVs the concentration was reduced to 0.1 mg.L^{-1} and from the area under the leaching curve it was calculated that 30% of the total Mo was removed from the fly ash. As the flow rate was decreased a second peak of Mo concentration appeared between 4 and 6 PVs (Fig. 10). This peak accounted for a further 10 and 30% of total Mo leached out at flow rates of 0.08 and 0.02 PV.h^{-1} respectively. It is probable that at the lower flow rates, the extra contact time of leaching solution with fly ash enables dissolution of a fraction of Mo which is not soluble at the high initial pH (above 12.4).

The amount of Se leached out from the ash was very low at all flow rates and did not exceed 0.01 mg.L^{-1} .

- (4) The interaction of Ca and B with fly ash-amended soils as measured by a) shaking mixtures of soil, ash and distilled water, and b) leaching columns of ash-amended soil with distilled water

(4a) Shaking mixtures of soil, ash and water

The solution concentration of Ca decreased with increasing time of shaking suspensions of ash and inert sand in distilled water (Fig. 11). This behaviour was explained in section 1 and was attributed to low soluble precipitates of Ca formed from dissolution of Ca(OH)_2 from the fly ash. A minimum Ca concentration in solution of 2 mmol. L^{-1} was reached at between 3 and 7 days shaking (Fig. 11) and thereafter increased slightly. The solution pH continued to decrease after Ca had reached a minimum concentration and only in suspensions containing not more than 10 g ash did pH decrease to an equilibrium of 8.5 within 14 days shaking (Fig. 12).

It is probable that the formation of CaCO_3 plays a significant part in the precipitation of low soluble Ca salts. The value of the constant ($\log K^0$) for the formation of CaCO_3 (calcite) which would determine pH and Ca concentration in solution is 9.74 (Lindsay, 1979). At 14 days of shaking the ash suspension, solution pH of 8.5 and Ca concentration of 2.0 mmol.L^{-1} require a CO_2 partial pressure ($p\text{CO}_2$) of $4 \times 10^{-5} \text{ atm}$. This value is an order of magnitude lower than the $p\text{CO}_2$ of air at 25°C of $3 \times 10^{-4} \text{ atm}$. and if the formation of CaCO_3 is the main Ca precipitate, then the $p\text{CO}_2$ of bubbling air through the ash suspension is much less than the atmospheric $p\text{CO}_2$. Therefore before a mechanism can be attributed to the precipitation of Ca salt it is necessary to control the suspension $p\text{CO}_2$ at known values.

Assuming a suspension $p\text{CO}_2$ kept constant at about an order of magnitude below atmospheric $p\text{CO}_2$ then it is possible that the observed rise in solution Ca concentration after reaching a minimum while the pH continued to drop, is due to maintaining solution concentrations of Ca and pH in equilibrium with CaCO_3 .

When distilled water extracts of fly ash and loamy sand soil were shaken, initial Ca solution concentrations (after one hour shaking) were slightly lower than initial Ca concentrations in ash and inert sand extracts (c.f. Figs. 11 and 13). This is probably due to the buffering capacity of the loamy sand soil.

The drop in pH while shaking the ash-loamy sand soil suspensions is also buffered by the soil and therefore the rate of decrease is less than in the ash-inert sand suspensions (c.f. Figs. 12 and 14). Therefore the corresponding decrease in Ca concentration was also at a lower rate than in the ash-inert sand suspensions (Fig. 13).

The buffering capacity of the clay soil is much higher than the loamy sand soil, e.g., higher CEC and clay content (Table 1) and therefore the initial Ca concentration is much lower (c.f. Figs. 13 and 15) and the rate of decrease in pH is also lower (c.f. Figs. 14 and 16).

The drop in pH of fly ash-water suspensions (containing either inert sand or soil) with increased time of shaking, as described above, caused increased dissolution of B from the fly ash (Figs. 17, 18 and 19). In suspensions containing inert sand, the amount of B dissolved was a function of the amount of ash added only when the latter reduced pH (Fig. 17). Hollis et al. (1986) showed that by

reducing the pH of ash-water extracts by neutralizing CaO in the ash with dilute HCL, B dissolution was increased. Therefore B dissolution was not affected by dissolution of Ca salts or their precipitation but was a function only of pH.

By increasing the amount of loamy sand soil added to the ash-water suspension from 50 g to 95 g, more B was dissolved (Fig. 18). This extra B was probably dissolved from the soil itself. At each addition of soil, the slope of the curve of B concentration vs. pH remained approximately the same (Fig. 18) suggesting that the dissolution of B from the loamy sand soil is not a function of pH. Dissolution of B also increased with increasing addition of clay soil (Fig. 19) and the slopes of each curve of B concentration versus pH changed, indicating that B dissolution from the clay soil was a function of pH.

In conclusion, dissolution of B from fly ash is a function of pH and doesn't depend on the texture of the soil, except when the buffering capacity of the amended soil affects the pH.

(4b) Leaching columns of ash-amended soil

Fig. 20 shows the concentration of Ca leached out of loamy sand soil amended with up to 10% ash. In the first 4 pore volumes (PVs) of leachate, 11% of the total soluble Ca in fly ash was leached out (calculated from the area under the curve of soil + 10% ash) compared to 40% of the total soluble Ca from fly ash mixed with inert sand. It is probable that the buffering capacity of the loamy sand soil prevents initial leaching out of a large amount of Ca dissolved from the fly ash. In a further 46 PVs of leachate, 32% more of the soluble

Ca in fly ash was leached out. This is a similar amount to that leached out of an inert sand-fly ash mixture and therefore after the initial 4 PVs of leachate the buffering capacity of the loamy sand soil becomes saturated and has no further effect in preventing the leaching out of Ca dissolved from the fly ash.

Fig. 21 shows the concentration of Ca leached out of a loam soil amended with up to 20% ash. In the first 4 PVs of leachate, 9% of the total soluble Ca in fly ash was leached out (calculated from the area under the curve of soil + 10% ash). As in the loamy sand soil, the buffering capacity of the loam soil also prevents initial leaching out of a large amount of Ca dissolved from the fly ash. In a further 46 PVs of leachate, 14% more of the soluble Ca in the fly ash was leached out. This is much less than that leached out of ash-amended loamy sand soil and suggests that the buffering capacity of the loam soil continues to prevent leaching of Ca dissolved from the ash. The higher buffering capacity of the loam soil than the loamy sand soil is mainly due to its higher CEC (Table 1).

Fig. 22 shows the ratio of concentration of OH to Ca in the leachates from ash mixed with inert sand and ash mixed with soil. From ash mixed with inert sand this ratio was slightly above 2 which corresponds to the dissolution and leaching out of $\text{Ca}(\text{OH})_2$. In the first 6 PVs of leachate from ash mixed with a loamy sand soil, this ratio was lower than 2 (Fig. 22) suggesting that OH was exchanged for some other anion in the soil, probably Cl. In the case of ash mixed with a loam soil, during 23 PVs of leachate the ratio was much less than 2 (Fig. 22). Therefore exchange of OH by the loam soil is

greater than by the loamy sand soil probably because if the CEC of the loam is higher, then also its anion exchange capacity (AEC) is higher than that of the loamy sand soil.

The pH of the ash-amended loamy sand rises to a maximum after 6 PVs of leachate (Fig. 23). During this rise in pH, the values are much lower than those from ash mixed with inert sand (Fig. 9). This lower pH enables greater initial leaching out of B from the ash-amended loamy sand soil (Fig. 24) compared to the ash mixed with inert sand (Fig. 9). The leachate pH from loamy sand soil amended with 5% was lower than that from soil with 10% ash (Fig. 23). Therefore more B was initially leached out of loamy sand soil amended with 5% ash even though the amount of amendment was lower and therefore contained less soluble B. After reaching peak concentration B decreased more gradually from 10% ash-amended soil than from 5% (Fig. 24). In 50 PVs of leachate B concentration had decreased to 0.23 mg.L^{-1} and 0.13 mg.L^{-1} from 10% and 5% ash-amended soils, respectively.

The loamy sand soil contains soluble B, as mentioned earlier in this section with a maximum concentration of 0.4 mg.L^{-1} in the leachate (Fig. 24). By measuring the area under the B leaching curve of soil + 10% ash and subtracting from it the amount of B leached from the soil alone, the amount of B released from the ash can be calculated. In 50 PVs of leachate 30% of the total soluble B in fly ash was leached out compared to 37% from a mixture of ash and inert sand. The high amount of soluble B not leached out was due to the

high leachate pH at 50 PVs, 10.5 and 11.0 from a mixture of ash + loamy sand soil and ash + inert sand, respectively.

In the first 6 PVs of leachate, the pH was similar in both 5% and 10% ash-amended loam soil (Fig. 25). Therefore, more B was initially leached out of the higher ash amendment (fig. 26). Increasing the ash amendment from 10 to 20% increased the initial pH (Fig. 25) and therefore decreased the amount of B initially leached out (fig. 26). From the highest ash amendment (20% ash) leachate concentration of B only slowly decreased reaching 0.34 mg.L^{-1} at 50 PVs whereas in lower ash amendments (10% and 5%) B decreased to 0.13 and 0.15 mg.L^{-1} , respectively.

There was much less B in the loam soil than in the loamy sand and its concentration did not exceed 0.2 mg.L^{-1} (Fig. 26). In 50 PVs leachate, 65%, 70% and 27% of the soluble B in fly ash were leached out of 5, 10 and 20% ash-amended loam soil, respectively. More B was released from 5 and 10% ash amendments because of the overall lower leachate pH than from a 20% ash amendment (Fig. 25).

Fig. 27 shows the EC of leachates from clay soil amended with up to 10% ash. Peak salt concentration of the leachate was reached at 1 PV and within 4 PVs the EC of ash-amended soil had decreased to the same value of EC of soil alone. Only a few measurements of Ca and Na concentrations in the leachates were made but an estimation showed that between 5 and 10% of the total soluble Ca in the fly ash was leached out in the first 4 PVs of leachate. No more Ca was leached out of the ash in further PVs of leachate. Therefore less Ca was leached out of ash in amended clay soil than in amended loamy sand or

loam soils due to the higher buffering capacity of the clay soil (higher clay content and CEC, Table 1).

The pH of leachates from ash-amended clay soil did not rise above 9.6 (Fig. 28) due to the high buffering capacity of this soil. This explains the high concentration of B leached out of these amended soils (Fig. 29). A lot of B was leached from the clay soil alone with a maximum concentration at about 0.6 mg.L^{-1} . After subtracting the amount of soluble B in the soil, it was calculated that 65% and 64% of the soluble B in fly ash were leached out of 5% and 10% ash-amended soils, respectively in 20 PVs of leachate. In this volume of leachate the concentration of B had decreased to about 0.2 mg.L^{-1} (Fig. 29).

It is clear that all three soils (loam sand, loam and clay) only affect leaching out of B by changing the leachate pH and not by their own properties.

(5) Effect of Fly Ash on the Infiltration Rate and Hydraulic Conductivity of Ash Amended Calcareous Smectitic Soils

(5a) Hydraulic Conductivity Study

The initial HC of loamy sand soil in the first PV of leachate decreased when fly ash (up to 10%) was added (Fig. 30). Fly ash particles (mainly $<20 \mu\text{m}$ in diameter) are smaller than loamy sand particles (mainly $>20 \mu\text{m}$, Table 1) and therefore the ash particles reduce soil pore size causing the reduction in initial HC. The decrease in bulk density of the loamy sand soil with addition of fly ash (Table 2) was only apparent since the standard deviation of the bulk density at each ash amendment was higher than this decrease.

During the leaching of the loamy sand soil with distilled water (DW), the HC was reduced almost 90% below its initial value after 50 pore volumes (PVs) had been passed through (Fig. 30). When 0.01 N SAR 2 solution was leached through the loamy sand soil, there was no reduction in HC (Fig. 30). This is probably because the EC of the leaching solution (Fig. 31) was high enough to prevent swelling and dispersion of soil clay particles. The EC of the distilled water leached through the soil column (Fig. 31) was not high enough to prevent swelling and dispersion of soil clay even though the exchangeable sodium percentage (ESP) of the loamy sand was low (3.9).

A large reduction in HC was also observed when distilled water was leached through a loamy sand soil amended with 10% ash (Fig. 30). The leachate EC was increased (Fig. 31) due to the dissolution of salt (mainly $\text{Ca}(\text{OH})_2$) from the fly ash but this was not enough to prevent the swelling and dispersion of soil clay which caused the reduction in HC.

The initial HC of a loam soil was decreased slightly when fly ash (up to 20%) was added (Fig. 32). Again the small size of the fly ash particles (mainly $<20\ \mu\text{m}$) reduces the pore size of the loam soil even though the loam soil particles are much closer in size to the ash particles than the loamy sand particles are (Table 1).

There was no reduction in HC when the loam soil was leached with distilled water (Fig. 32). One of the reasons for this is that the low ESP of the loam (1.9) which is lower than the ESP of the loamy sand soil, helps to prevent dispersion and swelling of soil clay. However, addition of between 10 and 20% ash to the loam soil,

decreased HC 40 and 50%, respectively, below its initial value when distilled water was leached through (Fig. 32). The increase in EC of the leachates by adding ash to the loam soil (Fig. 33) would be expected to prevent the observed decrease in HC. However, the leachate pH was increased above 10 (Fig 25) and since this is known to reduce the HC of soils (Suarez et al., 1984), it is probable that the effect of pH on the HC of ash-amended loam soil dominates.

The HC of the clay soil decreased when distilled water was leached through. Compared to the loamy sand soil this decrease was much faster since the HC was reduced to 30% its initial value after leaching through only 3 PVs water (Fig. 34) whereas 35 PVs water were necessary for the same HC reduction in the loamy sand soil (Fig. 30). The ESPs of the two soils are both about 4 (Table 1) which does not account for their difference in behaviour. The much higher sensitivity of the HC of the clay soil than the loamy sand soil to distilled water is probably due to its much higher clay content. (Table 1).

The addition of 5% ash to the clay soil improved its HC slightly by increasing its initial HC and by lessening the reduction in HC during leaching (Fig. 34). The addition of 10% ash also increased the initial HC of the clay soil and completely prevented any reduction in HC during the leaching of distilled water (Fig. 34). When ash was washed of most of its soluble salts and 10% added to the clay soil, there was no improvement in initial HC although there was about 30% improvement in the final HC compared to soil alone. Assuming negligible dissolution of salts from washed ash, the improvement in HC

is due to a physical effect of washed ash. It is probable that the larger size of the fly ash particles than the clay particles (table 1) increases soil pore size and thus increases HC. When comparing soils amended with 10% untreated ash and 10% washed ash (fig. 34), the most noticeable effect of fly ash on the HC of the clay soil is due to dissolution of salts (mainly $\text{Ca}(\text{OH})_2$) from the fly ash. Some of the Ca dissolved exchanges with Na in the soil thus reducing the soil ESP enough to prevent clay swelling and dispersion and the resultant decrease in HC. This effect is enough to counteract the effect of increased pH in amended clay soil (Fig. 28) which would be expected to lower the HC (Suarez et al., 1984).

0.5N, 0.05N and 0.01N SAR 20 solutions were successively leached through the clay soil producing a soil ESP of about 20. It was necessary to leach through about 2 PVs of each solution in order to reach equilibrium HC prior to leaching distilled water.

When distilled water was leached through clay soil alone, 3 PVs were enough to almost completely seal the water conducting soil pores (Fig. 35). Amending the soil with 10% fly ash prevented the sealing of soil pores when distilled water was leached and maintained the HC at about 50% its initial value (Fig. 35). The addition of 10% ash washed of most of its soluble salts, to the clay soil also prevented sealing of soil pores and maintained the HC at about 10% its initial value (Fig. 35). The effect of fly ash on the HC of the clay soil at ESP 20 was similar to its effect at the natural ESP of the clay soil (4). The washed ash raises the HC 10% due to the increased soil pore size caused by the fly ash particles and there was a further raise in

HC of 40% by the untreated ash due to dissolution of salt (mainly $\text{Ca}(\text{OH})_2$).

Fig. 36 shows the leachate EC after displacing 0.01N SAR 20 solution with distilled water in clay soil alone and amended with 10% ash. One PV of distilled water displaced SAR 20 solution and further PVs resulted in a final EC of about 0.4 dS.m^{-1} in both soil alone and Ash-amended. Na is the main cation in the leachates from both soil alone and ash-amended (Fig. 36). Exchangeable Na is removed from the soil, therefore lowering the soil ESP, by exchange of Na with Ca dissolved from fly ash and also by hydrolysis of Na. The former process can occur in the ash-amended soil throughout leaching with SAR 20 solutions and distilled water whereas the latter mainly occurs when leaching with distilled water. Therefore amending the clay soil with fly ash prevents a high rise in soil ESP when leaching SAR 20 solutions and protects the soil structure when displacing SAR 20 solutions with distilled water. In soil alone the hydrolysis of Na when displacing SAR 20 solution with distilled water is not enough to prevent clay swelling and dispersion caused by the high ESP.

The leachate pH increased up to 10.8 when 12 PVs of distilled water were leached through the ash-amended soil (fig. 37), due to dissolution of $\text{Ca}(\text{OH})_2$ from the fly ash. This high pH would be expected to reduce HC but, as also was the case at the natural ESP of the clay soil, the dominant effect on HC was from the exchange of Na in the soil by Ca dissolved from the fly ash preventing a large reduction in HC.

Fig. 38 shows the different effect on the HC of the clay soil of small particles of ash (3-8 μm diameter) and of large particles of ash (45-120 μm diameter). Amending the soil with 10% large particles gave a much higher initial HC (obtained by leaching 0.05N SAR 20 solution) than by amending the soil with 10% small particles (Fig. 38). After displacing 0.01N SAR 20 solution with distilled water, the HC of the soil amended with small ash particles decreased 75% and the HC of the soil amended with large ash particles decreased 55% (Fig. 38). The final leachate EC of the large particle amended soil was higher than the final EC of the small particle amended soil and the difference was mainly due to the higher concentration of Na leached from the large particle amended soil (Fig. 39). Adding large particles of fly ash to the clay soil improved its HC more than by adding small ash particles because the pore size of the soil was increased and there was greater exchange of Na by Ca dissolved from the ash, leading to a lower soil ESP.

(5b). Infiltration Rate Study

Fig. 40 shows the drop in infiltration rate (IR) of the loam soil to a final infiltration rate (FIR) of 3 mm/h. This sharp drop in IR was due to crust formation in the upper 2 mm of the soil (Agassi et al., 1981). Application of phosphogypsum (5 ton/ha) lessened this drop and the FIR was increased to 11 mm/h (Fig. 40). This improvement in IR was due to contribution of Ca-electrolytes from the phosphogypsum to the soil solution preventing chemical dispersion of the clay (Agassi et al., 1982).

Adding fly ash on top of the soil also improved the IR and raised the final infiltration rate (FIR) of the loam soil to 6 mm/h (Fig. 41). This improvement was partly due to dissolution of Ca-electrolytes from the fly ash and partly to a physical effect of fly ash particles. Addition of pure sand improved the FIR to 7 mm/h (Fig. 41) also due to a physical effect of reducing rain impact on the soil

Since the improvement to loam soil IR of adding fly ash was only slightly above that of pure sand and much less than the improvement caused by phosphogypsum, it was concluded that fly ash cannot replace phosphogypsum in amending the IR of a loam soil.

Fig. 42 shows the drop in IR of the clay soil and its improvement by adding phosphogypsum. The FIR was increased from 2 to 7 mm/h in the phosphogypsum amended soil. This improvement was caused by dissolution of Ca-electrolytes from the phosphogypsum as described in amended loam soil.

Mixing the soil with 5% ash improved its IR (Fig. 43) and FIR was risen slightly from 2 to 3 mm/h. After drying the amended soil 43 days and running another "rainstorm", there was no noticeable improvement in IR above the control (Fig. 43).

Mixing the clay soil with 7.5% ash raised the FIR slightly to 4 mm/h but reduced the initial IR considerably (fig. 44). This was probably because of a cementing effect of Ca(OH)_2 in the fly ash (Plowman et al., 1984) which reduces soil permeability before a crust is formed on the soil surface. After drying the amended soil one

week, this cementing effect was still evident (Fig. 44) although the FIR had decreased to 3 mm/h.

Mixing the clay soil with 10% ash had a similar effect to adding 7.5% ash on the IR of a "rainstorm" before and after drying the amended soil one week (Fig. 45). When the amended soil was dried two weeks after the initial "rainstorm" and another "rainstorm" applied, the cementing effect had disappeared (Fig. 45). This was probably because one week of drying was not enough to break down the soil-ash cement formed in the first "rainstorm" whereas two weeks was. In 10% ash-amended clay soil, the FIR was maintained at 4 mm/h after one week and two weeks drying (Fig. 45).

Afer 4 cycles of wetting and drying the clay soil alone and amended with 10% fly ash, the drop in IR and the FIR of 4mm/h was the same in both cases. Therefore the slight effect of fly ash in improving the FIR of the clay soil in one "rainstorm" would be expected to disappear over several seasons of wetting and drying.

10% fly ash has a large effect on the texture of the clay soil and after one cycle of wetting and drying or one "rainstorm", the amended soil behaved like a much lighter soil. Therefore, the fly ash improves the workability of the clay soil.

CONCLUSION

Leaching of a loamy sand soil with distilled water reduced the soil's hydraulic conductivity (HC) due to clay swelling and dispersion. Mixing up to 10% fly-ash with 90% loamy sand soil improved the soil by lowering its HC in the first pore volume (PV) of water leached. Calcium and hydroxide ions dissolved from fly ash,

increased the leachate pH and electrolyte concentration from the ash amended loamy sand soil. The beneficial effect of ash on soil structure (increased electrolyte concentration) was countered by the detrimental effect of higher pH and therefore the addition of ash to the loamy sand soil did not prevent clay swelling and dispersion.

The clay soil structure was much more susceptible to leaching distilled water than the loamy sand, due to its higher clay content. Mixing 10% fly ash with 90% clay soil increased its HC and prevented swelling and dispersion. This was due to a physical effect of fly ash increasing the pore size distribution in the soil and a chemical effect of Ca dissolution from the ash which prevented clay swelling and dispersion.

Boron dissolved from the fly ash was leached out of the ash-amended loamy sand soil relatively slowly. The total soluble B content of fly ash was 120 mg.kg^{-1} ash. In 50 PVs of leachate only 30% of the soluble B in fly ash was released from a soil amended with 10% ash, because of the high leachate pH (above 10.5). The buffering capacity of the clay soil is much higher than the loamy sand soil and therefore concentrations of Ca and OH leached out of ash-amended clay soil were much lower. The lower pH (9.6) allowed faster and greater leaching out of B from ash-amended clay soil. In 20 PVs of leachate 65% of the total soluble B in fly ash was leached out of a clay soil amended with 10% ash.

B dissolution from fly ash and its mobility in ash-amended soils were functions of pH. Precipitation of low soluble Ca salts on to the fly ash surface and the texture of the amended soil only affected the

mobility of soluble B by affecting the pH. Sorption of soluble B by fly ash was shown to take place at high pH and two mechanisms were suggested: (1) co-precipitation of B with Ca(OH)_2 or some other low soluble Ca salt on to the fly ash surface and (2) adsorption of CaB(OH)_4^+ ion pairs by the fly ash.

The interactions of Mo and Se dissolved from fly ash with amended soils were not studied. these interactions can be estimated from the dissolution and mobility of Mo and Se in water suspensions and columns of fly ash. The total Mo content of fly ash was 13.5 mg.kg^{-1} ash. 60% of the total was dissolved and most of this was leached out of the fly ash in the first 6 PVs of leachate. By adding fly ash to soil, the lower pH than from fly ash alone would be expected to slightly enhance dissolution and mobility of Mo.

Only a low concentration of Se (less than 0.01 mg.L^{-1}) was leached from fly ash alone which would be expected to be increased in fly ash-amended soil because of the lower pH. Analysis of Se and Mo in the leachates of ash-amended soils is necessary to check these hypotheses.

Mixing large particles of fly ash in a clay soil improved its HC more than bulk ash due mainly to their physical effect on increasing the pore size distribution of the clay soil. The advantages in this amendment are that much less soluble B and Mo are present in the large ash particles. However, the leachate pH was even higher than that of bulk soil (11.3 compared to 10.5). Although neither pH showed any adverse effect upon soil structure, they are both very high for plant growth. Therefore, further work is necessary to make use of the

processes in the fly ash which will reduce this pH, for example precipitation of low soluble Ca salts by fly ash.

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Table 1: Description and some properties of the soil and fly ash used.

	Soil type			Fly ash
	Loamy sand	Fine sandy clay loam	Clay	
Location	Zeelim	Alumim	Kfar Menachem	
USDA	Xeric	Calcic Mollic	Typic	
Identification	Torrip-samments	Haploxeralf	Chromoxerert	
% CaCO_3	6	20	8	0
% sand > 20 μm	82	47	31	28
% silt 2-20 μm	8	36	22	70
% clay < 2 μm	10	17	47	2
CEC mmol kg^{-1}	49	200	470	60
ESP	3.9	1.9	4.2	0

Table 2: The bulk density of the packed fly ash-amended soils and the flow rate of leaching solution

Soil	Ash amendment	Bulk density g.cm ⁻³	Flow rate pore volume.h ⁻¹
Loamy sand	None	1.48 ± .02 [*]	0.32
	5%	1.47 ± .04 [*]	0.32
	10%	1.46 ± .04 [*]	0.32
Loam	None	1.30	0.29
	5%	1.31	0.26
	10%	1.27	0.25
	20%	1.27	0.25
Clay	None	1.16 ± .01 [*]	0.02
	5%	1.15	0.21
	10%	1.20 ± .01 [*]	0.20

* Standard deviation

Table 3: The effect of time on the pH and concentration of Ca, B, Mo and Se dissolved in aqueous suspensions of fly ash.

Shaking time	pH	Ca mmol L ⁻¹	B mg L ⁻¹	Mo mg l ⁻¹	Se mg L ⁻¹
Hours					
0.2	12.44	19.7	-	0.31	0.024
0.5	12.44	21.6	0.40	0.37	0.008
1.0	12.44	23.7	0.40	0.47	0.003
4.0	12.50	23.6	0.44	0.75	0.002
24	12.48	22.8	0.21	0.95	0.001
days					
4	12.38	14.3	0.07	0.16	0.001
12	12.23	11.3	0.07	0.13	0.001

Table 4: Effect of fly ash particle size on Ca, Mg, B, Mo and Se dissolved from neutralized suspensions of 6 g ash in 30 ml solution while shaking for 24 hours.

Particle size um	Mass fraction %	pH	Ca mmol.L ⁻¹	Mg mmol.L ⁻¹	B mg.L ⁻¹	Mo mg.L ⁻¹	Se mg.L ⁻¹
<3	1.7	6.5	41	-	13.6	-	-
3-8	24.7	7.4	65	11	24.8	2.60	0.12
8-15	29.6	8.4	93	15.5	20.0	1.04	0.03
15-20	16.1	8.1	95	11	9.6	0.68	0.01
20-45	14.3	8.5	103	8.5	2.9	0.23	0.04
45-120	13.5	6.8	93	6.5	0.9	0.16	0.18
45-120*	-	8.8	110	-	1.3	0.23	-
Bulk	-	8.0	90	9	14.0	1.20	0.05

All values are means of two replicates

45-120* um particles crushed to <10 um

Fig. 1. Effect of pH on the concentration of Ca released from acidified suspensions of fly ash

Fig. 2. Effect of pH on the concentration of Mo released from acidified suspensions of fly ash

Fig.3. Effect of pH on the concentration of Se released from acidified suspensions of fly ash.

Fig. 4. Effect of ash particle size on the rate of sorption of boron by a suspension of washed ash and $\text{Fe}(\text{OH})_3$ in an ash to water ratio of one to five

Fig.5. Effect of ash particle size on the rate of precipitation of low

Fig. 6 Effect of pH on the sorption of Molybdenum by washed ash where the pH is adjusted by $\text{Ca}(\text{OH})_2$ in an ash to water ratio of one to five shaken for 24 hours

Fig. 7. Effect of ash particle size on the rate of sorption of selenium by a suspension of washed ash and $\text{Ca}(\text{OH})_2$ in an ash to water ratio of one to five

Fig. 8. Calcium leached from a mixture of ash and inert sand (8% ash) under different fluxes.

Fig. 9. pH and B concentration of leachates from washed sand mixed with 8% ash and leached with 0.88 PV.h^{-1} of distilled water.

Fig. 10. Molybdenum leached from a mixture of ash and inert sand (8% ash) under different fluxes.

Fig.11. The concentration of calcium dissolved in distilled water extracts of fly ash + inert sand at different amounts of fly ash to 500 ml distilled water.

Fig. 12. The pH of distilled water extracts of fly ash + inert sand at different amounts of fly ash to 500 ml distilled water

Fig. 13. The concentration of calcium dissolved from extracts of fly ash and loamy sand soil in 500 ml distilled water

Fig. 14. The pH of extracts of different amounts of fly ash and loamy sand soil in 500 ml of distilled water

Time of shaking days

Fig. 15. The concentration of calcium dissolved from extracts of different amounts of fly ash and clay soil in 500 ml distilled water.

Fig. 16. The pH of extracts of different amounts of fly ash and clay soil in 500 ml distilled water

Fig. 17. The effect of pH on the amount of boron dissolved from different amounts of fly ash mixed with inert sand in 500 ml distilled water

Fig. 18: The effect of pH on the amount of boron dissolved from different amounts of fly ash mixed with loamy sand soil in 500 ml distilled water.

Fig. 19: The effect of pH on the amount of boron dissolved from different amounts of fly ash mixed with a clay soil in 500 ml distilled water.

Fig. 20: Calcium concentration in leachates from loamy sand soil amended with fly ash and leached with distilled water at 0.3 PV.h⁻¹.

Fig. 21: Calcium concentration in leachates from loam soil amended with fly ash and leached with distilled water at 0.3 PV.h⁻¹.

Fig. 22: Ratio of hydroxide concentration to calcium concentration in leachates from ash-amended sand and soil.

Fig. 23. pH of leachates from loamy sand soil amended with ash and leached with distilled water at 0.3 PV. h⁻¹

Fig. 24. Concentration of boron in leachates from loamy sand soil amended with fly ash and leached with distilled water.

Fig. 25. pH of leachates from loam soil amended with ash and leached with distilled water at 0.3 PV.h^{-1}

Fig. 26. Concentration of boron in leachates from loam soil amended with fly ash and leached with distilled water

Fig. 27. The electrical conductivity of leachates from clay soil amended with fly ash and leached with distilled water.

Fig. 28. The pH of leachates from day soil amended with ash and leached with distilled water.

Fig. 29: The concentration of boron in leachates from ash-amended clay soil leached with distilled water.

Fig. 30. The relative hydraulic conductivity of a loamy sand soil amended with fly ash and leached with water of different salt concentrations.

Fig. 31: Electrical conductivity of loamy sand soil amended with fly ash

Fig. 32: Effect of fly ash on the relative hydraulic conductivity of a loam soil leached with distilled water.

Fig. 33: Effect of fly ash on the EC of leachates from columns of loam soil + fly ash leached with distilled water.

Fig. 34: Effect of fly ash on the relative hydraulic conductivity of clay soil leached with distilled water

Fig. 35: Effect of fly ash on the relative hydraulic conductivity of a clay soil leached with SAR 20 solutions followed by distilled water.

Fig. 36: Electrical conductivity of leachates from clay soil amended with fly ash after SAR 20 solution followed by distilled water was passed through.

Fig. 37: pH of leachates from clay soil amended with fly ash and leached with SAR 20 solutions followed by distilled water.

Fig. 38: Effect of ash particle size on the relative HC of a clay soil leached with SAR 20 solutions followed by distilled water.

Fig. 39: Electrical conductivity of leachates from clay soil amended with different size fractions of flay ash and leached with SAR 20 solutions followed by distilled water.

Figure 40

Fig. 41
LOAM (LOESS) SOIL

Fig. 42
Clay Soil

Fig. 43
Clay Soil

Fig. 44
Clay Soil

Fig. 45
Clay soil

BORON RELEASE AND ADSORPTION BY FLY ASH AS AFFECTED BY pH AND
PARTICLE SIZE

J.F. Hollis, R. Keren and M. Gal

Introduction

Fly ash is a major solid residue produced from the combustion of coal in modern coal-fired power plants. Although several beneficial effects from the use of fly ash as a soil amendment have been demonstrated (Rees and Sidrak, 1956; Martens, 1971), the extent of fly ash utilization in agriculture has been negligible because of the release of elements injurious to plants (Hodgson and Holliday, 1966).

Greenhouse experiments have demonstrated that addition of fly ash to soil tends to increase boron levels as well as pH and soil salinity (Page et al., 1979). Boron is of special concern in soil because of the relatively small range between levels causing deficiency and toxicity symptoms in plants (Philipson, 1953). Page et al. (1979) found that for some crop species a yield improvement occurred in ash-amended calcareous soil when ash was added up to 8% by weight, but this improvement was reduced in ash-amended acid soil. This yield reduction can be attributed to the difference in soil pH since the dissolution of B is increased by lowering the pH of an aqueous fly ash suspension from 12.3 to 6.0 (Phung et al., 1979).

Readsorption of dissolved B occurred in an ash suspension at its original pH of 12.3 (Elseewi et al., 1981). Since the B adsorption by Fe and Al oxides at this pH is very small (Sims and Bingham, 1968; Keren and Gast, 1983), the adsorption of B by these oxides as suggested by Elseewi et al. (1980), cannot account for the adsorption of B by fly ash.

The objective of this study is to determine the effect of particle size, pH and $\text{Ca}(\text{OH})_2$ presence on B dissolution and adsorption by fly ash in aqueous media.

Materials and Methods

The fly ash used was obtained from the Hadera M.D. Power Station (Hadera, Israel) and was derived from an English coal. Details of the main elemental composition and mineralogy of this ash sample are given in Table 1.

The fly ash particles were separated into different size fractions (using a zig-zag air classifier) and were used for dissolution and adsorption studies as described below.

Boron and calcium dissolution from fly ash were studied in suspension by shaking 6g ash in 50 ml polypropylene centrifuge tubes containing 30 ml solution at various compositions. Distilled water was used for the systems at natural pH and the pH was adjusted by adding 1.0 M HCl. At predetermined time intervals the fly ash suspensions were centrifuged, filtered through a Whatman No.42 paper and the filtrate analyzed for B, Ca and pH.

Boron adsorption by fly ash was studied in suspension by shaking fly ash in solution at a solution to solid ratio of 5 (as used for the dissolution study). The fly ash was washed prior to boron addition in order to remove most of the boron which is associated initially with the solid phase. The ash was washed by sequential neutralization with dilute HCl at a suspension pH of 6.5 until there was no further change in B and Ca concentration from one washing to the next. The washed

ash was dried at 40°C and solution of either NaCl or CaCl₂ was added at appropriate amounts to form a final solution having an ionic strength of 0.15 M. Suspension pH was adjusted prior to boron addition with NaOH, Ca(OH)₂ or HCl until there was no pH change after 24 hours of shaking. Boron was added to the suspensions making an initial concentration of 0.925 mmol.L⁻¹ and then the suspensions were shaken, centrifuged and filtered as detailed above.

All solution extracts were analyzed for pH using an El Hama pH meter, Ca by EDTA titration (USDA, 1954), Na and K by flame photometer, Cl by chloridometer, Al, Fe, Mg and Si by a Perkin Elmer 460 flame, atomic, absorption spectrophotometer and B colorimetrically using Azomethine-H (Gupta and Stewart, 1975).

Calculations

Ion pair concentration of CaOH⁺ was calculated using the equilibrium constant for their formation (Lindsay, 1979) and the extended Debye Huckel equation (Stumm and Morgan, 1970).

Results and Discussion

The relative amount of B in solution (the amount of B in solution over the total extractable B in fly ash) as a function of pH is given in Fig. 1. The solubility of B in water was greatly influenced by the equilibrium pH of the fly ash suspension, being extremely low at pH 12. However, as the equilibrium pH decreased, B solubility was greatly increased. A similar pH effect on trace element solubility was reported by Phung et al. (1979). Comparison of 24 hour and 4 day extractions indicates that an equilibrium was established at less than 24 hours.

The results also indicate that the extractability of B from alkaline fly ash is pH dependent. For example, at pH 9, only 60 percent of the B was removed after 3 extractions, whereas at pH 6 100 percent was removed after 2 extractions. At this pH, about 85 percent of the extractable B in fly ash was removed from the solid phase at the first extraction and the rest (15 percent) was removed at the second extraction.

Since soil pH is among the more important chemical properties governing the availability of B to plants (Keren and Bingham, 1985), adding fly ash (alkaline) to acid soils may elevate the B concentration in soil solution to levels above the toxicity threshold of B for plants. However, to alkaline soil (at the same clay content and clay mineral composition) higher rates of fly ash can be used.

Element composition of fly ash - water extracts is given in Table 2. It is evident that the dissolution of some of the elements is pH dependent. For example, the Ca and B concentrations increase about 4 and 100 times, respectively, when the pH is decreased from 12.5 to 7.0. It is also evident that the dominant cation in solution is Ca^{2+} which is mainly balanced by OH^- anions (Table 3). The Ca in fly ash primarily exists in the form of calcium oxide. Thus, when the fly ash interacts with water, the following reaction may occur:

The dissolution rate of Ca from fly ash at pH 12 is relatively fast (Table 3). The maximum ^{Ca²⁺} concentration was obtained at 4h of shaking

and from then a decrease in concentration was observed. The ion activity products (IAP) are also presented in Table 3. It is evident that the solution is supersaturated with respect to Ca^{2+} and OH^- ions at their maximum concentration (between 1 to 24 hours) and becomes undersaturated with time. This may indicate that low soluble precipitates of Ca other than $\text{Ca}(\text{OH})_2$ are present in the system.

B and Ca concentrations in neutralized fly ash-water extracts as function of particle size are given in Table 4. Whereas, Ca was present in all 8 particle size fractions, B was concentrated in the smaller size fractions and only a small amount was dissolved from particles $>20 \mu\text{m}$ diameter. The contribution of the largest particles to B concentration in solution was very small even after crushing the particles to a size range smaller than $10 \mu\text{m}$ (Table 4). These results indicate that the small particles are the important ones as far as B is concerned especially since about 70 percent of the particles are in the clay and silt size range.

The B concentration (on solid basis) which is released from the solid phase of a bulk fly ash into solution after 24h is 7.9 mol.kg^{-1} . By knowing the fraction of each particle size range and its contribution of B concentration in solution after 24h interaction, it is possible to calculate the total B concentration in solution of a bulk fly ash suspension. The calculated value is 6.6 mol.kg^{-1} which is close to the experimental result (7.9 mol.kg^{-1}).

The effect of pH on B adsorption by washed ash at two different solution compositions ($\text{NaCl} + \text{NaOH}$ and $\text{CaCl}_2 + \text{Ca}(\text{OH})_2$) is given in Fig. 2. Although the results indicate that the B adsorption at pH 7

is independent of solution composition (Ca^{2+} vs. Na^+), a great *difference* was observed in the alkaline range. B adsorption decreases with increasing pH in the NaCl + NaOH system whereas B adsorption increases in the CaCl_2 + $\text{Ca}(\text{OH})_2$ system.

The decrease in B adsorption by the NaCl + NaOH system can be explained as follows: Boric acid acts as a Lewis acid due to its electron configuration:

The first hydrolysis constant, K_h is 5.8×10^{-10} at 20°C (Owen, 1934) and the other K_h values are 5×10^{-13} and 5×10^{-14} (Kanopik and Leherl, 1949). These constants indicate that the main B species in solution at the studied pH range are $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$.

It was found that fly ash contains the minerals mullite, hematite and maghemite as well as amorphous material such as Fe and Al oxides (Table 1, Grossman, 1983). The edges of these minerals contain ions not fully coordinated by structural oxygens which make possible discrete sites capable of specific interaction with the adsorbate species. Hydroxyl groups in the coordination sphere of the adsorbate may act as bridging ligands between adsorbate and adjacent surface groups. Thus boron can be specifically adsorbed by fly ash through a mechanism referred to as ligand exchange, whereby the adsorbed species displace OH^- (or H_2O) from the surface. Such specific adsorption can occur theoretically for any species capable of coordination with the surface metal ions. A possible complex configuration for B with

surface Al is given in Fig. 3 (as suggested by Keren and Bingham, 1985). The increase in pH results in an enhanced OH^- concentration relative to B and as a result of the increased OH^- competition, B adsorption decreases rapidly.

Although B adsorption decreases when the pH increases in the presence of $\text{NaCl} + \text{NaOH}$, the opposite is true when $\text{CaCl}_2 + \text{Ca(OH)}_2$ is present and the amount of sorbed B increases with pH at least up to pH 12. At this pH 80 percent of the total B in the system was sorbed by the fly ash - Ca(OH)_2 complex. It is important to note that the amount of added Ca(OH)_2 at the highest pH, was about the same as the removal of base during the washing of fly ash. These results suggest that the high capacity of the complex to sorb B is connected with the presence of Ca(OH)_2 . This conclusion is supported by the fact that B adsorption by ash at pH 7 is independent of solution composition ($\text{NaCl} + \text{NaOH}$ vs. $\text{CaCl}_2 + \text{Ca(OH)}_2$), since at this pH no Ca precipitation occurs. It was found that B was not sorbed by an aqueous suspension of Ca(OH)_2 in the absence of fly ash. There are therefore two possibilities on how the B interacts with the fly ash - Ca(OH)_2 complex: 1) B is co-precipitated with Ca(OH)_2 or some other low soluble solid phase of Ca on to the fly ash surface, and 2) ion pairs containing B and Ca react with the fly ash surface at pH 12. However, it is difficult at this stage to attribute any mechanism to Ca(OH)_2 - B interaction.

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Table 1: Main elemental composition and mineralogy of fly ash^{*}

Compound	Total percent	Mineral form
SiO ₂	50.4	Quartz malite
Al ₂ O ₃	36.8	
Fe ₂ O ₃	5.6	Hematite, Magnetite
CaO	6.7	Free lime

30 percent amorphous glass

^{*} Grossman, 1983

Table 2: Element compositio of fly ash - water extracts after 24 hours of shaking at two pHs.

Element	Solution concentration	
	mmol.L ⁻¹	
	pH 12.5	pH 7.0
Ca	22.5	100
Mg	0	17
Al	<0.1	<0.1
Fe	<0.001	<0.001
Si	<0.1	1.8
Na	1.1	2.0
K	0.4	-
Cl	<0.1	1.9
B	0.02	1.9

Table 3: The effect of time on the concentration of Ca and Oh ion species present in fly ash-water extracts.

Equilibrating time -h-	pH	Free OH ⁻ mmol.L ⁻¹	Free Ca ²⁺ mmol.L ⁻¹	CaOH ⁺ mmol.L ⁻¹	IAP [*] 10 ⁶ mol ³ .L ⁻³
0.2	12.44	34	15	5	5.2
0.5	12.44	34	16	5	5.6
1.0	12.44	34	18	5	6.2
4.0	12.50	40	17	6	8.2
24	12.48	38	17	5	7.4
96	12.38	29	11	3	3.3
290	12.23	20	9	2	1.4

* Ion Activity Product, $IAP = (Ca^{2+})(OH^{-})^2 M^3 = 6.3 \times 10^{-6} mol^3.L^{-3}$.

Table 4: The effect of fly ash particle size on the concentration of B and Ca in neutralized fly ash-water extracts after 24 hours of shaking.

Particle size -um-	Mass fraction percent	pH	Ca mmol.L ⁻¹	B mmol.Kg ⁻¹
<3	1.7	6.5	41	6.3
3-8	24.7	7.4	65	11.5
8-15	29.6	8.4	93	9.2
15-20	16.1	8.1	95	4.4
20-45	14.3	8.5	103	1.3
45-120	13.5	6.8	93	0.4
45-120 [*]		8.8	110	0.6
Bulk		7.1	105	7.9

* 45-120 um particles crushed to <10 um.

Fig 1 Effect of pH on the B solubility and extractability in fly ash

Fig 2 - Effect of pH on the sorption of B by 'washed' ash where the pH is adjusted by NaOH or $\text{Ca}(\text{OH})_2$ in an ash to water ratio of one to five

Boric acid

Borate ion

SEPARATION AND IDENTIFICATION
OF COMPOUNDS IN FLY ASH

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Description of the cooperation in meeting the original objectives

1. Israel is expected to get about 3.4 million metric tons of coal annually from four different countries. It is expected that, depending on its source, the composition of the coals will vary. The first objective will be to make a comprehensive mineralogical and chemical analysis of fly ashes of different coals.
2. To study the chemical stability and the rate of dissolution of various constituents, especially B, Mo, and Se in fly ash.
3. To study the interaction of fly ash with calcareous smectitic-vermiculitic sandy soils of Israel. Based on this study, the beneficial as well as the detrimental effects of fly ash on these soils can be evaluated.
4. To conduct laboratory studies on the long term application of fly ash and irrigation on the mobilities of B, Mo and Se.

The original objectives were mostly met. The first objective was dealt with by the American group. A comprehensive mineralogical and chemical analysis was made of a fly ash derived from a western U.S. coal.

Total elemental analysis was determined in three ashes from different western U.S. coals and total Se analyzed in ashes from five different U.S. coals.

The other three objectives were dealt with by the Israeli group on a fly ash derived from an English coal which was burnt in the Hadera power station (Israel). These objectives were defined in other terms written in the introduction to the report by the Israeli group. In the third objective three soils were studied ranging in texture from loamy sand to clay soil. The different soil textures were chosen because of the different effect on each soil expected from fly ash which consists mainly of silt size particles.

Benefit to Agriculture

A major problem with coal-fired power plants is that of disposing of large quantities of solid waste (mainly fly ash) for which there is only a limited use.

This project investigated using fly ash to improve certain properties of agricultural soils. A range of soil texture was studied from loamy sand to clay soils. In the former, water retentivity is low and therefore crop growth requires frequent irrigation with a resulting high drainage and waste of water. In the latter case, infiltration rate (IR) and hydraulic conductivity (HC) are low and often less than irrigation or rain intensity. This leads to run-off of water over the soil surface causing soil erosion and also wasting water.

It was shown that by mixing up to 10% fly ash with the loamy sand soil, the soil's HC was lowered leading to less water drained away. By mixing up to 10% fly ash with the clay soil, the soil's HC was increased and maintained which should result in greater infiltration of water and a lower rate of run-off. Crust formation on the soil surface was not prevented by adding fly ash and therefore application of phosphogypsum to fly ash-amended clay soil would be necessary to maintain permeability in the soil surface (Agassi et al., 1982). The energy cost of initially mixing fly ash with the clay soil in the field should be offset in the following seasons by the increased workability of the ash-amended clay soil.

By amending the clay soil with large particles of ash instead of bulk ash, an improvement in HC was maintained with the release of negligible concentration of B and Mo into solution. Although the solution pH was high (above 11), this project demonstrated its reduction due to the precipitation of low soluble Ca salts. Further work is necessary to investigate the use of this reaction in non-shaking conditions (in the field).

In the case where only bulk ash is available for amendment, careful water

management in the field would probably avoid any adverse effects to crops. An initial leaching of amended soils with 4-6 pore volumes of water could leach out the soluble Mo prior to crop growth. A significant amount of B would probably also be leached out if a means of reducing the high pH was found.