University of Alberta

Characterization of Precipitation Products from Reaction of Phosphogypsum Leachate with Calcareous Subsoil

by

Laila Poulsen ©

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Master of Science

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for my wonderful brother John

ABSTRACT

A sequential batch experiment was conducted in which 10 successive treatments of acidic process water (PW) from a phosphogypsum (PG) repository were reacted with 23 homogeneous samples of a calcareous soil. pH, redox, electrical conductivity (EC), and total soluble F were monitored in PW leachates during the experiment. Soils were analysed for selected properties and total elemental content in order to determine attenuation along the sequence. Through a variety of mechanisms, most elements of environmental concern in PW were attenuated by calcareous soil: soil may contain unacceptable concentrations of F, P, Cd and U as a result. With continued leaching, some elements may be remobilized. PW leachates may present a regulatory concern with respect to total dissolved solids and Se, but not F after reaction with calcareous subsoils. The findings of this laboratory analog of a PW leaching scenario have implications in the long-term decommissioning of PG waste repositories.

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I've been browsing through Shakespeare, trying to find some good quotes about soils. Well, you may not be surprised to hear there aren't many! Poor guy, didn't know what he was missing out on, did he? However, Macbeth did say, "The deed is done." I haven't slain many kings recently, but I do feel as though I've made a great leap from one of life's stepping stones to the next. And like Macbeth, there's no going back for me now. I wouldn't have gotten here without guidance and friendship from so many good people.

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CHAPTER I

INTRODUCTION

Phosphogyspum (PG) is an acidic, gypsum-based byproduct of the manufacture of phosphate fertilizer. In Alberta, 40 Mt of PG are stockpiled at four plant sites underlain by calcareous soils. Impurities associated with PG limit its potential uses and the waste product will likely remain stockpiled at plant sites indefinitely. Process water (PW) used to slurry PG to stockpiles is recycled and becomes extremely acidic (pH < 2) and highly concentrated with contaminants derived from the solid PG. During and after slurrying operations, PW infiltrating through the porous PG to clay materials and soils below could contaminate soils and groundwater.

The present research is a continuation of studies initiated by Arocena et al. (1995a) into attenuation of dissolved constituents in PW by soils. In repeated batch equilibrations of calcareous and noncalcareous soils with PW, these researchers found that two-thirds of total clays and 100% of expandable clays dissolved. Decreased clay content and associated decreases in surface area and cation exchange capacity of the PW-treated soils led to concerns about the effectiveness of clay liners as impermeable barriers to leaching below PG repositories. PW-soil interactions would occur with each slurrying operation at an active PG repository; at inactive sites infiltration of more benign leachates may impact soils when substantial atmospheric precipitation events occur.

The general objective of the present research is to develop information on the attenuation of environmentally sensitive elements originating from PW as PW interacts with and is neutralized by a typical Alberta calcareous soil. PW is known to contain trace elements, F, Fe, Si and Al at elevated concentrations. This project was intended to provide information about the form which potential contaminants acquire as soil minerals dissolve and combine with soluble constituents concentrated in PW. Specifically, the objective is to quantitatively and qualitatively identify precipitates and residual materials which form along a pH gradient as acidic PW is neutralized by calcareous soil.

CHAPTER II

LITERATURE REVIEW

A. Stockpiling of Phosphogypsum

The byproduct phosphogypsum (PG) results from manufacturing phosphate fertilizer from phosphate rock using the wet acidulation process. The wet acidulation process is used for over 90% of phosphate fertilizer production, and involves digestion of raw phosphate rock by sulfuric acid, as illustrated by the following simplified reaction (Becker 1989):

$$Ca_{10}(PO_4)_6F_2 + 10H_2SO_4 + 20H_2O \rightarrow 10CaSO_4 \bullet 2H_2O + 6H_3PO_4 + 2HF$$

For every tonne of phosphoric acid produced as P_2O_5, 4.5 to 5.5 tonnes of the byproduct PG results, and worldwide production of PG is expected to reach 280 Mt by the year 2000 (Ferguson 1988). About 28% of PG is dumped into water bodies, 14% is reprocessed and 58% is stockpiled (Carmichael 1988). Containing up to 96% gypsum ($CaSO_4$), PG can be used as a building material or as a soil amendment to alleviate aluminum toxicity in acidic soils, to replenish the nutrient status of highly weathered and calcareous soils, and to reclaim sodic soils (Rutherford et al. 1994). However, due to the large supply of gypsum relative to demand worldwide, coupled with concerns about the elevated concentrations of impurities in PG, this waste product will probably remain stockpiled indefinitely. As of 1980, over 300 Mt of PG were stockpiled in Florida in 17 stacks which averaged an area of 92 ha and ranged from 9 to 43 m in height (May and Sweeney 1984). Of the 64 Mt of PG stockpiled in Canada, 40 Mt are stockpiled in Alberta at four plant sites. The largest PG repository in Alberta covers an area of 160 ha.

B. Process Water

Stockpiling of PG involves the recycling of process water (PW) from a cooling/settling pond at the PG stack to the plant where it is repeatedly used for scrubbing fumes and for sluicing PG back out to the stack (Kennedy et al. 1991). Because of this continuous recycling, PW becomes highly acidic (pH 1.4-1.9) and enriched with contaminants released from the phosphate rock, including trace metals, fluoride, uranium, sulfate, phosphate, silica, iron and aluminum (Kennedy et al. 1991; Ball 1994; Arocena et al. 1995a).

Impurities exist in the solid PG, in PG pore water, and in the phosphoric acid product; however PW contains the highest concentrations of potentially toxic elements. Readers interested in environmental issues associated with the solid byproduct PG or PG pore water should refer to Rutherford et al. (1994). Interaction of acidic PW with soil and groundwater systems represents the worst case scenario where contamination from a PG repository is concerned. Such interactions would occur repeatedly with each sluicing operation over the lifetime of an active PG repository.

C. Acid-Induced Clay Mineral Weathering and Precipitation Processes

Natural and anthropogenic inputs of acidity to soils compromise soil mineral stability and advance weathering processes. Acid sulfate soils generate acidity through the oxidation of sulfide-bearing minerals such as pyrite (FeS_2) to H_2SO_4. Podzolic soils receive inputs of organic acids from the decomposition of coniferous forest litter. With time, acidic inputs are responsible for eluviation of Fe, Al, Si and humic material from surface horizons. Reprecipitation of dissolved constituents results in formation of the illuvial B horizon which may be enriched in humic material, organo-metallic complexes, allophanic and Fe-oxide coatings, either in combination or as distinct horizons. Anthropogenic acidic wastes stockpiled on soils create conditions which parallel pedogenic soil weathering processes. Warren (1991) and Warren and Dudas (1992a; 1992b) investigated mineral weathering adjacent to an elemental sulfur stockpile and described acid-induced selective dissolution of carbonates, Fe-containing primary minerals, chlorite, smectite and plagioclase feldspars in surface horizons. Selected trace elements were mobilized in the acidified zone. A subsurface indurated layer enriched in Fe formed which had characteristics similar to an ortstein (Bfc) horizon observed in Podzols.

D. Fluoride-Induced Clay Mineral Weathering and Precipitation Processes

Extremely acidic wastes advance soil mineral weathering processes but this phenomenon is intensified in the presence of fluoride. HF acid is commonly used alone or in conjunction with other acids to digest soil minerals for total elemental analysis (i.e. Jackson 1979; Warren et al. 1990). Dissolution of silicate and aluminosilicate minerals by the highly electronegative element fluoride (F) has been widely reported in the literature and is proposed by Arocena et al. (1995a) as the mechanism for dissolution of clays by PW. PW can contain as much as 1.34 % F by weight (Kennedy et al. 1991), or up to 12 000 mg L^{-1} (Becker 1989), depending upon the phosphate rock source. Arocena et al (1995a) found that 100% of expandable clays and two-thirds of total clays in calcareous and noncalcareous soil samples dissolved upon repeated batch equilibrations with PW.

A predominant sink mechanism for F in soils is the exchange of F^- for OH^- on the surface of amorphous solids such as Al and Fe hydroxides (Omueti and Jones 1977; Fluhler et al. 1982; Elrashidi and Lindsay 1987). In a study of mechanisms of reaction of neutral fluoride solution with layer silicates and oxides of soils, Huang and Jackson (1965) deduced that disruption of minerals occurred to form complex Al and Fe ions and release OH^- into solution. They suggested F ions bring structural Al^{3+} or Fe^{3+} ions into solution via the following equations:

$$Al(OH)_3 + 6MF \rightarrow M_3AlF_6 + 3MOH$$
$$Fe_2O_3 + 10MF + 3H_2O \rightarrow 2M_2FeF_5 + 6MOH$$

This is supported by a strong stoichiometric relationship between Al and Fe released into solution and OH released. Omueti and Jones (1977) found a significant correlation between adsorption capacity and amorphous Al concentration, and the shape of isotherm curves closely followed abundance of amorphous Al species. Fluhler et al. (1982) found significant positive correlations between oxalate extractable Fe and Al and F sorptive capacity. Peek and Volk (1985) demonstrated that F released Al and OH into solution from various phyllosilicate clays and amorphous Al oxyhydroxides, suggesting degradation of mineral structure.

There are a variety of studies of F-induced dissolution/precipitation. Fluorite (CaF_2), sellaite (MgF_2), NaAlF $\bullet 1.3H_2O$, $MgAlF_5 \bullet 2.7H_2O$, and $Fe(II)(Al,Fe(III))F_5 \bullet 3.7H_2O$ have been identified as precipitates in a study of F-induced weathering of silicate rock (Langmyhr and Kringstad 1966); hieratite (K_2SiF_6), ralstonite ($Na_{0.88}Mg_{0.88}Al1.12(F,OH)_6 \bullet H_2O$) and $NaUZrF_{12}$ precipitated from dolerite dissolved in HF-HNO_3-$HClO_4$ (Boer et al. 1993). These researchers observed that silica fluoride precipitates formed during the dissolution stage. Upon reaction of kaolinite with acid sodium fluoride solutions, Semmens and Meggy (1966a) identified precipitates of sodium fluorosilicate (Na_2SiF_6) and cryolite (Na_3AlF_6) which were not present in unreacted samples. Colloidal silica formed from sodium fluoride solutions as well as aqueous HF solutions reacted with kaolinite (Semmens and Meggy 1966a and 1966b). Irrigating soil with leachate containing 7 mg $F^- L^{-1}$, Tracy et al. (1984) found 75 - 85% of fluoride in leachate was adsorbed or precipitated by an unknown mechanism, after which 15 - 25% precipitated as CaF_2. From speciated data, Ball (1994) predicts CaF_2 to be the solubility controlling solid for F in noncalcareous soil-PW systems. Elrashidi and Lindsay (1986) suggest AlF_3 is the solubility controlling solid for F at low pH values. Ball (1994) proposes jarosite ($KFe_2(SO_4)(OH)_6$) and amorphous $Fe(OH)_3$ as solubility controlling solids for Fe; $Cd_3(PO_4)_2$ and $CdCO_3$ for Cd at low and high pH values respectively; and $(Cr_xFe_{(1-x)}(OH)_3$ for Cr at low pH. All the above precipitates could possibly form in the soil-PW system in the present study.

E. Process Water-Soil Clay Mineral Interactions

Expandable clays are commonly chosen for use as liners under waste repositories because they attenuate electrically charged elements, and they swell to form a physically impermeable layer. Such liners would be ineffective under PG waste repositories, however, if, as reported by Arocena et al. (1995a), reaction with PW causes complete dissolution of expandable clays. In an investigation of seepage at a PG repository, Smith (1987) reported failure of a natural clay liner and attributed it to HF acid attack on clay. In one area clay materials investigated were hard and brittle with loss of plasticity; red-brown gelatinous material was observed in other locations. Further sluicing operations were discontinued on the existing stack and a new extension was constructed which was lined with an acid-resistant, artificial membrane.

In Alberta and in selected locations elsewhere, PG repositories are underlain by calcareous parent material. During sluicing operations, acidic PW containing soluble, mobile constituents would leach through the porous PG to calcareous soils below. Initially dissolution of clay minerals would occur as PW reacted with soils. PW would become neutralized as it migrated through calcareous soils and PW-derived contaminants and dissolved clay mineral constituents would precipitate.

Thermodynamics can be used to predict mineral stability in weathering environments (Rai and Lindsay 1975); studies have shown that contaminant behaviour in PW systems is pH dependent (Murray and Lewis 1985; Ball 1994). Using $Ca(OH)_2$ to neutralize PW up to pH 10, Ball (1994) identified decreases in soluble F^-, SO_4^{2-}, PO_4^{3-}, Fe(III), U(VI), As(V), Cd^{2+}, Cr(III), Se(IV) and Se(VI) as precipitates formed along the pH gradient. In a study of suspended solids removed from PW ponds at four Florida sites, Kennedy et al. (1991) identified gypsum, alkalifluorosilicates ($NaSiF_6$, $NaKSiF_6$), chukhrovite ($Ca_4SO_4SiAlF_{13} \bullet nH_2O$), and the compound $Fe_3(NH_4,K,H)H_8(PO_4)_6 \bullet 6H_2O$, where the NH_4-N form was most common. An amorphous silica gel was identified in this study as well as by Arocena et al. (1995a). Frazier et al. (1977) investigated methods of precipitating fluoride compounds from PW and found that chukhrovite was preferentially formed under high Al conditions but F precipitation was suppressed when Mg concentrations were high. They suggested competitive reactions existed between Si and Al for F and between Mg, Na and Ca for fluoroaluminates and fluorosilicates.

It is important to gain fundamental knowledge of the precipitation mechanisms in soil-PW systems: with repeated PW-soil interactions following sluicing operations, zones concentrated with precipitates may exist below PG repositories. Not only may precipitation products pose environmental concerns if they are produced at elevated concentrations in soils, but it is also necessary to determine their long-term stability, and whether leachate passing through such zones could potentially threaten groundwater quality.

The study reported herein was designed to simulate a scenario in which PW has induced dissolution of clays and leachates containing the dissolved clay component have migrated through a calcareous soil which typifies that underlying PG repositories in Alberta. This study is intended to quantify selective attenuation of elements through precipitation and coprecipitation mechanisms. As decommissioning of phosphogypsum waste repositories in Alberta and elsewhere occurs, this information will be useful in predicting the long-term leaching potential of contaminants from PG waste repositories.

CHAPTER III

MATERIALS AND METHODS

A. Sample Collection

1. Process Water

Process water (PW) was collected as a slurry (approximately 1:4 solid:solution ratio) from a sluice pipe at a phosphogypsum repository near Redwater, Alberta. The slurry was allowed to settle and the PW was poured off and stored in plastic buckets at 25°C for two years. PW was passed through a Type GS 0.22 μm Millipore™ filter immediately prior to use in the present study. Table 3.1 describes characteristics for PW used in this study. pH and EC were measured by glass electrode and conductivity cell, respectively. Fluoride analyses were conducted by ion specific electrode Orion™ Model 96-09 using total ionic strength buffer (Larsen and Widdowson 1971) at a 1:10 buffer:sample ratio. Al, Ca, Fe, K, Mg, Na, and Si were analysed by atomic absorption spectroscopy. Phosphate was determined by Technicon Autoanalyser II™. Sulfate was determined by turbidometry (Clesceri et al. 1989). Table 3.2 includes trace element

Table 3.1. Electrical conductivity (EC), pH, and total concentration (mg L^{-1}) of selected elements in PW (revised from Arocena et al. 1995a).

Property	Process Water
EC (dS m^{-1})	9.0
pH (mol L^{-1})	1.4
Al	190
Ca	790
Fe	120
K	62
Mg	100
Na	490
Si	1400
F^-	6070
PO_4^{3-}	13700
SO_4^{2-}	9930

Table 3.2. Selected trace element concentrations (mg L^{-1}) in PW from the same sampling site as PW used for this study (revised from Ball 1994).

Element	Process Water
As	1.3
Cd	2.0
Cr	1.8
Cu	1.1
Mn	5.5
Ni	187
Pb	0.3
Se	0.7
U	3.5
Zn	5.7

concentrations in PW measured by inductively coupled plasma - atomic emission spectroscopy (ICP-AES) for PW sampled from the same site but at an earlier sampling date.

2. Soil

A soil was selected which would typify calcareous soils beneath PG repositories in Alberta, although this study is relevant anywhere where PG repositories are underlain by calcareous material. Soil samples were collected from the Ck horizon of an Orthic Grey Luvisol (Typic Cryoboralf) at Cooking Lake, Alberta. A profile description of this soil and the surrounding area can be found in Crown and Greenlee (1978). Table 3.3 provides selected soil characteristics.

Table 3.3. Selected characteristics of the Ck horizon of an Orthic Grey Luvisol collected at Cooking Lake, Alberta (modified from Luther et al. 1996).

Property	Ck horizon
pH (0.01 M $CaCl_2$)^z	7.6
pH (H_20)^y	7.7
Total C (g kg^{-1})^y	1.5
$CaCO_3$ equivalent (g kg^{-1})^y	75.6
Clay content (g kg^{-1})^y	270
Clay mineralogy^{xw} (%)	
Kaolinite	20 - 40
Mica	2 - 20
Montmorillonite	60 - 80

[z] Crown and Greenlee (1978)
[y] examined in the present study
[x] Arocena et al. (1995a)
[w] Estimated from x-ray diffractograms

B. Sequential Batch Procedure

Soil was air dried and sieved to 2 mm using a brass sieve. Thirty g samples of air dry soil were weighed into 250 ml plastic centrifuge bottles. The bottles served as the reaction vessels for the batch experiment. Soils were wetted using distilled water (DW) so that PW was not consumed in the batch experiment by being added to air dry soil. The batch experiment therefore simulated replacement of soil pore water with PW. Soils were centrifuged at 10°C for 15 minutes at 15 000 x *g* RCF and supernatant DW was discarded. Soils contained an average of 8.7 % H_2O by weight prior to use in the batch procedure.

Figure 3.1 (p. 12) gives a visual description of the experimental design of the batch procedure. The experiment was conducted in triplicate and included DW treatments as controls. PW was mixed with wet soil samples at a 1:5 ratio (30 g soil:150 ml PW). A milkshake mixer was used to break up soil clods and the soil plug formed on centrifugation. Slurries were periodically mixed over an 18 to 24 hour period until the pH of the supernatant was constant. Constant pH was used to determine when to pass leachates on to the next sample. Samples were centrifuged at 10°C for 15 minutes at 15 000 x *g* RCF and the supernatant was analyzed for pH (glass electrode), electrical conductivity (EC) (conductivity cell); redox (platinum electrode) and total fluoride (ion specific electrode). Fluoride analysis was conducted as described in Section A.1, p. 7. A maximum of 2 ml of supernatant was consumed for fluoride analysis. Supernatant PW was decanted into a fresh wet 30 g soil sample and reacted as above. The weight of supernatant transferred was recorded and a quantity of DW was added to maintain approximately a 1:5 solid:solution ratio. The quantity of DW added varied from 0 - 5 ml generally but was as high as 16.5 ml for the initial transfer from the first to second soil sample. Altogether, each of the 10 fresh PW samples was passed sequentially through the 23 subsamples of the calcareous soil. The 23 subsamples were intended to represent equivalent depth intervals of calcareous soil underlying a PG repository. The batch procedure was concluded when pH, fluoride and EC levels in supernatants remained constant over several sequential equilibrations, suggesting a steady state had been reached in the soil-PW system.

C. Soil Physical and Chemical Analyses

Wet soil samples were stored in plastic centrifuge bottles at -10°C for up to 8 months.

1. Particle Size Separation

Approximately 20 g air-dry bulk soil samples sieved to 2 mm (brass sieve) were washed repeatedly with deionized water until dispersed. Ultrasonification was not used for dispersion because the technique may destroy some precipitation products and coatings. Clay separation was achieved through successive dispersion and gravity sedimentation cycles (Jackson 1979). Sand and silt fractions were separated by wet sieving, oven-dried at 105 °C for 24 hours and weighed. Clay content was calculated by difference. Clays were further separated into coarse (0.2 - 2 μm) and fine (< 0.2 μm) fractions by centrifugation (Jackson 1979).

2. Elemental Analysis of Bulk Soils

Five g bulk samples were ground to pass through a 100 mesh sieve using a pestle and mortar. Powdered soil samples were digested and analysed for trace and major elements (Activation Laboratories Ltd., Ancaster, Ontario) using inductively coupled plasma - atomic emission spectroscopy (ICP-AES), instrumental neutron activation analyses (INAA), and fusion specific ion electrode (Table 3.4). Untreated soils were included to provide background concentrations.

3. Selected Chemical Analyses of Bulk Soils and Clays

Twenty g bulk soil samples were air-dried and sieved to 2 mm (brass sieve). pH was measured with a glass electrode in deionized H_2O using a 1:1 solid:solution ratio (McKeague 1978). Soil samples were also tested for the presence of amorphous clays by measuring pH (glass electrode) in 1M NaF (Fieldes and Perrott 1966). Inorganic carbon and total carbon in powdered soil samples were measured by titrimetric (Bundy and Bremner 1972) and Leco Carbon Determination (Tabatabai and Bremner 1970) methods, respectively. Carbonates were removed from powdered soil samples using Na-acetate-acetic acid treatment (McKeague 1978). Organic matter content was sufficiently low (TOC < 10 g kg^{-1}; Table 3.3) that its removal was not considered necessary. Powdered soil samples were tested for the presence of alkali soluble Si and Al using boiling 0.5N NaOH (Hashimoto and Jackson 1960). Fine and coarse clay separates and powdered bulk soil samples were analysed for the presence of amorphous Fe, Al and Si using acid ammonium oxalate (McKeague and Day 1966) and dithionite-citrate-bicarbonate (DCB) (Mehra and Jackson 1960). Extracts were analysed for Si, Al and Fe using reduced molybdate (Weaver et al. 1968), catechol violet (Dougan and Wilson 1974; McAvoy et al. 1992) and flame atomic absorption spectroscopy (AAS), respectively. Cation exchange

Table 3.4. Techniques and detection limits for elemental analysis of bulk soils.

Element	Detection Limit (mg kg^{-1})	Element	Detection Limit (mg kg^{-1})
Ag^u	0.4	MnO^p	100
$Al_2O_3^p$	100	Mo^n	2
As^n	1	Na_2O^p	100
Au^n	0.002	Nd^n	0.1
Ba^u	1	Ni^u	1
Be^u	2	$P_2O_5^p$	100
Bi^u	5	Pb^u	5
Br^n	0.5	Rb^n	10
CaO^p	100	Sb^n	0.1
Cd^u	0.5	Sc^n	0.1
Ce^n	1	Se^n	0.5
Co^n	0.1	SiO_2^p	100
Cr^n	0.5	Sm^n	0.01
Cs^n	0.2	Sr^u	1
Cu^u	1	Ta^n	0.3
Eu^n	0.05	Tb^n	0.1
$Fe_2O_3^p$	100	Th^n	0.1
F^v	0.5	TiO_2^p	100
Hf^n	0.2	U^n	0.1
Hg^n	1	V^u	1
Ir^n	0.001	W^n	1
K_2O^p	100	Yb^n	0.05
La^n	0.1	Y^u	1
Lu^n	0.01	Zn^u	1
MgO^p	100	Zr^u	1

^{n}Instrumental Neutron Activation Analysis
^{p}Fusion Inductively Coupled Plasma Emission
^{u}Total Digestion Inductively Coupled Plasma Emission
^{v}Fusion Specific Ion Electrode

capacity (CEC) of powdered bulk soil samples and clay separates was measured at pH 3.5 and 9.5 after extraction by DCB as a further test for precipitates displaying amphoteric behaviour (Aomine and Jackson 1959). Surface area of clays was determined using adsorption of ethylene glycol monoethyl ether (Carter et al. 1965; Dudas and Pawluk 1982).

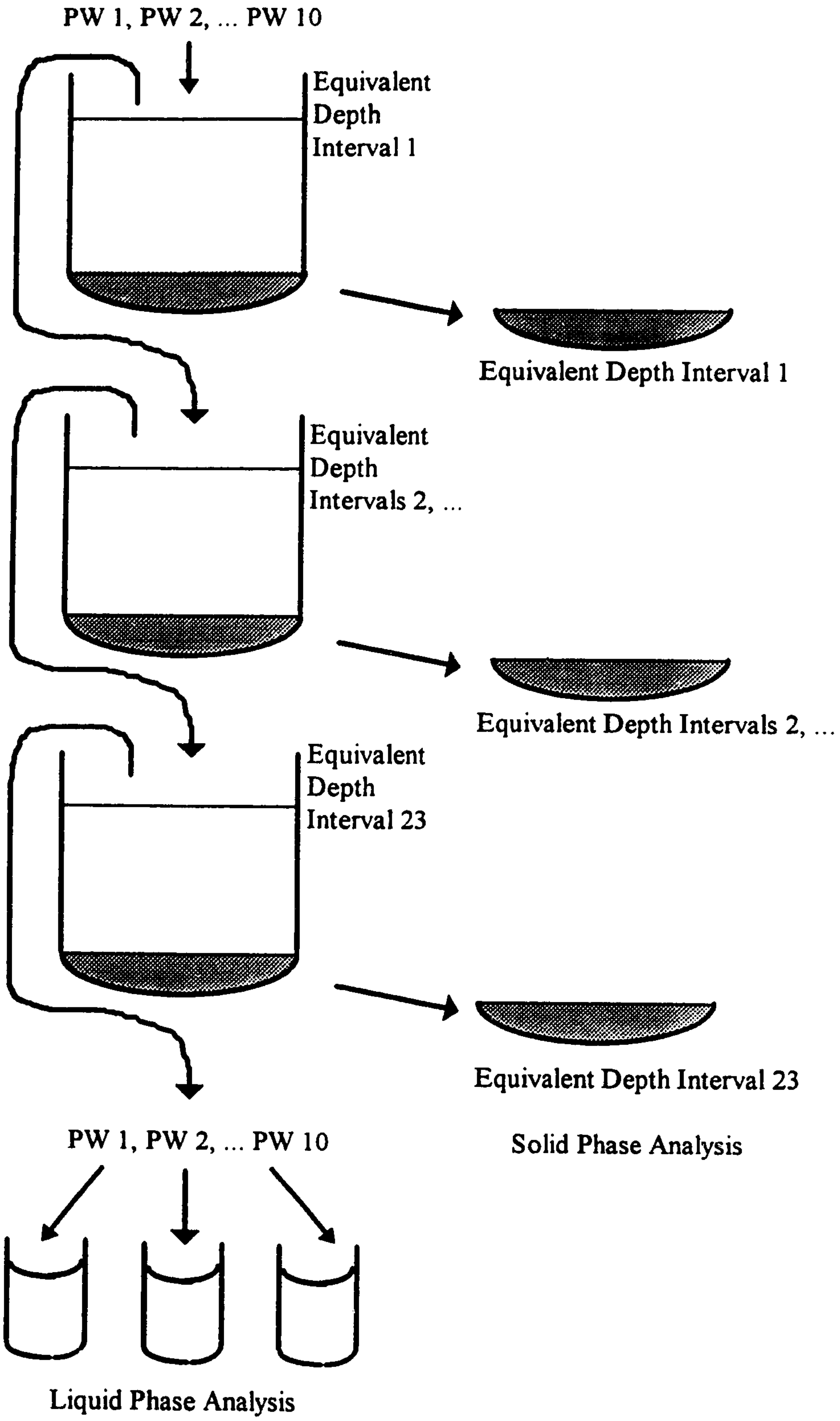

Figure 3.1. Design of sequential batch procedure.

CHAPTER IV

RESULTS AND DISCUSSION

A. Solution Chemistry

In the following section, results of solution analyses obtained during the batch procedure will be presented and discussed. pH, EC, redox and F were monitored in leachates as the batch procedure progressed. Complete solution analyses were not performed and thus a complete discussion of solution chemistry is not possible. Readers interested in solution phase analyses for PG leachates should refer to Luther et al. (1996). This section provides a backdrop to solid phase analyses presented in sections B and C.

1. pH

During the batch procedure, pH was monitored after each 18 - 24 hour equilibration period, prior to the leachate being decanted into the next soil sample in the sequence. At pH 1.4 (Table 3.1), PW is below Canadian Maximum Allowable Concentrations (CMAC) for drinking water by at least 5 orders of magnitude (Health and Welfare Canada 1993). pH is important as it provides information on the equilibrium status of the soil-PW system. The activity of many elements in solution, including trace metals , sulfate, phosphate and fluoride, decreases with increasing pH; thus mobility of contaminants can be roughly inferred from pH measurements. Also, the presence of solubility controlling solids can be predicted using thermodynamic constants and pH measurements. In order to understand pH of the solutions in this system, a discussion of the role of carbonates in influencing soil solution pH must be considered. $CaCO_3$ dissolves in acidic solutions, according to the following reactions:

$$\begin{array}{lcl} CaCO_{3(s)} + 2H^+ & \leftrightarrow & Ca^{2+} + CO_{2(g)} + H_2O \\ CO_{2(g)} + H_2O & \leftrightarrow & H_2CO_3{}^0{}_{(aq)} \\ \hline CaCO_{3(s)} + 2H^+ & \leftrightarrow & H_2CO_3{}^0{}_{(aq)} + Ca^{2+} \end{array} \qquad (1)$$

Initially, dissolution of carbonates consumes H^+, raising solution pH (equation 1). Basic pH promotes dissociation of the weak acid, H_2CO_3. Factors which control a soil's buffering capacity include amount of incoming acidity, initial soil carbonate content, soluble (Ca^{2+}), and partial pressure of $CO_{2(g)}$ (equation 1).

Figure 4.1 shows pH of the 10 PW treatments over the sequence of 23 depth intervals. All PW leachates follow the same trend of decreasing acidity throughout the sequence. The first PW treatment, designated PW 1, reached pH 7.7 by the 16th depth interval. Acidity in PW 1 was exhausted by reaction with carbonates but by the 16th depth interval pH of leachates was controlled by carbonate equilibria. PW leachates 2 through 10 retained pH values below 2 after reaction with the initial depth interval, indicating that carbonate content was exhausted in the initial depth interval after reaction with PW 1. Loss of carbonates was visibly evident by the presence of bubbles, as $CO_{2(g)}$ was evolved initially upon reaction of PW 1 with calcareous depth intervals 1 and 2 (equation 1). Theoretical considerations indicate that one 150 mL PW treatment at pH 1.4 (Table 3.1) should contribute 6.0 me (+) to the calcareous soil; a 30-g calcareous soil sample with $CaCO_3$ content of 75.6 g kg^{-1} (Table 3.3) should have 45 me (-) to counteract acidity. Thus 10 fresh PW treatments would input 60 me (+), enough to exhaust the carbonates present in depth interval 1 only. This is consistent with pH values reported in Fig. 4.1, as all PW leachates increased in pH after depth interval 1. PW 2 reached pH values near PW 1 by the 23rd depth interval. pH of PW 3 and 4 increased steadily throughout the sequence. $CaCO_3$ in soils further along the sequence may control pH of initial PW leachates. PW leachates 5 through 10 leveled off near pH 5.5 by depth interval 16. This suggests $CaCO_3$ did not control pH after equilibrium conditions developed in the soil-PW system. Using chemical equilibria models based on thermodynamic constants, Ball (1994) and Kennedy et al. (1991) have independently shown that PW is at equilibrium or oversaturated with respect to gypsum ($CaSO_4$) and fluorite (CaF_2). Addition of PW to the calcareous soil raised the activity of Ca, SO_4, PO_4, Si and F in particular (Table 3.1). Over the pH range described in the present study, solubility controlling solids would have formed in place of or in conjunction with calcite. A more extensive discussion of mineral stability in the present study can be found in Sections B and C.

PW leachates in the present study leveled off near pH 5.5 (Fig. 4.1). This is an order of magnitude below CMAC for drinking water (Health and Welfare Canada 1993), and at least two orders of magnitude more acidic than pH of pore water would be if controlled by $CaCO_3$ in the absence of PW.

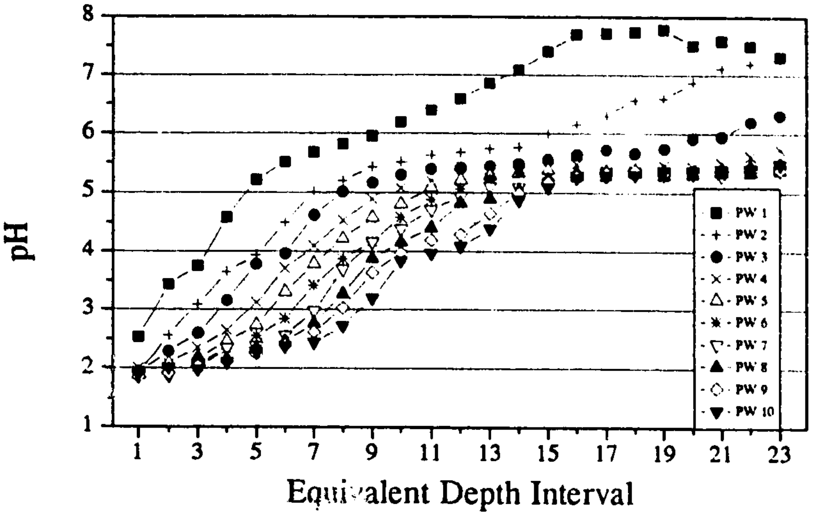

Fig. 4.1. pH of 10 process water (PW) leachates.

DW batch experiments were undertaken to simulate leaching conditions in calcareous soils in the absence of PW leachates, and provide information about equilibrium conditions in soil-DW systems for comparison purposes. Figure 4.2 shows pH values of

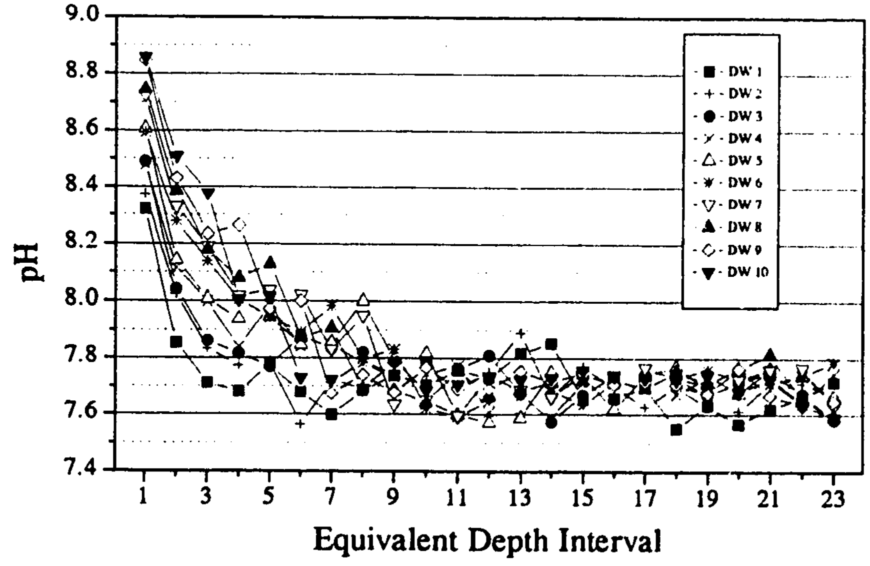

Fig. 4.2. pH of 10 distilled water (DW) leachates.

DW treatments passed through the 23 calcareous soil samples. pH of DW treatments followed the opposite trend from PW treatments. Leachates became slightly more acidic as they were passed through the soil sequence. DW 1 decreased from pH 8.3 in the first equilibration to near 7.7 in the 23rd equilibration. Subsequent leachates followed a similar trend until DW 10 dropped from pH 8.8 - 8.9 to near pH 7.7. Initially, pH in DW would be elevated due to minor accumulation of soluble salts. As leachates containing soluble carbonates were passed through the sequence, pH steadily decreased until solutions reached a steadv state typical of the soil-carbonate system. The pH at which this occurs is predictably above pH 7.5 but depends upon the partial pressure of $CO_{2(g)}$ in the system (Lindsay 1979). Fig. 4.2 shows that in the soil-DW batch experiment, a steady state was reached at pH 7.7; all leachates leveled off near pH 7.7 from the 12th to the 23rd depth interval. This is consistent with the pH value measured for the untreated calcareous soil in water (1:1 ratio; Table 3.3). Figure 4.1 shows that the initial PW leachate was buffered to pH 7.7; in Figure 4.3 pH values of the first and tenth PW and DW treatments are combined for comparison purposes. Distinct pH outcomes for DW treatments and 1 PW treatment versus 10 PW treatments are evident, again suggesting the presence of solubility

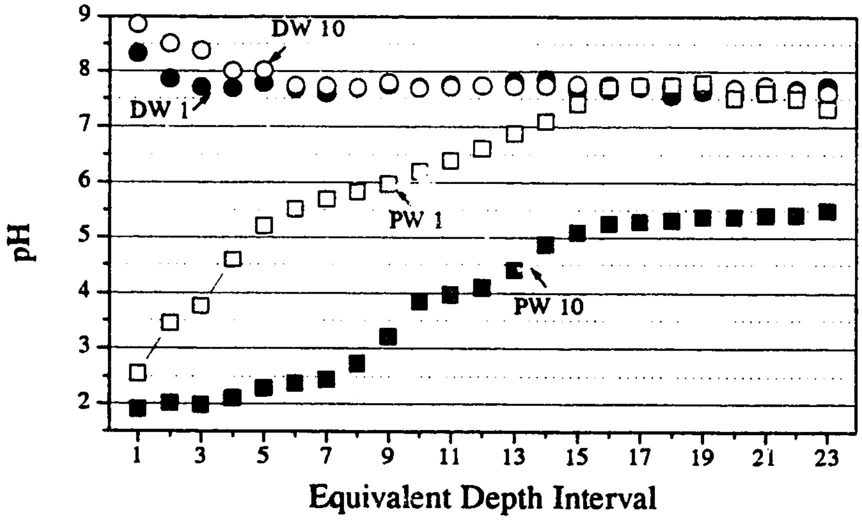

Fig. 4.3. pH in leachates 1 and 10 for process water (PW) and distilled water (DW) treatments.

controlling solids other than calcite developed in the PW-soil system after a steady state had been reached.

2. Redox

During the batch procedure, redox was monitored after each 18 - 24 hour equilibration period, prior to leachate being decanted into the next soil sample in the sequence. Redox was not monitored in the control experiment. Redox describes oxidation and reduction reactions in soils, and can be expressed in terms of activity of electrons in a system. Redox is an important consideration when describing the mobility of species such as Fe, Mn and Cr for which more than one oxidation state is possible. Soils are subject to spatial variability in redox conditions although reduced conditions are normally considered dominant because of the influence of aerobic respiration processes by plants and soil organisms which release electrons. Lower redox equilibria are expected in saturated soils such as those in the present study. Figure 4.4 shows redox values in millivolts for the 10 PW leachates passed through 23 equivalent depth intervals of calcareous soil. All 10 PW leachates followed a similar trend; initially redox potential

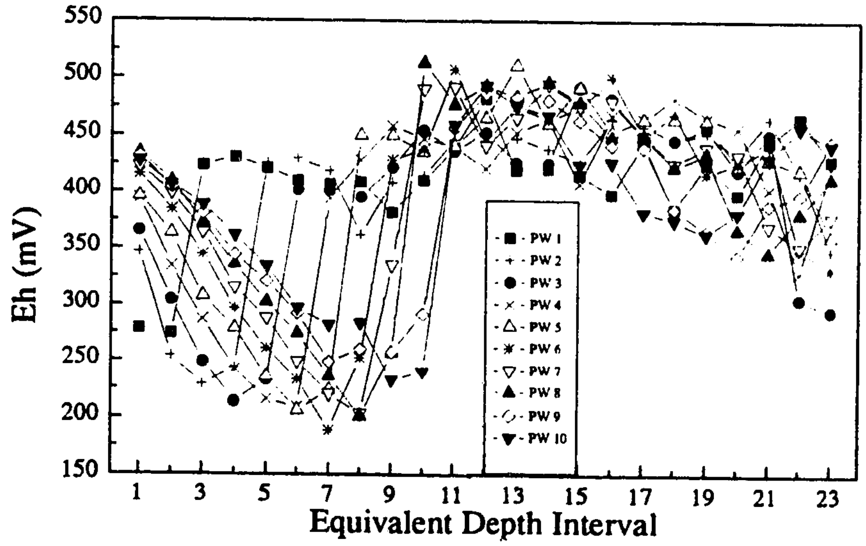

Fig. 4.4. Redox potential (mV) for 10 PW treatments reacted sequentially with 23 equivalent depth intervals of calcareous soil.

decreased, then rose sharply and leveled off before developing a decreasing trend throughout the latter half of the soil sequence.

Redox status of the soil samples can be more clearly explained by converting raw Eh values to *pe*, where *pe* refers to the negative log of electron activity, according to the following relationship (Lindsay 1979):

$$\text{Eh (millivolts)} = 59.2\,pe$$

Figures 4.5 and 4.6 show *pe*-pH relationships for selected PW leachates. All PW samples fell within the normal range for soils between $pe + \text{pH} = 2$ to $pe + \text{pH} = 18$. As PW leachates were successively passed through the soil sequence, they partitioned into two distinct groups with respect to redox potential. Group 1 consisted of those leachates in the early portion of the sequence which demonstrated a constant $pe + \text{pH}$ value near 8.0, while Group 2 consisted of those in the later part of the sequence which demonstrated a constant $pe + \text{pH}$ value near 12.5 (Fig. 4.7). As the experiment progressed and more leachates were passed through the sequence, redox potential of leachates gradually shifted from Group 2 to Group 1 (Figs. 4.5 and 4.6). This trend reflects the expected decline in oxidizing conditions as soils were exposed to continuous leaching. By the time PW 10 had been passed through the sequence, the first 10 equivalent depth intervals had partitioned into Group 1, while depth intervals 11 through 23 remained in Group 2 (Fig. 4.7). Selected soil properties and elemental analyses described in Sections B and C of this chapter confirm that soils along the sequence partitioned into two general groups. Lindsay (1979) suggests many redox-associated mineral transformations in soils occur at fixed $pe + \text{pH}$ values. The development of fixed $pe + \text{pH}$ parameters suggests the soil-PW system had reached equilibrium with respect to redox by the conclusion of the batch procedure. The role of redox with respect to behaviour of specific elements will be further discussed in Section C of this chapter.

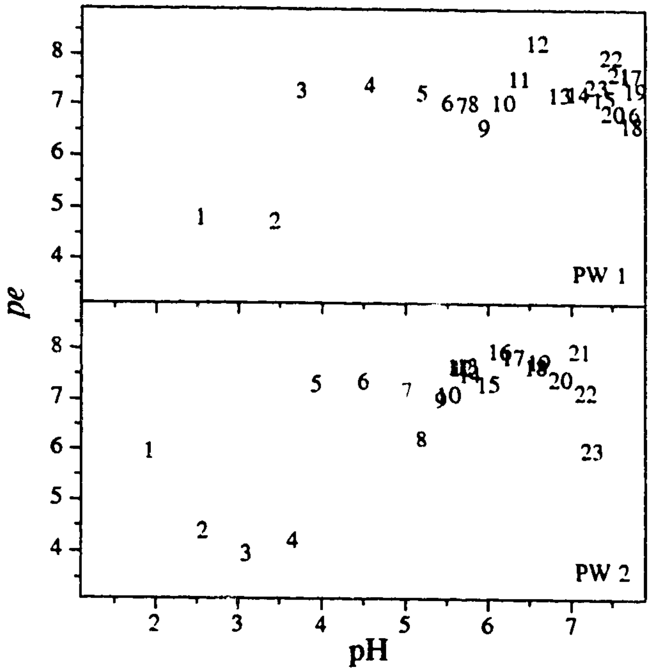

Fig. 4.5. *pe*-pH diagrams for PW treatments 1 and 2.

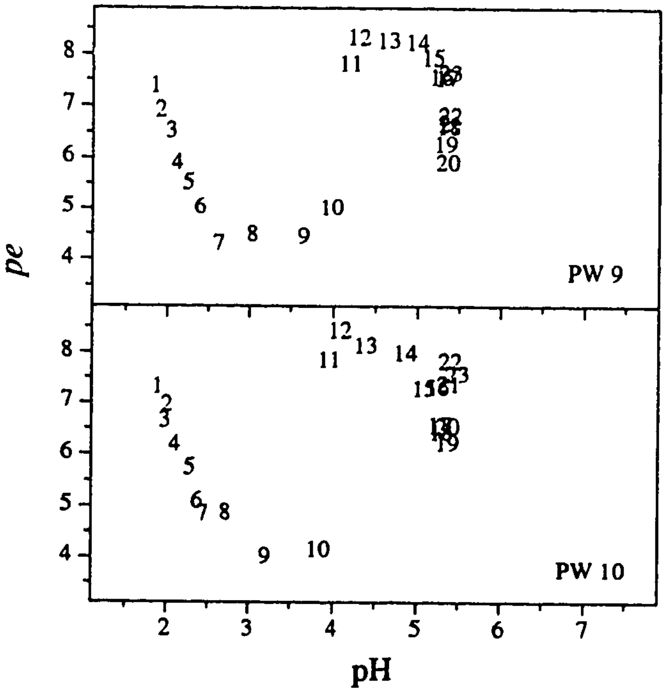

Fig. 4.6. *pe*-pH diagrams for PW treatments 9 and 10.

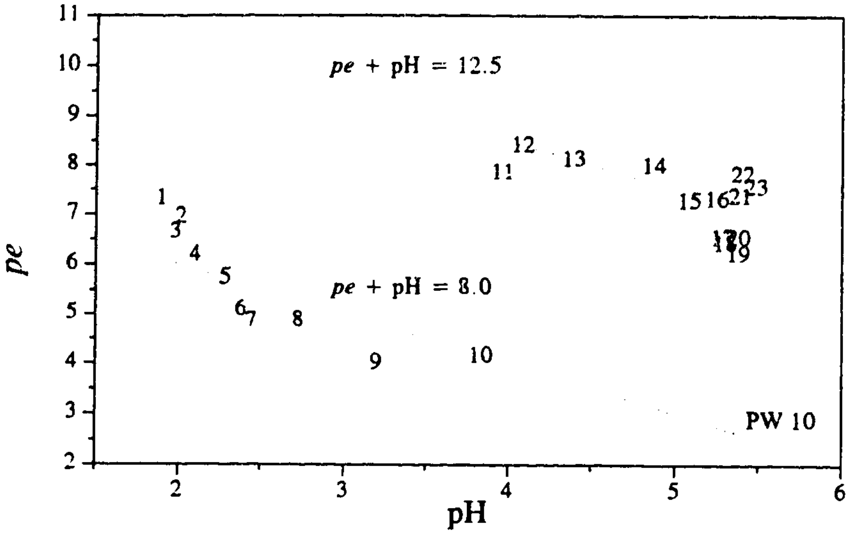

Fig. 4.7. *pe*-pH diagram of PW 10 with standard *pe* + pH parameters of 8.0 and 12.5.

3. Electrical Conductivity

During the batch procedure, electrical conductivity (EC) was monitored after each 18 - 24 hour equilibration period, prior to PW leachate being decanted into the next depth interval in the sequence. Electrical conductivity of soil solutions provides an estimate of their ionic strength using the following empirical relationship (Griffin and Jurinak 1973):

$$I\ (\text{mol L}^{-1}) \cong 0.013 \times \text{EC}\ (\text{dS m}^{-1})$$

Ionic strength can in turn be used to estimate activity of soluble species. Total dissolved solids (TDS) can be approximated from EC using the following (Rhoades 1982):

$$\text{TDS}\ (\text{mg L}^{-1}) \cong 640 \times \text{EC}\ (\text{dS m}^{-1})$$

Estimates of ionic strength and TDS from EC are based on data collected from solutions equilibrated with noncontaminated soils. Values calculated for PW leachates are therefore subject to error and should be considered as rough approximations only. Figures 4.8 and 4.9 show EC measurements for the 10 PW and DW leachates reacted sequentially with 23 equivalent depth intervals of calcareous soil respectively.

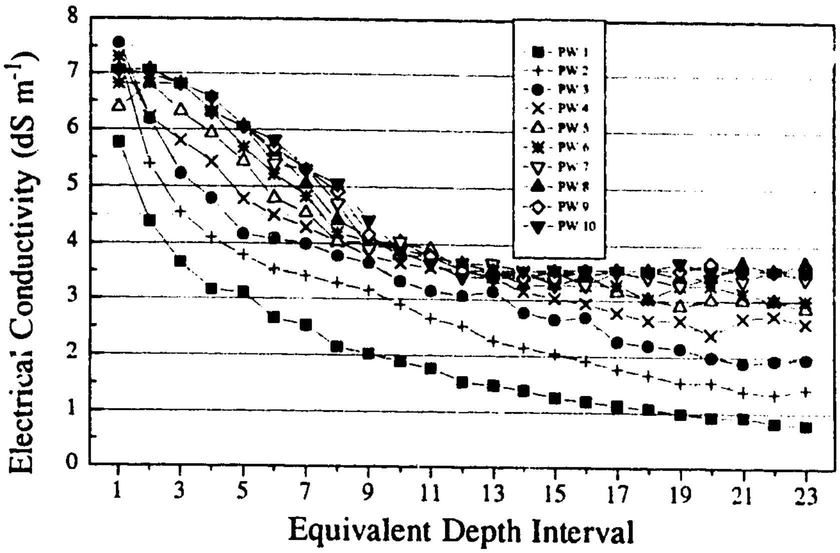

Fig. 4.8. Electrical conductivity (dS m^{-1}) for 10 PW leachates.

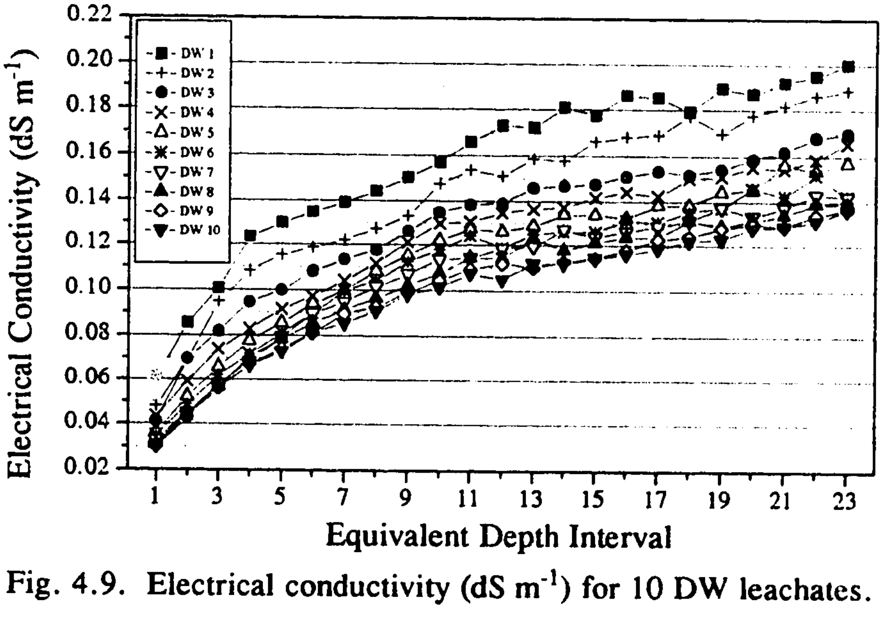

Fig. 4.9. Electrical conductivity (dS m^{-1}) for 10 DW leachates.

EC in all PW treatments decreased steadily as PW was equilibrated with the 23 depth intervals in the sequence, reflecting precipitation and adsorption processes which removed soluble constituents from PW leachates (Fig. 4.8). Leachate treatments early in the sequence (i.e. PW 1) decreased more than later leachates (i.e. from 5.7-0.7 dS m^{-1} in PW 1 and from 7.0-3.5 dS m^{-1} in PW 10). PW leachates 8-10 leveled off at 3.5 dS m^{-1} in depth intervals 13-23. An EC value of 3.5 dS m^{-1} corresponds to a TDS value of approximately 2200 mg L^{-1}, in excess of CMAC for drinking water at 500 mg L^{-1} (Health and Welfare Canada 1993). EC in PW 1 declined below 1 dS m^{-1}, and fell within acceptable TDS guidelines for drinking water in Canada. Thus although calcareous soils reduced the activity of ions in solution generally to within acceptable limits for the initial leachate, continued PW leaching resulted in a steady state condition in which activity of ions was elevated above acceptable levels.

EC in the DW experiment followed the opposite trend to the PW batch experiment, increasing steadily as DW leachates were reacted with the series of depth intervals of calcareous soil but still remaining one to two orders of magnitude below corresponding PW treatments (Fig. 4.9). Increases in EC with continued DW leaching occurred due to the continued dissolution of salts as calcareous soils were equilibrated with the dilute leachate. However, this resulted in a maximum increase in EC of only 0.14 dS m^{-1} over the sequence of 23 depth intervals for DW 1, a negligible change compared with that incurred by PW (Fig. 4.8). Repeated equilibration of soils with DW caused dispersion of fine clays which were decanted from one soil to the next and may have contributed to increasing EC values. The overall change in EC in the DW experiment decreased as the batch procedure progressed. This may have been due to a decreasing supply of soluble salts with continued leaching of DW, suggesting the system was approaching equilibrium. However, EC continued to increase slightly throughout the experiment and did not level off as in the case of the PW experiment. This may have been due to loading of fine clays and soluble salts as solutions were passed from one depth interval to the next. Equilibrium conditions are suggested by the observation that pH leveled off at 7.7 by the end of the DW experiment (Fig. 4.2).

Decreasing EC from 9.0 dS m^{-1} in fresh PW to 3.5 dS m^{-1} in final PW leachates suggests that soluble salts precipitated throughout the batch procedure until EC reached a constant value at depth interval 13. By calculating decrease in EC each time leachate was passed from one depth interval to the next, and using the approximation for TDS from EC provided by Rhoades (1982), the mass of salts precipitated in each depth interval can be roughly approximated. Figure 4.10 provides the results of these calculations.

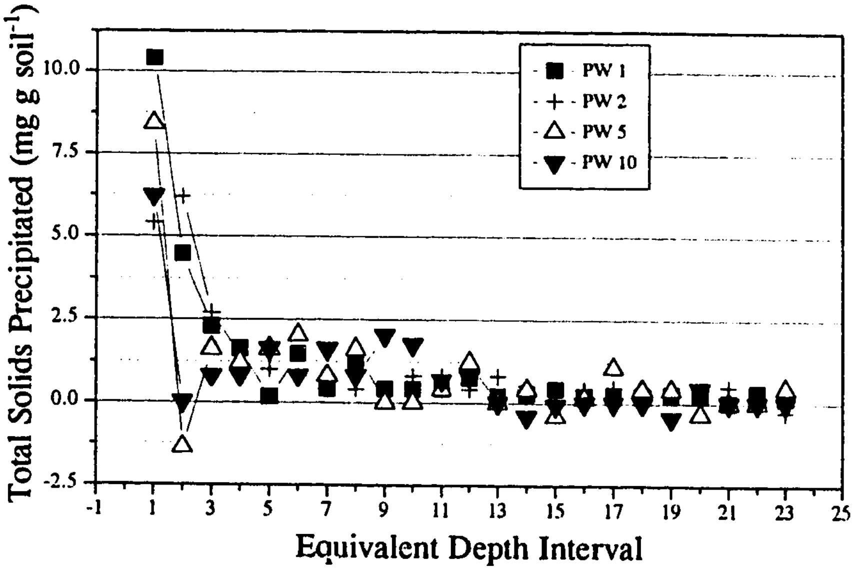

Fig. 4.10. Total solids precipitated from selected PW leachates. Values approximated from EC measurements.

Fig. 4.10 shows that initial depth intervals received most inputs of solids and solids continued to precipitate in depth intervals 3 through 9. In subsequent depth intervals solid inputs leveled off near zero. By the 5th equilibration with PW however, solids were no longer input in depth interval 2 and dissolution of some precipitates may have occurred when PW 5 was equilibrated with depth interval 2, indicated by the negative value reported for this leachate. The data reported in Fig. 4.10 show that as continued leaching took place, some salts may have been reintroduced to leachates, suggesting instability of some precipitation products. It should be emphasized however that the TDS values reported in Fig. 4.10 are rough approximations and should be interpreted in terms of trends only.

Constant EC measurements toward the end of the PW batch experiment indicate a steady state condition also developed in the PW-soil system. This is consistent with observations made with respect to pH (Fig. 4.1). By the end of the batch procedure, sorption sites may have become exhausted after several equilibrations with fresh PW. If stable precipitation products formed which were in equilibrium with soluble species, further sorption would not occur and EC would remain constant. Higher concentrations of soluble salts would be expected to be maintained in the presence of a relatively soluble controlling solid such as gypsum ($K_{sp} = 10^{-5}$) compared to calcite ($K_{sp} = 10^{-9}$). High EC in soil solutions correspond to high ionic strength (Griffin and Jurinak 1973). Dissolution is favored in conditions of high ionic strength because increased interferences among ions reduce their activity and promote undersaturation with respect to solubility controlling solids. Davies (1962) developed the following empirical relationship between ionic strength and activity of ions in solution:

$$\log_{10} \gamma_i = -A * z_i^2 * [((\sqrt{I})/(1 + \sqrt{I})) - 0.3 * I]$$

where γ_i = activity coefficient for the ion i; A = 0.511; z_i = valence of the ion i; and I = ionic strength in mol L^{-1}. Using the Davies equation and assuming a constant EC of 3.5 dS m^{-1}, activity coefficients of 0.466 and 0.826 can be calculated for divalent and monovalent ions respectively. Activity coefficients can be multiplied by the known concentration of an element to express the activity of an ion in solution. While these coefficients are indirectly derived from empirical equations and consequently are subject to error, it is nevertheless important to note that activities of divalent ions such as Ca^{2+} and SO_4^{2-} would be reduced to approximately half their concentration in PW leachates at the end of the batch experiment. This reduced activity enables twice the concentration of soluble, mobile ions to be present in solution than would be expressed using K_{sp} values, and assuming predicted values would be equivalent to measured concentrations. Conditions of high ionic strength interfere with sorption processes which may attenuate major and trace elements of environmental concern. High ionic strength and the corresponding elevated amounts of soluble, mobile ions would be maintained in soil solution as long as PW leaching continued. If dilute leachates such as rainwater subsequently infiltrated through the system, activity of ions in solution would initially increase as ionic strength decreased and precipitation would occur until activity of ions in solution reached equilibrium with the solid phase. Further leaching of dilute solutions would then promote dissolution as conditions became undersaturated with respect to the solid phase. Results shown in Fig. 4.10 suggest this may have occurred in some leachates toward the end of the batch procedure in the present study. Potential contaminants such as F and SO_4 below PG repositories may become remobilized during and after slurrying operations involving PW had ceased. With continued influence of dilute leachates the solid phase would eventually adjust to an equilibrium condition with the solution phase, and EC values would approach those measured in the DW experiment.

4. Total Soluble Fluoride

During the batch procedure, total soluble F was monitored after each 18 - 24 hour equilibration period, prior to PW leachate being decanted into the next depth interval in the sequence. Fluoride is regulated in drinking water in Canada at 1.5 mg L^{-1} (Health and Welfare Canada 1993); F mobility is of great concern in the present study as concentrations in PW are elevated to 6070 mg L^{-1} (Table 3.1). DW leachate had no detectable F concentrations and was not monitored in the control experiment.

Fig. 4.11 shows the results of F analysis for PW leachates. Although the detection limit for F analysis was 0.02 mg L^{-1}, a maximum of 2 ml of PW leachate was consumed for F analysis in order to preserve leachate. With dilution, this resulted in an effective detection limit for the batch procedure of $50 * 0.02$ mg L^{-1} = 0.5 mg L^{-1}. Decline in F concentrations was rapid and consistent as PW was passed through the calcareous soil sequence. Steep decreases at the beginning of the sequence are consistent with increasing total solids precipitated (Fig. 4.10) and increasing clay content (Section 4B), suggesting the formation of F-containing precipitates. F concentrations in PW 1 and 2 were reduced to 3400 and 4500 mg L^{-1} respectively upon the initial equilibration with calcareous soil; however subsequent PW treatments showed little change in F concentrations upon reaction with depth interval 1, indicating that sorption mechanisms for F were exhausted in the initial soil after two equilibrations with PW. This is consistent with the observation that pH was also not buffered by the initial soil after 2 equilibrations with PW (Fig. 4.1). However, as PW was passed through the sequence, F concentrations in all PW solutions fell below detection by the 16th equivalent depth interval (Fig. 4.11). Selected PW leachates monitored at the end of the batch procedure without dilution were consistently below 1 mg L^{-1}. Thus F concentrations in all PW leachates were within the CMAC of 1.5 mg L^{-1} after equilibrating with 23 depth intervals of calcareous soil. This is in contrast with other studies in which PG leachates were equilibrated with solid PG or with soils and F concentrations were consistently maintained above drinking water guidelines (Ball 1994; Rutherford et al. 1995; Luther et al. 1996).

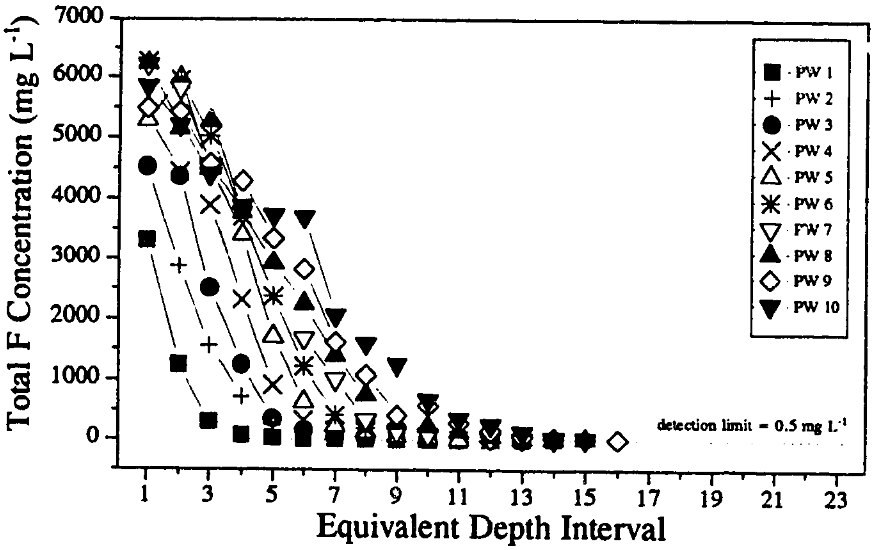

Fig. 4.11. Mean total soluble F concentrations in 10 PW leachates.

Although soluble F in PW leachates was reduced to acceptable limits in the present study, the possibility of redissolution of F precipitates and subsequent F mobility may be a concern for reasons related to ionic strength, as discussed previously in Section 3.

Luther et al. (1996) provide a thorough review of attenuation processes for F. Precipitation is a major mechanism for F attenuation in soil-PW systems. Murray and

Lewis (1985) found that F solubility is pH-dependent, with most F precipitating as CaF_2 by pH 4.5 in a pure PW-carbonate system. Using a geochemical model, Ball (1994) predicted CaF_2 controlled F solubility above pH 3.6 in a neutralization experiment which utilized PW similar to that in the present study. Aluminum complexes with F were hypothesized to control F at lower pH values. In the present study F concentrations were probably reduced below detection limits primarily due to attenuation by Al; sources of Al would be from PW and from F attack on aluminosilicate clays. Luther et al. (1996) reported CaF_2 and fluorapatite ($Ca_5(PO_4)_3F$) were oversaturated in PG-derived leachates equilibrated with calcareous and noncalcareous soils respectively; however clay mineral dissolution was minimal in their study. Kennedy et al. (1991) modeled PW from various sources and determined acidic PW (< pH 2) was consistently oversaturated with respect to CaF_2, chukhrovite ($Ca_4SO_4AlSiF_{13} \cdot 10H_20$) and alkali fluorosilicates (Na_2SiF_6 and K_2SiF_6). These latter minerals may control F solubility below pH 3.5 in the present study. A further discussion of F-containing minerals is included in Section C.

5. Summary

Solution pH was not neutralized beyond pH 5.5 although a steady state appeared to be reached at that pH value by depth interval 15. pH of a carbonate-controlled system would be expected to be higher. Redox was within the normal range for soils and a steady state condition with respect to redox was also achieved by the end of the batch procedure. EC values declined from approximately 9 to 3.5 dS m^{-1}, leveling off near depth interval 13. Except for the initial PW leachate, EC values translated to a TDS value above the accepted drinking water guidelines in Canada (Health and Welfare Canada 1993). Examination of solids removed from leachates suggests some precipitation products were unstable and redissolved with continued leaching. A steady state soil-PW system in which high ionic strengths are maintained may result in dissolution and mobility of elements as leachates eventually become more dilute. Sequential reaction of PW with calcareous soils effectively reduced fluoride concentrations to below detection limits in all PW leachates, probably through precipitation with Al. Reduced F concentrations were consistent with decreases in EC.

B. Physical, Chemical and Mineralogical Properties

1. Particle Size Distribution

Sand and silt sized fractions from the C horizon of this Cooking Lake soil developed on glacial till are dominated by the primary minerals quartz, Na/Ca-feldspars and K-feldspars (Pawluk 1961). Arocena et al. (1995a) determined the clay sized fraction was dominated by smectite, followed by kaolinite and a small amount of mica. The clay mineral composition reported by Arocena et al. (1995a) was consistent with clay mineralogy of soils formed on the plains region of Alberta (Dudas and Pawluk 1982). Organic matter content is negligible in the soil used for the present study; thus the clay sized fraction dominated by smectites provides virtually all the surface area for ion exchange and other sorption processes. Alterations to the amount and kind of minerals in the clay sized fraction of PW-treated soils would influence the soil's sorptive capacity. Predictions about the mobility of contaminants below PG repositories may be in error if only the clay characteristics of the original subsurface soil material are considered.

Fig. 4.12 gives a graphical representation of clay content for selected depth intervals. Table 4.1 shows particle size distribution and corresponding texture classes for

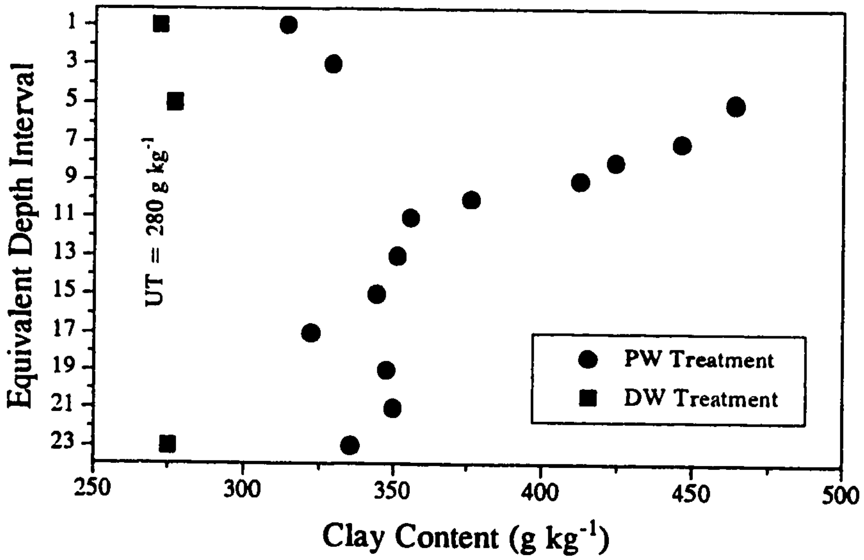

Fig. 4.12. Clay content in selected equivalent depth intervals treated with PW and DW. Clay content for an untreated (UT) sample is shown as a dotted line.

selected equivalent depth intervals treated with PW and DW, and for untreated (UT) samples.

Table 4.1. Mean particle size distribution (n = 3) of selected equivalent depth intervals of calcareous soil sequentially reacted with 10 PW treatments. Untreated (UT) samples and selected control samples treated with DW only (c1, c5 and c23) are also shown.

Equivalent Depth Interval	Mean Sand (>50 µm) (g kg^{-1})	±	Mean Silt (50-2 µm) (g kg^{-1})	±	Mean Clay (< 2 µm) (g kg^{-1})	±	Texture Class[†]
1	375	16.6	308	5.46	314	12.4	CL
3	346	22.8	324	17.5	329	24.1	CL
5	294	6.15	242	0.570	464	5.64	C
7	298	6.27	255	3.28	446	9.53	C
8	279	20.4	296	14.7	424	6.20	C
9	314	2.32	273	6.12	412	8.31	C
10	329	21.6	295	11.5	376	33.1	CL
11	348	0.750	296	3.11	356	3.76	CL
13	338	14.3	311	14.5	351	1.62	CL
15	345	5.91	311	19.5	344	14.4	CL
17	351	10.6	326	22.7	322	12.8	CL
19	365	3.18	287	5.99	348	7.93	CL
21	338	19.5	312	6.00	350	17.2	CL
23	357	5.90	307	14.1	336	9.55	CL
UT[‡]	381	0.150	338	16.6	280	16.7	L/CL
c1	391	12.1	337	14.2	272	25.9	L/CL
c5	380	4.20	343	2.78	277	3.81	L/CL
c23	382	4.80	343	10.9	275	15.3	L/CL

[†] CL = clay loam; C = clay; L/CL = borderline between loam and clay loam (Agriculture Canada Expert Committee on Soil Survey, 1987).

[‡] Two replicates only.

Clay content increased in PW treated samples from a low of 314 g kg^{-1} in the first depth interval to a maximum of 464 g kg^{-1} in depth interval 5. Clay content was highest in depth intervals 5, 7, 9 and 10, with corresponding texture classes changing to clay from clay loam earlier in the sequence (Table 4.1). Enrichment of the clay-sized fraction is consistent with decreases in EC (Fig. 4.8) and soluble F concentrations (Fig. 4.11). Absolute sand and silt content was consistent throughout the sequence; changes in sand and silt content expressed as percentages (Table 4.1) probably reflected masking by increased clay content and were not an indication of dissolution of sand- and silt-sized particles. Dominated by quartz and feldspars (Pawluk 1961), the sand- and silt-sized fractions in soils used in the present study would be expected to be relatively stable compared to minerals in the clay-sized fraction. Arocena et al. (1995a) reported complete dissolution of smectites and preferential dissolution of kaolinite compared to mica in the clay sized fraction of soils treated with PW. They hypothesized that preferential dissolution of smectites was due to the availability of interlayer area and overall high surface area, providing sites for F attack. Minerals in the sand- and silt-sized fractions would have the least surface area on which to provide opportunities for F attack. There was no alteration in the particle size distribution induced by DW treatments, indicated by the similar particle size distribution in DW-treated and UT samples.

There was a slight increase in clay content from 272-280 g kg^{-1} in UT and DW-treated samples to 314 g kg^{-1} in depth interval 1. This is in contrast with Arocena et al. (1995a) who reported 2/3 less clay in PW-treated samples versus DW-treated samples. The study by Arocena et al. (1995a) was designed to focus on dissolution reactions and not on precipitation products which is the focus of this study. Overestimation of clay content in depth interval 1 might result from losses in sand and silt fractions since the amount of clay was determined by difference. However, there was visible evidence of mineral dissolution in depth interval 1 during the batch procedure; as soils were repeatedly treated with fresh PW, samples became less aggregated and soil clods did not readily form after centrifugation. It is more likely that underestimation of clay in UT and DW-treated samples is responsible for the discrepancy. Carbonate-free samples of soils from the Ck horizon at the same site as the present study have been previously reported to have clay contents of 34 % (Crown and Greenlee 1973) and 330 g kg^{-1} (Arocena et al. 1995a). Table 4.1 shows 272-280 g kg^{-1} clay for UT and DW-treated soils in the present study. Different methods were used for particle size analysis; in the present study bulk soils containing the carbonates were washed repeatedly with DW for dispersion because the ultrasonic dispersion technique used by Arocena et al. (1995a) may have destroyed precipitation products and coatings which formed in PW treated samples. Repeated washing of samples for dispersion may fail to completely dislodge fine clays attached to silt and sand sized particles, and the presence of carbonates may contribute to incomplete dispersion, resulting in overestimation of sand and silt. During batch experiments, it was observed that poor dispersion was more of a problem in DW treated and UT than in PW treated samples.

Coarse/Fine (c/f) clay ratios show that precipitation products contributed mostly to the fine (< 0.2 μm) clay size fraction and occurred mainly in depth intervals 5, 7, 8 and 9 (Fig. 4.13). C/F ratios decreased until depth interval 7 and then rose to a plateau from depth interval 9 to 23. Although c/f ratios were not determined for depth intervals 11 through 22, total clay content was relatively constant in those samples (322-355 g kg^{-1}; Table 4.1) and it was assumed that c/f ratios were also constant. PW treated depth intervals had lower c/f ratios than DW treated and UT samples. This could be caused by poor dispersion due to carbonates in UT and DW treated samples as previously discussed. Also, precipitates in PW treated samples formed primarily in the fine clay fraction; a comparison of total clay content (Fig. 4.12) and c/f ratios (Fig. 4.13) for PW treated depth intervals shows that they are negatively correlated.

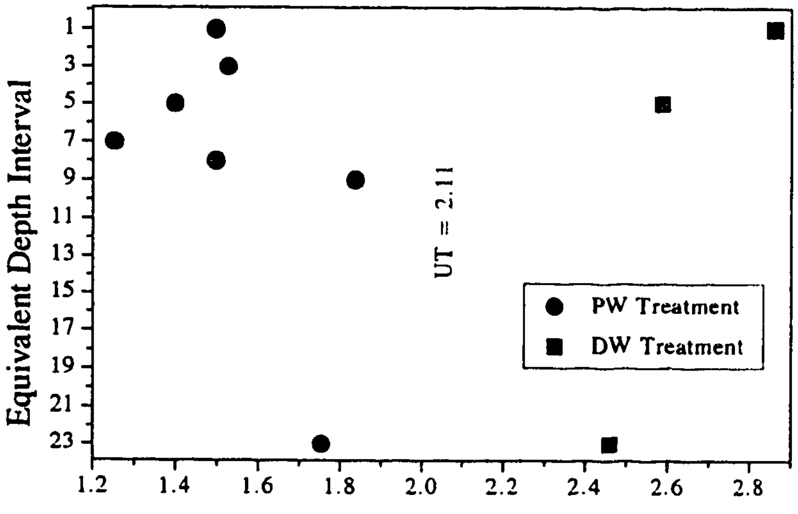

Fig. 4.13. Ratio of coarse clay to fine clay for selected equivalent depth intervals. Untreated (UT) samples are included as a dotted line.

Although enrichment of contaminants in the fine clay fraction was not directly determined in the present study, it is a strong possibility based on the analysis of clay content presented here. Enrichment of trace and rare earth elements has been reported in fine (< 20 µm) size fractions of solid PG compared to bulk soils and shale (Arocena et al. 1995b). Several authors have reported enrichment of trace and rare earth elements in soil clays, attributed not to differences in source clay minerals but to chemical weathering processes (i.e. Xing and Dudas, 1993; Duddy 1980; Cullers 1975). The fine clay fraction of unreacted soil in the present study is dominated by smectites (Arocena et al. 1995a) and would have a large surface area on which sorption mechanisms such as ion substitution and formation of co-precipitates with PW constituents could take place. Considering the short (18-24 hour) equilibration times used in the present study, PW constituents which precipitated as pure mineral phases may not have had time for crystal growth beyond the nucleation stage. Trace quantities of some of the contaminants may limit crystallization of coarse sized precipitates (Arocena et al. 1995b).

Enrichment of contaminants in the fine clay fraction is important because these contaminants may not have to be soluble to be mobile. In a review of colloid-facilitated contaminant transport, Nepfumbada (1995) states that five types of colloids (< 10 µm) could interact with metal contaminants and either mobilize or immobilize them: clay colloids, oxides and hydroxides of iron, aluminum and silica, other mineral colloids and precipitated colloids that form when a supersaturated aqueous phase exists. All of the above phases are possible in the system currently under study. Pedogenic studies have shown clay particles less than 0.2 µm in size are preferentially translocated within a soil solum (Pawluk 1961; McKeague and St. Arnaud 1969). Transport of colloidal particles may widen the zone of contaminant enrichment below PG repositories and impact groundwater quality.

2. pH of Solid Phase

Figure 4.14 shows pH values for selected equivalent depth intervals. The trend corresponds with that of solution pH reported in Section A.1. pH gradually increased with equivalent depth interval until it stabilized around 6.5 after the 15th interval. DW-treated and UT samples had constant pHs between 7.8 - 8.0 throughout the experiment. Under the conditions of this experiment, constituents within PW counteracted the buffering capability of calcareous soils even after 23 equilibrations. Further discussion of solid phases controlling pH in this system is in Section A.1.

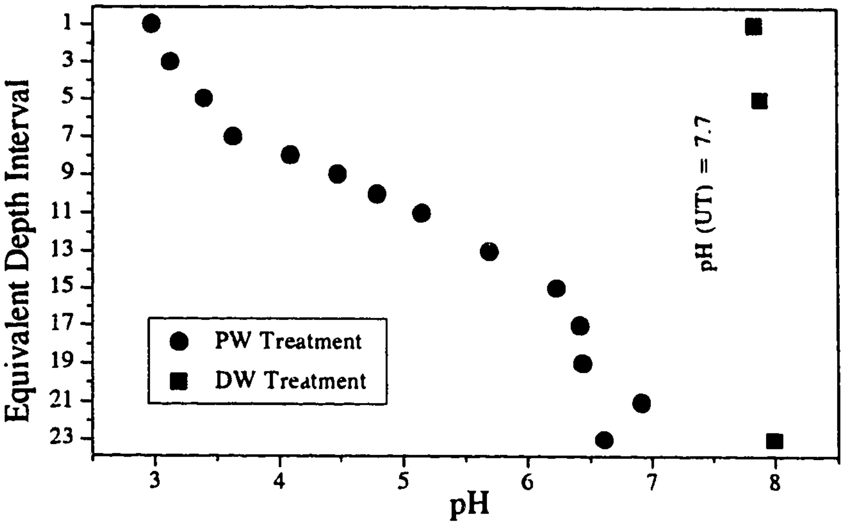

Fig. 4.14. pH of selected equivalent depth intervals sequentially reacted with PW and DW treatments. Untreated (UT) sample is included as a dotted line.

3. pH in NaF

Fig. 4.15 shows results of pH measured in 1N NaF. This test was designed to analyse for the presence of allophane in soils (Fieldes and Perrott 1966), based on the theory that F would replace surface OH groups in allophane and the resulting increase in soluble (OH) could be detected by measuring pH. Fig. 4.15 shows a jump in pH of PW-treated depth intervals from approximately 8 to 9.4 after depth interval 9. Fieldes and Perrott reported soils known to contain allophane gave high pH values between 9.4 and 10.4 in NaF. DW treatments and UT samples displayed pH values of 10 and above, due to the presence of free carbonates which would react with with NaF to produce Na_2CO_3. The NaF test in the present study probably did not reflect the presence of allophane; based on analyses of total and inorganic carbon (Section B.4), it is more likely that that the rise in pH observed after the 9th depth interval was due to carbonates. Competition by F for soluble Al probably prevented the formation of allophane.

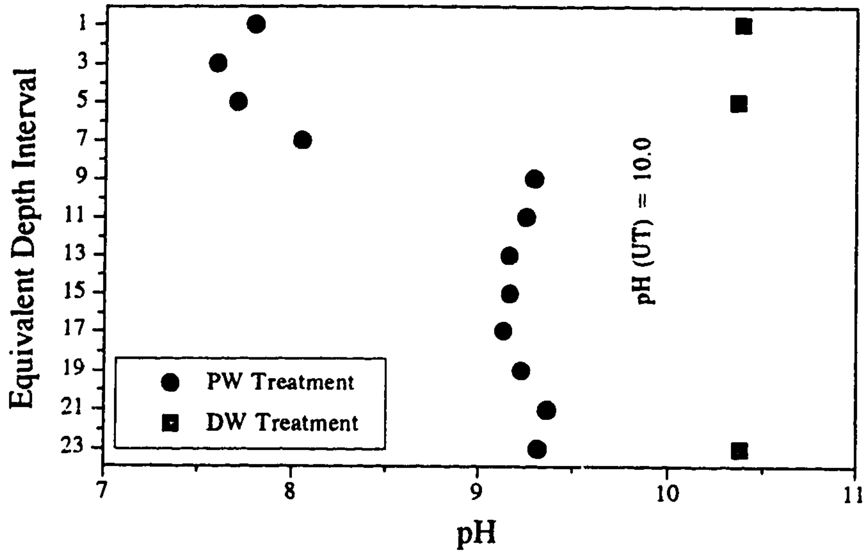

Fig. 4.15. pH in NaF for selected equivalent depth intervals. Untreated (UT) sample is included as a dotted line.

4. Total and $CaCO_3$ Equivalent (Inorganic) Carbon

Figures 4.16 and 4.17 show that total carbon and inorganic carbon expressed as $CaCO_3$ both leveled off after depth interval 15 in PW treated samples. After depth interval 15, $CaCO_3$ in PW-treated depth intervals reached the level of UT samples at about 75 g kg^{-1}. Total carbon in PW-treated samples did not reach the level of UT samples. The difference between total carbon and equivalent $CaCO_3$ can be attributed to organic carbon. PW leachates were light yellow in colour after equilibration, indicating some organic carbon dissolved and was decanted off during the sequential batch procedure. Inorganic carbon was not analysed in depth intervals treated with DW.

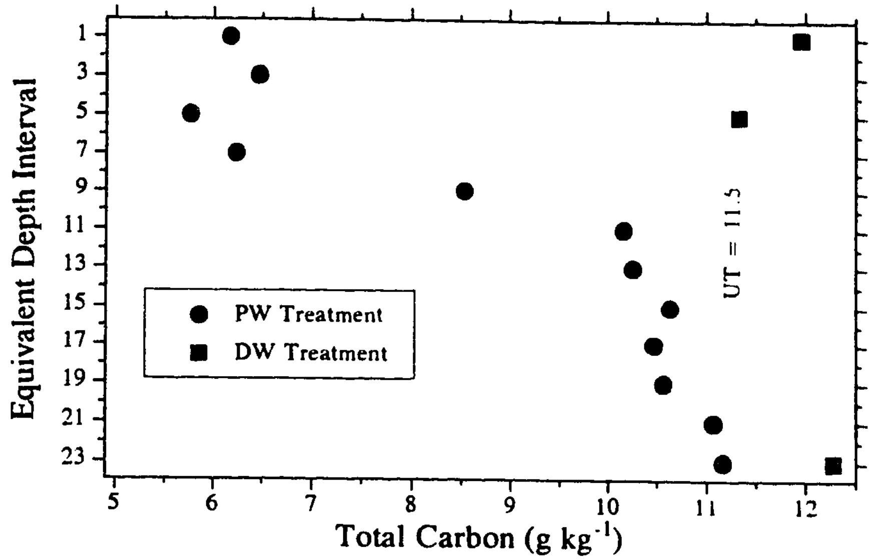

Fig. 4.16. Total carbon for selected equivalent depth intervals. Untreated (UT) sample is included as a dotted line.

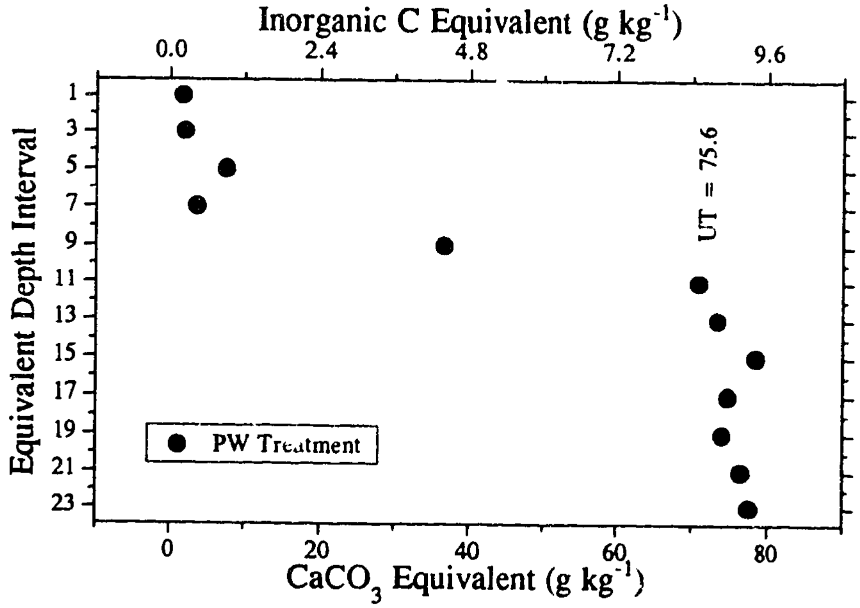

Fig. 4.17. $CaCO_3$ and inorganic C equivalents for selected equivalent depth intervals. Untreated (UT) sample mean is included as a dotted line.

PW treatments did not result in complete dissolution of $CaCO_3$ after approximately depth interval 7, even though pH of depth intervals 11 through 23 did not exceed 7.0 and pH of PW leachates leveled off near 5.5 (Figs. 4.1 and 4.14). As discussed in Section A.1, acidic inputs from one PW treatment would be about 6.0 me (+), compared with about 45 me (-) provided by $CaCO_3$ in one 30-g depth interval of calcareous soil. Theoretically there would only be enough acidity input by 10 PW treatments to destroy carbonates in the initial depth interval and in one-third of the second depth interval. However, Figs. 4.5 and 4.6 show that as PW was leached through depth intervals, soil *pe* decreased as pH increased, resulting in a fixed *pe* + pH value near 8.0 up to depth interval 10. Carbonates would have been oxidized to CO_2 as long as the fixed *pe* + pH condition was maintained: the jump in redox potential after depth interval 9 in Fig. 4.4 corresponds with the persistence of carbonates in depth interval 9 (Fig. 4.17).

pH would be expected to be around 7.7 if controlled by $CaCO_3$ for the soils used in the present study. Stable gypsum-calcite equilibria are possible; Lindsay (1979) predicts they occur at pH 7.8 but could be lower with increased (CO_3^{2-}). Ball (1994) suggested $CaSO_4$ controlled (Ca^{2+}) in PW throughout a pH range from 1.6 through 10 in the absence of $CaCO_3$. Murray and Lewis (1985) found that PW was neutralized to levels comparable to pure $CaCO_3$ in pure phase montmorillonite + calcite mixtures. $CaSO_4$ did not form in the system until pH 6, Ca-phosphate or Ca-fluorophosphate precipitated all orthophosphate out of solution between pH 3.5 and 8.5. In the absence of $CaCO_3$, all orthophosphate was removed by pH 4.0. Kennedy et al. (1991) consistently identified $CaSO_4$ and alkali fluorosilicate ($Na_xK_{(2-x)}SiF_6$) precipitates in strongly acidic (< pH 2) PW pond sediments. Barrows et al. (1966) and Barrows (1966) reported the formation of surface complexes on calcite when it was added to acid soils with elevated amounts of P, Al, or Mn. They postulated that surface coatings containing P, Si, Al and Fe may prevent calcite from dissolving. In a study of calcite additions to soils with elevated P, Barrows (1966) reported surfaces of calcite particles were coated with a porous, white granular material. The dissolution rate of calcite in coated particles was reduced by 31% compared to uncoated particles. Conditions in the soil-PW system in the present study may be conducive to the formation of similar coatings since PW leachate is high in P, Si, Al, Fe and Mn (Tables 3.1, 3.2; Section A.1). Dissolution of clay minerals at the start of the sequential procedure would contribute additional concentrations of these elements to the PW leachate. Coatings on calcite particles may be responsible for the failure of carbonates to buffer depth intervals at the end of the sequence in the present study. If present, a phosphate-containing coating would persist in PW-treated depth intervals until the supply of soluble P was exhausted. Coatings would dissolve with time in the absence of PW and soils may recover to an alkaline pH as $CaCO_3$ became available to react in solution.

5. Cation Exchange Capacity

Figs. 4.18 and 4.19 show the results of cation exchange capacity (CEC) determinations in selected equivalent depth intervals for bulk soils and coarse and fine clays respectively. This section will first discuss general CEC trends, followed by pH-dependent CEC.

Low CEC values for depth interval 1 of bulk samples reflect the dissolution of smectites incurred by the F-enriched waste (Arocena et al. 1995a). For bulk samples, CEC increased relative to depth interval 1 in subsequent depth intervals as leachates were neutralized and major precipitation products formed. CEC was increased in depth intervals 5 and 7 relative to controls. Fresh precipitates of Fe, Al and Si would result in high CEC values characteristic of amorphous clay minerals (Section B.7). Constant CEC values after depth interval 9 in bulk PW treated samples are in keeping with other chemical, mineral and solution analyses reported here, suggesting stable mineral phases formed with ion exchange properties similar to control and UT samples.

Fig. 4.19 shows decreased CEC in all clay separates relative to control sample c5. Coarse clays displayed lower CEC than fine clays for all depth intervals studied. CEC of coarse clays rose from near 20 cmol(+) kg^{-1} in depth intervals 1, 5 and 7 to near 30 cmol(+) kg^{-1} in depth interval 9, but remained less than the CEC of the control sample, c5. CEC of fine clays was less than 30 cmol(+) kg^{-1} for the initial depth interval, again reflecting the dissolution of smectites primarily found in the fine clay fraction (Arocena et al. 1995a). CEC of fine clays exceeded that of coarse clays by at least two times for all other depth intervals and increased through the depth sequence. None of the PW-treated clays studied reached CEC values as high as control samples; however, only depth intervals 1, 5, 7 and 9 were studied.

CEC determinations were made at pH 3.5 and 9.5 as a check for amphoteric clays. The CEC of allophane decreases with decreasing pH of the index and replacing cation solutions (Aomine and Jackson 1959). CEC indirectly determines the amount of negatively charged exchange sites on a soil by measuring the centimoles (cmol) of positive charge required to neutralize it. Amphoteric clays have a greater number of negatively charged sites and therefore their CEC rises with increasing pH; as [OH$^-$] increases in solution, H$^+$ dissociates from clay particle surfaces. In the present study, however, CEC for bulk soil in depth intervals 5 and 7 increased with decreasing pH. These results are not consistent with theoretical considerations and may be due to analytical error. In bulk samples, CEC increased from 6 to 27 cmol(+) kg^{-1} at pH 3.5 in depth intervals 1 and 7 respectively, and leveled off to 13-[illegible] cmol(+) kg^{-1} in depth intervals 9-23. At pH 9.5, CEC increased from 6 to 18 cmol(+) kg^{-1} in depth intervals 1 and 7, then rose slightly from 14-16 cmol(+) kg^{-1} between depth intervals 9-23. CEC of DW and UT samples was consistent at both pH values between 12-14 cmol(+) kg^{-1}.

pH treatments at 3.5 and 9.5 may have altered the mineralogy of some depth intervals. Al, Si and Fe are soluble at both low and high pH values; thus dissolution in the CEC procedure may have occurred. Parfitt and Kimble (1989) state that allophane requires pH > 4.7 to precipitate but may precipitate under more acidic conditions if soluble Al and Si are high. In the present study, competition for Al by F may have prevented the formation of allophane. If noncrystalline minerals dissolved during CEC analysis, precipitates may have formed with higher or lower CEC properties than the original minerals. Studies of extractable Fe, Al and Si (Section 4.7) showed fresh amorphous precipitates of Fe, Al and Si in depth intervals 1 through 9 likely occurred. Analysis of the clay sized fraction (Fig. 4.19) did not provide any evidence for amphoteric clay minerals. Bulk samples may have contained precipitates not present in the clay sized fraction, or clay sized particles may not have been completely removed from bulk samples during the gravity sedimentation process. Fixation of K by weathered micas may have influenced

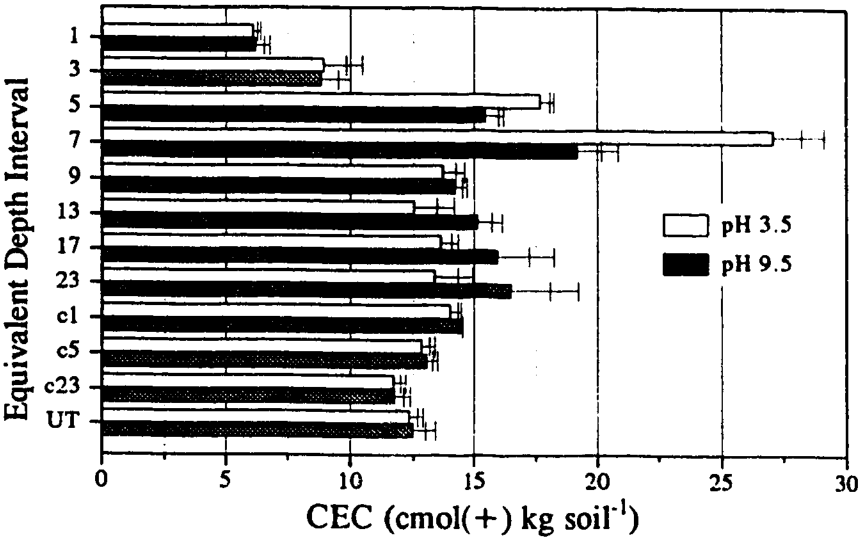

Fig. 4.18. Cation exchange capacity (CEC) at pH 3.5 and 9.5 for selected equivalent depth intervals including PW-treated, controls (c1, c5, c23) and untreated (UT) samples.

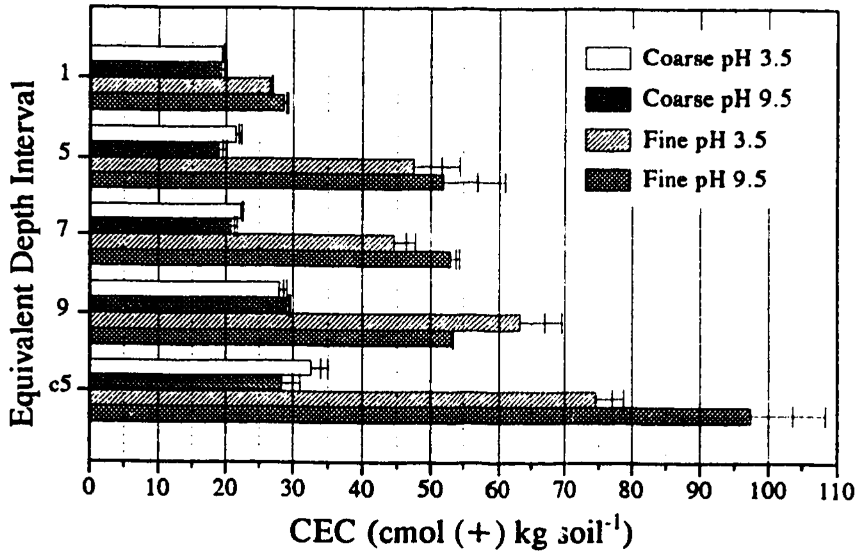

Fig. 4.19. Cation exchange capacity at pH 3.5 and 9.5 for selected fine and coarse clay separates.

CEC determinations; however Arocena et al. (1995a) observed that micas were resistant to weathering under PW treatment.

6. Surface Area

Fig. 4.20 shows surface area (SA) measurements for coarse (0.2 - 2 μm), fine (< 0.2 μm) and total clay fractions of selected equivalent depth intervals. SA of the total clay fraction was calculated from c/f ratios and SA data for coarse and fine fractions. SA of the coarse clay fraction was lowest in depth intervals 1 through 8 (200 - 230 $m^2 g^{-1}$) and increased to depth interval 23, where it was near that of the UT sample (330 - 340 $m^2 g^{-1}$). In the fine clay fraction, SA was lowest in depth interval 1 (510 $m^2 g^{-1}$) and increased to 730 $m^2 g^{-1}$ in depth interval 7. As in the coarse clay fraction, SA in the fine fraction was highest in depth interval 23 and the UT sample (760 and 770 $m^2 g^{-1}$, respectively). Total SA increased to depth interval 7 and by the end of the sequence was near the level of the UT sample.

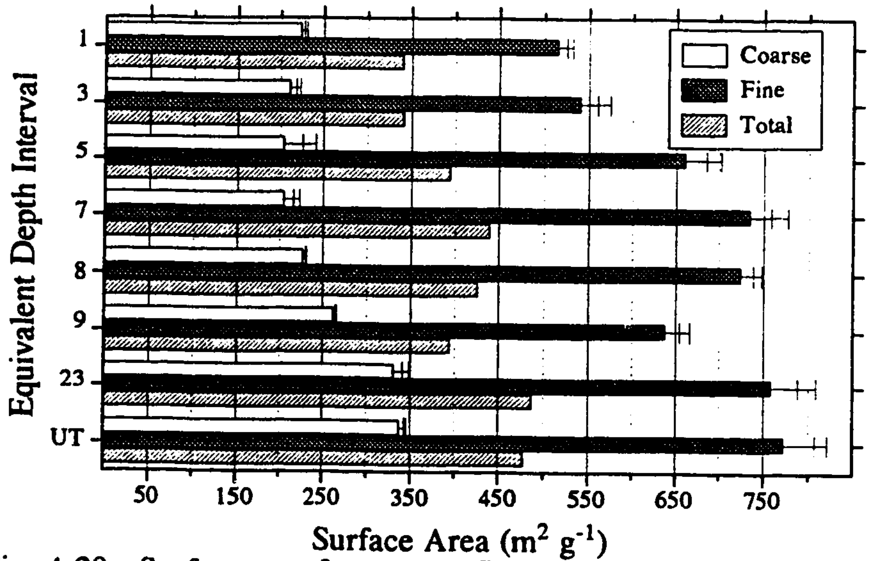

Fig. 4.20. Surface area for coarse, fine and total clay separates in selected equivalent depth intervals. Untreated (UT) sample is included as a control.

Coarse clays displayed less than half the SA of fine clays throughout the depth sequence. This was expected since smectites dominate the fine clay fraction (Arocena et al 1995a). Reduced SA in both coarse and fine clays was due to PW-induced clay mineral dissolution. Arocena et al. (1995a) provide a discussion of dissolution phenomena for PW treatments similar to those in the present study. Increased SA from depth interval 3 to 7 relative to depth interval 1 in the fine clay fraction was probably due to the formation of pure phase and amorphous precipitates or coatings around existing minerals. This is supported by a corresponding decrease in coarse/fine clay ratios between depth intervals 1 to 7 (Fig. 4.13). SA in depth interval 23 of both coarse and fine clay fractions was highest relative to other PW-treated samples and was comparable to the level of the control sample. Gradual inputs of precipitation products along the sequence from depth intervals 10 through 23 probably increased SA in these samples relative to those earlier in the sequence.

Overall, SA of PW-treated bulk clay samples during the sequential batch procedure was about 2.5 times greater in fine versus coarse clay fractions. Higher SA in depth intervals 5 and 7 relative to depth interval 1 occurred in the fine clay fraction only and were assumed to be due to the formation of precipitation products. SA of both fine and coarse clay fractions was comparable to the level of UT samples by the end of the sequential batch procedure. SA values reported for the total clay fraction were not directly measured and are subject to multiple error in SA measurements and particle size analysis. Thus they should be considered in terms of general trends only.

7. Extractable Fe, Al and Si

Amorphous and poorly crystalline Fe, Al and Si minerals are common products of pedogenesis in naturally acidic, highly weathered and volcanic environments. Similar conditions are present when extremely acidic wastes are introduced to soils through anthropogenic activity. In related studies of acidic waste/soil interactions, amorphous Fe-oxyhydroxides, amorphous Si gel, and allophane have been identified (Ball 1994; Warren and Dudas 1992; Arocena et al. 1995a; Murray and Lewis 1985; Kennedy et al. 1991). There are a number of methods which can aid in describing the continuum of amorphous, poorly crystalline and crystalline minerals formed in acidic weathering environments. The sodium dithionite-citrate-bicarbonate (DCB) extraction primarily removes coatings and precipitates of free Fe oxides such as goethite and hematite. To a lesser extent Al coatings and associated free Si are removed but destruction of iron silicate clays is minimized (Mehra and Jackson 1960). The acid ammonium oxalate (oxalate) extraction is generally less effective than DCB for iron oxides but more effective for amorphous forms of Al (McKeague and Day 1966; Dudas and Harward 1971). Oxalate extractable Al and Si can be used to estimate allophane and imogolite in soils (Parfitt and Kimble 1989). Oxalate also removes some Fe and Al organic complexes. The United States Department of Agriculture uses oxalate extractable Al and Fe to classify spodic and andic horizons (USDA 1994). Pyrophosphate specifically dissolves Fe and Al associated with organic matter and gives results comparable to the oxalate procedure (McKeague 1966). In the Canadian System of Soil Classification, pyrophosphate-extractable Fe and Al are used to differentiate Podzolic B horizons (Agriculture Canada 1978). Boiling 0.5N NaOH (NaOH) dissolves Si and Al which may be attributed to allophane, gibbsite and amorphous SiO_2 and Al_2O_3 (Hashimoto and Jackson 1960). Since there is overlap among the forms of Fe, Al and Si extracted by each method, the results of the extractions must be carefully interpreted.

Three extraction procedures, DCB, oxalate and NaOH, were used to characterize precipitation products of Fe, Al and Si resulting from neutralization of PW constituents and from dissolved clay mineral constituents in the first depth interval which were subsequently passed along in PW leachates. Pyrophosphate extractable Fe and Al were not examined because of the low organic carbon content in the Ck horizon used in the present study (see Figs. 4.16 and 4.17; Section B.4). Results are reported in Table 4.2 for bulk soil; Tables 4.3 and 4.4 report results of DCB and oxalate extracts in coarse and fine clay separates only. For all extractions, UT and DW-treated samples designated as c1, c5 and c23 were included as controls. Fe was not reported for NaOH extracts in bulk samples as it was below detection. Total elemental Fe, Al and Si are reported in Table 4.5 for comparison purposes and will be referred to as "total Fe, Al, and Si".

The DCB procedure extracted more Fe than oxalate for all samples. Depth interval 3 had the greatest amount of DCB and oxalate-extractable Fe, followed by depth interval 5, indicating Fe was sparingly mobile in the sequential batch procedure. By the 13th depth interval, extractable Fe was comparable to controls for bulk samples. Clay analysis did not include depth intervals 13 and 17, but extractable Fe was also comparable to controls in coarse and fine clays by the 23rd depth interval. Fine clays extracted more Fe overall than coarse clays. Extractable Fe was concentrated in fine and coarse clays by about three times compared to bulk samples. Since clay content was between 300-460 g kg^{-1} for PW-treated clays (Table 4.1), most enrichment of extractable Fe occurred in the clay sized fraction. Total Fe in the first depth interval was depleted by nearly 40 % compared to UT samples. Depletion of extractable Fe did not occur in depth interval 1 for bulk or clay samples, suggesting PW treatment depleted structural Fe. Structural Fe may have been reprecipitated as amorphous oxyhydroxides in depth interval 1 since extractable Fe exceeded controls in depth interval 1 for bulk and clay sized fractions. Inputs of Fe from PW leachate may have precipitated immediately in depth interval 1.

The Fe data presented suggest PW treatment depleted the initial depth interval of structural Fe, some of which may have reprecipitated *in situ* as extractable Fe, together with Fe introduced in PW (120 mg L^{-1}; Table 3.1). Depth interval 3 had most extractable Fe, concentrated in the clay fraction. *In situ* dissolution/reprecipitation may have occurred in depth intervals 3 and 5, since over 70% of total Fe was DCB extractable. Soluble Fe passed along the sequence formed extractable precipitates by depth interval 13 (pH 5.6, Fig. 4.14); most Fe precipitated in depth intervals 3 and 5 (pH 3.0 - 3.5). This is consistent with redox considerations (Figs. 4.4-4.6) which show that for the initial PW leachate, potential increased after depth interval 2. Fe probably was reduced and solubilized when depth interval 1 reacted with PW 1 and precipitated in depth interval 3 when redox potential increased and Fe became oxidized. Subsequent PW treatments may not have resulted in further solubilization of Fe in depth interval 1, as initially leachates were more oxidized than in PW 1. However, solubilization of Fe may have occurred in subsequent depth intervals with lower redox potentials in which fresh precipitates of Fe had already formed. Inputs of Fe with PW treatments probably precipitated in depth intervals 5 through 11 for subsequent leachates as redox potentials shifted from low to high (Fig. 4.4). While extractable Fe was present to depth interval 13, total Fe was negatively enriched compared to UT samples for all depth intervals except 3 and 5.

Table 4.2. Mean concentration (n = 3) of Fe, Al, and Si in extracts from bulk soil samples by citrate-bicarbonate-dithionite (DCB), acid ammonium oxalate (Ox), and boiling 0.5N NaOH (NaOH) from selected equivalent depth intervals (Depth) including controls c1, c5, c23 and untreated (UT) samples.

	$g\ kg^{-1}$							
	Fe		Al			Si		
Depth	DCB	Ox	DCB	Ox	NaOH	DCB	Ox	NaOH
1	9.9	3.3	0.17	0.049	1.1	0.11	1.7	17
c1	9.2	1.7	0.15	0.0095	0.82	0.59	1.1	2.2
3	21	16	0.49	0.19	1.4	0.65	0.78	19
5	19	13	0.39	0.18	2.6	0.47	3.9	19
c5	9	1.7	0.15	0.010	0.84	0.61	1.1	2.1
7	16	10	0.36	0.32	2.7	0.53	4.2	17
9	11	5.9	0.18	0.25	0.70	0.70	0.69	4.1
13	8.9	2.4	0.094	0.073	0.94	0.73	0.68	4.0
17	9.2	2.0	0.12	0.055	0.91	0.86	0.62	2.9
23	8.8	2.2	0.11	0.054	1.3	0.75	0.51	4.0
c23	8.6	1.7	0.15	0.011	0.93	0.85	1.1	3.3
UT	10	2.2	0.15	0.019	1.3	0.69	1.2	3.8

Table 4.3. Mean concentration (n = 3) of Fe, Al, and Si in extracts from coarse (0.2 - 2 µm) clay size fraction by citrate-bicarbonate-dithionite (DCB) and acid ammonium oxalate (Ox), from selected equivalent depth intervals (Depth) including controls c1, c5, c23 and untreated (UT) samples.

	$g\ kg^{-1}$					
	Fe		Al		Si	
Depth	DCB	Ox	DCB	Ox	DCB	Ox
1	21	8.4	0.30	0.89	0.66	0.18
c1	13	3.6	0.18	0.086	1.0	0.45
3	62	45	1.1	2.9	1.3	0.39
5	53	39	0.90	2.7	0.81	0.29
c5	14	3.6	0.16	0.087	1.2	0.51
7	45	30	0.86	2.5	0.87	1.2
9	23	12	0.53	2.2	0.31	1.4
23	14	3.7	0.13	0.10	0.64	0.48
c23	13	3.5	0.14	0.086	1.2	0.45
UT	14	3.4	0.27	0.083	1.2	0.44

Table 4.4. Mean concentration of Fe, Al, and Si in extracts from fine (< 0.2 μm) clay size fraction by citrate-bicarbonate-dithionite (DCB) and acid ammonium oxalate (Ox), from selected equivalent depth intervals (Depth) including controls c1, c5, c23 and untreated (UT) samples.

	g kg^{-1}					
	Fe		Al		Si	
Depth	DCB	Ox	DCB	Ox	DCB	Ox
1	35	15	0.67	1.1	0.44	0.45
c1	26	6.9	0.53	0.15	1.46	0.53
3	73	58	2.1	4.6	0.82	0.87
5	61	48	1.9	3.7	1.0	1.6
c5	28	6.7	0.64	0.15	1.5	0.78
7	46	34	1.15	3.2	0.85	1.7
9	32	20	0.61	6.9	1.7	3.2
23	26	6.4	0.53	0.14	1.3	0.72
c23	27	6.9	0.60	0.15	1.6	0.80
UT	27	6.8	0.87	0.10	1.4	0.76

Table 4.5. Mean concentration of Fe, Al, and Si in bulk soil digests of selected equivalent depth intervals (Depth) including untreated (UT) samples.

	g kg^{-1}		
Depth	Fe	Al	Si
1	16.37	39.75	349.4
3	29.65	41.67	33[illegible]
5	25.41	51.29	30[illegible].1
7	23.52	57.05	291.3
9	24.13	58.66	305.1
13	24.18	53.72	324.4
17	24.71	54.20	325.8
23	24.95	54.20	333.9
UT	26.46	54.97	324.0

Comparison of DCB, oxalate and NaOH extractable Al shows that in bulk samples, NaOH extracted most Al, followed by DCB and oxalate. In clay samples, oxalate extracted more Al than DCB. The most Al was extracted in depth intervals 3, 5, 7 and 9; as for Fe, extractable Al was comparable to controls by depth interval 13 for bulk soils and by depth interval 23 for clays. Oxalate extractable Al was about 10 times greater in fine clays than bulk samples. More DCB and oxalate extractable Al was extracted from fine versus coarse clays and from clays versus bulk samples, indicating enrichment of extractable Al occurred in the fine clay sized fraction. As for Fe, total Al was depleted in depth interval 1 compared to UT samples (Table 4.5). In fine and coarse clays, oxalate extractable Al was an order of magnitude higher in depth interval 1 compared to controls but DCB and NaOH extractable Al were comparable to controls in depth interval 1 for all samples. Like Fe, crystalline Al was likely dissolved in depth interval 1 due to PW treatment (Arocena et al. 1995a) and reprecipitated *in situ* as well as further along the sequence of depth intervals.

Fluoride is a well-known scavenger for Al; PW treatment probably depleted the initial depth interval of structural Al, some of which reprecipitated *in situ* as amorphous Al extractable by oxalate. Inputs of Al from PW (190 mg L^{-1}; Table 3.1) may also have precipitated immediately in depth interval 1. Depth interval 3 had most oxalate extractable Al in clays, but bulk samples had more NaOH extractable Al which was highest in depth interval 7. The oxalate extraction was effective in removing Al from clay samples but not from bulk samples. Even though inputs of Al from PW were greater for Fe than Al (190 and 120 mg L^{-1} respectively; Table 3.1), depletion of Al and concentrations of extractable Al were much less than for Fe, suggesting Fe was more susceptible to redistribution in the depth sequence after PW treatment. Soluble Al which passed along the sequence was precipitated as oxalate-extractable Al by depth interval 13 (pH 5.6, Fig. 4.14); most Al precipitates formed between depth intervals 3 and 9 (pH 3.0 - 4.5). Soluble F concentrations were depleted in corresponding depth intervals and formation of fluoroaluminate precipitates likely occurred. Unlike Fe, total Al was only depleted in depth intervals 1, 3 and 5 and was enriched relative to UT samples in depth intervals 7 and 9. Through the remainder of the sequence total Al was comparable to controls.

Most Si was extracted using NaOH in bulk samples, followed by oxalate and DCB for bulk samples. Although the DCB extraction is not intended for Si, it is worth noting DCB extractable Si was less than UT samples in depth interval 1 for all samples studied. In fine and coarse clay fractions, oxalate extracted comparable amounts of Si. In bulk samples, most NaOH extractable Si was in depth intervals 1, 3, 5 and 7 and was similar to control samples in subsequent depth intervals. Oxalate extractable Si was generally highest in depth intervals 5, 7 and 9 for bulk and clay samples, and was at or lower than control samples after depth intervals 9 and 23 for bulk and clay samples, respectively. Overall, oxalate extracted more Si from bulk depth intervals than from fine and coarse clays. Comparison of oxalate extractable Al and Si in coarse and fine clays indicates the presence of allophane in depth intervals 1 through 9 (Parfitt and Kimble 1989). Enrichment of total Si was positive in depth intervals 1 and 3 but negative in depth intervals 5, 7 and 9 relative to controls (Table 4.5). Total Si in subsequent depth intervals was comparable to controls.

Based on NaOH extractable data for bulk soils (Table 4.2), precipitation of amorphous Si probably occurred in depth intervals 1 through 7; negative enrichment of Si in depth intervals 5 and 7 may have been due to formation of other precipitation products. This is likely considering clay enrichment described in Section B.1. Unlike Fe and Al, total Si was not depleted in depth interval 1; this may be due to high Si inputs from PW leachate (1400 mg L^{-1}) which may have precipitated *in situ* along with Si previously dissolved from crystalline clays. Based on NaOH and oxalate extractable Si, amorphous Si precipitated by depth interval 7 in bulk samples (pH 3.7; Fig. 4.14) and by depth interval 9 (pH 4.5, Fig. 4.14) in clay samples.

8. Summary

Extractable Fe, Al and Si were generally greatest in depth intervals 1 through 9. Formation of amorphous or poorly crystalline constituents in these depth intervals was consistent with increased CEC and SA in depth intervals 5 and 7 relative to depth interval 1 (Sections B.5 and B.6) and may contribute to enrichment of the fine clay fraction observed in Section B.1. Fine clay enrichment was consistent with decreases in EC and soluble F (Sections A.3 and A.4) which occurred mainly up to depth interval 9. Extractable Fe, Al and Si were no longer evident after depth interval 9, suggesting amorphous precipitates formed by depth interval 9 (pH 4.5; Fig. 4.14). Carbonate content reached the level of untreated samples by depth interval 11 but some total carbon was lost from the system. Oxalate extractable Al:Si ratios indicated the presence of aluminosilicate precipitates in depth intervals 1 through 9 but pH in NaF and CEC hysteresis tests did not reveal allophanic properties in those depth intervals. Fluoride probably competed for Al and prevented allophane formation. Comparisons of total and extractable Fe, Al and Si show PW attack on clay minerals mobilized more Fe than Al or Si but PW-induced depletion of both Fe and Al was evident in depth interval 1. Mobilization and precipitation of Fe was influenced by fluctuating redox potentials which showed initially Fe was oxidized and precipitated early in the sequence but could be reduced and mobilized in leachates later in the sequence. Negative enrichment of total Al and Si occurred due to formation of precipitates primarily in the fine clay fraction (Fig. 4.13). Data for depth intervals 11 through 23 was uniform for most parameters studied, indicating steady state conditions had been reached.

C. Elemental Distribution

Over time, natural chemical and physical weathering processes result in elemental redistribution in soils. Development of clay enriched horizons is a result of illuviation of fine textured materials over time. Mottled and ferric horizons can form *in situ* from continuous wetting and drying cycles which alternately mobilize and immobilize Fe as it is reduced and oxidized. Podzolic B horizons form as a result of leaching and deposition of Fe, Al and humic materials mobilized by acidic inputs from surface horizons. Acidic conditions promote the solubility of many elements; pH dependent mobility may partition elements throughout the soil profile. Dissolved constituents can be sorbed and/or eventually form stable precipitates depending on their own properties and the surface characteristics of the solid matrix. Pedogenic studies, and, more recently, studies of anthropogenic weathering processes have documented elemental partitioning (Pawluk 1961; McKeague and St. Arnaud 1969; Duddy 1980; Koons et al. 1980; Dudas and Pawluk 1980; Warren and Dudas 1992a, 1992b; Xing and Dudas 1993).

An examination of elemental redistribution is an important step in achieving the objectives of the present study; that is, to determine the forms and stability of elements of environmental concern in order to predict the long-term consequences of decommissioning PG repositories. The following sections will describe and discuss the results of total elemental analysis of the calcareous soils sequentially reacted with PW in the present study. By definition, trace elements are those elements present in concentrations < 1000 mg kg^{-1}. For the purpose of the present study, major elements will consist of those elements present at concentrations > 1000 mg kg^{-1}. Rare earth elements (REE), also known as the lanthanide series, refer to the 15 elements on the periodic table between La (atomic number 57) and Lu (atomic number 71).

1. Major Elements

Elemental content of bulk soils from selected equivalent depth intervals was determined in order to assess redistribution of major elements. Extractable Fe, Al and Si were discussed in Section B.7 with reference to formation of new precipitates of noncrystalline and paracrystalline minerals in some depth intervals. The following section will refer to total elemental content and redistribution of major elements, with some reference to Section B.7 where applicable.

Table 4.6. Mean concentration (n = 3) of major elements in bulk samples from selected equivalent depth intervals. Detection limit for each element listed is 0.1 g kg^{-1}. Values for untreated samples (UT) are included for reference.

Depth	Al_2O_3	CaO	Fe_2O_3	F[†]	K_2O	MgO	MnO	Na_2O	P_2O_5	SiO_2	TiO_2
						g kg^{-1}					
1	75.1	17.6	23.4	5.97	17.2	3.80	0.133	10.2	10.1	748	5.13
3	78.7	11.8	42.4	11.7	15.9	5.00	0.167	10.2	30.2	720	5.17
5	96.9	33.8	36.3	45.3	15.5	5.47	0.200	10.5	28.2	659	4.27
7	108	39.1	33.6	54.0	15.4	6.57	0.200	10.5	26.5	623	4.23
9	111	29.2	34.5	26.0	16.1	13.2	0.400	9.77	22.3	653	4.47
11	106	25.3	35.4	4.50	16.5	14.6	0.500	9.37	9.83	695	4.73
13	101	25.7	34.6	2.10	16.6	14.9	0.600	9.50	6.37	694	4.77
15	101	24.6	34.2	0.82	17.2	14.6	0.700	9.70	4.97	705	4.83
17	102	25.1	35.3	0.74	17.0	14.8	0.667	9.53	6.17	697	4.87
19	100	26.2	35.0	0.62	16.0	14.8	0.800	9.47	7.00	706	4.70
21	101	25.7	34.8	0.65	16.4	14.7	0.600	9.43	5.63	713	4.77
23	102	24.9	35.7	0.60	16.4	15.1	0.567	9.47	4.93	714	4.83
UT	104	26.8	37.8	0.65	14.8	15.2	0.533	8.27	1.23	693	4.90

[†] detection limit = 0.01 g kg^{-1}

Table 4.6 shows distribution of major elements expressed as oxides for selected equivalent depth intervals and untreated (UT) samples. F is included in Table 4.6 due to its elevated concentrations in PW. Mn is also included in Table 4.6 as soil average values indicate its status as a major element. Elemental analysis in the present study will be discussed in the context of enrichment factors (EF). EFs for major elements were calculated from the values in Table 4.6 using the following relationship:

EF = concentration in treated sample/concentration in untreated sample

Figs. 4.21 through 4.23 show EFs for the major elements, including F. EFs greater than 1 are considered positive enrichment while EFs less than 1 are considered negative enrichment. All EFs for major elements will be considered because they provide information about precipitation products and the fate of contaminants in soil-PW systems.

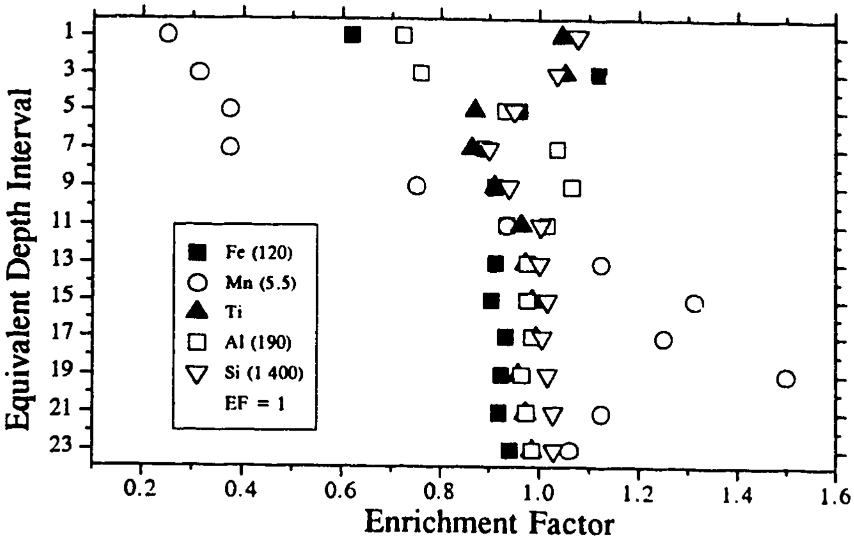

Fig. 4.21. Enrichment factors for some major elements in selected equivalent depth intervals. If available, concentrations in PW (mg L^{-1}) are included in brackets in the legend.

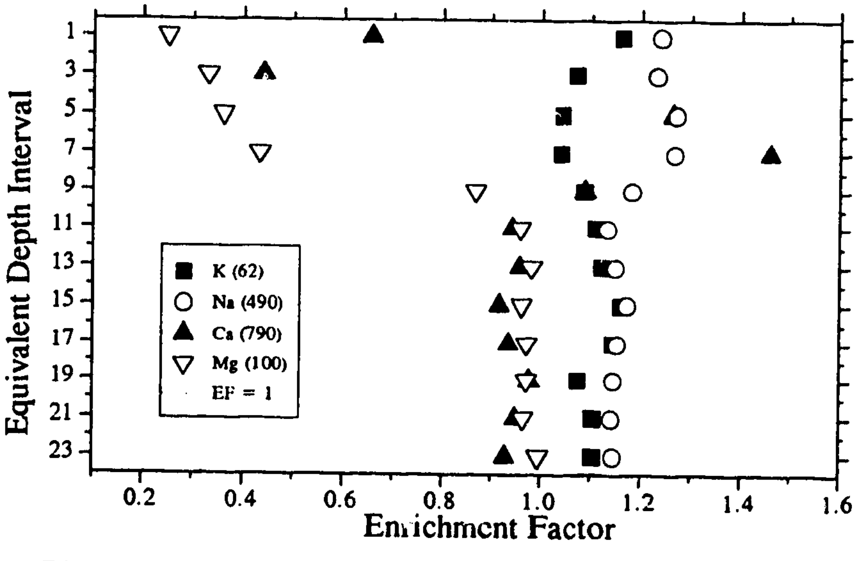

Fig. 4.22. Enrichment factors for some major elements in selected equivalent depth intervals. Concentrations in PW (mg L^{-1}) are included in brackets in the legend.

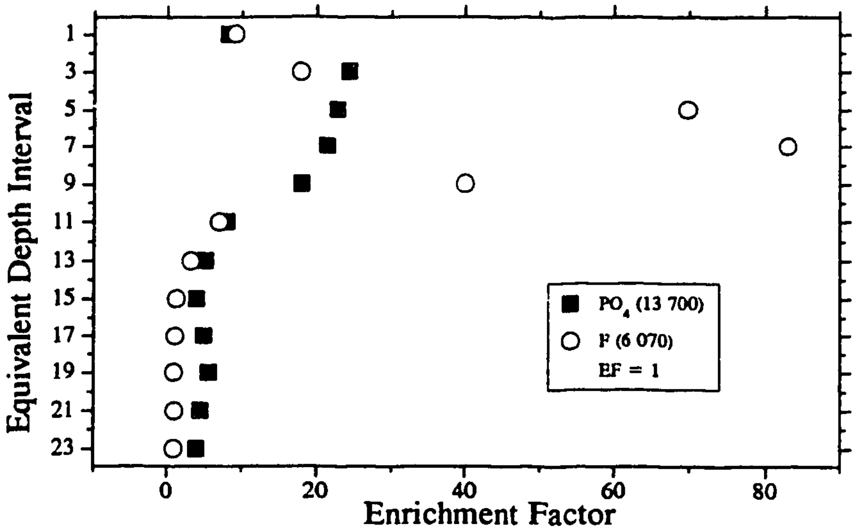

Fig. 4.23. Enrichment factors for some major elements in selected equivalent depth intervals. Concentrations in PW (mg L^{-1}) are included in brackets in the legend.

Elevated concentrations of major elements in PW would have resulted in elemental loading in initial depth intervals, and if precipitation products formed immediately as PW reacted with soil, positive EFs in initial depth intervals would result. Dissolution of clay minerals by reaction with PW would have resulted in negative enrichment at initial depth intervals. Both processes could have taken place in the same depth interval; for example, at acidic pH levels in depth interval 1, Si may have dissolved in smectites and reprecipitated in an amorphous form. Examination of EFs and NaOH-extractable Si (Section B.7) indicates that this may have occurred. Also, relatively high enrichments of one element would mask enrichments of all other elements since elemental concentrations were determined relative to total sample weight. Positive enrichments later in the depth sequence would be due solely to formation of precipitates as most mineralogical properties examined were stable after depth interval 11 (Section B).

Except for P and F, EFs were between 0.2 and 1.5 (Figs. 4.21 and 4.22). Fig. 4.21 shows EFs for Fe, Mn, Ti, Al and Si. Mn, Al and Fe were negatively enriched at the start of the sequential batch procedure, while Si and Ti were positively enriched. Fe remained negatively enriched except at depth interval 3. After depth interval 5, Al became positively enriched. Enrichment of Si and Ti was negative after depth interval 3. All elements except Mn leveled off near EF = 1 after depth interval 11. Mn displayed unusual behaviour relative to other elements as it was negatively enriched at the start of the sequence until depth interval 13 when it became positively enriched. EF for Mn was near 1 by depth interval 23.

Fig. 4.22 shows K and Na were positively enriched throughout the 23 depth intervals. The enrichment pattern shows that competitive interactions existed for these elements: when EF for Na increased, EF for K decreased and vice versa. Mg was negatively enriched throughout the depth intervals studied, while Ca was positively enriched in depth intervals 5, 7 and 9. After depth interval 11 EF for all elements leveled off, with Ca and Mg slightly below 1 and K and Na near 1.1.

Fig. 4.23 shows EFs for F and P. Enrichment of these elements was dramatically greater than for any other element studied. For both elements EFs were positive initially, rising to 83 for F in depth interval 7 and to 24 for P in depth interval 3. By depth interval 15 EF for F had dropped to 1 but remained slightly above 1 for P.

Negative enrichments in initial depth intervals (i.e. Al, Fe, Mn, Mg and Ca) could have occurred because (1) elements loaded into the system by PW did not precipitate initially and dissolved species remained soluble at least in initial depth intervals; or (2) that precipitation products formed but not at high enough concentrations to mask negative enrichment due to dissolution. The former explanation may apply to Ca, Mg and Mn; Ca and Mg would have occurred in untreated soils primarily in the form of carbonates and would have been dissolved under acidic conditions in treated depth intervals. With neutralization, precipitates of Ca and Mg in the soil-PW system would form as coatings or pure precipitates in association with F^-, PO_4^{3-}, SO_4^{2-}, or CO_3^{2-} (Murray and Lewis 1985; Ball 1994; Barrows 1966; Barrows et al. 1966). Evidence for the formation of precipitates is shown by increasing EFs up to depth intervals 7 and 9 for Ca and Mg respectively. Mn behaviour is consistent with redox considerations, which indicate Mn may have been reduced and mobilized in initial depth intervals in the absence of carbonates but by depth interval 9 when carbonates became present and redox conditions became more oxidized Mn also became oxidized and began to precipitate. Mn is commonly known to partition from Fe under reduced conditions in soil because of its high capacity to oxidize other species. Mn would have been present as oxyhydroxide coatings on mineral surfaces or as nodules (McKenzie 1977), and would have been mobilized upon being reduced to Mn^{2+} until precipitating as an oxyhydroxide in the higher *pe*-pH environment.

Al and Fe were also negatively enriched in initial depth intervals. Both would have been present originally in phyllosilicate minerals and oxyhydroxides. Both Fe and Al would have been mobilized and reprecipitated in noncrystalline or paracrystalline forms or as oxyhydroxides, evidenced by DCB and oxalate-extractable forms of Fe and Al (Section B.7) in similar depth intervals as those for which increasing EFs of Fe and Al are reported.

Si, Ti, Na, K, P and F were positively enriched initially, indicating they may have precipitated out of PW immediately upon reaction with soil. Except for Si, major amounts of these elements would not have been solubilized in soils by PW. Arocena et al. (1995a) reported that mica was stable relative to smectites and kaolinites in soils reacted with PW. Loading of these elements from PW may have been high enough to force precipitation products to form even at initial depth intervals. Si and Ti were the only elements in this group which did not maintain EFs > 1 throughout the depth intervals studied. Ti is an extremely stable mineral and its analysis involves removal of silicate minerals by hydrofluoric acid (Hutton 1977); thus its redistribution in the present study is not expected to occur. Variations in Ti concentrations can be attributed to sample variation only and negative EF values observed for Ti were probably due to positive enrichment of other elements rather than dissolution of Ti. Noncrystalline forms of Si precipitated up to depth interval 9, evidenced by NaOH-extractable Si (Section B.7). Negative enrichment of Si in depth intervals 5, 7 and 9 may have been a result of positive enrichment of other precipitates, particularly F (Fig. 4.23).

Na and K are known to be relatively soluble due to low surface charge density but precipitates containing these elements formed, evidenced by the constant positive EF values for those elements throughout the depth sequence. Competition between Na and K in sorption/precipitation processes was evident in depth intervals 1 through 9; by depth interval 11 coprecipitates containing the two elements may have formed or each may have formed its own stable phase. Kennedy et al. (1991) found alkalifluorosilicates including cryolite (Na_3SiF_6), $NaSiF_6$, and $NaKSiF_6$ were consistently present in a suite of sediments from PW ponds (pH <2). Possible precipitates under oxidized conditions include jarosite ($NaFe_3(SO_4)_2(OH)_6$) and natrojarosite ($KFe_3(SO_4)_2(OH)_6$). Precipitates with PO_4 and SO_4 such as Na_2SO_4 are possible under conditions of high ionic strength.

As indicated earlier, F and P EFs were higher than for any other major element. Examination of PW concentrations for these elements indicates high EF values were due to loading from PW. Increasing enrichment of Ca, Mg, Mn, Na and Al in conjunction with maximum EFs for F and P in depth intervals 3 through 9 provides indirect evidence for coprecipitation of these elements. F enrichment peaking in depth interval 7 was consistent with decreases in soluble F concentrations (Section A.4; Fig. 4.11) and clay enrichment (Section B.1; Fig. 4.12). Possible precipitation products for F in PW-soil systems include aluminum fluoride, alkalifluorosilicates, fluorite (CaF_2), chukhrovite ($Ca_4SO_4SiAlF_{13}$) and fluorapatite ($Ca_5F(PO_4)_3$ (Elrashidi and Lindsay 1985; Kennedy et al. 1991; Ball 1994; Luther et al. 1996). Besides fluorapatite, the orthophosphate ion could form complexes with almost any other ion present in PW leachates (Fe, Al, Mg, K, Na, and many trace elements).

2. Trace Elements

Examination of extractable Fe, Al and Si provided evidence of non- and paracrystalline precipitates which may act as scavengers for trace elements of environmental concern (Koons et al. 1980; Rajan and Watkinson 1976; Livesey and Huang 1981). Alternatively, trace elements could form insoluble complexes with phosphate and sulfate (Lindsay and Vlek 1977; Ball 1994). Trace elements are also known to substitute for ions of like size and valence in crystal matrices of stable phyllosilicate minerals in the process known as isomorphic substitution.

The results of trace element analyses of selected equivalent depth intervals are reported in Tables 4.7a and 4.7b. EFs above 10 are considered to represent potential environmental concern and are reported in Fig. 4.24 for Cd and U. EFs were calculated

Table 4.7a. Mean concentration (n = 3) of trace elements (A-N) in bulk samples from selected equivalent depth intervals. Values in parentheses indicate detection limits for each element. Values for untreated (UT) samples, soil average (SA), and crustal abundance (CA) are included for reference.

Depth	As	Ba	Br	Cd	Co	Cr	Cs	Cu	Hf	Hg	Mo	Ni
	mg kg^{-1}											
	(1.0)	*(1.0)*	*(0.5)*	*(0.5)*	*(0.1)*	*(0.5)*	*(0.2)*	*(1.0)*	*(0.2)*	*(1.0)*	*(2.0)*	*(1.0)*
1	8.33	687	2.03	3.17	2.87	43.8	2.57	21.3	4.43	nd[†]	6.33	9.33
3	9.67	595	1.57	3.00	3.47	59.6	2.77	24.0	5.13	nd	nd	9.67
5	9.00	557	1.37	3.77	5.23	60.7	2.80	22.7	4.37	nd	nd	12.3
7	9.00	544	1.40	4.80	6.73	65.0	2.73	26.3	4.10	nd	nd	13.7
9	9.00	578	1.63	12.6	11.2	74.9	2.77	35.3	4.53	nd	5.33	25.0
11	9.33	617	1.57	19.8	15.2	66.1	2.97	22.3	5.07	nd	nd	35.3
13	9.00	612	1.63	13.9	15.1	61.3	3.10	22.3	4.87	nd	3.00	41.7
15	8.00	615	1.77	4.10	14.0	58.2	3.07	17.7	4.83	nd	nd	41.0
17	8.00	623	1.67	nd	10.8	55.2	2.97	18.7	4.50	nd	nd	35.3
19	7.33	630	1.70	nd	11.0	55.8	3.03	16.3	4.60	nd	nd	31.3
21	7.33	615	1.87	nd	9.60	58.5	3.07	19.0	4.67	nd	nd	27.7
23	7.33	638	1.70	nd	9.30	57.6	3.33	22.3	4.63	nd	nd	30.3
UT	8.00	599	1.87	nd	10.1	56.2	3.13	18.3	4.80	nd	4.00	32.7
SA[‡]	6	500	10	0.35	8	70	4	30	6	0.06	1.2	50
CA[‡]	1.5	500	0.37	0.11	20	100[§]	3	50	5.3	0.05	1.5	75[§]

[†] nd: not detectable

[‡] source: Bowen (1979)

[§] source: Taylor (1964)

Table 4.7b. Mean concentration (n = 3) of trace elements (P-Z) in bulk samples from selected equivalent depth intervals. Values in parentheses indicate detection limits for each element. Values for untreated (UT) samples, soil average (SA), and crustal abundance (CA) are included for reference.

Depth	Pb	Rb	Sb	Sc	Se	Sr	Ta	Th	U	V	Y	Zn	Zr
							mg kg^{-1}						
	(5.0)	*(10.0)*	*(0.10)*	*(0.10)*	*(0.50)*	*(1.0)*	*(0.30)*	*(0.10)*	*(0.10)*	*(1.0)*	*(1.0)*	*(1.0)*	*(1.0)*
1	19.7	55.3	0.80	5.70	nd[†]	140	0.40	7.57	5.93	49.0	22.0	33.0	169
3	18.7	56.3	0.97	11.0	nd	140	nd	10.2	14.4	57.7	31.3	35.0	193
5	15.3	57.3	0.77	9.97	nd	220	0.40	7.37	17.8	61.0	60.7	38.3	179
7	16.0	59.0	0.80	8.60	nd	193	nd	6.57	19.7	73.0	32.3	42.7	162
9	15.7	61.3	0.87	8.10	nd	143	nd	7.27	9.70	109	20.3	92.0	171
11	12.7	63.3	0.80	8.47	nd	133	0.77	7.63	2.53	78.7	19.0	130	175
13	16.0	64.3	0.83	8.50	nd	129	0.57	8.30	1.93	72.7	19.0	105	168
15	10.7	59.3	0.73	8.43	nd	132	0.50	7.43	1.70	70.7	19.0	61.0	162
17	14.3	62.0	0.67	8.37	nd	133	nd	7.03	1.57	72.0	19.0	53.3	156
19	14.3	62.3	0.63	8.30	nd	136	0.50	7.03	1.57	69.3	19.3	48.0	181
21	10.7	60.0	0.73	8.47	nd	137	0.77	6.97	1.53	70.7	19.0	48.0	165
23	15.3	62.3	0.70	8.53	nd	142	0.67	7.07	1.43	75.3	19.7	59.7	166
UT	12.3	63.7	0.70	8.47	0.93	145	0.60	7.27	1.57	75.7	21.3	56.0	167
SA[‡]	35	150	1	7	0.4	250	2	9	2	90	40	90	400
CA[‡]	14	90	0.2	16	0.05	370	2	12	2.4	160	30	75	190

[†] nd: not detectable

[‡] source: Bowen (1979)

for Cd based on a soil average value of 0.2 mg kg^{-1} reported by Soon and Abboud (1990) as untreated samples had background concentrations below the detection limit of 0.5 mg kg^{-1}. Fig. 4.25 shows EFs for selected trace elements Co, Cu, Pb, Y and Zn to emphasize the variety and extent of enrichment patterns over the 23 depth intervals. Because of the low concentrations of trace elements, most EFs were likely masked by enrichment of major elements and therefore most of the discussion on trace elements will be in terms of absolute concentrations.

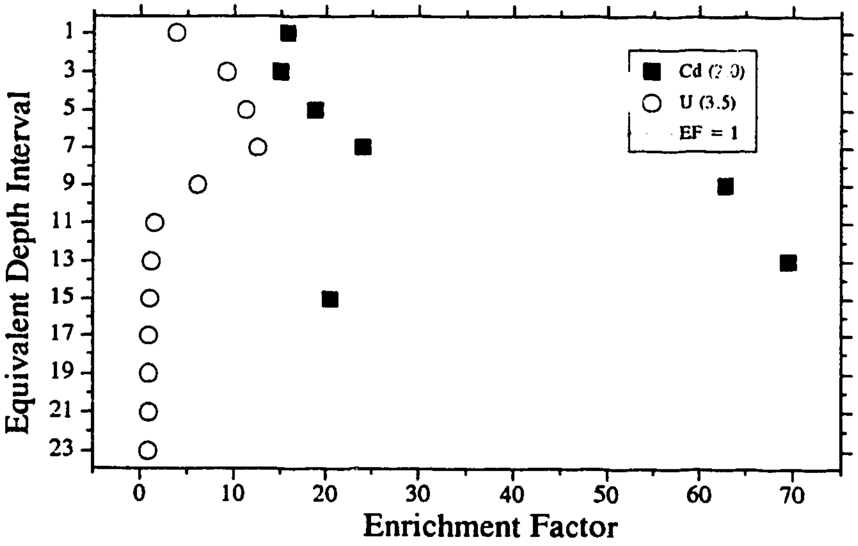

Fig. 4.24. Enrichment factors for Cd and U in selected equivalent depth intervals. Concentrations in PW (mg L^{-1}) are included in brackets in the legend.

Enrichment of Cd and U was greater than for any other trace element studied, reaching maximums of 69 and 12 relative to background values respectively. Maximum Cd concentrations occurred in depth interval 11, corresponding to soil pH 5.2 (Fig. 4.14). Similar size and valence allows Cd to mimic the behaviour of Ca and coprecipitates of Ca/Cd with sulfate, fluoride, phosphate and carbonate may have formed (McBride 1980; Papadopoulos and Rowell, 1988). Ca may compete with Cd for sorption sites (Christensen 1984); Ca enrichment was greatest in depth interval 7 and fell below 1 by depth interval 11 where Cd enrichment was greatest. Ball (1994) predicted phosphate complexes would be the solubility controlling solids for Cd but these did not match experimental data above pH 3.5. Phosphate complexes may have been responsible for enrichment of Cd in initial depth intervals; nonsilicate precipitation products may have sorbed Cd as pH increased to depth interval 7. Carbonate probably attenuated Cd at greater depth intervals. Carbonates were present in depth interval 9 and peaked and leveled off after depth interval 11 (Fig. 4.17); Cd enrichment also rose in depth interval 9 and peaked in depth interval 11. Calcareous soils have been shown to effectively attenuate Cd (McBride 1980; Papadopoulos and Rowell 1988). Octavite ($CdCO_3$) is predicted to be the solubility controlling solid for Cd at neutral to alkaline pH values (Ball 1994). By the 17th depth interval (pH 6.5), Cd was below detection limits.

Uranium enrichment was greater than 10 also and may present an environmental concern. Positive enrichment of U peaked at depth interval 7 at about EF = 12, corresponding to a concentration of 19.7 mg kg^{-1} (Table 4.7a); by depth interval 13 U concentrations had reached background. Although +4 and +6 valence states for U are possible, redox potentials in the present study were not low enough for U to become reduced (Fig. 4.24). U would be present as UO_2^{2+} or may form complexes with carbonates above pH 5.5 (Langmuir 1978). Coffinite ($USiO_4$) may have precipitated in initial depth intervals as soluble Si was high; uranitite (UO_2) or coprecipitates with phosphate or carbonate may also have formed. Langmuir (1978) and Hsi and Langmuir (1985) showed that UO_2^{2+} was readily sorbed by Fe-oxyhydroxides but sorption processes would be mitigated by complexation with anions in solution such as F^-, PO_4^{3-} and SO_4^{2-}. Ball (1994) found U precipitation was a more important mechanism than sorption for removing U from solution; both processes may have occurred simultaneously in the present study due to the presence of amorphous constituents up to depth interval 9 which coincided with maximum EF for U.

Some trace elements (Cu, Sb, Sr, Ta, U, Y) were positively enriched up to depth interval 9 and concentrations dropped later in the sequence to background levels. Other elements (Cd, Co, Cr, Ni, V, Zn) were negatively enriched up to depth interval 9 after which concentrations peaked by depth interval 17 and then dropped to background levels. A third group of elements (As, Ba, Cs, Hf, Mo, Pb, Th, Zr) showed no clear trend but had concentrations near background values by the 23rd depth interval. Fig. 4.25 gives a graphical representation of EFs for selected trace elements showing the three general trends.

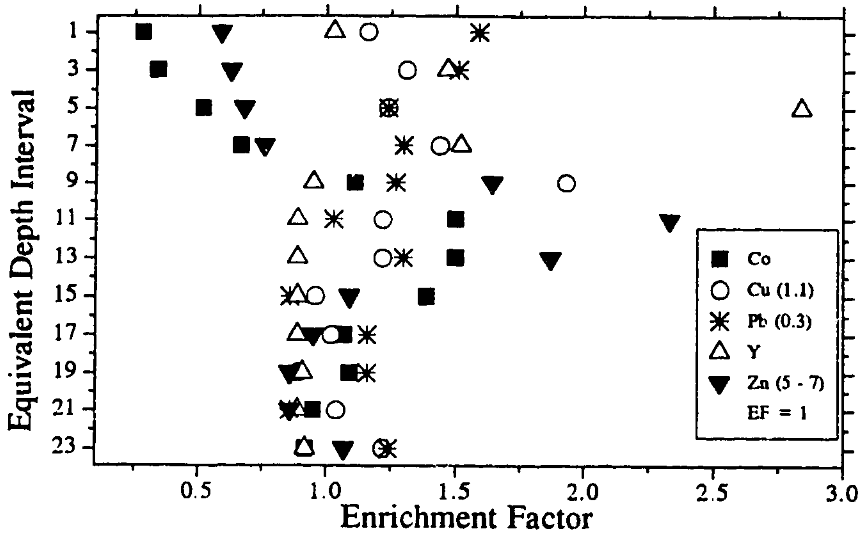

Fig. 4.25. Enrichment factors for some trace elements in selected equivalent depth intervals. If available, concer[illegible]ns in PW (mg L^{-1}) are included in brackets in the legend.

The three general trends in movement of trace elements through the depth sequence can be explained with reference to pH (Fig. 4.14), existence of amorphous constituents and other precipitation products (Section B.7), and presence of carbonates (Fig. 4.17). Carbonates became detectable in depth interval 9; the elements in the second group in which concentrations peaked after depth interval 9 (pH 4.5) probably formed precipitates with carbonates or required higher pH values for precipitation to occur. Elements in the first group formed precipitates at pH < 4.5. Trace elements may have formed as coprecipitates with P or F (Fig. 4.23), or may have sorbed to or coprecipitated with amorphous constituents present up to depth interval 9. The third group may represent elements which were not mobilized by PW treatment. Alternatively, some elements may have been precipitated or sorbed and were subsequently redissolved as ionic strength decreased with repeated PW treatments (Fig. 4.8). A third explanation could be that positive enrichment of elements in this group was masked by precipitation of other elements. For example, thorium concentrations peaked in depth interval 3 and again in depth interval 13 at 10.2 and 8.3 mg kg^{-1} respectively but generally Th concentrations were close to background values of 7.27 and 9 mg kg^{-1} for untreated soils and soil averages respectively (Table 4.7b). Harmsen and de Haan (1980) state that under acidic conditions, Th would exist as Th^{4+} and $Th(OH)_2^{2+}$ above pH 4. Th was probably sorbed to negatively charged sites in depth intervals 1 through 13, even though positive enrichment of Th did not occur throughout the profile.

Detection limits for Hg in the present study were not low enough to detect background concentrations, but it was assumed Hg did not accumulate in any of the depth intervals studied.

Accumulation of Ni occurred in association with the presence of carbonates after depth interval 9 but concentrations in the solid phase were inconsistent with concentrations measured in unreacted PW samples (Table 3.1).

Selenium was unique among the trace elements studied, as concentrations were below the detection limit of 0.50 mg kg-1 for all depth intervals studied but background concentrations were within detection limits. Se concentrations in PW were 0.7 mg L^{-1}; thus Se was not only depleted in all depth intervals relative to background but dissolved Se and inputs of Se from PW also remained mobile throughout the experiment. Elrashidi et al. (1987) state that Se forms H_2Se^0 below pH 3.8 and under typical *pe*-pH conditions forms SeO_3^{2-} or $HSeO_3^-$ complexes. Neutral and negatively charged species would be mobile in the soils used in the present study; any anion exchange capacity associated with the noncrystalline fraction apparently did not sorb Se. Alrichs and Hossner (1987) reported Se was readily sorbed over a range of pH values in column studies. Ball (1994) found Se from a PW leachate was sorbed by noncalcareous soils up to pH 2.75 but sorption decreased to pH 4.5, after which Se was released back into solution. Rajan and Watkinson (1976) report phosphate displacement of Se sorbed to allophane. Se may have been attenuated in the present study but anionic species of F^-,

SO_4^{2-} or PO_4^{3-} present in PW leachates may have promoted desorption. The results of Se analysis in the present study show that Se may be mobile in a leaching scenario below PG repositories. Se is toxic to animals at elevated concentrations and is regulated in drinking water at 0.01 mg L^{-1} (Health and Welfare Canada 1993). Mobility of Se would therefore pose an environmental and regulatory concern.

3. Rare Earth Elements

Table 4.8 shows concentrations of some REE in selected depth intervals. REE generally behave similarly but can be differentiated as light (La to Eu) and heavy (Gd to Lu). Table 4.8 shows that except for Sm and Tb, all REE were enriched relative to background concentrations up to depth interval 15 where concentrations dropped to background. No differences between heavy and light fractions were evident. Sm was depleted in depth interval 1 relative to background and reached peak concentrations by

Table 4.8. Mean concentration (n = 3) of rare earth elements in bulk samples from selected equivalent depth intervals. Values in parentheses indicate INAA detection limits for each element. Values for untreated samples (UT), soil average (SA), and crustal abundance (CA) are included for reference.

Depth	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu
				mg kg^{-1}				
	(0.10)	*(1.0)*	*(1.0)*	*(0.010)*	*(0.050)*	*(0.10)*	*(0.05)*	*(0.010)*
1	29	57	25	3.7	0.95	0.57	2.2	0.33
3	33	68	30	4.8	1.2	0.77	2.9	0.45
5	42	84	40	6.7	1.7	1.3	4.5	0.69
7	30	64	32	5.6	1.5	1.1	4.3	0.64
9	26	55	26	4.1	1.0	0.63	2.3	0.35
11	28	58	27	4.1	1.0	0.60	2.2	0.32
13	28	59	26	4.1	1.0	0.67	2.2	0.31
15	27	55	24	4.1	0.96	0.60	2.1	0.31
17	25	53	22	4.1	0.89	0.70	2.1	0.32
19	26	54	22	4.1	0.92	0.53	2.0	0.31
21	26	54	21	4.1	0.92	0.53	2.0	0.33
23	26	54	25	4.2	0.91	0.57	2.1	0.32
UT	27	55	24	4.3	0.93	0.53	2.1	0.32
SA[1]	40	50	35	4.5	1	0.7	3	0.4
CA[1]	32	68	38	7.9	2.1	1.1	3.3	0.51

[1] source: Bowen (1979).

depth interval 5 and background concentrations by depth interval 9. Tb did not reach background concentrations until depth interval 19 although by depth interval 9 Tb was at concentrations comparable to the soil average of 0.7 mg kg^{-1}. Yttrium (Y) is usually considered together with REE since it displays similar behaviour. Table 4.7b shows Y concentrations follow the trend observed for REE; by depth interval 9 Y concentrations were similar to background.

Studies of weathering and translocation of REE in association with clays have been documented (Duddy 1980; Cullers et al. 1975; Xing and Dudas 1993). In the present study, REE and Y in soils probably were not dissolved by PW treatment but inputs from PW quickly formed precipitates as depth intervals neutralized the acidic leachate. REE and Y concentrations in PW were not available but enrichment in depth interval 1 for all REE and Y except Sm suggests loading from PW occurred. Sm was unique among the REE studied as it must have undergone dissolution and solubilization due to the negative enrichment for that element in depth interval 1.

In a review of aqueous geochemistry of REE and Y, Wood (1990) states that F^-, SO_4^{2-}, PO_4^{3-}, CO_3^{2-} and OH^- are both theoretically and experimentally established to be ligands for these elements. In the present study, enrichment of REE and Y was greatest in depth intervals 3, 5 and 7, corresponding with enrichment of the suggested ligands F^- and PO_4^{3-}. REE concentrations had generally reached background by depth interval 9. Sm was unique because concentrations were depleted in the first depth interval relative to background although in subsequent depth intervals this element followed similar behaviour to the other REE studied.

4. Summary

Of the major elements analysed, all except Mn displayed stable EF values near 1 after depth interval 11. This supports other analyses in the present study which indicate a steady state condition formed in the soil-PW system. Positive enrichment of F (EF = 83) and P (EF = 24) occurred in depth intervals 3 and 7, respectively. Increasing pH probably controlled precipitation of F with Al up to depth interval 9 (pH 4.5). Na, K and P were positively enriched throughout the sequence, indicating PW leachates were oversaturated with respect to these elements even after 23 equilibrations with the solid phase. Mn displayed unique behaviour in relation to the other elements and did not reach steady EF values near 1. Low redox potentials may have prevented Mn from oxidizing and precipitating.

Results from trace element analysis show that except for Se, trace elements formed precipitates or were sorbed at different points along the sequence of 23 depth intervals studied. All trace elements were at background concentrations by the 23rd depth interval. Cd and U were positively enriched in separate depth intervals by more than 10 times background concentrations and soils may pose an environmental concern as a result. Se did not appear to be attenuated in any of the depth intervals studied and concentrations in excess of drinking water guidelines may be present in PW leachates even after leachates passed through 23 equivalent depth intervals of calcareous soil.

Rare earth elements and Y were attenuated by depth interval 9 and their mobility was probably controlled through formation of precipitates with F and P. Except for Sm, REE did not appear to be dissolved and mobilized by PW treatment; REE enrichment was probably due to loading from PW only.

CHAPTER V

CONCLUSIONS

The present study was intended to describe precipitation products and residual materials which form when acidic PW is reacted sequentially with calcareous subsoil, in order to assist in predicting the fate of elements of environmental concern which may leach from PG repositories. A sequential batch procedure was undertaken in which 23 samples of a calcareous soil (representing 23 depth intervals) were reacted sequentially with 10 samples of a PW leachate. Solution and solid phase data analysis provides insight into potential contamination from PW leachates interacting with calcareous subsoil below PG repositories.

Solution analyses indicated that pH of the initial leachate was buffered by carbonates but with subsequent leaching, pH reached a steady state value of 5.5. Electrical conductivity leveled off near 3.5 dS m^{-1} from an initial value in fresh PW of 9.0 dS m^{-1}, and leachates may pose an environmental concern due to elevated TDS as a result. Redox potentials in leachates monitored during the study were within the normal range for soils. By the end of the leaching procedure a stable *pe*+pH value near 8.0 was achieved for the initial 10 depth intervals while *pe*+pH of 12.5 described subsequent depth intervals. Calculations of total solids removed from leachates suggest redissolution and precipitation occurred in some depth intervals during the leaching process. Total soluble F in all leachates was below detection by the conclusion of the sequential batch procedure.

Extractable Fe, Al and Si were concentrated in depth intervals 1 through 9. Redox controlled mobility of Fe; all three elements probably experienced dissolution and precipitation within a depth interval. Negative enrichment of total Al and Si occurred as a result of positive enrichment in the fine clay fraction. Tests for CEC hysteresis and pH in NaF did not confirm the presence of allophane in any of the depth intervals studied; competition by F for Al derived from PW and from dissolved phyllosilicate clays inhibited the formation of allophane. CEC and SA were decreased relative to control samples due to F-induced clay mineral dissolution but increases relative to the initial depth interval were observed up to depth interval 9. Carbonate content persisted in PW treated samples after depth interval 11 but total carbon was lost from the system prior to depth interval 9.

Of the major elements analysed, all except Mn had reached stable concentrations by depth interval 11. Mobility of Mn was controlled by redox conditions and Mn precipitated after depth interval 7 in conjunction with the presence of carbonates. Soils were enriched with respect to P, Na and K throughout the sequence. Environmental concerns may exist due to enrichment of F, P, Cd and U at more than 10 times background concentrations. F enrichment early in the sequence was consistent with enrichment of the fine clay sized fraction, and with decreases in soluble F and EC. F attenuation in this study occurred in conjunction with Al, Si, Ca and P enrichment. Trace and rare earth element mobility was controlled in initial depth intervals through precipitation with P, S and F, and by sorption to fresh precipitates of Fe, Si and Al. In later depth intervals some trace elements including Cd, Ni and Zn were precipitated with carbonates. Se did not appear to be attenuated anywhere along the calcareous soil sequence.

The results of the present study show that through a variety of attenuation mechanisms, most elements of environmental concern in PW leachate are effectively attenuated by an Alberta calcareous soil. Immediately below a PG repository, an acidic, noncalcareous soil may exist which is enriched with U, P and F, as well as amorphous Al, Si, and Fe, and which displays variable CEC and SA properties. This may be underlain by calcareous soil with a near neutral pH in which more oxidized conditions prevail, and which is enriched with trace metals and displays CEC and SA properties comparable to a typical Alberta calcareous soil. This laboratory analog of a PG repository shows that (1) issues with respect to radioactivity, F and trace elements in soil must be considered before soil below PG repositories is moved or exposed; (2) PW leachate may present a regulatory concern with respect to TDS and Se, but not F after leaching through calcareous soil; (3) with continued leaching, remobilization of some elements of environmental concern may occur; and (4) some trace metals, including Cd, Ni and Zn, will not be attenuated below repositories underlain by noncalcareous soil.

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