

# **Aging reactions in residues**

## **Final report**

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## SAMMANFATTNING

Syftet med denna studie var att undersöka om väsentliga vittringsreaktioner uppträder vid åldring av vanligt förekommande slagger och askor och om sådana reaktioner inverkar på utlakningen av miljömässigt intressanta ämnen från dessa material.

Materialen i studien var finfraktionen (<4 mm) av prover på åldrad bottenaska från avfallsförbränning samt på åldrad stålslagg. Bottenaskan var ursprungligen en sorterad (2-35 mm) omagnetisk fraktion från en avfallförbränningsanläggning för 200 000 ton avfall per år och stålslaggen var ursprungligen den omagnetiska 0-300 mm fraktionen från en skrotbaserad, låglegerad stålsproduktion i ljusbågsugn. Båda materialen hade lagrats utomhus i lysimetrar i 4,5 år innan prov från fyra olika nivåer togs ut från vardera lysimetern för detta projekt. Även torkade och lagrade arkivprover ingick i undersökningen.

Porvatten extraherades i centrifug i speciella Teflon-burkar med Teflon filter. Materialen extraherades med olika extraktionsmedel enligt operationellt definierade metoder för amorf järnhydroxid (askorbinsyra), kristallin och amorf järnhydroxid (dionat), amorfa aluminiumsilikater (oxalsyra), karbonater (ättiksyra) och utbytbar fraktion (magnesiumklorid). Utlakningen som funktion av pH bestämdes genom pH-statiska lakteter. De geokemiska reaktionerna i porvattnen såväl som i lakvattnen från pH-statiska lakförsök modellerades i MINTEQA2. Alla vattenanalyser gjordes med ICP. Koncentrationerna och förekomstformerna av huvudkomponenterna i den fasta fasens partikelytor bestämdes med hjälp av röntgenfotoelektron-spektroskopi (XPS).

Undersökningarna med XPS visade att båda materialen innehöll amorfa och kristallina glasfaser associerade med en  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-Fe}_2\text{O}_3$  högttemperatursmälta. Det totala innehållet av Ca, Fe och Si i de provtagna fraktionerna (<4 mm) skilde sig från analyserna av respektive ursprungligen undersökt material. Proven innehöll både faser från den ursprungliga högttemperaturprocessen (Al- och Ca-silikatglas och kristallina silikatmaterial innehållande Al och Ca) och typiska vittringsprodukter såsom hydroxider och karbonater. Resultaten tydde även på att det hade bildats lerliknande aluminiumsilikater. Amorfa aluminiumsilikater återfanns i större grad i de övre lagren av bottenaskan än i de lägre lagren, samtidigt som förekomsten av karbonater var mindre i de övre lagren. I proverna från stålslagg var kalciumkarbonat mer förekommande i de vittrade proverna än i arkivprovet. I de vittrade proverna erhöles även amorfa och kristallina aluminiumoxider samt låga koncentrationer av kristallina och amorfa Fe-faser. I stålslaggen erhöles endast små skillnader mellan de olika nivåerna vad gäller identifierade faser av vittringsprodukter.

Extraktionerna med olika extraktionsmedel visade på vilka ämnen som hade inkorporerats i de nybildade faserna. I bottenaskan erhöles Al, Si och Fe huvudsakligen bundna i amorfa aluminiumsilikater, medan Mn till största delen extraherades från den kristallina järnfasen. De amorfa aluminiumsilikaterna innehöll vidare den huvudsakliga delen av de extraherbara mängderna As, Ba, Cu, Mo, Ni, V och Zn samt lika mycket Co och Cr som i den kristallina järnfasen. Karbonatfasen innehöll huvuddelen av Ca och Mg samt Cd och Pb. I stålslaggen var huvudkomponenterna Ca, Al, Si och Fe bundna i olika faser, där Fe huvudsakligen återfanns i den amorfa aluminiumsilikatfasen och Al och Si i den kristallina järnfasen. Karbonatfasen innehöll främst Ca samt även Mg, Pb och V. Några ämnen (Cr, Zn, Cu, As och Mo) var lika distribuerade mellan den kristallina järnfasen och den amorfa aluminiumsilikatfasen. Den kristallina järnfasen innehöll dessutom huvuddelen av extraherbar Ba och Cd och i den amorfa

aluminiumsilikatfasen återfanns även den största delen av Ni och Co. Endast några få ackumuleringsfronter återfanns i lysimetrarna. Innehållet av Ca, Cd och Pb i den amorfa järnfasen var förhöjd hos det översta lagret i stålslagglisimetern. Halten av Mo var för samtliga extraherade faser förhöjd i näst översta nivån i lysimetern med bottenaskan.

Geokemisk modellering med programmet MINTEQA2 indikerade löslighetskontroll av koncentrationerna i porvattnet för ett flertal ämnen. I bottenaskan visade utfallet att lösligheten kontrollerades av sulfater för Ba, Cr, Ca och K, av karbonater för Cd, Cu, Mn och Mg, av oxider för Cu, Mn och Si samt av silikater för Na. I porvattnen från stålslaggen var motsvarande resultat att lösligheten kontrollerades av oxider för Cu, Al, Si och Fe, av karbonater för Cd och Mg, av sulfater för Ba och Cr och av silikater för Mg, Ca, K och Na.

Sammanfattningsvis visade studien att åldringsprocesser hade väsentligt förändrat materialen under de 4,5 år som de lagrats utomhus och att nya faser och mineral hade bildats. I bottenaskan dominerade vittringsprodukterna amorfa aluminiumsilikater, kristallina järnhydroxider och karbonater. I dessa nybildade faser inneslöts ett antal intressanta ämnen såsom Cu, Cr och Cd. För stålslaggen var karbonater de dominerande vittringsprodukterna vilka innehöll bl a Cd, Pb och V. De vittringsprodukter som identifierats i denna studie kommer att ha betydelse för det fortsatta utlakningsförloppet vid nyttiggörande av materialet eller vid deponering.

## ABSTRACT

**Objectives:** The purpose of this study was to determine if beneficial aging reactions are occurring in commonly produced ashes and slags, and if they are important in controlling the environmental leaching behavior of contaminants of concern.

**Materials:** Fine size fractions (< 4 mm) from samples of aged municipal solid waste bottom ash and steel slag. The bottom ash was originally the non-magnetic 2-35 mm fraction from a 200,000 tonne/year facility and the steel slag was originally the screened, non-magnetic 0-300 mm fraction from an electric arc furnace plant designed to produce low alloy steel from scrap steel. The materials had been stored outdoor in lysimeters for four and a half year before samples from four depths in each lysimeter were taken. The raw, archived materials were also studied.

**Methods:** Pore waters were extracted in specially constructed Teflon centrifuge tubes and Teflon filter supports. Elements were extracted from operationally defined phases such as hydrous ferric oxide (ascorbic acid), crystalline and amorphous iron oxide (dithionite), amorphous aluminum silicates (oxalic acid), carbonates (acetic acid) and exchangeable fraction (magnesium chloride). Element concentrations and speciation of the major elements were determined from particle surfaces by X-ray photoelectron spectroscopy (XPS). The pH static leaching behavior was tested. The thermodynamic equilibrium source code MINTQA2 was used to model geochemical reactions in the pore waters as well as in the pH-dependent leaching. Analysis of leachates were made on Inductively Coupled Plasma Spectrometry with High Resolution, Mass Spectrometry or Emission Spectrometry.

**Main outcome measures:** Concentrations in pore waters and pH-static leachates, identified phases and total concentrations in the XPS analysis, extracted amounts of elements from extraction tests and saturation indices as indicated from the geochemical modeling.

**Results:** The XPS speciation data suggested that both wastes were glassy materials containing typical glass and crystalline phases associated with a CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub> high temperature, low pressure melts. The total content of Ca, Fe and Si were different in the <4 mm fraction in both materials in comparison to the original analysis of the material. The samples contained both phases from the original high temperature process, Al and Ca silicate glasses and crystalline silicate minerals containing Al and Ca, and typical weathering products such as hydroxides and carbonates. There was also evidence for clay like aluminosilicates. Amorphous aluminum silicates were more abundant in the upper sample levels of the bottom ash lysimeter and carbonates were less abundant in the same samples. There was more calcium carbonate present in the steel slag lysimeter samples than in the raw archived sample. There was also a clear presence of amorphous and crystalline aluminum hydrous oxides. Low concentrations crystalline and amorphous Fe phases were also present. There were small differences with depth in the amounts of weathering products between sample levels in the steel slag samples. In the bottom ash the components Al, Si and Fe were mainly bound in amorphous Al silicates. The amorphous Al silicates contained the major part of extractable amounts of As, Ba, Cu, Mo, Ni, V (raw material) and Zn, and equal part of Cr as in the crystalline Fe phase. Ca and Mg were mainly found in the carbonate phase and together with these were also Cd and Pb extracted in that phase. The major part of Mn was found in the crystalline Fe phase. Cr and Co was equally distributed between the amorphous Al silicates and crystalline Fe phase. In the steel slag the main components Ca, Al, Si and Fe were bound in different phases. Fe was mainly bound in amorphous Al silicates and Al and Si mainly found in the crystalline Fe phase. The major part of Ca was found in the carbonate phase. In addition the carbonate phase included the major part of

Mg, Pb and V. Cr, Zn, Cu, As and Mo were found in the crystalline Fe phase and in the amorphous Al silicate phase. Also a major proportion of Ba was found in the crystalline Fe phase. The amorphous Al silicate phase contained the major part of Ni and Co. Cd was found to a larger extent in the crystalline Fe phase than in the carbonate phase. Few accumulation fronts were seen in the lysimeter samples. The contents of Ca, Cd and Pb in the amorphous Fe oxide phase were elevated at the top sample level in the steel slag lysimeter. The content Mo was elevated at the upper middle sample level in the bottom ash lysimeter in all extracted phases. Geochemical modeling by use of MINTEQA2 indicated solubility control of the concentrations in the pore waters of several elements. In the bottom ash pore waters solubility control was indicated for sulfates containing Ba, Cr, Ca and K, carbonates containing Cd, Cu, Mn and Mg, oxides containing Cu, Mn and Si and finally silicates containing Na. In the steel slag pore waters solubility control was indicated for oxides containing Cu, Al, Si and Fe, carbonates containing Cd and Mg, sulfates containing Ba and Cr, and silicates containing Mg, Ca, K and Na.

**Conclusions:** The study showed that aging had occurred in the materials at storage over 4 years outdoors, and that new phases and solids had developed. For bottom ash, amorphous aluminosilicates, crystalline iron oxides and carbonates were the dominant weathering products; associated with the retention of many elements of concern e.g. Cu, Cr and Cd, respectively. For steel slag, carbonates were the dominant weathering products, associated with the retention of Cd, Pb and V. These types of weathering products are considered to be beneficial with respect to utilization or long term disposal.

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## 1 INTRODUCTION

One of the basic aspects of the AFR program on waste materials is the use of these materials, where suitable, in the construction of highways, etc. Swedish society has discussed recycling of materials into infrastructure construction for decades as a means to conserve natural resources and make use of inherent properties in certain waste materials. However, the concern from environmental authorities has so far not made a wide use of these materials possible.

Wastes from high temperature processes are very good secondary materials suitable for utilization in highway environs; these include slags from smelting operations and steel recycling operations, bottom ash from coal combustion and municipal solid waste incineration (MSWI), fly ash from coal combustion, clinker from cement calcining, etc. These types of wastes are widely used in other countries in Europe as well as in Japan and North America (OECD, 1997). These types of materials possess the necessary engineering properties that allow them to be used as aggregate substitutes in asphalt and Portland cement, as structurally sound aggregates, and as admixtures in Portland cement (Goumans et al., 1991, Goumans et al., 1994, Goumans et al., 1997). In many countries their environmental properties are also acceptable with respect to leaching behavior (Goumans et al., 1991, Goumans et al., 1994, Goumans et al., 1997).

However, waste from high temperature processes are geochemically unstable and require aging before they can be used (Chandler et al., 1997). This is a common requirement for waste that crystallize quickly after being in a molten state (Chandler et al., 1997). Disequilibrium is usually the case because the mineral phases within the waste material are neither in equilibrium with each other nor with moisture or oxygen present in the environment that they are eventually exposed to.

There are a variety of aging reactions that can occur in a waste material. These can include swelling reactions such as the formation of expansive crystals of  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  in bottom ash (Chandler et al., 1997) or  $\text{Ca}(\text{OH})_2$  in blast furnace slags (Farrand and Emery, 1995). These have been studied for steel slags, coal ash, bottom ash, etc. because they prevented the use of waste materials and can be, in part, rectified by altering the high temperature process. These types of reactions might be considered deleterious and can be controlled by altering components in the melt system of aging the material prior to use.

Other types of aging reactions can be considered to be beneficial in that they can immobilize contaminants in the waste. They involve the (i) weathering of particle surfaces and the formation of secondary minerals that can immobilize contaminants of concern via co-precipitation processes into stable mineral phases or (ii) the formation of sorptive surfaces that can sorb contaminants of concern. These are not as well studied.

Knowledge as to the magnitude and importance of these beneficial reactions is necessary to fully understand the environmental impact/benefit of using these types of waste materials. Methods such as surface spectroscopy (Eighmy et al., 1994) and sorption modeling (Meima and Comans, 1998) can be used to identify if these processes are occurring in aged materials and how important they may be for waste materials.

In this project the aging phenomena is studied in two different types of waste materials from high temperature processes—MSWI bottom ash and scrap steel slag. The wastes have been aging for over 4 years in outdoor lysimeters exposed to precipitation and to the atmosphere.

The bottom ash is a not fully oxidized material containing trace elements of concern such as Pb, Zn and Cu. When it weathers, minerals in the residue transform into carbonates, aluminum oxyhydroxides, ferric oxyhydroxides, allophane-like hydrous silicates, and neoformed clays. These are potential sorptive surfaces and secondary minerals. Bottom ash also has relatively high levels of organic carbon that may promote sorption or mobilization of the trace elements.

The steel slag is a slightly reduced material containing trace elements such as Cr and V. When it weathers, elemental and ferrous iron presumptively oxidize to hydrous ferric oxides. These are potential sorptive surfaces and secondary minerals.

In addition to studying these two wastes, we are also looking at aging as a function of depth within the lysimeter. This may show phenomena associated with sequential dissolution and precipitation of constituents in “fronts” as leachate migrates downwards in the lysimeters. Such phenomena are important in deposits and have been seen for coal fly ash (Warren and Dudas, 1985, van der Hoek, 1994) and in MSWI bottom ash (Meima, 1997).

These two waste have been previously studied in an earlier AFR project by Fällman (1997). The total composition of the two materials, as determined in that project, is presented in Table 1. The leachates from the lysimeters were followed over a period of 3.5 years. The pH in the leachates were close to 8 initially from the MSWI bottom ash and increased on occasions towards 8.4. The pH in the leachates from the steel slag was closer to 9 initially and decreased towards pH 8.4 over time. The dominating constituents in the leachates (>99%) were Ca, Mg, K, Na, Cl, S and for the steel slag also Si and V. Major components leached to the greatest extent in comparison to the total content were Mg and Si from the steel slag and Mg and Ca from the MSWI bottom ash. Fe was leached only in insignificant amounts. From the salts 3-5 % of the total content of Na, K and S were released from MSWI bottom ash. The steel slag also leached 3% of Na, but less of S and K, 0.4 %. Oxyanions (Cr, V and Mo) were leached in greater amounts from the steel slag than from MSWI BA and the opposite was seen for cations where Zn, Cu and Ni were ones leached to greatest amounts from the MSWI bottom ash.

## **2 OBJECTIVES**

The purpose of this present study was to determine if beneficial aging reactions are occurring in these two wastes, and if they are important in controlling the environmental leaching behavior of contaminants of concern.

## **3 MATERIALS AND METHODS**

### **3.1 Waste Materials**

The municipal solid waste incineration (MSWI) bottom ash was obtained from a 200,000 tonne/year facility. The plant is a mass burn type with moving grates. Grate siftings are generated along with the bottom ash. The ash is water quenched before it is screened and magnetic material is removed at an ash processing facility. The size fraction obtained for this work was 2-35 mm. Approximately 15 m<sup>3</sup> of material was collected. The steel slag was obtained from a plant designed to produce low alloy steel from scrap steel. The steel slag is generated by periodic dumping of molten material from the electric arc furnace. The slag is excavated from below the furnace and transported to an intermediate storage area while still in a hot, plastic state. It is then cooled by sprinkling. The slag was screened and magnetic materials were

removed prior to sample collection. The size fraction obtained was 0-300 mm. A 15m<sup>3</sup> sample was collected. The steel slag sample was collected in December 1992 and the MSWI bottom ash sample in February 1993. For the purposes of this study, we focus on the finer size fractions (<4 mm) as this constitutes the most significant size fraction with respect to surface area. Data on the total content of the materials are presented elsewhere (Fällman 1997).

### **3.2 Lysimeters**

The approximate 10 m<sup>3</sup> of each material were placed in specially constructed lysimeters located at the Lysimeter Facility at SGI. Samples were introduced into the lysimeter on December, 1992 (steel slag) or February, 1993 (bottom ash). At that time, representative samples (0.3 m<sup>3</sup>) of each material were collected for further analysis (see below).

The lysimeters were constructed to dimensions of 3.0 x 3.0 x 1.2 m so that the largest particle size was less than 1/10 the width of the lysimeter as is custom for flow through leaching systems (Hjelmar, 1991). The walls of the lysimeter were made with plywood (externally braced) and covered with a preformed HDPE liner. A geotextile with a fixed synthetic drainage layer was used to prevent fines from infiltrating the leachate collection lines. The leachate was collected at the center bottom of the lysimeter and directed through a PVC pipe to the basement of the adjacent SGI building. A water trap was used to prevent the atmosphere from entering the pipe. A tipping bucket system was used to measure leachate quantity over time. Leachate was then collected from a proportional sampler maintained under Ar to minimize the impact of O<sub>2</sub> or CO<sub>2</sub> on leachate quality. A nearby meteorological station was used to record adjacent precipitation amounts. Data about leachate quality over time has been presented elsewhere (Fällman, 1997).

### **3.3 Lysimeter Coring**

Aged samples with depth in each lysimeter were collected using coring and manual excavation procedures. The bottom ash lysimeter was cored on September 18, 1997 in two locations using a manual screw auger (diameter of 20 cm). Samples were collected at the following four depth intervals: 0.03-0.12 m, 0.35-0.45 m, 0.70-0.80 m and 1.00-1.10 m. As material was excavated it was placed in a bucket under N<sub>2</sub>/Ar and mixed prior to storage in 2 L plastic bags under N<sub>2</sub>/Ar before transport to an N<sub>2</sub> glovebox for further handling.

The steel slag was excavated with depth on October 7, 1997. A trowel was used to carefully excavate samples. However, given the large grain size distribution, it is likely that some materials near the surface of the lysimeter sifted downwards during the excavation. Samples were taken from a corner of the lysimeter to facilitate collection with depth. The footprint of the excavation was 0.7 x 0.7 m at the lysimeter surface decreasing to about 0.3 x 0.3 m at the deepest part of the excavation. The following four depth intervals were used: 0-0.15 m, 0.17-0.32 m, 0.43-0.57 m and 0.68-0.83m. Similar N<sub>2</sub>/Ar procedures to those used for the bottom ash were used for sample handling. However, because of the large particle sizes, field sieving using a 4 mm sieve was first necessary.

### **3.4 Raw material**

The original raw materials were used a reference point for this present study, they were processed as follows. The bottom ash was collected from the same pile used to fill the lysimeter.

It had been exposed once to water in the quench tank prior to collection. In 1992, the bottom ash was cone and quartered such that a representative sample was stored in a sealed plastic bags exposed at atmospheric pressures. In September, 1997, test sample of (2 kg) the laboratory sample was sieved to collect g of the < 4 mm fraction. This fraction constituted the raw bottom ash working sample. The steel slag was collected from the same pile used to fill the lysimeter. It had been air cooled outdoor and possible exposed to precipitation prior to collection. In 1992, the steel slag was cone and quartered and a 150 kg subsample was stored in a covered plastic barrels. In September, 1997, a barrel was cone and quartered so that a subsample (15 kg) was collected, sieved with a 4 mm sieve, producing a 3 kg sample of the <4 mm fraction. This fraction constituted the raw steel slag working fraction.

### **3.5 Sample preparation**

The samples were stored under N<sub>2</sub> in the glove box. The bottom ash samples were also sieved in the glove box under N<sub>2</sub> to produce <4mm fractions for each sample depth. The samples were split to produce (i) a slurried sample for measuring field pH and Eh (see below), (ii) a sample for pore water extraction (see below), (iii) a sample for measurement of the water content (SS-ISO 10390) and (iv) a sample for drying for subsequent use.

The samples for subsequent use were dried in N<sub>2</sub> glovebags in the presence of Drierite to produce dried test samples. Test samples were then ground (<250 um) for XPS analyses using an agate ball mill. Samples collected for pore water extraction were stored inside 1 L gas tight mason jars while in the glovebox under nitrogen. The glovebox and glovebags were periodically tested for O<sub>2</sub> content and photosynthetic activity using a gas probe for oxygen (GasTech Gas Monitor CO<sub>2</sub> version).

### **3.6 pH and Eh Measurements of Field Sample**

The samples with depth from both of the bottom ash cores and steel slag core were measured for pH using the probe/slurry method (SS-ISO 10390). Approximately, 10 g of moist material was added to 50 mL of deionized water (<0.2 mS/m). A combination electrode, standardized with a two point calibration, was used to measure pH in an open beaker. The beaker was stirred. Stable pH values were recorded three times for each sample. Readbacks on standards were also conducted.

Eh was measured on the same slurry as used for the pH measurements using the platinum electrode/slurry procedure described by Fällman and Aurell (1996). The platinum probe with separate reference cell (Radiometer Ref 401) was checked to a reference solution at pH 7 made from Na<sub>2</sub>HPO<sub>4</sub> and KH<sub>2</sub>PO<sub>4</sub> giving a E<sub>KCl</sub> of 47 mV at 20° C. The beaker was not stirred during measurement. Stable Eh values were recorded three times for each sample. Readbacks on standards were also conducted.

### **3.7 Pore Water Extractions**

Samples were sent to the Netherlands Energy Research Foundation (ECN) in Petten, the Netherlands. The procedure was developed at ECN (van der Hoek et al., 1996; Meima et al., 1997). The pore water extraction procedure uses specially constructed large (500 mL) Teflon (PTFE) centrifuge tubes and Teflon filter supports. The filters were 0.20 um membranes. Approximately 500 g of as received (containing field moisture) material was centrifuged.

Centrifugation (6,000 g for 20 minutes) is used to separate the pore water from the solid material. Yields were about 50 mL per 500g of sample.

### 3.8 Sorbent Surface Extractions

The sequential exchangeable ions and carbonate extraction procedure comes from Tessier et al. (1979). Exchangeable ions were extracted in a 1 M MgCl<sub>2</sub> solution giving a pH 7. The extraction was carried out on 20 g of material in 160 ml of extraction solution. The extraction process was subjected to agitation (end over end rotation at 10 rpm) for 24 hours. The extractant was filtered using a 0.2 µm filter. The material and filter were then subjected to the carbonate extraction step. In this step 160 ml of 1 M Na-acetate adjusted to pH 5.0 with acetic acid is added to bottle with the material and the filter. The extraction is done for 5 hours with an end over end agitation of 10 rpm.

The hydrous ferric oxide (HFO) extraction procedure comes from Meima & Comans (1997). It is based on the use of ascorbic acid as a solvent for the HFO as described by Kostka and Luther (1994). The original method was developed by Ferdelman (1988). It is “operationally selective” for amorphous HFO. The method of Meima & Comans has been modified slightly to extract a larger volume of material. On a L basis, the extraction solution is made with 50 g of sodium citrate and 50 g of sodium bicarbonate added to the deionised water. The mixture is deaerated with N<sub>2</sub> and then 20 g of ascorbic acid is added. The solution should have a pH of 8. 20 g of <4mm dried sample was placed in the bottle with 400 mL of the extractant. The extraction was done at room temperature. The extraction process was agitated (end over end rotation at 10 rpm). The extraction took place for 24 hours.

The crystalline and amorphous iron oxide extraction procedure comes from Meima & Comans (1997). It is based on the use of dithionite as a reductive solvent for the oxidized iron as described by Kostka and Luther (1994). It is “operationally selective” for both crystalline and amorphous iron. Used with the ascorbic acid method, the amount of crystalline iron and amorphous HFO can be determined (by difference). The method of Meima & Comans has been modified slightly to extract a larger volume of material. On a L basis, the extraction fluid is made of 0.35 moles of sodium acetate and 0.2 moles of sodium citrate added to the deionised water. The solution should have a pH of 4.8. Then 50 g of sodium dithionite is added to the buffered solution. 20 g of <4mm dried sample was placed in the bottle with 400 mL of the extractant. The extraction was done at 60 C in a temperature controlled oven. The extraction process was subjected to periodic hand agitation. The extraction was done for 4 hours.

The short range order material aluminium, iron and silica extraction procedure comes from Meima & Comans (1997). It is based on the use of an acidic ammonium oxalate extraction of aluminum and silicate amorphous and partially crystalline phases as described by Blakemore et al. (1987). The original method comes from Tamm (1922). It is “operationally selective” for aluminium, iron and silica in short range order materials. The method of Meima & Comans has been modified slightly to extract a larger volume of material. On a L basis, the extraction fluid is made of 16.2 g of ammonium oxalate and 10.8 g of oxalic acid added to the DDW. The solution has a pH of 3. In the extraction 9 g of <4mm dried was placed in the bottle with 900 mL of the extractant. The extraction was done at room temperature in the dark. The extraction process was subjected to agitation (end over end rotation at 10 rpm) for 4 hours.

All extractions were done in PE bottles (500 or 1000 mL). The bottles were acid cleaned using SGI procedures (6 M HCL (Pro analysi) for two weeks, then 0.05 M HNO<sub>3</sub> (Pro analysi) for one

week or until use. The extraction solution were made from the highest possible grade of reagent. The use of extensive cleanings procedures and high grade reagents is to avoid potential contamination from trace metals in the bottles or reagents. The extractants were filtered using 0.2  $\mu\text{m}$  filters before analysis.

### 3.9 XPS

The determination of element concentrations and speciation of the major elements from particle surfaces was done using X-ray photoelectron spectroscopy (XPS). For this work, the MOSES XPS spectrometer, located at the Department of Physics and Measurement Technology at Linköping University, was used. The instrument is a specially designed and built ultrahigh vacuum electron spectrometer system. It consists of three vacuum chambers: a small sample introduction chamber (with roughing and turbomolecular pumps), a sample prep chamber (with turbomolecular and ion pumps), and a sample analysis chamber (with turbomolecular and ion pumps). A sample transfer shaft is used to move samples between the three chambers. Typical base pressures in the analysis chamber were between 5 and  $10 \times 10^{-9}$  torr. A Mg k-alpha x-ray source was used (1400 eV, 15kV, 300 watts); it was situated in line with the sample shaft. The target surface is tipped 45 degrees relative to the x-ray illumination and 45 degrees relative to the entrance lens to the electron detector. The Scienta detector is a 180 degree hemispherical analyzer with a retarding four element electron lens. A simulated multi-channel electron detector is used.

Ground bottom ash or steel slag powder samples (<250  $\mu\text{m}$ ) were pressed onto the sticky side of copper tape. The tape is conducting; it facilitates the loading of powders into the sticky adhesive while allowing for charge conduction. Two pieces of copper tape were used to provide sufficient coverage of the sample holder target surface. Samples were carefully tapped clean to prevent any loose particulates from contaminating the vacuum system.

Initially, a broad scan at a pass energy of 150 eV was collected between 1,100 and 0 eV to identify photoelectron peaks of interest. Typical scan times were 20 to 30 minutes. Then detailed, high resolution scans of photoelectrons of interest were collected at a lower pass energy (50 eV) to permit better resolution of spectral features. Typically, high resolution scans were collected within 15 to 25 eV regions. Typical scan times ranged from 30 minutes to 2 hours for each region.

The results from the investigation contains information on the elements that were detected and a statistical measure (goodness of fit) about the quality of the curve fitting exercise, the concentration of the element, the type of photoelectron that was analyzed, the charge-corrected binding energy of the photoelectron peak, any spin orbit separations that were fixed during curve fitting, the full width, half maximum (FWHM) of the peak, the area counts for the peak and their relative abundance, and the likely mineral phase identified using the National Institute of Standards and Technology (NIST) XPS database.

The calculation of atomic concentrations in the powdered samples used the quantification procedure and atomic sensitivity factors established by Scienta. For Ca, the sensitivity factor of 0.44 was reduced by a third, as only the Ca 2p<sub>3/2</sub> was quantified.

Curve fitting of the complex spectra was facilitated using the adventitious carbon energy referencing method to correct for charging (Barr et al., 1995). Charging was observed at values between 3.5 and 5.5 eV; fairly typical for insulated samples. Generally, the largest C 1s peak was

assigned the binding energy of 284.65 eV for a spectrometer calibrated to a gold standard of 83.85 eV for the Au 4f<sub>7/2</sub> peak.

The process of curve fitting complex spectra containing peaks from multiple species was facilitated using FWHM values from the literature as starting values (Eighmy et al., 1997). The assignment of mineral phases to each peak was also done so that the data were internally consistent; for a mineral such as wollastonite (Ca<sub>3</sub>Si<sub>3</sub>O<sub>9</sub>) the mineral would be identified by the Ca 2p<sub>3/2</sub>, Si 2p and O 1s photoelectrons. Despite using this criteria, it is still difficult to actually discriminate between certain minerals as their component photoelectrons have similar binding energies.

### 3.10 pH-Dependent Leaching

pH static tests for the bottom ash and the steel slag were conducted using the procedure outlined in Fällman & Aurell (1996). It is based on the use of a low L/S (5) ratio that ensures near chemical equilibrium while still allowing for mixing. The extraction occurs over 24 hours at fixed pH values. The pH static tests was used for examining the pH dependent leaching of elements at four environmental pH values for two of the four lysimeter samples from each lysimeter—the top sample and the upper middle sample.

Extractions were done using the Radiometer TIM 90 titrator. The vessel was a PE beaker (1000 mL). It was stirred with a PTFE-coated propellar. The beakers were acid cleaned and acid-soaked using SGI procedures (6 M HCL (Pro analysi) for two weeks, then 0.05 M HNO<sub>3</sub> (Pro analysi) for one week or until use. HNO<sub>3</sub> (0.1 to 0.5 M) or NaOH (0.5M) were used to control the pH at +/- 0.05 pH units. The acid and base were made of Pro analysi grade materials. During the extraction, the beakers were covered. A LS of 5 was used, 50 g of dried <4mm material was placed in the bottle with about 230 mL of deionised water. This allows for about 20 mL of acid/base to be used to control the pH. The extraction was done for 24 hours at room temperature.

The tests were conducted at pH values of 6, 8, 10, and 12. These were selected to bracket the pH between freshly aged ash and slag, and potential future pH values. For the sorbed concentration test on the bottom ash, the test was conducted at a pH of 2. This allowed the recovery of Pb and Zn. For the sorbed concentration test on the steel slag, the test was conducted at a pH of 10. This allows the recovery Cr and V.

The leachants were filtered through 0.2 um filters (using cleaned filters and cleaned filter apparatus) and then split into three samples. One split was preserved with HNO<sub>3</sub> for analysis by AAS, GFAAS, or ICP-MS for the elements of interest (e.g. Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, Pb, S, Si, V, and Zn). Additionally, Na and K were analyzed. The second split was left unpreserved and analyzed by IC for Cl and SO<sub>4</sub>. The third split was analyzed for carbonates using an IR procedure.

### 3.11 Pore Water, Extract and Leachate Analyses

All routine analyses were conducted by SGAB AB in Luleå. ICP-AES, -MS or high resolution methods were used for the elements of interest (Al, As, Ba, Ca, Cd, Cl, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, Pb, SO<sub>4</sub>, Si, V, and Zn). Samples were always split into three subsamples: (i) those for metals analysis by ICP (preserved with HNO<sub>3</sub>), (ii) those anions for analysis by ion

chromatography (unpreserved), and (iii) those for carbon analysis by TOC or TIC (unpreserved). TOC and TIC in the pore water was analyzed by an IR-based method.

### **3.12 Geochemical Modeling of Pore Waters and pH-Dependent Leachates**

The geochemical thermodynamic equilibrium source code MINTQA2 ( Allison et al., 1990 ) was used to model both geochemical reactions (solid phase control) occurring in the pore water as well as the reactions (solid phase control) occurring during pH-dependent leaching. Methods are based on those detailed elsewhere (Fällman, 1997, Meima, 1997).

For modeling solid phase control in the pore water samples, pore water constituents were entered into the model. pH was fixed at the measured pH of the sample. The Davies equation was used to calculate activity coefficients. Temperatures were also set at 25° C. All constituents were entered into the model, no solids were allowed to precipitate, no sorption reactions were specified, and the principal outputs were the saturation index (SI) for minerals of interest and the speciation of aqueous components.

## **4 RESULTS**

### **4.1 Samples and Pore waters**

#### **4.1.1 Water Content, pH and Eh**

##### **4.1.1.1 Bottom ash**

Samples collected during the coring operation of the bottom ash lysimeter were subjected to moisture analysis, pH determination, and redox measurements in an attempt to better describe major geochemical system parameters with respect to depth in the lysimeter. The bottom ash lysimeter was cored in duplicate. In the bottom ash lysimeter, there was a distinct possibility of having a more oxidized zone at the top of the lysimeter and a more reduced zone at the bottom of the lysimeter because of the lower hydraulic conductivity of the bottom ash (especially compared to the steel slag). Further, the presence of organic carbon and microbial activity could generate a reducing zone in the lysimeter; similar to ones seen by Meima (1997). This required further evaluation.

As shown in Tables 2-3, the water contents of the bottom ash samples as a function of depth was fairly constant and low; about 100 to 150 ml of pore water per kg dry matter of the < 4 mm material ( $w_n = 0.10-0.15$ ). Both cores were similar in the values that were observed. This indicates that at all levels, the larger pores were not saturated and some of the smaller pores were saturated. Such conditions are conducive to the diffusion of oxygen and carbon dioxide into open pores and into saturated pores at all depths in the lysimeter.

The pH values of the bottom ash slurries (7.69 to 7.84) indicate that  $\text{HCO}_3$  and gypsum probably are the principal buffers in the sample-pore water system. The pH ranges observed in the replicate samples excavated with depth show some no significant differences with depth.

The Eh measurements of the bottom ash slurries indicate that the bottom ash is oxidized (see Tables 2-3). Such values are similar to those observed by Fällman (1997) in earlier studies on the bottom ash. The Eh ranges observed in the two cores are very similar. However, there is no direct connection between the organic carbon content in the pore waters and the redox

measurements. The redox conditions in the bottom ash samples are slightly more reduced than the steel slag samples.

#### **4.1.1.2 Steel Slag**

Samples collected during the coring operation of the steel slag lysimeter were subjected to moisture analysis, pH determination, and redox measurements in an attempt to better describe major geochemical system constraints on the samples with respect to depth in the lysimeter. Even though the lysimeter had no apparent perched water table, the possibility of having a more oxidized zone at the top of the lysimeter and a more reduced zone at the bottom of the lysimeter required evaluation. Furthermore, concentrations of metals, salts and carbon, inorganic and organic, were determined.

As shown in Table 4, the water contents of the samples as a function of depth was fairly constant and low; about 60 to 70 ml of pore water per kg dry matter of the < 4 mm material. This indicates that at all levels, the larger pores were not saturated and only a fraction of the smaller pores were saturated. Such conditions are conducive to the diffusion of oxygen and carbon dioxide into open pores and into saturated pores at all depths in the lysimeter. One would therefore expect that if significant pH or Eh gradients existed, they would be inside large particles themselves and not as a function of depth in the lysimeter.

The pH values of the steel slag slurries (9.5 to 9.7) indicate that  $\text{CaCO}_3$  is probably the principal buffer in the sample-pore water system. The pH ranges observed in the replicate samples excavated with depth show some slight differences with depth; the top layer (exposed directly to the atmosphere) has pH values slightly lower than the rest of the samples with depth. This could be due to greater  $\text{CO}_2$  reaction with  $\text{Ca}(\text{OH})_2$  and the formation of  $\text{CaCO}_3$  or the preferential leaching or acid-base reaction of  $\text{CaCO}_3$  with the acidic precipitation, resulting in the preferential loss of  $\text{CaCO}_3$ . There was more organic carbon in the pore water of the steel slag than expected. The largest amount of organic carbon was found in the upper part of the lysimeter and could be a source of  $\text{CO}_2$  for the formation of  $\text{CaCO}_3$  followed by the decrease in pH.

The Eh measurements of the steel slag slurries indicate that the slurries overall are oxidized (see Table 4). Such values are similar to those observed by Fällman (1997) in earlier studies on the steel slag. The original slag is a reducing material (dominated by  $\text{Fe}^{2+}$ ,  $\text{S}^0$ , and  $\text{Cr}^{3+}$  redox couples) so clearly there has been some oxidation reactions occurring as the material has oxidized slowly over time in the presence of  $\text{O}_2$ . The redox conditions evaluated in relation to pH (pe+pH) in the samples excavated with depth show some slight differences with depth; the two upper layers have pe+pH values slightly lower than the rest of the samples with depth. This is likely due to the higher TOC content in the pore water of the upper layers and a decrease in redox potential due to microbial activity.

#### **4.1.2 Concentrations in pore waters**

Pore waters collected from sampled material by centrifugation were analyzed for inorganic components and total organic content (TOC). Results are presented in Tables 2-3 and in Figures 1-10 for bottom ash samples and in Table 4 and Figures 11-15 for steel slag samples.

#### **4.1.2.1 Bottom ash**

##### **Major components (Al, Ca, Fe, Mg, Mn, Si)**

Pore water concentrations are commented in the order from the most abundant to the least abundant component (see Figures 1-2). Pore waters from the bottom ash samples contained Ca in the highest concentrations (650-900 mg/l). There was some difference in concentrations with depth where the highest concentrations were found in the top layers. Similar patterns were found in the two cores. Mg was the second most abundant component (40-220 mg/l). The concentrations increased with depth in both profiles. Si was evenly distributed in the profile with a concentration of 3-4 mg/l. Mn was more abundant (0.01-2.9 mg/l) than Fe but with a concentration profile that was dependent on the TOC content. The Mn concentration in the upper middle level in profile 1 decreased drastically where the TOC concentration was high probably due to reduction of Mn. Some decrease was also seen in profile 2 but not with the corresponding increased TOC concentration. Al concentration (0.06-0.2 mg/l) decreased with depth in profile 1 but was fairly constant in profile 2. Finally, Fe content (0.01-0.2 mg/l) in pore water decreased with depth in profile 1 but showed a varied concentrations in profile 2.

##### **Salts (Na, K, Cl, SO<sub>4</sub>)**

Salts concentrations generally increased with depth see (Figures 3-4). Concentrations of Na, K and Cl were close together at levels of 60 –640 mg/l. SO<sub>4</sub> on the contrary generally had higher concentrations and less pronounced increase with depth (1700-3000 mg/l). However, a comparison made on the sulfur content gave more similarities between the different salt components. Sulfur was together with Na, K, Ca and Cl the most abundant components in the pore waters.

##### **Oxyanions (As, Cr, Mo, V)**

Concentrations of oxyanions are shown in Figures 5-6. Mo was most abundant of the oxyanions at concentrations of 60-450 µg/l. Concentrations increased with depth with a pronounced peak in profile 2 at the lower middle level. Cr concentrations increased in the upper middle level in both profiles, but most pronounced (600µg/l) in profile 1 where also the TOC concentration was high. Below this level the concentrations of Cr in the two profiles came to more similar levels (0.9-3.7 µg/l). The concentrations of As (1.6-4.1 µg/l) gave an inverted but less pronounced pattern in comparison to Cr with some decrease in concentration at the upper middle level. Finally, the V concentrations in the pore water was very low 0.8-1.6 µg/l with fairly constant values in relation to depth.

##### **Trace elements (Cd, Cu, Ni, Pb, Zn, BA, Co, Hg)**

Concentrations of trace elements are presented in Figures 7-10. Concentrations of Zn reached the highest levels of these elements (160-310 µg/l). The levels increased somewhat with depth. The concentrations of Cu was generally higher in profile 1 (59-92 µg/l) than in profile 2 (38-52 µg/l). Ni concentrations (14-28 µg/l) increased with depth and were similar in the two profiles. Cd concentrations (1.4-3.2 µg/l) increased slightly with depth which also was the case for Pb (0.8-2.3 µg/l). Ba concentrations were similar in the entire profile with concentrations of 43-53 µg/l. The content of Co in the pore waters (1.8-23 mg/l) varied within one order of magnitude in the profiles and with different patterns for the two profiles. Finally, Hg concentrations (0.03-0.23 µg/l) increased with depth in both profiles.

##### **Carbon content (TOC, TIC)**

The content of organic (TOC) and inorganic (TIC) carbon in the pore waters are presented in Figures 11-12. The TIC content was similar in the two profiles (30-50 mg/l) and did not change

with depth to any great extent. The TOC content differed between the two profiles. Profile 1 generally contained more organic carbon in the pore water than what was obtained in profile 2. Especially the upper middle sample in profile 1 had a very high TOC content (520 mg/l) in comparison to the other samples. In profile 2 there was an increase in TOC content with depth and a maximum content was obtained at the lower middle level.

#### **4.1.2.2 Steel slag**

##### **Major components (Al, Ca, Fe, Mg, Mn, Si)**

Pore water concentrations are commented in the order from the most abundant to the least abundant component (see Figure 13). The highest concentrations of a single element in the pore waters from the steel slag samples was Ca (61-73 mg/l). There was some difference in concentrations with depth where the highest concentration was found in the top layer. Si was the second most abundant component (34-43 mg/l). Si was evenly distributed in the profile. Mg was found in the concentrations of 5.5-9.6 mg/l and also here was the highest value found in the top layer. This gave a similar behavior of Mg as for Ca. The three remaining elements ( Fe, Al and Mn) were grouped at a lower concentration level ( 0.003-0.03 mg/l) where the values mainly were parallel. The highest concentrations were found in the upper middle level for Al and Fe while the top sample held the highest value of Mn.

##### **Salts (Na, K, SO<sub>4</sub>)**

Salts concentrations generally increased with depth see (Figure 14). Concentrations were spread between the substances. SO<sub>4</sub> had the highest concentrations, 36-48 mg/l, corresponding to 15-20 mg S/l. Na and K concentrations were relatively low 5-12 mg/l and 1.4-2.7 mg/l respectively. K concentrations increased slightly in the top level.

##### **Oxyanions (As, Cr, Mo, V)**

Concentrations of oxyanions are shown in Figure 15. V was the most abundant oxyanion with concentrations of 1.1-3.5 mg/l in the pore water. Concentrations increased steadily with depth. Mo and As concentrations were relatively constant at a level of 120-140 µg/l and 8-10 µg/l respectively in the profile. Cr content was lower in the two upper levels ( 25-28 µg/l) and increased in the two lower levels to 39-48 µg/l.

##### **Trace elements (Cd, Cu, Ni, Pb, Zn, Ba, Co, Hg)**

Concentrations of trace elements are presented in Figures 16 and 17. Concentrations of Cu reached the highest levels ( 17-280 µg/l) of these components with a pronounced decrease with depth. A similar pattern was seen for concentrations of Ni ( 1.7-12 µg/l). Zn and Pb (6-18 µg/l and 0.4-1.0 µg/l, respectively) concentrations increased from the top to the upper middle level and decreased thereafter. Ba, Cd and Co concentrations were relatively constant in the profile with some increase at the top level. The concentrations were for Ba 105-155 µg/l, Cd 0.47-0.60 µg/l and for Co 0.05-0.15 µg/l. Concentrations of Hg was 0.09-0.12 µg/l with highest values in the top layer.

##### **Carbon content (TIC, TOC)**

The inorganic and organic content in the pore waters are presented in Figure 18. The inorganic content (TIC) in the pore waters was relatively low (<10 mg/l) in the entire profile. The content was not detectable in the upper middle sample. Higher concentrations were expected since the pH indicated a possible pH control by calcite. The organic content in the pore waters were on the contrary higher than expected with the highest values in the top layers (>100 mg/l) with a decrease to a constant value at the lower levels.

### 4.1.3 Modelling of pore waters

The geochemical thermodynamic equilibrium source code MINTEQA2 was used to model the geochemical reactions occurring in the pore waters. All analysed inorganic components except Co were used in the simulations. The result was used to identify solids at saturated conditions and which element concentrations they may control. The saturation index ( $SI = \log IAP - \log K_s$ ) was used for identifying solids appearing at solubility controlling conditions screened by the criteria  $SI = [-2, 2]$ . These values are presented in Table 5 and 6 for bottom ash and steel slag respectively. The solids with SI closest to 0 are marked in these tables and also graphically presented divided on different solids categories. Pore water from profile 2 from the bottom ash (Figures 19-23) and the steel slag samples (Figures 24-28) was simulated. The simulations were conducted at the measured pH and redox potential.

The redox couples Mn(II)/Mn(III) and Fe(II)/Fe(III) were allowed to adjust to the measured redox potential.

#### 4.1.3.1 Bottom ash

Solubility controlling solids in the bottom ash lysimeter appeared in the simulations as oxides and hydroxides, silicates, carbonates, sulphates and molybdates. Some elements appeared in more than one of these groups of controlling solids and the likeliness of the different possibilities needs further confirmation. The solids indicated by the simulations are either primary solids contained in the original matrix or secondarily formed solids.

**Ca** appeared in sulphate and molybdate solids (see Figures 21 and 23). Anhydrite seemed to be the dominant controlling solid for Ca with an SI close to 0. No carbonates appeared as controlling solids for Ca.

**Na** and **K** appeared in the solids analbite (silicate) and alunite (sulphate), respectively. However, the top layer was under saturated with respect to both these minerals (see Figures 20 and 21).

**Mg** appeared in magnesite, which is a carbonate (see Figure 22). The SI was varying with depth but relatively close to  $SI=0$ .

Concentrations of **Si** seem to be controlled by quartz or chalcedony/cristobalite which all are different forms of  $SiO_2$  and possibly also by analbite (see Figures 19 and 20).

The simulations of **Mn** concentration included a reduced Mn(II) and oxidised form defined as Mn(III). The oxyhydroxide manganite and oxide bixbyite controlling Mn(III) (Figure 19) were close to saturation at the two lower levels as well as rhodocrosite containing Mn(II) (Figure 22). At the two upper layers the pattern was unclear. All solids were over saturated at the top level and under saturated at the upper middle level. Other processes might control the concentrations of Mn at these levels.

**Ba** appeared in sulphates,  $BaSO_4$ , and in solid solutions with  $BaSO_4$  and  $BaCrO_4$  at varying ratios (see Figure 21). The SI for the solid solutions  $Ba(S, Cr 0.23)$  and  $Ba(S, Cr 0.04)$  are positioned on either side of  $SI=0$  indicating that a solid solution with a ratio between these would be controlling concentrations of both Ba and Cr in the pore waters. No difference was found throughout the profile.

**Cd** appeared in otavite, a carbonate (see Figure 22) with a SI close to 0 in the entire profile. No other controlling solids at saturation were found that contained Cd.

Solids with **Cu** were found among carbonates and oxides/hydroxides (see Figures 19 and 22). Malachite ( $\text{CuCO}_3$ ) had an SI somewhat closer to 0 than tenorite ( $\text{CuO}$ ), but both solids may be controlling the Cu concentrations. Cu is also easily bound to dissolved organic carbon, but these substances and the TOC content was not simulated in this modeling. However, the identified solids were close to saturation which would not be likely if a substantial concentration of Cu was dissolved in TOC.

**Pb** appeared only in one identified solid, wulfenite. This is a molybdate (see Figure 23). However, the SI was varying with depth in the profile and in parallel with the Ca-molybdate with the highest grade of saturation at the lower middle level.

**Zn** appeared in the silicate willemite. However, willemite was under saturated in the whole profile indicating other concentration controlling mechanisms.

No solids containing **Al**, **Fe** or **Hg** appeared with  $\text{SI} = [-2, 2]$ .

#### 4.1.3.2 Steel slag

Solubility controlling solids in the steel slag lysimeter were indicated by the simulations among oxides and hydroxides, silicates, carbonates, sulphates and molybdates. Some elements appeared in more than one of these groups of controlling solids and the likeliness of the different possibilities need to be discussed. The solids indicated by the simulations are either primary solids contained in the original matrix or secondarily formed solids. The solids with  $\text{SI} = [-2, 2]$  for steel slag are presented in Table 6.

The solids wollastonite and pseudo-wollastonite seemed to control the concentration of **Ca** in the pore waters (see Figure 25). The SIs in the top level was somewhat smaller than in the rest of the profile. Wollastonite appeared to be over saturated while pseudo-wollastonite appeared as under saturated. Calcium molybdate also appeared in SI close to 0 but is not likely to be controlling Ca (see Figure 28). However, it is likely that Ca through this solid is controlling **Mo**.

**Si** appeared to be controlled by amorphous  $\text{SiO}_2$  (a, gl), which had an SI close to 0 (see Figure 24). However, silicates which appeared to control other elements such as Ca, Mg, Na and K are also likely to control Si as the concentrations of these elements in the pore water were substantial (see Figure 25).

**Mg** appeared to be controlled by two solids namely forsterite (silicate, see Diagram Silicates SS) and magnesite (carbonate, see Diagram Carbonate SS). It is in this case possible that the silicate is a primary controlling solid and the carbonate is a secondary controlling solid. The silicate appeared to be the least saturated in the top sample indicating weathering of the material when at the same time the carbonate was over saturated in the same sample. This sample was most in contact with air carbon dioxide.

Solids indicated to control **K** and **Na** were found among silicates (see Figure 25). Leucite appeared to control K. Analchime and analbite appeared to control Na where the SIs were parallel and close to 0 in the top sample but more to the over saturated side in the bottom sample.

The oxide diaspore appeared in the simulations as the solid controlling **Al** (see Figure 24). SIs were somewhat over saturated in the two upper layer but came closer to SI=0 in the lower part of the lysimeter.

**Fe(III)** appeared to be controlled by ferrihydrite ( $\text{Fe}(\text{OH})_3$ , see Diagram oxides and hydroxides SS). No solids were found that could control Fe(II).

**Ba** was found in solids with sulfate and chromate in different ratios as was also the case in the bottom ash (see Figure 27).  $\text{BaSO}_4$  (c) and low chromium concentration solid solution of chromate and sulfate ( $\text{Ba}(\text{S}, \text{Cr } 0.04)\text{O}_4$ ) were the solids closest to saturation. The SIs were similar throughout the depth of the lysimeter. No other solids close to SI=0 were found containing **Cr**.

The carbonate otavite appeared as the controlling solid for **Cd**. The SI was very close to saturated conditions in the entire profile (see Figure 26).

Three different solids were candidates for controlling the concentration of **Cu** namely malachite (carbonate, see Figure 26), brochantite (sulfate, see Figure 27) and dioptase (silicate, see Figure 25). In all three the SIs of the two upper sample levels were considerably over saturated. It is possible that the TOC content in the pore water has mobilized the copper to concentrations above these solids saturation concentrations at the two upper sample levels. The silicate and sulfate gave for the two lower sample levels the SIs closest to 0.

**Pb** appeared in three different solids close to SI=0, where two were vanadates and one a hydroxide (see Figures 24 and 28). However, all three were only close to saturation in the sample at the upper middle level. It seems that they represent secondary solids and that there was an enrichment at this level of **Pb** that had been leached from the top level.

No solids close to saturation that contained **Mn**, **Ni** or **Zn** appeared in the simulations.

## 4.2 XPS

### 4.2.1 Bottom ash

#### 4.2.1.1 General

The data on the characterization of the mineral phases in the fine fraction (<4 mm) of the bottom ash by XPS is given in Table 7 for the raw sample and in Tables 8-11 in the four samples from the lysimeter. As can be seen in Tables 7-11; a large amount of information was collected using this technique. The elements C, O, Ca, Al, Si and Fe were routinely detected. The XPS speciation data also suggest that the bottom ash is a glassy material containing typical glass and crystalline phases associated with a  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-Fe}_2\text{O}_3$  high temperature, low pressure melt. Further, these phases show evidence of some aging during the four or so years they were stored outdoors in the lysimeter. However, the raw sample also shows evidence of some weathering, though not as extensive as the lysimeter samples. This is likely as the bottom ash was water quenched prior to collection and use in the original AFR study. Finally, like the steel slag, there do not appear to be large differences in weathering products with depth in the bottom ash samples in the lysimeter.

#### 4.2.1.2 Element Concentrations

The data presented in Tables 7-11 with respect to element concentrations are summarized in Table 15. There are significant differences from the original material and either the archived raw material or the lysimeter samples analyzed four years later. The concentrations of Ca are much lower and the Fe and Si much higher in the original material. This difference is likely related to the particle size ranges that were used for analysis by Fällman (1997) where the whole size distribution of the material was used; particularly if Fe and Si were preferentially in the larger particles.

The higher concentrations of Ca in the raw and lysimeter samples in comparison to determination on the whole sample suggests enrichment of Ca in the smaller particles or possibly that aging reactions accumulated Ca over time in both the raw sample (stored dry for 4 years after initial wetting) and the lysimeter samples. The lower concentrations of Si and Fe in raw and lysimeter samples compared to the original sample is likely due to a sampling artifact based on the exclusion of particles larger than 4 mm. There were some decrease in the concentrations of C in the lysimeter samples in relation to the raw and archived sample and the contrary, larger amounts in the lysimeter in comparison to the archived was seen for O. Al seemed to be slightly enriched in the two upper layers in the lysimeter in comparison to the lower layers and the raw archived sample.

There trends or changes in element concentrations between the raw sample and the four lysimeter samples are however small but the changes for C, O and Al may be indicative of aging reactions and leaching or re-precipitation.

#### 4.2.1.3 Types and Abundances of Mineral Phases

As shown in Tables 7-11, a large number of candidate mineral phases were seen. These include for C: hydrocarbons and organic matter, carbonates, carbides, and  $\text{CaCO}_3$ ; for Ca:  $\text{CaO}$ ,  $\text{CaCO}_3$ ,  $\text{Ca}_3\text{Si}_3\text{O}_9$ ,  $\text{CaSiO}_3 \cdot 2\text{H}_2\text{O}$ , and Ca silicates; for Al:  $\text{Al}(\text{OH})_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{AlOOH}$ ,  $\text{Al}_2\text{Si}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ ,  $\text{Al}_2\text{SiO}_5$ ,  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ,  $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$ , and Al silicates; for Si:  $\text{SiO}_2$ ; for Fe:  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{FeO}$ ,  $\text{FeOOH}$ ,  $\text{Fe}(\text{OH})_3$ , and Fe salts.

Some phases are oxides likely present in the original material ( $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{FeO}$ ,  $\text{SiO}_2$ ). Some of these phases are more closely associated with high temperature, low pressure glasses (Al silicates, Ca silicates) and silicate crystalline minerals ( $\text{Al}_2\text{SiO}_5$ ,  $\text{Ca}_3\text{Si}_3\text{O}_9$ ,  $\text{SiO}_2$ ) that precipitate out of glass melts. Others are clearly hydroxide and carbonate weathering products ( $\text{Al}(\text{OH})_3$ ,  $\text{AlOOH}$ ,  $\text{CaCO}_3$ ,  $\text{FeOOH}$ ,  $\text{Fe}(\text{OH})_3$ ). Finally, there is also evidence of aluminosilicate weathering products like clays ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ,  $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$ ).

Table 13 depicts the relative abundance with depth in the lysimeter of phases detected by XPS most likely associated with sorptive processes or co-precipitation phenomena in the lysimeters. They also correspond to the classes of phases derived from the extraction methods. There is a small decrease in carbonates in the two upper layers as well as a small increase in amorphous Al-silicates. For the other classes of mineral phases there are no discernable trends present.

## **4.2.2 Steel slag**

### **4.2.2.1 General**

X-ray photoelectron spectroscopy (XPS), some times known as ESCA, is a useful analytical spectroscopy for determining atomic concentrations and chemical speciation in environmental samples (Perry et al., 1990; Linton et al.; 1983). It was chosen to look particularly at weathering products in the steel slag containing Al, Ca, Si, and Fe. These amorphous phases and re-precipitates would be surface associated and likely involved in sorption or re-precipitation reactions involving metals of concern. Since XPS is a surface spectroscopy that interrogates only the top 30 angstroms, some caution is required in interpreting the data presented here. Steel slag samples less than 4 mm in size were ground to pass 250  $\mu\text{m}$  for analysis. Grinding, necessary for analysis by XPS, destroys any surface heterogeneity associated with the particles. As shown below, evidence suggests that the 4 mm particles were probably fairly homogeneous and weathering products associated with the particle surfaces could be identified.

The data on the XPS characterization of the mineral phases in the fine fraction (<4 mm) is given in Table 14 for the raw sample and in Tables 15-18 in the four samples with depth from the lysimeter.

As can be seen in Tables 14-18; a large amount of information was collected using this technique. The elements O, Ca, C, Si, Al and Fe (ranked in decreasing abundance) were routinely detected in the steel slag samples. Other elements were detected, but below quantifiable limits. These include Cr, Mg, and Mn. The data suggest that the steel slag is a glassy material containing both typical glass and crystalline phases associated with a  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-Fe}_2\text{O}_3$  high temperature, low pressure melt. Further, these glasses show evidence of aging during the four or so years they were stored outdoors in the lysimeter. However, the raw sample also shows evidence of some weathering, though not as extensive as the lysimeter samples. This is likely as the slag was air cooled outdoors prior to collection and use in the original AFR study. Finally, there do not appear to be large differences in weathering products with depth in the steel slag samples in the lysimeter. This may be attributed to the construction and operation of the lysimeter as a flow through reactor where pores are partially saturated with depth but where atmospheric oxygen is available for diffusion into the pores. The lysimeter was not operated where leachate accumulates in the bottom and offers the potential for reducing conditions to develop. The pH and Eh data support this observation.

### **4.2.2.2 Element Concentrations**

The data presented in Tables 14-18 with respect to element concentrations are summarized in Table 19. There are significant differences from the original material and either the archived raw material or the lysimeter samples analyzed four years later. The concentrations of Ca are much lower and the Fe much higher in the original material. This difference is related to the particle size ranges that were used for analysis by Fällman (1997); particularly if Fe were preferentially in the larger particles.

The higher concentrations of Ca in the raw and lysimeter samples suggests enrichment of Ca in the smaller particles or possibly to aging reactions that accumulate Ca over time in both the raw sample (stored dry for 4 years after initial wetting) and the lysimeter samples.

There are some trends or changes in element concentrations between the raw sample and the four lysimeter samples that may be indicative of leaching or re-precipitation. C, Ca, Al, and Fe are all less prevalent in the lysimeter samples compared to the raw sample. C and Fe may be accumulating with depth in the lysimeter. Si may be preferentially leaching with depth. O may be more prevalent in all of the lysimeter samples. These are potential trends; however, they are confounded by the interrelation between all the elements when quantification is done with XPS on samples when relative loss (leaching) or relative gain (re-precipitation) is occurring.

#### 4.2.2.3 Types and Abundances of Mineral Phases

As shown in Tables 14-18, a large number of candidate mineral phases were seen. These include for C: hydrocarbons and organic matter, carbonates, carbides, and  $\text{CaCO}_3$ ; for Ca:  $\text{CaO}$ ,  $\text{CaCO}_3$ ,  $\text{Ca}_3\text{Si}_3\text{O}_9$ ,  $\text{CaSiO}_3 \cdot 2\text{H}_2\text{O}$ , and Ca silicates; for Al:  $\text{Al}(\text{OH})_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{AlOOH}$ ,  $\text{Al}_2\text{Si}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ ,  $\text{Al}_2\text{SiO}_5$ ,  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ,  $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$ , and Al silicates; for Si:  $\text{SiO}_2$ ; for Fe:  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{FeO}$ ,  $\text{FeOOH}$ ,  $\text{Fe}(\text{OH})_3$ , and Fe salts.

Some phases are oxides likely present in the original material ( $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{FeO}$ ,  $\text{SiO}_2$ ). Some of these phases are more closely associated with high temperature, low pressure glasses (Al silicates, Ca silicates) and silicate crystalline minerals ( $\text{Al}_2\text{SiO}_5$ ,  $\text{Ca}_3\text{Si}_3\text{O}_9$ ,  $\text{SiO}_2$ ) that precipitate out of glass melts. Others are clearly hydroxide and carbonate weathering products ( $\text{Al}(\text{OH})_3$ ,  $\text{AlOOH}$ ,  $\text{CaCO}_3$ ,  $\text{FeOOH}$ ,  $\text{Fe}(\text{OH})_3$ ). Finally, there is also evidence of aluminosilicate weathering products like clays ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ,  $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$ ).

There is more  $\text{CaCO}_3$  present in the four lysimeter samples than in the raw sample. This is a clear indication that carbonation is more prevalent in the continually wetted and  $\text{CO}_2$ -exposed lysimeter specimens. There is a clear presence of amorphous and crystalline aluminum hydrous oxides ( $\text{AlOOH}$ ). Though present at low concentrations, there are also crystalline and amorphous Fe phases present that can promote sorption as well ( $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{FeO}$ ,  $\text{FeOOH}$ ,  $\text{Fe}(\text{OH})_3$ ).

Table 20 depicts the relative abundances with depth in the lysimeter of phases detected by XPS most likely associated with sorptive processes or co-precipitation phenomena in the lysimeters. They also correspond to the classes of phases derived from the extraction methods.

The first class of mineral phases, crystalline iron oxides like  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  (from individual Fe peaks), shows some changes with depth, being absent in the bottom sample. The second class of mineral phases, amorphous iron oxides like  $\text{FeOOH}$  (from individual Fe peaks), shows an increasing trend with depth. The third class of mineral phases, amorphous and crystalline aluminum silicates (from all the Al peak), shows a decline with depth. The last class of mineral phases, carbonates, shows a pronounced increase in the lysimeter samples relative to the raw and archived sample. One might expect that amorphous Al phases and carbonates were more important for controlling sorption and co-precipitation than either of the Fe phases by virtue of their greater abundance.

### 4.3 Extractions

Selective extractions were used to recover operationally defined phases from the < 4 mm material; both the raw archived material and the samples with depth in the lysimeters. Five types of extractions were used: (i) an exchangeable ions extraction ( $\text{MgCl}_2$  extraction), (ii) a sodium acetate/acetic acid-based extraction (NaAc extraction) to recover carbonates (iii) an ascorbic

acid-based extraction (Asc. acid extraction) to recover amorphous hydrous ferric oxides (HFO), (iv) a dithionate-based extraction (Dithion. extraction) to recover crystalline and amorphous iron oxides where the difference between the Dithion. and NaAc extractions would therefore be the crystalline iron oxides, and (v) an oxalic acid-based extraction (Ox. acid extraction) to recover amorphous aluminosilicates.

### 4.3.1 Bottom Ash Extractions

Elements are presented in order of general abundance within general categories for the bottom ash. The extracted amounts from each sample and for all the extraction procedures are presented in Tables 21-25. The graphs are provided in Figures 29-47. The graphs depict extractable concentrations in the raw, archived samples (at 0 meters below surface), and at the top, upper middle, lower middle and bottom sample locations. The discussion addresses the relative importance of the extraction phases in retaining an element, differences between the raw archived sample and the lysimeter samples as an indicator of aging transformations, differences with lysimeter depth, and the overall dominant phase for an element.

#### 4.3.1.1 Major Components (Fe, Mn, Al, Si, Ca, Mg)

**Fe** is present in the bottom ash at high concentrations (108,000 mg/kg; Fällman, 1997). The extractable Fe concentrations are much less than this; likely because of the fact that Fe is associated with larger particles and not with the <4 mm fraction.

Surprisingly, the predominant extraction for Fe was amorphous aluminum silicates, see Figure 29. Only one of the two fractions designed to recover Fe oxides (Asc. acid and Dithion.) recovered similar quantities to the Ox. acid extraction. As expected, there was more crystalline and amorphous iron oxides in the Dithion. extraction than amorphous iron oxides in the Asc. acid extraction. There appears to be significantly more crystalline iron oxide than HFO.

There were differences between the raw archived sample and the lysimeter samples. This was particularly evident in the MgCl<sub>2</sub>, NaAc, and Ox. acid extractions. This means from a weathering perspective either that the bottom ash has lost exchangeable Fe, carbonate-associated Fe, and increased Fe-associate amorphous aluminosilicates during aging. The variation in extractable Fe material with depth in the lysimeters was low for all extractions except the exchangeable fraction.

Based on the high concentrations of extractable Fe compared to other elements, the role of iron oxides in sorption processes may be more important than amorphous aluminum silicates and carbonates in providing sorption sites.

**Mn** is present in the bottom ash at much lower concentrations than the Fe, at 1,360 mg/kg (Fällman, 1997). The extractable Mn concentrations are in the same magnitude as this; perhaps indicating a preference of Mn for the smaller particle fraction or by Mn participating in weathering reactions producing surface-associated phases.

Mn was mainly recovered in the dithionite extraction designed to recover crystalline and amorphous iron oxides, see Figure 30. As expected, there was more manganese in the crystalline and amorphous iron oxides in the Dithion. extraction than in the amorphous iron oxides extraction.

There were differences between the raw archived sample and the lysimeter samples. This was particularly evident in the  $\text{MgCl}_2$  and Ox. acid extractions. This means from a weathering perspective that the bottom ash may have lost exchangeable Mn and produced amorphous aluminum silicate Mn during aging.

The variation in extractable Mn material with depth in the lysimeters was low for all of the extractions except the  $\text{MgCl}_2$  extraction.

Mn is largely associated with crystalline iron oxides.

**Al** is present in the bottom ash at fairly high concentrations (56,900 mg/kg; Fällman, 1997). The extractable Al concentrations are significantly less than this; likely because of the fact that Al is associated with larger particles and not with the <4 mm fraction.

The Ox. acid extraction designed to recover amorphous aluminum silicates recovered the highest quantities of Al, see Figure 31. The Dithion. extraction designed to recover crystalline and amorphous iron oxides also extracted Al.

More Al was extracted in the  $\text{MgCl}_2$ , NaAc, and Ox. acid extractions from the lysimeter samples than from the archived raw material. This indicates from a weathering perspective that a modest enrichment of Al has occurred. There were no significant differences with depth in the lysimeter for all of the extractions.

Given the low extractable Al concentrations, it is likely that amorphous aluminum oxides are less important than iron oxides and carbonates at element retention.

**Si** is present in the bottom ash at high concentrations (208,000 mg/kg; Fällman, 1997). The extractable Si concentrations are significantly less than this; likely because of the fact that Si is associated with larger particles and not with the <4 mm fraction.

The Ox. acid extraction designed to recover amorphous aluminum silicates recovered the highest quantities of Si, see Figure 32. The Dithion. extraction designed to recover crystalline and amorphous iron oxides also extracted Si.

Most of the extractions showed no differences between the archived raw sample and the lysimeter sample. A modest increase in extractable amounts were seen for the oxalic extraction of the lysimeter sample in comparison to the raw archived sample. Amongst the five extractions, there were no discernable differences with depth in the lysimeter.

Given the relatively low Si extraction concentrations, amorphous silicates are not likely to be as important as carbonates or iron oxides in element retention.

**Ca** is present in the bottom ash at moderately high concentrations (87,900 mg/kg; Fällman, 1997). The extractable Ca concentrations are significantly less than this; likely because of the fact that Ca is associated with larger particles and not with the <4 mm fraction.

The NaAc extraction designed to recover carbonates recovered larger quantities of Ca than the other extractions, see Figure 33. The amorphous and crystalline iron oxide fraction was also prevalent.

There were differences between the raw archived sample and the lysimeter samples. This was particularly evident in the  $\text{MgCl}_2$  and Asc. acid extractions. This suggests from a weathering perspective either that the bottom ash has lost exchangeable Ca during aging. The variation in extractable Ca material with depth in the lysimeters was significant for the Asc. acid and  $\text{MgCl}_2$  extractions. Smaller extractable amounts were found in the top level.

Based on the high concentrations of extractable Ca compared to other elements, the role of carbonates in precipitation processes may be as important as iron oxide sorption sites for element retention.

**Mg** is present in the bottom ash at moderate concentrations (11,300 mg/kg; Fällman, 1997). The extractable Mg concentrations are less than this; likely because of the fact that Mg is associated with larger particles and not with the <4 mm fraction. However, Mg was not analysed in the  $\text{MgCl}_2$  since the reagent contained Mg.

The NaAc extraction designed to recover carbonates recovered the largest quantities of Mg, see Figure 34. The crystalline iron and the amorphous aluminum silicates extractions recovered smaller amounts of Mg.

There were differences between the raw archived sample and the lysimeter samples. This was particularly evident in the Asc. Acid and Dithion. extractions. This suggests from a weathering perspective that the bottom ash has lost Mg during aging. No significant variation in extractable Mg material with depth in the lysimeters was seen.

Mg is principally associated with carbonates.

#### **4.3.1.2 Trace Elements (Ba, Cd, Co, Cu, Pb, Ni, Zn)**

**Ba** is present in the bottom ash at moderately low concentrations (1,660 mg/kg; Fällman, 1997). The extractable Ba concentrations are much less than this; likely because of the fact that Ba is associated with larger particles and not with the <4 mm fraction.

Ba was principally associated with the amorphous aluminum silicate fraction, see Figure 35. The NaAc extraction designed to recover carbonates recovered lesser quantities of Ba than the other extractions.

There were differences between the raw archived sample and the lysimeter samples for all extractions. This suggests from a weathering perspective that the bottom ash has retained Ba during aging.

The variation in extractable Ba with depth in the lysimeters was significant for the  $\text{MgCl}_2$  and carbonate and Asc. acid extractions.

Ba is largely associated with the amorphous aluminum silicate fraction in the bottom ash.

**Cd** is a trace element in the bottom ash; present at 5.8 mg/kg (Fällman, 1997). The extractable Cd concentrations are in this order of magnitude; perhaps indicating a preference of Cd for the smaller particle fraction or by Cd participating in weathering reactions producing surface precipitates.

The NaAc extraction designed to recover carbonates recovered larger quantities of Cd than the other extractions, see Figure 36.

There were differences between the raw archived sample and the lysimeter samples for all of the extractions. The data generally suggest some modest enrichment from a weathering perspective. The variation in extractable Cd material with depth in the lysimeters was significant for the Dithion. and NaAc extractions.

These data suggest that Cd is largely associated with the carbonates as a sorbed species.

**Co** is present in the bottom ash at trace levels (19.1 mg/kg; Fällman, 1997). The extractable Co concentrations are the same magnitude; perhaps indicating a preference of Co for the smaller particle fraction or by Co participating in weathering reactions producing surface associated phases.

Co was found largely associated with all fractions except the MgCl<sub>2</sub> fraction, see Figure 37. Amorphous aluminosilicates and crystalline iron oxides are important phases.

There were differences between the raw archived sample and the lysimeter samples for only the MgCl<sub>2</sub> extraction. The data generally suggest some modest enrichment from a weathering perspective. The variation in extractable Co material with depth in the lysimeters was significant for the Mg, Asc. acid, and Dithion. extractions.

These data suggest that Co is largely associated with the amorphous aluminum silicates and crystalline iron oxides as a sorbed species.

**Cu** is present in the bottom ash at moderate levels (3,400 mg/kg; Fällman, 1997). The extractable Cu concentrations are the same magnitudes as this; perhaps indicating a preference of Cu for the smaller particle fraction or by Cu participating in weathering reactions producing surface-associated phases.

Cu was extracted with all five extractions; principally the Ox. acid extraction, see Figure 38. This suggests an association with amorphous aluminum silicates.

There were differences between the raw archived sample and the lysimeter samples for all five extractions. The data suggest both modest enrichment and depletion from a weathering perspective.

The variation in extractable Cu material with depth in the lysimeters was significant for the carbonate and Ox. acid extractions.

Cu is largely associated with the amorphous aluminosilicate fractions in the bottom ash.

**Ni** is present in the bottom ash at minor levels (138 mg/kg; Fällman, 1997). The extractable Ni concentrations are the same magnitude as this; perhaps indicating a preference of Ni for the smaller particle fraction or by Ni participating in weathering reactions producing surface associated phases.

Ni was found largely associated with the Ox. acid extraction, indicating an affinity for amorphous aluminosilicates, see Figure 39. The crystalline iron oxides are also prevalent.

There were differences between the raw archived sample and the lysimeter samples for all extractions. The data suggest some modest enrichment from a weathering perspective. The variation in extractable Ni material with depth in the lysimeters was significant for all extractions.

Ni is largely associated with the amorphous aluminosilicates and crystalline iron oxide fractions in the bottom ash.

**Pb** is present in the bottom ash at moderate levels (737 mg/kg; Fällman, 1997). The extractable Pb concentrations are in this order of magnitude; perhaps indicating a preference of Pb for the smaller particle fraction or by Pb participating in weathering reactions producing surface-associated phases.

Pb was associated with all fractions except the MgCl<sub>2</sub> fraction, see Figure 40. Carbonates, amorphous HFO, and amorphous aluminosilicates are the important phases.

There were differences between the raw archived sample and the lysimeter samples for all of the extractions. The data suggest some modest enrichment from a weathering perspective. The variation in extractable Pb material with depth in the lysimeters was significant for the MgCl<sub>2</sub> and carbonate extractions.

These data suggest that Pb is largely associated with carbonate and amorphous HFO as a sorbed species.

**Zn** is present in the bottom ash at moderate levels (3,080 mg/kg; Fällman, 1997). The extractable Zn concentrations were similar this; perhaps indicating a preference of Zn for the smaller particle fraction or by Zn participating in weathering reactions producing surface precipitates.

Zn was found significantly associated with all extractions except the MgCl<sub>2</sub> extraction, see Figure 41. The amorphous aluminosilicates were more prevalent.

There were differences between the raw archived sample and the lysimeter samples for the Ox. acid extraction. The data suggest some enrichment in the amorphous aluminosilicate phase from a weathering perspective.

The variation in extractable Zn material with depth in the lysimeters was not significant except for the MgCl<sub>2</sub> extraction.

Zn is largely associated with the amorphous aluminosilicate fractions in the bottom ash.

#### **4.3.1.3 Oxyanions (As, Cr, V, Mo, S)**

**As** is present in the bottom ash at trace levels (16.0 mg/kg; Fällman, 1997). The extractable As concentrations is of the same magnitude; perhaps indicating a preference of As for the smaller particle fraction or by As participating in weathering reactions producing surface precipitates.

As was found associated with all fractions except the  $\text{MgCl}_2$  fraction, Figure 42. Amorphous aluminosilicates is the most important phase.

There were little differences between the raw archived sample and the lysimeter samples for all the extractions.

The variation in extractable As material with depth in the lysimeters was not significant for any of the extractions.

These data suggest that As is largely associated with the amorphous aluminum silicates as a sorbed species.

**Cr** is present in the bottom ash at minor levels (274 mg/kg; Fällman, 1997). The extractable Cr concentrations are smaller than this; likely because of the fact that Cr is associated with larger particles and not with the <4 mm fraction.

Cr was found associated with all fractions except the exchangeable fraction, Figure 43. Crystalline iron oxides and amorphous aluminosilicates are the most important phases.

There were differences between the raw archived sample and the lysimeter samples for the  $\text{MgCl}_2$  and NaAc extractions. The data generally suggest some modest depletion from a weathering perspective. The variation in extractable Cr material with depth in the lysimeters was not significant for any of the extractions except the exchangeable fraction.

These data suggest that Cr is largely associated with the amorphous aluminosilicates and crystalline iron oxides as a sorbed species.

**V** is present in the bottom ash at trace levels (58.7 mg/kg; Fällman, 1997). The extractable V concentrations are smaller than this; likely because of the fact that V is associated with larger particles and not with the <4 mm fraction.

V was found associated with the  $\text{MgCl}_2$ , NaAc, and Ox. acid fractions, see Figure 44. Amorphous aluminum silicates is the dominant phase. However, V was not analyzed in extracts from Dition. and Asc. acid extractions.

The variation in extractable V material with depth in the lysimeters was not significant except for the exchangeable fraction.

These data suggest that V is largely associated with the amorphous aluminum silicates as a sorbed species.

**Mo** is present in the bottom ash at trace levels (16.0 mg/kg; Fällman, 1997). The extractable Mo concentrations are similar to this; perhaps indicating a preference of Mo for the smaller particle fraction or by Mo participating in weathering reactions producing surface precipitates.

Mo was found associated with all fractions, see Figure 45. Amorphous aluminosilicates and amorphous HFO are the most important phases.

There were modest differences between the raw archived sample and the lysimeter samples for the  $\text{MgCl}_2$  and Asc. acid extractions. The data generally suggest some modest depletion from a

weathering perspective. The variation in extractable Mo material with depth in the lysimeters was significant for all extractions.

These data suggest that Mo is largely associated with the amorphous aluminosilicates and amorphous HFO as a sorbed species.

S is present in the bottom ash at moderate levels (8,560 mg/kg; Fällman, 1997). The extractable S concentrations are similar to this; perhaps indicating a preference of S for the smaller particle fraction or by S participating in weathering reactions producing surface precipitates.

S was measured in all the extractions, see Figure 46. Exchangeable and amorphous iron are the most important phases.

There were differences between the raw archived sample and the lysimeter samples for all of the extractions. The data generally suggest some depletion from a weathering perspective. The variation in extractable S material with depth in the lysimeters was significant for all of the extractions.

These data suggest that S is largely associated with the exchangeable and amorphous HFO fractions.

#### **4.3.1.4 Carbon (TIC, TOC)**

The organic carbon content of the bottom ash measured as loss on ignition at 550 °C was moderate (43,000 mg/kg; Fällman 1997). The extractable carbon was only measured in the exchangeable fraction, see Figure 47.

There were differences in TOC content with depth. The top sample had the lowest content of exchangeable TOC which increased to the upper middle sample where the highest amounts occurred. Less change with further depth was seen in the lower part of the lysimeter.

The exchangeable amounts of TIC differed to a lesser extent with depth. The highest amount of exchangeable TIC was found in the top sample. The deeper samples showed smaller exchangeable amounts with less variation with depth.

#### **4.3.1.5 Bottom Ash Extraction Summary**

Table 26 summarizes the extraction data by element; describing the dominant phase the element is associated with, the degree of association, the presence of discernable differences between the raw archived samples and the lysimeter samples, and differences with depth in the lysimeter samples. There are a number of important observations.

First, the extractions that should have extracted the highest levels of Fe did not do so. This may be a selectivity problem. It may also indicate that these elements were actually associated with the phases that they came from. Second, there are few discernable patterns. Amorphous aluminosilicates, crystalline iron oxides, and carbonates were generally the most important phases for element retention. Invariably, all extractions showed differences between the archived raw sample and the lysimeter samples. This suggests that significant transformations had occurred after aging and leaching. The ion exchangeable fraction was the predominant fraction to

show differences with depth. The importance of using multiple extractions is also shown; all five phases play a role in controlling the availability of elements.

### 4.3.2 Steel Slag Extractions

Elements are presented in order of general abundance within general categories for the steel slag. The extracted amounts from each sample and for all the extraction procedures are presented in Tables 27-31. The graphs are provided in Figures 48-66. The graphs depict extractable concentrations in the raw, archived samples (at 0 meters below surface), and at the top, upper middle, lower middle and bottom sample locations. The discussion addresses the relative importance of the extraction phases in retaining an element, differences between the raw archived sample and the lysimeter samples as an indicator of aging transformations, differences with lysimeter depth, and the overall dominant phase for an element.

#### 4.3.2.1 Major Components (Fe, Mn, Al, Si, Ca, Mg)

**Fe** is present in the steel slag at high concentrations (242,000 mg/kg; Fällman, 1997). The extractable Fe concentrations are much less than this; likely because of the fact that Fe is associated with larger particles and not with the <4 mm fraction.

Fe was mainly recovered in the Ox. acid extraction designed to recover amorphous aluminum silicates; perhaps indicating association of Fe with aluminosilicates, see Figure 48. The two fractions designed to recover Fe oxides (Asc. acid and Dithion.) recovered smaller quantities than the Ox. acid extraction. As expected, there was more crystalline and amorphous iron oxides in the Dithion. extraction than amorphous iron oxides in the Asc. acid extraction. There appears to be larger amounts of crystalline iron in comparison to amorphous iron oxides. There was relatively little exchangeable Fe.

There were differences between the raw archived sample and the lysimeter samples. This was particularly evident in the MgCl<sub>2</sub>, NaAc, and Dithion. extractions. This means from a weathering perspective either that the slag has lost exchangeable Fe and crystalline Fe during aging. The variation in extractable Fe material with depth in the lysimeters was low for all five extractions.

Based on the high concentrations of extractable Fe compared to other elements, the role of iron oxides in sorption processes may be more important than amorphous aluminum silicates and carbonates in providing sorption sites.

**Mn** is present in the steel slag at much lower concentrations than the Fe, at 39,300 mg/kg (Fällman, 1997). The extractable Mn concentrations are less than this; likely because of the fact that Mn, like Fe, is associated with larger particles and not with the <4 mm fraction.

Mn was mainly recovered in the dithionite extraction designed to recover crystalline and amorphous iron oxides, see Figure 49. However, manganese oxides may be extracted in the same extraction procedure as iron oxides. As expected, there was more manganese in the Dithion. extraction than in the amorphous iron oxides extraction.

There were differences between the raw archived sample and the lysimeter samples. This was particularly evident in the MgCl<sub>2</sub>, Asc. acid, and NaAc extractions. This means from a

weathering perspective either that the slag has produced exchangeable and amorphous Mn during aging.

The variation in extractable Mn material with depth in the lysimeters was low for all five extractions.

Mn is largely associated with the crystalline phases and in amorphous HFO.

**Al** is present in the steel slag at fairly low concentrations (21,900 mg/kg; Fällman, 1997). The extractable Al concentrations are much less than this; likely because of the fact that Al is associated with larger particles and not with the <4 mm fraction.

Surprisingly, the Ox. acid extraction designed to recover amorphous aluminum silicates recovered smaller quantities of Al than the Dithion. extraction, see Figure 50. Al was also associated with the amorphous HFO fraction.

There were differences between the raw archived sample and the lysimeter samples; particularly in the exchangeable fraction and carbonate fraction. There were no marked differences with depth in the lysimeter for the different extractions except for the exchangeable fraction.

Given the low extractable Al concentrations, it is likely that that amorphous aluminum oxides are less important than iron oxides and carbonates at element retention.

**Si** is present in the steel slag at fairly low concentrations (57,700 mg/kg; Fällman, 1997). The extractable Si concentrations are somewhat less than this; likely because of the fact that Si is associated with larger particles and not with the <4 mm fraction.

Si was associated with all of the extraction phases except the exchangeable phase, see Figure 51. Surprisingly, it was not as associated with the amorphous aluminum silicates of the oxalic fraction, as with the crystalline and amorphous iron oxide fraction.

Most of the extractions showed differences between the archived raw sample and the lysimeter sample; with an increase of exchangeable Si in the weathered samples and a decrease in the crystalline iron oxide and amorphous aluminum silicate phases. Amongst the five extractions, there were no discernable differences with depth in the lysimeter.

Given the relatively low Si extraction concentrations, amorphous silicates are not likely to be as important as carbonates or iron oxides in element retention.

**Ca** is present in the steel slag at fairly high concentrations (221,000 mg/kg; Fällman, 1997). The extractable Ca concentrations are significantly less than this; likely because of the fact that the extraction is operationally weak.

As expected, the NaAc extraction designed to recover carbonates (including calcium carbonates) recovered significantly larger quantities of Ca than the other extractions, see Figure 52. Ca was also associated with crystalline and amorphous iron oxides. There was less exchangeable, amorphous HFO associated, than amorphous aluminum silicate-associated Ca.

There were differences between the raw archived sample and the lysimeter samples. This was particularly evident in the MgCl<sub>2</sub> extraction. This suggests from a weathering perspective that

the slag may have lost exchangeable Ca during aging. The variation in extractable Ca material with depth in the lysimeters was low for all five extractions except the Asc. Acid extractable fraction.

Based on the high concentrations of extractable Ca compared to other elements, the role of carbonates in precipitation processes may be as important as iron oxide sorption sites for element retention.

**Mg** is present in the steel slag at fairly high concentrations (45,200 mg/kg; Fällman, 1997). The extractable Mg concentrations are similar to this; perhaps indicating a preference of Mg for the smaller particle fraction or by Mg participating in weathering reactions producing surface precipitates.

Mg was principally found in the carbonate fraction and to a lesser extent in the crystalline iron oxide fraction, see Figure 53. However, Mg was not evaluated in the exchangeable fraction due to reagent containing Mg.

There were differences between the raw archived sample and the lysimeter samples. This was particularly evident in the Asc. Acid and Ox. acid extractions. This suggests from a weathering perspective that the slag has lost Mg from amorphous aluminum silicate and amorphous HFO phases during aging. The variation in extractable Mg material with depth in the lysimeters was low for all five extractions except the Asc. Acid extractable fraction.

Mg is principally associated with carbonates and crystalline iron oxides.

#### **4.3.2.2 Trace Elements (Ba, Cd, Co, Cu, Ni, Pb, Zn)**

**Ba** is present in the steel slag at fairly high concentrations (728 mg/kg; Fällman, 1997). The extractable Ba concentrations are about one magnitude less than this; perhaps indicating a preference of Ba for the smaller particle fraction or by Ba participating in weathering reactions producing surface precipitates.

The NaAc extraction designed to recover carbonates recovered larger quantities of Ba than all of the other extractions except the crystalline and amorphous iron extraction, see Figure 54. The amorphous HFO extraction also recovered significant quantities of Ba.

There were differences between the raw archived sample and the lysimeter samples. This was particularly evident in the Asc. Acid and MgCl<sub>2</sub> extractions. This suggests from a weathering perspective that the slag has lost exchangeable Ba and produced amorphous HFO during aging. The variation in extractable Ba with depth in the lysimeters was not significant for the five extractions.

Ba is largely associated with the crystalline iron oxide and carbonates fractions in the slag.

**Cd** is a trace element in the steel slag; present at 0.45 mg/kg (Fällman, 1997). The extractable Cd concentrations are the same magnitude or exceed this; perhaps indicating a preference of Cd for the smaller particle fraction or by Cd participating in weathering reactions producing surface associated phases.

Cd was found associated with all fractions, see Figure 55. Carbonates and crystalline iron oxides are the most important phases.

There were differences between the raw archived sample and the lysimeter samples for all of the extractions. The data generally suggest some modest enrichment from a weathering perspective. The variation in extractable Cd material with depth in the lysimeters was significant for the Asc. Acid extraction; decreasing with depth.

These data suggest that Cd is largely associated with the carbonates and crystalline iron oxides as a sorbed species.

**Co** is present in the steel slag at trace levels (5.8 mg/kg; Fällman, 1997 ). The extractable Co concentrations are the same magnitude or exceed this; perhaps indicating a preference of Co for the smaller particle fraction or by Co participating in weathering reactions producing surface associated phases.

Co was found largely associated with all fractions except the  $MgCl_2$  fraction, see Figure 56. Amorphous aluminosilicates and crystalline iron oxides are important phases.

There were differences between the raw archived sample and the lysimeter samples for all of the extractions. The data generally suggest some modest enrichment from a weathering perspective. The variation in extractable Co material with depth in the lysimeters was not significant for any of the extractions

These data suggest that Co is largely associated with the amorphous aluminum silicates and crystalline iron oxides as a sorbed species.

**Cu** is present in the steel slag at minor levels (166 mg/kg; Fällman, 1997 ). The extractable Cu concentrations are one tenth of this; perhaps indicating a preference of Cu for the smaller particle fraction or by Cu participating in weathering reactions producing surface-associated phases.

Cu was measured only in the  $MgCl_2$ , Dithion., and Ox. Acid extractions and largely associated with the latter two, see Figure 57. The concentrations were below detection limit in the two not reported extractions.

There were differences between the raw archived sample and the lysimeter samples for all three extractions. The data suggest some modest enrichment from a weathering perspective. The variation in extractable Cu material with depth in the lysimeters was significant for the  $MgCl_2$  extraction.

Cu is largely associated with the crystalline iron oxide and amorphous aluminosilicate fractions in the slag.

**Ni** is present in the steel slag at minor levels (45 mg/kg; Fällman, 1997). The extractable Ni concentrations are the same magnitude or exceed this; perhaps indicating a preference of Ni for the smaller particle fraction or by Ni participating in weathering reactions producing surface associated phases.

Ni was found largely associated with the Ox. acid extraction, indicating an affinity for amorphous aluminosilicates, see Figure 58. The crystalline iron oxides are also prevalent.

There were differences between the raw archived sample and the lysimeter samples for the  $\text{MgCl}_2$  extraction. The data suggest some modest enrichment from a weathering perspective. The variation in extractable Ni material with depth in the lysimeters was not significant for the five extractions.

Ni is largely associated with the amorphous aluminosilicates and crystalline iron oxide fractions in the slag.

**Pb** is present in the steel slag at minor levels (21.5 mg/kg; Fällman, 1997 ). The extractable Pb concentrations are the same magnitude as this; perhaps indicating a preference of Pb for the smaller particle fraction or by Pb participating in weathering reactions producing surface precipitates.

Pb was found largely associated with carbonates, crystalline iron oxides, and amorphous aluminosilicates, see Figure 59. Only minor fractions were associated with the  $\text{MgCl}_2$  fraction.

There were differences between the raw archived sample and the lysimeter samples for all of the extractions. The data suggest some modest enrichment from a weathering perspective. The variation in extractable Pb material with depth in the lysimeters was significant for the  $\text{MgCl}_2$  and Asc. acid extractions.

These data suggest that Pb is largely associated with carbonates and crystalline iron oxides as a sorbed species.

**Zn** is present in the steel slag at minor levels (244 mg/kg; Fällman, 1997). The extractable Zn concentrations exceeded this; perhaps indicating a preference of Zn for the smaller particle fraction or by Zn participating in weathering reactions producing surface precipitates.

Zn was found associated with all extractions except the  $\text{MgCl}_2$  extraction, see Figure 60. The crystalline and amorphous iron oxides and the amorphous aluminosilicates with most prevalence.

There were differences between the raw archived sample and the lysimeter samples for all extractions. The data suggest some modest enrichment from a weathering perspective. The variation in extractable Zn material with depth in the lysimeters was not significant for the five extractions.

Zn is largely associated with the crystalline iron oxide and amorphous aluminosilicate fractions in the slag.

#### **4.3.2.3 Oxyanions (As, Cr, Mo, V, S)**

**As** is present in the steel slag at trace levels (5.3 mg/kg; Fällman, 1997). The extractable As concentrations is of the same magnitude; perhaps indicating a preference of As for the smaller particle fraction or by As participating in weathering reactions producing surface precipitates.

As was found associated with all fractions except the  $\text{MgCl}_2$  fraction where concentrations were below detection limit, see Figure 61. Crystalline iron oxides and amorphous aluminosilicates are the most important phases.

There were differences between the raw archived sample and the lysimeter samples for all the Asc. acid, Dithion., and Ox. acid extractions. The data generally suggest some modest enrichment from a weathering perspective.

The variation in extractable As material with depth in the lysimeters was not significant for any of the extractions.

These data suggest that As is largely associated with the crystalline iron oxides and amorphous aluminum silicates as a sorbed species.

**Cr** is present in the steel slag at major levels (7,760 mg/kg; Fällman, 1997). The extractable Cr concentrations are smaller than this; likely because of the fact that Cr is associated with larger particles and not with the <4 mm fraction.

Cr was found associated with all fractions, see Figure 62. Crystalline iron oxides, amorphous aluminosilicates and amorphous HFO are the most important phases.

There were differences between the raw archived sample and the lysimeter samples for the MgCl<sub>2</sub>, Ox. Acid, and Dithion. extractions. The data generally suggest some modest depletion from a weathering perspective. The variation in extractable Cr material with depth in the lysimeters was not significant for any of the extractions.

These data suggest that Cr is largely associated with the aluminosilicates and crystalline iron oxides.

**Mo** is present in the steel slag at trace levels (20.6 mg/kg; Fällman, 1997). The extractable Mo concentrations are smaller than this; likely because of the fact that Mo is associated with larger particles and not with the <4 mm fraction.

Mo was found associated with all fractions, see Figure 63. Crystalline iron oxides and amorphous aluminosilicates are the most important phases.

There were differences between the raw archived sample and the lysimeter samples for the MgCl<sub>2</sub>, NaAc, and Asc. acid extractions. The data generally suggest some modest depletion from a weathering perspective. The variation in extractable Mo material with depth in the lysimeters was significant for the Asc. Acid extraction; decreasing with depth.

These data suggest that Mo is largely associated with crystalline iron oxides and aluminosilicates.

**V** is present in the steel slag at trace levels (1210 mg/kg; Fällman, 1997). The extractable V concentrations are smaller than this. However, V was not measured in the extractions for amorphous and crystalline iron oxides, and amorphous aluminosilicates

V was found associated with the MgCl<sub>2</sub> and NaAc fractions, see Figure 64. The variation in extractable V material with depth in the lysimeters was not significant with depth.

These data suggest that V is associated with the carbonates as a sorbed species.

**S** is present in the steel slag at minor levels (1,260 mg/kg; Fällman, 1997). The extractable S concentrations are equal or smaller than this.

S was measured in the NaAc, Asc. Acid, and Ox. acid extractions, see Figure 65. Carbonates and amorphous HFO are the most important phases.

There were differences between the raw archived sample and the lysimeter samples for all three of the extractions. The data generally suggest some depletion from a weathering perspective. The variation in extractable S material with depth in the lysimeters was not significant for any of the extractions.

These data suggest that S is largely associated with the carbonates and amorphous HFO.

#### **4.3.2.4 Carbon (TIC, TOC)**

The organic carbon content of the steel slag kg measured as loss on ignition at 550 °C was below detection limit (<1,000 mg/kg; Fällman 1997). The extractable carbon was only measured in the exchangeable fraction, see Figure 66.

There were no significant differences in neither TOC nor TIC content with depth. The amounts of exchangeable TIC was rather high (700-800 mg/kg) where smaller amounts of exchangeable TOC was found (50-70 mg/kg). However, the occurrence of organic carbon in the leachate is probably a product of the storage of the material since the slag realistically can not contain any greater contents of organic material

#### **4.3.2.5 Steel Slag Extraction Summary**

Table 32 summarizes the extraction data by element; describing the dominant phase the element is associated with, the degree of association, the presence of discernable differences between the raw archived samples and the lysimeter samples, and differences with depth in the lysimeter samples. There are a number of important observations.

First, the extractions that should have extracted the highest levels of Fe, Al and Si did not do so. This may be a selectivity problem. It may also indicate that these elements were actually associated with the phases that they came from. Second, there are few discernable patterns. Amorphous aluminosilicates, crystalline iron oxides, and carbonates were generally the most important phases for element retention. Invariably, all extractions showed differences between the archived raw sample and the lysimeter samples. This suggest that significant transformations had occurred after aging and leaching. The ion exchangeable fraction was the predominant fraction to show differences with depth. The importance of using multiple extractions is also shown; all five phases play a role in controlling the availability of elements.

### **4.4 pH-Static tests**

#### **4.4.1 Bottom ash**

Concentrations obtained in the pH-static tests are presented by element category. Diagrams of the concentrations in relation to pH are presented in Figures 67-89. The pH-static tests aim at chemical equilibrium or near chemical equilibrium between the solid phase and leachate. It is therefore relevant to present and discuss the concentrations in the leachate and to look for

patterns in the change of concentration with pH for the different samples. The concentrations are shown in logarithmic scale as the changes may be of several magnitudes and the major patterns are of interest. The pH-static tests of the bottom ash samples were carried out the pH values of 2, 6, 8, 10 and 12. The resulting pH after control with addition of acid or base differed in some cases essentially from the target pH. The resulting pH values were 2.2, 6.8, 7.3, 9.6 and 12.2 for the top samples and 2.4, 6.1, 7.0, 8.6 and 11.1 for the upper middle samples. At both sample levels there was a tendency for the samples to drive the pH in the neutral area towards pH around 7.

#### 4.4.1.1 Major components (Fe, Mn, Al, Si, Ca, Mg)

**Fe** concentrations in the leachates decreased with increasing pH and a minimum was reached at pH 7 in the samples from the upper middle level, see Figure 67. In the top level concentrations continued to decrease with increasing pH. There was a steeper decrease in concentrations to the minimum of 20 µg/l in the upper middle level than the decrease in the top level. The lowest concentration in the top level was 3 µg/l. The highest concentrations, which occurred at pH 2, was around 1000 mg/l.

**Mn** concentrations in the leachates decreased from a high level of above 100 mg/l at pH 6 to a low level of 10 µg/l at pH 11, see Figure 68. There was a plateau with little decrease between pH 2 and 6, but a steep decrease in the concentrations of Mn at a modest decrease in pH from 6 to 7. There were similarities between the two sample levels at pH values between 2 and 7. At a further increase in pH the concentrations in the top samples decreased more than the corresponding upper middle samples. Concentrations of Mn were below detection limit (<1.5 µg/l) in the top sample at pH 12.

**Al** concentrations in the leachates varied with pH in a u-shaped pattern for the both sample levels up to pH 10, see Figure 69. At a further increase above pH 10 there was a further increase in the concentrations in the upper middle sample whereas the concentration in the top decreased at pH 12. The highest concentrations ( 2700 mg/l) were found at pH 2 and the lowest at pH 8 (0.1 mg/l) which occurred in the upper middle sample.

**Si** concentrations in the leachates decreased generally with increase in pH in the entire tested pH interval, see Figure 70. The decrease in concentration was less between pH 10 and 12 in the top sample and an small increase in concentration was seen in the upper middle samples at the same pH interval. The concentrations also dropped more in the upper middle samples at an increase of pH from 6 to 7 in comparison to the decrease in concentrations seen in the top samples. The highest concentrations occurred at pH 2 (2600 mg/l) and the lowest concentrations at pH 10 (0.5 mg/l).

**Ca** concentrations in the leachates responded differently to changes in pH for the two sample levels, see Figure 71. In both sample levels only small decreases in concentrations occurred at an increase of pH from 2 to 6 followed by a steep fall in concentration at a further increase of pH to 7. From that point a further increase in pH resulted in different behavior of the concentrations at the two levels. In the top level samples an increase in pH from 7 to 12 resulted in a continuous decrease in concentrations of Ca. At the upper middle level a new plateau for the concentration of Ca occurred at an increase of pH from 7 to 10, followed by a steep drop in concentration of Ca when pH increased further to 12. The highest concentrations were found at pH 2 (10 000 mg/l) and the lowest at pH 12 in the top samples (1 mg/l). The plateau between pH 2 and 6 were at

5000-10000 mg/l and the second plateau for the upper middle sample were at concentrations of Ca of about 600 mg/l.

**Mg** concentrations in the leachates generally decreased with an increase in pH, see Figure 72. The highest concentrations were 620 mg/l and the lowest below the detection limit of 0.09 mg/l. In the top samples there was a steep decrease in the concentration of Mg between pH 6 and 7. This fall in concentration was not seen in the upper middle sample where concentrations decreased more evenly at an increase of pH.

#### **4.4.1.2 Salts (Cl, SO<sub>4</sub>)**

**Cl** concentrations differed between the two sample levels, see Figure 73. The highest concentration were found in the top sample at pH 2 (1800mg/l). The increase in pH resulted in decrease in Cl concentration in the top level samples with a local maximum at pH 10. The lowest concentrations in the top samples were around 200 mg/l. In the upper middle sample the concentrations increased at an increase of pH between 6 and 7 where also the maximum for that sample level was found (390 mg/l). A small decrease of the Cl concentrations occurred at a further increase of pH to 10 and 11.

Concentrations of **S** and **SO<sub>4</sub>** followed similar pattern but the behavior at the two sample levels differed, see Figures 74 and 75. The change in concentrations were generally small at an increase of pH. However, at the increase of pH from 6 to 7 there was an increase in concentrations of **S** and **SO<sub>4</sub>** in the upper middle samples but a decrease in concentrations in the top level samples. Concentrations of **SO<sub>4</sub>** ranged between 500–1000 mg/l in the top level samples and between 1000-3400 mg/l in the upper middle samples.

#### **4.4.1.3 Organic and inorganic carbon (TOC, TIC)**

Concentrations of organic carbon (**TOC**) in the leachates decreased to a minimum level at pH 7 at an increase of pH from 2 to 7, see Figure 76. The decrease in TOC concentration was steep between pH 6 and 7 in the top sample, a corresponding strong response was not seen in the upper middle samples. At a further increase of pH from 7 to 12 there was a similar increase in concentration of TOC in the leachates from the two levels. The highest TOC concentrations were found at pH 12 (170 mg/l) and the lowest at pH 7 ( 7 mg/l).

Concentrations of inorganic carbon (**TIC**) in the leachates showed the same shape of pH dependency as was seen for the TOC concentrations, see Figure 77. However, the decrease in TIC concentration in the top level samples at an increase in pH from 6 to 7 was even sharper for TIC than for the TOC concentrations. The TIC concentrations in the upper middle sample also increased sharply at an increase in pH between 10 and 11. However, this increase in concentration can be due to contact with CO<sub>2</sub> in air during the test. The lowest concentration of TIC was 1 mg C/l and the highest 320 mg C/l.

#### **4.4.1.4 Trace elements (Ba, Cd, Co, Cu, Ni, Pb, Zn)**

**Ba** concentrations in the leachates generally decreased at an increase of pH, but the fall in the concentration was greater for the samples from the top level, see Figure 78. The fall in concentration was greatest between pH 6 and 7 which was followed by a plateau between pH 7 and 10. This plateau was more marked for the upper middle sample than for the top sample. At a

further increase of the pH above pH 10 the concentrations of Ba decreased further. The highest concentrations were found at pH 2 (5.3 mg/l) and the lowest concentrations at pH 12 (0.6 µg/l). There were similarities between the pattern for Ba the upper middle level and the concentrations of Ca in samples from the same level.

**Cd** concentrations decreased in three different steps in the tested pH interval, see Figure 79. There was a similar decrease in the concentration at the two sample levels at an with increase of pH from 2 to 6. Between pH 6 and 7 there was a steep decrease in concentration of Cd at both sample levels which flattened at a further increase in the upper middle sample. The steep decrease in concentration continued in the top levels samples at a further increase of pH and reached a new plateau at pH between 10 and 12. The maximum concentrations of Cd in the leachates was 1.1 mg/l which occurred at pH 2 and the minimum concentration was 0.2 µg/l which occurred at pH 12.

**Co** concentrations in the leachates followed largely the same pattern as Cd in relation to pH up to pH 7, see Figure 80. A further increase from pH 7 to 10 decreased the concentrations further and between pH 10 and 12 there was a modest increase in the concentrations of Co. The maximum concentration of Cd reached the level of around 1 mg/l and the minimum concentration was around 0.1 µg/l.

**Cu** concentrations in relation to pH showed a U-shaped curve in samples from both levels, see Figure 81. However, the U-shape was more pronounced in the upper middle sample where concentrations decreased more than three orders of magnitude with an increase in pH from 2 to 7. The concentration was almost constant between pH 7 and 10 and increased quite sharply at a further increase in pH to 11. The concentrations in the top samples decreased from pH 2 to a minimum at pH 10 and increased modestly at a further increase to pH 12. The highest concentrations of Cu occurred at pH 2 (400 mg/l) and the lowest concentrations occurred at pH 7 in the upper middle samples (0.1 mg/l).

Concentrations of **Ni** in the leachates decreased about one magnitude of order at an increase of pH from 2 to 6, see Figure 82. At a further increase in pH from 6 to 7 the concentrations at both sample levels dropped almost two orders of magnitude. Further increase in pH resulted in concentrations below detection limit (<2.5µg/l) in the leachates. The maximum concentrations was 11.5 mg/l.

**Pb** concentrations in the leachates decreased with pH to a minimum at pH 10 in the upper middle samples, see Figure 83. At a further increase in pH to 11 there was an increase in concentration of Pb. The concentrations in relation to pH showed a U-shaped curve. The concentrations of Pb in the leachates from the top level samples decreased almost seven orders of magnitude in the tested pH interval 2-12 ( 530 mg/l to 0.1 µg/l).

**Zn** responded to the variation in pH in the leachates with a decrease in concentration at an increase of pH from 2 to 6, See Figure 84. This was followed with a drop in concentrations at a further increase in pH from 6 to 7 and a less step decrease in concentration at further increase in pH to 10. In the upper middle samples a further increase of pH to 11 resulted in an increase in Zn concentration in the leachates whereas the concentration in the top level samples continued to decrease. The highest concentrations of Zn in the leachates was 750 mg/l and the lowest concentration was 6 µg/l.

**Hg** was measured in most of the leachates from the bottom ash, see Figure 85. The concentrations were only to a minor extent decreasing at an increase of pH in the interval 2 to 10. At a further increase of pH to 11 and 12 the concentrations of Hg increased significantly in samples from both levels. Concentrations in the leachates ranged from <0.02 µg/l to 6µg/l.

#### 4.4.1.5 Oxyanions (As, Cr, Mo, V)

Concentrations of **As** generally decreased at an increase of pH, see Figure 86. However, there was a local increase in concentrations between pH 6 and 7. A small increase in the concentration was also seen in the upper middle samples between pH 10 and 11. The maximum concentration was 50 µg/l and the lowest concentration was 0.5 µg/l.

Concentrations of **Cr** behaved generally in a U-shaped manner in relation to pH, see Figure 87. A local increase in concentration was found at an increase in pH from 6 to 7. Minimum concentrations occurred at pH 7 in the upper level samples and in the top level samples at pH 10. Maximum concentrations ( 3 mg/l) occurred at pH 2.

**Mo** concentrations in the leachates increased at an increase in pH, see Figure 88. This increase was mostly pronounced between pH 6 and 7 in the upper middle samples. A plateau in the concentrations was reached in the same samples at pH 7 to 10. In the top level samples this plateau occurred between pH 10 and 12. The maximum concentration in the leachates was 1200 µg/l and the minimum concentration was 4 µg/l.

**V** concentrations showed a U-shaped behavior in relation to pH, See Figure 89. Concentrations decreased from pH 2 to 7. In the upper middle sample a further increase in pH resulted in an increase in concentrations of V. In the top samples there was an increase in the concentrations of V from pH 7 to 10 which was followed by a decrease in concentration at a further increase in pH to 12. The maximum concentration of V occurred at pH 2 (1.2 mg/l) and the lowest concentration occurred at pH 7 (0.3 µg/l).

#### 4.4.2 Steel slag

Concentrations obtained in the pH-static tests are presented in categories of the substances. Diagrams of the concentrations in relation to pH are presented in Figures 90-111. The pH-static tests aim at chemical equilibrium or near chemical equilibrium between the solid phase and leachate. It is therefore relevant to present and discuss the concentrations in the leachate and to look for patterns in the change of concentration with pH for different substances. The concentrations are shown in logarithmic scale as the changes may be of several magnitudes and the major patterns are of interest. The pH-static tests of the steel slag samples were carried out the pH values adjusted to 6, 8, 10 and 12. After pH adjustment had stopped the pH-values drifted to some extent and the resulting pH values were 6.0, 8.1, 9.9 and 12.2 for the top samples and 6.6, 8.1, 9.8 and 11.9 for the upper middle samples.

##### 4.4.2.1 Major components (Fe, Mn, Al, Si, Ca, Mg)

**Fe** concentrations in the leachates decreased with increasing pH and a minimum was reached at about pH 9, see Figure 90. The pattern was similar for the two levels, but the concentrations in the upper middle level leachates were higher than from the top level sample. The concentrations increased with increasing pH in the interval pH 10-12 for the top sample. The corresponding

increase did not occur in the upper middle sample where concentrations remained at the same low level for pH 10-12. High concentrations of about 1 mg/l were found at pH 6. The lowest concentrations were in the interval 0.001 and 0.01 mg/l.

**Mn** concentrations in the leachates decreased from a high level of above 10 mg/l at pH 6 to a low level of 1-10 µg/l at pH 10, see Figure 91. Further increase in pH to 12 resulted in a small increase in concentration in the top sample leachate but in decreased concentrations in the leachate from the upper middle sample. Similarities were seen between the curves for Fe at corresponding sample level.

**Al** concentrations in the leachates varied with pH in a U-shaped pattern for the top level sample, see Figure 92. Similar pattern occurred at pH 10 and 12 for the upper middle sample, but the pH 8 leachate reached a higher concentration than in the top sample. The highest concentrations ( 1-10 mg/l) were found at pH 12 and the lowest concentrations in the upper middle sample at pH 8 (0.1-1 µg/l).

**Si** concentrations in the leachates did not vary to a great extent with pH between pH 6 and 10, see Figure 93. A modest increase occurred when pH was further increased to pH 12. The highest concentrations were around 100 mg/l and the lowest at about 20 mg/l. There were not any distinct difference between the curves for the samples from the two levels.

**Ca** in the leachates decreased in concentration with increasing pH in leachates of samples from both levels, see Figure 94. The highest concentrations at pH 6 was around 3000 mg/l which decreased to about 10 mg/l at pH 12. The decrease was greater between pH 8 and 10 in the leachate from the upper middle sample than from the top sample, but the same concentrations were reached at pH 12 for the two levels.

**Mg** concentrations in the leachates also decreased with increased pH as reported for Ca, but with less decrease in concentration between pH 6 and 8, see Figure 95. The highest concentrations were found at pH 6 ( around 150 mg/l) and the lowest at pH 12 where concentrations were below detection limit (<0.09 mg/l) in the top sample leachate. There were similarities in concentrations of Mg between the two levels, but the concentrations in the top level sample was slightly lower at pH 6 and 8 in comparison with those from the upper middle level.

#### 4.4.2.2 Salts (Cl, SO<sub>4</sub>)

**Cl** concentrations varied little with pH in the upper middle sample, see Figure 96. A little decrease was observed when pH increased from 6 to 8. The concentration in the top level samples firstly increased with increased pH up to pH 10 and decreased thereafter. But still these changes in concentrations were modest. The concentrations were at the highest 300 mg/l and at the lowest 200 mg/l.

Concentrations of **S** and **SO<sub>4</sub>** differed slightly, see Figures 97 and 98. The **S** concentrations decreased modestly with an increase in pH from 6 to 8. The concentrations varied within the magnitude of 1-10 mg/l. **SO<sub>4</sub>** also showed this small decrease in concentrations when pH increased from 6 to 8, but for the upper middle sample there was also an increase in concentrations at an increase in pH from 10 12. This increase was not seen in the top level sample. Concentrations of **SO<sub>4</sub>** were all within the magnitude of 10-100 mg/l.

#### 4.4.2.3 Organic and inorganic carbon (TOC, TIC)

Concentrations of organic carbon (**TOC**) in the leachates varied in a U-shape with increased pH, see Figure 99. The lowest concentrations ( around 1 mg/l) occurred at pH 8 and the highest ( around 10 mg/l) were found in leachates at pH 6 and 12. Concentrations in the upper middle sample were lower than those from the top sample, but there were no essential differences in shape of the curve between the two levels.

Concentrations of inorganic carbon (**TIC**) in the leachates showed the same shape of pH dependency for the two levels, see Figure 100. A local maximum was obtained at pH 8. Lower values of the concentration appeared at pH 6 and 10. A greater increase was obtained when pH was further increased to 12. However, at this latter pH CO<sub>2</sub> from the may be absorbed by the leachate. The top sample did not have measurable concentrations of TIC (<0.5 mg/l) at pH 6. The rest of the concentration were within the interval 10-140 mg/l.

#### 4.4.2.4 Trace elements (Ba, Cd, Co, Cu, Ni, Pb, Zn)

**Ba** concentrations in the leachates generally decreased at an increase of pH, see Figure 101. The patterns were similar at the two sample levels, but concentrations of Ba fell more between pH 8 and 10 at the upper middle level than at the top level. The highest concentrations were 7 mg/l and the lowest ones were 20 µg/l. The behavior of concentration in relation to pH was similar to the pattern observed for Ca.

**Cd** concentrations decreased with increase of pH from 6 to 10, see Figure 102. There was a small increase in concentration at a further increase of pH to 12. The variations between the two levels were not greater than what would be expected as a natural variation. The highest concentrations ( around 20 µg/l) were found at pH 6 and the lowest at pH 10 (0.04 µg/l).

**Co** concentrations in the leachates decreased with increasing pH and were at pH 10-12 at or below the detection limit for the instrument, see Figure 103. Similar patterns were seen at both levels.

**Cu** concentrations in relation to pH differed between the two sample levels, see Figure 104. The concentrations of Cu in the top level were similar at 2 µg/l at pH 6-10 and increased at pH 12 to above 10 µg/l. In the upper middle level there was a local maximum of 40 µg/l at pH 8 and clearly lower concentrations at pH 6 and 10. At a further increase of pH to 12 also the concentrations increased above 100µg/l. There were parallel curves at pH 10 and 12 between the levels, but with clearly lower concentrations in the leachate from the top level.

Concentrations of **Ni** in the leachates dropped at an increase of pH, see Figure 105. Only few of the leachates from both levels of samples had concentrations above the detection limits.

**Pb** concentrations in the leachates decreased with pH to a minimum at pH 10 ( 0.1-0.3 µg/l), see Figure 106. The concentrations increased again at further increase of the pH. Similar patterns were seen for the two sample levels, except for the upper middle level where a plateau was seen for the concentration between pH 6 and 8. The highest concentrations occurred at pH 6 in the top sample (about 20µg/l).

**Zn** responded strongly to the variation in pH in the leachates, see Figure 107. There was a steep decrease in concentration when pH increased from 6 to 10. The lowest concentration occurred in

the top sample (1µg/l) whereas the upper middle sample at the same pH had a concentration that was 6 times higher. The concentrations increased in samples from both levels at an increase in pH from 10 to 12. The highest concentrations were around 10 mg/l and appeared at pH 6.

#### 4.4.2.5 Oxyanions (As, Cr, Mo, V)

Concentrations of **As** varied only by small values with a change in pH, see Figure 108. Samples from the two levels differed in responses to pH. The upper middle level sample showed a U-shaped curve with a minimum at pH 8 and increase in concentration of As at a pH change to either sides from this pH. In the top level there was only a small decrease in concentration with an increase of pH up to pH 10 and a more marked increase in concentration of As at a further increase to pH 12. The maximum concentrations were found in the upper middle samples ( 10-20 µg/l) and the minimum concentrations were around 4µg/l.

Concentrations of **Cr** increased with an increase in pH, see Figure 109. The behavior was similar for samples from the two levels. Slightly lower concentrations were found in the upper middle sample at the low pH values. A smaller increase in concentrations were seen at an increase of pH from 10 to 12. The concentrations ranged between 1 and 80 µg/l.

**Mo** concentrations in the leachates varied with more than two magnitudes between pH 8 and 10 in the top level samples, see Figure 110. The concentrations at pH 6 and 12 were at intermediate levels. Concentrations of Mo in the upper middle sample varied less with a local minimum at pH 10. The concentrations for the sample from the top level varied between 0.5 and 220 µg/l and the corresponding variation for the upper middle level was 20-50 µg/l.

**V** concentrations increased at an increase of pH, see Figure 111. The steepest increase occurred between pH 8 and 10. The samples from the two levels did not differ significantly in response to pH.

#### 4.4.3 Modeling of pH-static tests

The geochemical thermodynamic equilibrium source code MINTQA2 was used to model the geochemical reactions occurring in the pore waters. All analysed inorganic components except Co were used in the simulations. The results were used to identify solids at saturated conditions and the element concentrations they may control. The saturation index ( $SI = \log IAP - \log K_s$ ) was used for identifying solids appearing at solubility controlling conditions screened by the criteria  $SI = [-2, 2]$ . These values are presented in Table 33-34 and 35-36 for bottom ash and steel slag respectively. The solids with SI closest to 0 are marked in these tables. The simulations were conducted at the measured pH and redox potential. The redox couples Mn(II)/Mn(III) and Fe(II)/Fe(III) were allowed to adjust to the measured redox potential.

##### 4.4.3.1 Bottom ash

Not all elements gave indications of solubility controlling conditions in the pH-static tests. It was also common that different solids indicated solubility control at different pH values. The tests have only been made on the two upper sample levels, but a difference can in some cases be seen between these levels in relation to the solids indicated for solubility control. This suggests that some weathering reactions can be discerned with depth in the lysimeter.

There were no significant differences between indicated solubility controlling solids at the two sample levels for Al, Si, Fe, Ba, Cr and Cd. **Al** seems to be controlled by hydroxides and oxides at different pH values in the interval 6-10. There were no substantial differences between the two sample levels. Several SiO<sub>2</sub> minerals were candidates for controlling the **Si** concentrations in the leachates at both sample levels. There were no differences seen between the sample levels. **Ba** and **Cr** seems to be controlled by Ba(S<sub>0.77</sub>, Cr<sub>0.23</sub>)O<sub>4</sub> in the pH-interval 6-10 and these was no difference between the two sample levels. This was the only sulfate that did not behave differently at the two sample levels. **Cd** may be controlled by the carbonate otavite, but there is no consistency between the SI-values in the pH-interval. The differences between the sampling levels were not convincing for this solid. There is only possibility to find solubility control of **Fe** at pH 2. There are both **V** (vanadates), oxides and sulfates that control the concentration. Ferrihydrite seem to control the Fe(III) concentration in the upper middle level at pH 6. The corresponding solubility control is not found at that pH in the top sample but rather at pH 9.6.

Differences between the sample levels occurred for solids including sulfate (not for Ba-S-Cr), carbonate, and molybdate. The solubility control was more pronounced at the upper middle samples in these cases than in the top level samples. In the top samples it was in these cases more likely oxides and hydroxides or silicates that were candidates for controlling the aqueous phase concentrations.

**Ca** seemed to be controlled by both carbonates ( aragonite and calcite) and sulfates ( anhydrite and gypsum) where the sulfates occurred at more saturated conditions in the upper middle sample level than in the top sample level. In addition it seems that Ca is controlling **Mo** through CaMoO<sub>4</sub>. The saturation of this solid was lower at the top sample level then in the upper middle sample level. **Mn** seem to be controlled by carbonate, but only at pH 6.8 in the top level and at pH 11 in the upper middle level. However the carbonate may be an artifact at this high pH as it can have entered from air contact. **Cu** may be controlled by the oxide tenorite or the carbonate malachite but only at pH 7 in the upper middle sample level. In the top level it seems that Cu(OH)<sub>2</sub> is controlling the Cu concentration at all pH-values but 9.6. **Pb** seemed to be controlled by hydroxide and vanadate at the top sample level. However, no solubility control occurred for Pb in the upper middle sample level. The silicate willemite was a candidate for controlling the concentrations of **Zn**. However, this control was more pronounced in the top sample level than in the upper middle sample level.

#### 4.4.3.2 Steel slag

Not all elements gave indications of solubility controlling conditions in the pH-static tests. It was also common that different solids indicated solubility control at different pH values. The tests have only been made on the two upper sample levels, but a difference can in some cases be seen between these levels in relation to the solids indicated for solubility control.

There were no differences seen between the sample levels for solids containing silicates (except Zn, see below). However, there were also solids containing carbonate, sulfate, chromate and vanadate that also did not show differences between the sample layers. **Si** appeared to be controlled by various forms of SiO<sub>2</sub> at both levels. No significant differences were seen. Among the carbonates solids with Cd and Mg showed consistency between the sample levels. **Cd** seemed to be controlled by otavite (carbonate), but only at pH 8. There was no difference between the sample levels. **Mg** seemed to be controlled by carbonate at both sample levels, at all pH values but pH 6. **Ba** was controlled by sulfates and the solid solution of sulfates and

**chromates.** There was no difference between the two sample levels. Vanadates (**V**) seemed to control the **Fe** concentrations at pH 6 and ferrihydrite (hydroxide) seem to control the concentration at pH 10. There were no minerals that occurred as solubility controllers at the other pH values.

For some solids with carbonate, sulfates, vanadates or silicate it seemed to be a depletion in the top layer that made the saturated conditions more likely in the upper middle samples. **Al** was controlled by silicates at both sample levels but in addition also a sulfate was indicated for solubility control at pH 6-8 at the upper middle level. Around pH 6 carbonates occurred as solids controlling **Ca** in the upper middle level but not at the top sample level. However, at higher pH these solids occurred at over saturated conditions at both levels. Silicates seemed also be controlling the concentrations of **Ca** and over the tested pH interval, with less likelihood at pH 8. In addition, **Ca** seemed to control the concentration of **Mo** at both levels and low pH-values. Hydroxide and carbonate seemed to control the concentrations of **Cu** in the upper middle samples whereas only the hydroxide seemed to control the concentration in the top levels samples. Carbonate and oxides seemed to control **Mn** at both sample levels. However, the carbonate control was more likely at different pH values in the upper middle level and only at pH 8 in the top sample level. **Pb** seems to be controlled by **V** at pH 6-8. More under saturated conditions were found in the top samples. **Zn** seemed to be controlled by a silicate at both levels. Less likely solubility control was seen in the top samples.

## 5 DISCUSSION

### 5.1 Bottom ash

The XPS speciation data suggest that the bottom ash is a glassy material containing typical glass and crystalline phases associated with a  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-Fe}_2\text{O}_3$  high temperature, low pressure melts.

Aging processes have clearly occurred in the material. This is supported both by the content of different mineral phases in the original, raw archived compared to the lysimeter samples and by the concentration of elements in the raw archived sample compared to the lysimeter samples. However, some aging had already occurred in the raw archived material due to quenching in water directly in the MSWI plant. The carbon content in the lysimeter samples and the archived samples were similar even though extensive contact with air would have increased the carbon content. Additionally, the oxygen (as a measure of the formation of carbonates, oxides, and hydroxides) content was clearly higher in the lysimeter samples than in the raw archived samples.

The composition of the finer particles (< 4 mm) that were used in this study was different from the composition measured on the whole sample. The concentration of **Ca** was higher in the finer grain sizes since materials in this study contained higher concentrations in comparison to the original analysis. The opposite conditions were found for **Fe** and **Si** where the finer particles contained less of these elements than the original analysis. No differences were found for **Al** between the original material and the materials used in this study.

The samples contained phases from the original high temperature melting process such as **Al** and **Ca** silicate glasses and crystalline silicate minerals containing **Al** and **Ca**. However, aging products such as hydroxides and carbonates were seen. There was also evidence for clay-like aluminosilicates; phases that form when glasses weather (Zevenbergen, 1994).

Solids that are weathering products and are likely involved in adsorption reactions were grouped in crystalline and amorphous iron oxides, amorphous aluminium silicates and carbonates. The two upper sample levels were clearly different from the two lower sample levels when it came to the abundance of the amorphous aluminium silicates, which were more abundant in the upper sample levels, and the carbonates, which were less abundant in the upper sample levels. This difference in content was confirmed by the carbon content in the different levels, but was not revealed in the total aluminium content which did not vary with depth. There was no clear variation in the iron containing oxides with depth.

Extraction tests designed to extract specific phases gave interesting information on in which phases the elements mainly were bound. The main components Al, Si and Fe were mainly bound in amorphous Al silicates. This was somewhat surprising when it came to Fe. However, a substantial, but not major, part of the Fe was also bound in the crystalline Fe oxides. The contents of Al, Fe and Si in these phases were higher in the lysimeter samples than in the raw, archived samples, which again indicate that these are weathering products. The amorphous Al silicates contained the major part of extractable amounts of As, Ba, Cu, Mo, Ni, V (raw material) and Zn, and equal part of Cr as in the crystalline Fe phase. The greater abundance of amorphous Al silicates in the two upper sample levels did not result in greater adsorption of these elements.

It is likely that As, which also was found in the two Fe phases, as well as Mo, Ni and Zn were controlled by sorption processes on the amorphous Al silicates (and Fe phases for As) since there were no direct indication of solubility control of these elements in the geochemical modeling of pore waters or pH-static tests. V was found in a solid with Pb in the top sample layer in the geochemical modeling of the pH-static tests. However, this does not exclude other forms of control of V, e.g. sorption control, in the other layers. The concentration of Cu was clearly identified as solubility controlled by the oxide tenorite and the carbonate malachite in the geochemical modelling of both pore waters and pH-static tests. However, the organic complexing component was not included which is likely increasing the concentrations of Cu. Ba and Cr does not seem to be controlled by sorption processes in the amorphous Al silicates since there was a clear indication of solubility control by the Ba-SO<sub>4</sub>-CrO<sub>4</sub> solid solutions from the geochemical modeling of pore waters and pH-static tests.

Ca and Mg were mainly found in the carbonate phase and together with these were also Cd and Pb extracted in that phase. However, the geochemical modeling of the pore waters and the pH-static tests indicated that sulfates (gypsum and anhydrite) also controlled the concentrations of Ca. Lower levels of carbon in the two upper levels neither had an impact on the content of Ca or Mg nor on the content of Pb and Cd in the carbonate phase. The content of Cd and Pb varied with depth in the lysimeter, but with a maximum extractable amount distinctly in the upper middle level for Cd and in the top level for Pb. The geochemical modeling of pore waters and pH-static tests indicated solubility control by a carbonate for Cd (otavite). Pb, on the contrary, showed only some solubility control by hydroxides, vanadates and molybdates. There is a possibility that these were adsorbed to the carbonate phase.

The Fe phases were not important as adsorption sites. Only for Mn was the major part was found in the crystalline Fe phase; however, this was probably because Mn oxides were reduced in this extraction and not that Mn was sorbed to the crystalline Fe oxides. Cr and Co was equally distributed between the amorphous Al silicates and crystalline Fe phase. It is possible that Cr sits in solid solutions of Cr and Fe oxides and therefore are released in the crystalline Fe extraction. S was found in equal parts in the amorphous Fe oxide fraction and the exchangeable fraction and was the only element that was found to some extent in the amorphous Fe phase. At the lower middle level there was also an increase in the Ni content in the extract.

There were differences between the extracted amounts of all analysed elements except Si and V, between the raw, archived sample and the lysimeter samples. The extractable Fe content changed by aging from being predominant in the crystalline Fe oxides in the raw, archived material to a major part in the amorphous Al silicates in the lysimeter samples. The amount of extractable Al and Si also increased by the aging in this phase. For many of the elements that were predominant in the amorphous Al silicates this increase in extractable amounts from this phase increased by aging.

Amorphous Fe oxides were a less important phase for containing the analysed elements. However, smaller amounts were included in this phase and interesting differences were seen within the lysimeter. Fe had been lost to other phases since the content of Fe in this phase was smaller in the aged samples than in the raw, archived sample, and lower levels of Fe in the top sample was indicated. Different variations in the content of other elements were seen in the amorphous Fe phase. The elements Al and Cd increased the content in the amorphous Fe phase with aging and the increase was stable with depth in the lysimeter. The opposite was seen for Cr and Mg where extracted amounts were lower in the aged material and stable with depth. The extractable contents of Ba and Pb increased in the top level. For some elements (Ca, Co, Mo, Ni, Si and Zn) an increase of the content had occurred in the profile except for the top level where a leaching of these elements seemed to have decreased the extractable amounts. It seems that the amorphous Fe phase is important for the release of elements from the aged bottom ash even though it is not the major phase containing the analysed elements.

There were no general accumulation fronts seen in the lysimeter except that the content Mo was elevated in the upper middle sample level in all phases. The increase was within one order of magnitude.

The study shows that aging has occurred in the material at storage over 4 years outdoors and that new phases, and solids have developed. These new solids are important as they contain elements of interest either as part of a solid or as adsorbed to the new solid.

## **5.2 Steel slag**

The data suggest that the steel slag is a glassy material containing both typical glass and crystalline phases associated with a CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub> high temperature, low pressure melts. Other elements were detected, but were below quantifiable limits. These include Cr, Mg, and Mn.

Aging reactions had occurred in the material that had been stored in the lysimeters, but also in the raw archived material. The slag was air cooled outdoors prior to collection and use in the original AFR study, which may explain why the raw archived material contained a substantial amount of carbon as an aging product. However, the aging had gone further in the lysimeter where the oxygen content was generally greater than in the raw archived sample.

The finer particles (< 4 mm) used in this study differed in composition in comparison to the original analysis on the whole sample. The Ca and Si content were higher in the smaller particles and the Fe content was lower in the smaller particles than in the whole sample. The total content of Al did not essentially differ between the grain sizes.

The samples contained both phases from the original high temperature process, Al and Ca silicate glasses and crystalline silicate minerals containing Al and Ca, and typical weathering products such as hydroxides and carbonates. There was also evidence for clay like aluminosilicates.

There is more  $\text{CaCO}_3$  present in the four lysimeter samples than in the raw archived sample. This is a clear indication that carbonation is more prevalent in the continually wetted and  $\text{CO}_2$ -exposed lysimeter samples. There is also a clear presence of amorphous and crystalline aluminum hydroxides ( $\text{AlOOH}$ ). Though present at low concentrations, there are in addition crystalline and amorphous Fe phases present that can promote sorption as well ( $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{FeO}$ ,  $\text{FeOOH}$ ,  $\text{Fe}(\text{OH})_3$ ).

There were no large differences in aging products between the sample levels. However, smaller amounts of the Fe phases were found in the top sample level and carbonates increased somewhat with depth until the lower middle sample. The bottom sample contained clearly smaller amounts of carbonates.

Extraction tests designed to extract specific phases gave interesting information on in which phases the elements mainly were bound. The main components Ca, Al, Si and Fe were bound in different phases. Fe was mainly bound in amorphous Al silicates. This was somewhat surprising when it came to Fe. However, the raw archived material contained equal parts of Fe in the crystalline Fe oxides and in amorphous Al silicates, but in the aged lysimeter samples the amount bound in the crystalline Fe phase had decreased substantially. On the contrary was Al and Si mainly found in the crystalline Fe phase. Si was also found in the amorphous Fe phase, but Al was in addition found in the amorphous Al silicate phase where it was expected to be. The aging of the material in the lysimeter had made changes in the content of Al, Si and Fe in the phases, but mainly to a decrease in content. This was the case for Al, Fe and Si in both the crystalline Fe phase and in the amorphous Al silicate phase. The major part of Ca was found in the carbonate phase and the carbonate extractions contradicted the XPS measurement by a results that there was no direct difference between the raw, archived sample and the lysimeter samples.

The trace elements were mainly found in the crystalline Fe phase either as the dominant phase or with an equal part found in the amorphous Al silicate phase. A minor part of the trace elements were found to a major extent in the amorphous Al silicates or in the carbonate phase.

Cr, which is one of the more interesting components leaching from the steel slag, was found in the crystalline Fe phase and in the amorphous Al silicate phase. The geochemical modeling of pore water and pH-static tests indicated solubility control of Cr and Ba in the system  $\text{Ba-SO}_4\text{-CrO}_4$ . Also a major proportion of Ba was found in the crystalline Fe phase. However, the Ba content in the amorphous Fe phase increased significantly in the lysimeter sample in relation to the raw archived samples and it is possible that the formed solid solution would be found in the amorphous Fe phase.

Zn, Cu, As and Mo were also present at equal amounts in the amorphous Al silicates and in the crystalline Fe phase. Zn was found to a substantial amount in all phases but the exchangeable phase. No solubility controlled minerals were found neither for Zn nor for As. The content of Zn, Cu and As increased in the amorphous Al silicate phase and in the crystalline Fe phase by aging in the lysimeter. These circumstances together with the lack of indicated solubility controlling solids imply that As would be adsorbed to these phases. There was some indication of solubility control of Zn by a silicate which them could relate to Zn in the amorphous Al silicate phase, but

it is still a possibility of adsorption to the crystalline Fe phase. The concentration of Cu in the pore water was elevated in the two top sample levels. No solubility controlling solids were indicated in the geochemical modeling of the pore water. However, the organic content in the pore water was high at these levels and it is likely that Cu is mobilized by TOC in the pore water. However, in the geochemical modeling of the pH-static tests Cu concentration seemed to be controlled by a hydroxide in the two upper levels and in addition by a carbonate in the upper middle level. There was only indications of solubility control of Mo by Ca at the upper middle level and it is likely that also here adsorption play a part in the control of Mo concentrations.

The amorphous Al silicate phase contained the major part of Ni and Co. For both of these elements there was a small increase in the content in the aged lysimeter material. Both these elements behave similarly in relation to the proportions extracted from different phases, although with a difference in the order of one magnitude.

Finally, the carbonate phase included the major part of not only Ca but also Mg, Pb and V. Even though Cd was found to a larger extent in the crystalline Fe phase than in the carbonate phase it seems more relevant to comment Cd here. Both Mg and Cd were found in the geochemical modeling of the pore water and of the pH-static tests to be controlled by carbonates. Pb and V seem to be interrelated and approach solubility controlled conditions at the upper middle level, but not at the other sample levels. Subsequently, there was a clear increase in the Pb concentration in the pore water at the upper middle level. However, it is possible that adsorption could be important for the retention of Pb and V in the carbonate phase.

There were no general accumulation fronts seen in the lysimeter except that the content of Ca, Cd and Pb was elevated in the top sample level in the amorphous Fe oxide phase. The increase was more than one order of magnitude for Pb and Cd, and about 3 times for Ca.

The study shows that aging has occurred in the material at storage over 4 years outdoors and that new phases, solids have developed. These new solids are important as they contain elements of interest either as part of a solid or as adsorbed to the new solid.

## **6 CONCLUSIONS**

Bottom ash and steel slag are both residues from high temperature processes. Both materials have aggregate properties that allow them to be used as materials in highway construction. However, concerns about the presence of contaminants in either material (e.g. Pb in bottom ash, Cr in steel slag) has tempered interest in their use. Both materials are geochemically unstable after they are produced. Aging reaction can occur in these materials that may enhance the environmental performance of the residues. Studies were carried out on bottom ash and steel slag that have been exposed in lysimeters to air and precipitation for over 4.5 years. The intent of the study was to better describe aging products, their role in contaminant retention, and the possible existence of weathering fronts with depth in the lysimeter samples.

Important weathering phenomena were observed for both waste materials. For the bottom ash, amorphous aluminum silicates, crystalline iron oxides, and carbonates were the dominant weathering products based on both extraction and spectroscopic data. These three products were more prevalent in the lysimeter samples than in the raw archived samples. Amorphous aluminum silicates was the most predominant weathering product; associated with the retention of Ba, Co, Cu, Zn, As, Cr and V. Crystalline iron oxides were the next dominant weathering product; associated with the retention of Mn, Ni and Cr. Carbonates were the next most predominant

weathering product; associated with the retention of Ca, Mg, Cd and Pb. Geochemical modeling of solid phase control of porewaters in bottom ash lysimeters further demonstrated the role of carbonates in controlling Mg and Cd leaching.

For the steel slag, the presence of crystalline iron oxides and amorphous aluminum silicates based on extraction data indicated that they were important phases. However, these phases are likely to be present in the original slag and thus can not be considered true weathering products. Crystalline iron oxides were the most predominant phases; associated with the retention of Mn, Ba, Cd, Cu, Pb, Zn, As, Cr, and Mo. Amorphous aluminum silicates were the next dominant phases; associated with the retention of Co, Cu, Ni, Pb, Zn, As, Cr and Mo. Carbonates, on the other hand, were the dominant weathering products based on extraction and spectroscopic data. This product was more prevalent in the lysimeter samples than in the raw archived sample. The substances associated with carbonates were Ca, Cd, Pb and V. Geochemical modeling of solid phase control of porewaters in steel slag lysimeters further demonstrated the role of carbonates in controlling Mg and Cd leaching.

There are some important distinctions in the weathering reactions observed in the two materials. In the bottom ash, the likely incongruent dissolution of the glassy aluminosilicates to form amorphous aluminosilicate precipitates was by far the most important weathering reaction to have occurred over the 4.5 years, influencing constituents of concern like Cu, Zn, Cr and V. Carbonate formation, though not as significant, was also important in controlling elements like Cd and Pb. These data are in general agreement with other studies on bottom ash weathering (Meima and Comans, 1997). In the steel slag, however, the alkaline nature of the slag promoted the formation of carbonates as the dominant weathering reaction. Carbonates control the behavior of Cd, Pb and V.

These weathering phenomena are considered to be beneficial with respect to both thermodynamic stability of the residues and in retention of elements of concern. These are both beneficial to the concept on use of these materials in construction applications or to long term storage.

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