



Recycled Materials Resource Center

Final Report for RMRC Research Project No. 3/4

- **Project Title :** Geochemical Weathering of Granular Byproduct Materials
- **Name of PI :** Kevin H. Gardner
- **Affiliation of PI :** University of New Hampshire

Research Products

1. Carter, R.K., K.H. Gardner, O. Hjelmar, S. Lopez, D.S. Kosson “Mineralogical and Leaching Characteristics of Weathered Industrial Ash” Proceedings of the Fifth International Conference on the Environmental and Technical Implications of Construction with Alternative Materials, G. Ortiz de Urbina, J.J.J.M. Goumans Eds, San Sebastian, Spain, June 4-6, 2003.
2. Gardner, K.H., R.K. Carter, T. Shimaoka, “Long-term Leaching Behavior Changes in Granular Waste Materials due to Chemical Weathering Processes: Implications for Beneficial Use,” *In Beneficial Use of Recycled Materials in Transportation Applications*, T.T.Eighmy Eds., Air and Waste Management Association Press, 335-344 (2003).
3. Shimaoka, T., K. Miyawaki, M. Hanashima, T. Yoshida, I. Ito, T. Uchida, K.H. Gardner, T.T. Eighmy, “Insolubility of Heavy Metals in Wet Scrubber Residues of Municipal Solid Waste,” *Waste Management and Research* 20(1), 90-98 (2002).
4. Gardner, K.H., R.K. Carter, “Impact of Chemical Weathering on Leaching from Coal Fly Ash,” Eighteenth Annual International Pittsburgh Coal Conference, Newcastle, New South Wales, Australia, December 4-7, 2001.

Mineralogical and Leaching Characteristics Of Weathered Industrial Ash

(Published in WASCON Proceedings, 2003)

Robert K. Carter¹, Kevin H. Gardner¹, Ole Hjelmar², Sarynna Lopez³, David S. Kosson³

¹ Recycled Materials Resource Center, University of New Hampshire, Durham, New Hampshire 03824 USA

² Water Quality Institute of Denmark, 11 Agern Alle, DK-2970 Horsholm, Denmark

³ Department of Civil and Environmental Engineering, Vanderbilt University, Nashville, Tennessee 37235 USA

ABSTRACT

It has been observed that waste materials from high-temperature processes are thermodynamically unstable in the natural environment and weather in a similar fashion to volcanic ash. The large surface area, small particle size and high pH enhance natural weathering processes. Experiments were conducted on municipal solid waste incinerator ash material to accelerate the individual mechanisms involved in this geochemical transformation process (dissolution, precipitation, carbonation and pH reduction) and pH-dependent leaching experiments were used to characterize changes in the availability of lead in the weathered materials. The development of crystalline mineral material with artificial weathering was compared with naturally aged pulverized coal fly ash, as well as previous experimental materials, to determine a concurrence in the artificial weathering method used to natural weathering products. Use of x-ray powder diffraction and scanning electron microscopy show more defined crystalline mineral composition of the naturally weathered and artificially weathered ash materials when compared to carbonated or fresh ash materials. The use of elevated temperatures in addition to increase pressures and varying moisture contents proved to be comparable to natural weathering processes in initial weathering product tendencies. However combined weathering methods of carbonation and artificial weathering proved more effective at reduction of lead leaching than did either method alone.

INTRODUCTION

Incinerator byproduct materials, both fly and bottom ash, are composed primarily of amorphous minerals, salts, and metals, and meet a non-biological definition of soil as an unconsolidated mineral material.¹ As such, the chemical and physical weathering characteristics of soils can be applied to ash, with the predictions and theories applied to the weathering of soils also applicable to these granular byproduct materials. Dissolution and precipitation are chemical weathering processes that impact the inorganic content and composition of unconsolidated mineral materials.² Dissolution of the soluble components of amorphous ash material and their subsequent precipitation leads to a crystalline mineral development in aging ashes, with maturation of the ash determinable by the speciation of crystalline mineral composition. Identifying the speciation and development of crystalline minerals with maturation of the ash will contribute to understanding the controlling mechanisms in their heavy metal leaching characteristics. To better understand the natural impact of natural weathering on ash materials a natural analog is used to assess the natural weathering progression and degree of mineralogical development of these industrial granular byproduct materials.

Volcanic ash has been used as a coal fly ash and bottom ash analog, as composition, size, and surface area are similar.³ However volcanic ash pH is typically near neutral, while coal and MSWI ashes may have typical pH values up to 13. Differences in pH aside, the weathering products of volcanic ash material will be similar in mineralogical and physical properties. The relatively large surface area of the ash materials permits more intense surface controlled dissolution than typical soils. This combined with the difference in initial pH values contribute to the natural rapid weathering rate of coal and MSWI ashes. Since unaltered coal and MSWI ashes weather rapidly, the possibility of enhancing and controlling the weathering rate of these ashes is high. The artificial accelerated weathering of ash materials in a laboratory setting allows for elucidation of the controlling mechanisms in heavy metal leaching properties.

The governing hypothesis for this work is that chemical weathering of industrial byproducts are important to understand in order to predict the long-term environmental impact and risk associated with their beneficial use. Furthermore, it is hypothesized that these chemical reactions can be controlled by monitoring and altering the variables in soil solution conditions, and that the reactions can be accelerated in the laboratory. This research is proceeding by collecting ash materials preserved in initial condition and comparing the mineralogical development of the fresh materials to that of naturally aged materials of similar or identical origin. The fresh ash materials are then subjected to accelerated weathering techniques with resultant relative age of this artificially weathered material determined by comparison to mineralogical and crystalline speciation and development of naturally aged materials. A number of analytical techniques are being employed to determine an equivalent weathering age, analogous to the weathering stages of soils based on the distributions of primary and weathered products.

MATERIALS AND METHODS

Sample Materials

Three sub-samples of municipal solid waste incinerator bottom ash (MSWI bottom ash) were received from Dr. David Kosson and Sarynna Lopez at Vanderbilt University: ash preserved in a nitrogen atmosphere in initial condition, ash preserved in a nitrogen atmosphere aged by carbonation for one month, and ash preserved in a nitrogen atmosphere naturally aged for one month. Pulverized coal fly ash (PCFA) was received from Dr. Ole Hjelmar of the Vandkvalitetsinstituttet, naturally aged for twenty years in an ash monofill.⁴ Samples from three depths of the monofill were analyzed for comparison. Although not of identical origin, similarities in both particle size and chemical composition of the MSWI bottom ash and PCFA sample materials allow for a limited comparison as to potential development of the younger ash material.

Experimental Design

The high temperature thermal processes involved in incineration are analogues to the high temperature processes involved in a volcanic event which results in formation of ash materials. These high temperature processes produce a byproduct that is thermodynamically unstable in the natural environment. After subsequent chemical weathering of these geochemically unstable reactants, the product materials have vastly different environmental properties. To examine the geomorphological development of the weathering ash and characterize this development as a function of time, analysis of the amorphous species, elemental composition, and crystalline phases of the fresh and aged ash materials must be determined.

Carbonation of granular byproduct materials, MSW incinerator bottom ash in particular, has been shown to reduce certain heavy metal leaching characteristics as well as the pH of the subjected material.⁵ The mineralogical development of the ash influenced by carbonation has yet to be well defined. Accelerated weathering by elevated temperature and pressure at 100% moisture holding capacity, potentially in conjunction with carbonation, would mimic the major chemical weathering conditions of naturally weathered mineral materials. Variables in the conditions that allow an acceleration of natural weathering without yielding products that would not occur in a natural weathering environment must be manipulated to best replicate an equivalent end product.

X-ray powder diffraction has been utilized to analyze crystalline mineral phases of fresh ash material, carbonated material, artificially accelerated weathered material, combined carbonated and artificially accelerated weathered material, as well as various naturally aged ash materials. Samples were ground by mortar and pestle, then sieved through a number 80 (177 micron opening) sieve. X-ray diffraction patterns were collected from 10° to $90^\circ 2\theta$, at a $.02^\circ$ step size and residence time of 2.5 seconds/step. The resultant diffraction patterns of these materials have then been compared. Scanning electron microscopy (SEM) has been used to visually validate the presence of the crystal mineral phases identified by XRD. Samples sieved through a number 80 sieve were mounted on a carbon coated (adhesive) sample stud then coated with gold palladium. Leaching characteristics of the carbonated material and combined carbonated and artificially weathered material were identified by batch pH dependant leaching tests, in the pH range of 2 to 12.

RESULTS AND DISCUSSION

Spectral data obtained from XRD analysis of the fresh, carbonated and artificially weathered ash material demonstrate differences in major compositional content. (Figure 1) Mineral components of each ash sample with figure of merits (FOM) as calculated by Jade Software used for interpretation of the spectral data, less than 20 are given in Table 1. Figure of merit is used in this application as an indicator of peak match when referenced with a tungsten standard for qualitative purposes. The intensity of calcite peaks (most notably at $23.041, 29.44 2\theta$) is the greatest for the carbonated sample, with relative intensity of 100%, followed by the fresh ash at 87%, and the artificially aged ash at 85%. Quartz (notable at $20.8 2\theta$) which only exists as a minor constituent of the fresh ash material, increases in relative intensity from the carbonated sample at 33%, to the artificially aged sample at 38%. With the exception of johannsenite and hedenbergite, both of which are inosilicates, the remainder of the major mineral constituents are sulfides(ates), phosphates, and (hydr)oxides, or variations of these three.

Minor constituents of the three samples consist of hydrates and (hydr)oxides of various metals, as well as quartz and calcite. The artificially weathered sample typically has better defined mineral phases, including alumino-silicate clays, as opposed to the fresh and carbonated ash materials containing more poorly defined metal (hydr)oxides.

XRD spectral data of the three PCFA samples aged naturally for 20 years show only slight differences in mineral composition with depth. (Figure 2) The spectral data are presented from top PCFA sample to bottom PCFA sample. Major constituents of the PCFA sample are quartz, calcite, gismondine, and mullite. Gismondine and mullite are typically products of high temperature processes; gismondine, a zeolite is typically found in cavities of igneous rocks, while mullite, a nesosilicate, is typically a ceramic product of high temperature alteration of kaolinite, andalusite, or other anhydrous aluminosilicates. It is possible the presence of these minerals is relic of the original material, or may be a natural weathering progression of initial ash components.

Comparing the XRD spectral results of the MSWI bottom ash and PCFA (Figures 1 and 2) the more weathered PCFA is evident by the reduction in background resulting from amorphous material. The younger MSWI bottom ash exhibits a greater number of less intense peaks indicative of the less defined crystalline mineral composition.

SEM micrographs of carbonated, artificially weathered, and naturally weathered ash materials present visual indications of the more defined mineral content of the artificially and naturally weathered materials. (Figures 3, 4 and 5) Figure 3 is representative of poorly crystalline metal (hydr)oxides.

The micrographs in Figures 4 and 5 are relatively characteristic of an aluminosilicate clay particle, such as halloysite, a minor constituent of the artificially weathered ash material.

The micrographs, in conjunction with XRD results, suggests the method of artificial weathering being used as acceptable in developing mineral phases that would occur under natural weathering conditions.

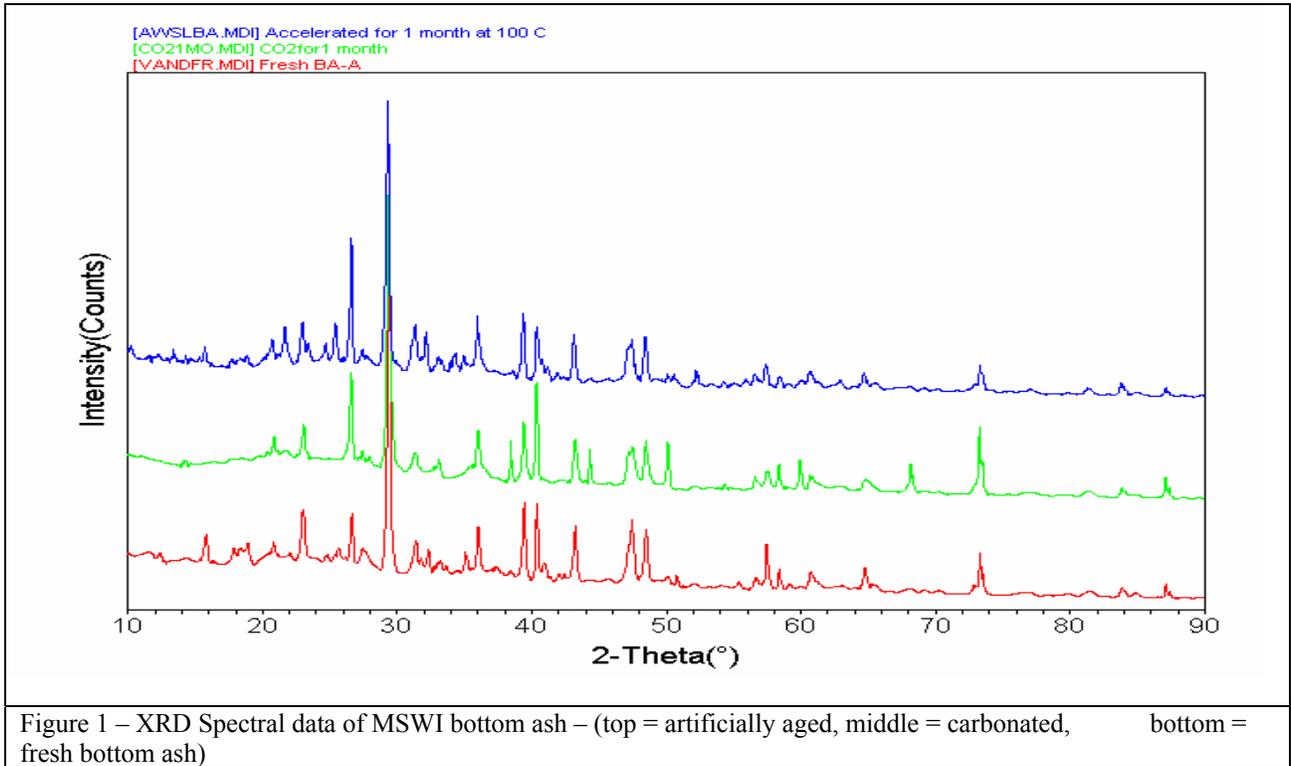
The implications of the weathering on lead leaching characteristics of the MSWI bottom ash were determined by pH dependant leaching tests. (Figure 6) The combined artificial weathering and carbonation has the greatest reduction in lead leaching in the range of 2 to approximately 10.

CONCLUSION

The development of a potential beneficial re-use of industrial byproduct materials is imperative. In order to ensure an environmentally stable product, better understanding of the entire morphological maturation process of these materials must be attained. The artificial weathering by elevated temperatures and pressures provides a practical and controllable means by which to evaluate the geomorphological development of incinerator residues, with potential application to a wide variety of industrial granular byproducts. In addition, by studying the crystalline mineral composition and phases of development, our knowledge of the long term leaching behavior and subsequent environmental stability will be better refined. The tendency for weathering ash materials to develop toward aluminosilicate materials is consistent with the use of volcanic ash as a natural analog, and consistent with observations of naturally weathered incinerator residues.

REFERENCES

1. Birkeland, Peter W., Soils and Geomorphology, Oxford University Press, New York, NY
2. Sparks, Donald L.; Environmental Soil Chemistry, Academic Press, San Diego, CA, 1995
3. Zevenbergen, C., Bradley, J.P., Ven Reeuwijk, L.P., Shyam, A.K., Hjelmar, Ole, Comans, Rob N., *Clay Formation and Metal Fixation during Weathering of Coal Fly Ash*, Environmental Science and Technology, 1999, 33, 3405-3409
4. Hjelmar, Ole, Hansen, Aagaard, Flemming, Larsen, Thomassen, Hanne,; Leaching and Soil/Groundwater Transport of Contaminants from Coal Combustion Residues, Denmark, Water Quality Institute
5. Lopez, Sarynna, Sanchez, Florence, Kosson, David, *Evaluation of the Impact of Environmental Conditions on Constituent Leaching from Granular Materials During Intermittent Infiltration*, Conference Proceedings, Beneficial Use of Recycled Materials in Transportation Applications, Nov. 2001



| Table 1 – Mineral Composition of Ash Materials with Figure of Merit < 20 | | | |
|--|--------------|--------------------------------|-----------------|
| Sample Source | Mineral Name | Chemical Formula/Mineral Group | Figure of Merit |
| Fresh Ash Material | Calcite, syn | CaCO ₃ /Carbonate | 4.9 |

| | | | |
|--|----------------------------------|--|------|
| | Cobalt Phosphate | Co ₂ (P ₂ O ₇)/Phosphate | 9.8 |
| | Piypite | K ₂ Cu ₂ O(SO ₄) ₂ /Anhydrous Sulfate | 10.4 |
| | Hedenbergite | CaFeSi ₂ O ₆ /Inosilicate | 11.7 |
| | Billingslevite, syn | Ag ₇ AsS ₆ /Sulfide-sulfosalt | 12.7 |
| | Brandtite | Ca ₂ Mn(AsO ₄) ₂ ·2H ₂ O/Hydrated Phosphate | 12.7 |
| | Silicon Sulfide | SiS ₂ /sulfide | 17.5 |
| | | | |
| Carbonated Material | Calcite, syn | CaCO ₃ /Carbonate | 4.5 |
| | Calcium Cobalt Vanadium Oxide | CaCoV ₂ O ₇ /Oxide | 7.8 |
| | Silicon Sulfide | SiS ₂ /Sulfide | 7.8 |
| | Magnesium Vanadium Oxide | MgV ₂ O ₆ /Oxide | 9.6 |
| | Billingslevite, syn | Ag ₇ AsS ₆ /Sulfide-sulfosalt | 10.2 |
| | Piypite | K ₂ Cu ₂ O(SO ₄) ₂ /Anhydrous Sulfate | 10.7 |
| | Johannsenite | CaMnSi ₂ O ₆ /Inosilicate | 10.7 |
| | Quartz, syn | SiO ₂ /Silicate | 12 |
| | Brandtite | Ca ₂ Mn(AsO ₄) ₂ ·2H ₂ O/Hydrated Phosphate | 14.2 |
| | | | |
| Artificially Weathered Material | Calcite, syn | CaCO ₃ /Carbonate | 3.7 |
| | Calcium Cobalt Vanadium Oxide | CaCoV ₂ O ₇ /Oxide | 4.2 |
| | Zinc Hydroxide | Zn(OH) ₂ /Hydroxide | 15.6 |
| | Ammonium Calcium Sulfate | (NH ₄) ₂ Ca ₂ (SO ₄) ₃ /Sulfate | 15.6 |
| | Burtite, syn | CaSn(OH) ₆ /Hydroxide | 15.6 |
| | Sodium Zinc Phosphate | NaZnPZnO ₄ /Phosphate | 16.1 |
| | Sodium Iron Selenite | NaFe(SeO ₃) ₂ /Selenite | 17.4 |
| | Magnesium Phosphate | Mg ₂ P ₂ O ₇ /Phosphate | 18.6 |
| | Potassium Sodium Manganese Oxide | K ₂ NaMnO ₄ /Oxide | 18.9 |
| | Quartz, syn | SiO ₂ /Silicate | 18.9 |

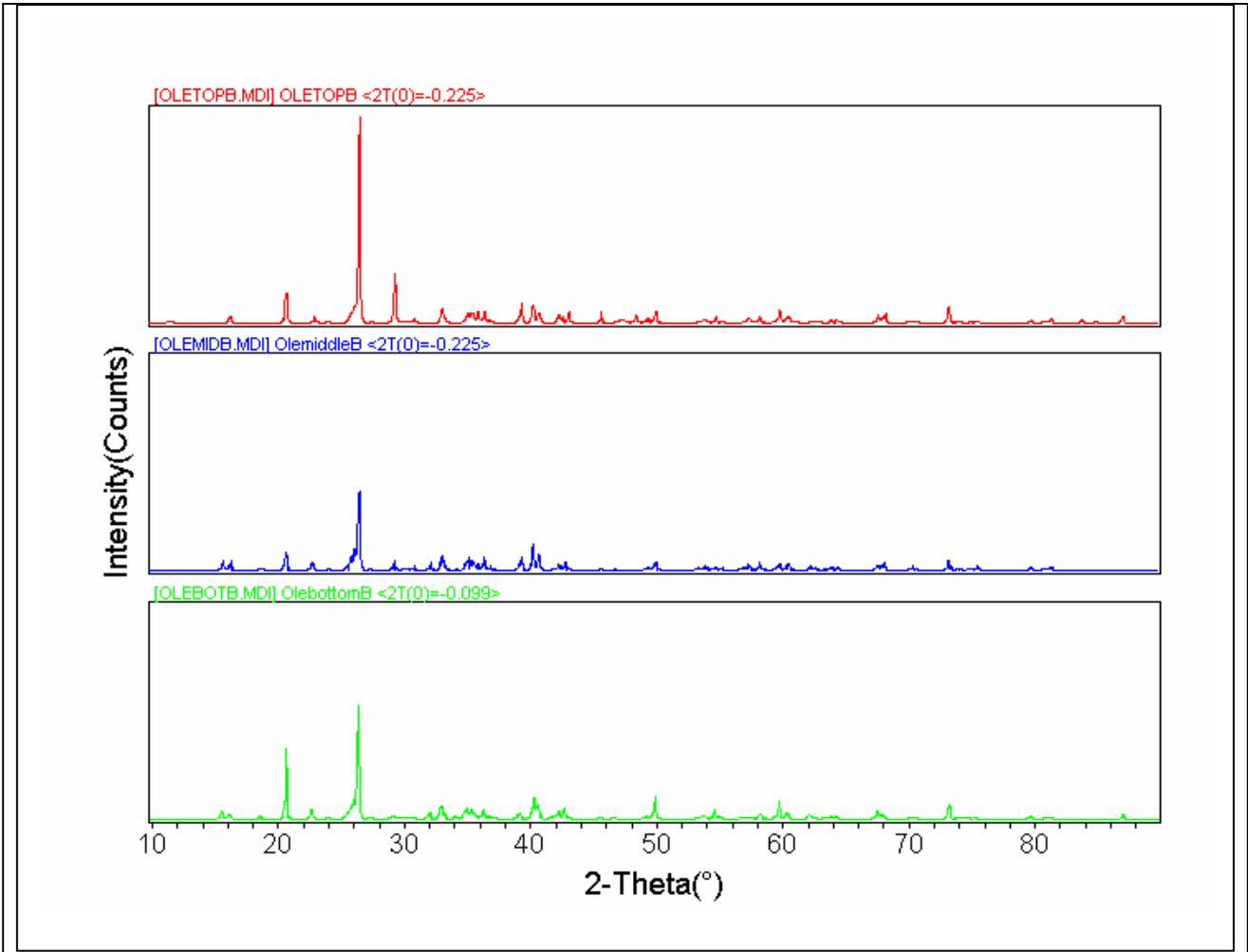


Figure 2 – XRD spectral data of PCFA aged 20 years

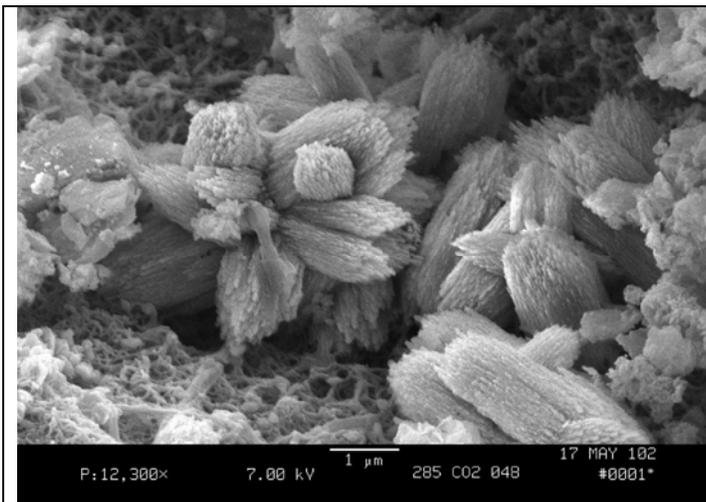


Figure 3 – SEM micrograph of carbonated ash

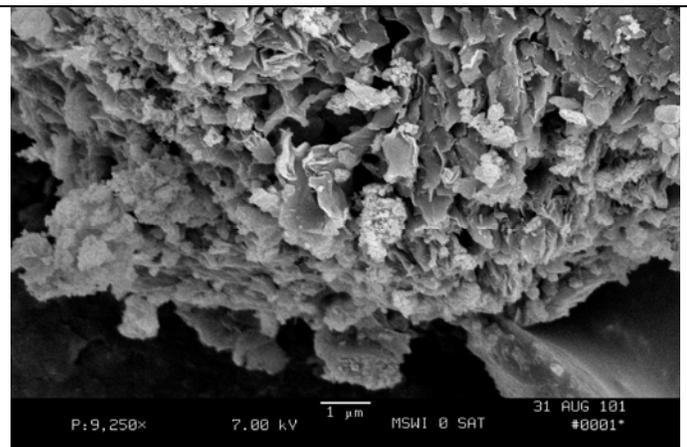


Figure 4 – SEM micrograph of artificially weathered ash

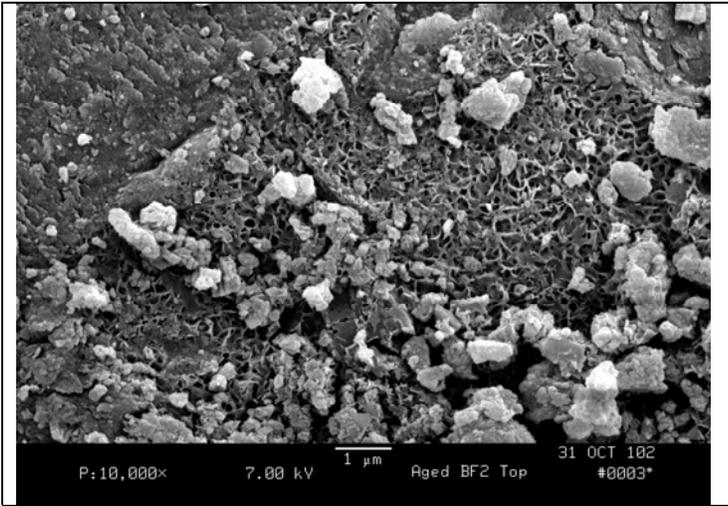


Figure 5 – SEM micrograph of PCFA aged 20 years+

Long-term Leaching Behavior Changes in Granular Waste Materials due to Chemical Weathering Processes: Implications for Beneficial Use

(published in Beneficial Use of Recycled Materials in Transportation Applications, 2003)

Robert Carter

Environmental Research Group, 330 Environmental Technology Building, University of New Hampshire, Durham, N.H. 03824, (603) 862-1197 rkcarter@unh.edu

Kevin Gardner *

Environmental Research Group, 330 Environmental Technology Building, University of New Hampshire, Durham, N.H. 03824, (603) 862-4334, kevin.gardner@unh.edu

Takayuki Shimaoka

Institute of Environmental Systems, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka, 812-8581, Japan, +81-92-642-4090, Fax: +81-92-642-3848, himaoka@ies.kyushu-u.ac.jp

Kentaro Miyawaki

Civil Engineering Department, Fukuoka University, 8-19-1 Nanakuma, Johnan-ku, Fukuoka, 814-0180, Japan, +81-92-871-6631, Fax: +81-92-863-8248, miuawaki@fukuoka-u.ac.jp

ABSTRACT:

One of the important aspects of using recycled materials in a beneficial manner in roadway construction is assurance of human health and environmental protection. Long-term leaching of metals from ashes, slags, and foundry materials, that are excellent candidates for base materials, is a process that requires further elucidation, particularly as these materials are subject to chemical weathering over time. Chemical weathering has the potential to significantly impact estimates of long-term leaching from byproduct materials, but the mechanisms by which this occurs are still not well understood or documented. This paper presents an investigative technique reliant largely on Fourier Transform Infrared Spectroscopy, in combination with complementary analytical techniques, to characterize phase changes in MSW bottom ash that has been weathered in a lysimeter for 3 years. FTIR results demonstrate the weathering of allophane and proto-immogolite allophane tending toward halloysite, which implies a limiting factor in the weathering process and further suggests that the weathering products of ash materials may be intentionally altered by control of the porewater chemistry.

INTRODUCTION

There are numerous granular byproduct materials, such as combustion ashes, and smelting and foundry byproduct materials, that are limited in their reuse potential by poor environmental performance. Concern over the leaching of contaminants may result in prohibition against a material's reuse, or may represent an unacceptable liability risk to the corporation, utility, or municipality interested in the reuse of a material. Furthermore, there is a need for greater accuracy in understanding how a material may leach in a given environment over time such that more precise, application-specific exposure scenarios can be developed. A lack of risk information has been cited as one of the largest barriers to the use of recycled materials in highway applications by a recent survey conducted by the Association of State and Territorial Waste Management Officials (ASTSWMO, 2000).

Many granular byproduct materials, however, have been observed to undergo natural transformations when left in an exposed environment for a number of years. These granular materials originate from high temperature processes that produce a byproduct that is thermodynamically unstable in the natural environment. After chemical weathering of these geochemically unstable "reactants," the product materials have vastly different environmental properties. These chemical weathering processes have not been well documented in the literature and have only been investigated for a small number of materials from high-temperature processes. Furthermore, mechanisms by which leaching processes are changed by these geochemical reactions have not been elucidated.

This research is focused on understanding these natural reactions so that there is a greater understanding of how leaching of contaminants changes with the geochemical weathering of the byproduct material. Furthermore, methods to accelerate the weathering process are being investigated, which offers the potential that beneficiation methods can be used to develop a useful and environmentally acceptable product. Changes in physical properties of these materials will also be investigated to document how the geochemical changes influence the physical and mechanical behavior of the materials, which is an important consideration for the beneficial use of these materials in highway construction.

HYPOTHESIS

Ashes and slags are composed primarily of amorphous minerals, salts, and metals, and meet a non-biological definition of soil as an unconsolidated mineral material.(Sparks, 1995) As such, the chemical and physical weathering characteristics of soils can be applied to ash, and the predictions and theories applied to the weathering of soils may also be applicable. Dissolution and precipitation are chemical weathering processes that impact the inorganic content and composition of unconsolidated mineral materials (Sparks, 1995). Alumino-silicate clay formation is derived from the dissolution of primary minerals and the subsequent precipitation secondary minerals. The concentrations of aluminum, silicon, other major and minor elements, moisture and the pH of the "soil" solution determine the speciation of the clay mineral formed(Buol, S.W, et.al., 1980)

“Surface-controlled” dissolution occurs when transport reactions occur more quickly than surface reactions, which occurs in silicates and oxides. This surface controlled rate is proportional to the surface area of the minerals. (Sparks, 1995) Fly ashes are usually fine particles, with relatively large surface areas, while bottom ashes, slags, and foundry and smelting byproducts may be large granular particles with lower surface areas. Volcanic ash has been used as a fly ash and bottom ash analog, as composition, size, and surface area are similar (Zevenbergen, C., et al, 1994; Zevenbergen, C., et al, 1999), but volcanic ash pH is typically near neutral, while coal and MSWI ashes may have typical pH values up to 13. The relatively large surface area allowing more intense surface controlled dissolution, combined with the difference in “parent material” pH values contribute to the accelerated weathering rate of coal and MSWI ashes. If unaltered coal and MSWI ashes weather rapidly, than the possibility of enhancing and controlling the weathering rate of these ashes is high. Other granular material that is being investigated is not expected to weather at the high rate of very basic fly ashes, although over the long term their weathering and alteration of leaching properties may be significant.

The governing hypothesis for this work is that chemical weathering of industrial byproducts are important to understand in order to predict the long-term environmental impact and risk associated with their beneficial use. Furthermore, it is hypothesized that these chemical reactions can be controlled by manipulating the soil solution conditions, and that they can be accelerated in the laboratory. This research is proceeding by first collecting waste materials that have been exposed to the natural environment for many years. A number of analytical techniques are then being employed to determine an equivalent weathering age, analogous to the weathering stages of soils based on the distributions of primary and weathered products.

Materials and Methods

STUDY MATERIALS

Although a fair amount of work has been conducted using coal ashes and MSWI bottom ash, these materials are the first materials being studied in this research in order to “calibrate” the methods and aging stages that will be used for these and other materials. Additional materials that will be investigated in this research are those for which beneficial use in the highway environment is likely, and will include aluminum dross and blast furnace slag. The research presented in this paper has been conducted on MSWI bottom ash mined from a lysimeter in Japan. MSWI bottom ash was placed in this lysimeter for a period of three years, and was left exposed to the environment in the city of Fukuoka, on the southern-most island of Japan. The lysimeter was sampled after 3 years and samples were taken from 7 depths - sample 1 – 0 c.m., sample 2 – 35 c.m., sample 3 - 85 c.m., sample 4 – 135 c.m., sample 5 – 185 c.m., sample 6 – 235c.m., and sample 7 - 285 cm.

EXPERIMENTAL METHODS

Fourier Transform Infrared Spectroscopy (FTIR) analysis was done by combining small amounts of sample (< 0.1g) crushed by mortar and pestle with potassium bromide and pressing into a slide. The slides were then analyzed by Colet FTIR Spectroscopy with results given in percent transmittance.

Two sets of samples were glued to a sample stud with carbon paint. One sample stud was coated with gold palladium for scanning electron microscopy (SEM). The other sample stud was coated with carbon for analysis by energy dispersive x-ray spectroscopy (EDS). SEM work was done on an Amray 3300 F.E. S.E.M., and EDS work was done by EDS P.G.T. EDS analysis was qualitative only, not quantitative.

For x-ray diffraction (XRD) work, 1g of each sample to be analyzed was crushed by mortar and pestle and sieved through a number 50 sieve (300 μm). Approximately 0.3g of the sample were placed on a slide without altering the surface of the sample, and placed in the slide tube. Data analysis was done by Jade software.

Leaching tests were conducted by suspending ash samples (crushed and sieved to <200 μm) in distilled, deionized water in a 1:10 liquid:solid ratio (e.g. 10 g solid in 100 ml solution). The suspension was agitated for 6 hours and filtered through a 0.45 μm filter and preserved as appropriate for chemical analysis. pH-dependent leaching was carried out in a similar fashion, maintaining a pH-stat condition at different pH values with the use of strong acid and strong base.

Post analysis of the initial materials, 15 g of sample 1 was subjected to 185 ° C under 100% saturation, for 96 hours, then analyzed by SEM and XRD to determine degree of crystallinity and effectiveness of hydrothermal treatment as method for acceleration of weathering reactions.

Results and Discussion

Previous research on MSWI Bottom Ash has determined the main crystalline phases to be silicates, oxides, carbonates, and salts (Speisser, C., et al, 2000). Our analysis of MSWI Bottom Ash aged for three years in a lysimeter, by FTIR, SEM, EDS, and XRD, shows preliminary results concurring with these findings.

Fourier Transform Infrared Spectroscopy (FTIR) has been used to monitor phase change in solids of contaminated weathering soils, though not widely used in analysis of ash materials. (Martinez, C.E., et al, 2001) Utilizing this approach to view solid phase change of naturally weathering amorphous ash materials will assist in defining the depth and extent of the weathering front, and rate of pedochemical and geochemical processes.

Spectral data for sample 1 (0 cm depth) strongly indicate the presence of silicates, carbonates, phosphates and possibly nitrates. Silicates are indicated with diagnostic peaks at 3450 cm^{-1} , 1050 and 1100 cm^{-1} , 940, 805, and 450 cm^{-1} (Smith, B., 1999). Peaks diagnostic of allophane (980 and 570 cm^{-1}), halloysite (1100 and 470 cm^{-1}) and possibly immogolite (690 and 430 cm^{-1}) are also present representing silicate minerals (Figure 1.1) (Martinez, C.E., et al, 2001). Similarly, FTIR spectral data indicated the presence of carbonates, with bands at 1540 to 1410 cm^{-1} , 880 to 860 cm^{-1} , and approximately 740 cm^{-1} . Phosphate bands are pronounced at 1100 to 1000 cm^{-1} , and at 600 to 500 cm^{-1} . Nitrate bands are less defined at 1400 to 1340 cm^{-1} , 840 to 810 cm^{-1} , and slightly more defined at 720 cm^{-1} (Figures 1.2 and 1.3) (8).

FTIR spectral data for sample 2 at 35 c.m. (Figure 2.1), show the silanol Si-O stretch is less defined, as well as a decrease in intensity for all silicate peaks. Diagnostic peaks for allophane, immogolite and halloysite are much less intense and less defined than in sample 1, indicating an overall phase change of the structural form of silica. Inorganic carbonates and nitrates do not have well defined peaks in sample 2 (Figures 2.2 and 2.3), lacking a C-O stretch peak, as well as a N-O out of plane bend. This implied decrease is consistent with expected retarded weathering rates with sample at depth considering limited exposure to atmospheric conditions.

Spectral data for samples 3 and 4, 135 c.m and 235 c.m., respectively, show similar trends: a decrease in intensity of diagnostic peaks of carbonates and nitrates, with silicates and phosphates maintaining the most significant presence of mineral structure. Sample 4 shows a slight increase in intensity of peaks of silicates and phosphates, indicative of higher concentrations of relic materials.

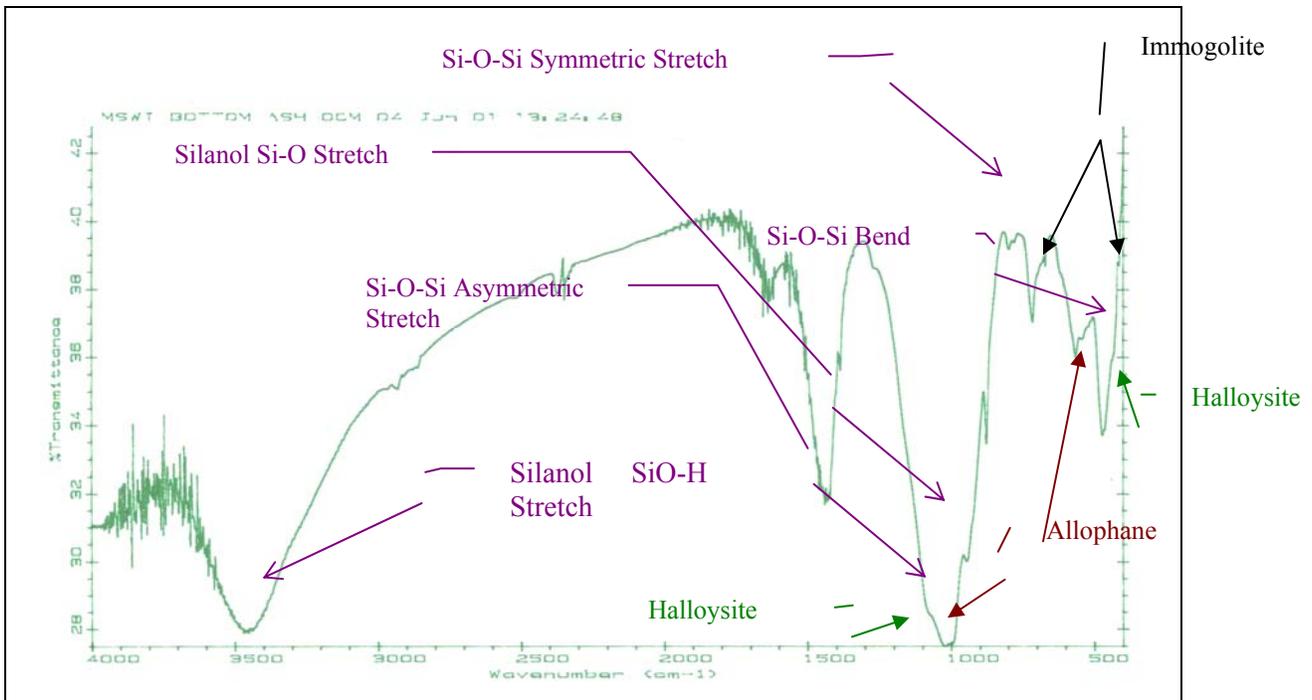
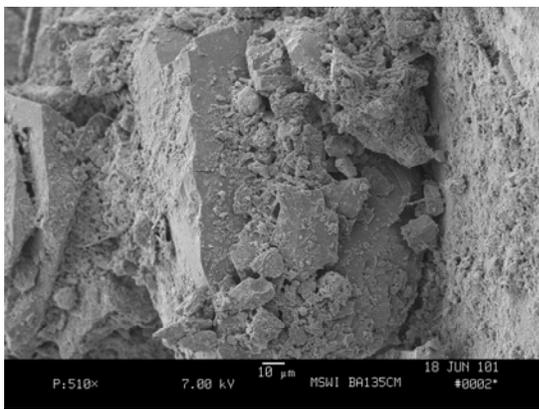
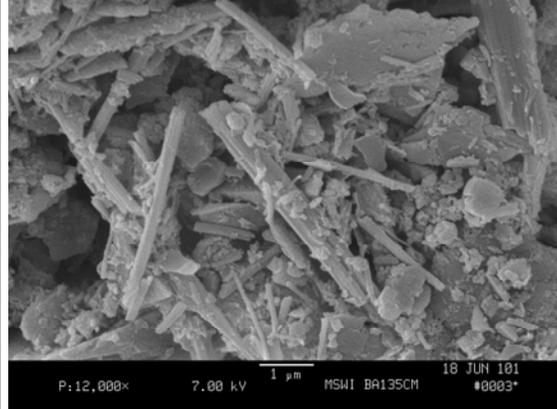


Figure 1.1 – FTIR Spectral Data of Sample 1 – MSWI Bottom Ash from 0 c.m., 3 yrs. Old

EDS determination of chemical composition by atomic percentage indicates the presence of Al, C, Ca, Cl, Cu, Fe, K, Mg, Mn, Na, O, P, Pb, S, Si, Ti, and Zn. XRD results for samples 1 and 7, 0 c.m. and 285 c.m., respectively, were reviewed for a comparison to view the lysimeter samples as a weathering profile, with sample 7 analogues to the “parent material”. The major composition of sample 7 is quartz, calcite, and gismondine ($\text{CaAl}_2\text{Si}_2\text{O}_8 \cdot 4\text{H}_2\text{O}$), with minor and trace constituents of metal oxides and hydroxides. The major constituent of sample 1 is calcite, with minor constituents of quartz, metal oxides and hydroxides.



SEM of ash material aged for 3 yrs.



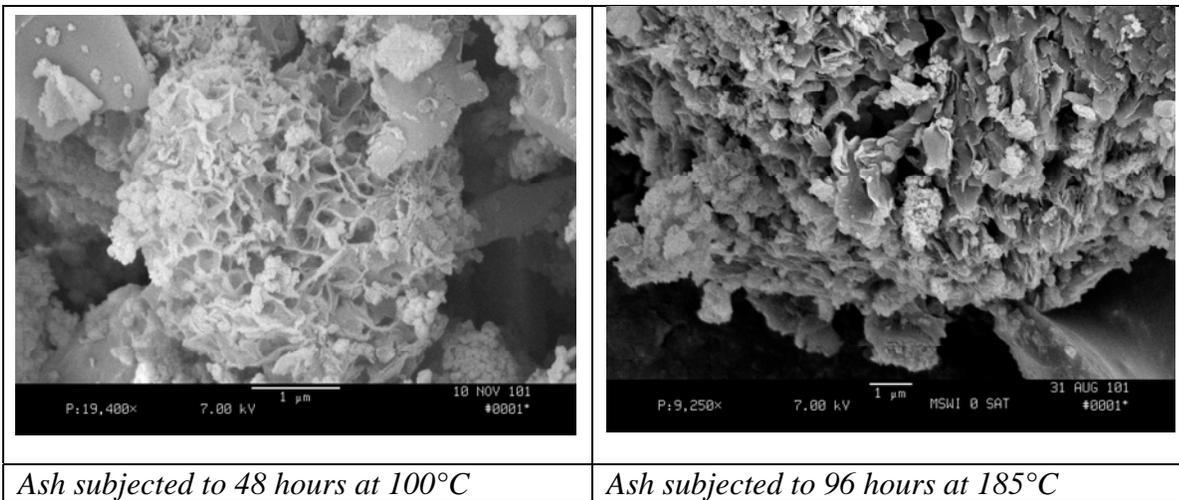
SEM of ash material aged for 3 yrs.

Gismondine ($\text{Ca}_2\text{Al}_4\text{Si}_4\text{O}_{16} \cdot 9(\text{H}_2\text{O})$), a tectosilicate zeolite (framework silicate), is an alteration of plagioclase feldspars (Gaines, R.V., et al, 1997). The presence of gismondine in the sample at

depth is likely relic as zeolites have typically been thought to form from rapid cooling of igneous rock. However zeolites may also occur as alterations of volcanic tuff and glass (Klein, C., et al, 1993); application of this theory to the glassy constituent of bottom ash allows the hypothesis of natural geochemical processes occurring. In the sample at depth, where pH values are more basic than at the surface, and exposure to CO₂ is limited, Ca is not bound by carbonate, and is able to be incorporated into silicate mineral structures.

Cation exchange capacity (CEC) and pH dependant leaching of Pb data support the development of alumino-silicate clay materials as well. CEC of the 0 c.m. sample is substantially higher than the subordinate samples, despite the smaller specific surface area. These factors may explain the drastic difference in Pb leachability at the higher (>10) pH levels.

XRD results for samples subjected to hydrothermal treatment indicated the presence of quartz, tridymite, anorthite, albite, calcium oxide as primary constituents. Anorthite, CaAl₂Si₂O₈, and albite, NaAlSi₃O₈, are plagioclase feldspars, while tridymite is part of the silicate group, ideally SiO₂, with possible incorporation of Na and Al.



CONCLUSION

The presence of allophane and immogolite, and their pedogenic subordinate halloysite, in three year old MSWI bottom ash leads to the hypothesis that alumino-silicate clay minerals will develop from the natural weathering of these ashes. The indication by FTIR analysis of phase changes at depth allows for determination of a weathering or pedogenic profile to be established. With the profile established, and the species of crystalline structures present within each profile, an approximate age may be applied to form a reference for leaching characteristics of materials at varying degrees of geochemical alteration. The weathering of allophane and immogolite to halloysite, as opposed to

gibbsite or kaolinite, implies a limiting factor in the weathering process. If these factors, pH, ionic concentrations, moisture, and temperature, are controlled in attempts to accelerate the weathering process, the speciation of the resulting aluminosilicate clay may be controlled. The positive results from hydrothermal treatment of the formation of plagioclase feldspars strongly concurs with the hypothesis of accelerating the weathering processes by manipulating the factors involved in the weathering process. This not only has implications for future conduct of research on these materials, but for potential long-term treatment methods as well.

Acknowledgments

This work was funded through a cooperative agreement (DTFH61-98-X-00095) between FHWA and the University of New Hampshire.

REFERENCES

- (1) ASTSWMO. 2000. ASTSWMO Beneficial Use Survey. Association of State and Territorial Solid Waste Management Officials, Washington, D.C.
- (2) Sparks, Donald L.; Environmental Soil Chemistry, Academic Press, San Diego, CA, 1995, 38-39
- (3) Buol, S.W., Hole, F.D., McCracken, R.J., Soil Genesis and Classification, Iowa State University Press, 1980, 2nd edition
- (4) Zevenbergen, C., Vander Wood, T., Bradley, J.P., Van Der Broeck, P.F.C.W., Orbons, A.J., and Ven Reeuwijk, L.P., Morphological and Chemical Properties of MSWI Bottom Ash with Respect to the Glassy Constituents, Hazardous Waste and Hazardous Materials, Mary Ann Liebert, Inc, 1994, Vol.11, no. 3
- (5) Zevenbergen, C., Bradley, J.P., Ven Reeuwijk, L.P., Shyan, A.K., Hjelmar, O., Comans, R.N.J., Clay Formation and Metal Fixation during Weathering of Coal Fly Ash, Environmental Science Technology, 1999, 3, 3405-3409
- (6) Speisser, C., Baumann, T., Niessner, R., Morphological and Chemical Characterization of Calcium-Hydrate Phases Formed in Alteration Processes of Deposited Municipal Solid Waste Incinerator Bottom Ash, Environmental Science and Technology, 34, 23, 2000, pp 5030-5037
- (7) Martinez, C.E., Jacobson, A., and McBride, M.B., Thermally Induced Changes in Metal Solubility of Contaminated Soils is Linked to Mineral Recrystallization and Organic Matter Transformations, Environmental Science and Technology, 2001, 35, 908-916

(8) Smith, Brian, Infrared Spectral Interpretation, a systematic approach, CRC Press, Boca Raton, FL, 1999, 165-174

(9) Gaines, R.V., Skinner, H.C., Foord, E.E., Mason, B., Rosenzweig, A., Dana's New Mineralogy, John Wiley and Sons, Inc, New York, 1997

(10) Klein, C., Hurlburt, C.S., Manual of Mineralogy 21st Edition, John Wiley and Sons, Inc, New York, 1993, 551

**MECHANISMS FOR THE AGING-INDUCED REDUCTION OF LEAD SOLUBILITY IN
SCRUBBER RESIDUES FROM MUNICIPAL SOLID WASTE COMBUSTION**

(Published in Waste Management and Research, 2002)

Takayuki Shimaoka, Kentaro Miyawaki, Masashi Soeda, Masataka Hanashima

Department of Civil Engineering, Faculty of Engineering

Fukuoka University

Fukuoka, Japan

Tsuneyuki Yoshida, Toshihito Uchida

Planning and Research Department, Environmental Division

Kurita Water Industries Ltd.

Tokyo, Japan

Kevin H. Gardner, T. Taylor Eighmy

Environmental Research Group, Department of Civil Engineering

University of New Hampshire

New Hampshire, USA

Abstract

This manuscript elucidates the mechanisms responsible for aging-induced reduction in lead leaching from scrubber residues. Leaching tests (JLT13) were conducted on 48 types of scrubber residues and lead solubility was found to be significantly reduced independent of incinerator type or type of gas treatment method. Reaction kinetics that result in lead solubility reduction were shown to be proportional to carbon dioxide partial pressure and in many cases were limited by mass transfer to the residue. With forced gas convection through the residue and a CO₂ partial pressure of 0.3%, the concentration of lead in leachate was reduced from 84 mg/L to < 0.5 mg/L in two days. Ettringite analogs (Ca₆Al₂(SO₄)₃(OH)₂·26H₂O) were identified by X-Ray Diffraction in the wetted scrubber residues early in the aging process; these appear to have been converted into gypsum (CaSO₄·2H₂O) and vaterite (CaCO₃) in the aged material. All of these solid phases are believed to substitute lead into their crystal structure and evidence for this attenuation mechanism is presented.

Keywords - lead; heavy metals; municipal solid waste; wetted scrubber residues; solubility; aging; leaching; XRD; EPMA

1. Introduction

Dry scrubber residues from combustion of municipal solid waste (MSW) typically have high pH values when brought into contact with water, and heavy metals such as Pb are readily leached. This raises the concern that the surrounding environment may be adversely affected if these residues are used as material for construction or are improperly landfilled.

It has been shown that there is a decrease in leaching of components such as heavy metals, the so-called *aging effect*, if wetted bottom ash or wetted scrubber residue is exposed to air over some period of time (Zevenbergen et al. 1996, Johnson et al. 1996, Steketee et al. 1997, Meima et al. 1997, Shimaoka et al. 1998, Whiting et al. 1998, Meima et al. 1998, and Fallman et al. 1999). If solubility reduction of heavy metals by natural mechanisms occurs universally, aging methodologies can be expected to find widespread application as economical treatment and landfill disposal technologies. There have been no studies to clarify mechanisms that cause a reduction in heavy metal leaching when scrubber residues are aged in contact with moisture and air. This paper quantifies the reduction of lead solubility from wetted scrubber residues in response to aging and clarifies the responsible mechanism.

2. Materials and experimental methods

A series of two experiments were conducted. First, leaching tests were conducted in order to confirm age-induced reduction of lead solubility in wetted scrubber residue from 48 MSW combustion facilities. Subsequently, the influence of water content on the aging reaction and the pH-dependent leaching of lead in the aged residues were investigated.

Secondly, as it was inferred that the solubility reduction was related to carbon dioxide gas in contact with the wetted residues, the influence of CO₂ gas concentration on lead leaching was investigated. Furthermore, studies were conducted to examine what changes in the morphology and mineralogy of the scrubber residue compounds occurred during wetting and aging. In this survey, XRD (X-ray diffraction), EPMA (electron probe X-ray micro analysis), and SEM (scanning electron microscopy) were used to analyze original, wetted, and aged scrubber residues. The methods used in the two sets of experiments are described in more detail below.

Scrubber residues from 48 combustion facilities in Japan were classified into the following three types: (1) Stoker furnace incinerator with "dry" exhaust gas treatment (HCl in exhaust gas is neutralized with powdered Ca(OH)₂ and is removed by the dust collector), (2) Stoker furnace incinerator with "wet"

exhaust gas treatment (HCl is neutralized by liquid NaOH sprayed into the scrubber), and (3) Fluidized bed furnace with dry exhaust gas treatment.

Aging was accomplished by first wetting each scrubber residue with 30 wt% of distilled water and then leaving the residues exposed to the atmosphere for 24 hours. Leaching was determined by Notification No.13 of the Environment Agency in Japan (JLT13): distilled water of ten times the scrubber residue weight was added (L:S=10), and was agitated in a rotary shaker for six hours. The solution was filtered through a 1 μm filter prior to analysis. Lead in leachates was analysed by an atomic absorption spectrophotometry.

The percentage of water added to scrubber residues and the time duration of aging are considered to have a significant impact on the solubility of the heavy metals in scrubber residues. Wetted scrubber residues were created by varying the percentage of water added from 10 to 60 %. Wetted residues were exposed to the atmosphere and sampled over time to investigate temporal changes in Pb leaching. In this experiment, the scrubber residues from three incinerators with different types of incinerators and exhaust gas treatment methods were used (SD1 residue representing stoker furnace with dry treatment, SW1 residue representing stoker furnace with wet treatment, and FD1 residue representing fluidized bed furnace with dry treatment). pH and alkalinity of solutions were measured by suspending the sample in distilled water at a 1 to 1,000 ratio, and titrating with a strong acid to the phenolphthalein endpoint. Alkalinity of the filtration residue was measured in the same way; the alkalinity reported is a summation of the filtrate plus filter residue alkalinities.

Finally, a pH dependent leaching test was conducted to determine the pH dependence of the lead phases formed by the wetting and aging process. The scrubber residue used in the test (FD2 residue) was from the fluidized bed furnace with dry gas treatment which was wetted with 30 wt% distilled water and aged for 90 days. The pH dependent leaching test was conducted with a liquid:solid ratio (L/S) of 10 and a shaking time of six hours. pH was adjusted using nitric acid and sodium hydroxide, and Ca, SO₄ and Pb were analyzed in the leachate after filtration through a 1 μm filter.

In an attempt to clarify the mechanism which provides the solubility reduction discussed above, the first step was to determine the contribution of CO₂ gas in the air. Scrubber residue SD2 was used in this set of experiments (stoker furnace, dry treatment). In order to pass air or CO₂ gas through the wetted

scrubber residues, the test equipment shown in Figure 1 was used. Wetted scrubber residues were made using 30 wt% of distilled water and were mixed by hand with a spatula for five minutes. After the bottoms of eight transparent acrylic resin-made columns (diameter = 25 mm, length = 250 mm) were filled with absorbent cotton, 30 g of sample was added so that the thickness would be 80 mm. Air or gas obtained by diluting CO₂ with N₂ to reach the specified partial pressures was forced through the sample at a flowrate of 20 L/kg/min (for 30 g sample this was 0.6 L/min), while being brought into contact with distilled water in order to prevent the sample from being dried. After the lapse of a specified period of time, all samples in the column were collected sequentially, and collected samples were subjected to the JLT13 elution test to measure pH, alkalinity, and Pb concentrations of the leachate.

Next, analyses using XRD, EPMA and SEM were made on the following three types of samples: (1) scrubber residues obtained by adding 10 wt% PbCl₂ (reagent) to the scrubber residue SD3 (the Pb content in the original scrubber residues was too small to analyse using these methods), (2) scrubber residues obtained by wetting the residues mentioned in (1), and (3) scrubber residues which were obtained by passing 3 % CO₂ gas through the residues mentioned in (2) for 48 hours (11 L/kg/min). XRD was used to investigate the crystalline compounds in each sample, SEM was used to photograph the portions containing a high concentration of Pb, and, EPMA was used to study the spatial distribution of elements.

3. Results and Discussion

Figure 2 shows the pH and Pb leachate (JLT13) concentration of the 48 scrubber residues from different types of incinerators and exhaust gas treatment methods, before and after being wetted and aged in air for 24 hours. Table 1 shows the minimum, maximum and average values of the pH and Pb concentration for three types of scrubber residues. The average pH of dry stoker furnace scrubber residues was 12.4, while the average pH of wet stoker furnace scrubber residues was 9.2. The average leachate concentration of Pb in the dry residues was 50.6 mg/L, greater by over an order of magnitude than that in the wet treatment residues that have a lower pH (maximum value 4.60 mg/L). However, the average Pb leachate concentration of the dry treatment residues mixed with water and aged for 24 hours was 26.2 mg/L, indicating the leachate concentration had been reduced to about half that of the original residue. This trend was observed consistently with all 48 residues investigated, which indicates the influence of wetting and aging seems to be consistent and universal.

Figure 3 shows the relationship between the Pb leachate concentration and pH for the residue from the stoker furnace with dry treatment (the same data as shown in Figure 2). The figure uses a solid line to show the theoretical solubility curve of $\text{Pb}(\text{OH})_2$ and PbCO_3 (total inorganic carbon = 10 mg/L). The Pb leachate concentration was greatly reduced upon wetting and aging, although it appears that concomitant pH reduction was small. This suggests that Pb solubility may be influenced not only by pH, but also by other chemical species in scrubber residues (for example, Ca and S). In fact, Figure 3 indicates little correlation between pH and Pb concentration in leachate, suggesting the primary mechanism responsible for the observed reduction in solubility is not controlled by pH. This observation is supported by the plots in Figure 2, where pH changes very little between wetted and dry, but Pb concentrations change significantly.

Figure 4 shows the relationship between the Pb leachate concentration, moisture content, and aging time for the three types of scrubber residues. For scrubber residues from the stoker furnace (SD1 and SW1 residues), Pb leachate concentration decreased as water added was increased. For the SD1 residue, Figure 4 shows a decrease in Pb concentration from 40 mg/L to 5.5 mg/L (average of percentages of added water), indicating a substantial reduction in Pb leachate concentration for the experimental period of 30 days. As shown, Pb elution characteristics after aging differ according to the type of scrubber residues and percentage of added water.

Lead leachate concentrations are typically controlled to a large extent by the solution pH. Figure 5 shows the pH and alkalinity of leachates from SD1 and FD1 residues as a function of aging time. In the case of the SD1 residue with a significantly higher alkalinity, alkalinity was reduced with time, but there was not much change in the pH of the leachate. As Figure 4 indicates, Pb solubility decreased significantly even though there was no change in pH: the solubility behavior seemed to be more closely associated with alkalinity changes. In the case of the FD1 residue with low alkalinity, by contrast, there was an abrupt reduction in pH and alkalinity with the start of the test. At the same time, the Pb concentration of FD1 residue was quickly reduced (see Figure 4). Note that the final alkalinity in the SD1 residue after 30 days of aging was still greater than the initial alkalinity in the FD1 residue.

Figure 6 illustrates the results of the pH dependent leaching test on wetted scrubber residue FD2 aged for 90 days and demonstrates the Pb solubility changes over a range of pH values. Pb solubility changed drastically on the alkaline side; it was 1.8 mg/kg after 90 days compared with 50 mg/kg initially at pH 12. Furthermore, elution of Ca and SO₄ was reduced in the range of pH from 8 to 12. In this pH range, elution of Ca was reduced from 9,800 mg/kg to 2,750 mg/kg, and that of SO₄ from 804 mg/kg to 5.9 mg/kg. As will be discussed below, the bound water of scrubber residue contains a high concentration of alkaline components, so it can be considered that CO₂ gas in air is absorbed to react with Ca dissolved in bound water, thereby forming insoluble carbonate phases. At the same time, it is likely that SO₄ reacted in the bound water to form insoluble sulfate phases.

Figure 7 shows the changes with time of the pH and Pb concentrations in leachates of the wetted SD2 scrubber residue aged in the atmosphere and in the column apparatus of Figure 1 (using air). Pb concentrations in leachates from residues where air was forced through in the column apparatus were reduced much more rapidly. In approximately two weeks, the limit of detection (0.05 mg/L) was reached in the column, whereas the Pb leachate concentration in the passively aged sample was reduced to 0.4 mg/l after 120 days. It is also interesting to note that pH was not reduced in the passively aged material even after 120 days, while pH began dropping after one week in the forced air system. It is clear that the speed of leachate concentration reduction can be increased substantially by promoting contact between wetted scrubber residues and air in this manner, which suggests mass transfer limitations in the passive aging experiments.

Similar experiments were conducted by changing the partial pressure of CO₂ that was transmitted through wetted scrubber residues in the columns. Partial pressures of CO₂ used were 0.03 %, corresponding to the concentration in the atmosphere, 0.3 % and 30 %. The CO₂ was mixed with N₂ to produce the appropriate partial pressures in this study. For comparison, pure N₂ gas and air were also used. Figure 8 shows the results of these experiments. Pb concentration was reduced slowly when CO₂ partial pressure was 0.03 %. At 0.3%, there was a significant increase in the rate of Pb leachate concentration reduction such that the time required for Pb concentration to fall below 0.1 mg/l was reduced from two weeks to two days. When the concentration of CO₂ gas was further increased to 30 %, the speed of concentration reduction in the initial phase were high, but no reduction in concentration was observed after

the second day. This is hypothesized to be the result of rapid CaCO_3 and CaSO_4 formation on the surface of the scrubber residue particles which acts as a barrier to CO_2 diffusion into particle pore spaces. The similarity between the N_2/CO_2 mix with 0.03% CO_2 and air (with approximately 0.03% CO_2) also suggests that the kinetics of the governing reactions are proportional to CO_2 partial pressure.

Close inspection of Figure 8 reveals a very significant phenomenon: that changes in Pb solubility are closely linked to changes in alkalinity, and do not appear to be associated with pH changes. Figure 8 demonstrates that pH decreases lag behind a reduction in alkalinity, as would be expected, but unexpectedly demonstrate that Pb leaching does not show such a lag. This observation has important practical implications for scrubber residue treatment processes.

Figure 9 shows the results of the pH dependent leaching test of scrubber residues from the experiments shown in Figure 8. The concentration of lead in leachate of wetted scrubber residues aged in the column apparatus was smaller than those of the wetted scrubber residues aged passively. The trend in solubility change was significant from pH 4 to pH 12. Data suggests that solubility may depend more on reactions brought about by CO_2 gas in the air, particularly reactions that reduce the alkalinity of the residue, than strictly on the pH of leachate.

It has been found that a reduction in Pb solubility can be accomplished by leaving wetted scrubber residues exposed to the atmosphere, and that alkalinity in the leachate and concentrations of Ca and SO_4 are simultaneously reduced. Based on these results, the following series of reactions can be hypothesized to effect solubility changes in Pb in scrubber residues:

- (1) Dissolution of lead into bound water (strongly alkaline water);
- (2) Generation of insoluble phases (such as CaCO_3 and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) by reaction between Ca (from $\text{Ca}(\text{OH})_2$, CaCl_2 and CaO) and CO_2 gas in the atmosphere and SO_4 in bound water;
- (3) Incorporation of lead into the solid phases formed during this process.

Figure 10 shows the XRD patterns of wetted scrubber residue and wetted scrubber residue after aging (note this experiment was conducted with the addition of 10 wt% PbCl_2). Table 2 shows the results of analysis by XRD and EPMA. Ettringite analogs ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_2 \cdot 26\text{H}_2\text{O}$) were found to be generated in wetted scrubber residues. In scrubber residues after aging, ettringite analogs appeared to have

been converted into gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and vaterite (CaCO_3). The spatial distribution of Pb and S were found to be the same in all residues.

Figure 11 (a) shows an SEM micrograph exhibiting a region in the residue with a very high Pb concentration (Pb concentration is 55 wt%). In the EPMA analysis of these materials, the angular crystals typical in the freshly wetted residues appear to be ettringite analogs. Figure 11 (b) shows an SEM micrograph of a region in the scrubber residue after aging (Pb concentration is 47 wt%). This micrograph shows almost no ettringite analogs, indicating that they have reacted to form different solid phases. It can be seen in Table 2 that new $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and CaCO_3 are generated which contain a high concentration of Pb. It can be hypothesized that Ca in $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and CaCO_3 is partially replaced by isomorphic substitution of Pb (McConnell 1973).

It was observed that in the XRD analysis of scrubber residues after aging, the peak diffraction angles for ettringite and gypsum were shifted from the theoretical diffraction angles of these compounds to slightly lower angles. When Pb, having an ion radius (0.119 nm), slightly greater than that of Ca (0.100 nm), is substituted for Ca in the above-mentioned compounds, the theoretical peak diffraction angles of those compounds will become smaller. Thus, the XRD results with the Pb-doped materials support the hypothesis that isomorphic substitution of Pb for Ca during the formation of gypsum and vaterite is a primary mechanism responsible for the observed reduction in Pb solubility.

4. Conclusions

Since scrubber residues generated as a result of incineration of MSW contain a high concentration of heavy metals, the surrounding environment may be adversely affected if these residues are used as material for construction or landfilled. A mechanism resulting in the reduction in leaching of lead contained in scrubber residues has been documented. The phenomenon is caused by wetting of the scrubber residue and subsequent reaction with gaseous CO_2 . This study has provided the following findings:

- (1) Elution tests (JLT13) were conducted on 48 types of wetted scrubber residues which were exposed to the atmosphere in the laboratory for 24 hours. The Pb leachate concentration

- for all scrubber residues was reduced, independent of the type of incinerator or the exhaust gas treatment method;
- (2) The kinetics of Pb leachate concentration reduction were proportional to the moisture content (in the range of 10 to 60 % by weight) and CO₂ partial pressure;
- (3) Alkalinity and pH in leachate are reduced as a result of wetting and exposure to CO₂ gas. Reduction of alkalinity, rather than pH, is indicative of lead stabilization;
- (4) Pb elution is reduced significantly through the pH range of 4 to 12, indicating that the Pb is incorporated into phases that are less soluble than the parent Pb phase throughout the pH range tested; and
- (5) XRD and EPMA analyses confirmed that ettringite analogs (Ca₆Al₂(SO₄)₃(OH)₂·26H₂O) were generated in wetted scrubber residues. After aging, ettringite analogs appeared to have been converted into gypsum (CaSO₄·2H₂O) and vaterite (CaCO₃). XRD peak shifts suggest Pb substitution for Ca in these minerals.

Acknowledgment

The authors wish to express their sincere gratitude to the people working in municipalities who were kind enough to provide scrubber residues for this study. We are also grateful to Mr. Shoji Kuba and Mr. Tomohiko Sakamoto of Mitsubishi Material Co., Ltd. for their assistance in XRD, EPMA, and SEM of scrubber residues and previous advice in executing this research work.

REFERENCE

- Fallman, A. N., Eighmy, T. T., and Salaneck, W. R. (1999) Aging reaction in residues (final report), Swedish Environmental Protection Agency, AFR-report 252
- Johnson, C. A., Kersten, M., Ziegler, F, and Moor, H. C. (1996) Leaching Behaviour and Solubility – Controlling Solid Phases of Heavy Metals in Municipal Solid Waste Incinerator Ash, Waste Management, **16 (1-3)**, 129-134.
- McConnell, D. (1973) Apatite: Its Crystal Chemistry, Mineralogy, Utilization, and Geologic and Biologic Occurrences, Applied Mineralogy, Springer - Verlag, N.Y.

- Meima, J. A. and Comans, R. N. J. (1997) Geochemical Modeling of Weathering Reactions in Municipal Solid Waste Incinerator Bottom Ash, *Environmental Science & Technology*, **31 (5)**, 1269-1276.
- Meima, J. A. and Comans, R. N. J. (1998) Application of Surface Complexation/Precipitation Modeling to Contaminant Leaching from Weathered Municipal Solid Waste Incinerator Bottom Ash, *Environmental Science & Technology*, **32 (5)**, 688-693.
- Shimaoka, T., Miyawaki, K., and Hanashima, M., et al. (1998) Insolubility of Hazardous Heavy Metals in Wet Fly Ashes of Municipal Solid Waste, *Proceedings of WASTECON/ISWA World Congress '98*, 419-431.
- Steketee, J.J., Duzijn, R.F., and Born, J.G.P. (1997) Quality Improvement of Bottom Ash by Enhanced Aging, Washing and Combination Processes, *The International Conference for the Environmental and Technical Implications of Construction with Alternative Materials, Proceedings of WASCON '97, Session BW1*.
- Whiting, K.J. (1998) An Overview of Current Practices and Future Alternative for the Management of Ash Residues from Waste-to-Energy Processes in Europe, *Proceedings of IT3 Conference, International Conference on Incineration and Thermal Treatment Technologies*, 459-464.
- Zevenbergen, C., Van Reeuwijk, L. P., Bradley, J. P., Bloemen, P., and Comans, R. N. J. (1996) Mechanism and Conditions of Clay Formation during Natural Weathering of MSWI Bottom Ash, *Clays and Clay Minerals*, **44 (4)**, 546-552.

List of Tables and Figures

Table 1. pH and Pb concentration of leachates from scrubber residues with different incineration methods.

Table 2. Changes in element speciation as determined by XRD and EPMA.

Figure 1. Device to test influence of carbon dioxide gas on scrubber residue aging.

Figure 2. Lead solubility changes in wetted scrubber residues aged for 24 hours under atmospheric conditions.

Figure 3. Relationship between lead concentration and pH in leachate.

Figure 4. Change of lead concentration in leachate with time and water content. Residues SD1, SW1, and FD1.

Figure 5. Change of pH and alkalinity in leachates with time. Residues SD1 and FD1.

Figure 6. pH-dependent leaching from wetted scrubber residues. Residue FD2.

Figure 7. Change of pH and lead concentration in leachates with time under forced air and atmospheric conditions. Residue SD2.

Figure 8. Changes of pH, alkalinity and lead concentration in leachates with time and carbon dioxide gas partial pressures. Residue SD2.

Figure 9. pH-dependent leaching of wetted scrubber residues with forced CO₂ gas. Residue SD2.

Figure 10. XRD patterns of wetted scrubber residue and wetted scrubber residue after aging. Residue SD3.

Figure 11 (a) SEM micrograph of wetted scrubber residue. Residue SD3.

Figure 11 (b) SEM micrograph of wetted scrubber residue after accelerated aging. Residue SD3.

Impact of Chemical Weathering on Leaching from Coal Fly Ash: Identification of Natural Weathering Reactions

(Published in Proceedings, Pittsburgh Coal Conference, 2001)

Robert K. Carter and Kevin H. Gardner

Environmental Research Group
Environmental Technology Building
University of New Hampshire,
Durham, N.H. 03824
United States

kevin.gardner@unh.edu

Abstract

It has been observed that waste materials from high-temperature processes are thermodynamically unstable in the natural environment and weather in a similar fashion to volcanic ash, although many times at a faster rate. Experiments were conducted with a variety of waste materials to accelerate the individual mechanisms involved in the geochemical transformation process (dissolution, precipitation, carbonation and pH reduction), and pH-dependent leaching experiments were used to characterize changes in the availability of heavy metals in the weathered materials. Mechanisms investigated for decreased heavy metal availability include increases in exchange capacity and substitution of heavy metals in newly formed mineral phases. This paper presents an investigative technique reliant primarily on Fourier Transform Infrared Spectroscopy, in combination with complementary analytical techniques, to characterize phase changes in bottom ash that has been weathered in a lysimeter for 3 years. FTIR results demonstrate the weathering of allophane and immogolite to halloysite, which implies a limiting factor in the weathering process and further suggests that the weathering products of ash materials may be intentionally altered by control of the porewater chemistry. Results presented are primarily for MSW bottom ash, although research with coal fly ash is also on-going and is making use of the same analytical methods.

Introduction

There are numerous granular byproduct materials, such as combustion ashes, and smelting and foundry byproduct materials, that are limited in their reuse potential by poor environmental performance. Concern over the leaching of contaminants may result in prohibition against a material's reuse, or may represent an unacceptable liability risk to the corporation, utility, or municipality interested in the reuse of a material. Furthermore, there is a need for greater accuracy in understanding how a material may leach in a given environment over time such that more precise, application-specific exposure scenarios can be developed. A lack of risk information has been cited as one of the largest barriers to the use of recycled materials in highway applications by a recent survey conducted by the Association of State and Territorial Waste Management Officials (ASTSWMO, 2000).

Many granular byproduct materials, however, have been observed to undergo natural transformations when left in an exposed environment for a number of years. These granular materials originate from high temperature processes that produce a byproduct that is thermodynamically unstable in the natural environment. After chemical weathering of these geochemically unstable “reactants,” the product materials have vastly different environmental properties. These chemical weathering processes have not been well documented in the literature and have only been investigated for a small number of materials from high-temperature processes. Furthermore, mechanisms by which leaching processes are changed by these geochemical reactions have not been elucidated.

This research is focused on understanding these natural reactions so that there is a greater understanding of how leaching of contaminants changes with the geochemical weathering of the byproduct material. Furthermore, methods to accelerate the weathering process are being investigated, which offers the potential that beneficiation methods can be used to develop a useful and environmentally acceptable product. Changes in physical properties of these materials will also be investigated to document how the geochemical changes influence the physical and mechanical behavior of the materials, which is an important consideration for the beneficial use of these materials in highway construction.

HYPOTHESIS

Ashes and slags are composed primarily of amorphous minerals, salts, and metals, and meet a non-biological definition of soil as an unconsolidated mineral material.(Sparks, 1995) As such, the chemical and physical weathering characteristics of soils can be applied to ash, and the predictions and theories applied to the weathering of soils may also be applicable. Dissolution and precipitation are chemical weathering processes that impact the inorganic content and composition of unconsolidated mineral materials (Sparks, 1995). Alumino-silicate clay formation is derived from the dissolution of primary minerals and the subsequent precipitation of secondary minerals. The concentrations of aluminum, silicon, other major and minor elements, moisture and the pH of the “soil” solution determine the speciation of the clay mineral formed (Buol et.al., 1980).

“Surface-controlled” dissolution occurs when transport reactions occur more quickly than surface reactions, which typically occurs in silicates and oxides. This surface controlled rate is proportional to the surface area of the minerals (Sparks, 1995). Fly ashes are usually fine particles, with relatively large surface areas, while bottom ashes, slags, and foundry and smelting byproducts may be large granular with quite low surface areas. Volcanic ash has been used as a coal fly ash and bottom ash analog, as composition, size, and surface area are similar (Zevenbergen et al., 1994; Zevenbergen et al., 1999), but volcanic ash pH is typically near neutral, while coal and MSWI ashes may have typical pH values up to 13. The relatively large surface area allowing more intense surface controlled dissolution, combined with the difference in “parent material” pH values contribute to the accelerated weathering rate of coal and MSWI ashes. If unaltered coal and MSWI ashes weather rapidly, then the possibility of enhancing and controlling the weathering rate of these ashes is high. Other granular material that is being investigated is not expected to weather at the high rate of very basic fly ashes, although over the long term their weathering and alteration of leaching properties may be significant.

The governing hypothesis for this work is that chemical weathering of industrial byproducts are important to understand in order to predict the long-term environmental impact and risk associated with their beneficial use. Furthermore, it is hypothesized that these chemical reactions can be controlled by controlling the soil solution conditions, and that they can be accelerated in the laboratory. This research is proceeding by first collecting waste materials that have been exposed to the natural environment for many years. A number of analytical techniques are then being employed to determine an equivalent weathering age, analogous to the weathering stages of soils based on the distributions of primary and weathered products.

MATERIALS AND METHODS

STUDY MATERIALS

Although a fair amount of work has been conducted using coal ashes and MSWI bottom ash, these materials are the first materials being studied in this research in order to “calibrate” the methods and aging stages that will be used for these and other materials. Additional materials that will be investigated in this research are those for which beneficial use in the highway environment is likely, and will include aluminum dross and blast furnace slag. The research presented in this paper has been conducted on MSWI bottom ash mined from a lysimeter in Japan. MSWI bottom ash was placed in this lysimeter for a period of three years, and was left exposed to the environment in the city of Fukuoka, on the southern-most island of Japan. The lysimeter was sampled after 3 years and samples were taken from 7 depths - sample 1 – 0 c.m., sample 2 – 35 c.m., sample 3 - 85 c.m., sample 4 – 135 c.m., sample 5 – 185 c.m., sample 6 – 235c.m., and sample 7 - 285 cm. However, it should be made clear at this point that the methodologies used are equally applicable to coal ashes, and that many of the findings are the same as are being found with coal ashes.

EXPERIMENTAL METHODS

Fourier Transform Infrared Spectroscopy (FTIR) analysis was done by combing small amounts of sample (< 0.1g) crushed by mortar and pestle with potassium bromide and pressing into a slide. The slides were then analyzed by Colet FTIR Spectroscopy with results given in percent transmittance.

Two sets of samples were glued to a sample stud with carbon paint. One sample stud was coated with gold palladium for scanning electron microscopy (SEM). The other sample stud was coated with carbon for analysis by energy dispersive x-ray spectroscopy (EDS). SEM work was done on an Amray 3300 F.E. S.E.M., and EDS work was done by EDS P.G.T. EDS analysis was qualitative only, not quantitative.

For x-ray diffraction (XRD) work, 1g of each sample to be analyzed was crushed by mortar and pestle and sieved through a number 50 sieve (300 μ m). Approximately 0.3g of the sample were placed on a slide without altering the surface of the sample, and placed in the slide tube. Data analysis was done by Jade software.

Leaching tests were conducted by suspending ash samples (crushed and sieved to <200 μ m) in distilled, deionized water in a 10:1 liquid:solid ratio (e.g. 10 g solid in 100 ml solution). The suspension was agitated for 6 hours and filtered

through a 0.45 μm filter and preserved as appropriate for chemical analysis. pH-dependent leaching was carried out in a similar fashion, maintaining a pH-stat condition at different pH values with the use of strong acid and strong base.

Results and Discussion

Previous research on MSWI Bottom Ash has determined the main crystalline phases to be silicates, oxides, carbonates, and salts (Speisser et al, 2000). Our analysis of MSWI Bottom Ash aged for three years in a lysimeter, by FTIR, SEM, EDS, and XRD, shows preliminary results concurring with these findings.

Fourier Transform Infrared Spectroscopy (FTIR) has been used to monitor phase change in solids of contaminated weathering soils, though not widely used in analysis of ash materials. (Martinez et al., 2001) Utilizing this approach to view solid phase change of naturally weathering ash materials will assist in defining the depth and extent of the weathering front, and rates of pedochemical and geochemical processes.

Spectral data for sample 1 (0 cm depth) strongly indicate the presence of silicates, carbonates, phosphates and possibly nitrates. Silicates are indicated with diagnostic peaks at 3450 c.m.^{-1} , 1050 c.m.^{-1} and 1100 c.m.^{-1} , 940 , 805 , and 450 c.m.^{-1} (Smith, 1999). Peaks diagnostic of allophane (980 and 570 c.m.^{-1}), halloysite (1100 and 470 c.m.^{-1}) and possibly immogolite (690 and 430 c.m.^{-1}) are also present representing silicate minerals (Figure 1.1) (Martinez, et al., 2001).

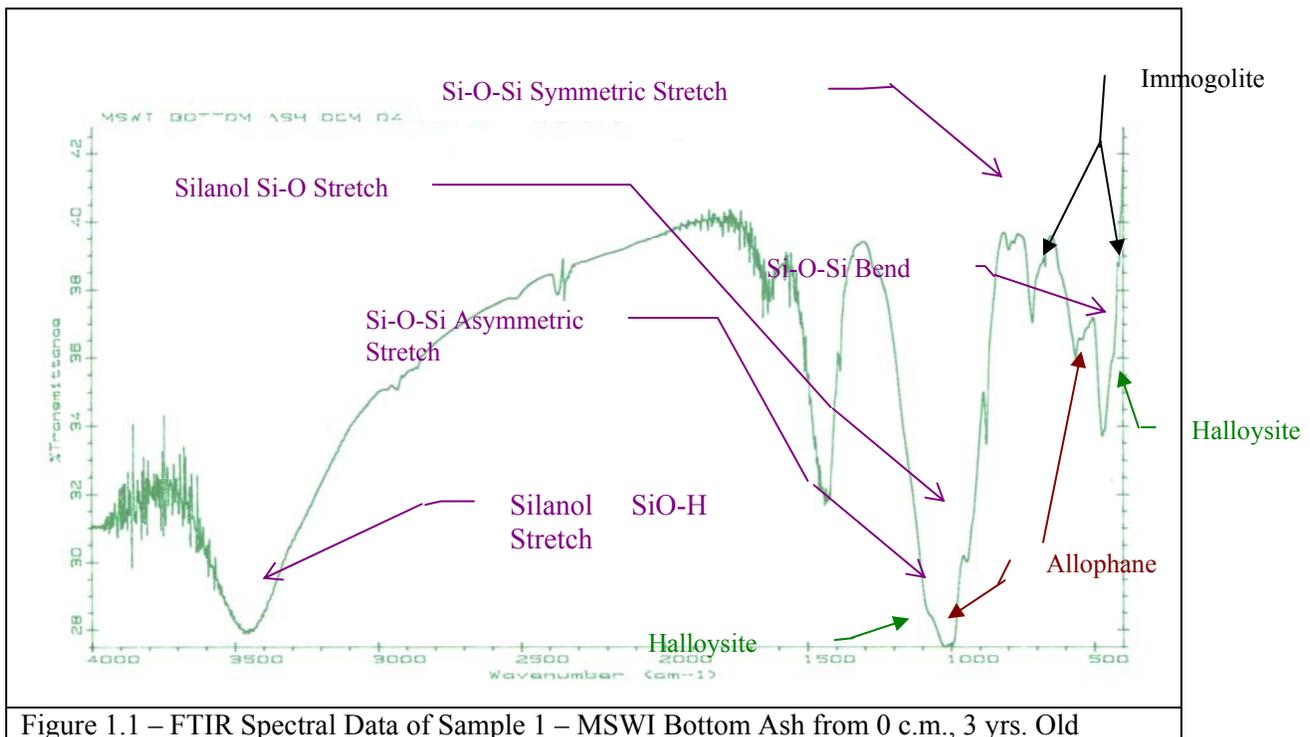


Figure 1.1 – FTIR Spectral Data of Sample 1 – MSWI Bottom Ash from 0 c.m., 3 yrs. Old

Similarly, FTIR spectral data indicated the presence of carbonates, with bands at 1540 to 1410 c.m.^{-1} , 880 to 860 c.m.^{-1} , and approximately 740 c.m.^{-1} . Phosphate bands are pronounced at 1100 to 1000 c.m.^{-1} , and at 600 to 500 c.m.^{-1} . Nitrate bands are less defined at 1400 to 1340 c.m.^{-1} , 840 to 810 c.m.^{-1} , and slightly more defined at 720 c.m.^{-1} (Figures 1.2 and 1.3) (Smith, 1999).

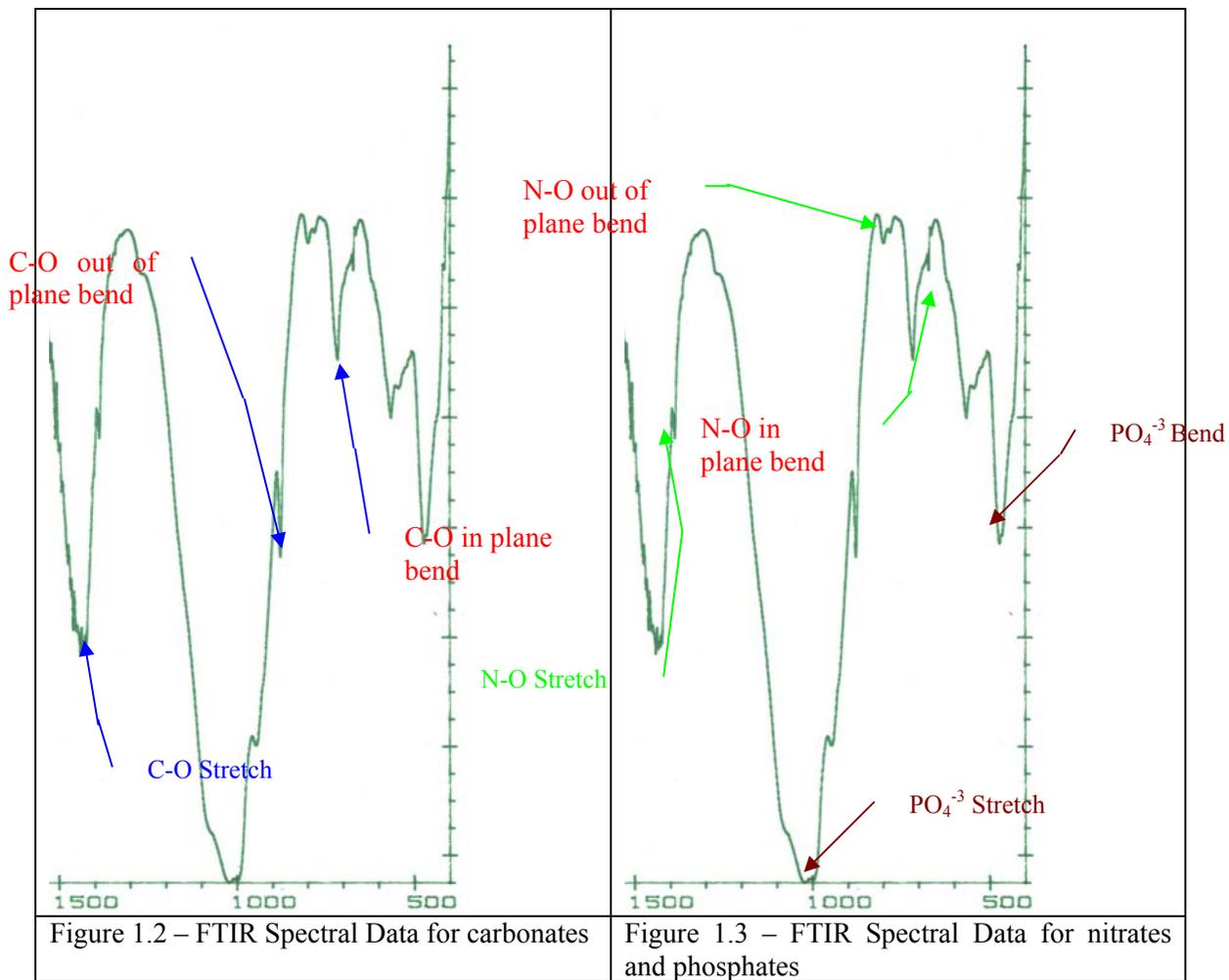


Figure 1.2 – FTIR Spectral Data for carbonates

Figure 1.3 – FTIR Spectral Data for nitrates and phosphates

FTIR spectral data for sample 2 at 35 c.m. (Figure 2.1), show the silanol Si-O stretch is less defined, as well as a decrease in intensity for all silicate peaks. Diagnostic peaks for allophane, immogolite and halloysite are much less intense and less defined than in sample 1, indicating an overall phase change of the structural form of silica. Inorganic carbonates and nitrates do not have well defined peaks in sample 2 (Figures 2.2 and 2.3), lacking a C-O stretch peak, as well as a N-O out of plane bend. This implied decrease is consistent with expected retarded weathering rates with sample at depth considering limited exposure to atmospheric conditions.

Spectral data for samples 3 and 4, 135 c.m and 235 c.m., respectively, show similar trends: a decrease in intensity of diagnostic peaks of carbonates and nitrates, with silicates and phosphates maintaining the most significant presence of mineral structure. Sample 4 shows a slight increase in intensity of peaks of silicates and phosphates, indicative of higher concentrations of relic materials.

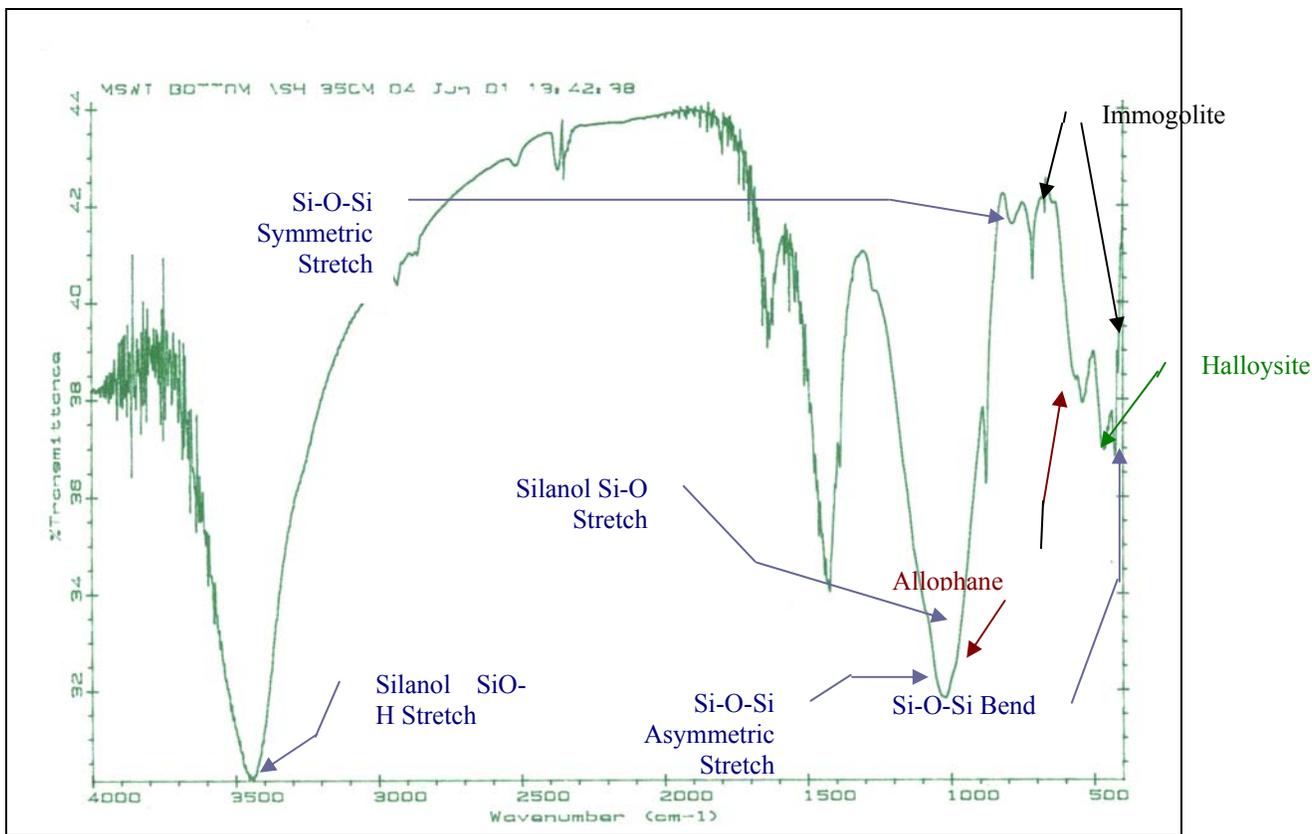


Figure 2.1 – FTIR Spectral Data of Sample 2 – MSWI Bottom Ash from 35 c.m., 3 yrs. Old

XRD results for samples 1 and 7, 0 c.m. and 285 c.m., respectively, were reviewed for a comparison to view the lysimeter samples as a weathering profile, with sample 7 analogues to the “parent material”. The major composition of sample 7 is quartz, calcite, and gismondine ($\text{CaAl}_2\text{Si}_2\text{O}_8 \cdot 4\text{H}_2\text{O}$), with minor and trace constituents of metal oxides and hydroxides. The major constituent of sample 1 is calcite, with minor constituents of quartz, metal oxides and hydroxides. The transition of quartz from a major constituent in the sample at depth to a minor constituent in the surface sample supports the hypothesis of a phase change of the silicate structures. Decrease in aluminum concentrations at the surface where pH values are lower, and aluminum is less soluble, furthers the phase change hypothesis of feldspars transitioning to clay size, amorphous, aluminosilicate minerals allopahne and possibly immogolite.

Gismondine ($\text{Ca}_2\text{Al}_4\text{Si}_4\text{O}_{16} \cdot 9(\text{H}_2\text{O})$), a tectosilicate zeolite (framework silicate), is an alteration of plagioclase feldspars (Gaines, R.V., et al, 1997). The presence of gismondine in the sample at depth is likely relic as zeolites have typically been thought to form from rapid cooling of igneous rock. However zeolites may also occur as alterations of volcanic tuff and glass (Klein, C., et al, 1993); application of this theory to the glassy constituent of bottom ash allows the hypothesis of natural geochemical processes occurring. In the sample at depth, where pH values are more basic than at the surface, and exposure to CO_2 is limited, Ca is not bound by carbonate, and is able to be incorporated into silicate mineral structures.

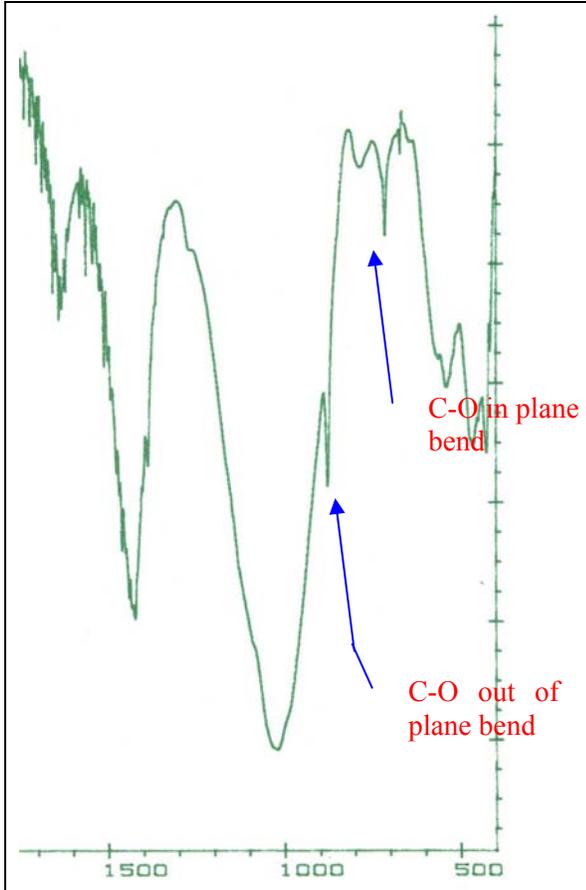


Figure 2.2 – FTIR spectral data for sample 2 – inorganic carbonates

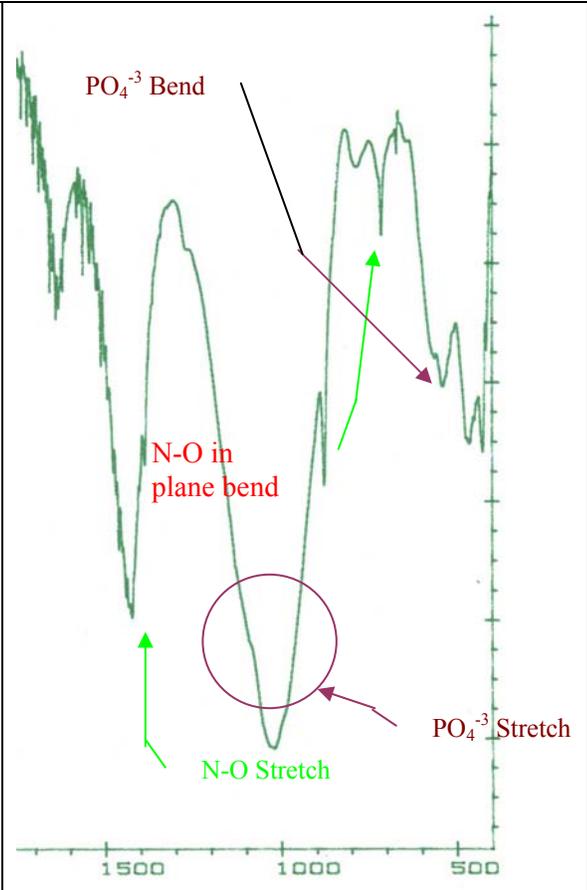


Figure 2.3 – FTIR spectral data for sample 2 – nitrates and phosphates

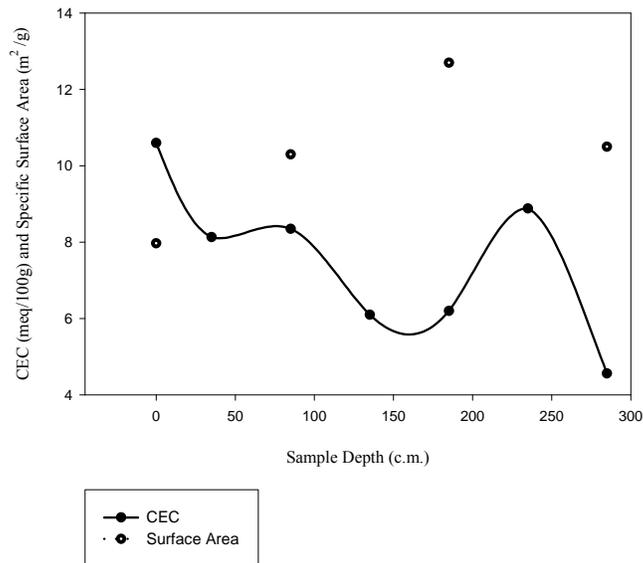


Figure 3.1 Specific surface area as a function of depth in the deposit.

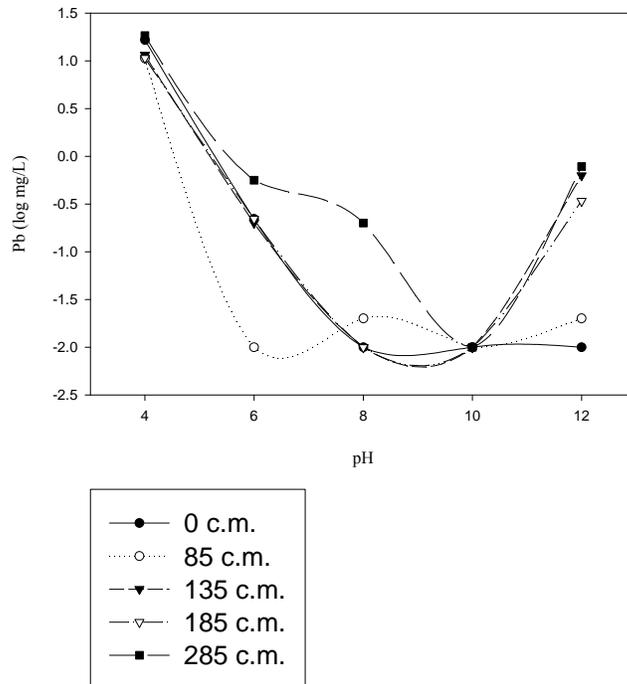


Figure 3.2 pH-dependent

leaching of Pb as a

function of depth in the ash deposit.

Cation exchange capacity (CEC) and pH dependant leaching of Pb data support the development of alumino-silicate clay materials as well. CEC of the 0 c.m. sample is substantially higher than the subordinate samples, despite the smaller specific surface area (Figure 3.1). These factors may explain the drastic difference in Pb leachability at the higher (>10) pH levels (Figure 3.2).

Conclusion

The presence of allophane and immogolite, and their pedogenic subordinate halloysite, in three year old MSWI bottom ash leads to the hypothesis that alumino-silicate clay minerals will develop from the natural weathering of these ashes. The indication by FTIR analysis of phase changes at depth allows for determination of a weathering or pedogenic profile to be established. With the profile established, an approximate age may be applied to form a reference for success of attempts to accelerate the weathering process. The weathering of allophane and immogolite to halloysite, as opposed to gibbsite or kaolinite, implies a limiting factor in the weathering process. If these factors, pH, ionic concentrations, moisture, and temperature, are controlled in attempts to accelerate the weathering process, the speciation of the resulting alumino-silicate clay may be controlled. This not only has implications for future conduct of research on these materials, but for potential long-term management methods as well.

ACKNOWLEDGEMENTS

This work was funded through a cooperative agreement (DTFH61-98-X-00095) between FHWA and the University of New Hampshire.

References

- ASTSWMO. 2000. ASTSWMO Beneficial Use Survey. Association of State and Territorial Solid Waste Management Officials, Washington, D.C.
- Buol, S.W., Hole, F.D., McCracken, R.J., Soil Genesis and Classification, Iowa State University Press, 1980, 2nd edition
- Gaines, R.V., Skinner, H.C., Foord, E.E., Mason, B., Rosenzweig, A., Danas New Mineralogy, John Wiley and Sons, Inc, New York, 1997
- Klein, C., Hurlburt, C.S., Manual of Mineralogy 21st Edition, John Wiley and Sons, Inc, New York, 1993, 551
- Martinez, C.E., Jacobson, A., and McBride, M.B., Thermally Induced Changes in Metal Solubility of Contaminated Soils is Linked to Mineral Recrystallization and Organic Matter Transformations, Environmental Science and Technology, 2001, 35, 908-916
- Smith, Brian, Infrared Spectral Interpretation, a systematic approach, CRC Press, Boca Raton, FL, 1999, 165-174
- Sparks, Donald L.; Environmental Soil Chemistry, Academic Press, San Diego, CA, 1995, 38-39
- Speisser, C., Baumann, T., Niessner, R., Morphological and Chemical Characterization of Calcium-Hydrate Phases Formed in Alteration Processes of Deposited Municipal Solid Waste Incinerator Bottom Ash, Environmental Science and Technology, 34, 23, 2000, pp 5030-5037
- Zevenbergen, C., Bradley, J.P., Ven Reeuwijk, L.P., Shyan, A.K., Hjelmar, O., Comans, R.N.J., Clay Formation and Metal Fixation during Weathering of Coal Fly Ash, Environmental Science Technology, 1999, 3, 3405-3409
- Zevenbergen, C., Vander Wood, T., Bradley, J.P., Van Der Broeck, P.F.C.W., Orbons, A.J., and Ven Reeuwijk, L.P., Morphological and Chemical Properties of MSWI Bottom Ash with Respect to the Glassy Constituents, Hazardous Waste and Hazardous Materials, Mary Ann Liebert, Inc, 1994, Vol.11, no. 3