MECHANISM AND CONDITIONS OF CLAY FORMATION DURING NATURAL WEATHERING OF MSWI BOTTOM ASH

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Abstract—Municipal solid waste incinerator (MSWI) bottom ash is the slag-like material produced by the incineration of municipal waste and is predominantly composed of glassy constituents, which include inherited manufactured glasses and glasses formed during incineration. Previous results indicate evidence of neoformation of well-ordered clay (illite) from glasses in MSWI bottom ash after 12 y of natural weathering. We investigated the mechanism and conditions of clay formation from glasses during natural weathering using transmission electron microscopy (TEM), experimental leaching experiments and ammonium oxalate extractions. It was concluded that the high surface area and initially high "active" Al and associated Si content predispose the ash to form clay minerals on a relatively short time scale. This work provides evidence that the composition of secondary amorphous aluminosilicate and thus, the type of clay mineral which may form, is determined by the pH of the pore solution rather than by the glass composition. Presumably alternate wetting and drying of the ash during disposal greatly accelerates the formation of well-ordered clays.

Key Words—Clay formation, Illite, MSWI bottom ash, Transmission Electron Microscopy.

INTRODUCTION

Glasses are metastable within an atmospheric environment and will transform into thermodynamically more stable secondary compounds (White and Claassen 1980; Zielinski 1980; Abrajano et al. 1990). Research has demonstrated that natural volcanic glasses provide insight into the weathering behavior of man-made nuclear waste glasses and glass-rich coal fly ash (Malow and Lutze 1984; White 1984; Warren and Dudas 1985; Crovisier et al. 1987; Janssen-Jurkovicova 1991; Bates et al. 1992). Thorough knowledge of the natural weathering mechanisms and rates of man-made glasses are prerequisites to determine their long-term environmental behavior and impact. However, information drawn from natural samples, is often limited due to slow alteration rates and uncertainties concerning the natural conditions during alteration (Magonthier 1992). In addition, the extrapolation of short-term hydrothermal weathering experiments require kinetic models to predict long-term weathering processes (Petit et al. 1990; Michaux et al. 1992).

Municipal solid waste incinerator (MSWI) bottom ash is the slag-like material produced by the incineration of municipal waste. Average flame temperatures in the primary incineration chamber may range from 800 to 1400 °C (Nelson and Schindler 1989). After the incineration process, the ash is quenched. Bottom ash is predominantly composed of glassy constituents, which include inherited manufactured ("primary") glasses and "secondary" glasses formed during incineration (Kirby and Rimstidt 1993). The heavy metal contents within bottom ash are usually higher than those reported for soils and common rocks (Ontiveros et al. 1989; Theis and Gardner 1990). We have noted that roughly 75% (wt/wt) of bottom ash consists of glass (Zevenbergen et al. 1994a). Secondary glass in bottom ash generally consists of relatively small particles, often aggregated, and adhering to larger particles. Within the discrete larger secondary particles, numerous vesicles can be discerned. These vesicles result from the rapid quenching. The major elemental composition of secondary glasses is similar to reported compositions of basaltic glasses (Kirby and Rimstidt 1993). Closer examination of the composition of individual particles has revealed that bottom ash consists of a heterogeneous mixture of different glass types (Zevenbergen et al. 1994a).

Published data on clay mineral formation within nature involves rocks and minerals generally exposed to at least thousands of years of weathering (Colman and Dethier 1986). Early formation of well-ordered clays in natural weathered volcanic glass of Precambrian origin was documented by Tazaki et al. (1989). We have reported direct evidence of neoformation of well-ordered clay illite, from glasses in MSWI bottom ash after 12 y from natural weathering (Zevenbergen et al. 1994b). The rapid formation of well-ordered clay had not previously been observed from nature. We observed two different mechanisms of glass weathering: 1) *in situ* transformation; and 2) congruent dissolution followed by precipitation outside the glass spheres. Since clay formation may contribute significantly to the retention

Table 1. Main characteristics of the two bottom ash deposits used in this study.

Type	Unsaturated deposit	Waterlogged deposit
Thickness of the deposit (m)	0.45	1.75
Hydrodynamic conditions	wet & dry cycles	waterlogged
Leaching	strong	very weak
pH*	8.2–8.5†	11.0–11.5‡
Age (years)	12	4

† Measured in a 1:5 ash/water (wt/wt) suspension after 2 h mechanical shaking.
‡ Direct measurement in the pore water.

of contaminants within these ashes, this process must be considered while evaluating its leaching behavior.

In order to elucidate the underlying mechanism and conditions, and to determine the rate of neoformation of clay minerals from MSWI bottom ash glasses, we have examined: 1) the compositional and mineralogical properties of alteration products of MSWI bottom ash glasses during weathering; 2) the solubility of fresh MSWI bottom ash with respect to silica and alumina from a waterlogged and in an air-purged leaching experiment; and 3) the "active" Al and associated Si, or short-range ordered hydrated aluminosilicate content, of MSWI bottom ash from different weathering stages, relative to that of natural and synthetic glasses and unheated and heated (550 °C) kaolinite.

METHODS AND MATERIALS

We have examined 2 types of naturally weathered MSWI bottom ash by transmission electron microscopy (TEM). One was obtained from a 0.30 to 0.35 m depth at a vegetated unsaturated deposit without containment, which has been allowed to weather in the open for more than 12 y. The general weathering features of this ash deposit, including clay formation, have recently been documented (Zevenbergen et al. 1994b). The other was taken from a 1.50 to 1.75 m depth at a 4 y old waterlogged ash deposit. The main characteristics of both deposits used in this study are given in Table 1. Size-fractionated samples of dried disaggregated ash were embedded into epoxy resin and thin-sectioned using an ultramicrotome (Bradley 1988). The thin sections (< 100 nm thick) were examined using brightfield/darkfield imaging, lattice fringe imaging, and selected area electron diffraction (SAED). Compositional trends were determined using energy-dispersive X-ray spectroscopy (EDS).

The leaching experiments were carried out with a fresh ash sample at a water to ash ratio (wt/wt) of 2.5:1. The extractions were carried out with deionized H_2O. For the air-purged experiment, the suspension was continuously purged with water-saturated air. The waterlogged experiment was carried out within a capped reaction vessel with no headspace. At selected time intervals, an aliquot of 25 ml was taken from the suspensions and the pH was measured. Each extract was filtered through a 0.45 μm filter prior to analysis. (Zevenbergen and Comans 1994).

Determination of Al and Si dissolved after a 4 h extraction in the dark with 0.2 M acid ammonium oxalate buffered at pH 3 and a liquid/solid ratio of 50 (Van Reeuwijk 1992) was used to estimate the "active" Al and associated Si content (Mizota and Van Reeuwijk 1989) of the bottom and of unweathered natural and synthetic glasses and of unheated and heated (550 °C, 4 h) kaolinite. Since it is well-established that ammonium oxalate extracts the amorphous products with little or no attack on the crystalline materials (Higashi and Ikeda 1974), the "active" Al and associated Si fraction is expected to include all short-range ordered hydrated aluminosilicates. All bottom ash samples used for this study originate from the same incinerator facility.

RESULTS AND DISCUSSION

TEM observations

In both naturally weathered ash samples, glass particles with and without crystalline domains are observed. On the surface of these particles and outside the glassy spheres, widespread decomposition of the glass phase and formation of secondary aluminosilicates are noted. Figure 1a shows a typical well-ordered 10 Å clay at the rim of a silica glass particle from the unsaturated deposit ash sample. The electron diffraction pattern suggests spacings of an illite structure. The glass phase contains only Si and O, whereas the weathered, amorphous rim contains hydrous aluminosilicate with a relatively high Si/Al ratio, molar Si/Al ratio ≈2.

The gradual transition from an amorphous to a crystalline phase indicates in situ transformation of glass. It is well-established that wetting and drying cycles enhance the formation of illite (Srodon 1984) and smectite (Van der Gaast et al. 1986). The prevailing hydrodynamic conditions may have stimulated the formation of a well-ordered clay that yields strong reflections in a SAED pattern, for this deposit.

In the ash sample from the waterlogged deposit, most glassy silicate particles have a thick alteration rim, 1 to 0.5 μm with a relatively low Si/Al ratio. An example of such a weathered particle is given in Figure 1b. The Al content of the alteration rim increases progressively to a maximum into the more weathered outer sphere (molar Si/Al ratio ≈0.5) indicating relative uptake of Al. The widespread observed discrete amorphous aluminosilicates exhibit similar low Si/Al ratios (Figure 1c). Well-ordered clays have not been observed within this ash type. We speculate that the Al content of the amorphous aluminosilicate of the waterlogged ash is too high to form well-ordered clays within the present relatively short time span.
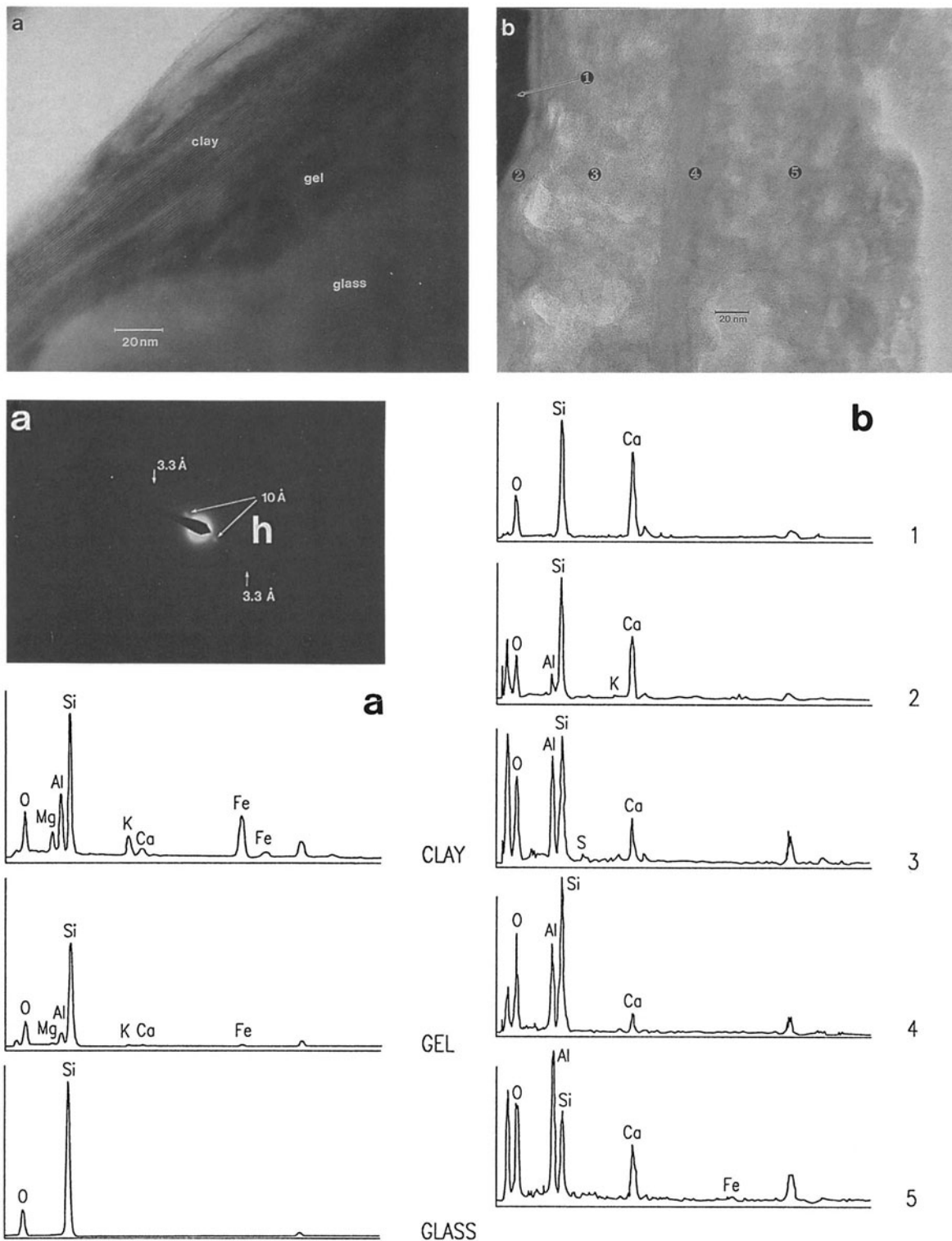
Figure 1.   Transmission electron micrographs of thin sections and corresponding EDS analyses showing a continuous alteration layer on the surface of bottom ash glasses (a and b) and a discrete hydrous aluminosilicate precipitate (c): a) Gel on a silicate glass with a region of well-ordered clay and a SAED pattern from the well-ordered clay, illite. The sample was taken from an open bottom ash deposit, which has been allowed to weather for 12 y; b) Gel on a calcium silicate glass; and c) a discrete amorphous aluminosilicate precipitate. Both neoformed phases exhibit similar compositions. The sample was taken from a 4 y old waterlogged bottom ash deposit. The gradual transition from glass to amorphous and/or crystalline material indicates *in situ* transformation of the glass.
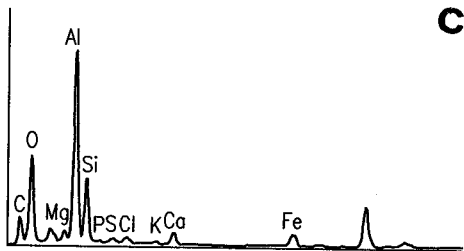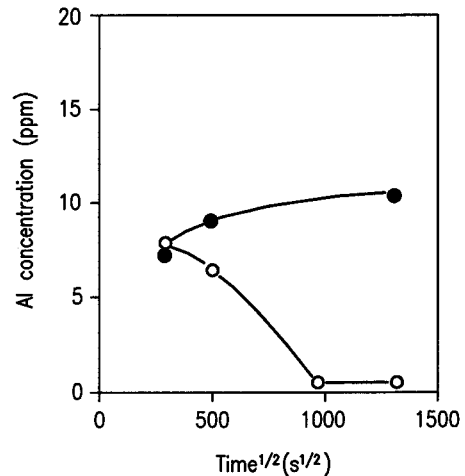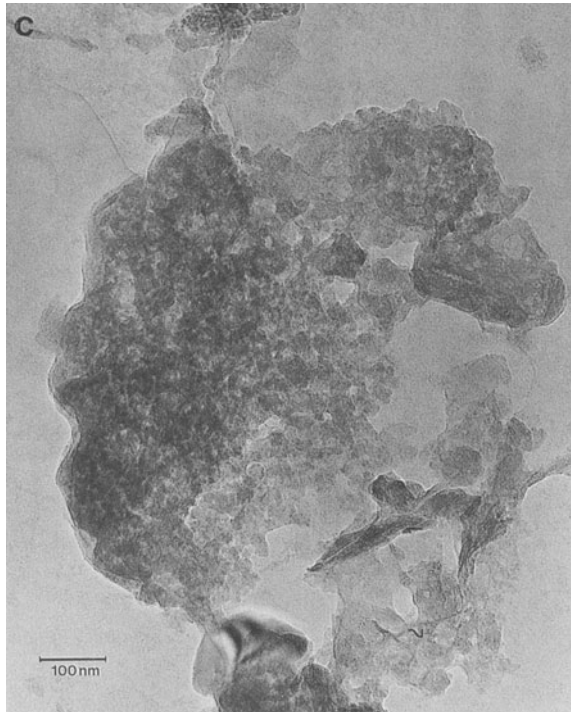
Figure 1.   Continued.

Figure 2.   The Si and Al concentration of air-purged and waterlogged leaching experiments with fresh bottom ash as a function of time ($\sqrt{t}$). The leaching experiments lasted 500 h at a temperature of 18 °C. Key: open symbols= the concentration within the air-purged suspension and closed symbols= the concentration in the waterlogged suspension. A high and constant pH of 10.5 was recorded within the waterlogged suspension. For the air-purged suspension the pH dropped within a few days to a constant value of 8.2.

Formation of well-ordered clay during experimental alteration of glass has been reported previously (Kawano and Tomita 1992; Mazer et al. 1992; Kawano et al. 1993). These studies reveal that hydrous aluminosilicate, allophane, appears to be the first reaction product of glass weathering. The formation of clays from glasses under low temperature conditions is not well understood. There are no reports concerning direct observations of the transitional process of clay formation in nature. Recently Tazaki and Fyfe (1988) and Tazaki et al. (1989) observed crystalline domains that already existed prior to deposition. These crystalline domains typically show 3 Å spacings within the non-crystalline volcanic glass matrix. They suggested that these domain structures may initiate the growth of clay products on the glass substrate. On the basis of low temperature experimental alteration of obsidian, Kawano et al. (1993) postulate that smectites may develop from vol-
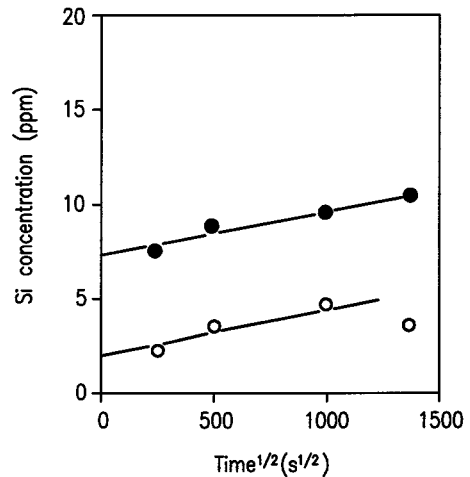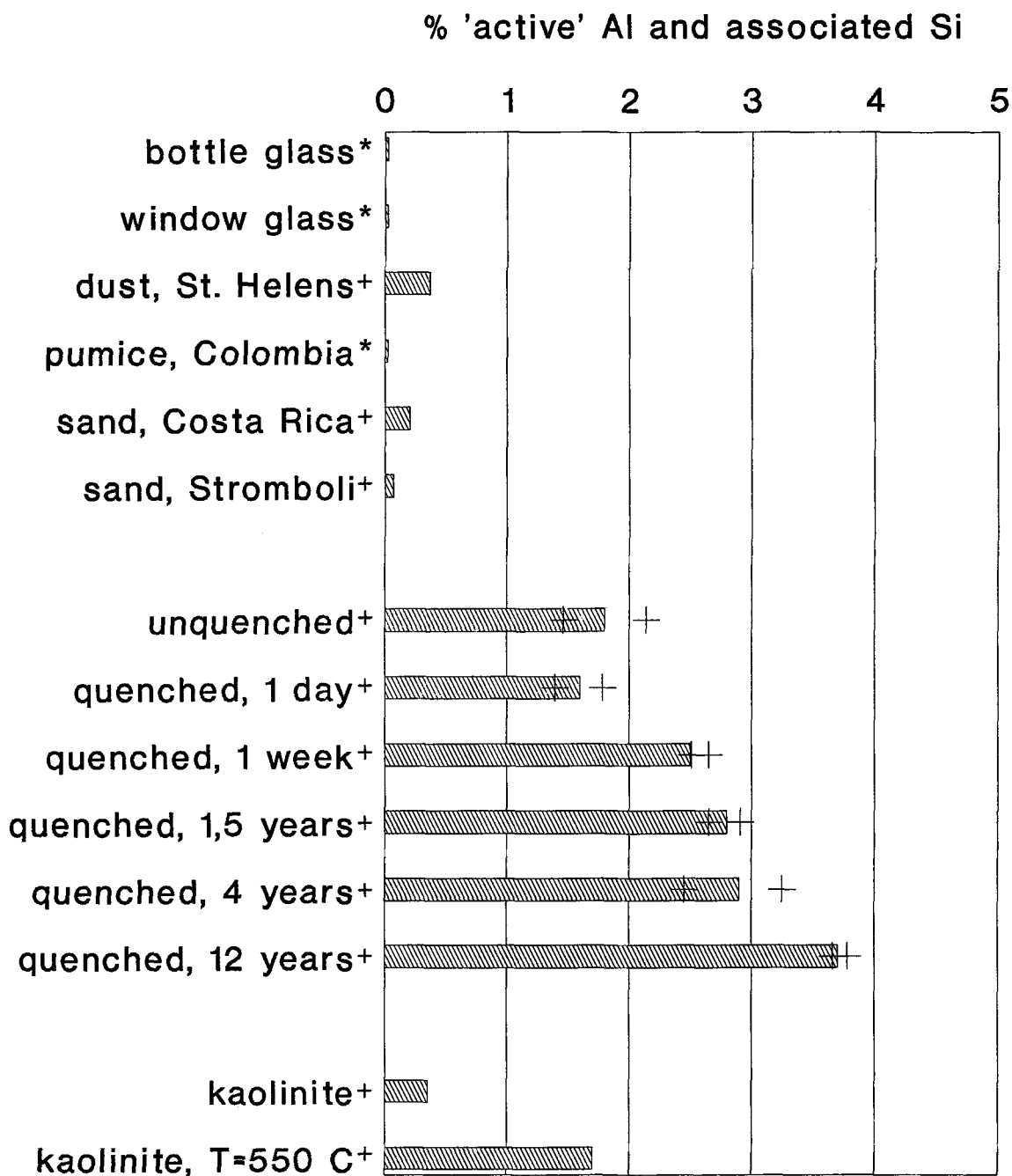
canic glass through a non-crystalline transitional phase rather than direct glass-to-clay formation.

Si and Al leaching

Purging with air decreases the pH of the ash suspension from 10.5 to 8.2 within a few days. The latter

Figure 3. "Active" Al and associated Si content in % (wt/wt) of fresh natural and synthetic glasses, bottom ash from different weathering stages, and unheated and heated (550 °C) kaolinite. The "active" Al and associated Si content was determined after extraction with ammonium oxalate according to Mizota and Van Reeuwijk (1989). Key: * = ground to pass 53 μm sieve; and + = passed through 2 mm sieve.

pH value is close to the pH of a solution in equilibrium with calcite and the atmosphere (Comans and Meima 1994). For both the air-purged and waterlogged experiments, a parabolic increase of dissolved Si is observed (Figure 2). The parabolic release of Si may suggest a diffusion-controlled release of SiO_2, or H_4SiO_4, molecules through an altered layer and is in accordance with the generally observed release pattern of Si for both artificial and natural glasses (Goossens 1990). The maximum amount of Si release after 500 h of leaching was approximately 1×10^{-6} molSi/g ash. The same Si release was found by Kirby (1993) from 40 °C bottom ash dissolution experiments. These values are substantially lower than the amount of Si released during dissolution experiments with quartz and glassy siliceous tuff and volcanic ash (Kirby 1993). We suggest that this difference is due to a precipitation reaction, which proceeds slightly more slowly than the dissolution of Si, thus allowing the Si concentration to rise continuously but much more slowly than from the leaching experiments with the natural solids. Our TEM observations of the widespread formation of amorphous aluminosilicates is consistent with the above suggestion that secondary precipitates form during ash leaching. For the waterlogged experiment, the Al concentration reaches a steady state, whereas for the air-purged solution the concentration drops rapidly to values below the detection limit (0.2 ppb). For the highly alkaline waterlogged suspension, the concentration of both Si and Al are high resulting in relatively low Si/Al ratio. By contrast, within the air-purged, less alkaline suspension, the concentration of Al is relatively low resulting in a relatively high Si/Al ratio. It is speculated from these observations that for the waterlogged suspension, the Al concentration is relatively high and may control the release of Si by the formation of hydrous aluminosilicates. Within the air-purged suspension, initially dissolved Al is removed from solution probably by precipitation of $Al(OH)_3$, because Al has a relatively low solubility at this pH range.

It would appear from our TEM observations and experimental leaching data that the alkalinity regulates the Si/Al ratio of the solution, which in turn controls the Si/Al ratio of the amorphous hydrous aluminosilicate phase. A similar correlation between the Si/Al ratio of the solution and the newly formed aluminosilicate phase has been observed by Mariner and Surdam (1970) during hydrothermal weathering of rhyolitic glass and recently after experimental leaching of MSWI bottom ash by Zevenbergen and Comans (1994).

"Active" Al and Associated Si Content

The results of the determination of the "active" Al and associated Si content are summarized in Figure 3. These results indicate that: 1) fresh bottom ash contains significantly larger amounts of these constituents than fresh, natural and manufactured glasses; and 2)

heat treatment at 550 °C increases the "active" Al and associated Si content of kaolinite. These results suggest that during incineration, part of the native clay minerals may decompose resulting in the formation of a more poorly ordered structure without forming a rigid glass. The latter implies that temperatures within the incineration chamber remain locally much lower (< 800 °C) and/or that the incineration is not long enough to completely melt these minerals. This suggestion is consistent with the noted inherited crystalline regions within the ash glass particles, which are observed with TEM and with previous oriented powder XRD data. These data reveal the presence of inherited kaolinite within the clay fraction of fresh bottom ash (data not presented). It follows that Al and Si extracted with ammonium oxalate from the fresh ash are part of a continuum from crystalline materials to highly disordered structures, for example, true glass. It is hypothesized that this fraction strongly contributes to the observed rapid process of clay formation.

The results of Figure 3 suggest that continued weathering of bottom ash causes a slow increase of the "active" Al and associated Si content as a result of hydration and hydrolysis of the glass matrix and/or breakdown of the glass particles through which new surfaces of the numerous vesicles are exposed.

CONCLUSIONS

This study shows that a substantial fraction of MSWI bottom ash consists of reactive glasses and reactive thermal decomposition products of primary clay minerals. Its large surface area and initially high "active" Al and associated Si content predispose the ash to form clay minerals within a relatively short course of time. The TEM observations, in conjunction with the experimental leaching data indicate that clay formation from bottom ash glasses occurs by reaction among dissolved species as well as by reaction with an altered layer. Hydrous aluminosilicate is found to be the intermediate reaction product. In comparison with natural systems, bottom ash is unique in that it is composed of glasses with different composition, which are subject to weathering within the same environment. The observation that the secondary aluminosilicates tend toward the same composition, leads to the conclusion that the mechanism of clay formation is determined by the external chemical environment, for example pH, rather than by the composition of the glass phase.

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