AGEING OF ASHES IN A LANDFILL TOP COVER

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SUMMARY: This paper is based on studies on the effects of accelerated ageing on refuse-derived-fuel (RDF) fly ashes, in experiments under controlled laboratory conditions, intended to derive models to predict the stability of RDF fly ashes used in a landfill liner and the mineralogical changes that occur in them. A reduced factorial design was applied, followed by multivariate data analysis, to evaluate the effects of five factors — carbon dioxide (CO_2) levels, temperature, relative air humidity (RH), time and the quality of added water — on mineral transformations within the ashes, and leaching behaviour.

The pH values of these ash specimens ranged from 7.2 to 7.6, indicating advanced carbonation. Ageing decreased pH values from 12.4 to 7.2, consequently affecting the leaching behaviour of most chemicals measured in the leachates. Levels of Ba, Ca, Cl, Cr, Cu, Pb, K and Na decreased over the study period while those of Mg, Zn and SO_4 increased.

Clay minerals could not be detected neither in fresh nor in aged ashes. However, geochemical modelling indicated that such minerals may precipitate.

1. INTRODUCTION

Currently, ashes are either landfilled or used as construction materials. They are subject to weathering processes, including physical, chemical and mineralogical changes caused *i. a.* by fluctuations of temperature and humidity, atmospheric gases or acid rain. Ofcourse it is not only the mentioned fluctuations that affect ash during the ageing, but also the fact that ash is generated at high temperatures and is therefore not in thermodynamic equilibrium in contact with water and air at room temperature. Ashes contain various potentially hazardous and non-hazardous chemical compounds. Therefore, precautions must be taken to avoid leaching of substances such as heavy metals into the surrounding environment. Mineral phases that are initially present and/or that form during the ageing are primarily responsible for the immobilization or leaching of vriousspecies. Newly formed mineral phases like clay minerals are of main interest, because of their very high cation exchange capacity, swelling and expansion properties. The conditions found in a landfill environment are likely to favour clay mineral formation.

Changes in mineralogical composition and leaching behaviour were investigated in ashes that were aged under accelerating conditions in the laboratory. The aim of this study is to evaluate the potential of refuse-derived fuel (RDF) ashes as liner material in a landfill top cover. The following specific questions have been addressed and are discussed below: How does ageing affect the chemical stability of RDF fly ash in terms of leaching behaviour and mineral composition of ashes? And under what conditions are clay minerals likely to form in RDF fly ashes?

2. MATERIALS AND METHODS

2.1 Material

The RDF fly ashes used in the experiment originated from Söderenergi AB (Sweden) co-incinerators 1 and 3; grate type and fluid bed type incinerators, respectively. Both incinerators had burned sorted industrial waste (crushed wood, paper, cardboard and plastic), waste from construction and demolition (plastic, gypsum and waste from finishing processes) and by-products from the cellulose industry (mill peat and creosote oil) as fuel to generate heat for district heating.

Ash specimens for the ageing experiment were prepared by adding ca 8% distilled water or leachate to a total solid (TS) content of 70% and compaction in two layers into cylinders (height and diameter, 4 cm). The specimens were then incubated under different conditions according to the experimental design described below.

2.2 Laboratory experiment

The influences of selected factors on the chemical and mineralogical changes that occur in RDF fly ashes were investigated in a laboratory experiment. It had a reduced factorial (D-optimal, 2^{5-1}) (Eriksson *et al*., 2008) design, in which the following five factors were varied at two levels and intermediate point (centre point) (Table 1). Triplicate samples were tested for every combination of factors except the intermediate point samples, for which there were no replicates.

Table 1. Factors varied, and their applied levels, in the reduced multivariate factorial design for the accelerated RDF ashes ageing experiment.

Factor	Level		
	Low	Intermediate	High
Carbon dioxide, CO_2 (%)	Atmosphere (0.038)	20*	100
Temperature, ºC	5	30	60
Relative air humidity, RH (%)	30	65	100
Time, months	3	10, 22	31
Water quality	Distilled	–	Leachate

* Mixture of 20% CO_2 and 80% N_2

2.3 Sampling and preparation

Samples for X-ray diffraction (XRD) and scanning electron microscopy (SEM) were taken from the surface of each specimen (top 2-3 mm). Then the rest of each specimen was crushed and samples for batch leaching test were taken. The samples were dried for 2h at 50ºC, ground and sieved to less than 50 μm for XRD analysis. Samples for the batch leaching tests were crushed to particle sizes of less than 4 mm.

2.4 Analysis

2.4.1 Batch leaching test

A standard one-stage compliance batch leaching test (SS-EN 12457-4) at a liquid to solid ratio of 10 l/kg (L/S 10) was used to estimate leachable fractions of elements in fresh and aged ashes.

The concentrations of dissolved organic carbon (DOC), total organic carbon (TOC), chloride (Cl⁻) and sulphate (SO_4^{2-}) in the eluates, in mg kg⁻¹ dry weight (dw), were compared with the leaching limit values for hazardous amd non-hazardous acceptance at EU landfills, listed in Annex II of the Landfill Directive (2003/33/EC).

2.4.2 X-Ray diffraction (XRD)

The mineralogical composition of each sample was determined qualitatively by X-ray diffraction using a Siemens D5000 X-Ray diffractometer at a current of 40 mA, 40 kV voltage, 30 rpm sample rotation, with CuKα₁ radiation, for Bragg-angles (2θ) between 5° and 70°, with 0.02° and 3s steps.

2.5 Geochemical modelling

A database compiled by Blanc et al. (2009) was used for geochemical equilibrium modelling with PHREEQC-2 (Parkhurst and Appelo, 1999), based on the composition of the leachates from fresh and aged ash specimens, in order to: (1) identify potential solubility controlling minerals and (2) to evaluate possible formation of clay minerals in the ashes.

The presented mineral phases were selected based on: calculated saturation indices (SI) that approach zero (-0.5 < log SI < 0.5). Elemental concentrations and pH were used to calculate the saturation indices. Saturation indices provide indications of whether a mineral is in thermodynamic equilibrium with the solution (SI ~), will tend to precipitate (SI > 0) or tend to dissolve (SI < 0).

3. RESULTS, DISCUSSION AND CONCLUSIONS

3.1 Mobility of metals and salts in ashes

Ashes contain various hazardous and non-hazardous metallic elements and salts. Therefore, precautions must be taken to avoid the latter (e.g. heavy metals) leaching into the surrounding environment. However, the presence of elements that may potentially form hazardous soluble species does not necessarily mean that the ash is dangerous, because their availability to the pore water and leaching depend on the mineral structure.

Leaching of major elements in the ash can change the mineral composition, and hence the chemical stability of a landfill top cover in which it is used. Thus, it is important to evaluate the leaching of elements and to identify potentially hazardous elements.

The leaching results show that the concentrations of Ba, Cr, Cu, DOC and SO_4^{2-} in the leachates of aged ashes were consistently below the limit values for accepting waste at landfills for non-hazardous waste (2003/33/EC, 2002). The concentrations of many other elements, e.g. Al, As, Cd, Co, Fe, Mn, Ni and S in the leachates were below the detection limits in most cases.

The leaching of Pb, Zn and Cl⁻ exceeded the limit values in some cases. Most of the samples aged at 20 % and 100 % CO_2 did not exceed the Pb leaching limit values for accepting granular hazardous waste at landfills for non-hazardous waste. However, the samples aged at atmospheric CO_2 exceeded the Pb leaching limit values. Concentrations of Cl⁻ in most of the aged ash leachates, and Zn in some of them, exceeded the leaching limit values even for acceptance of granular waste at landfills for hazardous waste.

3.2 Mineralogical changes during the ageing

Significant changes in leaching behaviour occurred during the ageing of the ashes, strongly indi-

cating that mineral transformations occurred.

The theoretically possible precipitation and dissolution of various mineral phases were estimated by geochemical equilibrium modelling of the leaching results. In addition, minerals in the samples were empirically identified by XRD. The results show that fresh and aged RDF ashes contain various mineral phases, like silicates, carbonates, hydroxides, oxides, chlorides and sulphates (Table 2).

Ageing conditions	Silicates		Carbonates, hydroxides, oxides, chlorides and sulphates											
	Quartz	Gehlenite	Calcite	Vaterite	Portlandite	Lime	Hematite	Halite	Hydrocalumite	Sylvite	Anhydrite	Bassanite	Ettringite	Gypsum
Fresh ash	x	x	x		x	x		x	x	x	x		x	x
3 months — 0.038% CO_2, 30 % RH, 60°C, L*	x		x	x	x			x	x	x	x			
3 months — 100% CO_2, 30% RH, 5°C, L	x		x	x				x		x		x		
3 months — 0.038% CO_2, 100% RH, 60°C, D*	x		x	x				x	x	x	x	x		
3 months — 100% CO_2, 100% RH, 5°C, D	x		x	x				x		x	x	x		
10 months — 0.038% CO_2, 30 % RH, 5°C, L	x		x	x				x	x	x		x		
10 months — 100% CO_2, 30% RH, 60°C, L	x		x					x		x	x			
10 months — 0.038% CO_2, 100% RH, 5°C, D	x		x	x				x	x	x		x		
10 months — 100% CO_2, 100% RH, 60°C, D	x		x					x		x	x			
10 months — 20% CO_2, 65% RH, 30°C, D	x		x					x				x		
10 months — 20% CO_2, 65% RH, 30°C, L	x		x					x				x		
22 months — 0.038% CO_2, 30% RH, 5°C, D	x		x					x		x			x	x
22 months — 0.038% CO_2, 100 % RH, 5°C, L	x		x					x		x		x		
22 months — 20% CO_2, 65% RH, 30°C, L	x		x					x						x
22 months — 20% CO_2, 65% RH, 30°C, D	x		x					x						x
22 months — 100% CO_2, 30% RH, 60°C, D	x		x					x			x			
22 months — 100% CO_2, 100% RH, 60°C, L	x		x					x			x			
31 months — 0.038% CO_2, 30% RH, 60°C, D	x	x	x					x	x		x			
31 months — 0.038% CO_2, 100 % RH, 60°C, L	x		x					x	x		x			
31 months — 20% CO_2, 65% RH, 30°C, D	x		x											x
31 months — 20% CO_2, 65% RH, 30°C, L	x		x											x
31 months — 100% CO_2, 30% RH, 5°C, D	x		x	x				x						x
31 months — 100% CO_2, 100% RH, 5°C, L	x		x	x				x						x

D- distilled water, L-leachate water

Table 2. Crystalline phases detected by XRD analysis in fresh and aged RDF fly ashes

However, the results of the XRD analyses only partially conformed to the geochemical equilibrium calculations. Geochemical modelling indicated that 429 different mineral phases and chemical compounds could be present in the ashes: 132 silicates; 68 oxides, hydroxides and oxyhydroxides; 48 clay minerals; 44 sulphates; 38 carbonates; 36 chlorides; 26 sulphides and others (Brännvall, 2010).

The calculated SI indicated that most of the carbonates could precipitate in the leachates of both fresh and aged ash (at 100 % CO_2) (Brännvall, 2010). All leachates were undersaturated with respect to chlorides and close to equilibrium with respect to most sulphates. For more details see Brännvall (2010).

3.2.1 Clay minerals

The leachates from fresh and 3 months-aged ashes were undersaturated with respect to clay minerals like dickite, halloysite, illite, imogolite, kaolinite, smectite and syngenite. Saponite-Na and vermiculite-K were very close to equilibrium in the leachate of fresh ash, while hydrotalcite was close to equilibrium in the leachate of aged ash (100% CO_2, 100% RH, 5°C, distilled water). Chrysotile, saponite-Na, vermiculite-K and hydrotalcite could potentially precipitate in leachates of ash aged for 3 months under most of the tested conditions.

The leachates of ash specimens aged for 10 months were mostly undersaturated with respect to clay minerals (Brännvall, 2010). For example, Ca, K, Mg and Na saponite were close to equilibrium and could precipitate, as well as chrysotile, hydrotalcite and vermiculite-Mg, in the leachate of ash specimens aged at 0.038 % CO_2, 100 % RH, 5°C, prepared with distilled water. Leachates of ash aged for 22 months at 0.038 % CO_2 were modelled to be oversaturated with respect to Ca and Na saponite, talc, Ca, Mg and Na vermiculite (Brännvall, 2010).

Most of the 31 months-aged ash leachates were oversaturated with respect to saponite and vermiculite (Brännvall, 2010). Smectite, montmorillonite and illite could precipitate in the leachates of ash specimens aged at 100 % CO_2, 100 % RH, 5°C prepared with leachate. Kaolinite was very close to equilibrium in the same ash leachates.

Clay minerals like smectite, montmorillonite and vermiculite have very high cation exchange capacities, which favour the stabilization/immobilization of heavy metals in the mineral.

3.4 Long-term chemical stability of ash liners

To assess the long-term stability of RDF FA used in a landfill cover liner, specimens were subjected to accelerated ageing under various conditions. Accelerated ageing affected the chemical stability of RDF fly ash in terms of changes in leaching behaviour and mineralogical transformations. The factors CO_2, ageing time, relative air humidity and (in some cases) temperature significantly affected the properties of the aged ash.

Hydration is the primary reaction that occurs in ashes when they come into contact with water, and several mineral transformations appear to have been driven by hydration processes, notably portlandite ($Ca(OH)_2$) formed when lime (CaO) and mixed oxides containing calcium reacted with water. Portlandite and lime were also responsible for the high alkalinity of fresh ash and their buffering at pH 12. In addition, hydrocalumite and ettringite formed as a result of hydration in the presence of chlorides and sulphates in the RDF fly ash. Ettringite usually forms when sulphate ions are available and may be converted into hydrocalumite as sulphate depletes (Zhang and Reardon, 2003). Both ettringite and hydrocalumite have structures that promote the immobilization of various hazardous chemicals, which is considered to be a favourable feature when using fly ash in liner constructions. The swelling of the material makes it denser when it is under pressure from the overlying layers. However, a possible risk is that the formation of ettringite may destabilise constructions due to its expansive (swelling) properties (Chrysochoou and Dermatas, 2006). Typically, the slopes of the landfill top cover can fail due to the accompanying reduction in strength.

Ettringite formation can be delayed if fly ash is exposed to temperatures higher than 70 °C (Newman and Choo, 2003). However, such conditions do normally not occur in landfill top covers, unless methane from the landfill body is oxidised, which can lead to the temperature rising to 90°C (Brundin et al. 2001). Carbonation of ettringite leads to the formation of calcite, gypsum and aluminium hydroxide. The disappearance of ettringite may also be related to reductions in pH, which may be caused by other factors in addition to carbonation (Sjöblom, 2007), e.g. silicate formation (Steenari *et al.*, 1999).

Carbonation of the RDF fly ash, which contained abundant Ca, resulted in the transformation

of soluble forms of oxides and hydroxides into less soluble carbonates. Carbonation causes clogging of the pores, thereby decreasing porosity (which is directly related to permeability) (Maurice and Lagerkvist 1998). Carbonation also stabilizes the material, by binding trace elements into carbonates and binding particles together, resulting in hardening and strengthening of the material and reducing leaching of trace elements from it (Chandler et al. 1997). Calcite is one of the carbonates that determine the long-term stability of RDF fly ashes used in landfill top cover construction.

Due to reductions in pH the carbonates can dissolve, releasing the bound trace elements. However, the presence of carbonates in RDF fly ashes results in high resistance to acidification by increasing the buffering capacity (Brännvall, 2010). This was confirmed by the high ANC of the ashes (up to 10.7 mmol/g) following the accelerated ageing treatments. The hazardous components immobilised in the ashes will not be released due to such a high buffer capacity, which will not be exhausted for 1,000 or even 10,000 years (Hirschmann and Förstner, 1997).

A quantitative description of calcite dissolution in very heterogenous systems in contact with water with high ionic strength is not currently possible (Krauskopf and Bird 1995). However, the ANC tests showed that some mineral phases in RDF fly ashes confer a high buffering capacity (Brännvall, 2010). It should be mentioned that the pH values of pure systems cannot be used to identify hydration phases in materials like ash, especially in the presence of contaminants (Polettini et al. 2002).

The geochemical equilibrium modelling indicated the potential occurrence of various solubility-controlling mineral phases that only partly conformed to results of the XRD analysis. This was expected because of the differences in the thermodynamics and kinetics of the formation of mineral phases. Thermodynamic parameters define the stability of one mineral state versus another, while kinetic parameters describe the reaction rates of species. Therefore, the geochemical equilibrium calculations indicate the mineral phases that could be formed after periods longer than the duration of the experiment.

According to the Swedish Environmental Protection Agency, covers for non-hazardous and hazardous waste landfills should be reliable for hundreds of years and a thousand years perspective, respectively. Clearly, tests with such durations cannot be applied. Therefore, the leaching behaviour of ashes is assessed by leaching tests.

Water is the main prerequisite for chemical reactions to occur in ashes, and a large amount of water increases the possibility for soluble compounds to dissolve (Kylefors *et al.*, 2003). A landfill top cover liner with low permeability hinders the percolation of large amounts of water through it and thus the leaching of hazardous compounds from the liner. About 22 l/m^2 yr of water percolates through a landfill top cover liner containing a 1 m layer of fly ashes in ca. 1.6 m deep examined by Tham and Andreas (2008). This corresponds to an increase of L/S by 0.022 per year. Assuming that this rate remains more or less constant, it will take about 1400 years to reach a L/S ratio of 10.

The batch leaching test at L/S 10 performed for 24 h hours is a very simple test for evaluating the solubility of contaminants in ashes. However, it does not reflect the real situation in the landfill top cover environment. Column tests, in which water percolates at low rates, can provide more accurate predictions of the long-term behaviour of ashes, but it was not possible to perform column tests in this study, because of the small amounts of material used in the ageing experiment. Furthermore, column tests also have limitations, as described by Kylefors at al. (2003) and Reid and Brooks (1999). For example, the reactions between material and water occurring in a laboratory leaching test differ from those that occur in the field (Reid and Brooks (1999). The conditions in the leaching tests are saturated when a large amount of water contacts a small amount of material, while in the field small amounts of water contact large volumes of material, creating unsaturated conditions. This (and other factors) affects the leaching behaviour of contaminants. Notably, smaller amounts of contaminants like Cl, Cu, Cr and Mo are released from

field lysimeters than from a homogeneous column (Sager and Heuss-Assbichler, 2009).

In addition, batch and column leaching tests are only applicable to substances that do not react with water (Andreas and Bilitewski, 1999; Kylefors *et al.*, 2003; 2003/33/EC). Thus, comparisons with leaching limit values are only valid for ash that has been aged to equilibrium conditions in an appropriate environment.

In summary, the use of RDF ashes in a top cover liner construction has the following advantages: most of potentially hazardous elements like Pb, Cl, Cr, Cu etc., will not be released from the ashes in the long-term. Nevertheless, the technical and environmental performance of an ash liner is expected to be stable in the long-term.

Clay minerals were not detected by XRD analysis, possibly because they were present at levels below the threshold concentration of a mineral for XRD detection ($\geq$ ca. 4%), and/or that clay minerals formed in the specimens that were non-crystalline or poorly crystalline, and thus not detectable by XRD. Another possibility is, of course, that no clay minerals were formed in any of the ashes during the ageing.

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