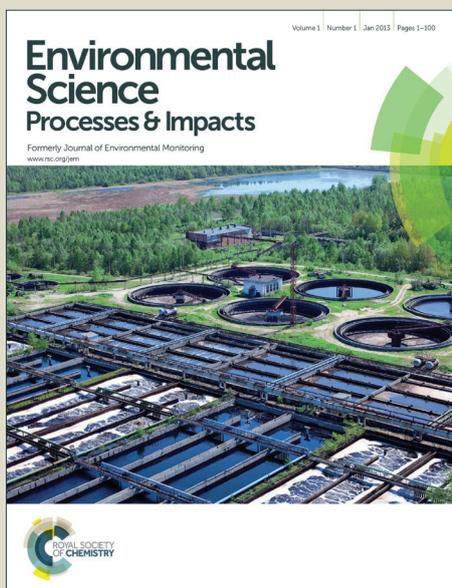


Environmental Science Processes & Impacts

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3 Fly ash is often landfilled or sent abroad for stabilization because it is
4 considered a hazardous waste. These approaches to fly ash are both costly, and
5 highlight the need for alternative and sustainable management solutions. Both
6 ash recycling and preservation of natural resources can be solved by using fly
7 ashes as a secondary construction material and as soil fertilizer. However, most
8 fly ashes cannot be applied on the forest soil because of the presence of
9 hazardous compounds. But those ashes that are not suitable for such application
10 can still be used e.g. in a vegetation layer of a landfill top cover. Still, a
11 responsible application of fly ashes is warrant and careful investigation of
12 ash properties before recycling is necessary.
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Fly Ash in Landfill Top Covers – a review

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Increase of energy recovery from municipal solid waste by incineration results in the increased amounts of incineration residues, such as fly ash, that have to be taken care of. Material properties should define whether fly ash is a waste or a viable resource to be used for various applications. Here, two areas of potential fly ash application are reviewed: the use of fly ash in a landfill top cover either as a liner material or as a soil amendment in vegetation layer. Fly ashes from incineration of three types of fuel are considered: refuse derived fuel (RDF), municipal solid waste incineration (MSWI) and biofuel.

Based on the observations, RDF and MSWI fly ash is considered as suitable materials to be used in a landfill top cover liner. Whereas MSWI and biofuel fly ashes based on element availability for plant studies, could be considered suitable for the vegetation layer of the top cover. Responsible application of MSWI ashes is, however, warranted in order to avoid element accumulation in soil and elevation of background values over time.

Introduction

Sweden's goal is to generate 100% of its energy from renewable resources.¹ During the last 5 years, energy recovery from renewable resources such as municipal solid waste (MSW) has increased by 8%. Almost 52% of all MSW being recycled is used for energy recovery by incineration.² Such increase can be attributed to the landfill ban of sorted combustible waste in 2002 and organic waste in 2005. This incineration reduces MSW volume by 90% and its weight by 75%. However, the remaining incineration residues (ashes) still have to be dealt with. According to EU Directive 2000/76/EC³ on the incineration of waste, the amounts and harmfulness of these residues must be minimised and the residues should be recycled where appropriate.

MSW is very heterogeneous, consisting of diverse unburned organic and inorganic materials. These wastes can either be mass burnt directly as received without pre-treatment, or sorted, separated and reduced in size prior to incineration. This separation results in a more homogeneous material called refuse-derived-fuel (RDF), which consists of wastes such as tainted wood (31–73%), recycled fuels (~30%); peat (~23%); plastics (~22%);

various oils (9%) and other materials (5.3–8%).^{4, 5} Wood (biofuel) fly ash, in contrast, originates from combustion of purely wood-based fuels. During combustion processes bottom and fly ashes are generated. Bottom ash (BA) is a non-combustible residue that remains in the incinerator, and fly ash (FA) comprises the fine particles that rise with the flue gases during combustion. In 2012, 0.85 Mt of bottom ash and ca 0.26 Mt of fly ash were generated from waste incineration in Sweden.⁶ Bottom ash is used in various applications, but fly ash is often landfilled or sent abroad for stabilization because it is considered a hazardous waste.⁷ These approaches to fly ash are both costly, and highlight the need for alternative and sustainable management solutions.

Large amounts of materials are needed in construction and land cultivation sectors. In Sweden alone about 87 Mt of natural material is required to cover ca 15–20 km² of landfills according to the data from 2008.⁸ In addition, the global demand for fertilizer nutrients (currently from natural resources) is rapidly increasing and it is estimated to increase up to 2% per year until 2015.⁹ Therefore using fly ashes as a secondary construction material and as soil fertilizer would contribute to the preservation of natural resources.

However, not all fly ashes are suitable for recycling. For example, most ashes cannot be applied on the forest soil because of the presence of hazardous compounds. But those ashes that are not suitable for such application can still be used e.g. in a vegetation layer of a landfill top cover. Here standard environmental monitoring systems such as leachate collection/treatment are installed, minimizing the risk for spreading of the hazardous compounds into the surrounding environment.

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Fly ash could also surpass other materials (e.g. clays) commonly used in landfill top cover liners for strength and endurance in construction, as shown in recent years.¹⁰⁻¹⁴ Therefore material properties should define whether fly ash is a waste or a viable resource to be used for various applications.

Fly Ash

The chemical composition of MSW may vary from source to source and also within the same incineration facility. Municipal solid waste incineration (MSWI) ashes are products of incineration at 850°C. This promotes the formation of amorphous glass phases (>40%), which play a key role in fly ash reactivity.^{15,16} The most abundant constituents of MSWI fly ash are oxides of Ca, Si, Al, Na and Fe, which frequently occur as mixed oxides (Figure 1).

MSWI and RDF fly ash also contain significant amounts of chlorine, originating from the various types of plastics like PVC (polyvinyl chloride) in the waste, and paper waste from bleaching processes.¹⁷⁻¹⁸ Also, heavy metals like Cr, Cd, Cu, Ni, Pb, Zn and etc., are accumulated in fly ashes.

The chemical composition of biofuel fly ash is difficult to generalize. Its properties not only depend on plant species and which parts are combusted, but also on the types of fuels that are co-combusted with wood, as well as the collection and storage conditions of that wood prior to combustion.¹⁹

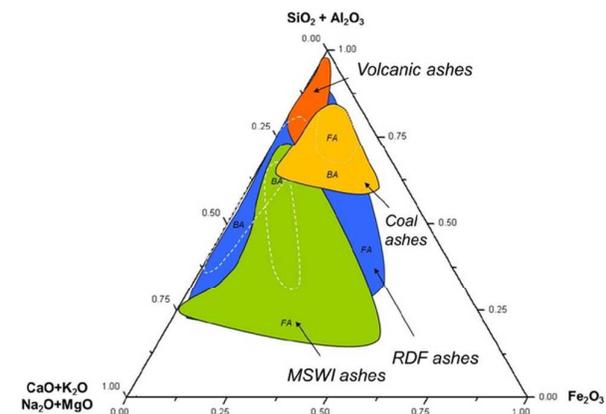


Figure 1. Ternary diagram showing relative proportions of SiO_2 , Al_2O_3 and CaO , K_2O , Na_2O , MgO and Fe_2O_3 in various fly (FA) and bottom (BA) ashes according to the chosen references.^{16,20-43}

Biofuel fly ash usually contains high concentrations of Si, Al, Fe, Ca, S, Mg, P, K, Na and Mn.^{44,45}

Mineralogical composition of MSWI as well as RDF fly ashes consists of mixtures of silicates, oxides, carbonates, sulphates and chlorides, while biofuel fly ash contains less chlorides, but more phosphates (Table 1).

Table 1. Mineralogical composition of RDF, MSWI and biofuel fly ashes according to the chosen references

Group/ Mineral name	Formula	RDF	MSWI	Biofuel (wood)
			Fresh <i>Aged</i>	
		FA		

Fly Ash in the Liner of a Landfill Top Cover

Design.

A landfill top cover is a multilayer construction that protects the environment from gas emissions from the landfill body and hinders water infiltration into the waste (Figure 2).

According to Swedish and EU legislation, the amount of percolating water must not exceed $50 \text{ l/m}^2 \text{ yr}$ for non-hazardous waste landfills and $5 \text{ l/m}^2 \text{ yr}$ for hazardous waste landfills.⁴⁶ The protection layer protects the liner from freezing/thawing, desiccation, root penetration and digging animals, while the upper drainage layer protects it from water percolating from above and the bottom drainage layer provides protection from gas penetrating from the waste body below the liner.

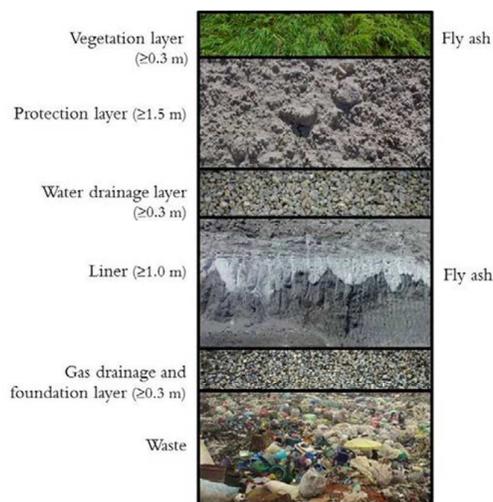


Figure 2. Illustration of a landfill top cover system.¹³

Prevailing conditions.

Air. The atmosphere below the liner contains water-saturated landfill gas, and the atmosphere above the liner may be affected by the run-off water from the layers above it. However the protection layer and vegetation on it retains the largest part of the moisture and only ca. 25% of precipitated water will reach the drainage layer above the liner.⁴⁷ Humidity is an important factor for hydration and carbonation reactions to occur, which in turn affect mineralogical changes in the fly ash used as a liner material. Maximal and rapid carbonation occurs at 50 to 70% humidity,^{48,49} while on either side of this range the carbonation rate decreases.^{50,51}

1	2	3	4	5
CARBONATES				
Calcite	CaCO ₃	65; <u>53</u>	52; 59; 61; 73; <u>15; 59; 60</u>	64; 66; 69; <u>63</u>
	Fairchildite K ₂ Ca(CO ₃) ₂			69; 73
	Huntite Mg ₃ Ca(CO ₃) ₄			<u>63</u>
	Magnezite MgCO ₃		61	
	Natrite Na ₂ CO ₃		<u>57</u>	
	Vaterite CaCO ₃	<u>53</u>	<u>60</u>	
CLAY MINERALS				
	Illite KAl ₃ Si ₃ O ₁₀ (OH) ₂		52	
	Syngenite K ₂ Ca(SO ₄) ₂ H ₂ O	70	<u>15</u>	64
CHLORIDES				
	Blixite Pb ₂ Cl _x (O,OH) _{2x}		74	
	Cotunnite PbCl ₂		74	
	Halite NaCl	65; 54; <u>53</u>	52; 55; 57; 58; 59-62; 67; 73; <u>15; 59;</u> <u>60</u>	
	Hydrocalumite (Friedel's salt) Ca ₈ Al ₄ (OH) ₂₄ (CO ₃) ₃ (Cl)(H ₂ O) _{9,6}	<u>53; 54</u>	52; 60; <u>3; 28</u>	
	Hydrophilite CaCl ₂	25		
	Sylvite KCl	54; <u>53</u>	62	66; 69
	Zinc Chloride ZnCl ₂		52	
HYDROXIDES				
	Boehmite ALOOH		<u>15</u>	
	Lepidocrocite FeOOH		52	
	Nordstrandite Al(OH) ₃		<u>60</u>	
	Portlandite Ca(OH) ₂	54; <u>54</u>	15; 57; 59; 60	64; 69
OXIDES				
	Calcium aluminum oxide Ca ₃ Al ₂ O ₆			<u>63</u>
	Calcium titanite CaTiO ₃		52	
	Corundum Al ₂ O ₃		60	
	Grossite CaAl ₄ O ₇		55	
	Hematite Fe ₂ O ₃	56	52; 61; <u>15</u>	
	Lime CaO		60; 73	69
	Magnetite Fe ₃ O ₄		52	
	Minium Pb ₃ O ₄		52	
	Periclase MgO	56		69
	Rutile TiO ₂		52; <u>15</u>	
	Ulvöspinel Fe ₂ TiO ₄		52; <u>15</u>	
PHOSPHATES				
	Aluminum phosphate AlPO ₄			<u>63</u>
	Hydroxiapatite Ca ₅ (PO ₄) ₃ (OH)			69
SILICATES				
	Akermanite Ca ₂ Mg(Si ₂ O ₇)			
	Albite NaAlSi ₃ O ₈			64; <u>63</u>
	Amorphous glass		52	64
	Anorthite CaAl ₂ Si ₂ O ₈		55	
	Augite Ca ₃ Na ₃ Mg ₃ FeAl _{1.6} Si ₇ O ₂₄		52	
	Calcium silicate hydrate Ca _{1.5} SiO _{3.5} ·xH ₂ O	56	<u>59</u>	
	Cristobalite SiO ₂		<u>15</u>	
	Diopside CaMgSi ₂ O ₆		52	
	Enstatite (Mg,Fe)SiO ₃		52	
	Feldspar		73	
	Ferrosilicate, magnesian (Fe,Mg)SiO ₃			<u>63</u>
	Forsterite (Mg,Fe) ₂ SiO ₄		52	
	Garnet Ca ₃ (Al,Fe) ₂ (Si,P) ₃ O ₁₂		52	

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Gehlenite	$\text{Ca}_2\text{Al}_2\text{SO}_7$	<u>53</u>	52; 59; 60; 73; <u>15</u> ; <u>60</u> ; <u>61</u>	<u>63</u>
Gismondite	$\text{CaAl}_2\text{Si}_2\text{O}_8 \cdot 4\text{H}_2\text{O}$		<u>57</u>	
Hatruite	Ca_3SiO_5		52	
Kalsilite	KAlSiO_4		52	
Kilchoanite	$\text{Ca}_3\text{Si}_2\text{O}_7$		16	
Larnite	Ca_2SiO_4		52; <u>58</u>	
Merwinite	$\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$			69
Microcline	$\text{K}_2\text{AlSi}_3\text{O}_8$			64
Mullite	$\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$			64
Nepheline	$\text{Na}_3\text{KAl}_4\text{Si}_4\text{O}_{16}$		52	
Plagioclase	$(\text{Na,Ca})((\text{Si,Al})\text{AlSi}_2\text{O}_8)$			69
Quartz	SiO_2	25; 54; 72; <u>53</u>	52; 59-61; 67; 73; <u>15</u> ; <u>57</u> ; <u>59</u> ; <u>60</u>	64; 66; 69; <u>63</u>
Sanidine	KAlSi_3O_8		52; 55	69
Sodalite	$\text{Na}_4\text{Al}_3\text{Si}_3\text{O}_{12}\text{Cl}$		52	
Tobermorite	$\text{Ca}_5(\text{OH})_2\text{SiO}_{16} \cdot 4\text{H}_2\text{O}$		52	
SULPHATES				
Allenite	$\text{MgSO}_4 \cdot 5\text{H}_2\text{O}$		55	
Alunite	$\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$		52	
Anhydrite	CaSO_4	25; 65; 56; <u>53</u>	52; 57; 59-62; 67; 71; 73 <u>15</u> ; <u>59</u> ; <u>60</u>	69
Aphthitalite	$\text{K}_3\text{Na}(\text{SO}_4)_2$			<u>63</u>
Bassanite	$\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$		52; <u>15</u>	
Caracolite	$\text{Na}_3\text{Pb}_2(\text{SO}_4)_3\text{Cl}$		52; <u>15</u>	
Ettringite	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$	54; <u>53</u>	52; <u>68</u>	<u>63</u>
Gordaitite	$\text{NaZn}_4(\text{SO}_4)(\text{OH})_6 \text{Cl}(\text{H}_2\text{O})_6$		52; <u>15</u>	
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	65	52; 59	
SULPHIDES				
Marcasite	FeS_2		52	
Pyrite	FeS_2		52	

At 100% humidity, carbon dioxide penetrates material very little due to the low diffusion rate of CO_2 in water.

Gas. The gas below the liner consists primarily of CH_4 , N_2 , CO_2 and O_2 . The typical concentration (by volume) of carbon dioxide in landfill gas is between 20 and 50% (Lagerkvist, 2003). The absorption of CO_2 by alkaline material leads to carbonation reactions, which in turn promote the pH decrease and affect leaching behaviour of various compounds in the liner material.

Temperature. The temperature in and around the liner is influenced by the heat generated and released from the waste below; the heat conductivity of the cover layers; and the climatic conditions of the location. As the rate of waste decomposition gradually decreases, heat production declines and, hence, the temperature below the liner falls over time. Heat generation from the landfill body can lead to evaporation and subsequent desiccation in both above and below the liner. Desiccation can cause crack formation in the liner, thereby allowing water to migrate into the waste and generate leachate (Dwyer, 2000). Temperatures between $+15^\circ\text{C}$ and $+40^\circ\text{C}$ below the liner (at about 3 m depth) and between -1°C to $+47^\circ\text{C}$ above the liner (at about 2 m depth) have been recorded.¹³ The high temperatures in the protection layer above the liner were probably caused by methane oxidation. Hydration and carbonation are also heat generating or exothermic reactions.²⁷ The generated heat enhances the short-term reactivity of material, and that affects

changes within mineral phases.⁷⁷ At temperatures up to 60°C carbonation of material increases, but at higher temperatures carbonation decreases due to decrease of water content.^{78, 79} The most beneficial temperature range for carbonation is from 20 to 30°C .^{49, 79}

Ageing of fly ash.

Fly ash properties depend on the environmental conditions they are exposed to. Whether they are simply landfilled, used as construction materials or applied on soil, ashes are subject to transformations, occurring when they are not in thermodynamic equilibrium with atmospheric or other conditions. Temperature and humidity fluctuations, atmospheric gases or acid rain are key factors influencing these changes.

Mineralogical transformations. Complex chemical and mineralogical transformations occurring in fly ash include hydrolysis/hydration of Al, Ca, K and Na oxides, dissolution/precipitation of salts and hydroxides, carbonation, neo-formation of clay-like minerals, oxidation/reduction, and formation of solid solutions^{71, 80-83} (Table 2).

Table 2. Mineral changes that occur during ageing of fly ash (adapted).⁸⁴

Process	Mineral changes	Chemical reaction
Hydration	Anhydrite to gypsum:	$\text{CaSO}_4 + 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
	Ettringite formation	$3\text{CaSO}_4 + \text{Ca}_3\text{Al}_2\text{O}_6 + 32\text{H}_2\text{O} \rightarrow \text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$
	Lime to portlandite:	$2\text{CaO} + \text{H}_2\text{O} \rightarrow 2\text{Ca}(\text{OH})_2$
Solution/ Dissolution	Dissolution of gypsum:	$\text{CaSO}_4 \rightarrow \text{Ca}^{2+} + \text{SO}_4^{2-}$
Hydrolysis	Dissolution of glass: (schematic reaction)	$\text{Me-Al-Si-O glass} + \text{H}_2\text{O} + \text{H}^+ \rightarrow \text{Me}^+ + \text{Al}(\text{OH})_3(\text{am}) + \text{SiO}_2(\text{am})$
Carbonation	Portlandite to calcite:	$\text{Ca}(\text{OH})_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$
	Ettringite to calcite and gypsum	$\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O} + 3\text{CO}_2 \rightarrow 3\text{CaCO}_3 + 3(\text{CaSO}_4 \cdot 2\text{H}_2\text{O}) + \text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O} + 25\text{H}_2\text{O}$
Oxidation	Magnetite to hematite:	$2\text{Fe}_3\text{O}_4 + 0.5\text{O}_2 \rightarrow 3\text{Fe}_2\text{O}_3$
Precipitation	Ferric hydroxide:	$\text{Fe}^{3+} + 3\text{OH}^- \rightarrow \text{Fe}(\text{OH})_3$
	Ettringite	$3\text{CaSO}_4 + \text{Ca}_3\text{Al}_2\text{O}_6 + 32\text{H}_2\text{O} \rightarrow \text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$
Adsorption	Heavy metals on oxides:	$\text{Fe-OH} + \text{Me}^{2+} \rightarrow \text{Fe-OMe}^+ + \text{H}^+$
Co-precipitation	Ideal solid solution between $\text{Fe}(\text{OH})_3$ and $\text{Me}(\text{OH})_2$:	$\text{Fe}(\text{OH})_3(\text{s}) + \text{Me}^{2+} \rightarrow \text{Me}(\text{OH})_2(\text{s}) + \text{Fe}^{3+} + \text{OH}^-$

Fly ash used in a landfill top cover will be subject to ageing and mineral transformation processes that are similar to those observed in previous studies of other ashes exposed to other conditions.^{83, 85-87} It might be expected that in the long-term, fly ashes could possibly transform into clay-like materials with similar advantageous chemical and geotechnical properties that are beneficial for the stability of the landfill top cover.

Formation of such solid phases as clay minerals, are of main interest because of their high cation exchange capacity (3–150 cmol/kg), which increases retention of trace elements.^{88, 89} The key factor in clay-like mineral formation is the high pH of ashes. The high pH promotes the prompt dissolution of certain compounds of aluminosilicate glass phase, which is a prerequisite for the formation of clay minerals over time.⁸⁶ Ageing causes pH to decrease, what strongly influences mobility of potentially hazardous compounds in fly ash.

Accelerated Ageing. Considering environmental impact on future generations, the requirements for a landfill top cover are that it would be stable for ca. 1000 years. However, in practice such a long-term evaluation is impossible. Therefore, accelerated ageing experiments in the laboratory by exposing ashes to extreme conditions, e.g. 100% of CO_2 atmosphere, 100% of relative air

humidity and high temperatures (up to 60°C)^{27, 90-93}, which initiate chemical reactions expected to occur over a long-term, may be a promising tool contributing to overcoming this practical obstacle.

Accelerated ageing of ash simulating *inter alia* conditions close to those found in a landfill top cover (20% CO_2 , 65% RH, 30°C T), resulted in the transformation of comparatively soluble forms of oxides and hydroxides into less soluble carbonates.^{91, 92} Hydration and carbonation were the main chemical reactions effecting the dissolution and precipitation of mineral phases in ashes during ageing (Figure 3).⁹³ Formation of carbonates can cause clogging of the ash pores thereby decreasing porosity directly related to permeability of a residue.⁹⁴ Carbonation also stabilizes the material by binding trace elements into carbonates and binding particles together, which results in hardening and strengthening of the material and reduced leaching of trace elements from it.^{55, 91, 92} In particular calcite (calcium carbonate) was the main mineral phase that formed abundantly in the RDF fly ash aged under elevated CO_2 conditions. Hence, in a landfill top cover where CO_2 concentration is higher than in the atmosphere, carbonates can easily form and partly control the leaching of trace elements such as Cu, Pb and Zn.

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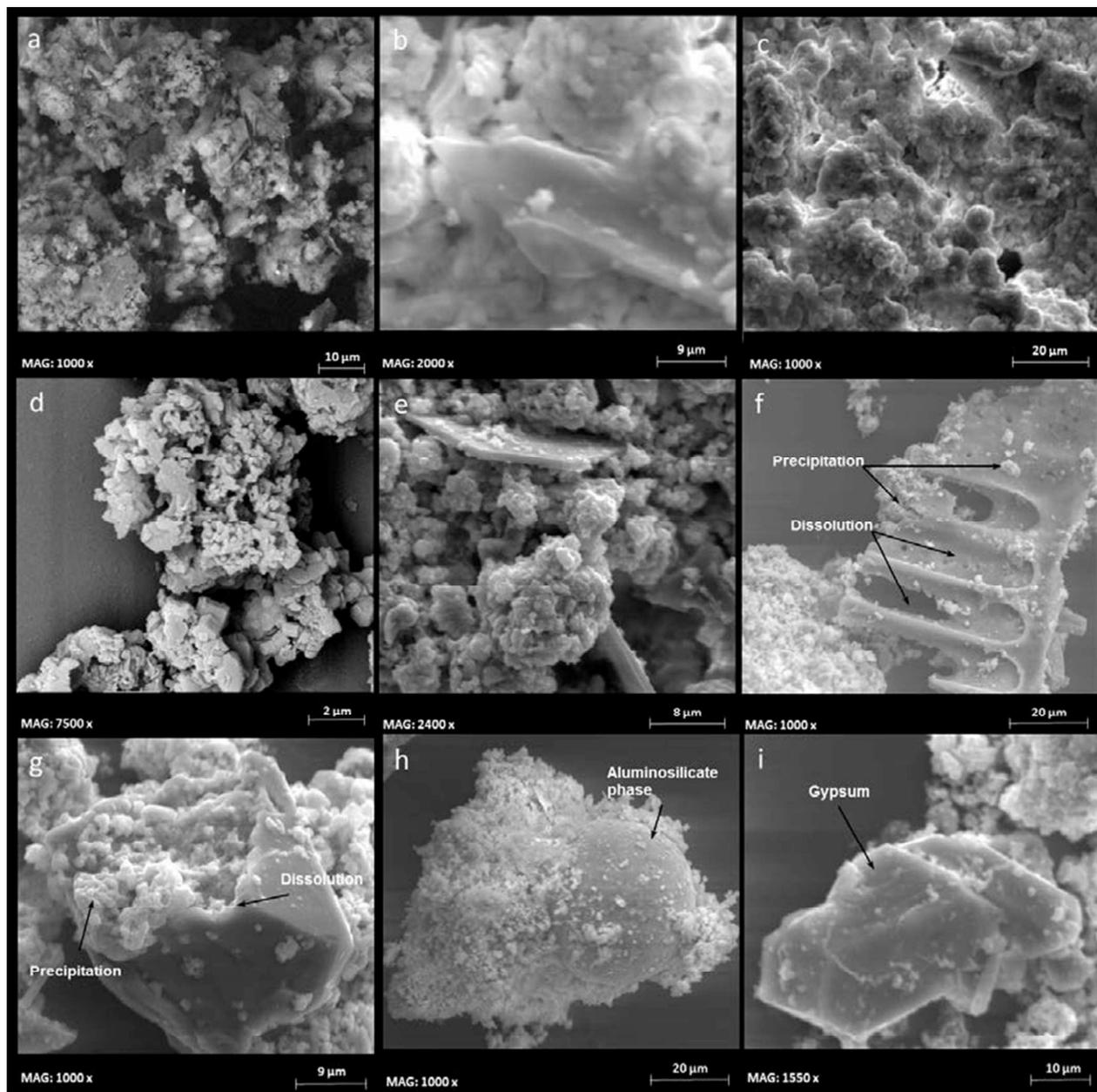


Figure 3. Fresh and aged ash SEM images: a) and b) Fresh ash. c) Ash aged for 10 months under 0.038% CO₂, 100% RH, 5°C with distilled water. d) and e) Ash aged for 22 months under 0.038% CO₂, 100% RH, 5°C with leachate. f) and g) Ash aged for 31 months under 0.038% CO₂, 30% RH, 60°C with

distilled water. h) and i) Ash aged for 31 month under 20% CO₂, 65% RH, 30°C with distilled water. All images were taken with 15 kV acceleration voltage at different magnifications.⁹³

The geochemical equilibrium modelling can indicate potential occurrences of various solubility-controlling mineral phases, whereas the XRD and SEM analysis can only partly confirm this.^{91,92} For example, clay minerals were not detected by XRD (or SEM) 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 were non-crystalline or poorly crystalline, and thus not detectable. There is also a possibility that no clay minerals were formed in any of the ashes during ageing.

Element solubility in aged ashes.

Another important property of fly ash is the acid neutralization capacity (ANC), which plays a substantial role in maintaining pH levels. The pH in turn is the most important factor governing the solubility of various mineral phases, heavy metals and trace elements in aged ashes.⁵⁵ ANC analysis indicate that ashes used in a landfill top cover might have the ability to buffer and keep the pH around 4.5 for a longer period of time compared to fresh ash.^{91,92} This may cause the carbonate dissolution and release of the bound trace elements e.g. Cu, Pb and Zn at pH below 6.²⁰ However, carbonates, particularly calcite (CaCO₃) in RDF fly ashes, resist acidification by increasing the buffering capacity of ashes.^{91,92} Consequently, the hazardous components immobilised in the ashes are not likely to be released due to the high buffer capacity, which will probably not be exhausted for 1000 or even 10000 years.⁹⁵

Both reaction time and level of CO₂ under which fly ashes were aged reduced the pH, which in turn affected the leaching behavior of most soluble constituents. In general, leaching of Ba, Ca, Cl, Cr, Cu, Pb, K, Zn and Na decreased while that of Mg increased in aged ashes.^{91,92} But fly ash exposed to the conditions similar to a landfill top cover liner (20% CO₂, 65% RH, 30°C T and under the influence of leachate from upper soil layers) leached 50% less chlorides and 200 times less Pb compared to fresh ash.⁹² Relative air humidity and the type of water used in the tests (distilled or leachate) did not cause any evident impact on the leaching behaviour. Concentrations of Ba, Cr, Cu, DOC, Pb, Zn and SO₄ in the leachates of ash aged under conditions similar to the landfill top cover were consistently below the limit values for accepting waste at landfills for non-hazardous waste.^{91,96} The concentrations of many other elements, e.g. Al, As, Cd, Co, Fe, Mn, Ni and S, in the leachates were below the instrument detection limits in most cases. Even though chloride leaching significantly decreased during ageing, concentrations of chlorides in most ash leachates remained above the leaching limit values.

Since a low permeability liner containing RDF fly ashes hinders the percolation of water through it, and thus the leaching of substances from it, therefore the leaching of potentially hazardous compounds from the liner material will be rather low.¹³ Still, special care should be taken to reduce water contact with the surface of the compacted ash layer to avoid salt washout by

mineral dissolution and thus preserving the overall stability of a liner.

Fly Ash in a Vegetation Layer

Ash as nutrient supplement. Several studies showed that fly ash can be used as a nutrient source to promote vegetation growth or to stabilize the contaminated soil used in a protection/vegetation layer (Figure 2).^{97,98} The main function of the vegetation layer of the landfill top cover is to sustain plant growth so that the landfill surface is protected against erosion. Plants help to minimise the amount of percolating water through evapotranspiration and nutrient-rich substrates are therefore desirable to ensure a high biomass development. Fly ash, as a source of P, Ca, Mg and K, makes it attractive as soil fertiliser. However, it lacks sufficient amounts of N.

Nitrogen is often the limiting nutrient for the biomass growth, therefore considering ashes as fertilisers, additional N source is needed, e.g. in the form of biosolids. Application of biosolids on soil increases the content of organic matter, improves the water-holding capacity of soil, and most importantly, supplies N and P. Thus, by combining ash with biosolids, a better balance between the macronutrients (N, P, K) in the material mixtures can be achieved. At the same time, such mixing may lead to chemical reactions which can be expected to reduce leaching of potentially toxic elements (e.g. Cd and Pb) in ash and biosolids by immobilizing them within the mixture matrix.

Due to the very high alkalinity of fresh ash (pH \approx 12), a direct application to soil is not recommended. Ashes must mature before application onto soil, in order to avoid disturbance of the nitrogen balance there.⁹⁹ For this reason granulation/pelletizing are frequently used in order to transform the raw ash into a product that has a lower pH and is easier to handle. Granulated materials have a smaller surface area compared to powdered ones leading to a reduced reactivity and a slower release of ash constituents.¹⁰⁰⁻¹⁰³ This in turn, might increase the possibility for plants to take up nutrients over a more extended period of time.

Currently MSWI fly ashes are classified as a hazardous waste due to the leaching of chemical elements from them, however ageing may transform fly ash into material having different properties compared to fresh ash. Based on the background described above it can be concluded that much of the internal and external factors influencing element availability in the fly ashes have yet to be understood.

Today EU policies encourage use of biofuel fly ashes on soil as an alternative to currently depleting mineral fertilizers. Contrary to MSWI and RDF fly ash, biofuel fly ash (BFA) from combustion of wood-based fuel is considered as clean and is readily used as nutrient-rich soil fertiliser in forestry^{19,104} provided it passes quality control requirements where the maximum allowable concentrations of certain elements (e.g. P, As, Pb, Cd and etc.) are defined.¹⁰⁵

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In another case, the use of MSWI fly ash on soil is limited, mainly because of the type of fuel incinerated, which may be hazardous wastes. Therefore potentially toxic elements concentrated in the MSWI fly ash may pose environmental risk for soil environment if such fly ash is applied on soil. However, it has been observed that element availability to leaching and plant uptake in soil often poorly correlates with the total element concentrations in materials.^{106, 107} The residue mixture experiments demonstrated that solubility of potentially toxic elements in MSWI ash might be as low as that of biofuel ash, as shown by leaching tests of materials, despite differences in total element concentrations.¹⁰⁸

Fly ash mixtures with organic waste. As nitrogen content in ashes may be too low to fulfil the plant demands, combining fly ash with N-rich biosolids or other materials is needed to balance the nutrients in potential fertilisers.¹⁰⁸ Indeed, combining ashes with biosolids had a positive effect on P and N availability as P and N solubility significantly increased compared to the fly ashes alone (Table 3-4)¹⁰⁸ Furthermore, the mixing of residues had a notable impact on the solubility of several potentially toxic elements; the leaching of Pb in the combined fly ashes with other materials was lower than in the single ashes, but for Cd this had an opposite effect. Leaching of Cd from material mixtures increased between 8 and 50 times compared with that from ashes alone (Tables 3-4)¹⁰⁸ Cadmium and Pb along with Hg and As are of particular interest since the use of these elements as well as their emissions is restricted in many countries due to their toxicity to animals and humans.¹⁰⁹ Cadmium, supplied from mineral fertilizers, is known to be one of the most problematic potentially toxic elements that tend to leach and accumulate in soil and plants.¹¹⁰ Therefore low leaching of potentially toxic elements would be an advantageous property of ash-based fertilisers. A further analysis of the reasons for the increased Cd mobility might help to adjust the proportions of the materials used in the mixtures.

Application of pelletized MSWI fly ash with biosolids on soil resulted in elevated total concentrations of As, Cd and Pb in soil (by 29%, 100% and 300%), but dissolved concentrations of these elements in pore water (0.08±0.04 mg/l, 0.004±0.001 mg/l and 0.006±0.003 mg/l respectively), besides the As, were in the range of drinking water concentrations (0.005 mg/l of Cd and 0.01 mg/l of Pb).¹¹¹⁻¹¹² Further, the concentrations of Cd and Pb in plant biomass were negligible regardless of the type of ash used (Table 2)¹¹² Even applications of fly ash containing extremely high concentrations of Cd (400 mg/kg) were shown to have no effect on e.g. microflora in the humus layer of a coniferous forest.¹¹³ It appears likely that the plant uptake of Cd and Pb is counteracted by the availability of major nutrients and particularly phosphorus. The ability of P amendments to reduce Pb availability and phytoavailability is frequently observed in Pb contaminated soils.¹¹⁴ Similar observations are reported for Cd.^{115, 116} The suggested mechanism responsible for the low concentrations of Cd and Pb in the above-ground biomass is a P-induced decrease in metal translocation from roots to shoots.^{117, 118} Furthermore, P is considered to be a chemical analogue for As in soil.¹¹⁹ and it might be expected that substantially higher P concentrations in the mixtures can suppress As uptake. This could be the reason for the observed lower uptake of As in soil amended with

biosolids compared with MSWI fly ash as the P/As ratio was higher in biosolids (778) compared to the MSWI fly ash (5).¹⁰⁸ This suggests that to reduce the accumulation of potentially toxic elements in vegetation, ashes should preferably contain substantial amounts of soluble P, which can be achieved by mixing ash with biosolids. Moreover, application of Zn-rich residue mixtures to soil might further help to counteract Cd uptake by plants. Zinc is known as a chemical analogue of Cd, exhibiting antagonistic behaviour for plant uptake,^{120, 121} possibly due to a larger ionic radius of Cd as compared to Zn.

High concentrations of chloride ions, on the other hand, have been shown to increase dissolved Cd concentrations and its plant uptake.¹²² This might explain why Cd concentrations in soil containing MSWI-mixtures were higher and the Cd uptake by plants was greater compared to other mixtures.¹¹² In spite of this, Cd concentration in plants remained low (0.3±0.1 mg/kg).

Phosphorus is one of the primary plant nutrients, but in most soils it is relatively unavailable for plant uptake. A strong P fixation in soil is an important reason why only a fraction of applied P fertilizers are taken up by plants. Phosphorus may be strongly bound to Fe and Al phosphates¹²³ or be adsorbed on Fe and Al oxyhydroxides.¹²⁴ Phosphorus availability depends on the incineration temperatures.¹²⁵ Phosphorus is commonly present in solid phase bound to insoluble basic oxides¹²⁵ and is not in a water-soluble form in ashes. However, P applied in the form of pelletized ashes and biosolids had a positive effect on P uptake by plants, despite the low dissolved P concentration in soil solution (Table 2).¹¹²

Plants are capable of solubilizing some of the strongly bound P, e.g. to Fe oxides, through exudation of organic acids¹²⁶ and by doing so increase P uptake even at lower availability. High P accumulation in plants might also be the reason for the observed low dissolved P concentration in soil containing pelletized residues.¹¹²

Fly ash contains a significant amount of calcium silicate and aluminosilicate phases. Dissolution of these phases may lead to the increased concentrations of Ca and Si (which are considered to have a positive impact on soil) and Al (which may have an undesirable toxic effect on plants). But Al is rarely a problem in neutral soils, as it can easily react with phosphates, sulphates and other organic and inorganic ligands at pH>5 that would keep dissolved Al in non-toxic concentrations.^{127, 128} Therefore application of slightly alkaline mixtures on acidic soil would be beneficial in reducing potential Al toxicity to plants by keeping the soil slightly alkaline. Indeed, in all soil mixtures containing fly ashes, concentrations of dissolved Al in soil pore water were below instrument detection limits. While in unamended soil, the dissolved Al concentration was the highest (0.048 mg/l), yet within the tolerable limits for plants (<1.6 g/l).¹²⁹ Furthermore, Al accumulation in plants grown on the soil containing MSWI fly ash was 70% lower than in soil containing biofuel fly ash.

The purpose of combining fly ashes with biosolids is to improve the nutrient balance and chemical properties of the fertilizer, and by this to increase the biomass production in the vegetation layer of a landfill top cover. Despite positive changes in chemical properties, such as decreased availability of potentially toxic elements and increased supply of nutrients, combination of

biofuel fly ash with biosolids can have a negative effect on biomass development. The plant biomass was lower in soil containing biofuel fly ash mixed with biosolids compared to unamended soil in both experiments with powdered¹³⁰ and pelletized¹¹² materials. The reasons for such results are not clear. Too short time given for plants to grow, changes in water balance in soil caused by these amendments could be possible reasons. Longer-term studies are needed to elucidate possible benefits of soil fertilization with fly ash and biosolids combinations.

Prediction of element availability in fly ash combined with other materials is not as straight forward as could be expected. Theoretical calculations of leaching potential showed the differences between the measured and calculated leaching potential of elements (Table 6).¹⁰⁸ This indicates that materials most likely interact with each other through various geochemical processes, such as dissolution, precipitation, complexation with organic matter and sorption to metal hydroxides, causing significant changes in element availability.

Application of both MSWI and biofuel fly ashes do not increase element accumulation in plants, therefore, total concentrations of elements in fly ash do not directly reflect their behaviour and potential impacts on soil and plants. Responsible application of MSWI ashes is, however, warranted in order to avoid element accumulation in soil and elevation of background values over time.

Conclusions

Application of fly ash in a landfill top cover can generally be considered as an advantageous practice of ash management. The environmental properties of the ash-containing constructions are expected to improve with ash ageing. For example, RDF fly ash ageing due to their exposed to the conditions found in a landfill top cover might lead to the chemical and mineralogical transformations that result in reduced leaching of most of the critical elements. Even if concentrations of Cl in the leachates may be an issue, because they are difficult to immobilise and might still exceed the leaching limit values, ageing of ash might significantly decrease Cl leaching (e.g. by 50%). Furthermore, published observations and modelling results indicate that clay minerals, which favour the immobilization of heavy metals, could form in ageing RDF fly ashes. Consequently, a landfill top cover containing these ashes can be expected to remain chemically stable over a long period of time.

Taking into account the chemical and mineralogical composition as well as leaching behaviour, even MSWI fly ash could be considered as a suitable liner material in the landfill top cover. Nevertheless, using MSWI ash as a soil amendment in the vegetation layer might lead to undesirable leaching of potentially toxic elements (e.g. As, Cd and Pb), requiring additional leachate management measures. Although element availability in ash changes when combined with other materials, e.g. biosolids, ash doses to be applied to soil should be adjusted to the type of ashes to avoid potentially toxic elements accumulation in soil over time.

Seeing as fly ashes from biofuel have properties that are beneficial for plants as a source of nutrients (e.g. P, K), as well as relatively low concentrations of potentially toxic elements, biofuel ashes should not be wasted in deeper construction layers, such as liners002E

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