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Possible applications for municipal solid waste fly ash

C. Ferreira [a,b,*], A. Ribeiro [c], L. Ottosen [a]

[a] Technical University of Denmark, Lyngby, Denmark
[b] CERNAS, Escola Sup. Agraria de Coimbra, Coimbra, Portugal
[c] Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Portugal

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Abstract

The present study focuses on existing practices related to the reuse of Municipal Solid Waste (MSW) fly ash and identifies new potential uses. Nine possible applications were identified and grouped into four main categories: construction materials (cement, concrete, ceramics, glass and glass–ceramics); geotechnical applications (road pavement, embankments); "agriculture" (soil amendment); and, miscellaneous (sorbent, sludge conditioning). Each application is analysed in detail, including final-product technical characteristics, with a special emphasis on environmental impacts. A comparative analysis of the different options is performed, stressing the advantages but also the weaknesses of each option. This information is systemized in order to provide a framework for the selection of best technology and final products. The results presented here show new possibilities for this waste reuse in a short-term, in a wide range of fields, resulting in great advantages in waste minimization as well as resources conservation.

Keywords: Fly ash; Hazardous waste; Waste management; Waste recycling; Incineration; Treatment of hazardous materials; Waste valorisation

1. Introduction

Incineration is a commonly accepted solution throughout the world for managing the increasing production of Municipal Solid Waste (MSW). There are two different types of incineration facilities: refuse-derived fuel, which involves pre-sorting MSW to remove glass and ferrous metals in order to obtain waste with higher calorific value, and mass-burn, in which MSW are incinerated as-received.

* Corresponding author. Tel.: +351-93-930-3952; fax: +351-23-980-2979.
E-mail address: celia@mail.esac.pt (C. Ferreira).

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Although incineration reduces the volume of MSW and provides energy, it is not a final solution since it generates bottom and fly ashes that must subsequently be disposed of. Bottom-ash is collected at the base of the combustion chamber and consists of a slag-type material. However, it is the finer fraction, collected from the flue gas by the air pollution control (APC) devices, and referred to as *fly ash*, that poses the more serious environmental problems. Fly ash consists of fine particles that contain leachable heavy metals, and is therefore classified as a toxic waste. In addition, highly toxic organic substances (dioxins, furans and PAHs) are also present, further adding to the problem. These aspects make fly ash management one of most important environmental issues related to the incineration of MSW. Bottom ash and fly ash are sometimes mixed for practical reasons, forming a residue referred to as combined ash. This practice occurs in some countries, such as the USA and Japan.

The use of landfills for fly ash disposal is currently the main option in many countries. However, more stringent measures for special waste landfills, in combination with an emerging *recycling philosophy,* have encouraged the recycle and reuse of this waste. Fly ash is rich in some elements and compounds (such as metals and salts) and therefore has some potential to be used as raw material. Each potential application for fly ash results in three main advantages: first, the use of a zero-cost raw material, secondly, the conservation of natural resources, and thirdly, the elimination of waste.

A large amount of information is available on the application of wastes such as coal fly ash, or blast furnace slag [1–7]. However, the same cannot be said about MSW fly ash. The main reason lays probably in the fact that only recently was incineration regarded as a promising solution for the problems of the increasing amounts of MSW and fewer landfilling spaces available.

The present study focuses on existing practices related to the reuse of MSW fly ash and identifies new potential uses. The paper is organized as follows: Section 1 is the introduction; Section 2 identifies potential areas for fly ash application and evaluates each individual use; in Section 3 a comparative analysis of the different applications is performed; and Section 4 presents the conclusions.

2. Main identified areas of fly ash application

In the current work, three main factors were considered relevant to evaluate fly ash suitability for each application: suitability for processing, technical performance and environmental impact:

- The first factor, suitability for processing, depends on physical–chemical characteristics of the fly ash, such as particle size and chemical properties, that may constitute a limitation for a specific process (although in some cases these characteristics can be adjusted so as to comply to processing requirements).
- Technical performance is the second factor considered. Even if fly ash can be easily processed, the final product cannot be used unless it presents good technical properties.
- Finally, the third factor considered is environmental impact. Toxicity does not necessarily disappear with fly ash valorisation. The risks imposed on the environment by each possible application must be carefully weighed against creating new pollution sources elsewhere.

Table 1
Potential use of MSW fly ash

(A) Construction materials
(A.1) Cement production
(A.2) Concrete
(A.3) Ceramics
(A.4) Glass and glass–ceramics
(B) Geotechnical
(B.1) Road pavement
(B.2) Embankment
(C) Agriculture
(C.1) Soil amendment
(D) Miscellaneous
(D.1) Sorbent
(D.2) Sludge conditioning

Taking these three factors as well as fly ash's characteristics into consideration, nine potential applications for fly ash were identified and grouped into four main categories (Table 1). A detailed description of each application is presented in the next lines, along with specific technical and environmental considerations.

2.1. Construction materials

One possible way to reuse fly ash is its incorporation in construction products. Options include cement/concrete, ceramics, and glass/glass–ceramics.

2.1.1. Cement production

Cement is a fine powder that hardens (sets) after being mixed with water. Portland cement is one of the most common types and is manufactured from limestone ($CaCO_3$) mixed with clays and other materials containing alumina and silica. This mixture is then heated in rotary kilns at temperatures between 1540 and 1600 °C. The resulting product is called "clinker" and consists of different proportions of tricalcium silicate ($3CaO{\cdot}SiO_2$), tricalcium aluminate ($3CaO{\cdot}Al_2O_3$), and dicalcium silicate ($2CaO{\cdot}SiO_2$), together with small amounts of magnesium and iron compounds. Gypsum is often added (4% (w/w)) to slow the hardening process.

Fly ash in cement production: Since MSW fly ash contains 24–27% of lime [8] and some silicates and aluminosilicates [9] it could potentially be used for the production of cement powder. Cement production is an activity that consumes large quantities of raw materials and energy and emits large amounts of CO_2, which is thought to be a major contributor to the greenhouse effect and the global warming of the planet. A large percentage of energy is spent in decomposing calcium carbonates ($CaCO_3$) to lime (CaO) and for each ton of cement produced approximately the same quantity of CO_2 is emitted, most of which resulting from the decomposition of carbonates. If fly ash was used as a source of lime, a reduction in CO_2 emissions could be achieved, thus contributing to minimize global warming.

A special application for MSW fly ash in this area could be in low energy cements, also called calcium sulfoaluminate cements. These are special cements that can be synthesized at low temperatures and which present high strength and rapid hardening [10]. Fly ash could potentially be used in these cements, as a source of both alumina, for the formation of calcium sulfoaluminates, and silica, for the formation of calcium silicates. The application of some other industrial wastes (coal fly ash, blast furnace slag, bauxite fines, and phosphogypsum) in low energy cements was already subject of research [10] but to the authors' best knowledge no testing was conducted on MSW fly ash.

Use of MSW fly ash in cement production can pose technical problems. Addition of MSW fly ash in cement kilns will most probably increase chloride and heavy metal concentrations in cement dust. Trace metal levels in cement may be subject to a maximum value for technical reasons while high chloride content can lead to *cycling*, that is, a repeated volatilization in the hot parts, followed by a condensation in the colder ones. Cycling can rapidly clog the battery of cyclonic heat exchangers and cause a plant shut-down. Care must be taken to prevent these problems, either by performing a pre-treatment in fly ash in order to remove heavy metals and chloride or by controlling the quantity of fly ash added to the process to such levels that no significant increase occurs.

2.1.2. Concrete

When water is added to cement a hydration reaction takes place. The hydration products crystallize and create a three-dimensional structure that binds together all the substances present into a hard mass. The reactions that occur are the basis for the stabilization/solidification (S/S) process, applied world-wide for the treatment of hazardous waste. The 3-dimensional structure formed, which comprises hydration products, water, small bubbles of air, and particles of sand or stone, can also include small particles ($<150\ \mu m$). Since fly ash particles have a small grain size they could fill these spaces and become encapsulated inside the concrete matrix.

Although S/S is a technology applied for waste treatment, it can also be oriented to promote waste reuse. The potential for MSW fly ash application in concrete is either as a replacement of cement or as an aggregate. Suitability for each purpose is discussed next.

Use of MSW fly ash as a replacement for cement in concrete: Fly ash contains some quantities of typical cement minerals, although in less quantity than in cement clinker. This could mean that fly ash could be used as partial replacement for cement in concrete mixes, as a supplementary cementitious material, similarly to what already happens for fly ash resulting from the combustion of coal, which is widely accepted for that purpose.

ASTM standards [11] defines the chemical and physical requirements of coal fly ash and natural pozzolans for use in Portland cement concrete. Hamernik and Frantz [12] investigated different types of MSW fly ash and revealed that they were very similar to class C pozzolans, as defined in the ASTM standard, but also that each type of fly ash failed to meet one or more criteria of the standard. For instance, refuse derived fuel (RDF) fly ash had high values for loss on ignition and coarse particle size, while mass-burn fly ash presented high SO_3 content and was slightly below the Class C requirement for (Si + Fe + Al)-oxides [12].

Although the purpose behind this standard is the protection against poor quality and deterioration of construction, its strict application can pose unnecessary restrictions on the utilization of new materials. Instead of material specific requirements, Swamy [13] proposed a performance-oriented approach, which would allow the utilization of a wide range of substitute materials without compromising quality requirements.

One important engineering property of concrete is its compressive strength. Hamernik and Frantz [14] studied the effect on compressive strength of replacing cement with MSW fly ash. While replacement levels of 45% (RDF fly ash) resulted in concrete with strengths comparable to control (no fly ash, all cement), for 15% replacement the concrete presented compressive strength higher than the control, which is noteworthy. The mass-burn fly ash did not perform so well, resulting in compressive strengths significantly lower than control. Acceptable replacement levels are therefore strongly dependent on the characteristics of fly ash, mainly its pozzolanic activity. One other relevant result from their work is that the higher setting time of concrete due to fly ash addition could be overcome by increasing the dosage of set-accelerating admixtures. Mangialardi et al. [9] propose another way to reduce setting time of fly ash concrete which consists in pre-washing the ash in order to partially eliminate water-soluble species responsible for delaying setting time (like sulfates, chlorides, alkalies and heavy metals).

Besides concrete strength and setting time there are other properties that are affected by fly ash addition such as air-entrainment, resistance to freezing and thawing and resistance to surface scaling. Results reported by Triano and Frantz [15] indicate that depending on the type of fly ash (mass-burn/RDF) and incinerator conditions these properties can be either improved or not. For instance, addition of one type of fly ash increased resistance to freezing and thawing, comparable to the control (no fly ash addition) while for the other type of fly ash it decreased. Another important technical issue is the possible reaction between alkalis and MSW fly ash. According to AbdulRashid and Frantz [16] aluminium in the ash can react with alkalis in the cement and produce efflorescences, resulting in expansion and cracking of concrete. This alkali-fly ash reactions must necessarily be evaluated in all MSW fly ash potential applications in concrete as cement replacement.

One final comment to mention the work done by Roethel and Breslin [17–19] on the utilization of solidified MSW combined ash. Although the current paper focuses on fly ash, it is worth mentioning their efforts for the application of combined ash in the construction of artificial reefs [17–19] and also in the construction of a boathouse demonstrator [20].

Use of MSW fly ash in concrete as aggregate: Sand is used as a fine aggregate in concrete mixes. Although utilization of combined MSW (bottom + fly) ash as aggregate in concrete has already been reported [16], replacement of sand for fly ash alone does not seem very promising, since fly ash grain size is smaller than the sand's. Although it could eventually be used to add to the finer fraction of the sand, a more promising use is in lightweight concrete as a substitute of commercially available lightweight aggregates. Lightweight concrete is less dense than gravel concrete but has a lower compressive strength. It presents improved thermal and sound insulation properties, which makes it suitable for non-structural applications, such as the interior of walls for insulating purposes. It can also be used for structural applications, provided compressive strength, density and water absorption values are adequate.

MSW fly ash could be processed into pellets and used as lightweight aggregates. The resulting product could be suitable for non-structural applications, such as those described above.

Environmental issues: Assessment of pollutant release can be conducted by standard short-term leaching tests and long-term release studies. There are several different tests that can be conducted to assess the environmental impact of products containing incinerator residues on soil and groundwater (see for example [21]). Barna et al. [22,23] present a methodology for the modelling of long-term release from a water storage reservoir for fire fighting, the bottom of which was constructed with MSW fly ash mixed with hydraulic binders and water. Although the scenario cannot be considered a common application, the methodology developed can be used in other applications. Triano and Frantz [15] evaluated the leaching behaviour of concrete containing up to 15% of fly ash. They report very small amounts of heavy metals in the leachate, below the toxicity limits according to the EPTOX toxicity procedure.

Application as lightweight aggregates is not expected to pose environmental problems, since heavy metal leaching is not significant as long as lightweight concrete is used under sheltered conditions, like in internal structures. Even so, a problem could arise after demolition of the structure, situation where rainfall is expected to come in contact with fly ash, resulting in metal leaching.

2.1.3. Ceramics

The ceramic industry includes the manufacture of pottery and porcelain and building ceramics, like bricks, tiles and stoneware. Ceramics are prepared from malleable, earthy materials (such as clay) that are made rigid by high temperatures. Besides clays, that confer cohesion and plasticity, ceramic pastes also include inert materials that provide structural support that helps to retain shape during drying and firing. Quartz (silica) is the most commonly inert used and is usually supplied either as sand or schist. Silica is also used in the glazing of ceramic bodies in combination with stiffeners and melting agents. When a glaze layer is applied to the ceramic body and then fired, the glaze ingredients melt and become glass-like. Ceramic industry is therefore a high consumer of silicate-based natural raw materials and this fact makes it a potential candidate for MSW fly ash application. Moreover, fly ash is presented as a fine dust so it can be directly incorporated into ceramic pastes, with almost no pre-treatment. Against this possibility is the fact that fly ash contains high amounts of iron oxide and metals, which according to [24] could negatively affect the properties of the ceramic product. However, according to [25] this industry traditionally uses heavy metal oxides (e.g. lead, chromium, cobalt, etc.) in the production process, so this problem could probably be solved by judicious choice of the amount of added fly ash.

Application of MSW combined ash in the production of ceramic tiles is reported in [26]. The tile contains 50% incinerator ash and presented good results in durability, with a fracture load in bending of 76.20 kgf/cm^2 which is higher than the reported JIS standard for floor tiles, which is 12.24 kgf/cm^2. Absorption coefficient values lay within normal range for ceramics. Leaching tests showed minimum releases for some of the tested heavy metals and organics. Produced tiles were applied in outside and inside pavement and exterior facing of walls.

2.1.4. Glass and glass–ceramics

One possible application for fly ash is to convert it to a glasslike substance by melting, at high temperatures (above 1300 °C). This process is called vitrification and is one of the currently available options for treating MSW fly ash [27–31]. During vitrification high temperatures destroy organic contaminants, like dioxins, with efficiencies over 99.9% [31,27], while heavy metals are either encapsulated in the silicate matrix or separated from the product by evaporation or differential precipitation [30]. Several companies build and install vitrification facilities around the world, especially in Japan, where this technology is widely used to treat MSW combined ash.

Some of the potential uses referred for vitrified fly ash are [27,29,30,32]: road base materials; embankments; blasting grit; partial sand replacement in concrete; in monolith blocks for coastal protection and, in the production of construction and decorative-materials, like water-permeable blocks, ceramic tiles, pavement bricks and decorative stones for gardens.

Among the possibilities enunciated, four were actually tested with relative success, even though on a limited scale: use as blasting grit [32]; production of ceramic tiles [27]; production of water-permeable blocks and pavement bricks [29]. These last two, however, refer to combined MSW ash (bottom + fly), which is a less toxic waste than plain MSW fly ash.

One of the main disadvantages of vitrification is the high cost involved, since it is an energy intensive process. To reduce processing costs Boccaccini et al. [33] suggest transforming MSW fly ash into a glass–ceramic, which is a product with improved properties and higher market value. Conventional glass–ceramics are formed by inducing crystallization in certain glasses by means of a carefully controlled heat treatment [34]. Glass–ceramics present improved mechanical strength and electrical insulating properties and are used for special applications such as in the aeronautic industry (e.g. rocket nosecones and heat-resistant tiles) or in high-efficiency electrical transformers.

Glass–ceramics from MSW fly ash can be obtained mainly by controlling the temperature of the vitrified product during the cooling down stage [33,35]. The resulting product presents better mechanical and technical properties than those of the amorphous product. According to Boccaccini et al. [33], improvements include: higher-hardness, better workability, and increased fracture toughness, strength (almost three-fold) and thermal shock resistance. Potential applications for the resulting glass–ceramic are [33]: floors of industrial buildings; outside and inside facing of walls; and, production of machine-tool parts. Effective testing of these possibilities has not been reported.

Environmental evaluation of MSW fly ash glass and glass–ceramics: Several tests have been conducted to determine the leaching behaviour and toxicity of vitrified fly ash [28,31–33,35]. As expected, vitrified fly ash was found to be less leaching than non-vitrified material [27], which attests the effectiveness of this treatment. Also, in general crystalline fly ash was reported as more toxic than amorphous vitrified fly ash [33,35], although the reasons for this were not made completely clear.

Although vitrified MSW ash usually passes the TCLP test (see [28,31]) investigations conducted on live cell cultures indicate that they could be toxic, as reported by Boccaccini et al. [33]. Haugsten and Gustavson [28] compared the results of leaching test conducted on vitrified fly ash with regulations from different countries. The results indicate that vitrified fly ash fulfils the German, French, Austrian, Swiss and US requirements for inert materials and also the Dutch Regulation for construction materials (class 1), with the possible exception of antimony, with leaching values varying around the legal limit [28].

2.2. Geotechnical

2.2.1. Road pavement

Road pavement is a stratified, multi-layered structure consisting of a surface layer (made of bitumen or asphalt), a middle layer (base course and subbase) and the lowest layer (subgrade).

The base course is the layer of material that lies immediately below the wearing surface of a pavement and has essentially a structural role. It consists of granular material (like stone fragments or slag) that can be stabilised with cementitious materials (cement, natural pozzolans, etc.). Between the base course and the subgrade there is sometimes another layer, called subbase, which supports the base and is built with the same type of materials, but is usually of inferior quality.

MSW fly ash possible application in road pavement is as a substitute for sand and/or cement in cement stabilized bases and subbases. Environmental issues related with this application are the contamination of the underlying soil and groundwater by substances leached from the road base.

Feasibility studies on sand replacement by fly ash in sand/cement base layers were conducted at TNO, in The Netherlands [36]. The product obtained after pre-washing followed by cementation meets Dutch standards for building materials. Although the report focuses on environmental issues it also includes an estimation of global costs, resulting that pre-washing + application is less expensive than ash disposal as hazardous material. However, this study does not include technical evaluation of the product, that is, if the cement-bound fly ash obtained is adequate as a road base from a technical standpoint.

Use of secondary raw materials (other than MSW fly ash) for road construction has also been reported for coal fly ash [37,38] and MSW bottom ash [39].

2.2.2. Embankments

Embankments are constructed from earth (soil) or stone materials and are used to keep back the water (retaining walls, land reclamation, etc.). When soils do not present the desirable geotechnical properties it is common practice to stabilize them with lime or cement. This reduces soil compressibility and increases shear strength, therefore improving engineering properties.

One potential application for MSW fly ash is in soil stabilization, as a substitute of lime or cement, taking advantage of MSW fly ash's pozzolanic characteristics. MSW fly ash's density is less than other fill materials used in the construction of embankments: typical values for MSW fly ash are 1.7–2.4 [40,41] while for sand is 2.65 [40]. In soft, compressible soils there is an advantage in replacing conventional fill materials with fly ash, since smaller loads would be imposed on soils thus resulting in less significant ground settlements [40].

Tay and Goh [40] investigated the possibility of using MSW fly ash in geotechnical applications as a substitute for filler. They report that fly ash displays the prerequisite properties for this type of application with high strength and free-draining, typical of granular material, and lower compacted densities than conventional earth fills. They also assessed the possibility of using fly ash in soil stabilization (instead of lime or cement) finding that soil-fly ash mixtures presented improved shear strengths and lower compressibility than other non-treated soils.

Environmental issues regarding MSW fly ash use in embankments: The main environmental issue arising from this application is the same as in road base, that is, the possible contamination of the soil and groundwater from the embankment construction.

Goh and Tay [41] compared leaching from fly ash with leaching from fly ash stabilized with either lime or cement. They report that initial leaching from non-stabilised fly ash exceeded drinking standards and that stabilised fly ash presented lower values, which is not surprising. However, they limited their study to leaching from fly ash and did not look into what happened for the soil/fly ash system, which could give a more precise indication of the leaching behaviour from embankments constructed with these materials. Pre-washing the ash could be a possible solution to the problem of leaching, similarly to what [36] reported for road construction.

2.3. Agriculture

2.3.1. Soil amendment

Application of fertilizers to enrich soil and promote plant growth is a common practice. Plants require more than a dozen different chemical elements. Nitrogen, phosphorus and potassium are the three main elements commonly supplied in fertilizers, while boron, copper, and manganese are sometimes also added in small quantities.

Fly ash is rich in two out of three of these main nutrients: phosphorous and potassium (nitrogen is lost during the combustion). This means that fly ash can potentially supply P and K, replacing commercial fertilizers.

The fertilizer potential of MSW fly ash was studied by Rosen et al. [42], who found that plant growth in fly ash amended soils was 1.5 to 2 times greater than in non-amended soils and greater than in either a P-fertilizer or a K-fertilizer amended soil. Another study by Giordano et al. [43] confirms the fertilizer potential of fly ash, registering positive Swiss chard growth responses to fly ash application when compared to control (no fly ash).

Besides the fertilizing potential fly ash could also be used in agriculture as a liming agent. Lime (calcium oxide) is often added to soil to reduce acidity. Fly ash presents high pH values and thus can substitute lime in reducing soil acidity. Rosen et al. have confirmed the effectiveness of fly ash as a liming agent [42].

The quantity of fly ash applied to the soil is important, since excessive amounts can introduce unnecessary dosages of nutrients (along with contaminants). Values in literature lay between 5 and 40 wt.% [42]. Rosen et al. [42] proposes that application rates should be based on the nutrient availability of the ash and on standard fertilizer recommendations for each crop.

Environmental issues of fly ash application in agriculture: Application of fly ash in soils either as fertilizer or amendment is a controversial subject. It raises questions of toxicity that must be carefully addressed, moreover since plants belong to the first trophic level of the food chain. Two main issues relate to the high levels of heavy metals and salts present in the ash and are addressed in more detail in the following paragraphs. Another important aspect is the mobility of the metals in the soil and the possible contamination of ground and surface waters.

Heavy metals: Regarding heavy metals, it is pertinent to start by establishing a difference between total concentration in soil and availability. In fact, only a fraction of the total content

Table 2
Desirable levels in plant tissue and risk conditions for the main micronutrients

Micronutrient	Desirable range (mg/kg)	Higher risk of phytotoxicity
Iron	40–250	Acidic anaerobic soil
Manganese	16–45	Acidic soil
Aluminium		Acidic soil, low organic matter
Copper	0.9–7	
Zinc	1–3.5	Acidic soil
Boron	0.4–1	[B] in soil >20 mg/kg
Molybdenum	0.15	Alkaline soil

Adapted from [44].

present in soil is available for plant uptake, and this depends on very specific interactions between the element, the plant, and the soil. Grass absorbs preferentially potassium over magnesium, while legumes (e.g. alfalfa) have a high absorption capacity for magnesium [44].

The main factor determining heavy metal mobility is pH. Availability of phosphorous can be a problem for very acidic or very alkaline calcareous soils since insoluble (hence immobile) forms are dominant for those conditions. Another factor affecting metal's mobility in soil is the chloride content. Chloride is commonly found in fly ash and can complexate some heavy metals, thus enhancing their mobility.

Excessive amounts of available elements in the soil lead to the accumulation of these elements in plant tissue. Some of these elements, like boron, copper, molybdenum and zinc are also essential plant nutrients, and in certain quantities can even improve plant growth. However, above a certain level they become phytotoxic. Acceptable levels of these elements in plant tissue are shown in Table 2. Several investigations conducted on plants grown on MSW fly ash-amended soils report accumulation in plant tissue of high levels of Zn [42,43], Cd and Pb [43], and Mo, B and Cu [42], some of which above the acceptable levels. However, in some of these studies there was no concern in trying to adapt the amount of fly ash added to the species requirements in nutrients. An interesting aspect is that although the plant tissue levels of some elements are sometimes higher than those in Table 2, plant growth was not affected and this may indicate that current limits are somewhat conservative and generalist.

In crops destined for animal consumption there is an additional concern: even if heavy metals are at acceptable levels regarding phytotoxicity, this does not mean that there is no risk for the animals that feed on these crops. For instance, Mo is very important to N-fixing crops and has a positive influence on growth. However, concentrations in plant tissue above 5–10 mg kg^{-1} may cause a condition called molybdenosis in ruminant animals that feed on these crops [42] and this limits the use of Mo-containing wastes as soil amendments.

Salinity: The addition of fly ash to the soil will most probably increase its salt content, due to the high levels of soluble salts present in the ash. These salts are of concern since they can induce salt stress in plants. Plant tolerance to salt levels varies with species, and plants can be classified accordingly as tolerant, moderately tolerant or moderately sensitive. The decrease in crop productivity with increasing salinity for several plants and levels of salinity is well documented [44]. Phytotoxicity due to high salinity is also reported [43].

In summary, the results presented in bibliography clearly demonstrate the potential of fly ash use as a fertilizer and as a liming agent. However, this is not probably a large-scale application due to the small amounts that can effectively be applied to the soil because of nutrient balance and environmental concerns. The potential for using MSW fly ash in agriculture depends on the specific crop and soil environment and an evaluation should be conducted case by case, with special emphasis on tissue concentration and ground water contamination by leaching. Although this last aspect can pose a major environmental impact, to the authors' best knowledge it has not been addressed by the investigators working on this field.

2.4. *Miscellaneous*

2.4.1. *Adsorbing materials*

The use of adsorbing materials, like for instance activated carbon, has recently been widespread, namely for treatment of effluents. Another example is zeolite (term referring to a group of minerals composed of hydrated aluminium silicates of alkali metals and alkaline earth metals), which used in ion-exchange processes, such as water-softening. Although natural zeolites appear in veins and cavities of basic igneous rocks (especially basalt), there are reports on the syntesis of artifical zeolite from coal fly ash by hydrothermal treatment with NaOH [45–47].

The idea of using coal fly ash to synthesize artificial zeolite is based on the fact that both materials have a similar chemical composition, namely a high content of aluminosilicate glass and high specific surface [45]. MSW fly ash also has a high specific surface and contains minerals, such as SiO_2 and Al_2O_3 (see Table 3), which are important in the synthesis of zeolite materials, although these appear in less quantity in MSW fly ash than in coal fly ash.

Yang and Yang [48] report the synthesis of zeolite-like materials from MSW fly ash by a hydrothermal alkaline processing, very similar to that reported for coal fly ash. They refer that although zeolite's quality is lower than that of commercially available adsorbents (such as natural zeolite and activated carbon-see Table 3), synthesized zeolite is environmental safe to use, according to the TCLP extraction procedure. However, the effluent that is generated during the synthesis contains high levels of heavy metals such as Pb and Zn, and must therefore be treated prior to discharge. Yao et al. [49] report the successful synthesis

Table 3
Sorbent-related properties of different materials

	MSW fly ash [48]		Coal fly ash [47]		Commercial adsorvents [48]
	Raw	Converted to zeolite	Raw	Converted to zeolite	
SiO_2 (%)	22	–	55.2	–	–
Al_2O_3 (%)	10	–	25.4	–	–
CEC (meq/100 g)[a]	7.80	50–90	8	72–210	200–300
Specific surface area (m^2/g)	2.54	20–50	3	94	600–1600

[a] Cation exchange capacity.

of a Al-substituted tobermorite from MSW fly. The use of this product to remove Cs^+ and NH_4^+ from wastewater resulted in removals of 0.40 and 0.35 mmol/g, respectively.

Although the results of the investigations referred previously are preliminary, it can be said that there is a possibility of converting MSW fly ash into zeolite-like materials. This synthesized zeolite could have industrial application as sorbent, for instance for the removal of different ions and molecules from solution. It could also be used in industrial wastewater treatment, to remove heavy metals from water, and also for the treatment of wastewater arising from farming activities, to remove NH_4^+.

Regarding gaseous pollutant treatment in combustion facilities, it is common practice to introduce hydrated lime in the flue gas duct, or/and use high specific surface sorbents, like activated carbon. One possible way to reduce costs is to use alternative sorbents, for instance mixtures of lime with a silica-containing material, such as clays and coal fly ash [50], in flue gas desulphurisation (FGD) and acid gas cleaning systems. Matsuda et al. [51] report that adsorption capacity is related to the calcium compounds present in the coal ashes and depends on surface area and pore volume. They report that treating coal fly ash with a calcium hydroxide aqueous solution greatly improves the absorption capacity. Although to the author's best knowledge no studies were conducted with MSW fly ash, this waste would most probably present similar behaviour to that of coal fly ash, moreover since excess lime is normally added to treat flue gas in waste incinerators. MSW fly ash could therefore be processed in a similar to coal fly ash and be reintroduced in the incineration process for acid gas cleaning.

2.4.2. Sludge conditioning

Sludge originating from wastewater treatment contains high amounts of water (up to 95 wt.%) and needs to be dewatered to reduce volume and disposal costs. Filtration is one of the more commonly used methodologies to dewater sludge. However, wastewater contains small amounts of oil that make dewatering difficult. To overcome this problem the sludge can be conditioned by the addition of filter aids. The use of MSW fly ash as a chemical conditioner has been investigated [52] with results indicating that fly ash does facilitates the filtering process since it decreases both specific resistance and capillary suction time. Heavy metal concentration in the filtrate increased, but values were found to be within permitted levels for effluent discharge [52]. Reported optimum fly ash dosage was 3–4% (w/w) [52].

3. Comparative analysis

Table 4 summarizes the major aspects regarding MSW fly ash applications. The following factors are analysed: current status of development, level of application, need for pre-treatment, degree of valorization, potential uses, leaching behaviour and major advantages/disadvantages.

Current status indicates the level of development of a particular use. As can be seen from Table 4 most applications are still being investigated. In some cases, a distinction should be made between the application and the technology underlying it. This happens for concrete and glass: while the cementation and vitrification technologies, respectively, are currently used in large scale throughout the world for treating fly ash, the product obtained cannot

Table 4
Comparison of different options for the applications for MSW fly ash

Application	Current status	Level of application	Pre-treatment	Valorization	Possible uses	Leaching behaviour	Major advantages	Possible disadvantages
Cement production	Not tested	High	Advised	Medium	Production of aluminosilicate cements; production of other cements	Low	Reduction of waste to dispose; energy saving; less CO_2 emissions; easy to implement	Possible corrosion due to chloride emission of air pollutants during the cement making process
Concrete	Under investigation	High	Advised	Medium/low	Coastal protection; house construction and insulation; low-density concretes	Low	Reduction of waste to dispose; resources conservation; improvement of concrete special characteristics	High setting times; possible strength reduction of concrete; regulations too restrictive and hinder implementation
Ceramics	Under investigation/ tested	High	–	Medium	Building bricks; pavement stoneware; wall tiles	Low	Reduction of waste to dispose; resources conservation	–
Glass and glass–ceramics	Under investigation	Medium/low	Not required	Low	Decorative materials, monolith blocks (coastal protection); water permeable blocks; ceramic tiles, pavement bricks; road construction; machine-tool pieces	Low/medium	Reduction of waste to dispose; natural resources conservation	Emission of air pollutants during the vitrification stage; high cost
Road pavement	Tested	Medium	Required	Low	Filler/cementitious	Low	Cost effective (less expensive than disposal)	–
Embankment	tested	Low	Advised	Low	Filler/cementitious	Medium/high	Easy to implement; low ground settlement	Leaching exceeds water standards
Soil amendment	Tested	Low/medium	Advised	High	Fertilizer, liming agent	Medium/high	Reduction of waste to dispose; natural resources conservation	Only small amounts of fly ash can be used; phytotoxicity by salt stress
Sorbent	Under investigation	Medium	Not required	High	Wastewater treatment; acid gas cleaner	Low	Reduction of waste to dispose; natural resources conservation	Poor quality of the product, compared with commercial adsorbents; remaining liquid needs to be treated
Sludge conditioning	Tested	Low	Not required	High	Chemical conditioner	–	Easy to implement	Possible increase of heavy metals in the wastewater

yet be considered safe to use. Therefore, a more product-oriented approach is needed and this requires further investigation.

The factor “level of application” (second column) measures the amount of fly ash that can be “used up” in a specific use. It results from a combination of two factors: amount of fly ash used per unit product and production rate. An application that uses small percentages of fly ash but has a high production will result in global quantities of fly ash used higher than one application that could use higher quantities per unit product but with low production rates. Examples of both cases are cement production (high) and sludge conditioning (low).

The need for pre-treating the ash is summarized in the third column. Although pre-treatment can increase process costs, it makes possible to use fly ash in a wider range of applications, thus increasing its recycling potential. As can be seen from the table, most of high-level applications (the ones that can use up more ash) either require or recommend this operation.

Level of valorisation depends on the type of use it is made of fly ash: undifferentiated use (such as filler) is not considered a high level application since it does not take advantage of the special characteristics of fly ash. On the other hand, use as a fertilizer agent strongly depends on fly ash’s content in special elements, and thus a high valorisation of the product occurs.

Leaching behaviour is one of the most important aspects conditioning MSW fly ash application. This column evaluates what happens with the contaminants present in fly ash after it is converted into useful products. Some applications imply processing the ash into an end-product where contaminants are either destroyed or encapsulated (e.g. glass). In most cases process parameters can be controlled and optimised so as to produce an end-product resistant to leaching. This explains why, in most cases, leaching is considered “low”. However, in some cases such as soil amendment and use in embankments, the ash is applied as-received and therefore leaching can pose a problem.

Advantages and disadvantages make up the last two columns. In most cases, disadvantages are related to technical problems of a specific application or to environmental issues. Among the advantages, there are some that are common to practically all applications, namely, reduction of waste to dispose and resources conservation. Others relate to low cost (e.g. road pavement), facility of implementation (e.g. sludge conditioning) or even improvement of end-product properties (e.g. concrete).

4. Conclusion

This work highlights several applications for MSW fly ash, and shows the relative advantages of these applications, according to current knowledge. These applications are confronted from an environmental/engineering point of view, showing the shortcomings of each method, but also stressing their advantages.

In most cases, there is no sufficient background knowledge to clearly define the conditions for a safe application, neither from an environmental point of view nor from a technical standpoint, and this has lead systematically to the rejection of waste in applications where it could be effectively recycled with great environmental benefits. It has been found that most of the environmental constraints regarding MSW fly ash applications are related to the leaching behaviour of the final products.

There is not one widely accepted use for MSW fly ash and the viability of most of the options here presented is still being investigated. Moreover, in most applications a pre-treatment is either required or strongly advised. Although this pre-treatment increases the cost it also makes utilization of fly ash possible for some high level uses.

The results presented here are encouraging, since they show new real possibilities for this waste's reuse in a short-term, in a wide range of fields, from ceramics and construction materials to road bases. Successful application of this waste will have great advantages in waste minimization as well as resources conservation and this fact seems to be pushing both the research community and the legislator to develop good alternatives to landfilling.

References

[1] V.G. Papadakis, Cement Concrete Res. 29 (1999) 1727.
[2] J. Bijen, Constr. Building Mater. 10 (1996) 309.
[3] L.J. Alemany, M.C. Jimenez, M.A. Larrubia, F. Delgado, J.M. Blasco, Adsorption Sci. Technol. 13 (1996) 527.
[4] D. Ravina, Mater. Struct. 31 (1998) 84.
[5] V.L. Rayzman, S.A. Shcherban, R.S. Dworkin, Energy Fuels 11 (1997) 761.
[6] G.G. Hollman, G. Steenbruggen, M. Janssenjurkovicova, Fuel 78 (1999) 1225.
[7] A.H. Lav, M.A. Lav, J. Mater. Civil Eng. 12 (2000) 157.
[8] N. Alba, S. Gasso, T. Lacorte, J.M. Baldasano, J. Air Waste Manage. Assoc. 47 (1997) 1170.
[9] T. Mangialardi, A.E. Paolini, A. Polettini, P. Sirini, J. Hazard. Mater. 70 (1999) 53.
[10] J. Beretka, B. Devito, L. Santoro, N. Sherman, G.L. Valenti, Resour. Conserv. Recycling 9 (1993) 179.
[11] ASTM C618-94a, Standard specification for coal fly ash and raw or calcinated natural pozzolan for use as a mineral admixture in Portland, Cement Concrete, 1994, pp. 304–306.
[12] J.D. Hamernik, G.C. Frantz, ACI Mater. J. 88 (1991) 294.
[13] R.N. Swamy, Mater. Struct. 26 (1993) 600.
[14] J.D. Hamernik, G.C. Frantz, ACI Mater. J. 88 (1991) 508.
[15] J.R. Triano, G.C. Frantz, J. Mater. Civil Eng. 4 (1992) 369.
[16] R. AbdulRashid, G.C. Frantz, J. Mater. Civil Eng. 4 (1992) 353.
[17] F.J. Roethel, V.T. Breslin, Solid Waste and Power, 1988, p. 43.
[18] V.T. Breslin, F.J. Roethel, Estuarine Coastal Shelf Sci. 40 (1995) 249.
[19] V.T. Breslin, F.J. Roethel, V.P. Schaeperkoetter, Marine Pollut. Bull. 11B (1988) 628.
[20] P.C. Renaud, R.F. Probstein, Physicochem. Hydrodyn. 9 (1987) 345.
[21] H.A. VanderSloot, G.J. deGroot, D. Hoede, J. Wijkstra, Mobility of trace elements derived from combustion residues and products containing these residues in soil and groundwater, The Netherlands Energy Research Foundation ECN, ECN-C-91-059, Petten, The Netherlands, 1991.
[22] R. Barna, Z. Rethy, A. Imyim, Y. Perrodin, P. Moszkowicz, L. TirutaBarna, Waste Manage. 20 (2000) 741.
[23] R. Barna, Z. Rethy, A. Imyim, Y. Perrodin, P. Moszkowicz, L. TirutaBarna, Waste Manage. 20 (2000) 751.
[24] I. Queralt, X. Querol, A. Lopezsoler, F. Plana, Fuel 76 (1997) 787.
[25] A.E. Rokhvarger, Environmental and waste management issues in the ceramic industry II, in: D. Bickford, S. Bates, V. Jain, G. Smith (Eds.), Ceramic Transactions, vol. 45, The American Ceramic Society, OH, 1994, pp. 125–135.
[26] GEC, Waste treatment technology in Japan, Committee for Studying Transfer of Environmental Technology, Global Environment Centre Foundation, 1996.
[27] S. Abe, F. Kambayashi, M. Okada, Waste Manage. 16 (1996) 431.
[28] K.E. Haugsten, B. Gustavson, Waste Manage. 20 (2000) 167.
[29] M. Nishigaki, Waste Manage. 20 (2000) 185.
[30] A.R. Boccaccini and H. Kern, in: A. Barrage, X. Edelmann (Eds.), Proceedings of the R'99 World Congress on R'99 Recovery Recycling Re-integration, vol. II, Geneva, Switzerland, 1999, EMPA, St. Gallen, Switzerland, 1999, pp. 152–157.

[31] M.L. Elliott, C.C. Chapman, C.J. Freeman, G. B. Mellinger (Eds.), Environmental and waste management issues in the ceramic industry, Ceramic Transactions, vol. 39, The American Ceramic Society, OH, 1993, pp. 83–90.
[32] H.A. VanderSloot and D. Hoede, Leaching characteristics of vitrified AVR fly ash, The Netherlands Energy Research Foundation ECN, ECN-C-96-095, Petten, The Netherlands, 1996.
[33] A.R. Boccaccini, M. Petitmermet, E. Wintermantel, Am. Ceramic Soc. Bull. 76 (1997) 75.
[34] A. Paul, Chemistry of Glasses, 2nd ed., Chapman & Hall, London, UK, 1990.
[35] H.A. VanderSloot, D. Hoede, Leaching behaviour of amorphous, mixed and crystalline vitrified MSWI fly ash, The Netherlands Energy Research Foundation ECN, ECN-C-97-003, Petten, The Netherlands, 1997.
[36] E. Mulder, Waste Manage. 16 (1996) 181.
[37] E. Mulder, Waste Manage. 16 (1996) 15.
[38] N. Bolt, A. Snel, Environmental aspects of fly ash application in The Netherlands, Kema Scientific and Technical reports, The Netherlands 4 (1986) 125.
[39] J. Rogbeck, J. Hartlen, Waste Manage. 16 (1996) 109.
[40] J.H. Tay, A.T.C. Goh, J. Environ. Eng. 117 (1991) 224.
[41] A.T.C. Goh, J.H. Tay, J. Geotech. Eng. 119 (1993) 811.
[42] C.J. Rosen, P.M. Bierman, D. Olson, J. Agric. Food Chem. 42 (1994) 1361.
[43] P.M. Giordano, A.D. Behel, J.E. Lawrence, J.M. Soileau, B.N. Bradford, Environ. Sci. Technol. 17 (1983) 193.
[44] J.C. Ferreira, A. Strcht, J.R. Ribeiro, A. Soeirp, G. Cotrim, Manual de agricultura biológica—fertilização e protecção das plantas para uma agricultura sustentável, 2nd ed., Associação Portuguesa de Agricultura Biológica, Lisboa, 1999.
[45] X. Querol, A. Alastuey, A. Lopezsoler, F. Plana, J.M. Andres, R. Juan, P. Ferrer, C.R. Ruiz, Environ. Sci. Technol. 31 (1997) 2527.
[46] G.G. Hollman, G. Steenbruggen, M. Janssenjurkovicova, Fuel 78 (1999) 1225.
[47] C.F. Lin, H.C. His, Environ. Sci. Technol. 29 (1995) 1109.
[48] G.C.C. Yang, T.Y. Yang, J. Hazard. Mater. 62 (1998) 75.
[49] Z.D. Yao, C. Tamura, M. Matsuda, M. Miyake, J. Mater. Res. 14 (1999) 4437.
[50] A. Garea, M.I. Ortiz, J.R. Viguri, M.J. Renedo, J. Fernandez, J.A. Irabien, Thermochim. Acta 286 (1996) 173.
[51] H. Matsuda, S. Ozawa, D. Hirabayashi, in: A. Barrage, X. Edelmann (Eds.), in: Proceedings of the R'99 World Congress on R'99 Recovery Recycling Re-integration, vol. II, Geneva, Switzerland, 1999, EMPA, St. Gallen, Switzerland, 1999, pp. 287–292.
[52] T.J. Hwa, S. Jeyaseelan, Water Sci. Technol. 35 (1997) 231.