A SYSTEMIC APPROACH ON CHARACTERISTICS AND TREATMENT PROCESSES FOR HAZARDOUS WASTES: THE CASE OF FLY-ASH FROM WASTE-TO-ENERGY FACILITIES FOR MUNICIPAL SOLID WASTES

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SUMMARY

Despite increased efforts to prevent, reduce, reuse and recycle, the appropriate management of municipal solid waste remains a major environmental issue. Currently, Waste-to-Energy facilities produce clean renewable energy through the combustion of municipal solid waste in specially designed power plants equipped with the most state-of-the-art pollution control equipment. Nevertheless, the management of solid combustion residues and especially of fly ash by-products remains a primary issue. The objectives of this work were the implementation of an inventory study regarding processes used for the management of Waste-to-Energy solid by-products, with emphasis on methods applied for the utilization of fly-ash residues and an assessment of existing practices for the stabilization of combustion residues. The work includes a survey of ash qualitative characteristics and their potential relation to the specific conditions (feed, type of furnace etc). Furthermore, existing methods are evaluated for the production of cleaner and stabilized materials that can be directly re-used, thus reducing the requirements for the construction of landfills for hazardous residues.

INTRODUCTION

In the last few decades of the 20th century it became obvious that the large quantities of waste produced by the modern consumer society cause serious environmental damage when they are disposed of without any treatment. Modern landfills for municipal solid waste (MSW) have a complex design and should be able to carry out several processes such as leachate and gas management and monitoring. This makes the disposal space for a volume unit of waste rather expensive. In order to minimise disposal space, it has become common practice to sort, reuse and incinerate waste materials. Incineration and landfilling are integral components of waste management in many countries across the world. The relative importance of incineration as opposed to direct landfilling varies substantially from country to country. Incineration is often the preferred option in countries with limited availability or accessibility of space for landfilling. Switzerland, Japan, France, Germany, Sweden and Denmark are examples of countries in which 50% or more of the un-recycled waste is being or will be incinerated; some of these countries have even passed legislation which will prohibit future landfilling of combustible waste.

Incineration reduces the volume of the waste by more than approximately 80% and allows for recovery of much of the energy bound in the waste. But the incineration process is not a final waste treatment stage. Combustion and air pollution control (APC) residues are produced and must subsequently be utilized or landfilled. In principle, at least in Europe, utilization of residues is generally preferred over landfilling, provided this does not give rise to unacceptable environmental impacts or health hazards. In practice, existing regulations, lack of economic incentives, liability issues, residue separation practices and uncertainty concerning the functional properties of the residues as well as uncertainties concerning the evaluation of the extent and acceptability of the environmental impacts and health hazards of municipal solid waste incinerator (MSWI) residue utilization often serve as obstacles to residue utilization. Due to the potential leaching of contaminants, landfilling of MSWI residues may have long-term consequences for the environment. The disposal solutions chosen for these residues should therefore be sustainable in terms of environmental impact and energy consumption. This may be achieved only through careful consideration of the characteristics of the residues and of the disposal strategies involved (ISWA, 2008).

The current disposal management practices for MSWI residues are rarely based on sustainability criteria and long-term strategies; instead, traditional sanitary landfilling techniques have generally been applied to the MSWI residues without any significant adjustments. The properties of MSWI residues are very different from those of uncombusted MSW, and while sanitary landfilling may be entirely appropriate for MSW, its application to MSWI residues may lead to disposal solutions which are less than optimal in terms of resource conservation and environmental safety, particularly in the long term. The purpose of this paper is to examinene alternative methods for disposal of MSWI residues considering the specific properties of these residues and based primarily on environmental/technical considerations.

WTE FACILITIES FOR MSW UTILIZATION

A number of demonstrated technology approaches are available for WTE projects today; the predominate ones are (1) modular incinerators, (2) refuse derived fuel (RDF) systems, and (3) mass-burning systems. The technology selection process begins with evaluating all plausible options, considering the quantity and quality of waste, the energy market options available, local environmental considerations, or other local factors that can affect selection decisions.

Modular combustion systems are usually factory-assembled units consisting of a refractory-lined furnace and a waste heat boiler. Both units can be preassembled and shipped to the construction site, which minimizes field installation time and cost. On the other hand, there are two primary types of RDF systems in operation: the shred-and-burn systems with minimal processing and removal of noncombustibles, and simplified process systems that remove a significant portion of the noncombustibles. Each of these systems uses a dedicated combustor to fire the RDF to generate steam.

A mass-burn WTE facility typically consists of a reciprocating grate combustion system and a refractory-lined, water-walled, steam generator. A typical facility is shown in Figure 1, and consists of two or more combustors that are sized to properly fire or burn the area's municipal solid waste during its peak generation period. Typically, at least two combustor units are included to provide a level of redundancy and to allow waste processing at a reduced rate during periods of scheduled and unscheduled maintenance. Mass-burn facilities today generate a higher quality steam, (i.e., pressure and temperature) compared to modular systems. This steam is then passed through a once-through turbine generator to produce electricity or through an extraction turbine to generate electricity and provide process steam for heating or other purposes. Higher steam quality allows the use of more efficient electrical generating equipment, which, in turn, can result in a greater revenue stream per ton of waste.

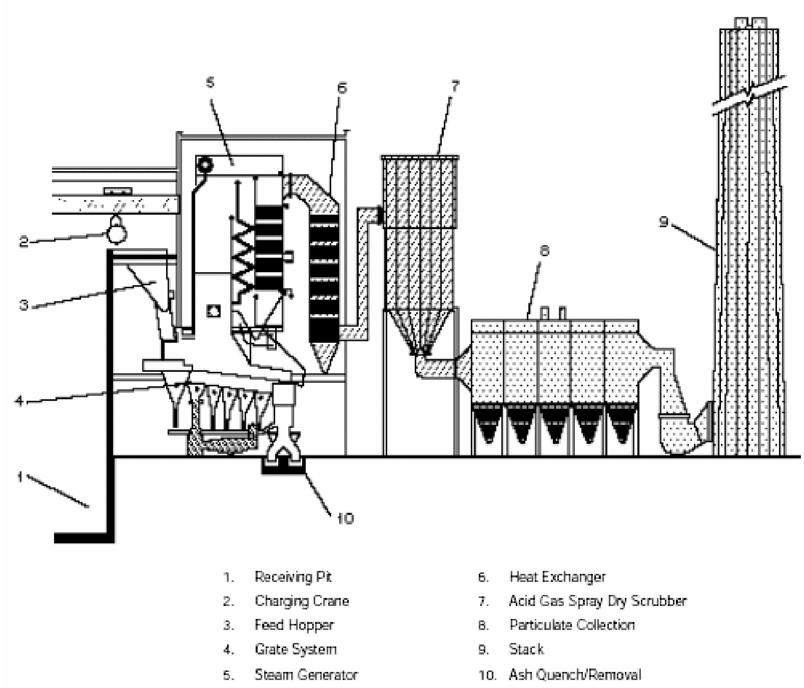

Figure 1. Schematic diagram of a typical WTE facility (EPA)

WTE residues can be divided in the following groups:

1. Bottom ash as discharged from the bottom of the furnace (mainly the grate) and fallen through the furnace grates;
2. Heat recovery ash (HRA) as collected in the heat recovery system including boiler, economizer and superheater. HRA is frequently discharged into the botrtom ash stream and thus is often included in a broader definition of bottom ash;
3. Fly ash carried over from the furnace and removed before sorbents are injected to clean the fuel gases;
4. Air pollution control (APC) residues as collected in the APC equipment (i.e. scrubbers, electrostatic precipitators, and baghouses) including fly ash, sorbents, condensates and reaction products. The term “fly ash” usually includes APC residues;
5. Combined ash as a mixture of the above categories.

The amount of each residue produced at an incinerator depends on several factors which may be summarized as feed waste composition, incinerator technology and operation, and air pollution control system technology and operation. Some typical amounts of MSWI residues produced are presented in Table 1 (Hjelmar, 1996).

Table 1. Typical amounts of residues produced per metric ton of waste incinerated

Type of residue	Typical amounts produced, kg/ton of feed waste
Bottom ash	250-420
Grate siftings	5
Boiler ash	2-12
Economizer ash	Small
Fly ash	10-30

Fly ash normally comprises only a small proportion of the total volume of residue from a WTE facility; the quantity ranges from 5 to 20 percent of the total ash. Distribution of bottom and fly ash is largely influenced by the type of combustion unit. Excess air systems produce the most fly ash; controlled air units produce the smallest amounts. Separate collection of the residue streams improves the utilization potential of the bottom ash (which constitutes 85-90% by weight of the residue stream), and limits the amount of more contaminated material (fly ash/scrubber residues) which must be managed more restrictively (Wiles, 1996; Stegemann, 2006).

CHARACTERISTICS OF FLY ASH FROM WTE FACILITIES

Fly ash consists of products in particulate form which are produced either as a result of the chemical decomposition of burnable materials or are unburned (or partially burned) materials drawn upward by thermal air currents in the incinerator and trapped in pollution control equipment. Constituents in both ash and scrubber product vary, depending on the materials burned. In systems burning a homogeneous fuel such as coal, oil, or tires, levels of pollutants in residuals may be relatively constant. Systems burning a more heterogeneous mixture, such as municipal, industrial, or medical waste, may experience wide swings in the chemical composition of residuals. The major constituents of concern in municipal waste combustion ash are heavy metals, particularly lead, cadmium, and mercury. These metals may impact human health and the environment if improperly handled, stored, transported, disposed of, or reused (for example, using stabilized ash in construction materials such as concrete blocks). Typical ranges of composition of MSWI fly ash is shown in Table 2 (Hjelmar, 1996; Zhang and Zhao, 2009). From Table 2 it is apparent that the major elements (those present in concentrations exceeding 10 g/kg) are nearly the same for all the residues: Si, Al, Fe, Ca, Mg, Na, K, S, Cl, Zn and Pb. Many of the elements are present as oxides and oxygen is therefore also a major element for all the residues. From the examination of the typical composition of various MSWI residues, including fly ash, bottom ash, acid gas scrubbing residues from the dry and semidry processes which consist of mixtures of fly ash, reaction products (predominantly calcium chloride) and excess lime, and a mixture of pre-collected fly ash and wastewater treatment sludge from the wet scrubbing process, it was observed that the concentration of the various trace elements varies between the different types of residues; some (e.g. Ba and Cr) are present at the same concentration level in all the residues, some (notably Cu) are usually enriched in the bottom ash, whereas several trace elements, particularly the more volatile elements (e.g. Cd, Hg, As, Pb and Zn) are enriched in the fly ash and acid gas scrubbing residues (Belvi and Moench, 2000).

However, earlier studies of the composition of fly ash residues revealed that the implementation of stricter emission limits, the development of improved air pollution control technologies and the incineration of MSW with controlled composition, resulted to the reduction of the various elements concentration in fly ash. According to EPA, typical composition in APC residues is for Cd: 30-300 mg/kg; Cr: 40-320 mg/kg; Ni: 10-80 mg/kg and lower than 200 mg/kg for Sn, As, Co, Mo, Sb and V (Stegemann, 2006).

Table 2. Typical composition of fly ash residues from MSWI facilities

Parameter	Fly ash	Parameter	Fly ash	Parameter	Fly ash
Si, g/kg	95-190	Ag, mg/kg	31-95	Se, mg/kg	6,1-31
Al, g/kg	49-78	As, mg/kg	49-320	Sn, mg/kg	1400-1900
Fe, g/kg	18-35	Ba, mg/kg	920-1800	Sr, mg/kg	80-250
Ca, g/kg	74-130	Be, mg/kg	Nd	V, mg/kg	32-150
Mg, g/kg	11-19	Cd, mg/kg	250-450	W, mg/kg	Nd
K, g/kg	23-47	Co, mg/kg	29-69	Zn, mg/kg	19000-41000
Na, g/kg	22-57	Cr, mg/kg	140-530	PCDD, μg/kg	115-140
Ti, g/kg	7,5-12	Cu, mg/kg	860-1400	PCDF	48-69
S, g/kg	11-32	Hg, mg/kg	0,8-7	Mn, g/kg	0,8-1,7
Cl, g/kg	45-101	Mo, mg/kg	15-49	Pb, mg/kg	7400-19000
P, g/kg	4,8-9,6	Ni, mg/kg	92-240		

The development of strategies for disposal of MSWI residues and management of the leachate should be based on extensive knowledge of both the short- and long-term leaching behaviour of the particular types of MSWI residues in question. In this context, ‘short term’ may cover a time period of 25-50 years and ‘long term’ consequently represents the following several hundred to thousands of years. Reasonable amount of information is available on the short-term behaviour of most MSWI residues, and the evaluation of the short-term behaviour may to a large extent be based on the results of laboratory and pilot-scale leaching experiments and field observations. The long-term behaviour of MSWI residues is much less understood. Due to the lack of direct observations, the evaluation of the long-term behaviour is more complicated and requires a synthesis of information obtained from laboratory testing of fundamental leaching behaviour, leaching tests simulating long-term disposal conditions, field measurements and hydrogeochemical modelling of mineral changes and speciation (Chandler, Eighmy et al., 1997).

The chemical composition of a product does not in principle allow evaluating its environmental impact. This is far more depending on the leaching stability of the material in question. Even if the matrix and the speciation of single elements were known, a reliable theoretical prediction of the short- and long-term behaviour is more or less impossible. The most important parameters influencing the leaching stability of a material are: a) chemical composition, b) chemical/geochemical/mineralogical speciation, c) the fraction of a species available for leaching, d) the particle morphology, e) the properties of the leachate, especially its pH or the presence of complexing constituents and f) the liquid-solid ratio (LS) in the leaching system.

The various MSWI residues differ substantially from each other in terms of water solubility. Only a small fraction, often less than l%, of the total mass of the bottom ash is soluble in water, whereas 20-25% of the total mass of the fly ash and 30-40% of the total mass of the dry/semidry acid gas scrubbing residues consists of salts which are readily soluble in water. The water solubility of an acid gas scrubbing residue from a wet scrubbing system (a mixture of sludge and fly ash) has been determined at 14 wt%. The water solubility of the residues and the potential leaching and release of components which may adversely affect the environment are obviously important properties in relation to disposal/landfilling of the residues and management of the leachate.

An overview of the maximum levels of concentrations of inorganic salts, trace elements and non-volatile organic carbon (NVOC) observed in initial leachates from the major types of MSWI residues is given in Table 3 including fly ash and mixtures of fly ash and acid gas scrubbing residues from the semidry process and dry lime injection process, and a mixture of fly ash and sludge from treatment of the wastewater from the wet scrubbing process. The maximum concentrations occur in the initial leachate for most parameters, and most of the concentrations have been observed in samples of leachate collected at or below L/S = 0.5 L/kg. For a particular disposal site S will be constant and L will increase as the leachate is formed; an L/S scale may therefore be transformed to a time scale if the rate of percolation or flow through the site is known. Such data may subsequently be used in conjunction with additional information (i.e. pH and redox conditions) to predict leachate quality as a function of time at a disposal site which contains waste/residues with similar properties and for which the rate of percolation of water is known. At low L/S values, the leaching of several contaminants, particularly trace elements, is solubility controlled and strongly influenced by the pH of the leachate (which in turn is governed by the major constituents of the MSWI residues and local conditions).

Table 3. Maximum concentration of substances in leachates from various MSWI residues

Typical max. concentration in leachate	MSWI fly ash and residues from dry/semidry APC processes	Mixture of MSWI fly ash and sludge from wet scrubbing process
>100 /L	Cl^-, Ca	
10-100 g/L	Na, K, Pb	Cl-, Na, K
1-10 g/L	Zn	SO_4^{2-}, Ca
100-1000 mg/L	NVOC, SO_4^{2-}	
10-100 mg/L		
1-10 mg/L	Cu, Cd, Cr, Mo	NVOC, Mo
<1 mg/L	As, Hg	As, Cr, Zn, Pb, Cd, Cu, Hg

TREATMENT OPTIONS OF FLY ASH FROM WTE FACILITIES

Boiler and even more filter ashes are classified as special wastes in many legislative regulations and their final destination is in most countries a disposal on special and expensive disposal sites. As a result, current management processes are generally based on less sustainable strategies involving total containment/entombment or containment and collection of leachate. Thus, a lot of effort is given to the development of alternative methods for the treatment and reuse of fly ash. A sustainable disposal solution for the APC residues must eventually be based on a controlled contaminant release strategy but it will almost certainly require extensive pretreatment of the residues. Several methods have been proposed for the stabilization of the APC residues and the reduction of their hazardous characteristics (Chang, Wang et al., 1999). Thermal immobilisation techniques, such as sintering/melting or vitrification have been proposed for the conversion of MSWI fly ash into ceramic type materials, although these processes are very expensive and problems may arise due to the presence of alkali chlorides and sulphates in raw fly ash (Wang, Chiang et al., 1998).

The conversion of MSWI fly ash into a non-hazardous material through a combination of chemical and thermal processes has also been proposed. The so-called 3R-process is one of these techniques, aiming at destroying chlorinated organic pollutants and recovering heavy metals from MSWI fly ash; it is based on a four step treatment, consisting of acid washing, recovery of metals by ion exchange, combination with neutral sludge and mixture recycle to the combustion chamber for mineralization and combination with bottom ash (Vehlow, 2002).

However, currently the most common technique consists the solidification/stabilization of residues through mixing with cement/ or inorganic binding agents. The primary drawback of such methods is the requirement for using a high binder/ash ratio resulting to an almost doubled amount of mass to be disposed. In addition, some elements like Cd, Cr, Mo and Zn may not sufficiently encapsulated to meet the required leaching standards. Several, pre-treatment options have been proposed for the conversion of MSWI fly ash to a cementitious material without an excessive release of metals, including washing by nitric acid at pH 4; mixing by salts of phosphorous (the so-called WES-PHix® method); washing with ferrous sulphate solution followed by ferrous sulphate oxidation (Satoshi, Van der Sloot, 2000; Bournonville and Nzihou et al., 2004; Malviya and Chaudhary, 2006).

The costs of the various filter ash treatment options have been estimated on the basis of published data and are given in Table 4. The costs of technical processes should be comparable in most industrialised counties whereas the disposal fees will change from country to country. Table 4 reveals that the specific costs of the technical measures are rather high, especially for thermal processes, but due to the small residue streams the expenses per ton of waste are low and similar for all disposal strategies. Hence the economy will not be the decisive factor for the selection of a specific process and local conditions like access to adequate disposal sites will be more important. In Germany the underground 'utilisation' looks economically promising s the gate fee has dropped down to approx. 40 - 70 € per ton of material. As a consequence dry scrubbing processes may be promoted which is in contradiction to the legislative demand for residue minimization. If the strategy gains wide application, however, it will change the management of residues from APC systems in future at least in Germany, where a great number of old mines is waiting to be filled (Vehlow, 2002).

Table 4. Cost estimation of the various APC residues treatment options (ISWA, 2008)

Process	**Weight change, %**	**Cost, €/ton of residue**
Cement stabilization	+ 20-50	25-50
Vitrification	+ 30-50	100-500
Melting	-	100-500
Acid washing + thermal treatment	-20	100-200
Stabilization by $FeSO_4$	-10	65
Stabilization by CO_2	- 10-20	80
Stabilization by PO_4	+ 10-20	25

CONCLUSIONS

In recent years, the public has been concerned about the changing characteristics of incineration with respect to the increase in heating value, incinerator emissions and ash properties. The MSW mass burn process is considered today as an efficient MSW treatment technique; modern plants are equipped with new technologies for the minimization of their environmental impacts, especially of toxic gas emissions. Nevertheless, WTE solid residues are produced, corresponding to about 20-30 percent of the feed material; these residues include mainly bottom ash, fly ash and air pollution control devices residues. Fly ash normally comprises only a small proportion of the total volume of residue ranging from 5 to 20 percent of the total ash. Separate collection of the residue streams improves the utilization potential of the bottom ash, and limits the amount of more contaminated material (fly ash/scrubber residues) which must be managed more restrictively. Fly ash is considered as a hazardous material by the European standards, and is enriched in the most volatile elements such as Cd, Hg, As, Pb and Zn. As a result, an appropriate management process of these residues should be based on methods for the reduction of their environmental impact due to the release of hazardous compounds. Most problems in the field of residue management are well understood today and in most cases appropriate technologies exist already. These technologies include in principal thermal processes (vitrification, sintering) or chemical transformation methods for solidification/stabilization of fly ash and transformation to a material with reduced release of contaminants. The costs of these processes are similar in most industrialised counties, whereas the disposal fees will change from country to country. In general, all processes intended for quality improvement have carefully to be analysed whether they result in real ecological benefits, whether all potential impacts upon the environment are taken into consideration, and whether these benefits pay in view of effort and expenses.

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