



Review

Treatment and use of air pollution control residues from MSW incineration: An overview

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Abstract

This work reviews strategies for the management of municipal solid waste incineration (MSWI) residues, particularly solid particles collected from flue gases. These tiny particles may be retained by different equipment, with or without additives (lime, activated carbon, etc.), and depending on the different possible combinations, their properties may vary. In industrial plants, the most commonly used equipment for heat recovery and the cleaning of gas emissions are: heat recovery devices (boiler, superheater and economiser); dry, semi-dry or wet scrubbers; electrostatic precipitators; bag filters; fabric filters, and cyclones. In accordance with the stringent regulations in force in developed countries, these residues are considered hazardous, and therefore must be treated before being disposed of in landfills. Nowadays, research is being conducted into specific applications for these residues in order to prevent landfill practices. There are basically two possible ways of handling these residues: landfill after adequate treatment or recycling as a secondary material. The different types of treatment may be grouped into three categories: separation processes, solidification/stabilization, and thermal methods. These residues generally have limited applications, mainly due to the fact that they tend to contain large quantities of soluble salts (NaCl, KCl, calcium compounds), significant amounts of toxic heavy metals (Pb, Zn, Cr, Cu, Ni, Cd) in forms that may easily leach out, and trace quantities of very toxic organic compounds (dioxin, furans). The most promising materials for recycling this residue are ceramics and glass–ceramic materials.

The main purpose of the present paper is to review the published literature in this field. A range of studies have been summarized in a series of tables focusing upon management strategies used in various countries, waste composition, treatment processes and possible applications.

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Acronyms

APC	air pollution control
BA	bottom ashes
CA	cyclone ash
CB	chlorobenzenes
DS	dry scrubbing residues
ESP	electrostatic precipitator ash
FA	fly ashes
FF	fabric filter or baghouse ash
IAWG	international ash working group
LWA	lightweight aggregates
MSW	municipal solid waste
MSWI	municipal solid waste incineration
PAH	polycyclic aromatic hydrocarbons
PCB	polychlorinated biphenyls
PCDD	polychlorinated dibenzo- <i>p</i> -dioxins
PCDF	polychlorinated dibenzo furans
S/S	solidification/stabilization
SDS	semi-dry scrubbing residues
WS	wet scrubbing residues

1. Introduction

The solid particles produced during municipal solid waste incineration (MSWI) in mass burning units may be grouped into bottom ashes (BA) and fly ashes (FA). Fly ashes are defined by the International Ash Working Group (IAWG, 1997) as “*the particulate matter carried over from the combustion chamber and removed from the flue gas stream prior to addition of any type of sorbent material*”. Incorrect terms are sometimes used in the literature when it is appropriate to identify the ash according to the unit that contributes to the waste (Sabbas et al., 2003). In our assessment, only studies using the following terminology have been taken into account:

- Heat recovery system ash, which is collected in hoppers below the boiler, superheater and economiser (sometimes referred to as fly ash – FA);
- Electrostatic precipitator ash (ESP);
- Fabric filter or baghouse ash (FF);
- Dry scrubbing residues (DS), semi-dry scrubbing residues (SDS) or wet scrubbing residues (WS), with sorbents such as Na_2CO_3 , $\text{Ca}(\text{OH})_2$ and activated carbon;
- Cyclone ash (CA);
- Air pollution control (APC) residues, which may include FA and the solid material captured downstream from the acid gas treatment units and before the gases are released into the atmosphere.

Therefore, the solid waste considered here consists mainly of particles produced in mass burning units, which are carried over by flue gases with or without chemical additives (sorbents). It includes combinations from different units, which will be referred to in the next sections as FA, ESP, FF, DS, SDS, WS, CA and APC residues.

Environmental legislation is becoming increasingly restrictive, and consequently industrial plants have to be constantly adapted to enhance control of gas emissions, in particular. Depending on the units used for post-combustion control, the resulting solid waste may have different characteristics, which means that different management strategies may be used. The next sections examine the strategies adopted in some countries where incineration processes are generally used for the management of MSW, and discuss the treatment and application of possible wastes (FA, ESP, FF, DS, SDS, WS, CA, APC). Some directions for future research in this field will also be suggested.

2. Waste management practices

Systems of integrated waste management may include the processes indicated in Fig. 1 (Sabbas et al., 2003). Recycling is generally agreed to be the best management strategy for waste that has already been created and collected, since it transforms the residue into a secondary raw material. However, while the utilization of waste is usually possible and desirable, the emissions produced during the life cycle of the new product should be carefully taken into account. According to the environmental policies of developed countries, disposal in landfills should be avoided as much as possible.

The present overview considers the solid residues produced during MSWI and carried over by the flue gases, summarized in Fig. 2. For each tonne of MSW that is incinerated in a mass burn unit, 15–40 kg of hazardous waste is produced, requiring further treatment and landfill as hazardous waste. Valorization may be an alternative, but it is important to ensure that the environment is properly protected against emissions into the earth, water and atmosphere. Since APC residues include the particulate matter captured after the acid gas treatment units, the waste may be a solid or a sludge, depending on the type of air pollution control equipment used (dry, semi-dry or wet processes), and is generally characterized by high concentrations of salts, heavy metals and organic trace-pollutants. These properties limit subsequent applications and require pre-treatment to improve their environmental characteristics. One of the most usual strategies for the manage-

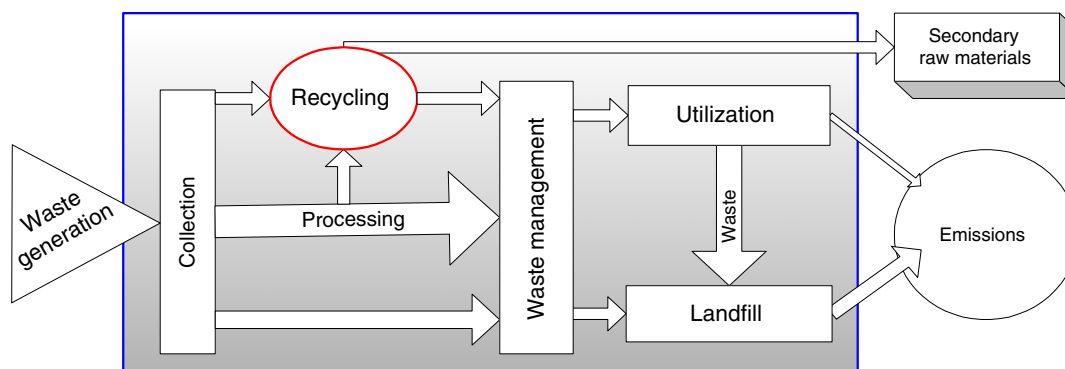


Fig. 1. Integrated waste management system, based on Sabbas et al. (2003).

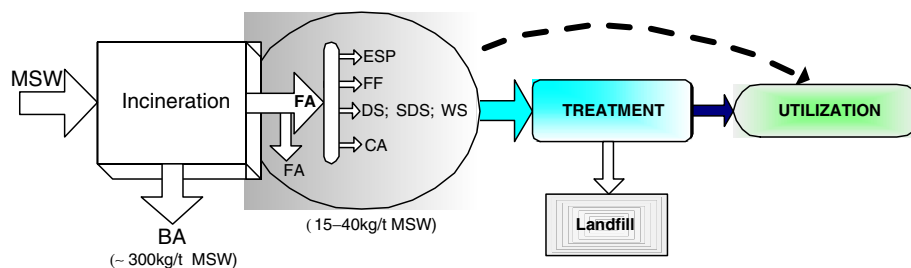


Fig. 2. Management of APC residues from MSW incineration.

ment of these APC residues is treatment followed by landfill.

In practice (as indicated in Table 1), the most common options for the management of fly ash/APC residues are permanent storage in hazardous waste disposal sites or

treatment followed by disposal with less stringent requirements. Temporary storage in big bags or disposal in underground sites are alternatives in some countries. Van der Sloot et al. (2001) claims that the beneficial utilization of residues from municipal solid waste incineration is an

Table 1
Waste management of FA/APC residues from MSWI processes in various countries

Country	Management strategies for FA/APC residues	Reference
USA	APC residues and bottom ash are mixed at most MSW incineration (MSWI) plants and disposed as a “combined ash”. The most frequent dumping option is disposal in landfills which receive only MSWI residues (monofills)	Eighmy and Kosson (1996) Sakai et al. (1996) Millrath et al. (2004)
Canada	APC residues are disposed in a hazardous waste landfill after treatment	Sakai et al. (1996)
Sweden	APC residues are disposed in secure landfills after treatment	Sakai et al. (1996)
Denmark	APC residues and fly ashes are classified as a special hazardous waste and are currently exported or stored temporarily in big bags. Significant efforts are being spent to develop treatment methods which can guarantee that APC residues can be landfilled in a sustainable way	Hjelmar (1996a,1996b) Sorensen et al. (2001)
Germany	The APC residues are mainly disposed of in underground disposal sites, such as old salt mines	Vehlow (1996) IEA (2000)
Netherlands	Flue-gas cleaning wastes are disposed temporarily in large sealed bags at a controlled landfill until better options are available. The utilization of APC residues is presently not considered. The re-use of the waste is subject to investigation	Van der Sloot (1996)
France	After industrial solidification and stabilization processes based on the properties of hydraulic binders, the waste is stored in confined cavities in a specific landfill (French class I and II). The high cost of this treatment is promoting the companies to search alternatives to disposal	Piantone et al. (2003)
Italy	Various technologies have been proposed, but the most widely adopted comprehends solidification with a variety of hydraulic binders (such as cement and/or lime, blast furnace slag, etc.)	Polettini et al. (2001)
Portugal	APC residues are treated with hydraulic binders (solidification/stabilization method) and landfilled in specific sites (monofills)	Quina (2005)
Japan	MSWI fly ash and APC residues are considered as hazardous, and before landfill intermediate treatments must be performed, such as melting, solidification with cement, stabilization using chemical agents or extraction with acid or other solvents. Melting slag may be used in road construction and the materials of S/S with cement are landfilled	Sakai (1996) Nagib and Inoue (2000) Ecke et al. (2000)

important goal for integrated waste management in some jurisdictions. However, the most significant potential environmental problems related to the disposal of MSWI residues are the short- and long-term leaching of contaminants (Hjelmar, 1996b). In particular, the high soluble salt content will be very difficult to stabilize in disposed waste without prior or simultaneous removal by aqueous extraction. In fact, removing salts makes the remaining inorganic residue much more manageable (van der Sloot et al., 2001). In a recent paper, the management of BA, FA and APC residues produced in Flanders, The Netherlands, Germany and France were compared, taking into account heavy metal contamination (Van Gerven et al., 2005). The main conclusion was that these residues may be managed differently in different countries, in accordance with management options available, leaching tests and limit values. In fact, European limit values for landfills have only become available recently, while recycling legislation has not been developed yet.

Some authors have stressed that the improvement of air pollution control devices shifts the focus from air emissions to incinerator residues (Sawell et al., 1995).

3. Characterization of the residues

In order to select the most appropriate method of treatment or application for any residue, it is extremely important to know its main characteristics, particularly chemical properties. Some physical characteristics may also be very important in some cases. Table 2 indicates the total contents of several elements and some organic compounds that were measured in diverse studies. Those compositions show that the major elements are Si, Al, Fe, Ca, Mg, K, Na and Cl. As regards heavy metals, Cd, Cr, Cu, Hg, Ni, Pb and Zn were the most frequent, with Zn and Pb generally found in the largest amounts. Trace quantities of very toxic organic compounds are usually present in these residues, namely polycyclic aromatic hydrocarbons (PAH), chlorobenzenes (CB), polychlorinated biphenyls (PCB) and polychlorinated dibenzo-*p*-dioxins (PCDD) and furans (PCDF).

Whenever the treatment, utilization or disposal of APC residues are considered, both Pb and Cl⁻ are of particular concern due to their leaching behaviour; Figs. 3 and 4 show the ranges of elemental composition for those species, based on the literature. It should be noted that some of these studies correspond to comprehensive analysis, where diverse properties are also indicated (Le Forestier and Libourel, 1998; Alba et al., 2001; Bodénan and Deniard, 2003; Li et al., 2003a, 2004). Additional works may also be referred in the context of characterization of the considered residues (Sawell et al., 1999; van der Sloot et al., 2001; Song et al., 2004; He et al., 2004; Geysen et al., 2006; Quina et al., 2007). Those (Figs. 3 and 4) were obtained from different residues (APC, FA, DS, SDS, WS, CA and FF) produced in several countries (Belgium, China, Denmark, France, Germany, Italy, Japan, Korea, Portugal, Spain, Taiwan, The Netherlands). An asterisk (*) in the caption of these fig-

ures means that the country of origin or type of residue being studied is not clear in the reference. The shaded area (Ref. b.1–b.3, c.1–c.3, d) correspond to typical ranges indicated in some references that review various other studies. By comparing the data for Pb (Fig. 3) from the shaded area (Hjelmar, 1996b; IAWG, 1997; Stegemann and Buenfeld, 2003), it can be concluded that, depending on the residues in question, the range may be very wide for this element. A glance at Fig. 3 shows that the amount of Pb in these residues may be lower than 1000 mg/kg or higher than 10,000 mg/kg. The concentration of Pb in the APC residues from Portugal is 1495–2453 mg/kg, which is lower than the ranges indicated in Hjelmar (1996b) and IAWG (1997) for similar residues. In studies conducted by the authors (Quina, 2005; Quina et al., 2007), the chloride concentration measured in 5 samples taken over 2.5 years was 101–138 g/kg, which is a considerable amount for APC residues. Nevertheless, other studies have revealed wider ranges, as in the case of Poletini et al. (2001), where the indicated amount of chloride may be 29–337 g/kg. These variations make it difficult to treat waste on the basis of general formulations. Therefore, careful characterization studies should precede any treatment or valorization procedure.

For many applications, particularly ceramics and glass-ceramics, it is important to know the quantities of oxide species. Some of the values given in the literature for CaO, SiO₂, Al₂O₃, Fe₂O₃, MgO, Na₂O, K₂O, Ti₂O, SO₃, P₂O₅, MnO and ZnO are indicated in Table 3. Oxide compositions are also given in many other studies, such as Quina et al. (2006), Qian et al. (2006a,b), Park et al. (2005), Carignan et al. (2005), Chimenos et al. (2005), Stegemann and Buenfeld (2003), Wang et al. (2002, 2004), Rémond et al. (2002a), Nishida et al. (2001), Poletini et al. (2001), Haugsten and Gustavson (2000) and Derie (1996). Although oxide composition may vary, a very high alkali content is generally observed, mainly due to the calcium hydroxide or sodium carbonate usually used for acid gas removal. Consequently, the natural pH of these residues is usually also very high, sometimes higher than 12.5, which may constitute a problem for some applications. It should be noted that 12.5 is the pH value of a saturated solution of Ca(OH)₂.

As indicated in Table 2, APC residues mainly consist of O, Si, Ca, Al, Cl, K, Na, S and Fe, and are mostly present as oxides (shown in Table 3), chlorides, sulphates and carbonates (Hong et al., 2000; IAWG, 1997; Wiles, 1996). However, due to the high concentration of several heavy metals, the reuse of APC residues as a secondary material is prohibited in many countries, with the ever more stringent legislation. Therefore, taking into account the potential environmental impact of these residues, the main problems that have to be solved concern toxic heavy metals (e.g., Pb, Zn, Cd, Cr, Cu, Ni, Hg), the high concentration of soluble salts (e.g., NaCl, KCl, salts of Ca), and organic micropollutants (e.g., dioxins, furans). Among other researchers, Hjelmar (1996b) pointed out that almost all APC residues produced are landfilled or placed in under-

Table 2
Total composition of FA/APC MSWI residues based on literature

Units		Quina (2005)	Hjelmar (1996b)		IAWG (1997)	Le Forestier and Libourel (1998)		Song et al. (2004)		Eighmy et al. (1995)
		APC + FA	APC +FA	FA	APC + FA	SD	ESP	SDS	FF	ESP
Si	g/kg	45–83	57–98	95–190	36–120	56	132	nd	nd	38
Al	g/kg	12–40	17–46	49–78	12–83	36	93	10	6.4	21
Fe	g/kg	4–16	3.6–18	18–35	2.6–71	8.4	12	2.0	0.76	1.6
Ca	g/kg	92–361	170–290	74–130	110–350	274	169	117	65	46
Mg	g/kg	nd	7.1–12	11–19	5.1–14	9.8	18	8.9	6.7	<1.1
K	g/kg	23–30	27–40	23–47	5.9–40	17	28	nd	nd	109
Na	g/kg	22–33	12–19	22–57	7.6–29	15	25	6.2	37	84
Ti	g/kg	nd	1.5–5.1	7.5–12	0.7–5.7	4.4	11	nd	nd	6
S	g/kg	nd	8–18	11–32	1.4–25	11	12	nd	nd	nd
Cl	g/kg	101–138	92–220	45–101	62–380	183	69	203	317	232
P	g/kg	nd	1.7–4.6	4.8–9.6	1.7–4.6	3.2	6.2	nd	nd	nd
Mn	g/kg	nd	0.3–0.7	0.8–1.7	0.2–0.9	0.9	0.8	0.6	0.3	0.4
Ag	mg/kg	nd	14–60	31–95	0.9–60	nd	nd	nd	nd	192
As	mg/kg	nd	40–260	49–320	18–530	19	28	nd	nd	960
Ba	mg/kg	nd	310–1400	920–1800	51–14000	804	1482	41	34	nd
Be	mg/kg	nd	0.5–0.9	nd	0.5–0.9	nd	nd	nd	nd	nd
Cd	mg/kg	49–87	140–300	230–430	140–300	126	166	16	190	1660
Co	mg/kg	nd	4–15	29–69	4–300	10	28	2.3	1.9	13
Cr	mg/kg	72–259	150–570	140–530	73–570	217	549	169	183	495
Cu	mg/kg	440–648	450–1100	860–1400	16–1700	434	741	407	602	2220
Hg	mg/kg	9–16	9.3–44	0.8–7	0.1–51	18	19	11	48	9.8
Mo	mg/kg	nd	9.3–20	15–49	9.3–29	nd	36	nd	nd	47
Ni	mg/kg	45–132	20–63	95–240	19–710	52	96	nd	nd	70
Pb	mg/kg	1495–2453	4000–6500	7400–19000	2500–10000	2780	2611	254	2055	27000
Se	mg/kg	nd	8.2–16	6.1–31	0.7–29	nd	nd	nd	nd	17
Sn	mg/kg	nd	620–780	1400–1900	620–1400	814	863	367	767	5900
Sr	mg/kg	nd	400–500	<80–250	400–500	337	388	138	109	nd
V	mg/kg	nd	26–62	32–150	8–62	38	40	7	4	35
Zn	mg/kg	4308–6574	12000–19000	19000–41000	7000–20000	8211	7339	9036	12814	104400
PAH	µg/kg	nd	18–5600	30–110	30	nd	nd	nd	nd	nd
CB	µg/kg	nd	220	50–890	0.03–0.4	nd	nd	nd	nd	nd
PCB	µg/kg	nd	<40	<40	nd	nd	nd	nd	nd	nd
PCDD	µg/kg	nd	0.7–1000	115–140	0.7–32	nd	nd	nd	nd	nd
PCDF	µg/kg	nd	1.4–370	48–69	1.4–73	nd	nd	nd	nd	nd
TCDD	eqv	nd	0.8–2	1.5–2.5	0.8–2	nd	nd	nd	nd	nd
TOC	g/kg	10	6–9	4.9–17	6–9	nd	nd	nd	nd	nd
LOI	g/kg	12–24	28–49	11–43	21–120	nd	nd	nd	nd	nd

nd – not determined or not indicated; PAH – polycyclic aromatic hydrocarbons; CB – chlorobenzenes; PCB – polychlorinated biphenil; PCDD – polychlorinated dibenzo-*p*-dioxins; PCDF – polychlorinated dibenzofurans; TCDD – tetrachloro dibenzo-*p*-dioxins as reference for toxicity equivalents determined according to Eadon's method; TOC – total organic carbon; LOI – loss on ignition (550 °C); SD – semi-dry absorber; BF – bag filter.

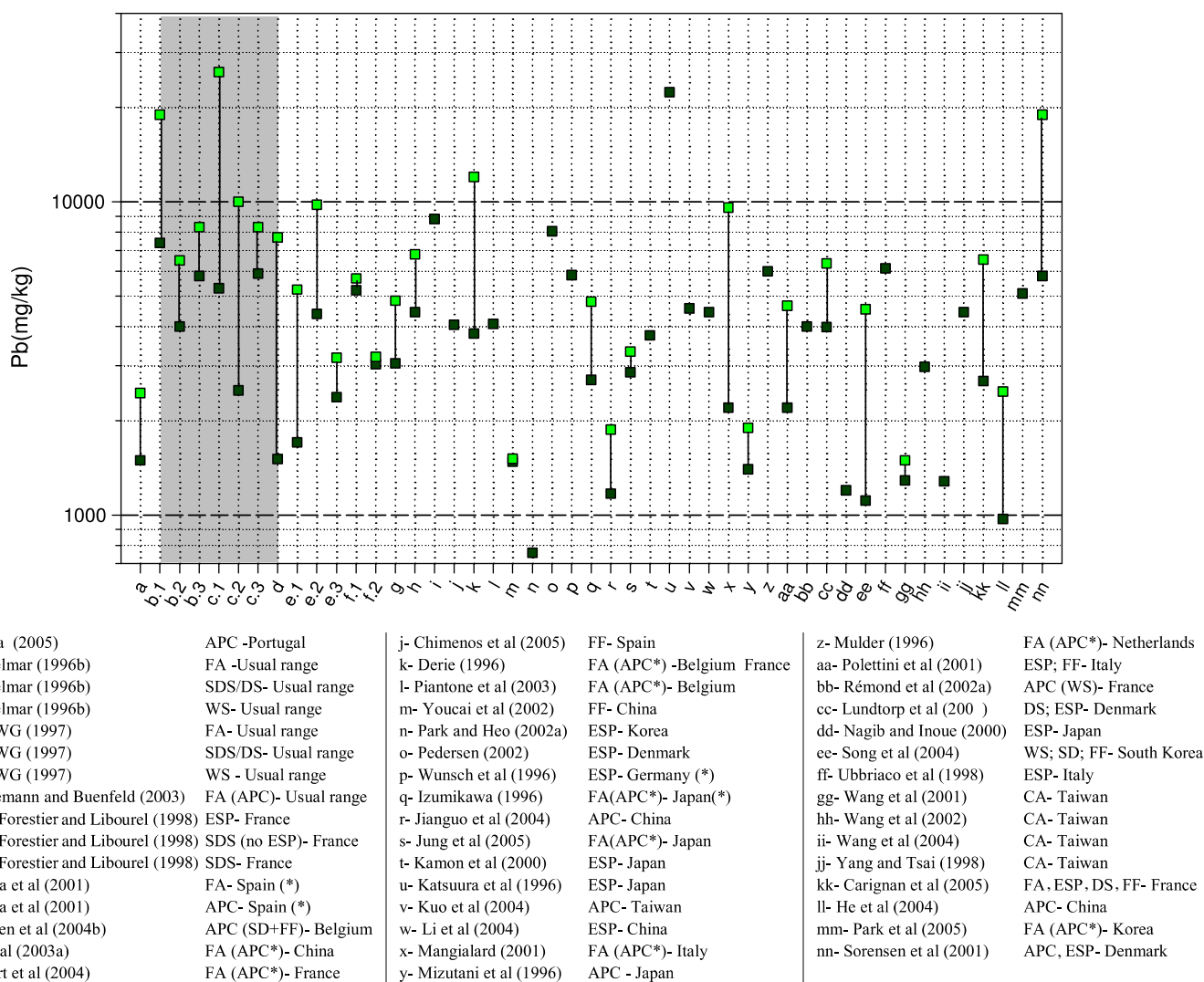


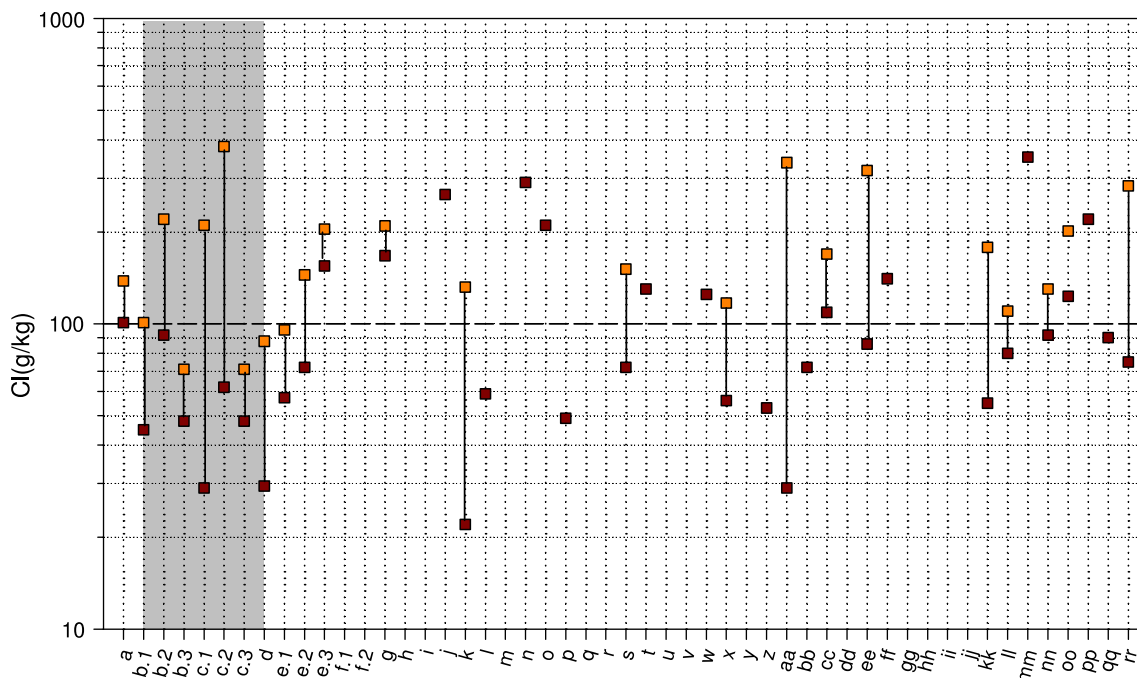
Fig. 3. Lead concentration in incineration residues from MSWI (APC, FA, DS, SDS, WS, ESP, FF, CA).

ground facilities, and because of the potential leaching of contaminants over long periods, the solutions chosen for these residues should be sustainable in terms of environmental impact.

4. Possible treatments

The appropriate treatments for APC residues can be grouped into three classes (IAWG, 1997): (i) separation processes; (ii) solidification/stabilization (S/S); (iii) thermal methods. Fig. 5 shows a scheme of this classification, where further subdivisions for each type of treatment is also indicated. In practice, it may be useful to start the treatment with separation techniques (mainly washing or leaching with fluid solutions that are more aggressive than water), followed by thermal treatments or stabilization/solidification methods. As pointed out by Sabbas et al. (2003), treatment strategies may vary; methodologies for reducing environmental impact may involve lowering the total content of the contaminant (e.g., through washing), reducing

the availability of contaminants for leaching (e.g., by stabilization methods), or decreasing the leaching rates (e.g., through S/S methods). Van der Sloot et al. (2001) present an overview of the methods of treatment for MSWI residues, indicating those which correspond to existing proven technology, those that have shown promising results, and the ones that are currently under investigation or have been found to be technically and/or economically feasible. Sakai et al. (1996) stressed that, in comparing different technologies, a cost assessment is needed in addition to a description of the characteristics of the products generated by each process. The high costs associated with vitrification or extraction processes may be considered acceptable if the potential use or volume reduction of the material being generated is taken into account. On the other hand, the lower costs of S/S methods must be counterbalanced by the shortcomings of the significant volume increase due to the need for solidification reagents (binders) and the potential long-term instability (mainly the high salt contents) of the treated material.



a- Quina (2005)	APC- Portugal	k- Derie (1996)	FA (APC*)- Belgium, France	bb- Rémond et al (2002a)	APC (WS)- France
b.1- Hjelmar (1996b)	FA- Usual range	l- Piantone et al (2003)	FA (APC*)- Belgium	cc- Lundtorp et al (2003)	DS; ESP- Denmark
b.2- Hjelmar (1996b)	SDS/DS- Usual range	m- Youcai et al (2002)	FF- China	dd- Nagib and Inoue (2000)	ESP- Japan
b.3- Hjelmar (1996b)	WS- Usual range	n- Park and Heo (2002a)	ESP- Korea	ee- Song et al (2004)	WS; SD; FF- South Korea
c.1- IAWG (1997)	FA- Usual range	o- Pedersen (2002)	ESP- Denmark	ff- Ubbricco et al (1998)	ESP- Italy
c.2- IAWG (1997)	SDS/DS- Usual range	p- Wunsch et al (1996)	ESP- Germany (*)	gg- Wang et al (2001)	CA- Taiwan
c.3- IAWG (1997)	WS- Usual range	q- Izumikawa (1996)	FA(APC*)- Japan(*)	hh- Wang et al (2002)	CA- Taiwan
d- Stegemann and Buenfeld (2003)	FA (APC)- Usual range	r- Jianguo et al (2004)	APC- China	ii- Wang et al (2004)	CA- Taiwan
e.1- Le Forestier and Libourel (1998)	ESP- France	s- Jung et al (2005)	FA(APC*)- Japan	jj- Yang and Tsai (1998)	CA- Taiwan
e.2- Le Forestier and Libourel (1998)	SDS (no ESP)- France	t- Kamon et al (2000)	ESP- Japan	kk- Carignan et al (2005)	FA, ESP, DS, FF- France
e.3- Le Forestier and Libourel (1998)	SDS- France	u- Katsuura et al (1996)	ESP- Japan	ll- He et al (2004)	APC- China
f.1- Alba et al (2001)	FA- Spain(*)	v- Kuo et al (2004)	APC- Taiwan	mm- Park et al (2005)	FA (APC*)- Korea
f.2- Alba et al (2001)	APC- Spain(*)	w- Li et al (2004)	ESP- China	nn- Sorensen et al (2001)	APC, ESP- Denmark
g- Geysen et al (2004b)	APC (SD+FF)- Belgium	x- Mangialard (2001)	FA (APC*)- Italy	oo- Qian et al (2006a,b)	FA- China
h- Li et al (2003a)	FA (APC*)- China	y- Mizutani et al (1996)	APC - Japan	pp- Kim and Kim (2004)	FA(APC*)- Korea
i- Aubert et al (2004)	FA (APC*)- France	z- Mulder (1996)	FA (APC*)- Netherlands	qq- Iretskaya et al (1999)	APC- France
j- Chimenos et al (2005)	FF- Spain	aa- Poletini et al (2001)	ESP; FF- Italy	rr- Bodéan and Deniard (2003)	APC- Several countries

Fig. 4. Chloride concentration in incineration residues from MSWI (APC, FA, DS, SDS, WS, ESP, FF, CA).

In the literature, the cost of the different treatments is seldom indicated. Ecke et al. (2000) claim that thermal processes may involve costs of over 367 € t⁻¹, which is a com-

pletely different order of magnitude to the other processes. In fact, since melting methods involve expensive equipment and high energy input, operating costs may be as much as

Table 3
Chemical composition of the major oxides that constitute the APC residues (wt.%)

	Auer et al. (1995)	Alba et al. (1997)		Romero et al. (2001)	Li et al. (2003a)	Piantone et al. (2003)	Song et al. (2004)		Cheng and Chen (2004)	Kim and Kim (2004)	
	ESP	FA	APC	FA	FA + APC	APC	SDS	FF	FA	ESP	ESP_wash
CaO	19.3	24.3	27.7	29.34	13.9	24.2	52.9	25.2	19.7	19.50	26.23
SiO ₂	20.2	18.8	15.0	11.47	8.57	33.6	5.8	4.7	19.4	7.30	21.94
Al ₂ O ₃	12.3	12.7	7.1	5.75	3.90	11.6	2.8	1.8	10.1	3.20	9.97
Fe ₂ O ₃	1.2	1.6	1.4	1.29	2.58	1.9	2.4	0.95	1.8	1.39	2.08
MgO	2.5	2.6	1.9	3.02	3.16	2.2	2.6	1.3	2.8	2.61	8.32
Na ₂ O	6.4	5.8	4.1	8.70	14.0	2.2	(a)	10.9	8.9	13.07	2.11
K ₂ O	6.2	4.3	4.4	7.02	8.77	2.6	1.5	10.6	8.1	11.21	0.84
TiO ₂	1.4	1.5	1.0	0.85	0.76	1.7	1.9	1.2	1.9	2.77	3.80
SO ₃	8.3	6.4	8.2	(a)	15.36	(a)	6.7	8.0	(a)	9.76	11.93
P ₂ O ₅	1.3	2.7	1.6	1.69	2.81	1.4	1.4	1.2	(a)	1.72	5.76
MnO	(a)	0.12	0.06	0.18	0.12	0.06	(a)	(a)	(a)	(a)	(a)
ZnO	3.0	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(a)	3.02	4.72

ESP – electrostatic precipitator; FA – fly ash; APC – air pollution control residues; SDS – semi-dry absorber; FF – bag filter; (a) – not indicated.

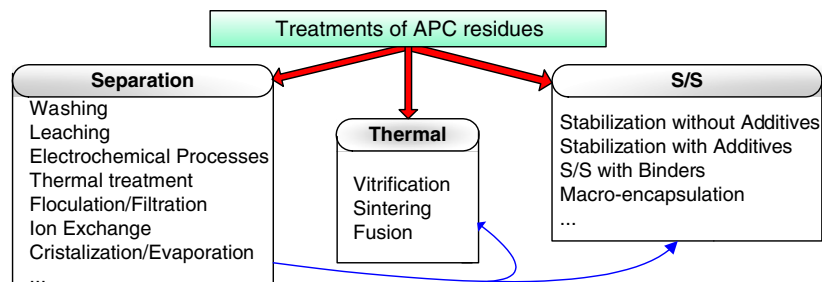


Fig. 5. Treatments for APC residues.

15 times higher than cementitious solidification/stabilization (S/S) processes. On the other hand, the addition of 2–3 wt.% of chelate agents in stabilization methods may result in a cost of 61–92 € t⁻¹. Chemical treatments are generally more expensive than cementitious S/S, but the increase in solid waste mass is lower. Therefore, if disposal costs are taken into account in this less expensive technology, separation methods such as acid extraction might be possible options, with the advantage that they enable the recovery of metals and salts. Alternative inorganic binding agents, when compared with ordinary Portland cement, may lead to treatment costs two to three times higher than for cementitious S/S. Based on industrial data from a Portuguese industrial incineration plant and excluding the landfill cost, the cementitious S/S treatment may cost 45 € t⁻¹ (Quina, 2005).

4.1. Separation methods

Separation methods include all techniques that allow the extraction of some species from the waste, aiming to improve the quality of the residue for further utilization and/or to recover the species in question. According to Mohapatra and Rao (2001), acid leaching, alkali fusion, ion exchange, solvent extraction and magnetic separation are some of the most widely used methods for extracting metal values from different types of fly ash. For APC residues from MSW incineration, several separation processes may also be applied (Fig. 5):

- (1) *Washing processes*: The objective in this case is generally to remove the soluble salts by using water as a leachant. This process may be used as a first step in more elaborate methodologies (Chimenos et al., 2005; Mangialardi, 2003; Piantone et al., 2003; Nzihou and Sharrock, 2002; Krebs et al., 2001; Lundtorp et al., 2003; Derie, 1996; Mulder, 1996). Kirby and Rimstidt (1994) studied the dominant chemical reactions between water and a mixture of ESP and bottom ash (BA), and concluded that 10 kg of anhydrous salts can be obtained from a tonne of waste. Studies by the author have shown that washing methods involving water alone are not very appropriate since large quantities of heavy metals (e.g., Pb and Zn) are also released simultaneously

with the soluble salts (Quina, 2005). Some chemical additives, such as soluble phosphates, may be used to overcome this problem.

- (2) *Leaching*: Aiming at the extraction of heavy metals for further recovery, leachant solutions other than water may be used. The main elements in this process are Pb and Zn, and the goal is to obtain a solution in which concentrations are high enough to enable further separation or recovery. When the released amounts are too low, two possibilities can be implemented for improving leaching efficiency: adding chemical additives or reintroducing the leachate into the process (Laethem et al., 1994). In the literature, various studies attempted to use chemical agents to improve heavy metal leaching (Hong et al., 2000; van der Bruggen et al., 1998; Katsuura et al., 1996). The efficiency of the extraction depends very much upon the heavy metal in question, the extracting agent, the pH and the liquid/solid ratio used. In Japan, nine acid extraction units for treating the MSWI residues are in operation (Ecke et al., 2000). According to some studies, the leaching of heavy metals can also be improved through bioleaching, by using bacteria leaching processes (Krebs et al., 2001; Bosshard et al., 1996).
- (3) *Electrochemical processes*: These methodologies involve reduction/oxidation reactions at the interface of electrodes and electrolyte, forced by a potential difference in the electrodes. During the electrochemical process, hydrogen is generated at the cathode, metals are deposited on its surface (through the reduction reaction) and oxygen is released at the anode (due to the oxidation reaction). The main advantage of these methods is that they do not require the addition of chemicals, but removing metals when the concentration is low is a major problem (Yang and Tsai, 1998). The variables that significantly affect this process are current density, temperature, mixing conditions, distance between the electrodes and the pH of the solution.
- (4) *Thermal treatment*: This method may be used for removing heavy metals through evaporation processes (using temperatures lower than melting point), while at the same time enabling the recycling of the metals (decontamination). In general, the heavy

metals of interest are Zn, Pb, Cu and Cd. In the literature, some studies have yielded promising results as regards the separation of heavy metals by thermal treatment (Auer et al., 1999; Jakob et al., 1995, 1996; Stucki and Jakob, 1997). The principal thermochemical reactions that control the evaporation of

heavy metals are: the evaporation of the metallic forms or reduction at the metal state followed by evaporation; the evaporation of the volatile chlorides, and the formation of stable compounds within the solid matrix, which remain as oxides in the residue (Jakob and Stucki, 1997).

Table 4
Separation processes for treatment of APC residues

Separation	Residue	Objective	Conclusion	Reference
Washing	ESP	Washing the residue at pH 6.5–7.5 and then solidified with a binder	The washed residue is less adverse to cement hydration	Mangialardi (2003)
	APC	Extraction of soluble salts, carried out at a pH close to 10.5 by adding HCl	Occur carbonation and partial trapping of Pb and Zn by calcite neoformed during washing	Piantone et al. (2003)
	FF	Washing with water for extracting soluble salts	Chlorides can be extracted and the solutions can be evaporated to produce salts	Derie (1996)
	APC	Washing is promoted through a ferrous-sulphate solution	A large amount of salts was removed from the residue, leading to a decrease in leaching	Nzihou and Sharrock (2002)
Leaching	APC	Evaluate the extraction process of metallic elements from FA under hydrothermal conditions	For a process consisting of two steps (pre-washing and hydrothermal extraction), the optimum conditions are 150 °C and a liquid/solid ratio of 10:1	Lundtorp et al. (2003)
	FF	Recover Pb by using a counter-current sorption process with peat moss	Peat moss is an excellent adsorbent for Pb in alkaline leachates	Zhang and Itoh (2006)
	APC	Recover Cr, Cu, Pb and Zn by chelating agents	The residue is detoxified after treatment with chelating agents	Hammy et al. (2005)
	ESP; FF	Recover of Pb and Zn through acid and/or alkaline leaching	Acid leaching is clearly more effective than the alkaline one	Hong et al. (2000)
	ESP	Simulation of acid extraction in order to remove heavy metals	For Pb an increase in solubility is obtained when EDTA is added to acid solution (HCl)	Nagib and Inoue (2000)
	ESP	Full-scale plant of an acid extraction process	It is possible to recover solid salts containing near 99% of NaCl	Van der Bruggen et al. (1998)
	APC	Study the release of metals and availability in alkali condition	The amount extracted depends on the pH of the solution	Katsuura et al. (1996)
	ESP	Integrated treatment regarding metal recovery. The influence on leaching processes of pH, L/S and extraction time is analysed	One of the most important factors for leaching processes is the solubility of the metal salts. Some metals quantities can decrease for longer extraction times. The solubility of Pb and Cu can be improved by adding EDTA	Mizutani et al. (1996)
	ESP	Bioleaching by <i>Aspergillus Niger</i>	The environmental quality of the residues can be improved with respect to a re-use	Laethem et al. (1994)
	ESP	Bioleaching by <i>Thiobacilli thiooxidans</i>	Extraction of higher than 80% for Cd, Cu, and Zn. Low efficiency for Pb (re-precipitate as PbSO ₄)	Bosshard et al. (1996)
Electro-chemical	APC	Assess the electrodialytic remediation for the removal of Zn, Pb, Cu and Cd	Experimental results showed low efficiencies for the electrodialytic removal of Zn, Pb, Cu and Cd	Krebs et al. (2001, 1997)
	ESP	Utilization of assisting agents (ammonium citrate) for electrodialytic removal of metals	The best compromise for removal of Cd, Pb, Zn, Cu and Cr was obtained with the 0.25 M ammonium citrate/1.25%NH ₃ solution. Up to 86% Cd, 20% Pb, 62% Zn, 81% Cu and 44% Cr was removed in electrodialytic remediation and the time of the experiments was 5–70 days	Ferreira et al. (2005)
	CA	Heavy metal extractability (Pb, Cd, Cr, Cu) and subsequent recovery	Solvent extraction and electrolytic recovery is technically feasible	Pedersen (2002)
Thermal	ESP	Recycling heavy metals by fractionated condensation	Heavy metals are volatile in the presence of HCl(g), and condensation is a promising method	Pedersen et al. (2005)
		Analysis of the evaporation of heavy metals through heat treatment	Evaporation rates higher than 98% are obtained for Pb, Cd and Cu at 1000–1100 °C, decreasing above this temperature	Yang and Tsai (1998)
		Influence of chlorides on evaporation rates of heavy metals	The amounts evaporated as well as the rates of evaporation are strongly influenced by chlorides	Auer et al. (1999)
		Analysis of the ZnCl ₂ evaporation	Several factors have influence on the degree of Zn evaporation (composition, surface area)	Jakob et al. (1995)

A summary of the recent literature concerning separation processes for the treatment of ESP, FF, CA and APC residues produced during MSW incineration is presented in Table 4. The information indicated in this table was structured according to the separation process, type of residue analysed, the objective of the study and the main conclusion(s) drawn by the author(s). From these studies, it can be concluded that several separation techniques were tested for APC residues, having been considered technically feasible. When the cost of the treatment is not an important issue, a sustainable solution can be found by using separation processes. In fact, some methodologies are very effective at removing the hazardous substances, and consequently non-hazardous materials can be obtained. On the other hand, separation processes may also be regarded as a first step for further treatments, promoting recycling strategies. In addition to the processes included in Table 4, several separation treatments have been patented (Kuramochi et al., 2005; Mercier et al., 2002; Sawell and Hetherington, 2001; Carre and Templier, 1995; Kauser and LaMastro, 1991).

In our opinion, the removal of the soluble salts is crucial or even almost inevitable for sustainable treatment or the use of waste as secondary material.

4.2. Solidification/stabilization (S/S)

The solidification/stabilization processes (S/S), Fig. 5, are those that use additives or binders in order to immobilize physically and/or chemically hazardous components initially present in waste (Wiles, 1996). Solidification involves the transformation of a liquid or sludge into solids, and may not lead to a chemical interaction of the constituent of concern with the solidifying agent. The process reduces the mobility of the contaminants in the treated

material through encapsulation, as a consequence of the reduced surface area and low permeability. On the other hand, the main goal of stabilization is to convert the contaminants into less soluble or less toxic forms, with or without solidification. In practice, the best approach to S/S technology involves firstly chemical stabilization and then solidification of the waste; inorganic materials, such as cements or pozzolanic materials, are the most common binders. S/S methods consist of mixing the binders with the waste and water, and sometimes with chemical additives (e.g., sodium silicate or soluble phosphates). The quantities involved are optimized as a function of the performance required for the final product (leaching behaviour, mechanical strength, setting time, etc.), which may be either solid massive (monolithic) or granular. When Portland cement or similar binders are employed, the product is monolithic and a significant increase in weight and volume may occur, which affects shipping and landfill costs. Moreover, it should be pointed out that, although S/S processes are one of the most used methods, they are not effective for treating soluble salts. Therefore, since APC residues contain high levels of salts, the leaching of these salts from the S/S matrix over time is likely to result in poor performance. The subsequent loss of physical properties and durability of the treated product may lead to an increase in metals released. In general, irrespective of the S/S method used, the treatment is carried out in order to comply with landfill criteria. Huang and Chu (2003) point out that bag filter precipitator residues and scrubber residues have cement-like compositions, and therefore can be easily immobilized by cement.

Conner and Hoeffner (1998a,b) present a synopsis of the history of the S/S technology and a critical review of these methods. The schema in Figs. 6 and 7 were prepared on the basis of their work, and we can conclude that S/S technology

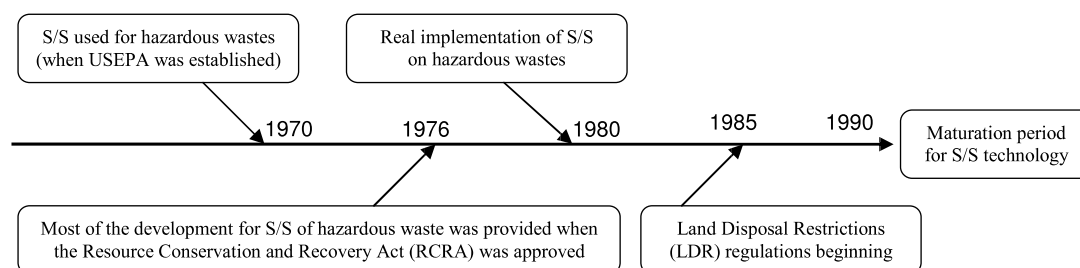


Fig. 6. Summary of the history of S/S technology (based on Conner and Hoeffner, 1998a).

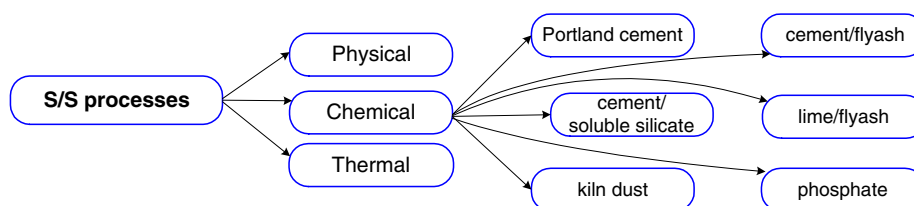


Fig. 7. Overview of the S/S processes (based on Conner and Hoeffner, 1998b).

Table 5
Treatment of APC residues by S/S processes – chemical stabilization (Group A)

S/S	Residue	Objective /methodology	Conclusion	Reference
Soluble phosphate-treatment	FF	Immobilization of heavy metals using soluble phosphates combined with “high specific surface area lime”	The “high specific surface area lime” allows to reduce to about 1/2 of the conventional lime injection rate, and the treatment costs by soluble phosphate can be remarkably reduced	Uchida et al. (1996)
Stabilization with soluble phosphates	DS	Stabilization of heavy metal by using soluble phosphate at a dosage of 1.2 mol of H ₃ PO ₄ /kg of residue. The chemical additive is mixed with the waste during 10 min at a L/S ratio of 0.4	The treatment with soluble phosphate is an effective stabilization method for divalent heavy metals (Pb, Zn), due to precipitation of metal phosphates rather than adsorption processes. The products formed are crystalline and amorphous calcium phosphates, tertiary metal phosphates and apatite family minerals	Eighmy et al. (1997)
Chemical stabilization(H ₃ PO ₄) and calcination at 900 °C	APC	Study of chemical and thermal treatments for APC residues. The procedure consists of mixing 1 kg of waste with 2 L of water, 20 g of Ca(OH) ₂ and 60 g of H ₃ PO ₄ . The suspension was stirred for 30 min, and after filtering and drying at 60 °C, the calcination in air at 900 °C of the solid was performed	Chemical treatment reduces heavy metal ion solubility. Thermal treatment affects also significantly the solubility of metal ions with respect to chelating ligands, due to the incorporation of the metals in a calcium phosphate matrix. The thermal treatments at 900 °C avoid metal loss by evaporation and contribute to apatite crystallization	Iretskaya et al. (1999)
Chemical stabilization with chelating agent, phosphate and ferrite	APC	Evaluation of treatments with a chelating agent, phosphate treatment, ferrite treatment. Analysis of leaching behaviour, the total availability	The treatment using a chelating agent is based on complexation of metals with an organic sulphide and a high reducing capacity and strong retention for metals is observed over a wide pH range. The treatment with phosphate showed a significant decrease in availability, mainly for Pb. The treatment with ferrite showed an increased physical retention	Mizutani et al. (2000)
Stabilization with chelating agent	SDS	Fly ashes are mixed with chelating agents	Chelating agents are more efficient than inorganic chemicals (sodium sulfide and lime)	Jianguo et al. (2004)
Stabilization with phosphate	APC	Monitoring the stabilization of fly ash by phosphatation. The treatment consist in three steps: removing the salts (chlorides, sulphates) by dissolution at basic pH, phosphation of the residue to trap metals, and its calcination to destroy dioxin-like compounds	Carbonation and partial immobilization of Pb and Zn by calcite neoformed occur during washing. Precipitation of calcium phosphates traps Pb and Zn during phosphation by destruction of the neoformed calcite. The calcination allows the stabilization of Pb and Zn by recrystallization of the mineral phases	Piantone et al. (2003)
Stabilization with ferrous sulphate solution and oxidation	APC FA	Treatment of the residue with a ferrous sulphate solution and subsequent oxidation of the suspension. The suspension was spread on a dedicated landfill which drains by gravity through the drainage system of the landfill	The wastewater from the process, collected through the drainage system, contained large concentrations of salts but low concentrations of trace metals. The concentrations of trace metals were reduced by up to four orders of magnitude. The effect on oxyanions (e.g. Cr) is very low	Lundtorp et al. (2002, 2003)
Stabilization with phosphates	APC	Immobilization of lead and zinc in APC residues by using soluble phosphates	With cement as well as with phosphates a reduction in Pb and Zn leaching was observed. However, with soluble phosphates, the Pb leaching was lower than with cement	Geysen et al. (2004a)
Stabilization with FeSO ₄ and Fe ₂ (SO ₄) ₃ solutions	APC	Study the effectiveness of mixing FeSO ₄ and Fe ₂ (SO ₄) ₃ solutions with APC residues in order to stabilize heavy metals	The solution reacted with the scrubber ash to form Ca ₄ Fe ₉ O ₁₇ , which coated the surface of ash particles, and therefore the heavy metal releasing is decreased	Hu (2005)
Stabilization with colloidal aluminate oxide	APC	Stabilize lead by using colloidal aluminate oxide (CAO)	CAO reveals a high reduction ratio for the leachability of Pb of 94.8% when compared with other commercial fixation agents. An immobilization mechanism is proposed, with the critical process being the formation of the Al(OH) ₃ /Pb(OH) ₂ crystals	Huang and Lo (2004)
Stabilization with FeSO ₄ and thermal treatment	DS ESP	Stabilization by coprecipitation with ferrous iron (Ferrox process), followed by thermal treatment (at 600 and 900 °C)	Ferrihydrite was formed initially but converted upon thermal treatment into more stable and crystalline compounds (maghemite and hematite). However, the overall effect of the Ferrox process followed by thermal treatment is an initially more contaminated leachate but the product obtained is more stable in the long term	Sorensen et al. (2000)

is at present in the maturing phase (Fig. 6), with a number of research projects aiming at optimizing the process. Fig. 7 shows that S/S processes can be classified into physical, thermal and chemical processes. S/S treatments that use chemical fixation/interaction may employ some possible combinations, the most common being those that use Portland cement, cement and fly ash from coal, cement and soluble silicates, lime and fly ash from coal, kiln dust, and soluble phosphates.

On the subject of cement solidification and stabilization, Glasser (1994, 1997) discusses the most important issues to be considered in this technology. Also related with these processes, Gougar et al. (1996) present a review concerning ettringite and calcium silicate hydrate (CSH) phases from Portland cement for waste ion immobilization, where the interaction with priority metallic pollutants (Cr, Pb, Ba, Se, Zn, Ag, Hg, As and Cd) was analyzed. Ettringite may interact with a number of these ions in both the columnar and channel sections of the crystal structure. Immobilization mechanisms for CSH include sorption, phase mixing and substitution. For heavy metals, the main factors in the immobilization process are pH, chemical speciation of metal, and redox potential control. Regarding organic compounds, immobilization can occur through reactions that destroy or alter organic structures or through physical processes such as adsorption and encapsulation.

An overview of the large body of recent research in the field of S/S methods applied to incineration residues (fly ashes and/or APC residues) is indicated in Tables 5–8. In addition, many more processes can be found in patents (Derie, 2000; Cartier et al., 1998; Sasae et al., 1996; Nicholson, 1978).

An analysis of the most frequently studied methodologies suggests that four groups can be formed:

- (1) Chemical stabilization (Group A) – with the addition of chemical compounds aiming at fixing the toxic species, Table 5;
- (2) Chemical fixation and solidification with binders (Group B) – in order to take advantage of Group A with those properties obtained when binders are used, Table 6;
- (3) Solidification with binders (Group C) – mainly using Portland cement of different types, involving the replacement of some amount of cement by other materials with a similar effect but lower price, Table 7;
- (4) Miscellaneous (Group D) – all other strategies (polymer-concrete, carbonation, aging, etc.), Table 8.

Van de Laar et al. (1994) present a study resulting from a project that involved five companies with different treatment strategies. The methods entail processes of 1, 2 or 3 steps, with or without chemical additives (silicates or others), with or without cement or thermal treatment. This study revealed that with the exception of chlorides, the immobilization of most toxic elements is possible through S/S processes.

From the literature, it is clear that nowadays the most dynamic research area is in the field of solidification with binders, using in particular Portland cement. In practice, at the industrial level in Europe, this is indeed the most important method for treatment of APC residues. It should be emphasized that the main disadvantages of

Table 6
Treatment of APC residues by S/S processes – chemical fixation and solidification with binders (Group B)

S/S	Residue	Objective/methodology	Conclusion	Reference
Cement and stabilizing agents	APC	Comparison of treatments with commercially stabilizing agents and cement. It is tested a solidifying powder (SFPA -mixture of inorganic agents). The residue is mixed with SFPA and pelletized in spheres	By using SFPA (Sumitomo Fine Powder Agent) the heavy metals can be immobilized. No toxic gases are formed during the chemical treatment	Kawakami et al. (1996)
Cement, Al ₂ (SO ₄) ₃ , Ca(OH) ₂ , coal fly ash	ESP	Treatment of fly ash for minimizing the geo-environment impact	The stabilized residue with cement and coal ash can be used for embankments	Kamon et al. (2000)
Stabilization with sodium sulphide and thiourea	FF	Development of a cost-effective stabilization process by chemical immobilization. Sodium sulphide, thiourea, sodium hydroxide, and ethylenediaminetetraacetic acid were used. The solidification effects of these chemicals were compared with those of cement and asphalt	Chemical stabilization processes, in particular by using sodium sulphide as the chemical agent, are strongly recommended, having advantages in terms of the low volume expansion and environmental safety of the stabilized products and cost balances. A combination of chemical stabilization and cement or asphalt solidification for fly ash is proposed	Youcai et al. (2002)
S/S with cement and with silica	APC	Comparison of immobilization of APC residues with different cements (CEM I 42.5, CEM I 52.5, CEM II 32.5, CEM III/A 32.5, CEM III/B 32.5, CEM III/B 42.5, CEM III/C 32.5) and with different silica-containing materials: pyrogenic silica –aerosil, micro-silica, waterglass, aluminosilicate, bottom ash and glass	The Pb leachability was reduced 3–50 times on the type and amount of cement used and on the curing time. The Pb leaching limit for landfilling (2 mg/L) could not be achieved for samples treated with cement. With silica-containing materials, that limit could be reached. The physical immobilisation of Pb is better in case of the cement-treatment than with micro-silica	Geysen et al. (2004b)

Table 7
Treatment of APC residues by S/S processes – *solidification with binders* (Group C)

S/S	Residue	Objective/methodology	Conclusion	Reference
Reactive calcium aluminates	ESP	Analysis of the hydration reactions taking place when the waste is stabilized and immobilized by reactive calcium aluminates. The new phases formed and the fixation mechanisms of SO_4^{2-} , Cl^- and heavy metals were investigated	The reactive calcium aluminates allow to fix heavy metals, SO_4^{2-} and Cl^- in hydration products. The formation of ettringite and Friedel's salt leads to fixation of toxic anions and cations. These aluminates can be the first step for solidification and fixation and can be followed by the addition of other binders	Auer et al. (1995)
Portland cement type I; blast furnace slag; superplasticizer	ESP	Statistical analysis of physicochemical properties of monoliths solidified with ASTM Type I portland cement alone; a partial replacement of Type I portland cement by powdered water-quenched blast furnace slag, by addition of Polymer SP (a superplasticizer) to cement, and by concurrent replacement of cement by slag and addition of Polymer SP	The results of analysis of variance showed that the weight ratio of water-to-binder(s) is the most important parameter for the compressive strength. The weight ratio of ESP to binder(s) is also important to the values of unconfined compressive strength, leaching toxicity, and acid neutralization capacity of some solidified specimens	Yang and Chen (1996)
Portland cement (ASTM type I)	CA+SDS or DS+FF	Study of the effects of the chelate EDTA addition on properties of cement-solidified municipal incinerator fly ash	EDTA does not have a significant effect in solidification process with cement. The Portland cement alone is capable of stabilizing the heavy metals contained on APC residues. The use of EDTA alone only slightly reduces the leaching of the residue	Yang et al. (1998)
Washing + Portland Cement ASTM Type III	Fly Ash	Optimization of the S/S process of cement based matrices. The washing process comprehends two stages (water at a liquid/solid ratio of 25, for 15 min for each stage). After each mixing step, the fly ash was filtered and dried in an oven at 105 °C	Washing treatment is a suitable means of improving the setting time of ash–cement mixtures. For untreated fly ash the quantities used should not be higher than 35% by weight, while after washing up to 75%–90% can be treated. A reduction of the S/S treatment cost by about 50%–63% can be achieved through pre-washing	Mangialardi et al. (1999)
Pozzolanic Cement type IV/A 42.5	ESP	Analysis of the influence of the residue on the S/S processes with cement paste, in particular of the hydration behaviour The hydraulic binder is pozzolanic cement formed by mixing ordinary portland cement (OPC) and an Italian natural pozzolan	The ESP provokes in the first curing period the slowing of hydration reactions of calcium silicates of cement and formation of gypsum and ettringite. With the increase of the fly ash on the mixture there is a lengthening of the period in which the hydration reactions of the calcium silicates are inhibited	Ubbriaco and Calabrese (1998, 2000)
Portland cement (type I)	FA APC	Treatment through S/S, and in particular study the durability of matrices as a function of carbonation	APC residues showed a rapid setting velocity in comparison with FA residues. Leaching test showed that heavy metals (Zn, Pb, Cd) and sulphates are immobilised within the paste, whereas chlorides are partially retained. The carbonation process increases the leachability of SO_4^{2-} , Zn, Cr	Alba et al. (2001)
Ordinary Portland cement class 42.5R (OPC)	ESP APC (FF; ESP)	Analysis of the relation among chemical composition of municipal solid waste incineration (MSWI) FA and its effect on cement hydration	The setting and hardening are strongly dependent on the technology used for flue gas treatment downstream of the combustion chamber. The mechanical properties of the stabilized residue could not be predicted based on the effect of heavy metals and anions	Polettini et al. (2001)

treatment with cement are related with the significant increase in the mass (almost double) disposed of, the low retention of salts, which may leach out in the short term, the possible release of heavy metals in the medium to long term, and finally the problem of the monolith formed at the landfill site that will hardly ever be used again. The main advantages come from the fact that this technology is well established and low cost. To our mind, it is advisable to remove the salts before adding the binders, whenever possible. The use of chemical additives may also be appropriate for solving some specific problems,

such as when the residue contains high quantities of a specific toxic element.

4.3. Thermal methods

Some thermal methods have also been considered for APC residues in order to obtain a material that is environmentally stable. In fact, these processes may result in a significant reduction in waste volume, requiring less space when the option is landfilling. On the other hand, the leaching processes are strongly reduced since the porosity of the

Table 8
Treatment of APC residues by S/S processes – *miscellaneous* (Group D)

S/S	Residue	Objective/methodology	Conclusion	Reference
Polymers (LDPE, PS, PVC) concrete double matrices	APC	S/S evaluation by using polymers through co-rotating twin-screw extrusion Retention properties of the polymers were compared with the concrete ones and polymer-concrete double matrices	The retention of pollutants follows the order: polymer-concrete > PVC > LDPE > two polymer blends > three polymer blends > concrete. This study shows that plastic waste can be used for fly ash solidification, being then the cost lower than by using only cement	Massardier et al. (1997)
Solidification with water	APC (ESP+BF+DS)	Investigation of the solidification with water as a method of treatment. The influence of the amount of water, time, and temperature to mechanical strength of solid material was studied	By adding water to APC residues, cementitious reaction can be initiated, leading to solidification. The compressive strength is dependent on the time and temperature, and on the interaction between water addition and time. The leaching processes are not diffusion controlled	Todorovic et al. (2003)
Carbonation	APC BA	Assess the effect of carbonation on the demobilization of critical components from the compacted residues	Carbonation proved to be an ineffective method for stabilize Cl^- and SO_4^{2-} . Carbonation was more effective in demobilising critical components in BA than in APC residues Reducing conditions may contribute to stabilize of Cr and Se in these residues	Todorovic and Ecke (2006)
Carbonation	BF	Assess the potentialities and limitations of adding CO_2 to fly ash as a stabilization method. Carbonation factors that were studied are the partial pressure of carbon dioxide, the addition of water, the temperature, and the reaction time	The carbonation is a good treatment for stabilization, especially with respect to Pb and Zn. The main factors were the partial pressure of CO_2 and the reaction time, while temperature and the addition of water were of minor influence	Ecke (2003)
Aging	APC	Study of the effect of water content on the aging processes, at a liquid to solid ratio (L/S) of 0.25 or 10, and with or without contact with ambient air	The releasing of Pb, Zn, Cd, Hg, and Cu decrease with age and Cr increase. For $L/S = 10$ controlling step is the dissolution and diffusion of CO_2 in the bulk solution. When $L/S = 0.25$ the limiting step is the dissolution of metals from ash particles	He et al. (2006)

produced material is very low. Due to the high temperatures used, these methods are very efficient at destroying dioxins, furans and other toxic organic compounds (Sakai and Hiraoka, 2000). In fact, the number of vitrification plants in Japan increased significantly when dioxins had to be taken into account, according to the criteria of *specialty controlled waste* established in 1999 (Jung et al., 2005). The final material has been considered suitable for reuse in practical applications, due to the fact that those thermal processes lead to the incorporation of elements of concern in the glass matrix through chemical bounding and/or encapsulation. In addition to the processes described, the reaction of CaO(soluble) to CaO (insoluble) at high temperatures leads to a decrease in the pH value and therefore to a change in the solubility of heavy metals.

In general, thermal methods can be divided into three groups (IAWG, 1997), Fig. 5:

- (1) Sintering – the temperature is increased until the chemical species of interest can achieve a reconfiguration. Usually the temperatures involved in this process are in the range of 900–1000 °C, and a denser product is obtained;
- (2) Vitrification – the material is melted with additives (glass precursors) in order to fix the contaminants in the final matrix (alumina-silicates). The temperatures involved are 1100–1500 °C and the material is

cooled to form a single solid phase (amorphous and homogeneous). Since the method is expensive, this treatment is not generalized for APC residues;

- (3) Melting (or Fusion) – although the process is similar to vitrification, in this case no additives are used, and the glass formed may not be homogeneous. Therefore, the product obtained can be used as a construction material, for example, as a sub-base in road construction or for pavements (Ecke et al., 2000). Sakai and Hiraoka (2000) divided the melting systems into two groups: fuel-burning melting systems and electric melting systems, and it is possible to subdivide each one further, as indicated in Fig. 8. At present, it is not clear which system is the best. In general, for large incinerators with a power generation facility, the electric melting systems may have advantages, since they can use the recovered electric power. In the case of small incinerators without power generation, the fuel-burning melting system may be preferable.

Kinto (1996) points out that, when the APC residues have significant quantities of unreacted lime, the melting process can be difficult because of the high flow point. It is important to note that during these thermal treatments, new fly ashes (dust) are produced which contain larger amounts of volatile species such as Hg, Cd, Pb, S, Cl, K, Na and Zn. Those elements may form simple salts (*e.g.*,

PbCl₂, ZnSO₄), and are then highly leachable. Therefore, these new residues are also hazardous, and require further treatment. Eighmy et al. (1998) showed that an efficient method for those hazardous ashes could be treatment with soluble phosphates, as that process is particularly efficient for Cd, Cu, Pb and Zn. The main phases formed are minerals such as Zn₃(PO₄)₂ and apatites such as Pb₅(PO₄)₃Cl. In fact, the use of soluble phosphates effectively transforms soluble metal salts into insoluble metal phosphate phases. Some of the separation techniques referred to earlier may also be applied to these ashes.

Tables 9–11 provide an overview of the recent literature in the field of thermal treatments (melting, vitrification and sintering) applied to incineration residues (fly ashes and/or APC residues). Moreover, many patented processes are well established for thermally treating the residues under analysis (Albus and Santora, 2003; Mechtersheimer,

2001; Swithenbank, 2000; Mechtersheimer and Wieckert, 1998; John, 1995; Harada et al., 1992).

The main conclusion is that, through these thermal treatments, an environmentally stable material can be produced for which applications may be easily found, including use as secondary raw material. The most important drawback of this process is the high cost that may be involved, due to the high power input required. It is important to stress that thermal processes constitute one of the best methods of destroying highly toxic trace organic compounds (e.g., dioxins and furans).

4.4. Combined methods

A possible strategy for the treatment of the residues produced during MSW incineration involves the combination of separation methods with S/S and/or thermal treatments.

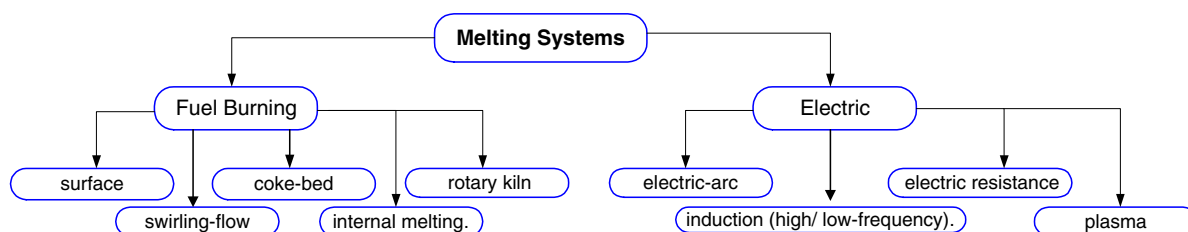


Fig. 8. Classification of melting systems (based on Sakai and Hiraoka, 2000).

Table 9
Treatment of APC residues by thermal (melting) processes

Thermal	Residue	Objective	Conclusion	Reference
Melting (rotating surface melting furnace)	FA (ESP)	Ash melting treatment	Fly ash melts without any additive at a temperature of 1280–1330 °C, being 88% of the residue converted to slag and 12% in dust (new fly ash). From the 10 ng TEQ/g of dioxins present in the residue, 99, 98% are destroyed. The produced slag is safe for the environment and adequate to be used for ceramics	Abe et al. (1996)
Melting (arc system)	FA BA	Overview of ash melting systems (by arc processing) and reuse of materials produced. Five plants are operating in Japan, and two were under construction	Melting FA mixed with BA is feasible, having lower melting point than only FA. Recycling of slags is possible for civil construction. The condensate dust contains high amounts of Pb and Zn and requires stabilization or separation methods	Kinto (1996)
Melting	FA	Overview of the melting technologies in Japan	Stable and non-toxic materials were obtained through melting processes, and the melted slag can be used as a resource. The PCDDs/PCDFs in residues are decomposed at the operating temperatures and the volatile heavy metals are concentrated in the fly ash of the melting process	Sakai and Hiraoka (2000)
Melting (fuel burning by rotary kiln)	FA	Development of a technology to crystallize melted slag (which has low strength) into higher strength stones	Good quality stones were produced and safe applications can be considered. Dioxins present in ash were 99.9% destroyed. Effective applications were tested for the produced stones as aggregates in pavement blocks and asphalt applications	Nishida et al. (2001)
Melting (several types of processes)	FA BA	Study of the metal behaviour in ash-melting and municipal solid waste (MSW) gasification-melting facilities	The behaviour of metals is mainly determined by its volatility. The chlorine content in feedstock can have a significant effect on Cu but not on Pb. The behaviour of Zn is influenced by the oxidizing condition in the furnace	Jung et al. (2005)

Some experimental studies have shown that some synergies can be obtained by taking advantage of each of the selected methods. In Table 12 some examples are given of such studies found in the literature. The main aspects that should be considered are, firstly, the fact that removing the soluble salts is advantageous and, secondly, that chemical stabilization can improve the results obtained through S/S or thermal methods, which generally aim to fix heavy metals.

5. Possible applications

Even though the treatments described above can be very effective at fixing the various potential toxic components of APC residues, another question is raised, namely what to do with the treated residue. Naturally, it would be better

to find a practical application than merely dump the material in a landfill site. To obtain a valuable product (according to Fig. 2), two strategies may be applied: either treating the residue in order to improve some of its characteristics and then producing a final product, or obtaining the final product directly.

According to Ferreira et al. (2003), nine potential applications were identified in the literature for incineration residues, which can be 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). The authors conclude that there is no evidence for selecting one particular application above the rest. On the other hand, although pre-treatment of the residue may increase the cost

Table 10
Treatment of APC residues by thermal (vitrification) processes

Thermal	Residue	Objective	Conclusion	Reference
Vitrification	ESP	Analysis of the vitrification process with plasma. In some cases, the addition of silicates and fusing agents) were used	The vitrification with a plasma technology is adequate for ESP from MSW. The obtained slags are inert and the heavy metals are fixed in the silicate matrix	Mugica et al. (1995)
Vitrification	FF	Demonstration of the vitrification of fly ash by swirling-flow furnace	The treatment is effective on reducing the volume, detoxification and stabilization of FF. A new technique for improving the quality of the slag and heavy metals recovery was developed	Ito (1996)
Vitrification	FA BA	Metal recovery from fly ash generated from vitrification processes (at 1350 °C). The process consists of pre-treatment, leaching, sulfurization and waste water treatment	Heavy metals (Pb, Zn, Cd) are concentrated into vitrification FA. Almost 100% of toxic heavy metals in vitrification FA can be recovered by chemical treatment and a detoxified FA is obtained	Izumikawa (1996)
Vitrification	FA	Studies in a pilot plant of vitrification with plasma in order to establish if it is possible to produce a slag that comply with the Dutch regulation for building materials	The VITROARC® process produces a slag material that complies with category I for almost all elements. In most cases well below the limit value. The slag is also tested according to German, Austrian and Swiss regulations and fulfils for disposal as inert material	Haugsten and Gustavson (2000)
Vitrification	FA	Study of the influence of composition variations of FA on the degree and kinetics of the vitrification and crystallization in the vitrified material	The composition of FA is very important on the degree and kinetics of the process of vitrification. The vitrification increases when the alkali content increases and as the silicon content decrease. Gehelinite can crystallize in high quantities giving a rock-like appearance	Frugier et al. (2002)
Vitrification	ESP	Vitrification of ESP at 1500 °C during 30 min by adding 5% of SiO ₂	The glass formed has a Vickers hardness of 4000–5000 MPa, bending strength of 60–90 MPa, and a significant leaching resistance. Therefore, vitrification is an effective treatment method	Park and Heo (2002a)
Vitrification	FA	Analysis of the metal behaviour during vitrification of incinerator ash in a coke bed furnace. Incinerator ash, coke, and lime were mixed at a ratio of 10:2.5:1, and melted at 1600 °C	Vitrification proved to be a useful technology for disposal of MSW incinerator ash. Metals with low boiling points (As, Cd, Hg, Pb, Zn) are volatilized and adsorbed in the fly ash, allowing safe reuse and recovery of metals in those fly ashes	Kuo et al. (2004)
Vitrification	APC BA	Convert (at 1450 °C for 1.5 h) a residue into a useful product, such as a material for construction	By increasing the bottom ash or cullet amounts added to the fly ash, the specimen basicity is decreased, leading to a more amorphous glassy matrix. The vitrification allows a volume reduction over 50%, and the slags have small porosity, low water absorption, high compressive strengths and are in compliance with the regulatory limits	Li et al. (2003b)

Table 11
Treatment of APC residues by thermal (sintering) processes

Thermal	Residue	Objective	Conclusion	Reference
Sintering/ Vitrification	ESP	Study of the binding of heavy metals in thermally treated ESP residues. Several temperatures were tested (400, 600, 800, 1000 and 1400 °C) for two hours in air	Thermal treatment leads to inertization for Zn, Cd, Pb, Cu, with the exception of Cr and Ni. Only for Cu vitrification (1400 °C) reveals higher inertization than sintering. The enthalpy of the solid/liquid transition is the decisive factor for choosing the thermal treatment, and sintering at high temperatures could be better than vitrification	Wunsch et al. (1996)
Sintering	CA	Study of the sintering process at various conditions, concerning the compact pressure, sintering temperature and time	The strengths of the material produced during sintering increase as the temperature rises from 1120 °C to 1140 °C, but decreases with an increasing ignition loss of CA. The heavy metals are fixed in the sintered material, and a ceramic-like solid with low metal leachability is obtained	Wang et al. (1998)
Sintering	CA	Thermo-treatment of the residue for obtaining aggregates. The temperatures tested were from 400 to 1000 °C, during 1–4 h	The sintering process provides an effective alternative for the treatment and recycling of MSWI fly ash. The compressive strength of cylinder sintered at 800 °C for more than 0.5 h, was greater than 68,5 MPa. The Cr can be converted in more extractable compounds after thermal treatment. The heavy metals released by leaching tests were in compliance with the current thresholds of legislation	Wang et al. (2002)
Sintering	ESP	Study of the Cr behaviour during thermal treatment. A mass of 0.5 g was preheated in a muffle furnace at 990 ± 10 °C for 1 h	Thermal treatment of fly ash was used to remove volatile metals such as Pb, Cd and Zn, but not Cr. After thermal treatment at 990 °C for 1 h, the leachable Cr was increased to about 12% of the Cr content. A mechanism explaining the increased solubilization was proposed	Kirk et al. (2002)
Sintering	FA	Investigate the continuous sintering behaviour of FA in a rotary kiln and reduce the concentrations of heavy metal to tolerable value	The sintering treatment in a rotary kiln can be fitted to incinerator plants and operated continuously. Water-washing pre-treatment is an effective process for decreasing both the sintering temperature (700–900 °C) and time, removing chlorides from FA	Wey et al. (2006)

and may create new problems, it is advantageous for most applications. Romero et al. (2001) identify several applications for this waste, mentioning particularly building materials, catalysts, refractories, pozzolanic materials, glasses and glass-ceramics. Mohapatra and Rao (2001) review some aspects related to the use and environmental effects of fly ashes in general, resulting from the burning of municipal solid waste, fossil fuel, coal, etc. Reijnders (2005) discusses disposal practices, uses and treatments for combustion ashes (from coal, wood, agriculture residues, MSWI, etc.), taking into account the associated pollution, which is mainly provoked by leaching processes.

Some of the applications that have been researched for cement or concrete materials are shown in Table 13, for ceramic or glass-ceramics in Table 14, and other applications such as chemical conditioner for sludges and zeolites in Table 15, indicating where possible the type of ash tested. A possible classification of tested applications for FA/APC residues from MSWI, in accordance with some of these recent studies, is indicated in Fig. 9.

Among possible applications, ceramic or glass-ceramic materials could be a good option, and indeed, some patented processes may be found (Talmy et al., 1996). Our research group is involved in a project to assess the possibility of producing lightweight aggregates (LWA) from

APC residues. Although the APC residues do not improve the technical properties of LWA, the results obtained show that when the amount of waste used is lower than 3% (wt), or for the case of pre-washed residues lower than 5%, the aggregates produced may have acceptable commercial properties. The amounts released through leaching processes for inorganic species are very low, and so the environmental impact is not significant.

The production of synthetic aggregates from combustion ashes has also been assessed in other research studies where several types of waste were tested (Wainwright and Cresswell, 2001). Concerning cement/concrete applications, the APC residue has limited performance, mainly due to the deleterious effect of the soluble salts, and in particular due to chlorides and sulphates. Moreover, the presence of materials such as aluminium may cause expansion due to the release of hydrogen; the ferrous metal can provoke staining of concrete; and soluble lead and zinc salts may interfere with the setting of cement. Ampadu and Torii (2001) state that the ecocement produced is designed to take advantage of the amount of chlorides in the incinerator ashes in order to obtain rapid-hardening cement. During the sintering process, chloride combines with calcium aluminate to form calcium chloroaluminate in place of tri-calcium aluminate. The performance of ecocement

Table 12
Treatment of APC residues by combined methods (separation, S/S and/or thermal)

Methods	Residue	Method/ Objective	Conclusion	Reference
Chemical (phosphate) Thermal (calcination)	APC	(i) Mix the residue with water ($L/S = 2$) and 2% of $\text{Ca}(\text{OH})_2$ and 6% of H_3PO_4 during 30 min at room temperature (ii) Filtration and drying at 60 °C. Calcination of the solid at 900 °C in a muffle	By combining both chemical and thermal treatments, an efficient stabilization of metals is found. The phosphate treatment reduces the heavy metals solubility, and calcination allows apatite crystallization without evaporation of heavy metals	Iretskaya et al. (1999)
Separation (washing) S/ S (Portland cement ASTM Type I)	ESP	<i>Washing process:</i> (2 stages with water, L/S ratio = 25, 15 min). The wastewater treatment is done by reducing of the pH and precipitating aluminium ion as metal hydroxide. The Cd, Pb and Zn are adsorbed onto flock particles of aluminium hydroxide <i>S/S process:</i> The sludge and washed residues were incorporated into cementitious materials (75 wt.%)	The combined washing and S/S process is an appropriate method of optimizing the disposal of this material in cementitious matrices. Washed fly ash is transformed into a material that adversely affects cement hydration to a much lower extent than unwashed fly ash	Mangialardi (2003)
Separation (washing) Stabilization (phosphate) Thermal (calcination) S/S(cement)	FA	A four stages treatment: (i) water extraction during 1 h (water:solid wt ratio 8:1) for removing alkali chlorides. Filtering and washing the cake with 2 part of water (ii) addition of a moderate quantity of phosphoric acid (10wt% H_3PO_4 – based on dry material) (iii) calcinations up to 800 °C in a oven, during 1 h (iv) solidification with Portland clinker or cement, for cement: ash ratios as low as 1:4	The principal advantages of the process are: the PCDD/PCDF destruction, the reactivity of the heavy metals is much lower, the final solids have satisfactory mechanical properties, and the increase in weight of the waste to be disposed of does not exceed 1/4	Derie (1996)
Separation (washing) Stabilization (phosphate) Thermal (calcination)	FA	A three stages treatment: (i) water extraction (water:solid wt ratio 2:1) in a stirred tank reactor of 10 L capacity; (ii) $\text{Ca}(\text{OH})_2$ (20 g) and 60 g of H_3PO_4 were added. The suspension was stirred for 30 min and then filtered with a filter-press. (iii) The filter cakes were air-dried in an oven at 60 °C and calcinated under air atmosphere at 900 °C in a muffle furnace	The alkali chlorides can be extracted by combining a calcium phosphate gel precipitation. NaCl and KCl can be obtained free from calcium salts, and the metals are immobilized in the calcium phosphate matrix. The calcination allows the formation of crystalline hydroxylapatite, which may trap toxic metals and prevent their evaporation during thermal treatments	Nzihou and Sharrock (2002)
Stabilization (iron oxide) Thermal (calcination)	APC ESP	The treatment consists of: (i) APC residues were washed in a FeSO_4 solution at a $L/S = 5$ (2.5–5gFe/100 g residue). (ii) The solids were filtered and dried at 50 °C. (iii) Bottom ash and dry iron-oxide-treated residues were mixed in a mass ratio of 9:1. (iv) Heat treatment occurs at 900 °C for 45 min (in a furnace with a static air atmosphere or in a tube furnace with a flow through of nitrogen).	During washing treatment iron hydroxides precipitate and Fe(II) was oxidized by oxygen supplied from atmosphere due to stirring and bubbling over 24 h. The sintering of the particles did not occur, but the process fixes the metals in the solid residue. This method of treatment produces a material that can be used as secondary road construction material	Sorensen et al. (2001)

is similar to the rapid hardening cement, but contains larger quantities of chlorides. Unlike the bottom ash produced during municipal solid waste incineration, which may be used under some circumstances for agricultural purposes (Zhang et al., 2001, 2002), APC residues are not recommended for this application due to their high concentration of heavy metals.

6. Conclusions

The main objective of this work has been to review possible management strategies, treatments and applications

of APC residues produced during MSWI processes. These types of residues may be produced in units such as heat recovery systems – boiler, superheater and economiser, electrostatic precipitators, fabric filters or baghouse, through dry scrubbing, semi-dry scrubbing or wet scrubbing, or cyclone. From the literature analyzed, some conclusions may be drawn:

- these residues are in general considered hazardous waste, which means that they should not be used directly as raw material in environmental applications, and should be properly treated before landfilling;

Table 13
Practical applications for valorization of APC in cement or concrete materials

Product	Residue	Process/Conclusions	Reference
Eco-cement	FA	This study refers the characterization of ecocement pastes and mortars produced from incinerated ashes. The technology for manufacturing ecocement was developed by <i>New Energy and Industrial Technology Development Organization</i> (NEDO) of Japan. The ecocement is produced similarly to the normal Portland cement by using up to 50% of municipal waste incinerator ashes	Ampadu and Torii (2001)
Cement	ESP FF	Recycling these residues is possible through cement production. In a pilot plant, with a capacity of 50 tons/day) 0.5 ton of incineration ash, 0.3 ton of dry sewage sludge and 0.3 ton of limestone were converted to 0.85 ton of cement clinker. By adding 0.15 ton of gypsum to the clinker, 1.0 ton of cement can be produced. It should be noted that an adequate treatment of the waste is able to fix the chlorine through calcium-chloroaluminate formation. The quality of the resulting cement is sufficient to enable the practical use, and no secondary pollution was produced	Kikuchi (2001)
Concrete (cement replacement)	APC (WS)	This study is centred on the analysis of the effects of the incorporation of APC ash in cement pastes and mortars, by replacing cement with up to 20% MSWI fly ash. XRD analysis revealed Friedel's salt, ettringite and thenardite resulting from the presence of APC. The waste may increase mortar setting times and the compressive strength. Strength reductions in the longer term (after 565 days) were observed in all the mortars containing MSWI fly ash. The diffusion coefficients of cement pastes containing MSWI fly ash were similar to the pure cement pastes	Rémond et al. (2002a,2002b)
Cement replacement	CA	The MSWI fly ashes were melted at 1300–1500 °C in an electrically heated furnace to obtain slag samples, which were water-quenched and further pulverized. Such slag could be recovered in a more valuable form as a cement replacement than as a roadbed aggregate	Wang et al. (2001)
Cellular mortar	FA from fluid sand furnace	The considered FA can be used for producing cellular mortar because a significant content of aluminium, lime, sand and anhydrite is present. A mortar with 0.74–1.09 kg/m ³ and a compressive strength of 3.9–8.5 N/mm ² was produced in laboratorial experiments. This application tries to explore the advantage of the high quantity of aluminium that is present in the FA	Alaejos and Leiro (2003)
Aggregates for concrete	FA	After treatment (Revasol process: washing, phosphation and calcinations) the stabilized waste can be used in concrete as aggregate. From mechanical and durable points of view, the ash incorporated in the concrete behaves similarly to ordinary sand. The leaching testes show that the process makes it possible to obtain materials without major risks for the environment	Aubert et al. (2004)
Aggregates for concrete	FA	A washing pre-treatment was applied to FA for removing sulfates and chlorides ($L/S = 10$, mixing during 20–30 min, settling for 24 h, filtration and drying solids at 105 °C for 24 h). In the S/S treatment, cement, lime, sodium silicate, bentonite, blast-furnace slag, and water dosage of 30–40% was used, and involves homogenization during 15 min and a curing phase during 15–20 days. The stabilized waste was ground (<1.5 mm) and the concrete is prepared with these aggregates	Collivignarelli and Sorlini (2001)
Cementitious building materials	FA	The FA of an incineration process, which previously separates metals, batteries, glass and ceramics were used to produce cementitious building materials. The considered FA exhibits pozzolanic action	Gerdes and Wittmann (1994)
Blocks and pavement bricks	FF + BA	Producing permeable blocks and pavement bricks from molten slag made by a surface-melting furnace. The raw material is a mixture of bottom ash and bag house ash in a ratio of 3:1. This study shows an effective way of re-use of incineration residue slag and fly ash	Nishigaki (2000)
Aggregate for concrete	ESP	A four-stage washing treatment (stirring; $L/S = 50$; mixing time = 30 min for each stage) was used for removing the water-soluble compounds almost completely. A compact pressure of 28 N/mm ² is used in order to obtain cylinders of 1.5 cm in diameter and 2 cm in height, which are sintered at 1140 °C for 60 min. The sintering of untreated MSW fly ashes proved to be unreliable	Mangialardi (2001)
Asphalt for road	FA	The use of FA as filler in asphalt for road construction, is technical and environmental acceptable	Hundales (1994)
Marine applications	ESP BA	The maximum quantity used is about 35% and a grinding phase is necessary	Hjelmar et al. (1994)
Base layer for roads	APC + FA treated (Ferrox-process)	Marine applications of ESP and BA can be acceptable for locations with scarce land space (e.g. Bermuda). The testes should include sampling and characterization of waste, laboratory leaching testes, analysis of acute and chronic toxicity, baseline studies, establishment of acceptance criteria; modelling of the release of contaminants and assessment of environmental impact	
		The ashes were washed in a ferrous sulphate solution and afterwards aerated to transform the precipitated ferrous hydroxide into ferrihydrite (high capacity for binding the heavy metals). After blend 50 kg of cement, 80–100 L of water, 2150 kg of gravel or 1800 kg of aged BA and 110 kg of Ferroxx-treated ash, the mixture was cast into 150-mm cubes that were sealed and cured at 20 °C. The obtained product would provide a base layer suitable for roads with the required strength	Cai et al. (2004)

Table 14
Practical applications for valorisation of APC in ceramics or glass–ceramics

Product	Residue	Process/conclusions	Reference
Lightweight aggregates	APC (SDS; FF)	The utilization of APC residues for producing lightweight aggregates is possible, if the quantities involved were lower than 5% or if the residue was previously washed. The incorporation of APC residues for producing lightweight aggregates exhibit slightly higher densities, but the material can be considered as environmental stable and safe	Quina et al. (2003)
Ceramic tile	FA	FA is used as a blending in production of ceramic tile by taking advantage of the high content of SiO ₂ , Al ₂ O ₃ and CaO. The results showed that the use of FA in this application constitutes a potential means of adding value	Haiying et al. (2007)
Brick	CA	Brick were heated to temperatures in the range of 800 to 1000 °C, for 6 h, with a heating rate of 10 °C/min. The results indicated that the residue is suitable for the partial replacement of clay in bricks	Lin (2006)
Glass and glass–ceramics	FA	A high frequency induction furnace was used for melting 3.5 kg of FA during 20 min at 1400 °C. After quenching, the glass was ground to < 149 µm and pressed at 11.8 MPa into 4 × 1.5 × 0.7 cm mould. The formed green bodies were sintered for 2 h at 850, 900, 950, 1000 and 1050 °C, being possible to produce glass-ceramic products. The crystallization takes place above 700 °C, and the glass-ceramic has optimum physical and mechanical properties when the sintering occurs at 950 °C for 2 h. This material has good characteristics to manufacture lightweight aggregates or bricks	Cheng and Chen (2004)
Glass–ceramics	FA	FA was vitrified in an dc arc plasma furnace at 1600 °C, followed by cooling. Crystallization was performed at 850, 900, 950, 1000 and 1500 °C for 2 h and cooled at 5 °C/min. This process yields a glass–ceramic product with outstanding properties (mechanical and chemical durability)	Károly et al. (2007)
Glass–ceramic	FA	By washing FA during 48 h it was possible to remove large amounts of chlorides, and to reduce in 100 °C its melting temperature. The glass was prepared by melting the washed fly ash at 1450 °C for 3 h. The glass was poured and heated at 950–1050 °C for 0.5–4 h to produce the glass-ceramic. It was found that the glass-ceramic has reliable properties for produce structural materials	Kim and Kim (2004)
Glass–ceramics	FA	The waste was melted in an electric furnace at 1500 °C for 30 min, being then poured onto a cold metal plate. The resulting glass was crushed and sieved to 0.75 µm. Cylinders with 10 mm × 15 mm were produced by cold-pressing at 250 MPa without using binder. Glass-ceramics were prepared by sintering the cylindrical glass compacts in the range 800 to 925 °C, for 4–120 min	Romero et al. (2001)
Glass–ceramics	ESP	By vitrification of the ESP with the addition of SiO ₂ , MgO and TiO ₂ a glass material is obtained in a first stage. Afterwards, a glass-ceramics material is produced, which can be used as a construction material. The optimum heat-treatment procedure for the ceramitization of glasses was 720 °C for 90 min (nucleation) and 870 °C for 10 h (crystal growth). Both glasses and glass-ceramics showed to be stable concerning heavy metals leaching processes with water	Park and Heo (2002b)
Porcelainized stoneware material	FA	The FA, granite muds, industrial feldspar and clay, silica and alumina were mixed and homogenized during 10 min, by using different formulations. Bodies of 20 mm diameter and 5 mm thickness were produced by cold axial pressing at 40 MPa., and heat treated on refractory tiles by using a single firing cycle at a 50 °C/min and held at the maximum temperature (1250 °C) for 6 min. The final materials could be used as a construction material with promising applications	Hernández-Crespo and Rincón (2001)
Diopside-based glass-ceramics	FA	Diopside-based glass-ceramics can be produced by combining MSWI fly ash with SiO ₂ , MgO and Al ₂ O ₃ or bottom ash as conditioner of the chemical compositions and TiO ₂ as the nucleation agent. The method involves melting at 1500 °C for 30 min, nucleating at 730 °C for 90 min, and crystallization at 880 °C for 10 h. The material has strong fixing capacity for Pb, Cr and Cd	Qian et al. (2006b)

- landfilling in a specific disposal site is the most common strategy in Europe and America, although thermal methods are usually preferred in countries such as Japan;
- the main problems with these residues concern the high quantities of soluble salts, the significant amounts of some toxic heavy metals (Pb, Cd, Cr, Zn), and some trace organic compounds (e.g., dioxins, furans);
- possible treatments can be grouped into: separation processes: solidification/stabilization (S/S) treatments, and thermal methods;
- reliable results in terms of treatment and application may be obtained by combining two or more methods, e.g., washing treatment (for removing salts) followed by S/S or thermal methods;
- although washing treatment can generate additional environmental problems, it results in a material that is suitable for further treatment or may have practical applications;
- in order to avoid landfilling, the valorization of the residues has been studied and several applications have been tested. The production of cement by using APC

Table 15
Practical valorisation of APC in miscellaneous applications

Product	Residue	Process/conclusions	Reference
Treatment of a waste sludge	FA	MSWI fly ash may be used as solidification binder to treat heavy metals-bearing industrial waste sludge. The heavy metals-bearing sludge and MSWI fly ash have a strong fixing capacity for Zn, Pb, Cu, Ni and Mn. By using only 5–15% cement content was sufficient to achieve a compressive strength of 0.3 MPa. By mixing 45% fly ash, 5% cement and 50% of the industrial sludge the required solidification and stabilization could be obtained	Qian et al. (2006a)
Zeolites	CA	The synthesis of zeolite-like materials by a hydrothermal alkaline processing is technically possible, which are environmentally safe to use. Experimental parameters studied were the mineralizer concentration, solid/liquid ratio, reaction time and operating temperature. The main drawback is the produced effluent during the synthesis, which may contain high levels of heavy metals (Pb, Zn) and require further treatment prior to discharge	Yang and Yang (1998)
Chemical conditioner for sludges	FA	The addition of fly ash can decrease the specific resistances and capillary suction time of oily sludges up to 3% dosage, during the filtering process. Beyond 3% fly ash, the decrease is less significant and the solids content in the sludge cake increases. The total suspended solids of filtrate decrease with fly ash dosage but the toxic concentrations of heavy metals increases considerably. However at the optimum dosage of 3%, concentrations of heavy metals are within the limits for discharging into the sewers	Tay and Jeyaseelan (1997)

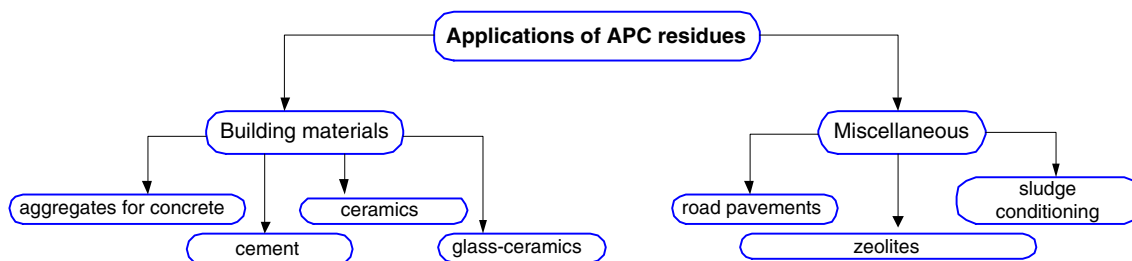


Fig. 9. Applications of APC residues tested in laboratory, pilot scale or industrial plants.

is unlikely to be a good solution due to the high quantities of soluble salts. Thermal treatments can produce a material that is environmentally stable, and may be further used for producing glass-ceramics;

- the production of lightweight aggregates by incorporating APC residues with natural clays is under investigation, and results have so far been promising.

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