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Management of Residues from Energy Recovery by Thermal Waste-to-Energy Systems and Quality Standards

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Abstract

All activities concerning waste handling are highly regulated in most countries. In the European Union a legislative framework has been established by a series of EU Directives which cared already or will in due time care for harmonised integrated waste management systems in the member states. These directives regulate the management of residues from waste-to-energy (WtE) systems, although in this area there are still more national initiatives possible.

This report concentrates mainly on management of residues from waste incineration in grate furnaces, since this technology has by far the widest application. Hence respective residues have well been studied. Fluidised Bed (FB) incinerators are not very common for waste incineration outside Japan and reliable data on their residue quality are rare. Furthermore they need pre-treatment of the waste and have more to be looked upon as refuse derived fuel (RDF) or solid recovered fuel (SRF) combustion plants.

The report covers the main legislative regulations on residues in the EU and the participating countries for the International Energy Agency Bioenergy Agreement's Task 36 on integration of energy into solid waste management. It describes briefly the most important quality parameters and the analytical tools that are generally applied before the single residues are treated with in more detail.

Bottom ashes are characterised, their potential for utilisation is discussed and the respective pre-treatment methods are described. This includes the commonly practiced recovery of ferrous and non-ferrous metals. This recovery is expected to increase in the future, especially the recovery of non-ferrous metals. Bottom ash production data and the amount of utilisation in Europe are listed.

The problem of disposal of filter and boiler ashes is their high inventory of heavy metals, dioxins and water soluble salts. Methods for rendering these ashes inert and their current status are described. An interesting aspect is the new development of Zn recovery from filter ashes, which is also described.

For residues from wet air pollution control (APC) systems recovery processes for Cl as HCl or NaCl have been developed, although their application is limited due to economic constraints and immature markets. Intelligent solutions in combination with the chemical industry may open new opportunities in the future. The recovery of gypsum is more common. Residues from dry scrubbing have to be disposed of. If $NaHCO_3$ is used as neutralising agent, the residues can be used in chemical industry.

Residues from FB combustion of RDF and SRF are only briefly mentioned; the availability of information limits clear statements in this area. More investigations and publication of detailed data are recommended.

Solid residues from WtE systems are in part well understood. However, the increasing application of WtE in industrialised countries means that their management is of growing importance.

Whether utilisation of bottom ashes will expand is difficult to predict; potential risks from heavy metal content may cause limitations. Metal recovery will remain important and will definitely be expanded. This should also be true for metal recovery from filter ashes.

The main question remaining concerns the sink for water soluble salts. Their final destination should be the ocean, but a simple technological solution of this problem is not currently available.

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List of Abbreviations

AAS	atomic absorption spectrometry
AFNOR	L'Association française de normalization (French standardization association)
ANC	acid neutralisation capacity
APC	air pollution control
BTEX	group of benzene, toluene, ethylbenzene and xylenes
c	concentration
CEN	Comité Européen de Normalisation (European Standardisation Committee)
CEWEP	Confederation of European Waste-to-Energy Plants
DepV	Deponieverordnung (German landfill ordinance)
DEV-S4	Deutsches Einheitsverfahren S4 (German leaching test for sludges and sediments)
DIN	Deutsches Institut für Normung (German Institute for Standardisation)
DOC	dissolved organic carbon
ESP	electrostatic precipitator
FB	fluidised bed
IAWG	International Ash Working Group
ICP-MS	inductively coupled plasma mass spectrometry
ICP-OES	inductively coupled plasma optical emission spectrometry
ISO	International Organization for Standardization
KRWG	Kreislaufwirtschafts- und Abfallgesetz (German close cycle economy and waste act)
LFD	EU landfill directive
LAGA	Bund/Länder-Arbeitsgemeinschaft Abfall (German working group on waste)
LOI	loss on ignition
L/S	liquid-solid ratio
MBT	mechanical-biological treatment
MDS	magnetic density separation
MSW	municipal solid waste
MSWI	municipal solid waste incinerator
NCV	net calorific value
NEN	Nederlandse norm (Dutch standardisation)
PAH	polyaromatic hydrocarbons
PCB	polychlorinated biphenyls
PCDD	polychlorinated dibenzo-p-dioxins
PCDF	polychlorinated dibenzofurans
RDF	refuse derived fuel
SEM	scanning electron microscopy
SRF	solid recovered fuel
STEM	scanning transmission electron microscopy
TASi	Technische Anleitung Siedlungsabfall (German technical ordinance for the disposal of waste from human settlements)
TCLP	toxicity characteristic leaching procedure
TDS	total dissolved salts
TOC	total organic carbon

TVA	Technische Verordnung über Abfälle (Swiss waste ordinance)
TRXRF	Total Reflection XRF
UK	United Kingdom
U.S. EPA	Environmental Protection Agency of the United States of America
WID	European waste incineration directive
WtE	waste-to-energy
XRF	X-ray fluorescence analysis
XRM	X-ray microprobe analysis
XRPD	X-ray powder diffractometry

1   Introduction and Scope

Incineration of municipal solid waste (MSW) started in the 1870s in England as a disposal route for residential waste that guaranteed complete disinfection and allowed safe disposal of the inert residues, the so-called grate or bottom ashes (in this report mainly the term bottom ash will be used). From early times the energy released from the combustion process was utilised and in some instances even the bottom ashes were compacted to form bricks for the building sector, e.g. in 1903 in the Frederiksberg incinerator in Copenhagen [de Fodor 1911].

In the wake of 'green' movements in the early 1980s in several European countries waste incineration plants became the subject of public and political discussions concerning their environmental impacts. These resulted in progressively tightened air emission standards in almost all countries and finally, to meet these standards, in the development and implementation of highly efficient gas cleaning systems.

Despite the discussion of potential environmental impacts, from the late 1990s there was increasing interest in energy recovery from MSW. Different routes were followed to optimise the energy efficiency of thermal waste treatment:
- the steam parameters of waste boilers were increased by the use of corrosion resistant wall materials such as Ni base alloys;
- boiler circuits of MSW incinerators (MSWI) were combined with power plants or gas turbines;
- MSW was used to produce waste-based fuels with higher energy and lower pollutants' inventory than mixed MSW.

This last strategy was favoured in many countries. The material was called refuse derived fuel (RDF). Since RDF production was not standardised, its combustion could be difficult due to varying quality. CEN, the European Standardisation Committee, has issued quality standards for such fuel which is now called solid recovered fuel (SRF) if it meets these standards [Frankenhäuser 2011]. The fuel is intended to be burnt in dedicated combustion plants, grate but also fluidised bed (FB) furnaces, equipped with APC systems.

Meanwhile the gas cleaning devices of MSWI plants are among the most effective ones found in any technical process. This development, however, created a new problem: how to care for safe and aftercare-free disposal of APC residues.

Hence the focus has currently changed from air emission quality onto the quality of solid residues and their sustainable - by which we mean aftercare-free - disposal. The actual objectives of waste incineration – apart from the improvement of energy recovery - are
- production of highly inert bottom ashes by adequate combustion control;
- reduction of the amount of fly ashes by adequate primary air control;
- achievement of excellent gas phase and fly ash burnout;
- rendering the boiler and filter ashes inert and safe for disposal or even utilisation; and
- management and safe disposal of the residues from the chemical APC systems.

The following report will briefly discuss
- the amount and quality of the various residues listed above;
- the legal aspects concerning their management, disposal or utilisation; and
- the actual practice in this area in selected countries.

Since the different types of fuel, MSW or SRF, control the amount as well as the quality of some solid residues the report will start with a short chapter describing the properties of MSW and SRF.

2   Properties of MSW and SRF/RDF

The major properties of a fuel are its calorific value, typically expressed as net calorific value (NCV), its moisture and its ash content. Apart from these parameters the inventory of pollutants is of interest in view of complying with environmental regulations.

In the context of this report residues from the combustion of MSW and SRF will be dealt with later, hence few characteristics of these fuels will be discussed in this section. Many data sets of MSW composition have been published which will not be listed here in detail.

The information is different for SRF. The above mentioned CEN standards rank SRF according to its NCV, chlorine (Cl) and mercury (Hg) content [CEN 2011]. Cl is an important in terms of air pollution and boiler corrosion; Hg is the most volatile heavy metal.

For estimating a fuel's combustion properties apart from the calorific value, in particular moisture and ash content have to be taken into account. The ash content is of course the key parameter in determining solid residue formation. These parameters and other heavy metals describing the quality of MSW and SRF but also influencing the quality of residues are compiled in Table 1.

Table 1   Selected quality parameters of Central European MSW and SRF (*: CEN standardisation parameters for SRF) [IAWG 1997, Wilén 2004, van Tubergen 2005, Garg 2007, Vainikka 2011]

parameter	unit	MSW	SRF
NCV*	MJ/kg	8 - 15	15 - >25
moisture	wt. %	20 - 50	1- 25
ash	wt. %	15 - 30	5 - 15
Cl*	wt. %	0.4 - 1	0.2 – 1.5
Cr	mg/kg	40 - 400	2 - 300
Cu	mg/kg	200 - 1000	90 - 500
Zn	mg/kg	600 - 2000	100 - 500
As	mg/kg	3 - 10	0.4 - 18
Cd	mg/kg	5 - 15	0.4 - 14
Hg*	mg/kg	0.5 - 5	0.1 - 5
Pb	mg/kg	400 - 1000	10 - 800

One surprising fact is the Cl level in SRF, which for CEN class CL3 can reach 1 wt. %, which means that it can be higher than that of MSW. This should be expected if SRF is mainly or to a greater extent produced from MSW [Rotter 2004].

Heavy metals can also reach concentration ranges typical for MSW in SRF, which implies that the abatement of volatile metals like Hg and Cd, as well as the quality of ashes, might be of similar relevance for both fuels.

The ash content in SRF is typically kept below 10 wt. % and with that significantly lower than that of MSW. This low ash content has of course consequences for the amount of solid residues.

3   Legislative Framework

3.1   EU Regulations

All waste management has to comply with legislative regulations which are inside the EU based on directives issued by the European Council and the European Parliament. The fundamental directive setting the standards for all EU waste policy was the so-called waste framework directive 1975/442/EEC, issued on July 15, 1975 [European Commission 1975]. This directive has been amended several times and was finally been replaced by the 'Directive 2008/98/EC of the European Parliament and Council of 19. November 2008 on waste and repealing certain directives' [European Parliament and Council 2008].

Another cornerstone in terms of assignment of the various different waste streams to the respective disposal, treatment, or utilisation strategy is the EU waste list, which identifies waste according to its source by a six-digit code [European Commission 2000].

For residue management the most important directive is the EU Landfill Directive 1999/31/EC (LFD) issued in 1999 [European Council 1999]. Its primary goal is to prohibit or at least reduce the disposal of untreated and reactive organic waste on landfills.

The LFD sets targets for reduction of disposal of biogenic waste compared to the situation in 1995:
- 25 % in 2006,
- 50 % in 2009, and
- 75 % in 2016.

Measures to achieve those targets include recycling, composting, biogas production, or materials and energy recovery. The latter option promotes waste incineration as the easiest efficient method combining total destruction of organic matter with energy recovery.

In 2003 the LFD was amended by the Council Decision 2003/33/EC [European Council 2003] which defines classes of landfills for
- inert,
- granular non-hazardous, and
- hazardous waste.

The Council Decision sets respective acceptance standards, together with protocols for sampling and testing. The main standards are organic inventory measured as TOC (total organic carbon) or LOI (loss on ignition), pH value, leaching of metals and other species as well as the inventory of some organic parameters.

Table 2   Limit values for the total content of organic parameters for the acceptance at an inert waste landfill in mg/kg of the material

	value
TOC (total organic carbon)	30,000[1]
BTEX (benzene, toluene, ethylbenzene and xylenes)	6
PCBs (polychlorinated biphenyls, 7 congeners)	1
Mineral oil (C10 to C40)	500
PAHs (Polycyclic aromatic hydrocarbons (total of 17)	Member states to set limit value

(1) In the case of soils a higher limit value may be admitted by the competent authority, provided the DOC value of 500 mg/kg is achieved at L/S 0 10 l/kg either at the soil's own pH or at a pH value between 7.5 and 8.0.

Table 2 compiles the limits of organic parameters for an inert waste landfill and Table 3 summarises the leaching limits for all three types of landfills. The basis for this is the CEN leaching test. L/S stands for liquid solid ratio.

Table 3 Limit values of total release regulating the acceptance of inert materials, of granular non-hazardous waste, and of hazardous waste on respective landfills, calculated at L/S = 2 and 10 l/kg in mg/kg and for c_0 (the first eluate of percolation test at L/S = 0.1 l/kg) in mg/l

	inert waste			*granular non-hazardous waste*			*hazardous waste*		
	L/S=2	*L/S=10*	*c_0*	*L/S=2*	*L/S=10*	*c_0*	*L/S=2*	*L/S=10*	*c_0*
As	0.1	0.5	0.06	0.4	2	0.3	6	25	3
Ba	7	20	4	30	100	20	100	300	60
Cd	0.03	0.04	0.02	0.6	1	0.3	3	5	1.7
Cr_{total}	0.2	0.5	0.1	4	10	2.5	25	70	15
Cu	0.9	2	0.6	25	50	30	50	100	60
Hg	0.003	0.01	0.002	0.05	0.2	0.03	0.5	2	0.3
Mo	0.3	0.5	0.2	5	10	3.5	20	30	10
Ni	0.2	0.4	0.12	5	10	3	20	40	12
Pb	0.2	0.5	0.15	5	10	3	25	50	15
Sb	0.02	0.06	0.1	0.2	0.7	0.15	2	5	1
Se	0.06	0.1	0.04	0.3	0.5	0.2	4	7	3
Zn	2	4	1.2	25	50	15	90	200	60
chloride	550	800	460	10000	15000	8500	17000	25000	15000
fluoride	4	10	2.5	60	150	40	200	500	120
sulphate	560[1]	1,000[1]	1500	10000	20000	7000	25000	50000	17000
phenol index	0.5	1	0.3	-	-	-			
DOC[2]	240	500	160	380	800	250	480	1000	320
TDS[3]	2500	4000	-	40000	60000	-	70000	100000	-

[1] If the waste does not meet this limit value for sulphate, it may still be considered as complying with the acceptance criteria if the leaching does not exceed either of the following values: 1500 mg/l as c_0 at L/S = 0.1 l/kg and 6000 mg/kg at L/S = 10 l/kg. It will be necessary to use a percolation test to determine the limit value at L/S = 0.1 l/kg under initial equilibrium conditions, whereas the value at L/S = 10 l/kg may be determined either by a batch leaching test or by a percolation test under conditions approaching local equilibrium.

[2] If the waste does not meet this value for DOC at its own pH value, it may alternatively be tested at L/S = 10 l/kg and a pH between 7.5 and 8.0. The waste may be considered as complying with the acceptance criteria for DOC, if the result of this determination does not exceed 500 mg/kg for inert waste respectively 800 mg/kg for granular non-hazardous waste.

[3] The value for total dissolved solids (TDS) can be used as an alternative to the values for sulphate and chloride.

The Council Decision 2003/33/EC specifies also the respective methods to be applied for sampling and measuring the various regulated parameters.

Another directive relevant to residue management is (to a limited extent) the Waste Incineration Directive 2000/76/EC (WID) of 2000, which addresses waste incineration and co-incineration of waste or waste derived fuels like SRF in industrial furnaces and utility boilers. Aside from its main topic, the regulation of emissions to air, it contains general instructions for residue treatment and plant operation.

3.2 National Regulations

3.2.1 Denmark

Denmark is a country that incinerates almost all of its residual waste and utilises almost all of the bottom ashes. This utilisation has been regulated since 1983 and the Danish road administration has a preference for the use of residues including bottom ash [Crillesen 2006].

Bottom ash use is based on pollution hazard by leaching and not on pollutant inventory. That is why all kinds of residues like contaminated soil, coal ash, and also bottom ash have to comply with the same standards. There are three categories of application, one for uncontaminated soil, the other two for inorganic residues; bottom ash falls into the regime of category 3, mainly due to its high salt inventory. The maximum TOC in bottom ash is 3 wt. %.

The leaching criteria measured by the CEN test EN 12457-3 at L/S = 2 l/kg for application category 3 are compiled in Table 4.

Table 4   Leaching limits for bottom ash utilisation in Denmark (application category 3)

	elution [mg/l]		*elution [mg/l]*
Cl⁻	3,000	*Cr (total)*	0.5
SO_4^{2-}	4,000	*Cu*	2
Na	1,500	*Hg*	0.001
As	0.05	*Mn*	1
Ba	4	*Ni*	0.07
Pb	0.1	*Zn*	1.5
Cd	0.04		

Bottom ash application is only allowed below watertight capping, above the highest ground water level and at least 30 m away from drinking water wells.

3.2.2 France

The 'Circular of 9th May, 1994' issued by the French Ministry of Environment regulates disposal as well as utilisation of bottom ash in road construction. The key parameter is the leaching stability of the material which is measure by the X31-210 AFNOR leach test which is equivalent to the EN 12457-4 [Normalisation française 1988]. Depending on the results of this test bottom ash falls into three categories:

- category V (valorisable, meaning recoverable) with low leaching values,
- category M (maturable, meaning can be improved by treatment), and
- category S (storable, meaning going to landfill).

Table 5   Criteria to classify bottom ashes

	category V	*category M*
TOC in wt. %	5	5
soluble fraction in wt.%	5	10
extractable organics in mg/kg	1,500	2,000
leaching results (X31-210) in mg/kg		
SO_4^{2-}	10,000	15,000
As	2	4
Pb	10	50
Cd	1	2
Cr(VI)	1.5	3
Hg	0.2	0.4

The criteria for the categories V and M are compiled in Table 5. Bottom ashes exceeding the limits of category M fall into category S. The quality improvement is typically performed by maturation for 3 months, eventually up to 12 months. Sometimes stabilizing additives are added [Soliman 2005].

3.2.3 Germany

In 1993 the German Minister of the Environment issued the Technical Instructions on Waste from Human Settlements [Bundesministerium 1993], also known as the TASi. This defined two types of landfills - class I and class II - for the disposal of non-hazardous waste and set standards for the access to these landfills. The TASi stipulated a ban on disposal of untreated organic waste within 12 years. Since this ordinance had no legal power, provisions for the ban were only slowly or not at all made.

The situation changed after the EU had issued the LFD, which Germany transposed into national law by the release of the Ordinance on Environmentally Compatible Storage of Waste from Human Settlements and on Biological Waste-Treatment Facilities (Abfallablagerungsverordnung, AbfAblV) [Bundesministerium 2001]. The standards for the access to landfills were the same as in the TASi. However, this ordinance had legal force. It repeated the time limit for the disposal of organic waste set in the TASi, which meant a total landfill ban of such material as of June 1, 2005.

The increasing use of mechanical-biological treatment (MBT) resulted in the definition of a new landfill class 3 for such residues as third type of landfills for waste materials.

Table 6   Selected acceptance criteria for German landfills class 1,2, and 3

no.	parameter	unit	class 1	class 2	class 3
1	*organic fraction of dry residue of original substance*				
1.01	*LOI*	wt%	≤3	≤5	≤10
1.02	*TOC*	wt%	≤1	≤3	≤6
2	*solid matter criteria*				
2.07	*extractable lithophilic substances*	wt%	≤0.4	≤0.8	≤4
3	*elution criteria(DIN EN 12457-4)*				
3.01	*pH*		5.5 - 13	5.5 - 13	4 - 13
3.02	*DOC*	mg/l	≤50	≤80	≤100
3.03	*Phenols*	mg/l	≤0.2	≤50	≤100
3.04	*As*	mg/l	≤0.2	≤0.2	≤2.5
3.05	*Pb*	mg/l	≤0.2	≤1	≤5
3.06	*Cd*	mg/l	≤0.05	≤0.1	≤0.5
3.07	*Cu*	mg/l	≤1	≤5	≤10
3.08	*Ni*	mg/l	≤0.2	≤1	≤4
3.09	*Hg*	mg/l	≤0.005	≤0.02	≤0.2
3.10	*Zn*	mg/l	≤2	≤5	≤20
3.11	*Cl*	mg/l	≤1,500	≤1,500	≤2,500
3.12	*SO_4*	mg/l	≤2,000	≤2,000	≤5,000
3.13	*CN*	mg/l	≤0.1	≤0.5	≤1
3.14	*F*	mg/l	≤5	≤15	≤50
3.15	*Ba*	mg/l	≤5	≤10	≤30
3.16	*Cr, total*	mg/l	≤0.3	≤1	≤7
3.17	*Mo*	mg/l	≤0.3	≤1	≤3
3.18a	*Sb*	mg/l	≤0.03	≤0.07	≤0.5
3.18b	*Sb, c_0 value*	mg/l	≤0.12	≤0.15	≤1
3.19	*Se*	mg/l	≤0.03	≤0.06	≤0.7
3.20	*water soluble fraction*	wt%	≤3	≤6	≤10

The AbfAblV was replaced in 2009 by the Waste Storage Ordinance (Deponieverordnung, DepV) to adjust to new EU regulations [Bundesministerium 2009]. This was amended in 2011. Furthermore the EU Waste Framework Directive forced Germany in 2012 to release a new Kreislaufwirtschafts- und Abfallgesetz (KrWG, Closed Substance Cycle and Waste Management Act), which regulates the entire waste management are, including the provisions concerning the end of waste regulation [Bundesministerium 2012]. The actual acceptance criteria for the three types of landfills for waste disposal are listed in Table 6. The table does not include the criteria for landfill class 0, the landfill for inert waste, since this one is not accessible for residues from thermal waste treatment.

In Germany the LAGA (a board of representatives of the ministers of environment of the country and of its federal states) has implemented memoranda to harmonise the implementation of the legal regulations concerning waste management. Of relevance in this actual context is the memorandum M19 which gives guidance for disposal and utilisation of residues from incineration of residential waste [LAGA 1994]. The memorandum sets standards for utilisation of bottom ash in road construction in terms of leaching stability. It also includes limits for pollutants in HCl, NaCl, Na_2SO_4, and gypsum recovered from gas cleaning residues.

The LAGA M20 memorandum defines so-called Z values for possible utilisation and disposal scenarios of mineral residues based on their pollutant inventory and leaching stability [LAGA 2003]. The three classes for utilisation are shown in Table 7. Bottom ash can only be utilised according to Z2.

Table 7   Z values for utilisation of mineral residues

Z0	Z1	Z2
application class 0	application class 1	application class 2
unlimited application	limited 'open' application	limited application with defined security measures

The respective concentration and leaching limits for mineral residues as laid down in the M20 memorandum are compared to the respective data laid down for bottom ash in M19 in Table 8. The test procedure is the old German DEV S4 protocol which is almost identical with DIN EN 12457-4.

Table 8   Allocation values for mineral residues (M20) and bottom ash (M19) for utilisation according to Z2

	M20		M19	
	concentration [mg/kg d. m.]	elution [mg/l]	concentration [mg/kg d. m.]	elution [mg/l]
As	150	0.06	-	-
Pb	700	0.2	6000	0.05
Cd	10	0.006	20	0.005
Cr (total)	600	0.06	2000	0.2
Cu	400	0.1	7000	0.3
Ni	500	0.07	500	0.04
Tl	7			
Hg	5	0.002		0.001
Zn	1500	0.6	10000	0.3
CN	10	0.02		0.02

Comparing the concentration and elution values for the two materials it can be stated that the concentration limits for raw bottom ash are typically much higher than those for mineral residues such as construction and demolition waste. The elution limits are sometimes higher, sometimes lower.

Both memoranda, especially M19, have been under revision for some years in order to harmonise them with the new DepV and the KrWG. For MSW bottom ash utilisation a so-called 'benchmark paper' published by LAGA in 2004 proposed new allocation values of 0.05 mg/l for Cr (total) and 0.2 mg/l for Zn [LAGA 2004]. Unfortunately the old memoranda have yet not been revised and actual practice of utilisation is based more on regulations of federal states and general requirements of the respective utilisation scenario, such as road construction regulations released by the federal research company for road and transportation (FGSV).

However, some requirements included in the old LAGA memorandum such as metal scrap separation and maturation by storage for at least 12 weeks under humid conditions are common practice today.

3.2.4 Italy

The 'Ronchi Decree', the Government Decree n°22 of February 5, 1997, regulates waste management in Italy, including disposal and/or utilisation of bottom ashes. Bottom ashes can be used as aggregates in concrete, as raw material for cement production, or as secondary building material. The criteria for utilisation and disposal are mainly based on leaching stability.

For access to landfill the EU test EN 12457-4 is mandatory, for utilisation a serial batch test has to be applied. In this test a sample is exposed to water at L/S = 5 l/kg for 2, 8, 24, 48, 72, 102, 168, and 384 hours. The eluate is always filtered and analysed, the accumulated leached portion has to comply with the limits given in Table 9 [Soliman 2005]. Compared to other countries the list of regulated elements is much longer in Italy.

Table 9 Criteria for landfilling and utilisation of bottom ashes in Italy (data in mg/kg)

	disposal *EN 12457-4 (L/S = 10 l/kg)*	*utilisation* *serial batch (L/S = 5 l/kg)*
Cl	15,000	1,000
F	150	7.5
SO$_4^{2-}$	20,000	1,250
NO$_3^-$	-	250
CN$^-$	5	0.25
As	2	0.25
Ba	100	5
Pb	10	0.25
Cd	0.2	0.025
Cr (total)	10	0.25
Cu	50	0.25
Hg	0.05	0.005
Mo	10	-
Ni	10	0.05
Zn	50	15
Sb	0.7	-
Se	-	0.05
Sr	0.5	-
Be	-	0.05
Co	-	1.25
V	-	1.25

Sweden

In Sweden waste handling, treatment facilities, and landfill sites are regulated by the Environmental Code [Regeringskansliet 1999]. The definition of waste and the access criteria to landfills are those of the EU Landfill Directive. Bottom ash is acknowledged as non-hazardous, whereas boiler and filter ashes as well as APC residues are classified as hazardous. Hence, for landfilling of bottom ashes the access standards of the Council Decision 2003/33/EC apply. The Swedish regulatory leaching test is EN 12457-3 (see 4.5.2).

The Swedish Environmental Protection Agency released standards for utilisation of waste materials in road or noise protection wall construction [SEPA 2007]. Materials for use category 1, which comply with the limits compiled in Table 10, can generally be utilised 'free' without report to the respective administration. If a material exceeds the limits a report and a permit are required.

These limits are valid for ashes from coal combustion, steel slags, and recycled building materials from construction and demolition waste. Bottom ashes from waste incineration fail for all metals in terms of their inventory. There are no general regulations for utilisation of bottom ashes. According to the Swedish National Road Administration's technical specifications for roads, ATB VÄG, evidence is required that the alternative aggregate is equivalent to the material it replaces in a standard construction.

Table 10   Limits for utilisation category 1 in Sweden for 'free' use of waste materials

	inventory *[mg/kg]*	*eluate (L/S = 10 l/kg)* *[mg/kg]*	*eluate c_0 (l/S = 0.1 l/kg)* *[mg/l]*
Pb	20	0.31	0.09
Cd	0.2	0.01	0.004
Hg	0.1	0.004	0.001
As	10	0.13	0.016
Cu	40	0.31	0.09
Zn	120	2.2	0.64
Cr (total)	40	0.42	0.09
Ni	35	0.6	0.18
Cl	-	147	84
SO_4^{2-}	-	227	78

Hence bottom ash utilisation requires case specific permits. Most applications are found in road construction on landfill sites or for cover of landfills.

3.2.5   United Kingdom

The standards of the European Landfill Directive were adopted by UK law and applied from 16 July 2005 under the Landfill (England and Wales) (Amendment) Regulations 2004 [Environment Agency 2004].

There are waste acceptance criteria for inert, non-hazardous and hazardous landfills. The Landfill Regulations solely reference the European Waste Catalogue (EWC) for the definition of hazardous and non-hazardous wastes. Two of the chapters in the European Waste Catalogue are relevant to biomass and waste-to-energy plants, i.e. Chapter 10: Wastes from thermal processes and Chapter 19: Wastes from waste management facilities [Environment Agency 2006]. Chapter 10 is restricted to non-waste treatment processes only, such as biomass plants. Waste-to-energy plants that are clearly designed to manage wastes are classified under Chapter 19. All solid residues from biomass plants are classified non-hazardous. In the case of waste-to-energy plants, APC residues are classified hazardous, whereas bottom ash and fly ash are classified minor hazardous, meaning that they have the potential to be either hazardous or not, depending on whether they contain "dangerous substances".

The waste acceptance criteria consist of:
- a list of inert wastes (which may be accepted without testing),
- leaching limit values according to the CEN test EN 12457,
- limit values for other parameters such as pH, acid neutralisation capacity and TOC.

The leaching limit values relate to specific leaching tests which are different for granular and monolithic wastes. The limits for granular waste are based on leaching test results expressed as mg/kg dry matter. Monolithic wastes are tested in a tank leaching test which tests the elution per exposed area; the standards are hence expressed in mg/m^{2}kg.

For granular hazardous waste, e.g. fly ash from WtE plants containing dangerous substances, the respective leaching limits at L/S = 10 l/kg of the Council Decision 2003/33/EC must be met. If the values for Cd or Hg are above 1 or 0.4 mg/kg respectively, a risk assessment must demonstrate that there will be no unacceptable discharge to groundwater. Furthermore a minimum load bearing capacity of 50 kPa has to be achieved.

There are also a number of special provisions relating to stable, non-reactive hazardous wastes (SNRHW) which are defined as hazardous wastes, the leaching behaviour of which will not change adversely in the long-term under landfill design conditions. These wastes can be deposited in special cells on landfills for non-hazardous wastes.

Table 11 Limits for monolithic wastes in the UK (tank leaching test NEN 7345)

	SNHRW	*hazardous waste*
	mg/m^2 kg (dry)	*mg/m^2 kg (dry)*
As	1.3	20
Ba	45	150
Cd	0.2	1
Cr$_{total}$	5	25
Cu	45	60
Hg	0.1	0.4
Mo	7	20
Ni	6	15
Pb	6	20
Sb	0.3	2.5
Se	0.4	5
Zn	30	100
Cl	10,000	20,000
F	60	200
SO$_4$[(1)]	10,000	20,000
Phenol index	-	-
DOC[(3)]	must be evaluated	must be evaluated
TDS[(2)]	-	-

[(1)] *This limit value for sulphate may be increased to 6,000, provided that the value of C0 from a percolation test does not exceed 1,500 mg/l at L/S = 0.1 l/kg. It will be necessary to use a percolation test to determine the limit value at L/S = 0.1 l/kg under initial equilibrium conditions (C0 is the concentration at L/S = 0.1 l/kg).*

[(2)] *The value for total dissolved solids (TDS) can be used as an alternative to the values for sulphate and chloride.*

[(3)] *If the waste does not meet this value for dissolved organic carbon (DOC) at its own pH value, it may alternatively be tested at L/S = 10 l/kg and a pH between 7.5 and 8.0. The waste may be considered as complying with the acceptance criteria for DOC, if the result of this determination does not exceed 500 mg/kg for inert waste, 800 mg/kg for SNRHW and 1000mg/kg for hazardous waste.*

In order to be accepted at a hazardous landfill, monolithic wastes (e.g. solidified APC residues from waste-to-energy plants) must not exceed the limit values provided in Table 11. The limit values for monolithic wastes apply to tests using the 64-day tank test developed in the Netherlands [NEN 7345]. The load bearing capacity has to reach at least 1.5 MPa; pH, electrical conductivity and the acid neutralisation capacity (ANC) have to be evaluated.

In conclusion, solid residues from biomass and WtE plants can be disposed of at a landfill site only if they comply with the waste acceptance criteria for the particular landfill site as proven by characterisation and testing.

4   Characterisation Principles

4.1   General Remarks

Characterisation of solid residues is important to decide on their most suitable disposal or utilisation strategies in view of protection of human health and lowest environmental impact. Hence the most important parameters are

- chemical composition,
- burnout,
- leaching properties, and
- physical (mechanical) properties.

Mineralogical characterisation is often helpful in explaining e.g. leaching characteristics and developing inertisation or stabilisation methods.

The International Ash Working Group (IAWG) discussed these items in detail compiling all kinds of practical methodologies applied for different types of materials [IAWG 1997]. Standardisation on such methods has been and is worked upon by various organisations like ISO, the International Organization for Standardization, CEN, the European Committee for Standardization, and the U.S. EPA, the Environmental Protection Agency of the United States of America. Furthermore many countries and organisations dealing with residues have issued their own utilisation or disposal specific standards, which have to be paid regard to.

Several standards concerning characterisation of e.g. grate ashes (the biggest and most important residue from waste incineration) are under approval at the CEN European Committee for Standardization at TC 154 Aggregates [CEN 2011].

4.2   Sampling Strategies

For characterising solid residues the sampling strategy applied is of paramount importance. This is particularly the case for coarse materials such as bottom ashes.

As a first estimate a statistical distribution of all parameters in one single sample of a given material has to be assumed. Of high importance for reaching this target is a documentation of all cyclical operation modes of the plant – e.g. soot blowing - to avoid any influence on the sampling scheme.

The number of increments or grab samples forming one composite sample depends upon the desired threshold of statistical error. A standard for sampling aggregates and coals suggests the precision should be within 10 % of the mean [ISO 1975].

The size of the grab samples is strongly dependent on the maximum grain size of the material to be sampled. This factor makes sampling of the coarse bottom ashes in particular more difficult than, for example, that of fine grained fly ashes.

4.2.1   Sampling of Bottom Ashes

For bottom ashes from MSW incineration 24 grab samples should be collected to obtain a representative gross sample, although for practical reasons a minimum of 10 samples is considered satisfactory. If parameters are normally distributed, a reduction of error by a factor of 2 requires an increase in the number of grab samples by a factor of 4. In other words: the reduction of increments from 24 to 10 is equivalent to an increase in error by approximately 50 % (e.g. from 10 up to 15 %). The German LAGA guideline for sampling of wastes and deposited materials recommends for each 50 tons of material in the case of fine grained (< 20 mm) three and for coarse matter (> 20 mm) five samples to be taken from a moving belt [LAGA 1984]. Of course the number of samples depends also upon the size of the single sample due to handling conditions. A good estimate for the size of an incremental sample found in the ISO norm cited above, but also in other sampling protocols is:

$$P = 0.06\ D$$

where P = mass of the increment in kg

D = the nominal upper size of the material, i.e. the square mesh screen size such that no more than 5 % of the material is oversize

On the basis of this equation the IAWG recommends a sample size of 10 kg for bottom ash grab samples, which is in practice about 5 to 7 litres of material. The LAGA recommends for the collective sample of homogeneous material with a maximum grain size of 120 mm approx. 50 kg and a size of 200 kg for heterogeneous matrices. If the maximum grain size is 30 mm, the respective numbers are 10 and 30.

Another factor of importance is the spacing of the incremental sampling in time. Although a random spacing is to be preferred from a statistical point of view, it is more convenient to use a systematic sampling with the increments evenly spaced in time. The sampling period has to be chosen in a way that it is not biased by any periodical operation of the plant (e.g. filter cleaning, soot blowing of the boiler etc.).

A further factor influencing the results is the sampling conditions. The best option is a stopped belt cut, with the loaded conveyor belt to be stopped and a full cross section to be removed. A second good option is the full stream cut, where a full cross section is removed from a moving belt. This is more easily accomplished if the fallen stream can be sampled by means of appropriate equipment.

The grab samples have to be mixed thoroughly to get a homogeneous and representative gross sample.

4.2.2   Sampling of Boiler Ashes

Boiler ashes fall into hoppers below the boiler segments and are periodically removed. Due to their higher homogeneity than grate ashes their sampling is less complicated. The easiest way is the collection of the entire boiler ash flow during the sampling procedure, which can then be mixed and a sample of few kg can be taken by e.g. coning and quartering or by taking a full depth tube core if the material is kept in a drum.

Boiler ashes should be separately collected during periods without and with tube cleaning. The mass flows of both operation modes have to be considered.

Since boiler ashes are hydroscopic care has to be taken to keep the material dry.

4.2.3   Sampling of Filter Ashes

Filter ashes are typically finely grained. They are permanently discharged into hoppers at the bottom of the electrostatic or fabric filter. As with the boiler ashes filters are periodically cleaned. These intervals might be short compared to the sampling period and have to be considered. An easy way of sampling is the implementation of an automatic e.g. rotary divider in the discharge stream, which takes a constant fraction out of the discharged ash flow. Filter ashes are hygroscopic as well.

4.2.4   Sampling of APC Residues

If dry gas cleaning is applied, sampling of residues can be performed the same way as described for filter ashes. In case of wet gas cleaning all effluents from the scrubbers have to be sampled. The content of solid matter in the solutions has to be measured.

4.3 Sample Pre-Treatment

4.3.1 Mechanical Pre-Treatment

The sampled residues need to be pre-treated for the various characterisation methods. The pre-treatment starts typically with the preparation of representative sub-samples from the total amount of collected material.

This is very challenging for bottom ashes, due to their material heterogeneity, their wide grain size distribution, and the size of the gross sample. The first step will always be the removal of iron and non-ferrous scrap. Iron scrap can be removed by magnetic separation, the latter by manual separation. Both fractions have to be weighed and recorded.

Oversized material has to be crushed and, if this is not possible, separated, characterised by observation and recorded.

The next step is size reduction to get a sample suited for the type of characterisation. For testing of mechanical parameters and for leaching tests the sample size should be in the order of some kg, whereas for chemical analysis small samples of eventually less than 1 g are required.

Sample size reduction goes along with grain size reduction and is an iterative procedure. The first reduction may be done by applying the cone and quarter technique, alternatively riffle boxes and other equipment are used. The grain size reduction starts with crushing, followed by grinding and milling until, in case of analytical samples, grain size <100 μm is achieved.

In the case of boiler ashes, filter ashes, and APC residues the composite sample of one test run is in the lower kg range and due to its fine grain size easier to handle.

It is common practice to seal and store 50 % of the final sample for replicate investigations.

Some samples, particularly those prepared for organic or Hg analysis should be stored in a refrigerator. Other samples for inorganic analysis are dried at 105°C, as the humidity has to be recorded.

4.3.2 Sample digestion

Many inorganic analytical methods require liquid samples. Since the major residues from waste incineration are solids they have to be dissolved before they can be analysed. However, highly annealed oxides and most silicates are extremely insoluble and require very aggressive agents and conditions to achieve total digestion.

Since bottom and filter ashes contain a significant share of silicatic matter, for total digestion of these materials fluorine containing agents with high oxidation potential at high temperature and high pressure are used. The typical method is a mix of HCl, HNO_3, and HF. The digestion is performed in sealed containers, called bombs, in a microwave furnace.

If this digestion leaves unsolved material it will probably be oxides of aluminium or tungsten. To dissolve such compounds fusion with a mix of Na_2SO_4 and K_2SO_4 can be used.

4.4 Chemical Analysis

Chemical analysis of waste incineration residues for inorganic ingredients can be performed by dry or wet analytical methods. If, for example XRF (X-ray fluorescence analysis) is applied, the material has to be finely ground and eventually compacted forming small pellets.

In many standards for regulatory tests specific analytical methods are prescribed. For scientific investigations the most convenient methods for most anions is ion chromatography. For metals atomic absorption spectrometry (AAS) or inductively coupled plasma mass spectrometry (ICP-MS) respectively inductively coupled plasma optical emission spectrometry (ICP-OES) are most

appropriate. Another sensitive method is TRXRF (total reflection XRF) which uses µl-samples of the digestate dried on a sample carrier [Härtel 1996].

The TOC, the amount of residual elementary and/or organic carbon species, is the measure of burnout of solid residues. In most cases it is measured by annealing the material under air atmosphere at 550 °C until constant weight is reached.

Organic analysis is much more complex, especially that of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F). Standardised sample pre-treatment and analysis protocols have been published and will not be listed here since in most cases this analysis is performed by specialised laboratories.

4.5 Leaching

4.5.1 Fundamentals of Leaching

All solid materials have a defined solubility in an aquatic environment. Some are easily dissolved (such as alkali chlorides); others are more insoluble (e.g. quartz or aluminium oxide). The solubility of the ingredients of a material in a specific disposal or utilization scenario where the access of water cannot be excluded is crucial for the impact this material can impose upon the environment.

The chemical composition of a product does not in principle enable an evaluation of its solubility in water, and even less in complex liquid media. Even if the matrix and the speciation of single elements were known, a reliable theoretical prediction of the short- and long-term behaviour of a material is difficult. The most important parameters influencing the leaching properties of a material are listed below:

- its chemical composition;
- its chemical/geochemical/mineralogical speciation;
- the fraction of a species available for leaching;
- the particle morphology;
- the properties of the leachant, particularly its pH or the presence of complexing components;
- the liquid-solid ratio (L/S) in the leaching system.

It seems evident, that no single - or simple - test procedure will deliver results that allow a sound evaluation of impacts upon the environment. In fact a great number of different tests have been developed to provide detailed information about the leaching properties of residues from waste incineration under various conditions.

Almost all regulations for the disposal or utilisation of waste products are based on standardised leaching tests; unfortunately these are different in different parts of the world. The situation has been improved in the EU where CEN, the European Committee for Standardisation, released the standard EN 12457 in 2002, which harmonised the testing in the member countries (see below). However, comparison and interpretation of test results obtained by different protocols is still a difficult task.

The key parameter controlling the leaching properties of a material is the pH value of the leachant. The pH influence on the elution out of silicatic and oxidic matter such as bottom ashes is shown in Fig. 1.

Metal cations have a relatively high solubility in an acidic environment. With increasing pH the solubility drops down and reaches a minimum at low alkaline conditions in the pH range of 9 to 11. Some heavy metals stay insoluble at further increasing pH. Examples are Cd, Cu or Sn. Others, however, undergo an again increasing solubility with increasing pH. The most important of these amphoteric metals in waste combustion is Pb. Zn and some other metals show a moderately increased solubility at high pH, too.
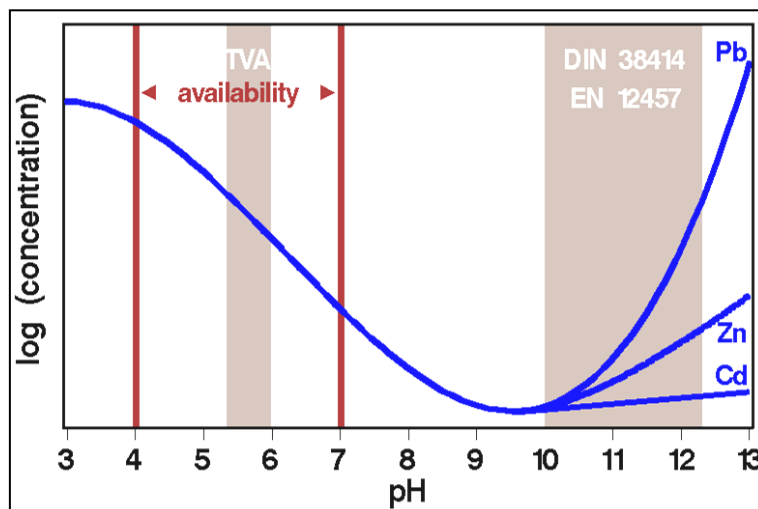
Fig. 1   pH dependency on the leaching of metal cations

Metals forming oxianions like V, Mo, W and to a certain extent also Cr and Mn show a rather different dependency with pH. These metals are characterized by a weak correlation with pH and a maximum solubility around the neutral point.

The shaded area at the right side of the diagram in Fig. 1 shows the pH range to be expected in the various standardized leaching tests performed on bottom ashes and will be discussed later. The two red vertical lines indicate the pH values controlled in the Dutch availability test and the shaded area on the left is the pH range establishing in the Swiss TVA test.

4.5.2   Standardised Leaching Tests

The elution stability is the preferred parameter to test the environmental compatibility of solid residues. At EU level CEN has defined the EN 12457 test as compliance test [European Committee for Standardization 2002]. This batch leaching test uses water as leachant.

The first step is performed at a liquid-to-solid ratio (L/S) of 2 l/kg with an equilibration time of 6 hours. It is followed by a second step at L/S 8 l/kg and an equilibration time of 18 hours. The combination of both tests resembles a test with an L/S of 10 l/kg and an exposition time of 24 h. The particle size is below 4 mm and the pH of the system is not controlled.

The results obtained have to be compared with specific reference values. These tests are intended to replace other national compliance tests in the EU and a number of countries have already based their regulations on CEN standards.

The third variant seems equivalent to the conditions of the German DEV S4 test [DIN 38 414] (water, LS=10, 24 h) or a similar protocol used in France with the X31-210 AFNOR leaching test [Normalisation française 1988]. However, the performance differs and with that the results of the combined tests cannot necessarily be expected to be identical with the German test [Bergfeldt 1998].

The pH, which is not controlled in the compliance tests described above, has a substantial influence upon the elution behaviour of almost all materials [IAWG 1997]. A test at controlled pH value is e.g. the pH-static leaching test according to CEN/TS 14997. This test is carried out as a 48 hour batch leaching test at L/S 10 l/kg at fixed pH values in the range of pH 4 to 12. The particle size is below 1 mm. The pH of the leachant is kept constant by means of a computer-controlled titration device with addition of nitric acid as described in the pre-standard WI 292015 [European Committee for Standardization 2000]. The pH-static leaching test contributes to the understanding of the influence of pH upon leaching and allows for comparison of leaching from different materials at fixed pH-values.

A better understanding of the leaching mechanism is provided by a number of scientific tests [IAWG 1997]. An important parameter in this respect is the availability (the amount of a species which is potentially available for leaching under worst environmental conditions). For this purpose the availability test according to the Dutch NEN regulation [NEN 7341] is often used. The cation solubility is tested at a pH of 4, that of the anions at a pH of 7. The sample is finely ground in order to exclude any inhibition of the leaching by diffusion and the liquid-solid ratio is kept at 100 to avoid saturation effects in the solution. The two solutions are combined and analysed.

The German DEV S4 test has no pH control. If bottom ashes are tested the pH ranges typically from 10 to >12. This range means that the mobility of Pb might be promoted in high alkaline materials. On the other hand the graph in Fig. 1 indicates that the access of acid rain (which may have pH values down to 4) carries the risk that it could shift the pH of the ashes into areas of increasing solubility.

Hence for evaluation of the long term leaching stability of a material not only does the primary pH of the leachant have to be taken into account, but the acid-neutralization capacity (ANC) of the material also has to be taken into account. The ANC is a measure of the buffering capability of the material. It gives an idea how much acid would be needed to change the pH from the desired weak alkaline area into more aggressive ranges.

In the Swiss TVA test the pH is controlled by CO_2 which is permanently injected into the system and establishes a $(CO_3)^{2-}/(HCO_3)^{-}$ buffering system with a pH of $5.5 - 6$ [Schweizerischer Bundesrat 1990]. This range is marked on the graph, too. It is evident that the strict compliance with this pH is of eminent importance for the interpretation of the TVA test results in relation to the legislative standards since in this pH range the solubility of cations is strongly influenced by pH changes.

Due to the chemical composition of the leachant in the TVA test there are minor problems to be expected with metals forming insoluble carbonates such as Pb. Some metals, however, form soluble hydrocarbonates and hence may be much more easily mobilized in that test than in reality by the access of acid rain. An example of this group of metals is Zn.

These different pH regimes explain some generic difficulties in the interpretation of test results obtained by different tests on the same samples of bottom ashes. The DEV S4 test often suggests problems with Pb in relation to its disposal on a German landfill class 1, whereas the TVA test indicates high leaching resistance for this element and allows the disposal on a Swiss residue landfill. The opposite situation is often found for Zn.

Table 12 Parameters of some leaching tests used in Europe

	EN 12457-3	*EN 12457-2/ DIN EN 12457-4*	*TVA*	*NEN 7343 (column)*	*NEN 7341 (availability)*
country	EU	Germany	Switzerland	Netherlands	Netherlands
type	serial batch	batch	serial batch	column	serial batch
max. particle size (mm)	10	actual size	10	4	0.125
leachant	H_2O	H_2O	CO_2 saturated H_2O	1 mol/l HNO_3	1st step: pH=7 2nd step: pH=4
number of steps	2	1	2	7	2
L/S (l/kg) per step	1st step: 2 2nd step: 8	10	10	0.1 - 10	50
contact time	1st step: 6 h 2nd step: 18 h	24 h	24 h per step	$\approx$ 16 d	3 h per step
agitation	end over end/ roller table	end over end/ roller table	CO_2 injection	leachant pumped through column	stirring

Table 12 compiles parameters of some leaching tests used in Europe. The EN 12457 tests are the EU compliance tests released by CEN. TVA is the respective test for Switzerland. The Dutch column and availability tests are integrated due to their importance for kinetic and mechanistic investigations.

The TCLP, the toxicity characteristic leaching procedure EPA Method 1311, uses different leachants depending on the original alkalinity of the sample [US EPA 2012]. The resulting pH at the end of the test procedure is not defined and should be expected to be in the range 5 - 12. This wide range is associated with substantial changes in the solubility of metal cations which implies that the test results depend strongly on the original alkalinity of the sample. Since this factor has not been taken care of in the establishment of the TCLP test procedure and the standards for classification, the TCLP protocol opens the chance to manipulate the test results by the addition of e.g. lime.

4.6 Mechanical Parameters

Mechanical parameters such as compressive and vane shear strength or axial deformation are important for landfilling of materials due to the stability of disposal sites. For utilisation of bottom ashes as secondary building material they are of crucial importance. The EU directives do not contain standards for mechanical parameters but these are found in some national regulations.

4.7 Mineralogy

In addition to chemical analysis mineralogical investigation is another useful tool to characterise solid residues. This can be done by microscopic methods: optical, scanning electron (SEM) or scanning-transmission electron microscopy (STEM), both latter methods eventually coupled with X-Ray microprobe analysis (XRM). Another powerful method is X-Ray powder diffractometry (XRPD).

Mineralogical investigations of the multi-phase system bottom ash are difficult regardless of the applied methodology and hence, in most cases, only semi-quantitative compositional data can be found in the literature.

Identification of the major mineralogical phases in bottom ashes can provide information on the long term behaviour, mechanical parameters, but also on general leaching properties [Pfrang-Stotz 1995].

Some mineral phases not only reveal information about the structure of the bottom ash but can (in some cases) also supply information about the temperature the material has been exposed to in the fuel bed. This important number controls mainly the fate of elements in the combustion chamber, but it is widely unknown in full scale plants. The knowledge of formation temperatures of single phases and the specific search for high-temperature phases are promising ways to obtain better information in this area [Pfrang-Stotz 1993].

5 Residues from Grate Type MSW Incineration Plants

5.1 Mass Flows

Grate furnaces are the preferred for high throughput waste incineration, especially in Europe. A grate system accepts untreated MSW and has almost no limit concerning particle size of the fuel. However, grate systems are also often used for burning SRF, especially in Germany.

The flow of solid masses in a grate type incinerators burning MSW is shown in Fig. 2. The graph compiles average ranges for these streams as found in modern mass burning systems [IAWG 1997, European Commission 2005]. The air consumption of approx. 4500 m^3/Mg of waste is not included in the graph. Although different types of grate systems and boilers are in use the amount, as well as the quality, of the respective residues is more dependent on the fuel quality and operation mode than on the different technologies.
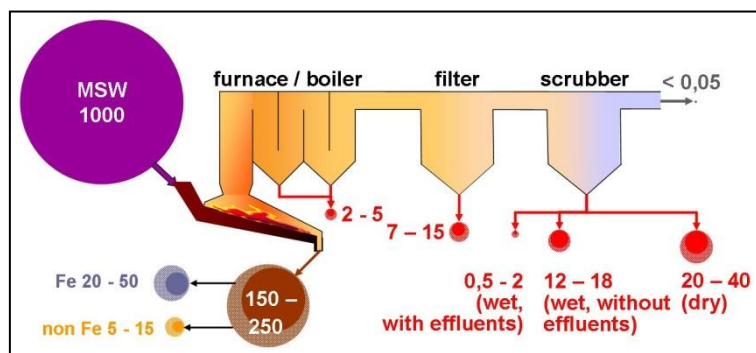

Fig. 2 Flow of solid mass in a modern grate equipped waste incinerator

State-of-the-art plants produce typically between 150 and 250 kg grate ashes per 1000 kg of burnt waste. Most published numbers include the grate siftings which are kept separate from the grate ash in a number of countries and fed, after metal separation, back into the furnace. The mass flow of siftings depends on the type of grate and its operation time. For modern incineration plants an amount in the order of 1 – 3 kg/Mg is typical. The mix of grate ashes and grate siftings is called bottom ash; however, this term is also typically used for pure grate ashes as well. In the following the term bottom ash will be used for the material discharged at the end of the combustion chamber.

Separation of grate siftings is obligatory in most countries since this material may increase the amount of unburnt matter in the bottom ash. For utilisation the inventory of metallic Al that drips through the grate voids is of even higher concern.

The production of boiler ash depends on the type of boiler and on the amount of dust originally released from the grate. Typical numbers in modern plants amount to 2 – 5 kg per Mg of waste as shown in Fig. 2. Boiler ashes should not be combined with the grate ash but be treated together with the filter ash. This has already been enforced by legislative regulations in a number of countries.

The fine particulate fly ashes are preferentially removed from the flue gas by an ESP or fabric filter. The amount given in the mass flow scheme in Fig. 2 is based on a fly ash concentration of 1.5 – approx. 5 g/m^3. Typical dust loads in modern waste incinerators which prefer a 'gentle' combustion e.g. in order to limit the PCDD/F formation in the boiler [Vogg 1991] are found at the lower end of that range.

The mass flow of APC residues shows the highest variation of all residues. Wet scrubbers are operated close to stoichiometry. The amount of 10 – 15 kg of residues from wet scrubbing is a mean value for such systems. The number comprises 2 - 3 kg/Mg of dry neutral sludge and 8 - 12 kg/Mg of soluble salts [Vogg 1984, Reimann 1987, IAWG 1997]. If the plant is allowed to discharge liquid

effluents into a sewer the only residue for disposal is the neutralisation sludge, a hazardous material requiring special supervision.

In semi-dry or dry systems the amount of residues is significantly increased because of not reacted additives. The 20 – 40 kg per Mg of waste is a typical value found in modern waste incineration plants [Reimann 1990 & 1991, IAWG 1997, Mark 2006].

5.2 Bottom Ashes

5.2.1 Ash Discharge

In grate systems bottom ash falls typically from the end of the grate directly into a water bath where it is quenched. The water bath serves also as seal between the combustion chamber and the ambient air. The bottom ash is then discharged by a hydraulic ram or a drag chain system. An example for wet bottom ash discharge is shown in Fig. 3 [Martin 2012].

Fig. 3 Conventional wet bottom ash discharge [Martin 2012]

Fig. 4 Bottom ash washing in the de-slagger at MVR Hamburg [MVR 2012]

The system is often operated with a surplus of water, which is not only used to replenish the evaporation losses but also to remove highly soluble salts, primarily chlorides, from the ashes

[Reimann 1994, Schneider 1994]. If wet gas cleaning is applied, the chloride-rich brine can be fed into the first acid scrubber of the plant. In the case of dry scrubbing it may be injected into the spray drier. A respective technical stage has been implemented at the Hamburg MSW incinerator Rugenberger Damm, a scheme of which is shown in Fig. 4 [MVR 2012].

In the 1990s first tests of the InRec[TM] process with dry bottom ash discharge were performed in a Swiss MSW incinerator [Simon 1995a]. Similar experiments took place in Japan and Germany [Koralewska 2010]. The main objective was more efficient metal separation. However, the economics of the process were not good at that time and the process was only used in Japan.

Increasing prices of metals over the last decade or so have resulted in a revival of optimised metal recovery, not just Fe scrap removal by magnetic separation. Increasingly waste incineration plants have started to install eddy current systems for non-ferrous metal recovery. Since non-ferrous metals in bottom ash in particular have typically small particle sizes their separation from wet ashes is much less efficient than from dry ones.

This fact was the driver to return to dry bottom ash discharge in the late 2000s. In 2009 two waste incineration plants in Switzerland – KEZO in Hinwil [Poldervaart 2009] and SATOM in Monthey [SATOM 2012] – were equipped with respective systems. The installed technology is slightly different as can be seen from the schemes shown in Fig. 5 and Fig. 6, the principles, however, are almost the same.
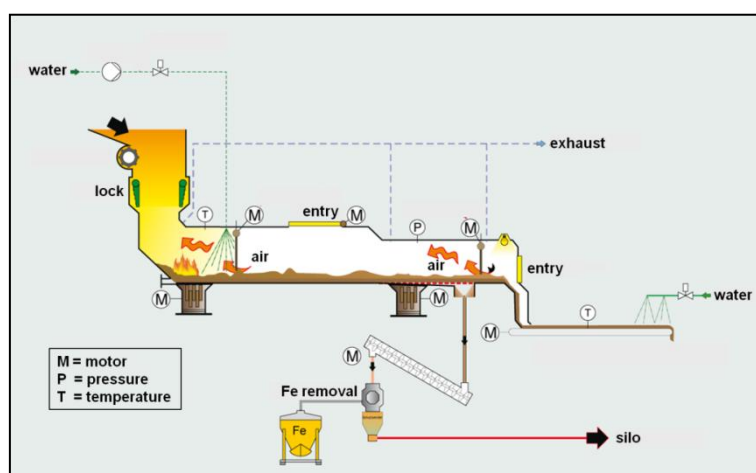

Fig. 5   Scheme of the dry bottom ash discharge at the KEZO Hinwil plant ([KEZO 2012], modified)

In the KEZO system (see Fig. 5) the hot ash falls onto a vibrating conveyor and is transported to a sieving machine where the fine fraction is separated. So-called tertiary air is introduced into the system which replaces approximately 10 % of the secondary air and promotes the burnout.

In the SATOM plant (see Fig. 6) a discharge system for wet deslagging is operated without water as shown in Fig. 3. The combustion chamber can be sealed against the ambient air by a lock. The separation of fine particles is done by wind sifting. Fine ash particles are recovered in a cyclone, the dust is injected with the air into the secondary air nozzles of the combustion chamber.

The advantage of both systems is improved metal recovery from the dry ashes. High efficiency is particularly achieved for metal separation from fine ash fractions. A secondary advantage is improved leaching stability of the coarse ash since water soluble metal compounds like chlorides are mainly found in the fine fraction which has partly been separated by sieving respectively wind sifting.
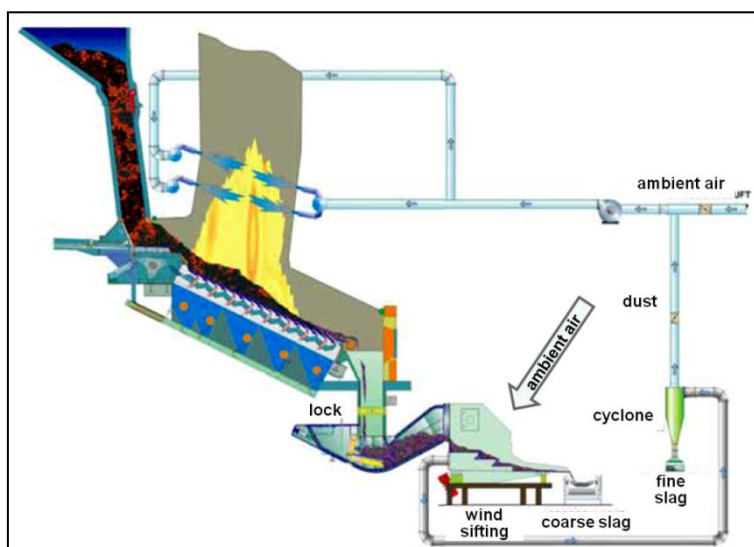
Fig. 6   Scheme of the dry bottom ash discharge at the SATOM Monthey plant ([Koralewska 2010], modified)

5.2.2   Characterisation

5.2.2.1   Gross Composition

Bottom ash is a rather heterogeneous material comprising widely varying fractions of ash, stones, metallic phases and unburnt matter. This 'gross' composition is mainly obtained by visual investigation or manual separation and weighing. Table 13 compiles published data of gross bottom ash composition from four countries at different times. It is evident that in the early 1990s as well as in the later 2000s the main components are ashes and mineral fractions.

Table 13   Gross bottom ash composition taken from literature (data in wt. %)

	Netherlands	*Sweden*	*Germany*	*Switzerland*	
ash <2 mm	27 - 32	45 - 56	81.5	45	43.1
ash >2 mm				40	47.4
stones	21 - 34	2 - 10		1	0.9
glass	20 – 27	36 - 45	12.3	5	1.8
ceramics	5 - 9	1.3 – 3.5	4.8	1 - 3	2.3
metals	3 - 7	-	1.1	5	3.5
organics	4 - 7	0.1	-	1 - 3	1.0
others	-	-	0.3		-
reference	Stoelhorst 1991	Hartlén 1991	Rübner 2007	Lichtensteiger 1996	Eggenberger 2010

The inventory of unburnt matter, i.e. organics, was significantly reduced with time (see below). The lower metal content with time reflects the improved efficiency of separate upfront collection of metals. The data indicate that the ashes of well operated waste incineration plants had reached high burnout quality already (at least partially) 20 years ago.

The water content of fresh bottom ashes from plants with wet ash discharge typically ranges between 15 and 25 wt. %. The bulk density of the fraction <100 mm is in the order of 1,500 – 2,000 kg/m3, that of the fraction >100 mm reaches 1,800 – 2,400 kg/m3 [Wiles 1996, IAWG 1997].

5.2.2.2 Burnout and Organic Micro-pollutants

Burnout is a key parameter for disposal as well as for utilisation of bottom ashes. The German Technical Ordinance Residential Waste sets a TOC limit of 1 wt. % for disposal on a class 1 landfill. The same number is found in the LAGA memorandum for utilisation in road construction.

In modern well operated MSW incineration plants the TOC in bottom ashes is typically well below 1 wt.-% [Schneider 1994, Bergfeldt 2000, Zhang 2004]. Special combustion trials at the Karlsruhe test incinerator TAMARA demonstrated that increasing the heating value of the feed and the resulting higher bed temperatures improve the burnout of bottom ashes (see Fig. 7) [Vehlow 1994].

The TOC of bottom ashes comprises mainly elementary carbon, but to a certain extent organic compounds are also found, which cover the spectrum from short-chain compounds [Köster 1998] to low volatile species such as PAH or PCDD/F. Typical concentrations of organic compounds in the various solid residues are compiled in Table 14.
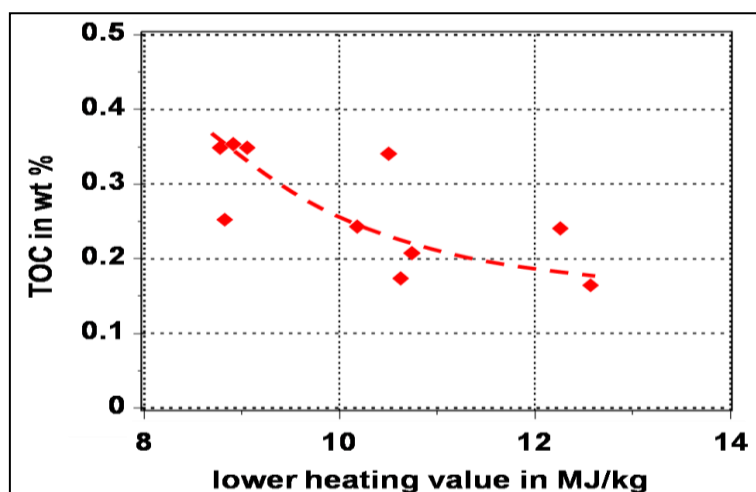

Fig. 7   Residual carbon (TOC) in TAMARA bottom ashes versus heating value of the feed

Table 14   Concentration ranges of organic compounds in bottom, boiler, and filter ashes in ng/g
            [Johnke 1995, Schneider 1994, Bergfeldt 1997, Huang 2003, Vehlow 2004, Öberg 2007]

	bottom ash	*boiler ash*	*filter ash*
PCDD/F (I-TEQ)	<0,001 - 0,01	0,02 - 0,5	0,2 - 10
PCB	<5 - 50	4 - 50	10 - 250
PCBz	< 2 - 20	200 - 1 000	100 - 4 000
PCPh	<2 - 50	20 - 500	50 - 10 000
PAH	<5 - 10	10 - 300	50 - 2 000

It is interesting to see the progress made in burnout of solid residues over the years. A major result of the research on PCDD/F formation during the 1980s and early 1990s was the recommendation to ensure a good burnout not only of the gas phase but also of all solid residues. As a consequence the PCDD/F inventory of bottom ashes was significantly reduced which can be seen in the compilation of literature data in Fig. 8 [Vehlow 2006].

The actual figures from state-of-the-art plants are generally in the range of PCDD/F concentrations in uncontaminated soils in Central Europe which range between<1 and 3 ng(TE)/kg [Fiedler 1996]. Hence PCDD/F are not critical constituents of bottom ashes any longer and should not impede the utilisation of this material as secondary building material.
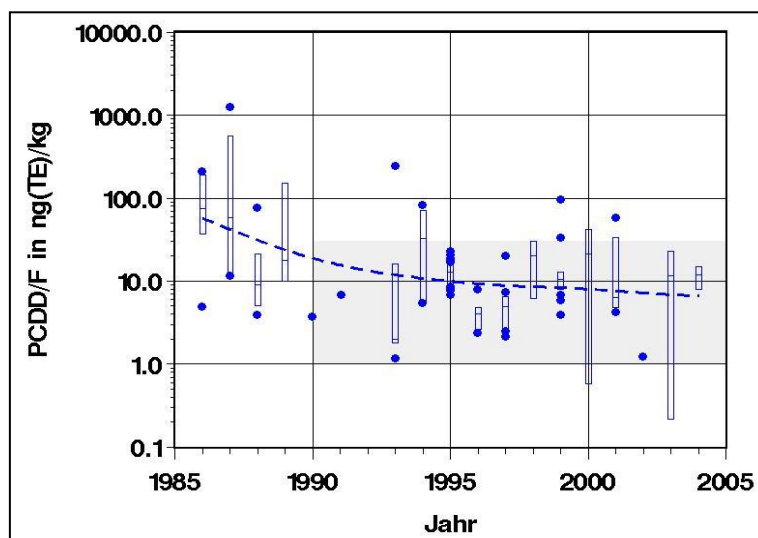
Fig. 8   PCDD/F inventory in bottom ashes between 1986 and 2005 [Vehlow 2006]

5.2.2.3   Inorganic Composition

Chemically the main inorganic components of bottom ashes are oxidic and silicatic compounds. When taking into consideration disposal or utilisation options other ingredients come are also important: heavy metals and salts.

Typical concentration ranges of Cl, S, and some heavy metals in bottom ashes are depicted in Fig. 9 [IAWG 1997, Belewi 2002, Zwahr 2005]. For comparison the respective concentration ranges In MSW [IAWG 1997] and in the lithosphere are added [Lide 1994].
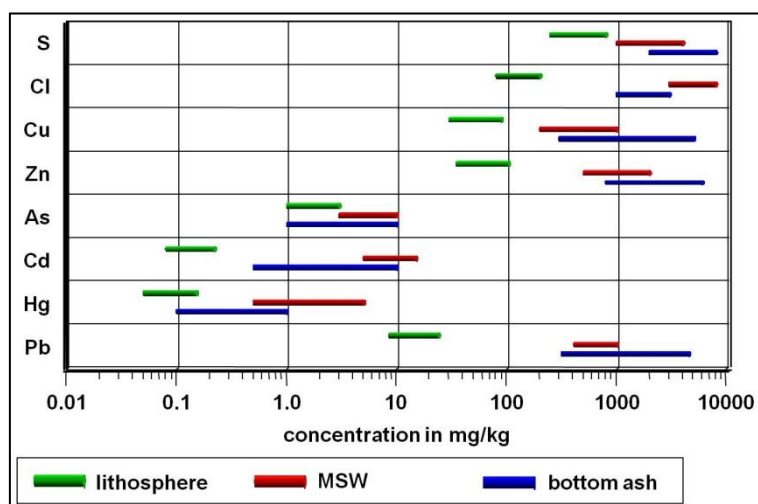

Fig. 9   Concentration ranges of selected species in bottom ashes and the earth's crust

The mass and volume reduction of waste incineration causes an enrichment of lithophilic species, e.g. Ti, Mn, or Fe, and moderately volatile metals such as Cu in the bottom ashes compared to their concentration in the waste feed. But even rather volatile metals such as Zn, and Pb often show higher concentrations in bottom ashes than in MSW. Only the highly volatile metals Hg and Cd are depleted in bottom ashes.

However, almost all of these metals are highly enriched in bottom ashes compared to their natural occurrence in the lithosphere which necessitates that their behaviour, e.g. their leaching properties on disposal sites or in utilisation scenarios, should be looked at critically. The high inventory of heavy metal compounds in bottom ashes is reason that in Switzerland bottom ash utilisation is prohibited; the ash has to be disposed of on a landfill for reactive materials.

5.2.2.4 Metallic Species

Analytical data on bottom ash composition are published in great numbers, but data on the inventory of metallic components are rare. Available data are often difficult to interpret. They have in most cases been obtained from operating technical separation systems and not from specific laboratory analysis. Hence the in Table 15 compiled concentrations of waste incineration bottom ashes reflect in most cases the amount of metals which are available with today common technology.

Table 15 Metal content in bottom ashes in wt. % (NF: non-ferrous metals)

	country	ash removal	metals	Fe	NF	Al	ref.
1991	Netherlands	wet	3-7				[Stoelhorst 1991]
1995	Switzerland	dry		15-20	2		[Simon 1995a]
1996	Switzerland	wet	5				[Lichtensteiger 1996]
2005	Germany	wet		10	0.9		[Zwahr 2005]
2007	Germany	wet	1.1				[Rübner 2007]
2010	Switzerland	wet	3.5				[Eggenberger 2010]
2010	Switzerland	wet		9		2.2-3.3	[Bunge 2010]
2010	Germany	wet		7.3	0.7		[Alwast 2010]
2011	Netherlands	wet		7	1.3		[AEB Amsterdam 2011]
2011	Switzerland	dry		11	3.2		[Ammann 2011]
2011	Belgium	wet			2.1	1.3	[Pruvost 2011]
	Denmark	wet			1.1–2.2	0.6-1.3	
	France	wet			0.65	0.37	
	Germany	wet			0.5-1.2	0.3-0.9	
	Netherlands	wet			2.0	1.6	

The data cover a wide range and should mainly be regarded as rough estimates. However, they seem to indicate that dry discharged bottom ashes enable better metal extraction than those from common wet systems. Investigations showed that up to 40 % of the metals, in particular the non-ferrous ones, are found in the fine bottom ash fraction [Ammann 2011]. It is obvious that fine-grained metals, especially the light-weight Al, are much more difficult to be separated from wet bottom ashes than from dry matter.

Heavy non-ferrous metals have come into focus over the past few years due to their industrial importance - e.g. Cu, Zn and Pb – or to their value – e.g. Ag, Au or even Pt. These latter ones will mainly originate from small electronic equipment in household waste. If these metals are present they will always be in the metallic state, their concentrations will be extremely low and they will be present in the very fine particle fraction. Data published for heavy non-ferrous metals in bottom ashes of the Amsterdam waste incinerator are compiled in Table 16 [Muchova 2009].

Table 16 Concentrations of selected metals in the Amsterdam bottom ash separated from the <2 mm fraction ([Muchova 2009], data in mg/kg)

	Cu	Pb	Zn	Sn	Ag	Au
concentration	920	480	10	80	2	0.11

5.2.2.5 Mineralogical Characterisation

Geochemical and mineralogical characterisation also provides useful information on the long term behaviour of a material. Bottom ashes can be characterised as a mixture of silicatic and oxidic phases. Some typical mineral phases found in these residues are shown in the micrographs in Fig. 10 [Pfrang-Stotz 1992].
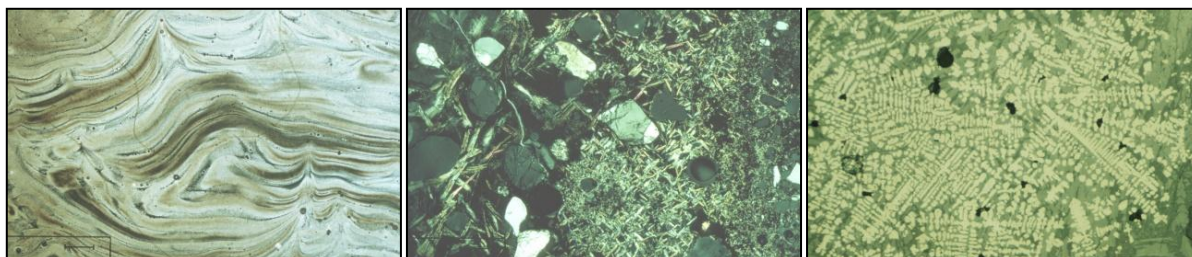

Fig. 10 Micrographs of minerals in bottom ashes: glass formed during combustion (left), gehlenite $Ca_2Al(AlSiO_7)$, in glassy matrix (centre), magnetite, Fe_3O_4 (right) [Pfrang-Stotz 1992]

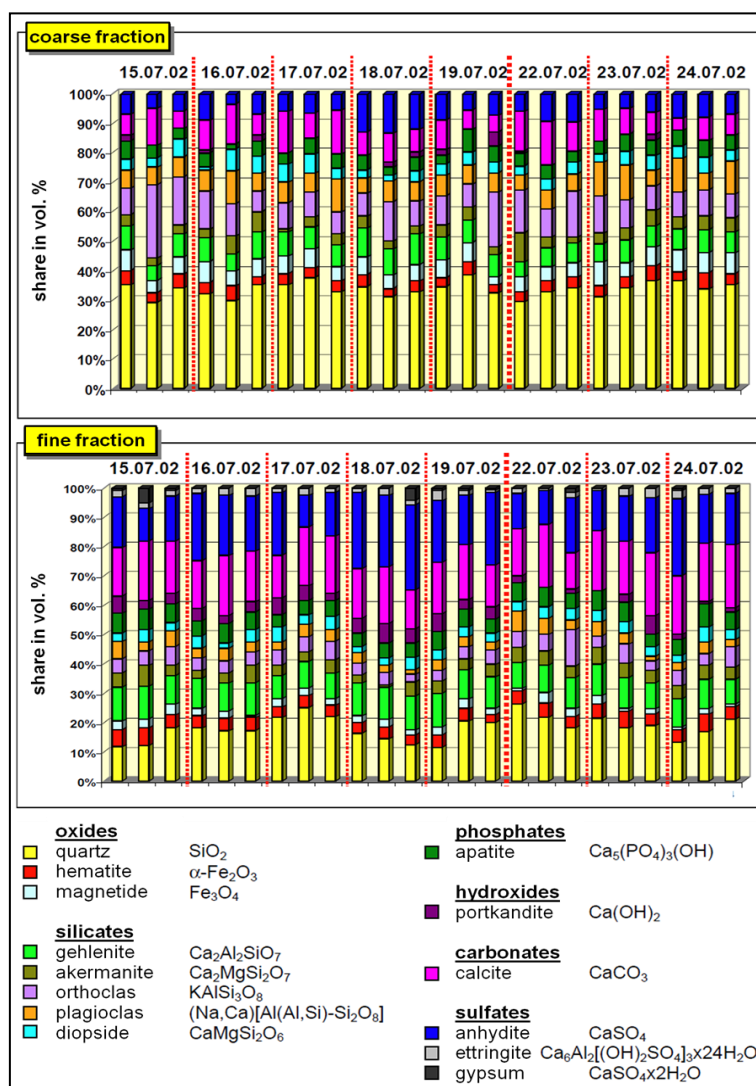|	oxides			phosphates	
	quartz	SiO_2		apatite	$Ca_5(PO_4)_3(OH)$
	hematite	$\alpha\text{-}Fe_2O_3$			
	magnetide	Fe_3O_4		**hydroxides**	
				portkandite	$Ca(OH)_2$
	silicates				
	gehlenite	$Ca_2Al_2SiO_7$		**carbonates**	
	akermanite	$Ca_2MgSi_2O_7$		calcite	$CaCO_3$
	orthoclas	$KAlSi_3O_8$			
	plagioclas	$(Na,Ca)[Al(Al,Si)\text{-}Si_2O_8]$		**sulfates**	
	diopside	$CaMgSi_2O_6$		anhydite	$CaSO_4$
				ettringite	$Ca_6Al_2[(OH)_2SO_4]_3x24H_2O$
				gypsum	$CaSO_4x2H_2O$

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Fig. 11 Mineralogical phases in bottom ashes from a German MSW incineration plant ([Pfrang-Stotz 2005], modified)

Most publications on mineralogical composition of bottom ashes distinguish between main phases (>20 %), secondary phases (<20 %), accessories (<10 %), and traces (<5 %). Main phases are typically quartz and glass, secondary phases are melilites (e.g. gehlenites and akermanites) [Pfrang-Stotz 1992, 1993 & 1995, Eighmy 1994, Lichtensteiger 1996].

In the early 2000s long-term bottom ash sampling campaigns were completed at a number of German waste incineration plants. Detailed mineralogical investigations of the ashes were part of the test program, in most cases separate investigations of their coarse and fine fraction were carried out.

The results depicted in Fig. 11 show the variability of phases identified in three 10 kg grab samples taken per day at a time interval of 2 hours [Pfrang-Stotz 2005]. The bar plots document a predominance of oxidic and silicatic phases - roughly 80 % - in the coarse ash fraction. These phases are mainly responsible for the mechanical properties of the ashes. In the fine fraction, however, they account only for approximately 50 % and the carbonates (e.g. calcite) and sulphates (e.g. anhydrite) are prevailing. These phases are more soluble and control to a certain extent the leaching stability of the ashes.

5.2.3   Bottom Ash Management

5.2.3.1   Management Options

All countries in Europe have stringent quality requirements for disposal of waste, as has been described above. Table 3 and Table 8, however, indicate that the required quality for utilisation is not that much more stringent that adequate combustion control and eventual post-combustion treatment could not meet it. A number of countries (including The Netherlands, Denmark, and Germany) decided to shoulder these efforts and use their bottom ashes as secondary building materials, preferentially in road construction.

A further utilisation option became of interest when prices of all kinds of raw materials including most metals started to escalate: metal recovery. Whether bottom ashes are landfilled or utilised, they undergo at least ferrous scrap removal by magnetic separation. For utilisation further treatment is needed, which will be described in more detail in chapter 5.2.3.3.

5.2.3.2   Separation Technologies

5.2.3.2.1   Size Fractionation

For separation of specific particle fractions all kinds of sieving machines are used, which will not be discussed in detail here. A method developed for gravel and sand classification and used in some treatment plants for combined washing and fractionation of fine ash fractions is the hydraulic belt or hydro-belt separator [Rohr 1987].
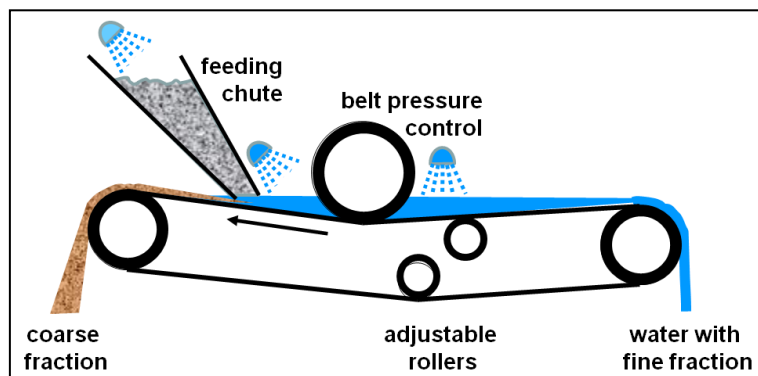
Fig. 12 Hydraulic belt separator for washing and fractionation on a belt ([Rohr 1987], modified)

A mixture of ash and water can be separated on a trough-like belt conveyer. The coarse and heavy particles sink to the base and are transported to the head of the conveyer whereas the lighter particles float along with the water in the opposite direction. The angle of the belt and the form of the trough allow adjustment of the particle size cut. The principle of the method is shown in Fig. 12.

5.2.3.2.2 Metal Separation Technologies

After the mid-1990s, when metal prices started to increase, metal recovery started to look profitable and it became clear that this did not only concern iron but even more non-ferrous metals [Simon 1996]. As a consequence waste incineration plant operators tried harder to improve their metal recovery systems not only by upgrading the magnet separators but also by adding eddy current separators for non-ferrous metals' sorting.

Metal separation from bottom ashes starts in most plants with ferrous scrap removal directly at the bottom ash discharge. The most common practice is the installation of an over-band magnet on top of the bottom ash conveyer. A conveyer belt running rectangular to the bottom ash discharge belt transports the ferrous material drawn out of the bottom ash by attraction of a strong permanent magnet to a silo or another belt conveyer. The operation mode of such system is schematically shown in Fig. 13. This method has limited efficiency only and can be regarded as pre-treatment stage.
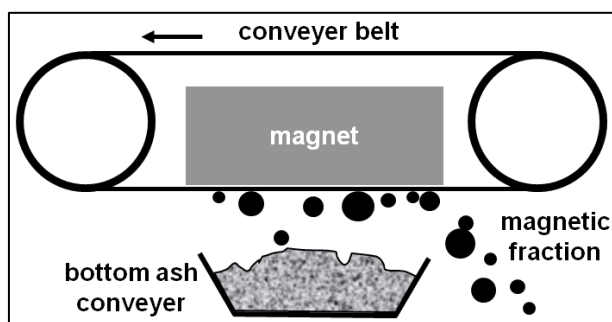

Fig. 13 Scheme of an over-band ferrous scrap removal system with a permanent magnet ([Bunge 2010], modified)

More efficient ferrous separation is done after storage of the raw bottom ashes for few days to reduce their water content. The most common technology is a drum separation system which is shown in Fig. 14.
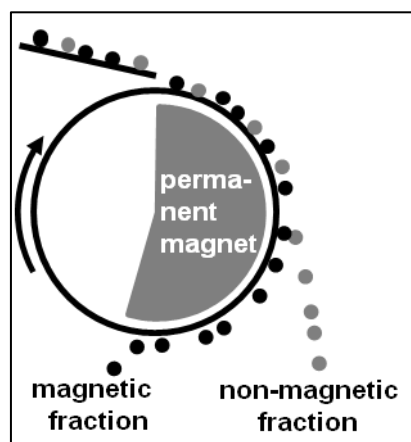
Fig. 14   Drum system for separation of ferrous scrap ([Bunge 2010], modified)

In such systems bottom ash passes over a rotating drum with a permanent magnet built in. Non-ferrous particles continue to fall down by gravity, whereas the ferrous particles are attached to the rotary drum to the end of the central magnet where they fall into a separate chute or container.

Non-ferrous scrap is typically removed by eddy current systems. A scheme of such system is shown in Fig. 15. The bottom ash passes a rotating drum in which a rotating electric coil generates eddy current. This eddy current induces a propellant force in non-ferrous metals and pushes such particles out of the ash. In fine-tuned systems even heavier metals, e.g. Cu, can be separated from lighter ones, such as Al. A problem arises with stainless steel which is not magnetic and also only little receptive for eddy current.
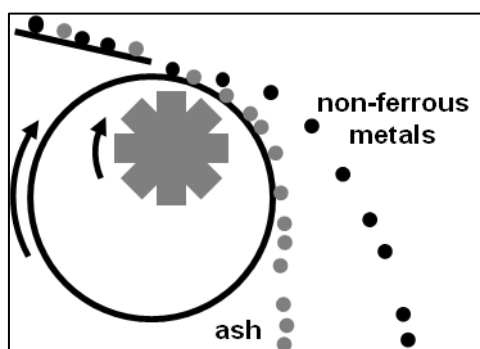

Fig. 15   Eddy current system for separation of non-ferrous metals ([Bunge 2010], modified)

New systems have been developed using a matrix sensor system which detects pieces of metals in a thin layer on a conveyor belt. The detector can be an electro-magnetic sensor for detecting metal pieces, an energy-dispersive X-ray fluorescence system for recognizing specific metals, or a camera for separating light coloured from dark coloured metals like Cu. The signal triggers another matrix of computer operated nozzles which blow the metal piece out of the ash falling down at the end of the conveyer [Eggenberger 2010]. A simplified scheme of such system is shown in Fig. 16.
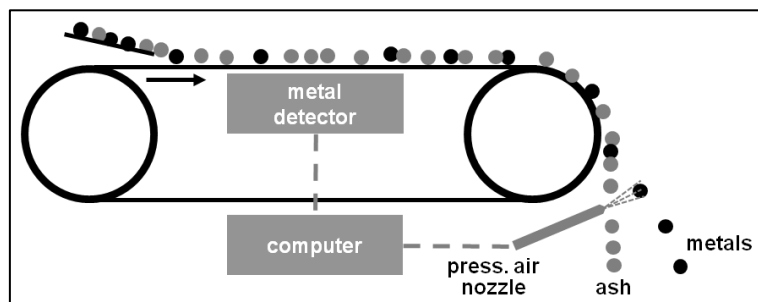
Fig. 16   Sensor operated metal separation system ([Bunge 2010], modified)

The separation technologies described above are those for getting access to the main metallic components in bottom ash. They result, in particular for the more valuable non-ferrous metals, in mixtures of metals which can be refined to get more homogeneous metal fractions.

Another separation method is the magnetic density separation (MDS) which is in principle a sink-float technique using a magnetic liquid in a magnetic field of specific geometry [Rikers 1998]. The magnetic liquid consists of finely grained iron oxide slurry which establishes a density gradient in height in a trough-like belt conveyer. The density gradient is induced by the field of magnets of special geometry located around the belt.
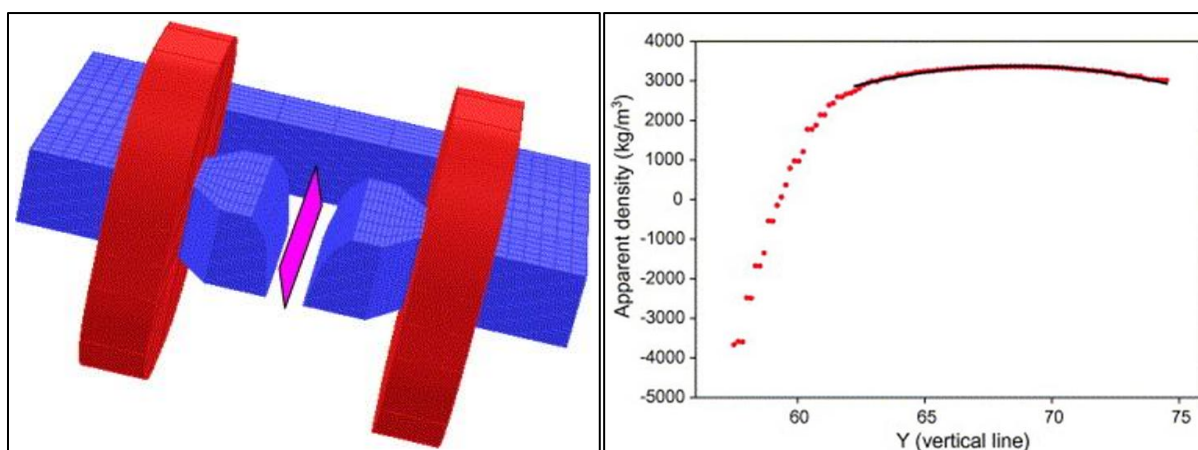

Fig. 17   Scheme of the magnet alignment in a MDS system (left) and characteristics of fluid density (right) [Murariu 2005]

A schematic design of the magnet alignment is shown in the left graph of Fig. 17. The pink plane symbolizes the centre of a trough or a respectively formed moving belt, which contains the magnetic fluid. The right graph in Fig. 17 shows the fluid density along a vertical line in that plane, which has been calculated for a specific magnet field design. In the modelled configuration the maximum density was 3 g/cm^3; in real systems densities up to 20 g/cm^3 have been realised. This enables float-sink separation of materials with very high densities. The graph points also out that close to the bottom and below the magnet the fluid density can also reach densities below 1 g/cm^3.

Such systems have been used for separation of several waste streams such as plastics and shredder residues. At the Amsterdam incineration plant the technology was successfully tested for separation of non-ferrous metals from fine ash fractions [Muchova 2009].

5.2.3.2.3   Metal Separation Systems

After pre-separation of ferrous scrap by an over-band magnet at the bottom ash discharge of the incineration plant and after short-term storage to reduce the water content, metal recovery from bottom

ashes is in most cases performed in special ash treatment facilities. Today's conventional metal separation system treats the coarse and fine ash fraction separately, as schematically shown in Fig. 18.
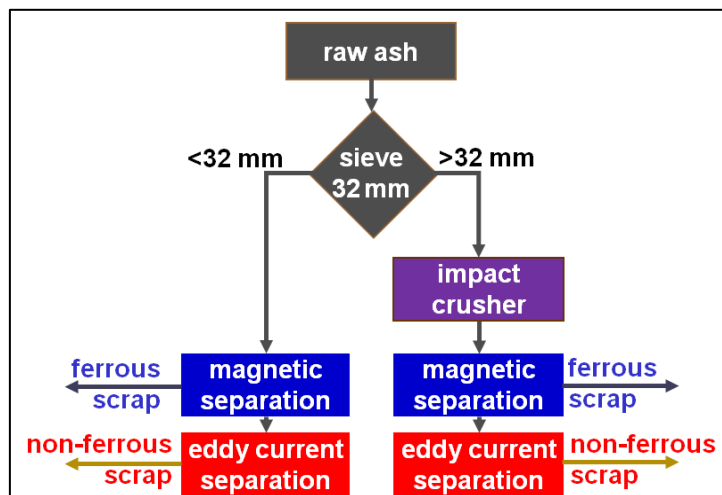

Fig. 18 Conventional system for separation of ferrous and non-ferrous metals ([MVR 2012], modified).

A more complex system designed and applied in Switzerland for optimized metal recovery is shown in Fig. 19 [Bunge 2010]. It separates a number of different metal fractions out of the bottom ash stream down to very fine particle sizes.
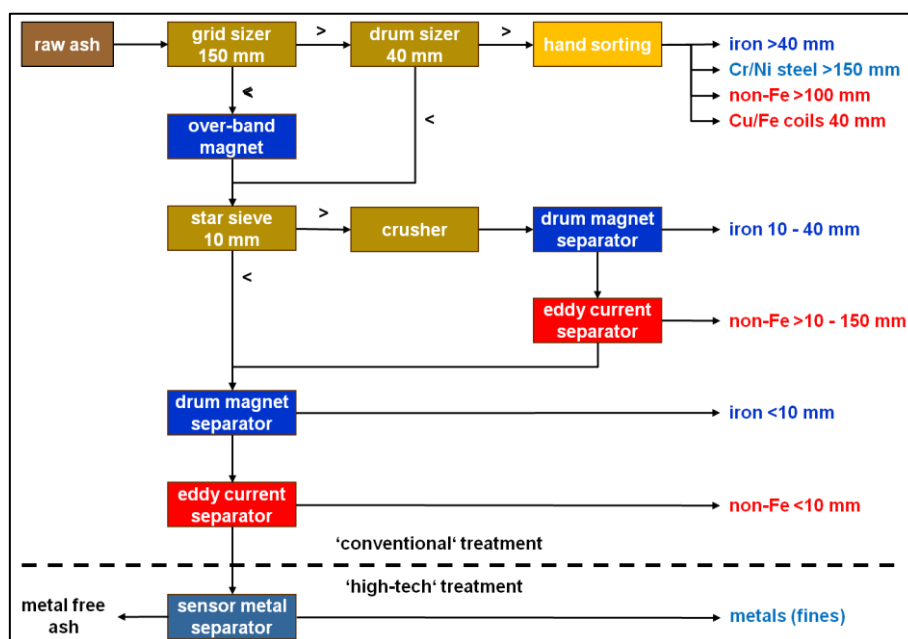
Fig. 19 Optimised metal separation system ([Bunge 2010], modified)

As mentioned above, this is not the final development. Incineration plants such as that in Amsterdam have installed or are going to install further metal refining stages, with the aim of improving the quality of valuable heavy metals and to become more profitable. The plants deliver their non-ferrous metal mix to special companies and get paid according to the analysed metal inventory.

5.2.3.2.4   Economic Relevance of Metal Recovery

To get a feeling about the potential of metal recovery from MSW incineration bottom ashes, the annual consumption of selected metals in Germany will be brought into perspective by comparing to the amount which could be recovered. A rough estimate is shown in Table 17. The data base on a bottom ash production of 4.76 mill. Mg in 2008 [Alwast 2010]. The concentrations of non-ferrous metals are estimated to be the same in Dutch and German ashes, since an analysis of Ag in bottom ash from one German plant showed almost the same result as found in Amsterdam [Muchova 2009]. Data on total metal consumption and metal scrap prices were collected from a report for the German Umweltbundesamt [Alwast 2010] and from several statistics and dealer offers found in the internet.

Table 17   Recovery potential of selected metals and their value on the scrap market in Germany

	Fe	*Al*	*Cu*	*Pb*	*Zn*	*Sn*	*Ag*
content in ash (kg/Mg)	100	10	0.9	0.5	0.01	0.08	0.002
total recovery (Mg)	474,100	47,410	4,267	2,370	47	380	9.5
total consumption (Mg)	20,000,000	3,300,000	1,700,000	320,000	350,000	300,000	1,230
potential (%)	2.4	1.45	0.25	0.74	0.013	0.13	0.77
value (1,000 €)	71,115	15,200	12,800	2,500	40	3,200	7,600

The table shows that only for iron does the amount of recoverable metals reach slightly more than 2 % of the annual consumption. For Al almost 1.5 %, for Pb and Ag about 1 % of the consumed metals may be recovered from bottom ash, the share of Zn is negligible.

The theoretical market value sums up to more than 100 million €, but this does not take the processing costs into account. A cautious estimate made for the Amsterdam plant came to the conclusion that the revenue to be realized by selling the non-ferrous heavy and precious metals could reach 3 – 5 € per ton of bottom ash. This would mean an annual extra profit for a medium size German waste incinerator with an annual throughput of 200,000 Mg of waste and a production of 40,000 – 50,000 Mg of bottom ash in the order of 200,000 €.

Actual data about the recovery of single metals are not available. However, it can be expected that at least the ferrous scrap is almost totally fed back into the economic cycle. For the 14.2 mill. Mg of bottom ash produced in Europe in 2008 [CEWEP 2012] this would account for approximately 1.5 mill. Mg recovered iron.

The recovery of non-ferrous metals is currently growing, although actual data are not available. The actual potential for recovery can be estimated to be in the order of 150,000 Mg. This amount could at least be doubled in the next ten years taking extension of waste incineration as well as better coverage and improvement of separation technologies into account.

The production of Al and Cu is very energy consuming (>30 MWh/Mg and >20 MWh/Mg respectively), which gives additional reason to recover these metals, even if the share of the recovered metals seems small compared to their consumption.

5.2.3.3   Treatment for Utilisation

Whereas metal separation is often the only pre-treatment of bottom ashes prior to final disposal, in the case of utilisation more effort has to be spent to reach the environmental requirements and to comply with the physical and mechanical properties required for the intended utilisation scenario. In most cases the wet discharged bottom ashes are stored for few days to reduce their humidity.

The next step is a sieving since utilisation requires specified particle sizes. The oversized material is often crushed to increase the yield of the usable fraction.

The next step is storage for roughly 3 months. According to German regulations such storage for aging or maturation is mandatory to improve the environmental and mechanical properties of the material. After this treatment the material has to be tested before it is delivered to the respective application scenario or it has to pass the entire procedure a second time.

The scheme of a technical bottom ash treatment plant, operated at the Hamburg MSW incinerator MVR, is shown in Fig. 20 [Zwahr 2005].
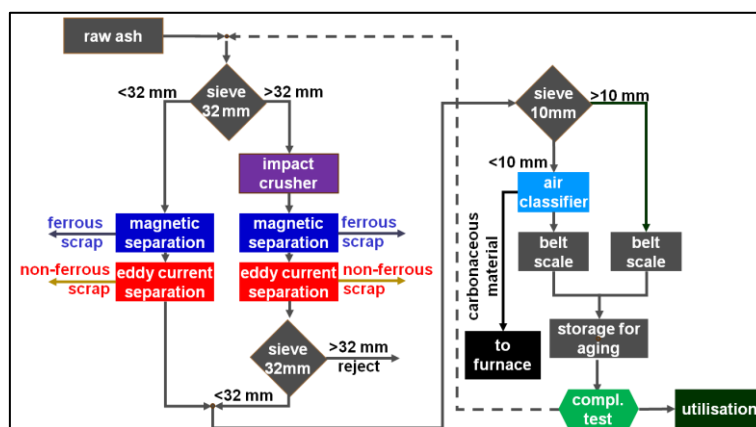

Fig. 20   Bottom ash treatment for utilisation at MVR Hamburg ([Zwahr 2005], modified)

At this plant the technology is optimised for metal recovery, including re-feeding of the aged bottom ashes (notified in the graph by the dotted line) and secondary processing along the whole line. After passing compliance testing the material is sent out for utilisation. This type of bottom ash treatment is often called 'dry' treatment.

Dry treatment as shown above can be followed by wet treatment of fine fractions. A hydraulic belt separator is used to separate water soluble salts, light-weight unburnt constituents and various fine aggregate fractions [Lück 2004]. An example for wet treatment of a < 22 mm fraction resulting from conventional bottom ash treatment is shown in Fig. 21. Similar treatment plants are operated at several waste incinerators. In Germany there are also some central treatment plants treating bottom ashes from a number of waste incineration plants.
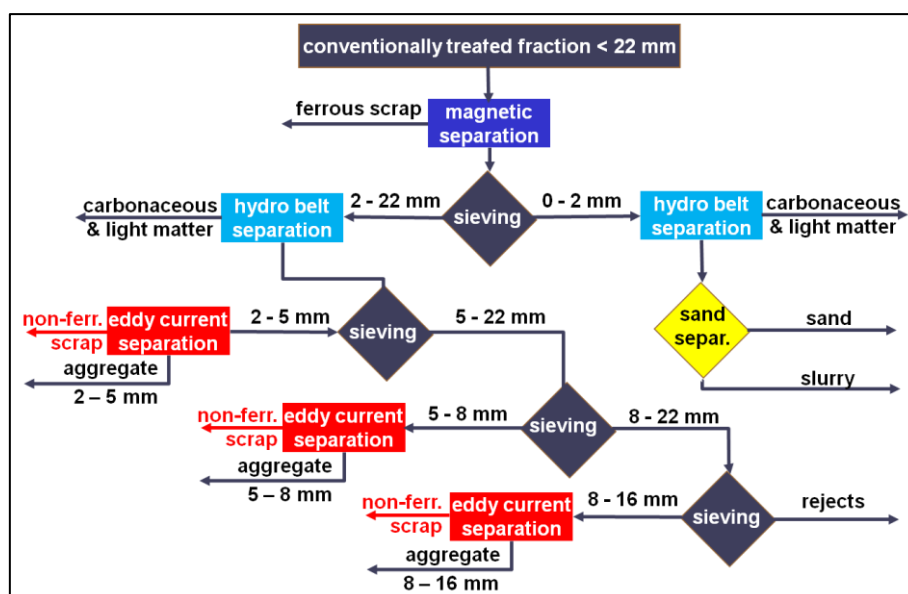
Fig. 21   Wet treatment of bottom ash fine fractions ([Lück 2004], modified)

5.2.3.4   Leaching Stability

Leaching stability is a key parameter for the disposal and the utilisation of MSW incineration bottom ashes. As mentioned above, fresh bottom ashes have a high inventory of alkaline compounds. The shaded area in the alkaline pH range in Fig. 1 indicates that in the actual German leaching test DIN EN 12457-4, the German adaptation of the CEN standard test, bottom ashes establish values between 10 and >12.5. These high pH values are common in modern plants where the fuel bed temperature is typically kept in the range of 800 to more than 1,000 °C. In this region many Ca compounds disintegrate and form strongly alkaline CaO, which is the main component controlling the pH value of fresh bottom ash.

In order to reduce this pH, the German LAGA memorandum requires bottom ashes to be stored for 12 weeks under humid conditions prior to utilisation in road construction. This process is called aging or maturing. During this time the uptake of CO_2 from air converts the alkali and earth-alkali oxides and hydroxides into carbonates which reduces the alkalinity of the ashes. Hence the pH of aged bottom ashes in aqueous solutions ranges typically between 10 and 11, a region where most heavy metals have low solubility.

Data from a test program in a German full scale MSW incineration plant illustrate the effect aging has on the pH of bottom ashes and on the test results obtained by the German test method [Bergfeldt 1997]. Fig. 22 shows that the pH of the fresh bottom ashes (red dots) in the test is typically exceeding 12, but drops down by about two units during the aging process (blue dots). The pH change has a significant effect on the leaching property of Pb which is improved by almost 2 orders of magnitude.
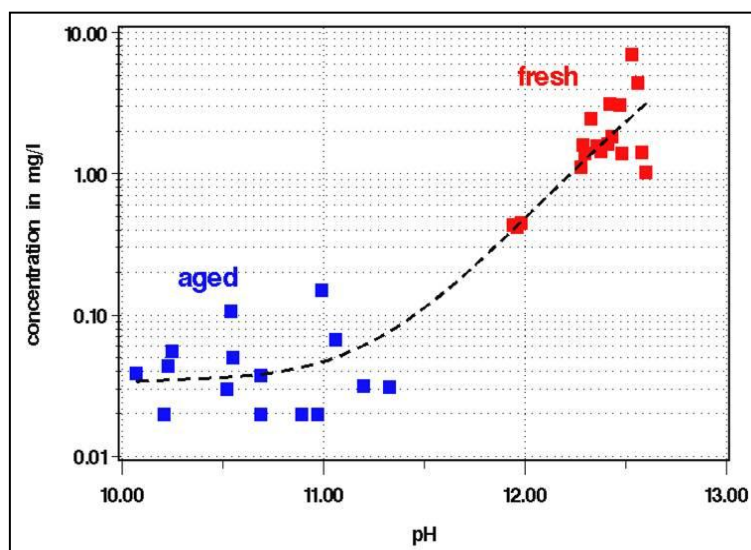
Fig. 22   pH dependency of Pb leaching from bottom ashes of a German MSW incinerator ([Bergfeldt 1997], modified)

There is no doubt that bottom ashes from modern MSWI plants comply easily with access criteria to landfills for granular non-toxic waste; after adequate treatment they can meet the much more stringent standards for utilisation as secondary building materials in road construction. As an example of the quality of treated bottom ashes Fig. 22 shows results of the old German leaching test DEV S4 (which is almost identical with DIN EN 12457-4) performed on 26 samples taken from a bottom ash treatment plant for regular final testing [Pfrang-Stotz 1995a].

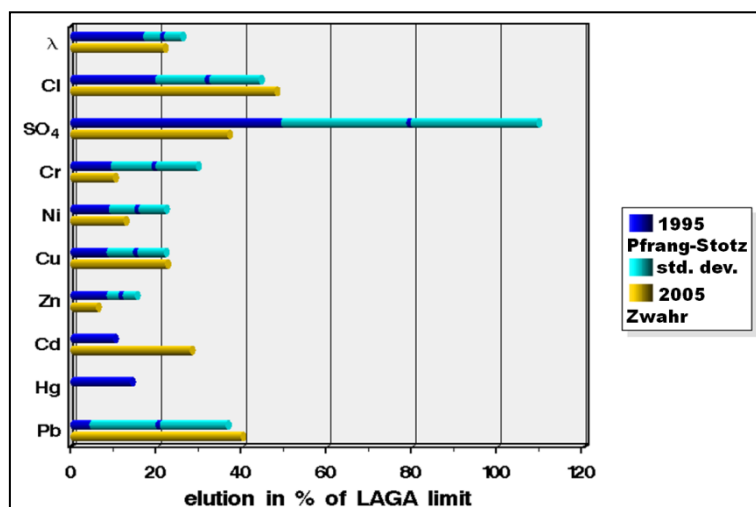**Fig. 23**   Leaching test results of 26 bottom ash samples [Pfrang-Stotz 1995a] and respective results of samples from a Hamburg MSW incinerator [Zwahr 2005] standardised to the limits of the German LAGA memorandum for utilisation

The data are standardised to the limits for utilisation in road construction as given by the LAGA memorandum. These limits are well below those set by the Council Decision 2003/33/EC for access to a granular non-hazardous waste landfill (compare Table 3 and Table 8).

The bar plot indicates that the obtained elution of heavy metals stays all the time below 50 % of the limit. The only value exceeding the limit few times was that of sulphate. The good performance of bottom ashes was ten years later confirmed by tests of Hamburg bottom ashes [Zwahr 2005]. These data are included in Fig. 23. These investigated ashes did meet the sulphate limit easily.

However, meeting legal standards does not tell us anything about the acceptability of the environmental impact. To understand this aspect the old German DEV S4 test was performed on bottom ashes ready for utilisation, on recycled concrete from a highway bridge, and on gravel from the river Rhine [Sauter 2000]. The results of these tests are compiled in the bar chart in Fig. 24. They document, that the leaching stability of matured high quality bottom ashes can be kept in the same order of magnitude as that of conventional building materials which is a strong argument for utilisation of those materials.
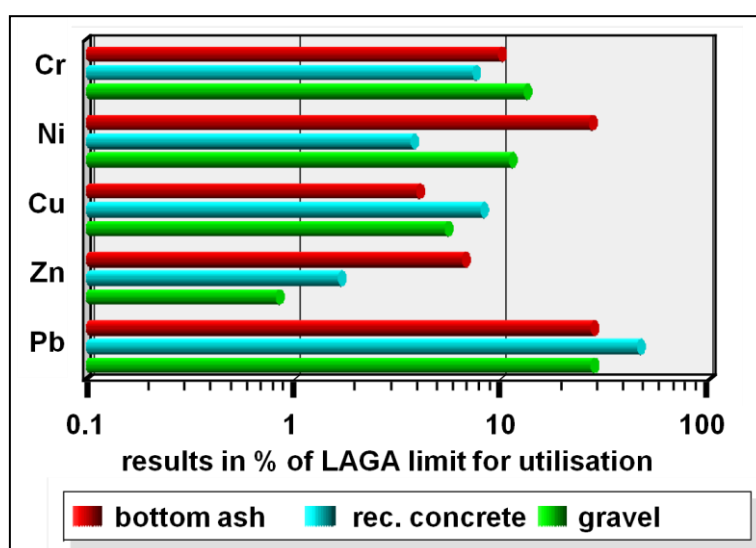
Fig. 24   Results of leaching tests on treated bottom ash, recycled concrete, and gravel [Sauter 2000]

However, it should always be kept in mind that the inventory of the selected metals in bottom ashes is always much higher than it is in comparative building materials. Roads are built for a lifetime of 30 – 100 years and the applied standardised leaching tests allow a prediction of the leaching effects of the tested materials for this lapse of time. They are of course not able to supply a realistic long-term forecast since the leaching properties can change drastically as soon as the matrix of the material in question disintegrates, e.g. by weathering. In this case the risk of total pollutant release cannot be excluded.

5.2.3.5   Processes for Quality Improvement

Although bottom ashes from state-of-the-art waste incineration plants comply already easily with the access criteria of landfills and also – after pre-treatment – in most countries with the standards for utilisation of inorganic residues, there have been efforts, particularly in the late 1980s and early 1990s, to improve their leaching stability.

In Japan fusion or vitrification of bottom ashes is practiced in order to reduce their volume and to improve their environmental quality [Nabeshima 1996]. However, by the early 1990s it was also demonstrated that fusion of bottom ashes from state-of-the-art MSW incineration plants does not improve the quality to the extent that would open new markets [Schneider 1994]. As documented in Fig. 25, the leaching stability of bottom ashes does not increase significantly if these are sintered at 850 or 1.000 °C and also not if they are fused at 1,300 °C.
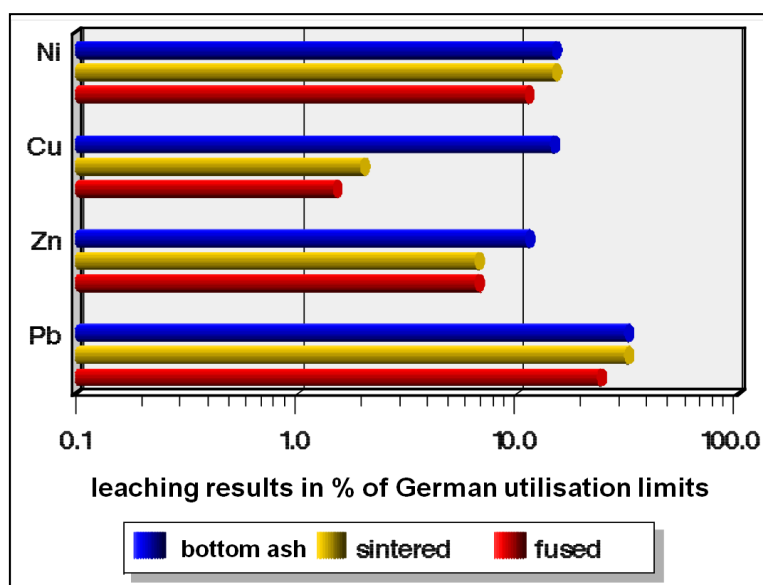
Fig. 25   Leaching results on aged, sintered and fused bottom ashes ([Schneider 1994], modified)

This fact and the economic disadvantage of high energy consumption are reason that the many proposed and pilot scale demonstrated fusion and vitrification processes during this time did not make it to the market in Europe [Faulstich 1995].

Another stabilisation process called WESPHIX[R] is often applied in the US market to immobilise heavy metals by addition of phosphates [Bradley 2002]. The process makes only sense for the US practice of co-disposal of bottom ash, filter ash and APC residues. Since this disposal strategy is prohibited in the EU the process is of no relevance in Europe.

To assess the usefulness of post-combustion treatment it is necessary to consider the environmental benefits of a measure and to understand the improvement obtained relative to the effort spent. The

measure for the effort should be the cost of the process. In other words: an eco-efficiency evaluation is strongly recommended.

The International Ash Working Group identified a number of principles which have to be considered when assessing the benefits but also the obstacles of a given treatment measure [IAWG 1997]:
- Does the process result in a significant quality improvement?
- Does the process impose any health, environmental, or safety impacts?
- Are there secondary residues and where do they end up?
- Is there a final product of high quality?
- Is there a long-term market for that product?
- What are the costs of the process?

It is not easy to answer these questions and even more so if the respective process has not been tested in full scale. This is particularly true for the costs. In view of the total process costs of waste incineration an expensive treatment process might be acceptable for a small residue stream like filter ashes; for the bottom ashes, however, even moderate process costs can be prohibitive.

5.2.4   Bottom Ash Disposal and Utilisation

With the exception of Switzerland which classifies bottom ashes as reactive materials due to their significant inventory of heavy metals and other critical constituents and landfills them, other European countries practice utilisation of treated ashes in the construction sector. The main applications are road construction (where the ash is used as basic layer under water-tight capping), noise protection walls, inner filling of dykes, or aggregates in cement production.

Other applications have been thought of such as production of pavement bricks, tiles, or stone wool. Those processes often required sintering or melting and the high energy cost prevented them to find a broad and stable market [Vehlow 1997]. New proposals to use bottom ash as raw material for glass also do not look promising economically [Monteiro 2008].

The situation in terms of disposal and utilisation in Europe is compiled in Fig. 26. The data are taken from country reports published by CEWEP, the Confederation of European Waste-to-Energy Plants [CEWEP 2012].
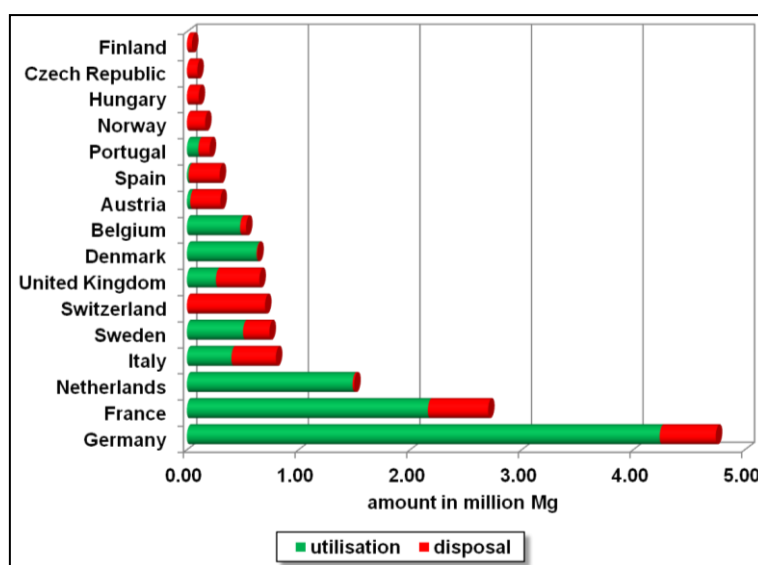

Fig. 26   Bottom ash disposal and utilisation in Europe in 2008/09

In The Netherlands and Denmark almost 100 % of bottom ash is used, preferentially in road construction. In Belgium all bottom ash is said to be applied as secondary building material. In Germany almost 90 % of bottom ash goes to road construction and the typical destination in France (80 % utilised) is 'civil engineering' [Bruder-Hubscher 2001, Bethanis 2004]. In these countries there are national standards regulating the properties and quality of materials for specific utilisation scenarios. Nevertheless, each actual application of treated and positively tested bottom ash needs a permit by the administration in charge.

There are other countries (e.g. Sweden) where no national strategy for bottom ash utilisation exists and each intended use of bottom ash for road construction needs a special permit which is decided upon site specific conditions. In 2008 approximately 590,000 Mg were utilised in road construction, by far the majority on waste treatment and disposal sites [Hjelmar 2009].

In Austria and Spain 90% or more of the bottom ash is landfilled, the rest is utilised as 'slag concrete for landfills' (Austria) and for road construction on landfill sites.

5.2.5   Future Development

For the time being there seems to be a tendency to extend utilisation of treated bottom ashes as secondary building material; the main reason is saving of landfill space. Of course a cheap contribution to building materials has its benefits; however, the share in this market is rather small. Meanwhile there are e.g. in Germany approximately 65 million Mg of material coming from construction and demolition waste recycling, furthermore there are almost 12 million tons of ashes from coal fired power plants which are also competing with the 4.2 million Mg of bottom ashes from waste incineration.

Since the other materials typically carry lower loads of heavy metals it has to be doubted whether (in spite of their excellent elution stability) bottom ashes will find a market in the future. Some countries might decide to follow Swiss philosophy and give up utilisation for safe disposal. Such a decision will not leave a big gap in the building material market behind, but end debates about environmental impacts.

5.3   Boiler and Filter Ashes

5.3.1   Characterisation

Boiler ashes are deposited inside the boiler at temperatures between approximately 800 and 200 °C and filter ashes typically at temperatures slightly below 200 °C in an electrostatic precipitator or a fabric filter. Due to their high inventory of volatilised heavy metals and dioxins these ashes are classified as hazardous materials and have to be disposed of on special and expensive landfill sites, preferentially in the underground, e.g. in caverns in old salt mines. The main problem for aftercare free disposal is their high inventory of water soluble salts, primarily chlorides, rather than that of the other pollutants.

Heavy metals that are volatilised inside the combustion chamber are increasingly condensed on the fly ash surfaces and the concentration of elements like Zn, As, Cd or Pb increases with decreasing temperature. The transfer of selected elements, metals as well as metalloids, into ashes deposited at different temperatures has been investigated in the Karlsruhe TAMARA test plant and is shown in Fig. 27 [Vehlow 1999].
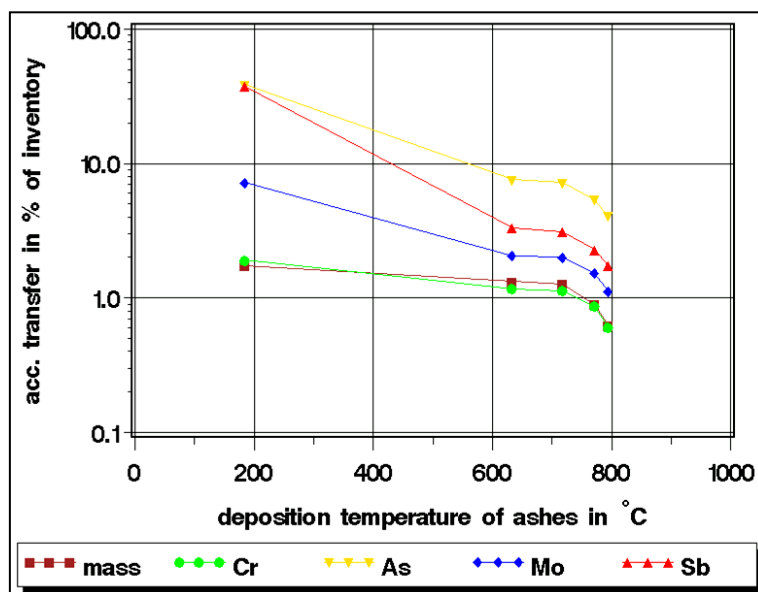
Fig. 27   Accumulated transfer of selected metals and metalloids into fly ash as a function of the ash deposition temperature ([Vehlow 1999], modified)

The graph depicts the accumulated amount of total mass, Cr, As, Mo, and Sb found in ashes deposited along a boiler and in the fabric filter of TAMARA as a function of the deposition temperature of the fly ashes. Approximately 1.5 % of the total ash content of the burnt fuel was transferred out of the combustion chamber. This is also the amount of the transfer of the lithophilic metal Cr. All ash samples contained almost the same concentration of that metal. This fact indicates that the Cr concentration does not change to a great extent between that in bottom and that in filter ashes.

Mo is moderately volatile; slightly less than 10 % were transported by the raw gas out of the combustion chamber. For the metalloids As and Sb this share accounted for approximately 40 %. Hence fly ashes carry high loads of volatile metals, but also boiler ashes are to a certain extent enriched by these metals. This fact and the elevated inventories of low volatile organic micropollutants (such as dioxins) cause boiler and filter ashes to be classified as hazardous materials. They are not allowed to be mixed with bottom ashes and require special measures for their disposal. An overview of the enrichment of selected metals and dioxins in filter ashes compared to their concentration in bottom ashes shown in Fig. 28 underlines the critical properties of these materials. In particular Cd and Pb, but also Zn, As, and Sb, can be enriched in filter ashes compared to bottom ashes by orders of magnitude.
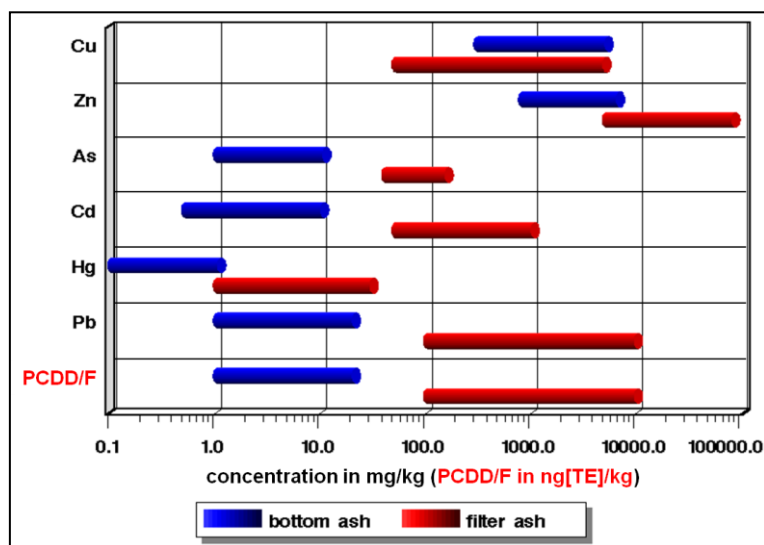
Fig. 28   Concentration ranges of selected species in bottom and filter ashes from grate systems

The concentrations of Zn (up to 10 wt. %) or Pb (up to 1 wt. %) are so high that recovery looks promising. Investigations in that direction started around 1990 but came to the conclusion that this was not commercially viable at that time. Due to rising metal prices on the world market the idea has recently become attractive again (see below).

The bar chart also documents rather high concentrations of PCDD/F in filter ashes. This is not surprising since these compounds are synthesised inside the boiler [Vogg 1990]. They were the major reason to classify filter ashes as hazardous materials in the 1980s.

5.3.2   Processes for Quality Improvement

The high expense of sustainable final disposal of boiler and filter ashes were the reason for numerous attempts to detoxify these materials in order to get access to less expensive disposal routes or even to utilisation scenarios. A broad spectrum of different processes has been proposed and tested in different scales. Table 18 provides a categorization of the various treatment options.

Without going into detail it seems evident that solidification or stabilisation does not alter the toxic inventory of the material. The established fixation or diffusion barrier only lasts for limited time. Two processes were in full scale application: the 'Bamberg Model', where filter ashes are stabilised on a landfill by mixing with the sludge of the wet scrubber discharge [Reimann 1990] and the Swiss filter ash cement stabilisation after washing [Tobler 1989].

The VKI Process uses water to extract soluble salts and stabilises the residue with CO_2 or sometimes also with H_3PO_4 [Hjelmar 1997]. The process has been tested in large pilot scale at three locations in Denmark.

Table 18   Procedures for treatment of boiler and filter ashes

principle	*process*	
solidification/ stabilisation	without additives	(Bamberg Model)
	cement based systems	(Portland cement, alinite)
	waste pozzolanic systems	(coal fly ash)
	chemical stabilisation	(sulphides, TMT 15™)
		phosphate, WESPHIX Process
	organic additives or matrix	(bitumen)
washing and stabilisation		(VKI Process)
thermal treatment	PCDD/F destruction	(Hagenmaier drum)

	sintering fusion vitrification	(mineral respeciation) (melting without additives) (melting with additives)
combined processes	acid extraction (+ sintering + metal recovery) stabilisation with FeSO$_4$, oxidation, sintering	(3R Process) FLUWA Process (Ferrox Process)

Thermal treatment can be performed at moderate temperature /400 – 450 °C) to destroy dioxins in the so-called Hagenmaier Drum [Hagenmaier 1987]. Another option is vitrification at high temperatures (>1300 °C) to produce glass products. Vitrification is mainly favoured in Japan where it was partly also practiced for bottom ashes. The molten products are distinguished by excellent elution stability. Care has to be taken to avoid air pollution by evaporation of metal compounds. The energy consumption of all of these processes, however, is very high and is not compensated by any benefits. That is why they – although developed as described for the bottom ashes - did not conquer the market in Europe.

A third strategy, more in line with the demand for simple and in-plant measures, is followed by the 3R Process which combines an acid extraction of soluble heavy metal compounds (by use of the acid flue gas cleaning solution after Hg separation) with a thermal treatment of the compacted extraction residues in the combustion chamber [Vogg 1984]. If this process is applied the incineration plant no longer exports filter and boiler ashes. A scheme of the process is shown in Fig. 29.
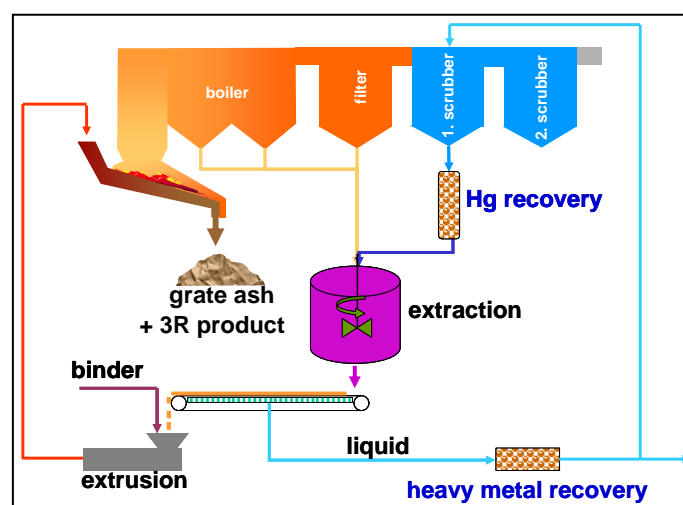
Fig. 29　Scheme of the 3R Process

The technical demonstration revealed that the grate ashes from a 3R Process that contain the leached filter ashes show excellent leaching properties of heavy metals and that the PCDD/F are almost totally destroyed [Vehlow 1990].

The concept of the 3R Process is also the basis of the FLUWA Process [Frey 2004, Schlumberger 2010]. The only difference is the direct mixing of the extracted residues with the bottom ash rather than its thermal treatment in the combustion chamber. The process is in full scale operation in a number of Swiss incineration plants.

The Ferrox Process for treatment of filter ashes and APC-residues involves washing of the residues in a ferrous sulphate solution and contemporary oxidation of the iron to form insoluble iron hydroxides and oxide hydrates [Lundtorp 2002]. The products are of the quality to be landfilled or they are fed back into the combustion chamber for further thermal treatment to improve quality. Tests in a pilot

plant documented the almost total destruction of PCDD/F and an excellent leaching stability of heavy metals after such sintering [Bergfeldt 2004, Baun 2004].

5.3.3 Material Recovery from Filter Ashes

When the 3R Process was developed in the mid1980s recovery of metals from the filtrate was already being considered. This looked especially promising for Zn. At that time, however, such recovery was not economically feasible and the research was not continued.

As mentioned above this situation has changed and the development of increased prices for raw materials has made recovery interesting again. That is why Swiss scientists came back to the old idea of metal recovery from filter ashes, now by using the FLUWA Process as basis [Frey 2004]. Since about 50 % of the Swiss waste incineration plants are equipped with the FLUWA Process, such recovery should be profitable.

Table 19 shows concentration ranges of selected metals in filter ashes as published in a review in 1997 [IAWG 1997] and new data from four Swiss incineration plants [Bühler 2010]. The third column of the table contains averaged data for estimation of recovery potential.

Table 19 Concentration ranges of selected metals in filter ashes (data in mg/kg)

	IAWG	*Swiss data*	*average*
Cu	50 – 5,000	1,200 – 1,350	1,300
Zn	5,000 – 80,000	40,000 – 44,000	45,000
Cd	50 - 450	550 - 650	600
Sn	1,700	--	1,500
Pb	5,300 – 26,000	15,000 – 18,000	16,000

Published extraction rates achieved in the FLUWA and 3R Process for selected metals are compiled in Table 20.

Table 20 Extraction rates in % obtained in the 3R Process at low pH and in the FLUWA Process

	3R Process	*FLUWA Process*
Cu	25 - 35	20 - 45
Zn	70 - 80	60 - 83
Cd	90	85 - 93
Sn	20 - 30	-
Pb	25 - 40	40 - 70

As the table shows, the efficiencies of both processes are, as expected, similar for Zn and Cd¸ those for Cu and Pb are higher in the FLUWA Process, most likely due to addition of H_2O_2 to the effluents from the acid scrubber.

There are a number of processes suited for recovery of metals from acid solutions. These are hydroxide precipitation, ion exchange, solvent extraction and electrolysis. Some of these processes have already successfully been tested in the early 1990s, but were given up for economic reasons. New investigations were started for Zn that resulted in the development of the FLUREC Process for electrolytic Zn recovery [Schlumberger 2010]. The process is operated in demo scale in Switzerland [Bühler 2010].

There are other proposals for recovering metals from fly ashes; however, they are no further forward than laboratory testing.

During the 1990s thermal processes for vitrification of bottom and filter ashes were developed, which often included stages for recovery of evaporated metals [Simon 1995b]. A special process to separate metals, in particular Zn, as chloride from filter ashes was studied in detail [Jakob 1996].

In Japan, where ash melting is widely practiced, a process was developed to leach Zn out of the fly ashes from the melting process with sulphuric acid; Zn was than precipitated as sulphide [Izumikawa 1996]. None of these processes has found industrial application yet, due to high energy costs.

5.3.4 Production and Management Practice

Actual data on the production and disposal of boiler and filter ashes are rarely found in literature. Most statistics do not separate the two ashes and often published figures only give APC residues as the sum of boiler and filter ashes as well as residues from chemical gas cleaning. Although mass flow diagrams of grate or fluidised bed based waste incinerators allow preliminary estimates of total production, the ranges depending on design and operation mode of individual plants can be broad.

In the context of this report, however, the management strategy practiced in the country is more interesting than the precise amount of ashes. Data on filter ash production found in 2006 annual reports published by CEWEP are compiled in Table 21.

Table 21 Filter ash production and management in selected countries [CEWEP 2012]

country	year	production [Mg]	comments
Austria	2004	40,000	mainly salt mine backfilling, hazardous landfill
Belgium	2004	50,000	solidification and hazardous landfill
Czech Republic	2004	6,000	5000 hazardous landfill, 1000 underground mine
Denmark	2004	86,834	100% recycled (salt mine after special treatment)
France	2004	400,000	hazardous landfill
Germany	2005	650,000	utilisation in salt mine, minor amount hazardous landfill
Hungary	2005	13,585	hazardous. landfill
Italy	2004	71,814	hazardous. landfill
Netherlands	2003	82,200	50% utilised in mines and construction (e.g. asphalt filler)
Portugal	2005	40,000	inertisation before hazardous landfill
Spain	2005	94,420	hazardous. landfill
Sweden	2004	138,000	landfilling + utilisation in Norway (Langøya)
United Kingdom	2000	78,125	hazardous landfill

As can be seen, most filter and boiler ashes in Europe are disposed of in hazardous waste landfills, in many cases in old salt mines. In Germany filter ashes packed in big bags can be permitted to be used for backfilling old salt mines [Plomer 1995]. This practice is acknowledged as utilisation respectively recovery. Similar regulation exists in Norway where filter ashes are used to fill an old quarry on the island of Langøya. On this island gas cleaning residues from Sweden are also accepted.

A peculiar management practice is performed in the Netherlands where filter ashes are partly used as filler in asphaltic layers in road construction.

5.4 APC Residues

5.4.1 Characterisation

In the context of this report APC residues are those from chemical gas cleaning, either from wet or dry systems.

Wet scrubbing comprises two stages: an acid scrubber for HCl followed by a neutral one for SO_2 abatement. The neutralising agents are either NaOH or Ca(OH). The neutralisation stoichiometry is for both agents and both acid gases close to 1. The neutralisation products of HCl are NaCl or $CaCl_2$;

those of SO_2 are finally Na_2SO_4 respectively $CaSO_4$. Other acid gases such as HF, HBr, or SO_3 which would also end up in the acid scrubber are present in the flue gas only in minor amounts.

Of greater concern in terms of its toxicity is Hg, the compounds of which are mainly in the gas phase in front of the scrubbing system. If the acid scrubber is operated at very high acidity, Hg is absorbed in the scrubbing solution. To a certain extent fine fly ash particles which have passed the filter also end up in the first scrubber.

If the incineration plant is allowed to discharge the scrubber effluents into a sewer system heavy metals have to be removed from the solution. This is done by precipitation of hydroxides at a pH regime of 9 – 9.5. For Cd and Hg in particular often inorganic sulphides (e.g. Na_2S) or organic ones (e.g. tri-mercapto triazole) are added to the neutralising agent. The amount of dried metal hydroxide sludge is in the order of 1.5 – 2 kg/Mg of waste. The sludge is often sent to metallurgical companies for recovery of metals.

Hg can be extracted from the washing solution of the first scrubber by ion exchange in a bypass to the circuit of that scrubber [Braun 1992].

In many countries the discharge of the neutralised scrubbing effluents is prohibited and the brines have to be evaporated, either in a separate system, or (as is usual) in a spray drier. This spray drier can be installed between filter and scrubber system, followed by a second filter. In this configuration filter ashes and APC residues are separated. The spray drier can also be installed directly at the boiler exit in front of the main filter resulting in a mix of filter ash and APC residues. In both cases the filter behind the spray drier is a fabric filter.

The amount of solid neutralisation products from wet scrubbing ranges between 10 and 20 kg/Mg of waste. A calculation using averaged mass flows of HCl and SO_2 for NaOH or $Ca(OH)_2$ as neutralising agents is presented in Table 22 [Vehlow 2010].

Table 22 Neutralisation products from wet scrubbing for NaOH and $Ca(OH)_2$ in kg/Mg of waste

	NaOH	*Ca(OH)₂*
acid scrubber	11.0	10.9
neutral scrubber	4.5	5.6
mixed effluents	15.5	16.5

Dry scrubbing processes based on Ca compounds are in use in many plants all over the world. They can be performed with different reagents. The most common ones are limestone, $CaCO_3$, calcium oxide, CaO, lime, $Ca(OH)_2$, or sodium hydrocarbonate, $NaHCO_3$, [Korte 1994], which are injected into the flue gas for neutralisation of acid gas components. The scrubbing products are in most cases removed from the flue gas by a fabric filter.

Table 23 compiles stoichiometric ratios and residue mass flows which have been calculated using a raw gas HCl mass flow of 6.5 kg/Mg waste and a raw gas SO_2 mass flow of 2 kg/Mg waste. Other gas components such as HF, HBr, or SO_3 are not taken into account since their contribution to the total residue stream is almost negligible.

Table 23 Stoichiometric ration (SR) and mass flow (M) of scrubbing residues from dry, semi-dry and semi-wet systems, operated with $Ca(OH)_2$ (data in kg/Mg of MSW)

	HCl		*SO₂*		M_{total}
	SR	M_{HCl}	*SR*	M_{SO2}	
Ca(OH)₂, dry	1.4	14.1	3.5	11.2	25.3
Ca(OH)₂, semi-dry	1.3	13.5	3.0	10.0	23.5
Ca(OH)₂, semi-wet	1.2	12.8	2.5	8.9	21.7

NaHCO₃	1.04	5.5	1.04	11	15.5

The resulting residue mass flows for Ca based systems are 25 to more than 50 % higher than those produced in wet systems with evaporation of the water. The residue mass flow if NaHCO$_3$ is used as reagent is because of the similar stoichiometry in the order of that found in wet scrubbing systems. These residues are shipped to a central processing plant where they are cleaned and used for Na$_2$CO$_3$ production. As in wet scrubbing systems with discharge of liquid effluents a small amount of precipitated heavy metal hydroxides or other compounds remain for final disposal.

Due to the high solubility of all residues from dry scrubbing their safe disposal can only be guaranteed on special and expensive sites. A different - and finally very cheap - way of disposal of APC residues is the same as has already been described for filter ashes: utilisation for backfilling of salt mine caverns in Germany and of an old quarry in Norway.

5.4.2 Recovery Options

Attempts have been made to utilise parts of the ingredients of these residues in order to minimize the disposal problem. The challenge is the closing of the chlorine cycle. Different processes for recovery of single salts have been tested. NaCl and Ca(Cl$_2$) can be recovered from the effluents of the acid scrubber by crystallisation [Karger 1990]. This technology is still applied in a few plants, e.g. in Germany.

Crystallisation is also applied to recover gypsum from the neutral scrubber effluents of Ca based wet scrubbing. In case the scrubber is neutralised using NaOH, lime is added [Kürzinger 1989].

HCl can be recovered from the effluents of the acid scrubber by distillation [Juritsch 1989]. To achieve a marketable product, however, several cleaning stages have to be added. The technology is applied at the Hamburg MVR waste incineration plant for HCl recovery is depicted in Fig. 30 [MVR 2012].

As the flow sheet shows, it requires a lot of effort to produce clean HCl. At the Hamburg MSW incineration plant the recovered HCl is used in processes inside other plants operated by the owner company.

An interesting option for closing the chlorine cycle is the production of elementary chlorine by electrolysis [Volkman 1991]. This process would be profitable if the gas could directly be delivered to a PVC factory; for the time being, however, no application is known.

All such processes can only be successful if they end up with high quality products and if there is a long-term market for the products. For example, today in Germany only a few MSW incineration plants produce HCl, NaCl, or CaCl$_2$ which can be marketed; a few are producing gypsum, which was preferentially used as cover on landfills, but sometimes used in the building sector.
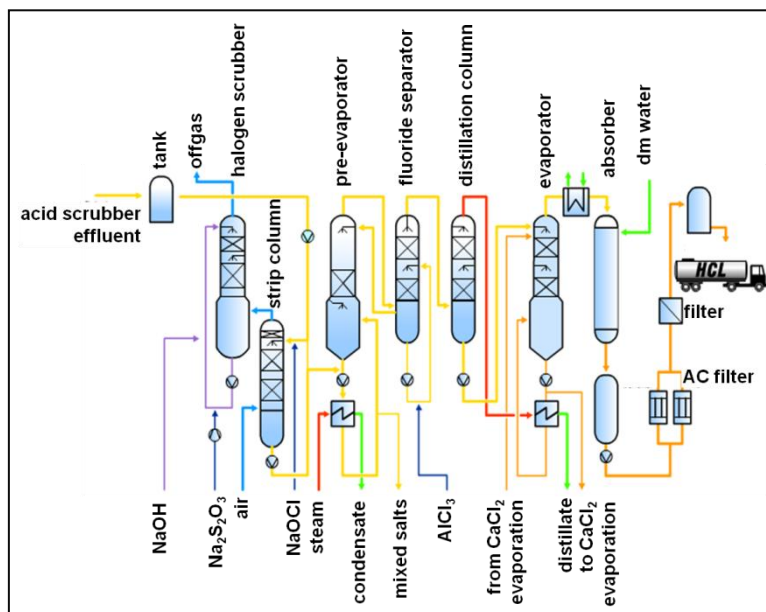
Fig. 30 HCl recovery at the Hamburg MVR plant ([MVR 2012], modified)

6   Residues from Fluidised Bed Systems

6.1   Mass Flows

Fluidised bed (FB) furnaces can only be operated with fuels of limited particle size, usually below 20 cm. If this technology is used for MSW incineration, the waste requires pre-treatment, at least size reduction, and, in most cases, metal separation, too. The technology was widely used in Japan, where waste is of a different quality compared to Europe.

The material is burned in a fluidised sand bed, sometimes with the addition of dolomite for the capture of acid gases. In such furnaces the amount of sand is typically 10 – 50 times higher than the amount of fuel.

The advantage of homogenous combustion in the sand bed is paid for by the limited particle size, the required pre-treatment of the fuel and the limited fuel bed temperature which has to be kept below 850°C to avoid a collapse of the bed by melting of ash ingredients.

Three types of furnaces are in use: stationary, circulating, and revolving or internally circulating fluidised beds. The amount of residues from all furnace types is similar, but, unlike grate systems, published data are not widely available. The few available data sets, one from a Swedish plant [Taherzadeh 2010, Schüssler 2011] and one from a Japanese plant [Granatstein 2000], both burning RDF, and another one from a Belgian plant burning 70 % RDF and 30 % dried waste water treatment sludge [van Caneghem 2010] show comparable mass flows.
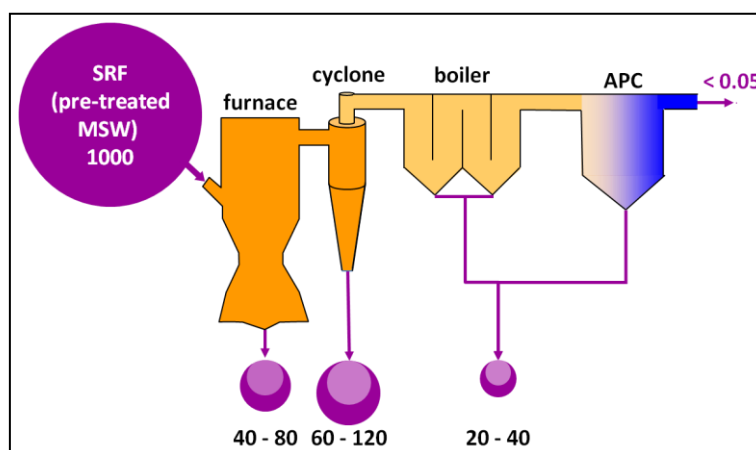

Fig. 31   Flow of solid masses in a fluidised bed incinerator burning SRF

6.2   Residues

6.2.1   General Remarks

Although FB combustion is common in many European countries, publications characterising residues from full scale plants are rare; in particular data describing combustion of mixed MSW is lacking. Since FB furnaces do only accept fuel of limited size, MSW is always pre-treated. The simplest treatment is shredding or crushing, but in most cases metal separation is also performed upfront. Hence in reality FB combustion of waste always refers to combustion of SRF or RDF, depending on the production of the fuel and its quality.

A significant number of available data have been generated in laboratory or semi-technical test facilities, in most cases not from combustion of pure RDF/SRF; but from its co-feeding to biomass or coal.

Since the chemical and physical processes taking place in a FB furnace are the same as in grate furnaces in principle the fate of elements is similar in both combustion systems. Significant differences arise from the typically lower bed temperature in FB than in fuel beds on a grate. This limits the volatilisation of several heavy metals and results in lower concentrations of these metals in the fly ashes.

The high transfer of inert fuel bed material into the fly ash flow adds to this effect. Hence fly ashes from FB systems are comparable to diluted fly ashes from grate systems.

In FB systems sulphur capture is often already performed by addition of CaO to the fuel bed which reduces the SO_2 concentration in the flue gas, hence the efforts in its abatement, and also the amount of respective residue, e.g. gypsum.

6.2.2 Bed Ashes

Fig. 31 shows that in FB furnaces the quantity of bed ash is relatively low compared to bottom ash in grate systems. The validity of published data is questionable since bed ash often contains varying amounts of bed material that cannot be totally separated out. Furthermore, use of CaO as additive for sulphur capture and $CaSO_4$ as neutralising product can be included in the data. These ingredients are obstacles for utilisation of bed ashes; hence bed ashes are typically landfilled.

Since fuel preparation for FB combustion contains a size reduction stage, the grain size distribution of bed ashes is lower than residues from combustion of untreated mixed MSW in grate furnaces.

6.2.3 Filter Ashes

As mentioned above the high entrainment of inert ashes and bed material out of the fluidised bed produces a fly ash which carries the similar amounts of volatilised species, the actual concentration of these species, however, is lower than in fly ashes from grate systems.

Table 24   Concentrations of selected elements in filter ashes

	Ragoßnig 2005	*Hernandez-Atonal 2007*	*Balampanis 2010*	*IAWG 1997*
Cr	83.7	255 - 360	400 - 1,070	100 - 1,000
Cu	-	1,500 - 2,070	360 - 470	50 - 4,000
Zn	1,646	1,800 - 2,090	800 - 1,230	5,000 - 80,000
As	6.4	14 - 25	-	40 - 120
Cd	6.8	<0.4 - 2.9	3 - 7	50 - 450
Pb	478	290 - 366	760 - 1,220	5,300 – 26,000

Table 24 compiles published concentrations of heavy metals and As in filter ashes from fluidised bed incinerators. The first data set was derived from full scale combustion of an RDF fuel mainly containing waste wood, bark, sawdust, fibrous residues, package waste, and a small percentage of residues from chipboard production; its net calorific value (NCV) was 11.3 MJ/kg [Ragoßnig 2005]. This fuel can generally be classified as biofuel.

The second data set is from pilot scale combustion of RDF produced from MSW which was shredded, its organic content was stabilised for 8 – 10 days in a digestion tower, then run through a magnetic and eddy current separator, screened and finally pelletised; its NCV was 20.8 MJ/kg [Hernandez-Atonal 2007].

For the third data set SRF according to CEN standard 'NCV 3, Cl 2, HG 1' was burnt in a 50 kW FB test rig [Balampanis 2010]. The CEN data translate to a NCV of 15 – 20 MJ/kg, Cl inventory 0.2 – 0.6 wt. %, and Hg ≤ 0.02 mg/MJ.

For comparison ranges of filter ash concentrations from grate incinerators burning mixed MSW as published by the International Ash Working Group [IAWG 1997] have been included in the table.

The filter ashes of the first biofuel-like fuel show the lowest concentrations. In the filter ashes from combustion of the comparably clean SRF almost equal concentrations of Cd and slightly higher ones of Zn were found, Cr and Pb were strongly enriched. The RDF filter ashes carried high loads of Cu, Zn, and As, whereas Cr ranged between the two other ashes and Pb showed the lowest figures.

Compared to filter ashes from MSW combustion in grate equipped incinerators, all concentrations of the volatile elements Zn, As, Cd, and Pb are much lower. This fact reflects that fly ashes from FB incinerators are diluted by high amounts of inert ashes; the volatilisation is the same in both furnaces if the Cl level and the bed temperature are of similar value.

The almost lithophilic Cr shows similar values in all filter ashes and the moderately volatile Cu has also comparable values in RDF filter ashes and those from grate systems.

7   Residues from Co-Treatment of Biomass and Waste Based Fuels

Co-incineration of fuels produced from waste with biomass is performed at industrial power stations. This practice is not common, except in Finland. These installations are usually FB incinerators with high combustion temperatures. Composition data for residues from such co-combustion are rarely found in literature. Table 25 compiles data of bed and filter ashes from 2 Finnish FB incinerators operated with biofuels and RDF.

Table 25   Selected elements in bed and filter ashes from three Finnish co-combustion plants (plant 1: forest residues + 12 % RDF from household and commercial waste; plant 2: solid biofuels, dried sludge and peat + 20 % RDF from demolition wood and industrial waste, [Ranta 2002]) and MSW incineration residues [IAWG 1997]

	bed ash from SRF co-incineration		MSW bottom ash	filter ash from SRF co-combustion		MSW filter ash
	pant 1	*pant 2*		*plant 1*	*plant 2*	
Cr	120	48	100 – 1,200	230	100	100 – 1,000
Mn	1900	2800	400 – 1,000	5000	7300	800 – 1,500
Ni	15	13	50 - 800	53	42	100 - 300
Cu	1200	120	450 – 4,500	2200	180	50 - 5000
Zn	1100	680	800 – 6,000	3300	1400	5,000 – 80,000
As	21	<30	1 - 80	51	<50	40 - 120
Cd	0.05	<10	<0.5 - 10	15	<10	50 – 1,000
Pb	55	<40	350 – 5,000	790	91	2,500 – 12,000

The grain size distribution of bed ashes from FB incineration is typically lower than that of grate systems due to the necessary pre-treatment with size reduction. This shift is should be expected, particularly if biomass and RDF/SRF are burnt.

The table shows that heavy metal concentrations in bed ashes – with the exemption of Mn – are always in the lower range of those found in MSW incineration plants. This should be expected since biomass or peat contain much lower heavy metals than MSW and the RDF has been produced from MSW based fractions, mainly paper, plastics, and wood and should hence also contain less pollutants than mixed MSW.

The same is valid for the filter ashes in which the volatile heavy metals present in the fuel are enriched compared to the bed ashes, but their concentrations are at the lower end or well below those found in MSW filter ashes.

Metallic constituents are typically not found in the bed ashes since metals have been separated already during the RDF production process.

8   Conclusions and Outlook

The 1980s were a decade of rapid tightening of air emission regulations for waste incinerators, which then became a strong driver for the development and implementation of highly efficient APC systems. Almost at the same time first attempts were seen to improve the quality of solid residues, too. These were mainly focussed on inertisation and safe disposal of APC residues, especially filter ashes.

Since that time intensive research and development activities have been aimed at improving the quality of the various residues and enabling their safe disposal or utilisation. The residues this work focused on were those from incineration plants equipped with grate furnaces. FB incinerators were not common for waste outside Japan and reliable data on their residue quality are rare.

In many countries the bottom ash (the main residue stream) has been used mainly as aggregate in road construction. Treatment technologies were developed to improve the ash quality and the standard achieved today guarantees no significant impact on the environment if the material is used correctly. However, whether such utilisation is accepted depends on the definition of acceptable environmental impact and is a political and societal decision rather than a technical one. Switzerland, for instance, landfills bottom ashes because of their high inventory of heavy metals, regardless of their leaching stability.

Another issue concerning bottom ashes that has come into focus since the late 1990s is their metal content. Ferrous scrap has always been separated, initially to improve the aggregate quality. With increasing metal prices this separation became profitable and recently the inventory of non-ferrous metals has become economically interesting. As a result all bottom ashes undergo intensive separation stages for both types of metals. The most attractive metals are Al and Cu. To improve metal recovery dry bottom ash discharge is being practiced in a number of plants and it should be expected that this technology will be used by more plants in future.

Filter ashes (including boiler ashes) are hazardous residues due to their high loads of water soluble salts, heavy metals, and PCDD/F. The main problem concerning disposal are salts, especially alkali chlorides. Technologies for stabilisation by washing, solidification, melting/fusion, or leaching have been developed. Melting is applied in Japan, leaching with eventual stabilisation of the leached ashes in Switzerland.

The latter technology lead to the revival of an idea already investigated in the 1980s, but given up due to missing economic interest: recovery of Zn from filter ashes. It is expected that this technology will be improved with time and will find widespread application, most likely in centralised treatment plants.

APC residues are also hazardous materials; their main problem is the salt content. Processes have been developed to recover Cl as marketable HCl or NaCl. Currently these processes are not economic and are practiced by few incineration plants only. It may be possible to achieve better use of gypsum and recovered chlorine products (the latter for industrial use) in centralised plants developed in co-operation with the chemical industry. Further research and development is required in this area.

The use of $NaHCO_3$ as neutralising agent, the residues of which can be utilised in chemical industry, could make handling of APC residues easier. The process is used in a number of plants, but its application depends on the conditions of the patent holder, which makes a forecast difficult.

The quality of residues from combustion of RDF, SRF or other waste derived fuels is less well investigated. It depends mainly on the quality of the fuel and of the combustion process. Production of high quality waste derived fuels is complex and expensive, especially if they originate from mixed municipal solid waste.

The major challenge in all residue management scenarios is the definition of final sinks of pollutants. PCDD/F and other organic pollutants can be thermally destroyed and heavy metals can to an extent either be recovered or widely stabilised. This is not that easy for water soluble salts, which cannot be stabilised and for which there is no stable and promising market to be seen today.

These problems have not only scientific and technical aspects, but essential prerequisites for long-term sound and aftercare-free solutions also have to take socio-economic effects into account and can only be realised with public involvement.

9   Acknowledgements

10   References

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