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Reststoffe aus der energetischen Verwertung von Abfällen und Biomassen

Zusammenfassung

In einer Literaturstudie wurden detaillierte Informationen zur Qualität fester Reststoffe aus thermischen Prozessen zur Behandlung von Siedlungsabfall und Biomasse gewonnen. Des weiteren wurden Möglichkeiten ihrer Verwertung und Anlagerung sowie die derzeit in der EU jeweils praktizierten Strategien untersucht. Die Ergebnisse bestätigen teilweise ein gutes Prozessverständnis, in anderen Bereichen aber auch Wissenslücken und weiteren Forschungsbedarf.

Reststoffe aus der Abfallverbrennung sind intensiv untersucht worden. Rostaschen aus modernen Anlagen haben eine hohe Qualität, die ihre problemlose Ablagerung auf Deponien gestattet. Maßnahmen zu Qualitätskontrolle und -sicherung sind entwickelt und werden angewendet. Die Verwertung als Baustoffe in bestimmten Szenarien ist heute mehr eine Frage der Akzeptanz durch Politik und Öffentlichkeit als ein technisches Problem.

Filterstäube und Gasreinigungsrückstände tragen ein hohes Inventar an Schwermetallen und organischen Schadstoffen. Sie sind als Sonderabfälle eingestuft und an ihre Ablagerung sind besondere Anforderungen zum Schutze der Umwelt zu stellen. Bei den Reststoffen der nassen Rauchgasreinigung verbleibt ein metallhaltiger Hydroxidschlamm. Das Problem bei Reststoffen aus der Eindampfung der Absalzlösungen nasser Wäscher sowie bei Reststoffen trockener Verfahren ist deren hoher Gehalt an löslichen Salzen. Überzeugende Entsorgungsmöglichkeiten außer der Verbringung in alte Salzstöcke fehlen.

Für diese Rückstände wurden verschiedene Verfahren zur Stabilisierung oder Inertisierung mit teilweiser Rückgewinnung einzelner Inhaltsstoffe entwickelt, die aber wegen mangelnder Wirtschaftlichkeit kaum angewendet werden. In diesem Zusammenhang könnte eine volkswirtschaftliche Betrachtung unter Einbeziehung langfristiger Kontroll- und Nachsorgenotwendigkeiten zu anderen Strategien führen.

Reststoffe aus der Mitverbrennung abfallbasierter Brennstoffe sind weniger gut untersucht, da ihre Qualität vom Brennstoffmix stark beeinflusst wird und eine Qualitätskontrolle von Brennstoffen, die Abfallkomponenten enthalten, oft nicht den technischen Anforderungen entspricht. Kritische Ingredienzien sind vor allem Chlor und Schwermetalle.

Wissensdefizite sind auch für Reststoffe aus der Vergasung von Biomasse zu konstatieren. Ein Verwertungspotential ist vorhanden, veröffentlichte Daten lassen aber eine Nachbehandlung angeraten sein, vor allem, falls kontaminierte Biomasse Verwendung findet. Gasreinigungsrückstände können wie die aus der Abfallverbrennung behandelt werden.

Ähnliche Schlüsse lassen sich in Bezug auf Reststoffe der Pyrolyse von Biomasse ziehen. Pyrolysekoks hat ein Verwertungspotential aber in vielen Fällen ist die ökologische Kompatibilität nicht abgesichert. Gleiches gilt für den Einsatz rückgewonnener P- und K-reicher Fraktionen als Dünger in der Landwirtschaft.

Auch bei Reststoffen aus der Vergärung von landwirtschaftlichen Abfällen und Biomasse ist weiterer Entwicklungsbedarf zu konstatieren. Zur Beurteilung des Kontaminationsrisikos, besonders falls Abfallfraktionen mit vergoren werden, aber auch bezüglich Menge und Qualität von Inhaltsstoffen mit Düngewirkung sind weitere Entwicklungen wünschenswert. Eine Reihe von Verfahren zur Verbesserung der Reststoffeigenschaften sind vorgeschlagen worden, eine Bewährung in der Technik steht noch aus.

Zusammenfassend kann auf nahezu allen Gebieten weiterer Forschungsbedarf festgestellt werden. Neben der Entwicklung praxisnaher technischer Verfahren ist den Anforderungen an eine akzeptable Senke für Schadstoffe, besonders solche mit hoher Wasserlöslichkeit, mehr Aufmerksamkeit zu widmen. Dieses Problem hat nicht nur einen wissenschaftlich-technischen Aspekt, nachhaltige und nachsorgefreie Lösungen müssen auch auf ihre sozioökonomischen Auswirkungen und ihre Akzeptanz in der Öffentlichkeit hin untersucht werden.

Summary

A literature review has been performed for getting in-depth information about quality of residues from thermal processes for waste and biomass as well as their disposal or utilisation options and current practices. This revue indicates partly a rather good knowledge, partly significant needs for more detailed information, but also for further research needs.

Residues from waste incineration have been subject to intense research programs for many years and it can be concluded that the quality of bottom ashes has meanwhile a high standard and that the measures to maintain and control this standard are well understood and widely applied. The question whether an utilisation as secondary building material is accepted or not depends on the definition of acceptable economic impact and is more a political and societal decision than a technical one.

For filter ashes and gas cleaning residues the situation is more complex. Their quality is known: due to their high inventory of heavy metals and organic micro-pollutants they are classified as hazardous waste which means they require specific measures for their safe long-term disposal. In case of residues from the chemical gas cleaning stages there is a distinct difference in quality concerning the residues from wet dry gas cleaning with liquid effluents and from those processes which end up with a high salt load. Wet scrubbing requires water purification and results in a final neutralisation residue containing mainly metal hydroxides the main obstacle in the solid residues from effluent evaporation or dry scrubbing is the high amount of soluble salts. For soluble salts no convincing disposal option aside from final storage in salt mines can be thought of. The salt problem is a difficult one since it depends strongly on the applied gas cleaning method. Unfortunately the water authorities in a number of countries, e.g. in Germany, restrict the discharge of effluents from waste incineration plants into sewers.

A number of stabilisation and treatment processes for filter ashes and gas cleaning residues including the recovery of species out of these materials have been developed but none has been implemented in full scale due to economic constraints. In this respect it might be useful to investigate treatment processes of gas cleaning residues including macro-economical aspects. There is reason to speculate that even recovery processes which are not profitable for private companies might point out economically useful if future and long-term costs which have to be covered of the society, e.g. for rehabilitation of contaminated sites, are taken into account.

The quality of residues from co-combustion of SRF or other waste derived fuels are less well investigated. Their quality as well as that of residues from combustion of contaminated biomass is mainly depending on the quality of the fuel. The inventory of critical ingredients in fuel produced from waste or waste fractions, especially of halogens and heavy metals, is often rather high and shows typically a wide range of variation. A reliable quality control for such fuels is very difficult, especially if they originate from mixed municipal solid waste.

Also little information is available for residues from gasification of biomass since only few data have been published. The main residue may have a potential for utilisation, however, the published data indicate that additional post-process treatment is necessary to reach the required properties. Such extra treatment will make any application scenario too expensive. Other residues can – like gas cleaning residues from waste incineration – be inertised in order to meet the criteria for the access to cheaper landfills than those for hazardous waste.

A similar conclusion can be drawn for the quality and management of residues from pyrolysis or carbonisation of biomass. A high potential of application of such charcoal is theoretically possible but the ecological compatibility of some of the proposed scenarios has not yet been shown. An open question is also the potential of such residues for the recovery of ingredients with fertiliser capabilities like potassium of phosphorous.

Limited sound information, too, was found for residues from anaerobic digestion of agricultural and other biomass and organic waste fractions. There are two main issues concerning their environmental compatibility: the potential pollution in case materials originated from waste is treated respectively co-treated and the inventory of nutrients in case 'clean' biomass from the agricultural

sector only was used. Published data indicate the risk of too high pollutant concentration in a number of analysed residues which endangers their typical utilisation as fertilisers in agriculture. There are also proposals for treatment technologies in order either to separate pollutants or nutrients, however, not much information is available about their efficiency and their application in real systems.

A final conclusion can be drawn that there is need for further research on long-term reliable management strategies, especially for all types of residues from gas cleaning in all processes. Additionally the residues from co-combustion of waste and coal, from combustion of SRF, from gasification and pyrolysis, as well as from fermentation of biogenic matter need more detailed investigation. The challenge in all residue management scenarios - especially if these residues derive from waste or contaminated fuels - is the definition of sinks for pollutants. This task has not only a scientific and technical aspect, essential prerequisites for long-term sound and aftercare-free solutions are also socio-economic effects and the public acceptance.

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1 Introduction

The management of process residues is an often overlooked but in terms of assessment of a process one of the most important aspects. Depending on the major purpose of a process its residues are

- unavoidable leftovers or
- sinks for unwanted ingredients in the products.

This implies that residues are in most cases a waste and their management contributes in an unwanted way to the economy of the process in question.

The topics of this report are residues from various bioenergy processes which include

- processes for municipal solid waste (MSW) like
  - waste incineration,
  - pyrolysis,
  - gasification,
- SRF (solid recovered fuel)
  - co-combustion
  - co-gasification
- processes for biomass combustion
  - in large scale plants, and
  - in small scale plants,
- processes for the production of liquid fuel for transportation, and
- anaerobic digestion processes for agricultural residues.

All residues from all major processes will be included. Their quantity and quality will be described as well as the current management practice in the countries of the NoE member states. In this context also eventual legislative regulations and standardisation methods will be included.

It is obvious that the quality of the various residues depends on the fuel and on the process which implies that also the management and the respective regulations will mainly depend on the process. Hence in the first part of this report the residue situation of the single bioenergy processes is described in detail.

For all processes a similar structure will be applied. A short description of the process and its types of residues is followed by detailed characterisation of the single residues according to their appearance in the process respectively their importance in view of their mass. The topics are

- quantity of the residue,
- quality in terms of major constituents and major pollutants,
- quality in terms of environmental compatibility including existing quality standards and qualification protocols, legislative regulations concerning the management on an EU and national level,
- existing management respectively disposal practice.

Each part ends with an identification of major problems associated with residues from the respective process.

The main objective of this paper is not only to create a solid data base but also to identify open questions and define research needs in that area. The cooperation in the NoE Bioenergy with partners dealing with the technologies in question and those who have great experiences in the field of technology assessment and socio-economic issues is well suited to expect that all aspects of the residue management are covered.

2 Legislative Framework for Residue Management

2.1 Regulations on the EU Level

2.1.1 Disposal

The fundamental directive regulating all aspects of waste management is the Council Framework Directive 75/442/EEC on Waste Disposal of 1975 [European Council 1975] which is currently in revision. All later waste related directives base on this one.

The EU Landfill Directive 99/31/EC and its amendment with the acceptance criteria of 2003 [European Council 1999] is the key regulative for the disposal of all kinds of waste and residues - hazardous, non-hazardous, and inert - in the EU. This directive is intended to prevent or reduce the adverse effects of the landfill of waste on the environment, in particular on surface water, groundwater, soil, air and human health and sets up a system of operating permits for landfill sites.

The most important part is Article 5 which requires a reduction of biodegradable waste going to landfills. The targets are a reduction of biogenic waste compared to the situation in 1995 by

- 25 % in 2006,
- 50 % in 2009, and
- 75 % in 2016.

Some countries have enacted such landfill ban already, e.g. Germany on June 1, 2005.

The Landfill Directive specifies only general criteria and principles to be obeyed for the acceptance of a waste or residue on a landfill but it does not contain specific parameters and their limit values. Each country is obliged to define procedures and set standards which have to be met by a material to be listed for a specific class of landfill. The hierarchy to be followed is

- basic characterisation,
- compliance testing, and
- on-site verification.

A specific instrument is the Hazardous Waste Directive [European Council 1991] which contains a list of waste types classified as hazardous. No. 22 in this list is 'ashes and/or cinders' and no. 28 is 'residue from pollution control operations (e.g. baghouse dusts, etc.)'. Whereas APC residues fall strictly under this directive, ashes and cinders may be exempted since in most cases they do not comply with the 'properties of wastes which render them hazardous' in Annex III of the directive.

The Waste Incineration Directive 2000/76/EC [European Parliament and Council 2000] is the legal framework for the incineration and co-incineration of waste or waste derived fuels like SRF (solid recovered fuel) in industrial furnaces and utility boilers. The main topic is the regulation of the emission to air. The instructions concerning residues are less specified.

There is a definition of residues found in Article 3:

(13) "residue" means any liquid or solid material (including bottom ash and slag, fly ash and boiler dust, solid reaction products from gas treatment, sewage sludge from the treatment of waste waters, spent catalysts and spent activated carbon) defined as waste in Article 1(a) of Directive 75/442/EEC, which is generated by the incineration or co-incineration process, the exhaust gas or waste water treatment or other processes within the incineration or co-incineration plant.

Their quality is addressed in Article 4.2:

(c) the residues will be minimised in their amount and harmfulness and recycled where appropriate;

(d) the disposal of the residues which cannot be prevented, reduced or recycled will be carried out in conformity with national and Community legislation.

and in Article 6:

1 Incineration plants shall be operated in order to achieve a level of incineration such that the slag and bottom ashes Total Organic Carbon (TOC) content is less than 3% or their loss on ignition is less than 5% of the dry weight of the material. If necessary appropriate techniques of waste pre-treatment shall be used.

The residues of co-incineration processes are mixtures of the combustion of the respective single fuels and their characteristics vary depending on the fuel mix. This aspect will be dealt with later.

2.1.2 Acceptance Criteria at Landfills

The Council Decision 2003/33/EC [European Council 2003] is an amendment to the Landfill Directive which lays down general criteria for the acceptance of waste on each landfill class. It defines also the methods to be used for sampling and testing of waste.

Table 1 Limit values for the leaching for the acceptance at an inert waste landfill, for granular non-hazardous waste accepted in the same cell as stable non-reactive hazardous waste, and for granular waste accepted at landfills for hazardous waste, calculated at L/S = 2 and 10 l/kg dry matter for total release in mg/kg of the material and directly expressed in mg/l for c_0 (in the first eluate of percolation test at L/S = 0.1 l/kg)

Component	***Inert waste landfill***			***Granular non-hazardous waste***			***Hazardous waste landfill***		
	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.*

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

Parameter	***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..

The acceptance criteria base first of all on leaching tests, but also other characteristic properties where necessary and available. These other criteria are mainly associated with the organic inventory of the waste. On top of that mechanical parameter limit should be set by the national authorities.

There are criteria for inert waste, for non-hazardous waste and for hazardous waste. For non hazardous waste the member states may create subcategories of landfills. A special one could be for municipal solid waste which is separately collected and can be admitted without testing.

The acceptance criteria at a landfill for inert waste and those for granular non hazardous waste on cells which also accept stable non reactive hazardous waste are compiled in Table 1 and Table 2.

For granular hazardous waste to be accepted at landfills for non-hazardous waste apply the same leaching criteria as for granular non-hazardous waste which is landfilled in the same cell as stable non reactive hazardous waste (see Table 1). For this waste, however, additional limiting criteria are

- a TOC value of 5 % (a higher value may be admitted by the competent authority, provided that the DOC value on 800 mg/kg is achieved at L/S = 10 l/kg),
- a minimum pH value of 6 and
- the ANC (acid neutralisation capacity) must be evaluated.

For hazardous landfills there are the following additional criteria to be met:

- a TOC value of 6 % (a higher value may be admitted by the competent authority, provided that the DOC value on 1000 mg/kg is achieved at L/S = 10 l/kg) or
- alternatively a LOI (loss on ignition)value of 10 % and
- the ANC must be evaluated.

These criteria are guidelines for the respective regulation in the member countries and some countries have already used these limits for new standards (compare chapter 2.2.4 United Kingdom).

2.1.3 Utilisation

The Council Framework Directive on Waste Disposal lists utilisation as one of the major objectives in waste management. The respective Articles in this respect are:

Article 3

1. Member States shall take appropriate steps to encourage the prevention, recycling and processing of waste, the extraction of raw materials and possibly of energy therefrom and any other process for the re-use of waste.

They shall inform the Commission in good time of any draft rules to such effect and, in particular, of any draft rule concerning: (a) the use of products which might be a source of technical difficulties as regards disposal or lead to excessive disposal costs; (b) the encouragement of: - the reduction in the quantities of certain waste,

- the treatment of waste for its recycling and re-use,
- the recovery of raw materials and/or the production of energy from certain waste;
(c) the use of certain natural resources, including energy resources, in applications where they may be replaced by recovered materials.

Article 4
Member States shall take the necessary measures to ensure that waste is disposed of without endangering human health and without harming the environment, and in particular: - without risk to water, air, soil and plants and animals,
- without causing a nuisance through noise or odours,
- without adversely affecting the countryside or places of special interest.

These are rather soft statements and a real demarcation between disposal and utilisation is not defined since Article 4 sets the same environmental and safety standards for both strategies: 'without endangering human health and without harming the environment'. However, whether a certain management option is accepted as utilisation or as disposal makes a big difference. Utilisation of residues is in most countries subsidised and the recycled or recovered materials are economic goods whereas the disposal of any material has to be paid for.

It became clear at least through a number of decisions of the European Court of Justice that this distinction between utilisation and disposal is not sufficiently clear. That is why in late 2005 the European Commission has drafted a new Waste Framework Directive which tries to clarify the terms disposal and utilisation. The standards for both routes will be based on environmental objectives which focus the Directive on the reduction of environmental impacts from waste generations and management, taking into account the whole life-cycle. For utilisation the savings and the replacement of resources will play a central role.

The Directive will harmonise and replace a number of Directives on waste management and there is hope that the regulations for utilisation of waste materials will be of about the same quality in all EU countries in due time.

2.2 National Legislative Regulations

2.2.1 Austria

The European Environment Agency (EEA) publishes annual reports on the environmental situation in its member countries. “Environmental Signals 2000” is based on “waste indicators” and compares the situation of waste management in Austria to that in other EEA member countries. It has shown that Austria takes a leading position with regard to almost all waste indicators. For example, Austria, together with one other member country, has reached the envisaged goal of the fifth environmental framework programme of the European Union with regard to the quantity of household waste per capita. Regarding the percentage of biodegradable waste deposited in landfills, Austria and Denmark have the lowest values and thus already comply with the targets set by the EU Landfill Directive for 2016. This success can partly be explained by the fact that Austria is one of those countries that increase the costs of landfilling by taking economic measures at the federal level. As far as recycling of packaging waste is concerned, Austria ranks among the three best EEA member countries with regard to all packaging materials analysed. Accordingly, Austria fulfils all requirements of the EU Packaging Directive – with regard to plastic waste recycling as one of only two countries. In addition, Austria has a legal obligation to collect biodegradable waste separately, which is then composted. Packaging waste must also be separately collected and reused or recovered. In larger construction projects the biodegradable waste must be separated [Umweltbundesamt Austria 2002].

With respect to the Directive 1999/31/EC on the landfill of waste Austria has already reached the last reduction target of Article 5 (a reduction of biodegradable municipal waste going to landfills to 35% by 16th of July in 2016) [Commission of the European Communities 2005]. The Austrian 'Landfill ordinance' [Bundesminister für Umwelt 1996] (Verordnung des Bundesministers für Umwelt über die Ablagerung von Abfällen (Deponieverordnung) StF: BGBl. Nr. 164/1996) prevents to landfill waste of a total organic carbon content (TOC) of more than 5%. It came into force on the 1st January 2004. Landfills may only accept waste which has been pretreated by incineration in order to attain a TOC of less than 5% or that has undergone biological mechanical treatment. Compared to thermal treatment plants processes of mechanical/biological treatment (MBA) of residual waste are cheaper due to higher investment costs of thermal treatment plants. The economical minimum potential of municipal solid waste for thermal treatment is assumed to exceed a capacity of 200,000 Mg/y. Even when the TOC of waste is higher than 5% municipal waste treated in mechanical biological treatment plants can still be landfilled.

2.2.2 Finland

In Finland a national regulation is set in force to allow utilisation of certain waste materials in soil engineering [VNA 2006]. These materials include ashes from biomass, peat and coal burning. The focus of these activities includes:

- public roads, streets, cycle ways and connecting structures, excluding noise barriers,
- parking areas,
- sport fields and connecting routes as well as outdoor routes,
- railway yards and certain industrial areas.

Table 3 Proposed maximum leaching values for waste materials used in covered and in coated structures in Finland (Pre-standard)

Substance	**Limit value, mg/kg dry matter** Basic study(1)			**Limit value, mg/kg dry-matter** Quality control study(1)		
	Content	Solubility (L/S = 10 l/kg) covered structure	Solubility (L/S = 10 l/kg) coated structure	Content	Solubility (L/S = 10 l/kg) covered structure	Solubility (L/S = 10 l//kg) coated structure
PCB(2)	1,0					
PAH(3)	20/40(4)					
DOC(5)		500	500			
Sb		0,06	0,18			
As	50	0,5	1,5	50		
Ba	3 000	20	60	3 000		
Cd	15	0,04	0,04	15		
Cr	400	0,5	3,0	400	0,5	3,0
Cu	400	2,0	6,0	400		
Hg		0,01	0,01			
Pb	300	0,5	1,5	300	0,5	1,5
Mo	50	0,5	6,0	50	0,5	6,0
Ni		0,4	1,2			
V	400	2,0	3,0	400	2,0	3,0
Zn	2 000	4,0	12	2 000		
Se		0,1	0,5		0,1	0,5
F^-		10	50		10	50
SO_4^{2-}		1 000	10 000		1 000	10 000
Cl^-		800	2400		800	2400

1) *In the basic study first the conformity with the scope of regulation is shown. Composition of waste is studied with standardized methods. This study is done at least every 5 years period or whenever the quality of waste has changed. In the quality control study quality of waste is followed over an adequate long period of time. During this period sampling and testing is performed according to quality control program. Special action plan is followed if given limits are not fulfilled.*

2) *Total of congeners 28, 52, 101, 118, 138, 153, 180*

3) *PAH (anthracene, acenaphthene, acenaphthylene, benzo(a)anthracene, benzo(a)pyrene, benzo (b)fluoranthene, benzo(g,h,i)perylene, benzo(k)fluoranthene, dibenzo(a,h)anthracene, phenanthrene, fluoranthene, fluorene, indeno(1,2,3-cd)pyrene, naphthalene, pyrene Chrysene) total*

4) *Covered structure/Coated structure*

5) *DOC, dissolved organic carbon*

Starting point for the acceptance is based on limit values given in the landfill directive and in the Council Decision [European Council 2003] for inert materials. Some specific limit values are given for filter and bottom ashes from wood based biomass, peat and coal combustion. These limit value are applied in basic and quality control studies. Limit values are given both for total concentration as well as in leaching values using L/S ratio of 10 for covered and coated constructions. Testing is done in accordance with the European standardisation EN 14405 [European Committee for Standardization 2004]. In Table 3 proposed limit values are given for covered and coated structures. For coated structures some upward deviations may be accepted which are based on leaching modelling taking into account low percolation rates in coated structures.

So far only limited number of material-specific information is available. It is foreseen that coal ashes will best fulfil the criteria while wood based biomass ashes have more problems in relation to limit values.

2.2.3 Germany

The German Technical Ordinance Residential Waste [Bundesministerium 1993] sets the standards for disposal of non-hazardous waste on landfills. It has been issued in 1993 and has been fully enacted on June 1, 2005. According to this ordinance there are two types of non-hazardous landfills, class 1 and class 2. The acceptance parameters for these two classes of non-hazardous waste in Germany are listed in Table 4.

Table 4 Acceptance criteria for German landfills and LAGA limits for the utilisation of grate ashes in road construction

Parameter	***Unit***	***Germany***			
		Landfill class 1	***Landfill class 2***	***Landfill class 3***	***LAGA***
Strength					
Vane shear strength	kN/m^2	≥25	≥25	≥25	≥25
Axial deformation	%	≤20	≤20	≤20	≤20
Uniaxial compressive strength	kN/m^2	≥50	≥50	≥50	≥50
Organic component of dry residues in original substance					
LOI	wt%	≤3	≤7	≤18	≤1
TOC	wt%	≤1	≤3	-	-
Extractable lithophilic substances in original substance	wt%	≤0.4	≤0.8	≤0.8	≤0.8
Elution criteria					
pH		5.5 - 13	5.5 - 13	5.5 - 13	5.5 - 13
El. conductivity	µS/cm	≤10000	≤ 50000	≤ 50000	≤ 50000
TOC	mg/l	≤20	≤100	≤250	≤250
Phenols	mg/l	≤0.2	≤50	≤50	≤50
As	mg/l	≤0.2	≤0.5	≤0.5	≤0.5
Pb	mg/l	≤0.2	≤1	≤1	≤1
Cd	mg/l	≤0.05	≤0.1	≤0.1	≤0.1
Cr-VI	mg/l	≤0.05	≤0.1	≤0.1	≤0.1
Cu	mg/l	≤1	≤5	≤5	≤5
Ni	mg/l	≤0.2	≤1	≤1	≤1
Hg	mg/l	≤0.005	≤0.02	≤0.02	≤0.02
Zn	mg/l	≤2	≤5	≤5	≤5
F	mg/l	≤5	≤25	≤25	≤25
Ammonium-N	mg/l	≤4	≤200	≤200	≤200
Cyanide	mg/l	≤0.1	≤0.5	≤0.5	≤0.5
AOX	mg/l	≤0.3	≤1.5	≤1.5	≤1.5
Soluble fraction	wt%	≤3	≤6	≤6	≤6
Biological degradability of dry residue in original substance					
as breathing activity (AT_4)	mg/g			≤5[1]	
or as gas formation rate in fermentation test (GB_{21})	l/kg			≤20[2]	
Upper thermal value (H_0)	kJ/kg			≤6000	

(1) *mg O_2 with respect to dry weight*

(2) *standard litre of gas with respect to dry weight)*

The increasing introduction of Mechanical-Biological Treatment (MBT) and the production of high-calorific fractions from waste for combustion in industry furnaces and utility boilers caused a further regulation of the disposal of residues from such processes which can never meet the TOC limits of the landfills class 1 and 2. The Ordinance on Environmentally Compatible Storage of Waste from

Human Settlements and on Biological Waste-Treatment Facilities [Bundesministerium 2001] defines for such residues a third type of landfills, class 3, the acceptance criteria of which are also listed in Table 4.

Germany has implemented a number of ordinances and memoranda which define the utilisation of residues from waste incineration. For grate ashes from waste incineration, for instance, the LAGA (a board of representatives of the ministers of environment of the federal states) has set standards for their utilisation in road construction. These standards are depicted in the fourth column of Table 4. They have to be met after a certain pre-treatment of the raw ashes which implies as major step the maturation of the ashes by storage for at least 3 months under humid conditions. Such storage alters the mineralogy of the ashes by uptake of CO_2 from the air – thus reducing the pH value - and changes the sulphate species [Pfrang-Stotz 1995, Zwahr 2005].

2.2.4 United Kingdom

The standards of the European Landfill Directive (1999/31/EC) have been adopted by UK law and apply 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 2005]. 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 as non-hazardous. In the case of waste-to-energy plants, air residues are classified as absolute hazardous, whereas, bottom ash, fly ash and pyrolysis wastes are classified as mirror 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 [European Committee for Standardization 2002] ,
- limit values for other parameters such as pH, acid neutralisation capacity and total organic carbon.

The leaching limit values relate to specific leaching tests which are different for granular and monolithic wastes. The limits for granular waste base on leaching test results expressed as mg/kg dry matter whereas monolithic waste are tested in a tank leaching test and the numbers are given in mg/m^2kg.

For the regulation of inert waste the leaching limits for L/S = 10 l/kg dry matter are used as laid down in the Council Decision 2003/33/EC (see Table 1 and Table 2). For inert waste and also for solid residues from biomass plants a PAH limit of 100 mg/kg is set. For solid non reactive hazardous waste (SNRHW) the leaching limits base on a L/S of 10 l/kg and are the same as those for granular non hazardous waste in the Council Decision. If the values for Cd or Hg for the waste are above 0.1 or 0.02 mg/kg respectively, a risk assessment must demonstrate that there will be no unacceptable discharge to groundwater.

Non-hazardous wastes (including inert wastes) of any other origin - i.e. wastes listed in the European Waste Catalogue, but not included in the Hazardous Waste List can be accepted at non-hazardous landfills. There are no limit values for non-hazardous landfills. Therefore, in any case solid residues from biomass plants can be accepted in non-hazardous landfills.

A permit from the Environment Agency may include conditions which authorise limit values for specific parameters other than for DOC that are up to three times higher for waste accepted in a mono-fill landfill - a landfill which is authorised to accept only a single waste type. The conditions will take into account the characteristics of the landfill and its surroundings and a risk assessment must demonstrate that emissions (including leachate) from the landfill will present no additional risk to the environment.

For granular hazardous waste, e.g. fly ash containing dangerous substances from waste-to-energy plants, also the respective leaching limits at L/S = 10 l/kg of the Council Decision 2003/33/EC are to be met. If the values for Cd or Hg are above 1 or 0.4mg/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 deposited in landfills for non-hazardous wastes, in cells not used for the deposit of biodegradable wastes. Stable, non-reactive hazardous waste (SNRHW) are defined as: hazardous waste, the leaching behaviour of which will not change adversely in the long-term, under landfill design conditions or foreseeable accidents:

- in the waste alone (for example, by biodegradation);
- under the impact of long-term ambient conditions (for example, water, air, temperature or mechanical constraints);
- by the impact of other wastes (including waste products such as leachate and gas).

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 5 (leaching and total content). The limit values for monolithic waste apply to tests using the 64-day tank test (NEN 7345) necessary to characterise the waste.

For monolithic wastes, blocks of the waste of specified dimensions are held in a tank of eluate for a period of time. The leaching of constituents is a function of the surface area of a monolith. The results are specified as milligrams per square meter.

The limit values provided in Table 5 should not be exceeded by monolithic SNRHW wastes in order to be accepted at a non-hazardous landfill. It is also mandatory that the load bearing capacity reaches at least 1.5 MPa. The pH, the electrical conductivity and the ANC have to be evaluated.

In conclusion, solid residues from biomass and waste-to-energy 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.

Table 5 Leaching limit values for different types of monolithic wastes

Component	***SNHRW***	***Hazardous waste***
	mg/m² kg dry wt	***mg/m² kg dry wt***
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 deter-

mine 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.*

3 Characterisation Methods

3.1 Characterisation Principles

For characterisation of the various residues it is necessary to get detailed information of a number of parameters. The major ones are

- chemical composition in terms of
    - heavy metals,
    - halogens,
    - alkali metals,
    - residual carbon,
    - organic compounds,
- mineralogical phases, and
- elution stability.

In some countries also standards of mechanical parameters like shear or compressive strength have to be met to fulfil the acceptance criteria for landfills or utilisation scenarios.

For all of the chemical and mechanical parameters there are standardised methods which are found in the respective national regulations or ordinances and will not be discussed in detail here.

3.2 Elution tests

The elution stability is the preferred parameter to test the environmental compatibility of solid residues. On the EU level the European Committee for Standardization has defined the CEN EN 12457 as compliance test [European Committee for Standardization 2002]. This batch leaching test uses water as leachate. 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 a 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 obtained results 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 based their regulations already 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 leach test [Normalisation française 1988]. However, the performance differs and with that the results of the combined tests can not necessarily be expected to be identical with the German test.

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 the pH-static leaching test for example according to CEN/TS 14997 which 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.

For better understanding of the leaching mechanism a number of scientific tests are in use [IAWG 1997]. An important parameter in this respect is the availability, the amount of a species which is potentially available under worst environmental conditions. For this purpose often the availability test according to the Dutch NEN regulation [NEN 7341] is 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.

This test is meanwhile often replaced by a pH-stat test which tests at a series of constant pH values (adjusted by automated titration) in combination with the measurement of the acid-neutralisation capacity (ANC) of the material.

For materials with a defined surface the Dutch tank leaching test provides a good simulation of the actual leaching progress [NEN 7345]. A monolith is placed in a tank with distilled water which is renewed after 0.5 days and than after always doubled exposition time till 64 days are reached. The test results enable the distinction between wash-off, diffusion controlled leaching and dissolution of the matrix and can be used for modelling.

The most realistic information about the leaching behaviour of granular material under field condition is obtained by the column test which is a compliance test in The Netherlands [NEN 7341] and meanwhile also a CEN standard for introduction in the EU countries [CEN/TS 14405 European Committee for Standardization 2004]. A glass column filled with the granular material is passed upwards by distilled water. The discharged leachate is collected in seven separate fractions by an automatic sample collector. The amount of species leached in each single fraction gives information about the time-wise behaviour of the leaching process.

An important parameter in addition to the leaching tests is the already above mentioned acid neutralisation capacity (ANC). The ANC is measured using an automatic titration device. The samples are titrated with 1 M HNO_3 until pH 3 is reached and give information about the buffer capacity of a material. This is important in view of the long-term evaluation of the leaching properties of residues which are often of alkaline nature.

4 Incineration of Municipal Solid Waste

4.1 Description of Processes

4.1.1 Furnaces

According to the EU Landfill Directive [European Council 1999] the direct disposal of reactive municipal solid waste has to be banned in future and some countries have already implemented this regulation in their national waste management strategies. The consequence is a pre-treatment process in order to inertise the waste prior to its final disposal. The prevailing inertisation method is the incineration of municipal solid waste which is in Europe mainly performed in so-called European Mass Burners, waste incineration plants based on grate technology. There are various grate systems on the market which can, however, be regarded as almost identical in view of the amount and for modern plants also of the quality of the residues. In various countries also fluidised beds are applied for waste incineration, especially in Japan, but also in Sweden and in Spain. Some common types of furnaces are compiled in Fig. 1.

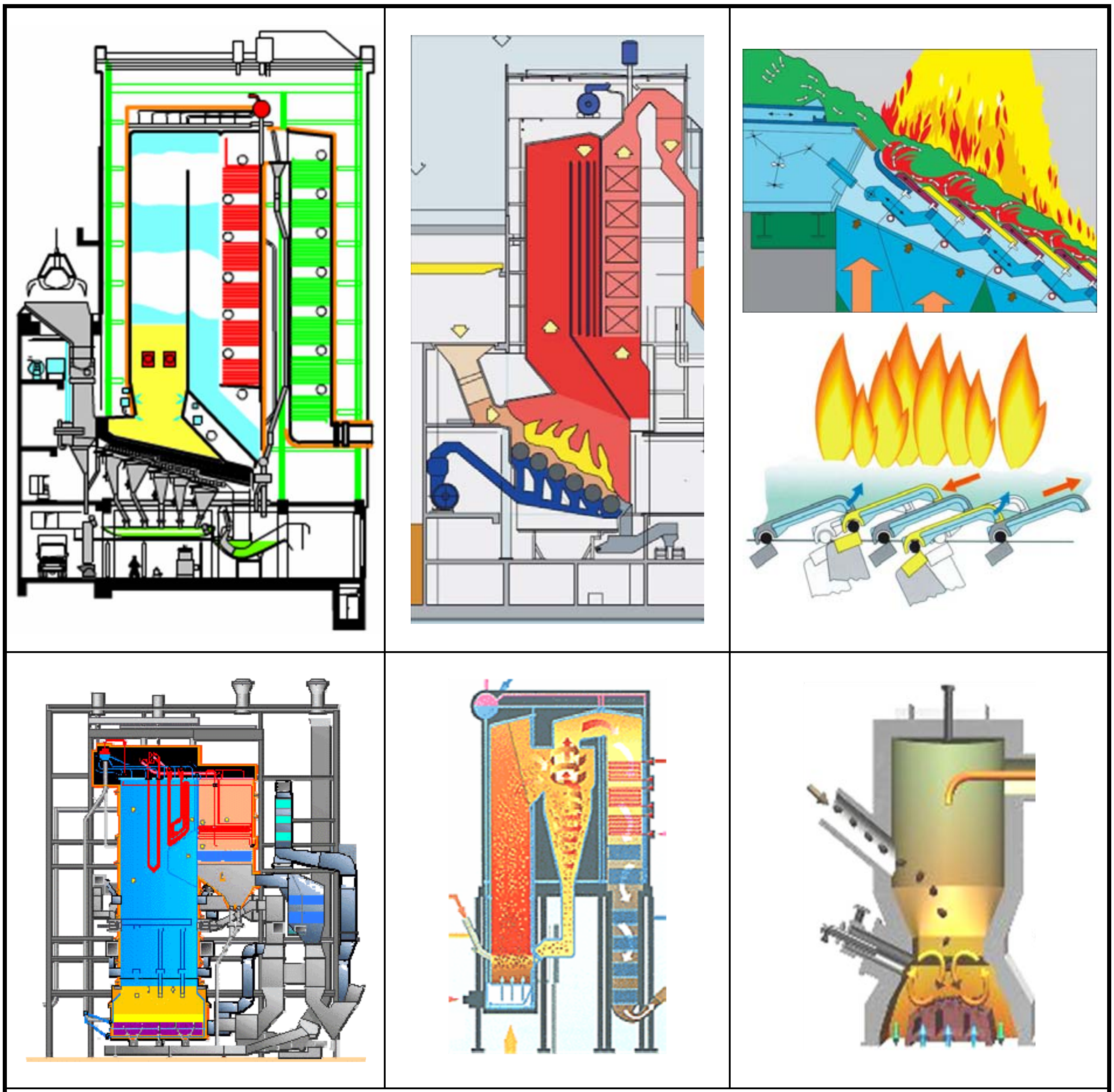

Fig. 1 Municipal solid waste incineration furnaces with reciprocating grate (top left, [MVR 2006], roller grate (top centre [Kiel 2006]), reverse acting grate (top right [Fischer 2006]), bubbling (bottom left [Finbioenergy 2006]), circulating (bottom centre [Takuma 2006]), and revolving fluidised bed furnace (bottom right [Ebara 2006])

4.1.2 Boilers

All modern waste-to-energy plants are equipped with heat recovery systems which are of different design and operate at different steam parameters. A critical component is the super-heater which is typically the section with the highest corrosion attack and hence various solutions to place the super-heater can be found. In grate systems the first part of the boiler is the radiation part followed by a convection section. There are vertical and horizontal boilers in use (see Fig. 2) and in fluidised beds parts of the heat exchange is done in boiler sections submerged in the bed or – in circulating fluidised beds - installed in the ash cycle below the cyclone.

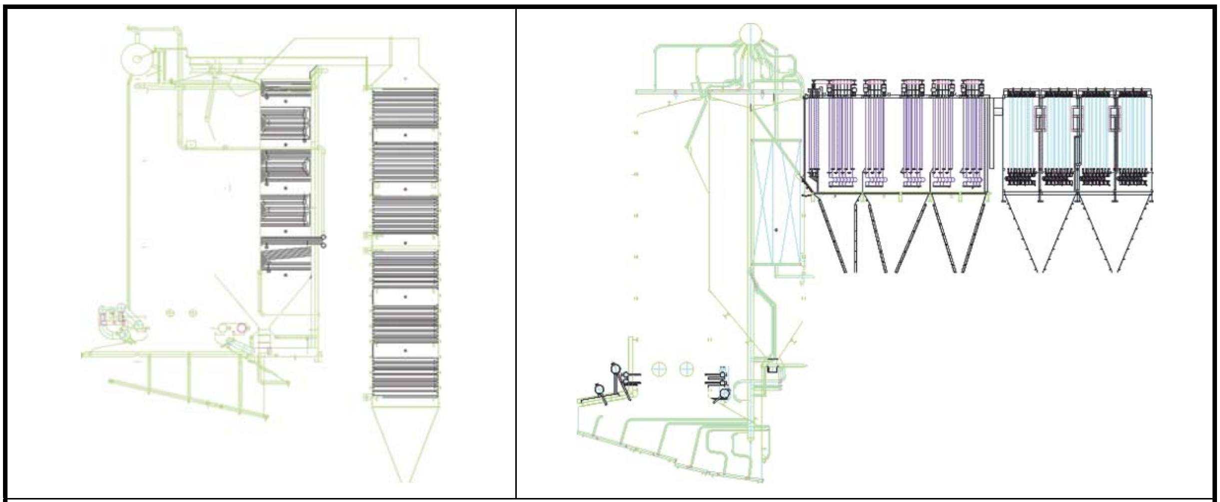

Fig. 2 Vertical (left) and horizontal boiler (right) [Vølund 2006]

4.1.3 Air Pollution Control Systems

4.1.3.1 Process Stages

In waste incineration the removal of pollutants from the flue gas is one of the most important and most expensive process stages. It can be achieved in many ways. The design of the various configurations found in full scale plants depends not that much upon the clean gas quality - which has to comply with about the same emission standards everywhere - but on investment and/or operation cost, utilisation or disposal option of the residues or on available space in the case of upgrading of old facilities.

Today all technologies and all kinds of combinations of abatement options can be found in full scale installations. Each configuration guarantees the compliance with the today's most stringent air emission standards. A selection of the most appropriate gas cleaning strategy depends to a great extent on local conditions. Important factors are administrative regulation (permit for liquid effluents, disposal of solid residues), options, and markets for an eventual recovery and finally the investment and operational costs of the entire system.

In waste incineration plants typically several technology stages are used for the removal of:

- fly ash,
- acid gases,
- specific contaminants like Hg or PCDD/F, and
- nitrogen oxides.

Following the tendency in modern plants to simplify the gas cleaning procedure some of the stages can be found combined.

4.1.3.2 Particle Removal

The first step in most APC systems is the fly ash removal which can be done by

- cyclone,
- electrostatic precipitator (ESP), or by
- fabric filter or baghouses.

A cyclone uses inertial impaction for fly ash separation. The gas is entering a cylindrical chamber tangentially at high velocity and is there forced into a cylindrical path. The centripetal force acting on the particles causes them to collide with the walls where they impinge and settle down into the discharge hopper. The gas is extracted through a central tube. A scheme of a cyclone is shown in the left graph of Fig. 3. Due to their limited removal efficiency for fine particles cyclones are not often found in modern plants or they serve for pre-deposition of the coarse fly ash.

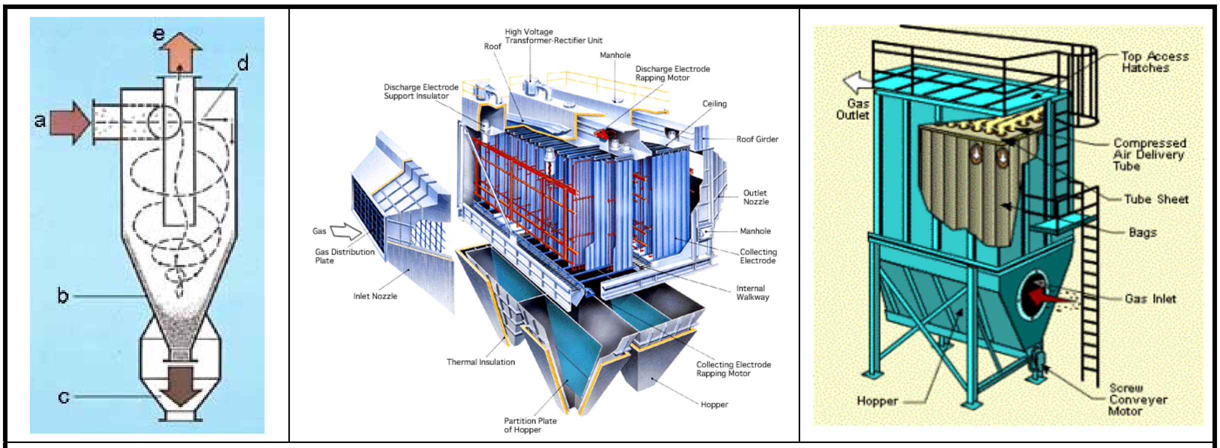

Fig. 3 Scheme of a cyclone (left [HDM 2006]), an ESP (centre [MHI 2006]), and a baghouse filter (right [Technical Felts Company])

Due to their simple design, low pressure loss and easy operation ESP are most widely used for fly ash separation in waste incineration but also in other combustion processes like in coal fired power plants. Schemes of the de-dusting principle and of a technical design are shown in the central graph in Fig. 3. A modern ESP which comprises at least two and often three sectors guarantees dust removal efficiencies of >99 % at particle sizes between 0.01 and >100 µm.

In few installations wet ESP are implemented at the back end for polishing purpose. In these ESP the collecting plates are cleaned with water instead of rapping. The residues from wet ESP are a sludge or suspension and their disposal may cause specific problems.

Even lower emission values than those of ESP can be achieved with fabric or baghouse filters. In a fabric filter the raw gas passes fabric bags which are supported by metal cages from the outside to the interior. The fly ash stays at the outer surface of the filter bags and is periodically removed by an air pulse blown into the bag from the inner side. This cleaning releases the particles, which fall into the discharge hopper. A scheme of a fabric filter is shown in the right graph of Fig. 3.

4.1.3.3 Chemical Gas Cleaning

4.1.3.3.1 Principles

The step following a primary fly ash deposition in the air pollution control system is usually the chemical gas cleaning which can be performed in two principal ways:

- wet-scrubbing and
- dry scrubbing.

A number of variations of these fundamental strategies – wet systems with and without liquid discharge, dry and semi-dry systems with different neutralising agents – have been developed and will be described below.

4.1.3.3.2 Wet Scrubbing

The principle of wet scrubbing is the absorption of gaseous components into a liquid. The efficiency of such absorption process depends first of all on the available surface of the liquid which controls the mass transfer out of the gas into the liquid phase. Different techniques are used to achieve this goal:

- venturi scrubbers,
- packed towers,

- plate and tray towers , and
- film absorbers.

Wet scrubbing is a common strategy in waste incineration in Central Europe, today in most cases performed as a two-stage installation with an initial acid scrubber followed by a neutral or weakly alkaline one. The acid scrubber is often of the spray or venturi type and reduces the flue gas temperature of 180 – 200 °C down to 63 – 65 °C. In the second stage mainly packed towers are used. Wet systems are operated with (see left graph in Fig. 4) or, which is the today preferred configuration, without discharge of liquid effluent effluents (see right graph in Fig. 4).

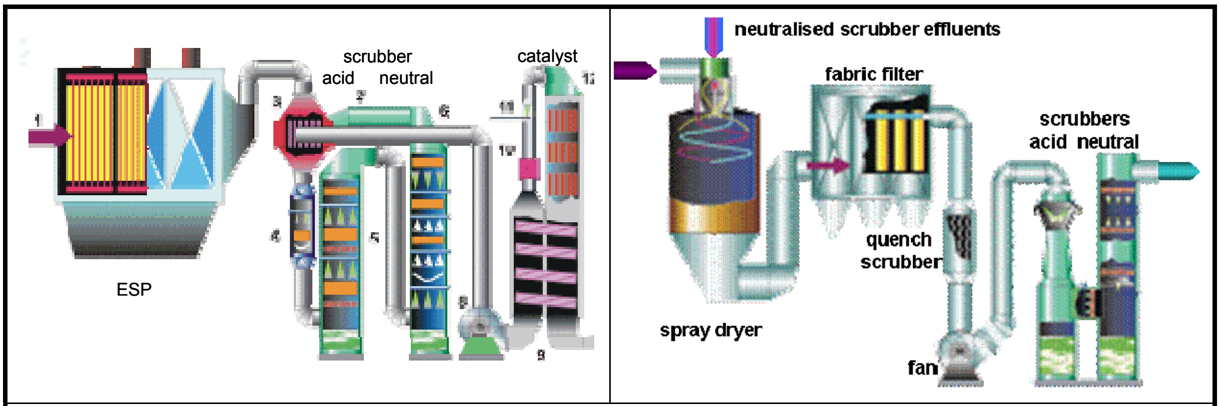

Fig. 4 Schemes of wet scrubbing systems with (Kempten, left) and without (Coburg, right) liquid effluents

Such two-stage systems have very high removal efficiencies for the halogen hydrides HF, HCl, and HBr, for mercury, and for SO_2. For these components the raw gas concentrations are easily reduced well below the emission standards.

In the first scrubber HF, HCl, and HBr are easily absorbed in water forming the respective strong acids. The reaction for HCl is

$$(HCl)_{gas} \rightleftharpoons (HCl)_{solution} \rightleftharpoons H^+ + Cl^-$$

This causes the establishment of a low pH in the scrubbing solution which is needed for an efficient removal of mercury [Braun 1986].

Hg which is mainly present in the flue gas as Hg^{2+} forms a stable chloride complex in an aqueous environment containing chloride ions according to:

$$Hg^{2+} + 4\,Cl^- \rightleftharpoons [HgCl_4]^{2-}$$

and stays also in the solution of the first scrubber.

The second scrubber is intended for SO_2 removal. SO_2 is first absorbed in the liquid but unlike HCl its dissociation into ions is a two-step reaction:

$$H_2O + SO_2 \rightleftharpoons H^+ + HSO_3^-$$

$$HSO_3^- \rightleftharpoons H^+ + SO_3^{--}$$

with the sum reaction

$$H_2O + SO_2 \rightleftharpoons SO_3^{2-} + 2\,H^+$$

An elevated pH drives the equilibrium to the ionic form. Hence the environment in the second scrubber is kept at neutral or weakly alkaline pH by controlled addition of NaOH or $Ca(OH)_2$ and SO_2 undergoes in fact a neutralisation reaction which is in case of NaOH as neutralising agent finally

$$SO_2 + 2\,NaOH \rightleftharpoons Na_2SO_3 + H_2O$$

and if $Ca(OH)_2$ is used:

$$SO_2 + Ca(OH)_2 \rightleftharpoons CaSO_3 + H_2O.$$

The dissolved sulphites are easily oxidised to sulphates by the oxygen surplus of the flue gas:

$$2\,SO_3^{2-} + O_2 \rightleftharpoons 2\,SO_4^{2-}$$

$Ca(OH)_2$ is often preferred as neutralising agent since the finally precipitating gypsum, $CaSO_4 \cdot 6\ H_2O$ is easily disposed of or can even be marketed.

Wet scrubbers were initially operated with discharge of liquid effluents which required a neutralisation and an efficient removal of heavy metals and other toxic contaminant. The standards for water discharge into a sewer are rather stringent and call for high efforts especially in view of Hg and Cd removal.

Often there is no suitable sewer available which tolerates the salt freight and in some Central European countries, especially in Germany, authorities try to prevent the discharge of liquid effluents. In these cases the scrubbing solutions need to be evaporated. The easiest way to evaporate the water in the scrubbing solutions is to spray them after neutralization in a so-called spray dryer directly into the hot flue gas downstream of the boiler. The solid scrubbing residues are removed from the gas flow in a subsequent - in most cases fabric - filter.

Sometimes a removal and separation of the primary fly ash may not be economical and the first filter is omitted. A typical configuration of a wet scrubbing system with internal evaporation is depicted in the right graph in Fig. 4. An alternative way to evaporate the scrubbing solutions is the external mode by drying in steam heated devices.

4.1.3.3.3 Dry Scrubbing

Dry and semi-dry scrubbing processes are simple and hence cheap concerning their investment and are in use in many plants all over the world. In most cases the adsorbent is either injected directly into the gas duct or into a spray dryer downstream of the boiler in dry form (dry process) or as a slurry (semi-dry process). The scrubbing products are in most cases removed from the flue gas by a fabric filter. In some installations a separation of the fly ashes prior to the spray dryer may be found. For such purpose in most cases cyclones are installed.

Dry scrubbing can be performed with different reagents, the most common ones are limestone, $CaCO_3$, calcium oxide, CaO, lime, $Ca(OH)_2$. Today dry processes using $CaCO_3$ have been phased out since they do not guarantee the compliance with the common air emission standards and CaO based processes are for the same reason only implied in cases where the flue gas is humidified prior to the CaO injection. Typical examples for modern waste incinerators equipped with Ca based dry scrubbing are shown in Fig. 5.

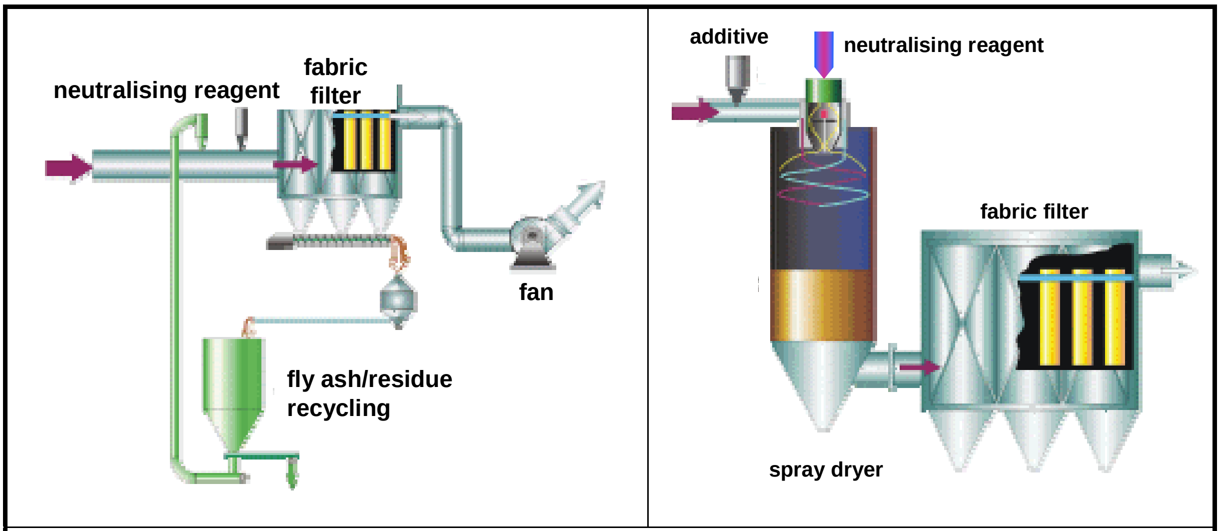

Fig. 5 Examples for dry scrubbing systems based on Ca: injection of reagent into the flue gas duct (left, Brescia) and into a spray dryer (right, Lee county) [Martin 2006]

Another option for dry scrubbing is the NEUTREC^R process which applies freshly ground $NaHCO_3$ for neutralisation of acid gas components has been developed to recycle the gas cleaning products and use them in other processes like metal melting or glass production [Korte 1994]. A scheme of this process is shown in Fig. 6.

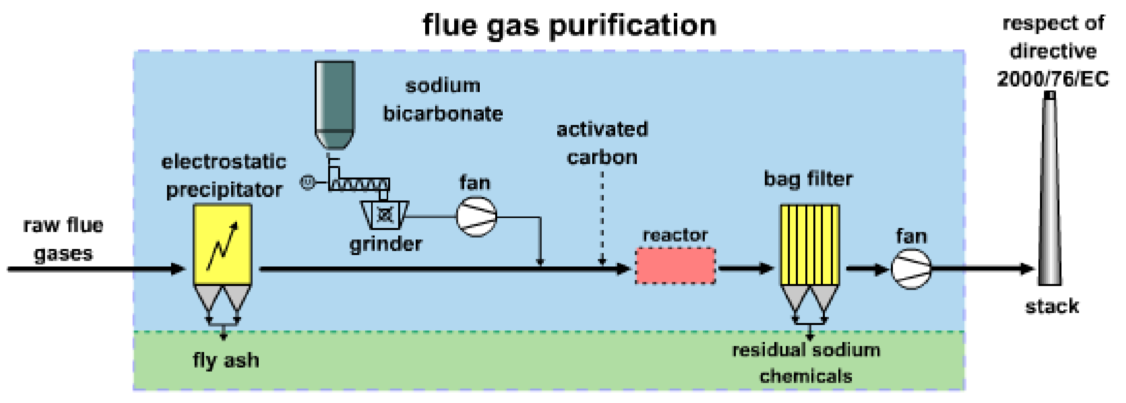

Fig. 6 Scheme of the NEUTREC^R process [Solvay 2006]

The principle neutralisation reactions of HCl and SO_2 with $Ca(OH)_2$, CaO, $CaCO_3$, and $NaHCO_3$ are compiled below in Table 6.

Table 6 Neutralisation reactions in dry scrubbing systems

Reagent	***Reactions with HCl***	***Reactions with SO_2***
$Ca(OH)_2$	$HCl + Ca(OH)_2 \rightleftharpoons CaOHCl + H_2O$ $HCl + CaOHCl \rightleftharpoons CaCl_2 + H_2O$ $2HCl + Ca(OH)_2 \rightleftharpoons CaCl_2 + 2H2O$	$SO_2 + Ca(OH)_2 \rightleftharpoons CaSO_3 + H_2O$ $2CaSO_3 + O_2 \rightleftharpoons 2CaSO_4$ $2SO_2 + 2Ca(OH)_2 + O_2 \rightleftharpoons 2CaSO_4 + 2H_2O$
CaO	$2HCl + CaO \rightleftharpoons CaCl_2 + H_2O$	$2SO_2 + 2CaO + O_2 \rightleftharpoons 2CaSO_4$
$CaCO_3$	$2HCl + CaCO_3 \rightleftharpoons CaCl_2 + CO_2 + H_2O$	$2SO_2 + 2CaCO_3 + O_2 \rightleftharpoons 2CaSO_4 + 2CO_2$
$NaHCO_3$	$HCl + NaHCO_3 \rightleftharpoons NaCl + CO_2 + H_2O$	$2SO_2 + 4NaHCO_3 + O_2 \rightleftharpoons 2Na_2SO_4 + 4CO_2 + 2H_2O$

4.1.3.3.4 Stoichiometric Ratios of Gas Cleaning

As has been mentioned above already the different gas cleaning processes operate with different stoichiometry of the neutralisation reaction. A survey on data published from full scale installations is compiled in Table 7.

Table 7 Specific stoichiometric ratios of HCl and SO_2 in the gas cleaning processes

Process	***Pauli 1990***		***Reimann 1991***		***Benassi 1997***	
	HCl	***SO_2***	***HCl***	***SO_2***	***HCl***	***SO_2***
Dry with $Ca(OH)_2$	1.1	1.3 – 3	1.1 – 1.5	1.8 – 3.5		
Semi-dry with $Ca(OH)_2$	1.1 5	1.3 – 2.5	1.1 – 1.5	1.3 – 2.6		
Dry with $NaHCO_3$					1.04 – 1.2	1.2 – 1.4
Wet process	1.05	1.05	1.05 – 1.15	1.05 – 1.15		

The data document that wet scrubbing systems do need almost no surplus of neutralisation reagent. For Ca based dry systems the abatement of HCl is much easier than that of SO_2. In terms of stoichiometric factors the NEUTREC^R process performs best.

4.1.3.3.5 Further Gas Cleaning Devices

Other stages like catalysts or adsorbents have no relevance in the context of this report and will not be included.

4.2 Mass Flows in Grate Systems

The flow of the different mass streams in a grate type municipal solid waste incinerator is shown in Fig. 7. The graph compiles average ranges for these streams as found in modern mass burning systems [IAWG 1997, European Commission 2005].

State-of-the-art plants produce typically between 150 and 250 kg bottom ashes per 1000 kg of burnt waste. Most published numbers include the grate siftings which are only recently and only in some countries kept separate from the grate ash and fed, after metal separation, back into the furnace. The mass flow of siftings depends on the type of grate and its time of operation. For modern incineration plants an amount in the order of 1 – 3 kg/Mg can be envisaged. The siftings may increase the amount of unburnt matter in the bottom ash. In view of utilisation, however, the inventory of metallic Al which drips through the grate voids is of much higher concern.

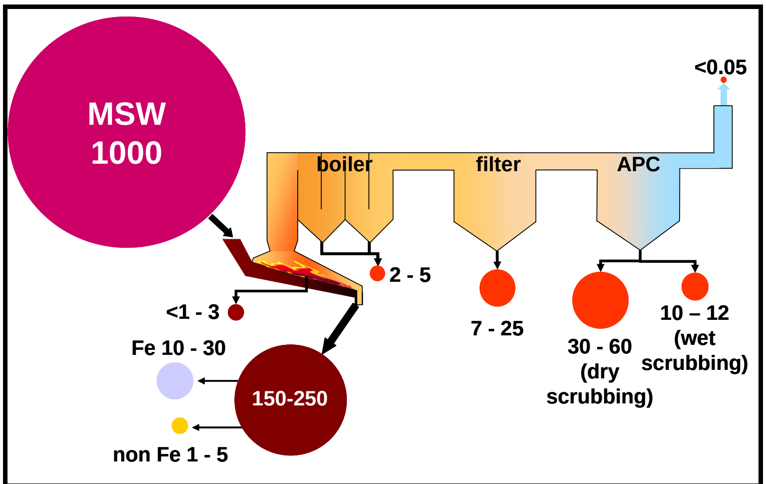

Fig. 7 Mass flows in a municipal solid waste incinerator in grate technology (values in kg)

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. 7. Boiler ashes should not be combined with the grate ash but be treated together with the filter ash which has in some countries already been enforced by legislative regulations.

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. 7 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 actually the highest variation of all residues. As described above a wet scrubber is operated close to stoichiometry. The amount of 10 – 12 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 surveillance.

In semi-dry or dry systems the amount of residues is significantly increased because of not reacted additives. The 30 – 60 kg per Mg of waste is a typical value found in modern waste incineration plants [Reimann 1990 & 1991, IAWG 1997, Mark 2006].

4.3 Characterisation of Residues

4.3.1 Bottom Ash Quality

4.3.1.1 Mineralogical Phases

Grate or bottom ashes can be characterised as a mixture of silicatic and oxidic phases. A geochemical and mineralogical characterisation provides useful information in view of their mechanical stability and their long term behaviour. Some typical mineral phases found in these residues are shown in the micrographs in Fig. 8 [Pfrang-Stotz 1992]. The graph documents that a number of natural phases but also those which have been newly formed at high temperatures in the combustion process, e.g. glasses or akermanit can be found.

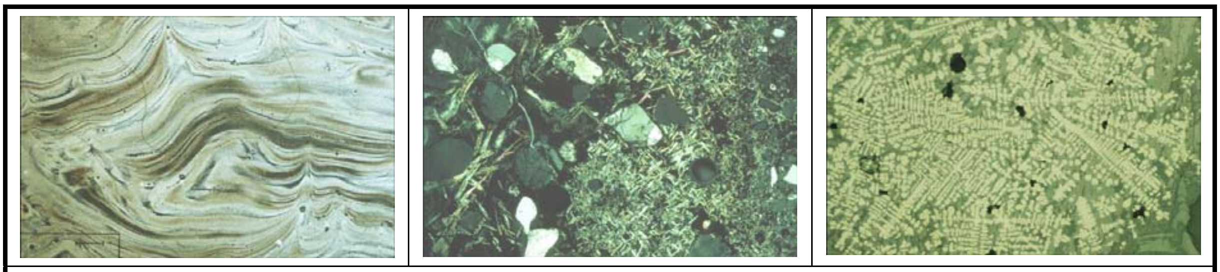

Fig. 8 Micrographs of minerals in bottom ashes: glass formed during combustion (left), gehlenite $Ca_2AlAlSiO_7$, in glassy matrix (centre), magnetite, Fe_3O_4 (right) [Pfrang-Stotz 1992]

There is a clear dependency between the grain size and the mineral phase composition of MSWI bottom ashes as can be seen in the listing in Table 8.

Table 8 Mineral compositions and grain size class of a typical German bottom ash (xxxx = main phases >20 %, xxx = secondary phases 10 – 20 %, xx = accessories 5 – 10 %, X = traces < 5% [Pfrang-Stotz 2002])

Mineral phase	***Formula***	***Grain size in mm***										
		0-0,063	***0,063-,09***	***0,09-0,25***	***0,25-0,71***	***0,71-2,0***	***2,0-5,0***	***5,0-8,0***	***8,0-11,2***	***11,2-16,0***	***16,0-22,4***	***22,4-32,0***
Quartz	SiO_2	xxx	xxx	xxxx	xxxx	xxxx	xxxx	xxx	xxxx	xxxx	xxxx	xxxx
Gehlenite	$Ca_2Al_2SiO_7$	xxx	xxx	xxx	xxx	xxx	xxx	xxx	xxx	xxx	xxx	xxx
Akermanite	$Ca_2MgSi_2O_7$	x	x	x	x		x	x	x	x		x
Calcite	$CaCO_3$	xxxx	xxxx	xxx	xxx	xx	xx	xx	xx	x		x
Portlandite	$Ca(OH)_2$	x	x									
Magnesite	$MgCO_3$	x	x									
Magnetite	Fe_3O_4	xx	xx	xx	xxx	xxx	xxx	xxx	xxx	xxx	xxx	xxxx
Marcasite	FeS_2	xx	xx	xx	xx	xx	x	x		x	xx	x
Hematite	α-Fe_2O_3		x								x	
Diopside	$Ca(Mg,Fe)(Si_2O_6)$	xx	xx	xx	xx	xx	xxx	xxx	xxx	xx	xxx	xxx
Feldspar	$(K,Na)[AlSi_3O_8]$	xx	xx	xx	xxx	xxx	xx	xx	xx	xx	xx	xx
Plagioclase	$NaAlSi_3O_8$- $CaAl_2Si_2O_8$	xx	xx	xx	x	xx	xx		xx	xx		xxx
Bassanite	$CaSO_4x0{,}5H_2O$	xx	xx	xx	x	xx	x					
Halite	$NaCl$	xx	xx	xx	x							
Ettringite	$3CaOxAl_2O_3x$ $3CaSO_4x30$-$32H_2O$	x	x									

A comparison of the constructionally relevant size ranges with the mineralogical composition shows clearly the following connections:

- the hard silicates and oxides which are substantially responsible for the mechanical characteristics are enriched in the coarser size classes,
- the carbonate calcite which is responsible for the alteration reactions is enriched in the finer grain classes,
- the sulphates which exert a considerable influence on the volume stability occur in the smaller particle size classes and
- the contents of the chlorides which control the salt release are enriched in the finer size classes.

4.3.1.2 Heavy Metals and Salts

The mass and volume reduction of waste incineration causes an enrichment of a number of heavy metals in the grate ashes compared to their concentration in the waste feed. This is demonstrated in Fig. 9 which shows the concentration ranges of selected metals in MSW, bottom ashes, and filter ashes [IAWG 1997]. With the exemption of As and Hg all heavy metals, even those with a significant volatility in waste incineration like Cd, are highly enriched in the grate ashes compared to the lithosphere. That is why these materials have to be looked thoroughly upon in view of their disposal or eventual utilisation. According to the Swiss regulation this high metal inventory is seen as a significant obstacle even for disposal.

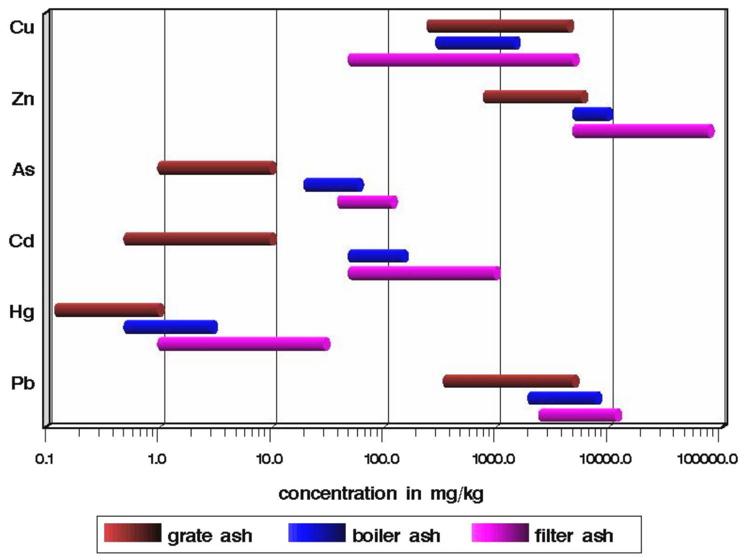

Fig. 9 Concentration ranges of selected elements in grate ash, bottom ash and fly ash (adopted from [IAWG 1997])

Another important ingredient aside of the heavy metals is the salt inventory in the grate ashes. For disposal the limitation of the salt content is in Germany only regulated by the soluble fraction and the electric conductivity whereas for utilisation specific standards are given for chlorides and sulphates.

Since grate ashes are typically discharged through a quench tank the very soluble chlorides are to a great extent washed out, especially if the quench tank is operated as a kind of washer with a slight water surplus [Reimann 1994, Schneider 1994]. In such cases Cl concentrations in grate ashes range from 1 – 5 mg/g [IAWG 1997, Belevi 2000]. Sulphates are far less soluble due to the high Ca inventory in the ashes and hence there is only a limited wash-out to be expected in the quench tank. Ranges of sulphate concentrations in grate ashes are reported to 3 – 50 mg/g [IAWG 1997, Belevi 2000].

4.3.1.3 Carbon and Organic Ingredients

The objective of waste incineration is the total conversion of all organic carbon or biodegradable matter into the stable carbon species carbonates and CO_2. The burnout is hence a key parameter for disposal as well as for utilisation of bottom ashes. The German Technical Ordinance Residential Waste sets a TOC (total organic carbon) limit of 1 wt.-% for disposal on a class I landfill. The same number is found in the LAGA memorandum for utilisation in road construction.

In modern well operated MSWI plants the TOC in bottom ashes is typically well below 1 wt.-% [Reeck 1991, Reimann 1994, Schneider 1994, Bergfeldt 2000]. Special combustion trials in the Karlsruhe test incinerator TAMARA demonstrated that an increasing heating value of the feed and the resulting higher bed temperatures improve the burnout of bottom ash [Vehlow 2000].

The TOC of bottom ashes comprises mainly elementary carbon, but to a certain extent also organic compounds are found which cover the spectrum from short-chain compounds [Köster 1998] up to low volatile species such as PAH or PCDD/F. Typical concentrations of organic compounds in grate ashes and other solid residues are compiled in Table 9 [Vehlow 2006].

Table 9 Concentration ranges of organic compounds in grate, boiler, and filter ashes

Parameter	***Grate ash ng/g***	***Boiler ash ng/g***	***Filter ash ng/g***
I-TEQ	<0.001 - 0,03	0,02 - 1	0.1 - 10
PCB	<5 - 50	4 - 50	10 - 250
PCBz	< 2 - 20	200 - 1 000	100 - 4000
PCPh	<2 - 50	20 - 500	50 - 10000
PAH	<5 - 10	10 - 300	50 - 2000

Only data from modern facilities have been used as basis [Vehlow 2006 and literature referred to there]. The PCDD/F numbers are given in terms of international toxic equivalence data (I-TEQ). The I-TEQ levels detected in the bottom ashes of modern incineration plants were in the same order of magnitude as found in uncontaminated soils in Central Europe [Fiedler 1996]. The concentrations of the other contaminants, too, are negligible in well burnt out grate ashes.

4.3.1.4 Post-combustion Treatment

The mass flow scheme in Fig. 7 documented that raw bottom ashes contain significant amounts of ferrous and non ferrous metal scrap. It is common practice that at least the ferrous, but nowadays in many plants also the non ferrous metals are recovered if the final destination of the bottom ash is a landfill.

If utilisation of the bottom ashes is envisaged the obligatory post-combustion treatment is much more extended. A typical flow sheet of advanced ash treatment as performed at the Hamburg waste incinerator MVR is shown in Fig. 10.

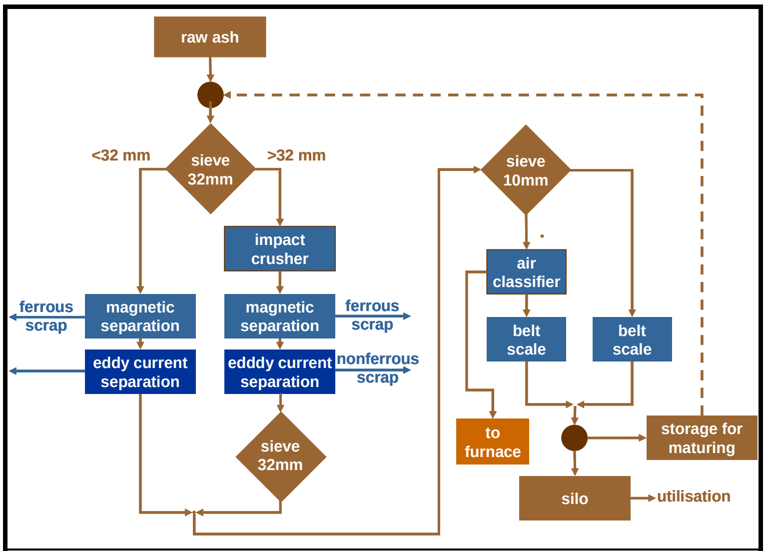

Fig. 10 Grate ash pre-treatment at the Hamburg waste incineration plant MVR (adopted from Zwahr 2005]

The procedure starts typically already in the quench tank of the incinerator where a surplus of water reduces the salt content. After discharge the ashes are stored for few days for de-watering before they undergo further treatment which consists of a sieving to remove bulky fractions and magnetic separation of ferrous scrap which is today in many plants amended by an eddy-current separation of non-ferrous metals. The metal fractions, up to 10 wt% of ferrous and approx. 1 wt% of non-ferrous scrap (compare Fig. 7), are sold to recycling companies. Considering the total amount of grate ashes of almost 10 million Mg in the six partner countries of the NoE where waste incineration is practiced to a greater extent, approx. 1 million Mg of iron scrap and some 100,000 Mg of non ferrous metals, mainly Al and Cu can be recovered. Especially the latter fraction accounts for a not unwanted revenue for the operator.

The ashes are than stored for aging or maturing a certain time, in Germany according to the LAGA memorandum 12 weeks [LAGA 1994]. After the respective compliance tests (see Table 4) the ashes can than be utilised as secondary building materials.

4.3.1.5 Elution Stability and Effect of Aging

The access to a landfill or a specific utilisation scenario depends not only on the residual carbon inventory but also on the leaching properties of the material in question. There is a number of standardised protocols for elution testing [IAWG 1997]. The EU countries will in future apply the CEN compliance tests [CEN 2002]. A comparison of various standards for disposal as well as for utilisation points out that the requirements for leaching stability are more or less of equal stringency in all countries all over the world.

The elution of a single element out of bottom ashes is in a complex way influenced by a number of parameters the most important ones are [IAWG 1997]:

- its chemical composition,
- its chemical/geochemical/mineralogical speciation,
- the fraction of a species available for leaching,
- the properties of the leachant, especially its pH or the presence of complexing constituents,
- the particle morphology, and
- the liquid-solid ratio (LS) in the leaching system.

In aqueous systems the pH of the leachant is in most cases the controlling parameter. All heavy metals have a solubility minimum at a slightly alkaline regime in the pH region of 9 – 10. A number of heavy metals, the amphotheric ones, are again solubilised at high pH values. The most important heavy metal of this sort is Pb which starts to become strongly soluble as soon as the pH exceeds11.5 (compare Fig. 11) [Bergfeldt 2000].

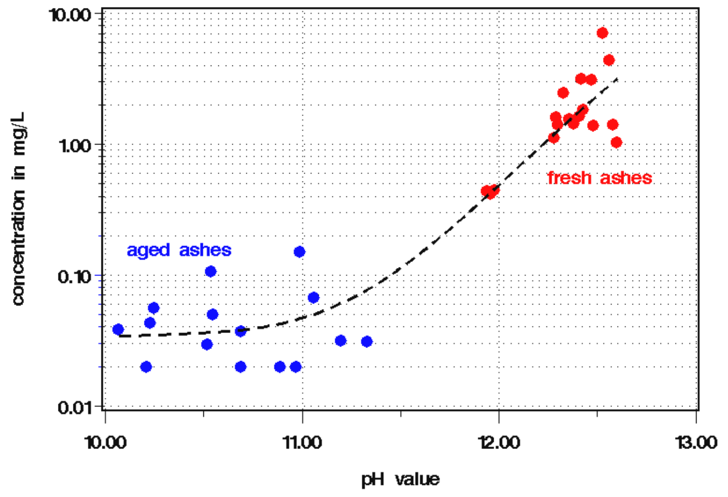

Fig. 11 Elution of Pb from fresh and aged bottom ashes (adopted from [Bergfeldt 2000])

The graph points out that the pH is significantly reduced if the ashes are aged. This is why aging or maturing is a mandatory pre-treatment in many legislative regulations before bottom ashes are allowed to be utilised. During the typical storage time the CaO in the bottom ashes reacts with CO_2 of the air according to

$$CaO + CO_2 \rightleftharpoons CaCO_3$$

This reaction is promoted by humidity since the intermediately formed $Ca(OH)_2$ adsorbs and reacts much faster with the CO_2 than the dry CaO.

Further main reactions during the aging process are corrosion reactions of finely dispersed metallic Fe and Al. All of these reactions are exothermic and the elevated temperature in the ash piles initiates further re-speciation of some mineral phases. Of special interest are the sulphates where anhydrite ($CaSO_4$) converts into the more stable gypsum ($CaSO_4x2H_2O$). A scheme of major changes in the mineral phase composition is shown in Fig. 12 [Pfrang_Stotz 1995].

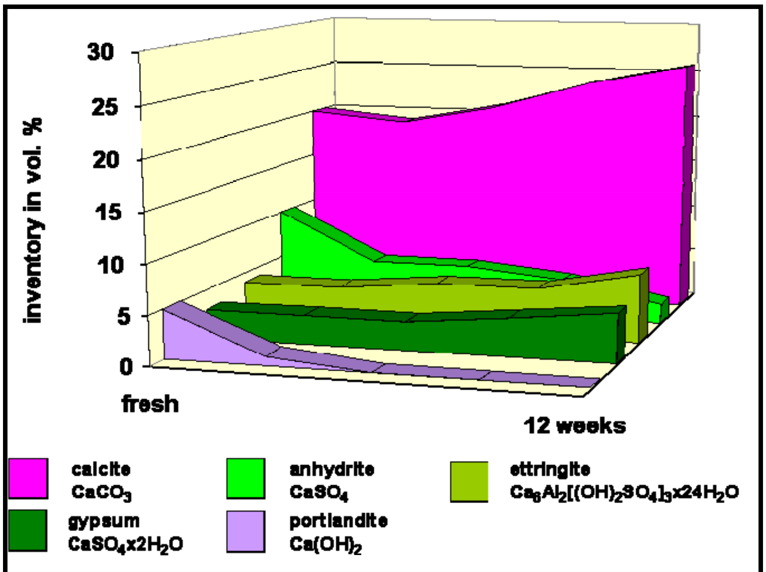

Fig. 12 Mineral changes during aging (adopted from [Pfrang-Stotz 1995])

Such aging is beneficial not only for the mechanical properties of the ash but also for its leaching stability. From a German plant which treats bottom ashes for utilisation in road construction a series of 26 compliance tests using the German DEV S4 protocol [DIN 38414] and taken through one year have been published [Pfrang-Stotz 1995] which comply well with the German LAGA limits for utilisation as is documented in the bar chart in Fig. 13.

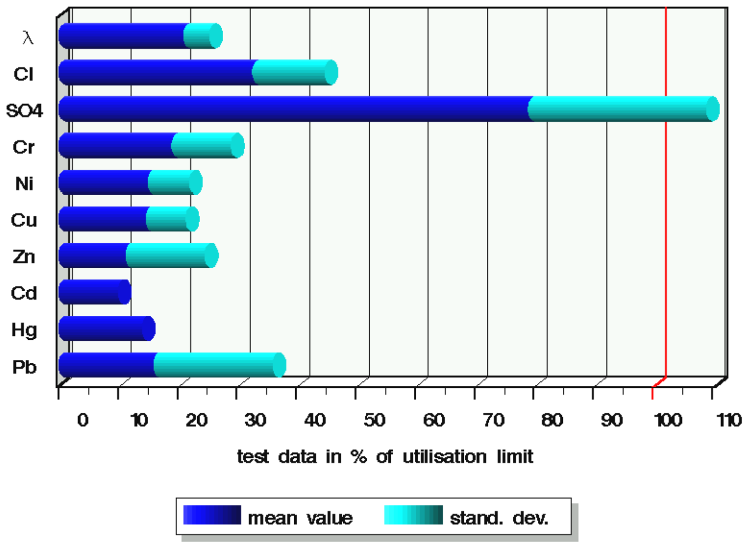

Fig. 13 DEV S4 results of 26 bottom ash samples standardised to the limits of the German LAGA memorandum

It is evident that the test results for the environmentally interesting heavy metals were always well below the respective standards. The only component exceeding the limit in few cases was sulphate. This limit has been set to protect concrete structures from corrosion attack. Hence it can be stated, that bottom ashes from modern and well operated MSWI plants do easily meet the LAGA limits for utilisation.

However, the compliance with standards fulfils the legislative requirements but does not necessarily tell about the acceptability of the environmental impact. To get a clue about this aspect the DEV S4 test was also applied to gravel from the river Rhine [Sauter 2000].

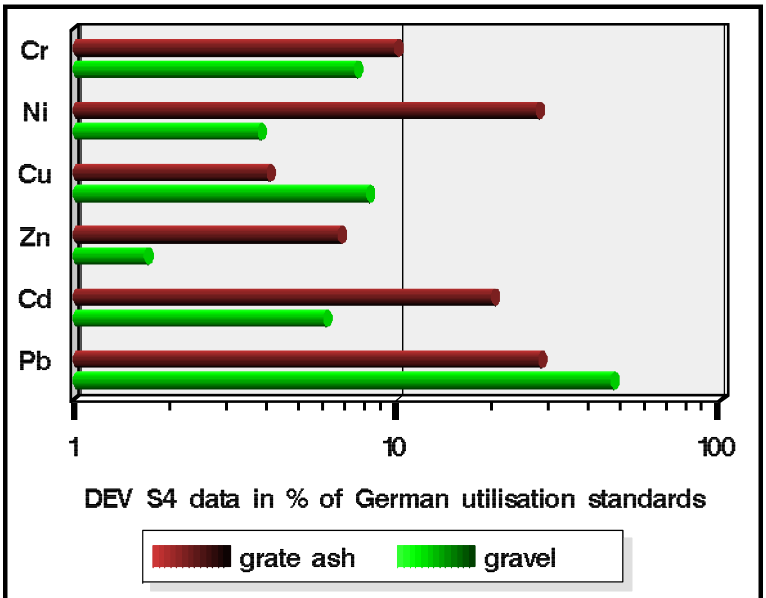

Fig. 14 DEV S4 results of 26 bottom ash samples and gravel from the river Rhine standardised to the limits of the German LAGA memorandum

The results for both materials in terms of percentiles of the German LAGA limits are displayed in Fig. 14. The bar chart documents 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 such materials.

4.3.1.6 Stabilisation Processes

Especially in Japan fusion or vitrification of bottom ashes is practised in order to reduce their volume and to improve their environmental quality [Nabeshima 1996]. As has been documented above, bottom ashes from modern waste incineration plants have the potential to be utilised as secondary building material in road construction - and there is a permanent requirement for such material in many countries in Central Europe. It has also been demonstrated that fusion of bottom ashes from state-of-the-art MSWI plants does not improve the quality to an extent which would open new markets [Schneider 1994]. This fact and the economic disadvantage of high energy consumption are reason that the many different fusion and vitrification processes which have also been proposed and partly even been demonstrated in pilot scale in Europe during the late eighties and early nineties of the 20th century did not enter the market [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]. This 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, not only to consider the environmental benefits of a measure but also to set the obtained improvement into relation to the spent effort. The measure for the effort should be the cost of the process. In other words: a real eco-balance is needed. 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:

- 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 is the cost of the process?

It is not easy to answer these questions in particular, the more so if the respective process has not been tested in full scale. This applies especially 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. This topic will be dealt with in a later chapter.

4.3.1.7 Disposal Practice

The latest available information on the production and management of residues from waste incineration is compiled in Table 10. The data are partly taken from CEWEP, the Confederation of European Waste-to-Energy Plants, which publishes results of annually performed member's questionnaires on the internet [CEWEP 2006].

Table 10 Bottom ash production and management in selected countries [CEWEP 2006, (1)Bethanis 2004, (2)Bruder-Hubscher 2001, (3)Environment Agency 2002]

Country	*Year*	*Production [Mg/a]*	*Recovered metals[Mg]*	*Utilisation [%]*	*Comments*
Austria	2004	300,000			mainly landfill, 'slag concrete for landfill'
Belgium	2004	250,000		100	secondary building material
Czech Republic	2004	114,000		0	landfilling
Denmark	2004	564,313		98	81% road construction
Finland	2005	20,000		no	landfilled
France(1,2)	2001	2,700,000	302000	30	civil engineering, 10% stockpiled
Germany	2005	4,100,000	≈330000	86	mainly road construction
Hungary	2005	69,628		0	landfilling
Italy	2004	827,310		20	
Netherlands	2003	1,100,000		75	mainly road construction
Portugal	2005	200,000		0	
Spain	2005	293,693			landfill, road construction
Sweden	2004	485,000			few sites for road construction
United Kingdom(3)	2000	625,000		40(2)	mainly landfilling

Some countries have established an extended utilisation of bottom ashes, i.e. Denmark, Germany and the Netherlands. For these countries data on the amount of utilisation as well as of the utilisation scenarios are available. The main application is road construction, other areas are noise protection walls, embanking, dykes and soil melioration. Countries which start to utilise or to extent their ash utilisation are France or the UK.

Table 11 UK applications and uses of recycled secondary aggregates [Greenspec 2006]

application	*examples*
Concrete	ready mixed concrete
Manufactured concrete products	wide range of products; examples include concrete blocks, kerbs, pipes, slabs
Geotechnical applications / civil engineering	fill
Roads, pavements, car parks and hardstanding	asphalt-bound and hydraulically bound mixtures

According to a study conducted by the Environment Agency in 2002 [Environment Agency 2002] over 40% (over 200,000 tonnes p.a.) of bottom ash from England's 11 municipal waste incinerators was being recycled as aggregate in 2000. The recycled ash is used in the building and road/pathway construction industries.

All the applications and uses of recycled secondary aggregates in the UK are presented in Table 11. The CEN Mandate for aggregates M125 applies to the preparation of concrete, mortar, grout and mixes for construction and for the manufacture of construction products as well as other bound and unbound mixtures for use in roads and other civil engineering works [ESA 2006]. Some of the standards under this mandate are presented in Table 12.

Table 12 UK standards for aggregates and uses [Greenspec 2006]

Standard	*Uses*
BS EN 12620 aggregates for Concrete	• structural concrete • roads, pavements • precast concrete products
BS 8500 – 2 specification for constituent materials & concrete; used in conjunction with BS EN 206 concrete – Part 1	• structures cast in situ • precast structures and structural precast products for buildings and civil engineering structures
BS 13139 aggregates for mortar	• mortar : masonry, floor/screed, plastering • rendering of external walls • special bedding materials
BS EN 13043 aggregates for bituminous mixtures and surface treatments for roads, airfields and other trafficked areas	• bituminous mixtures • surface treatments for roads, airfields and other trafficked areas.
BS EN 13055: lightweight aggregates – Part 1: lightweight aggregates for concrete, mortar and grout	• buildings • roads • civil engineering works
EN 13242 aggregates for unbound and hydraulically bound materials for use in civil engineering work and road construction	• buildings • roads • civil engineering works

4.3.2 Boiler and Filter Ashes

4.3.2.1 Chemical Characterisation

Boiler ashes are deposited at temperatures between approx. 800 and 200 °C, filter ashes typically at temperatures slightly below 200 °C. That is why heavy metals and other species which are volatilised inside the combustion chamber are to some extend condensated on their surfaces and their concentration of such elements like Cl, Zn, As, Cd or Pb can exceed that in grate ashes significantly as is shown in Fig. 9. Furthermore, since these compounds are synthesised inside the boiler, the inventory of low volatile halogenated organic micro-pollutants like PCDD/F or PCB is also increased compared to that in grate ashes. Since filter ashes are precipitated at lower temperatures than boiler ashes and since they have a much finer particle size distribution and offer higher surfaces for condensation their concentration of heavy metals, of halogenides and of organic micro-pollutants is typically higher. This fact can be seen in Fig. 9 and Table 9.

4.3.2.2 Disposal Practice

Due to their elevated pollutant inventory boiler and filter ashes have to be characterised as hazardous waste and must not be combined with the grate ashes. They are typically disposed of on special – and expensive – disposal sites, preferentially in the underground. In Germany they can be used in old salt mines for backfilling of caverns. This practise is according to national regulations acknowledged as utilisation. A compilation of filter ash production in selected countries is found in Table 13. Again the data are from CWEP member's questionnaires published in the internet [CEWEP 2006].

The preferential disposal site is the hazardous landfill.

Table 13 Filter ash production and management in selected countries [CEWEP 2006] ([1] estimated)

Country	*Year*	*Production [Mg]*	*Comments*
Austria	2004	40,000	mainly salt mine backfilling, hazardous landfill
Belgium	2004	50,000	solidification and haz. landfill
Czech Republic	2004	6,000	5000 hazardous landfill, 1000 underground mine
Denmark	2004	86,834	100% recycled (salt mine after special treatment)
France		400,000	
Germany	2005	650,000	utilisation in salt mine, minor amount haz. landfill
Hungary	2005	13,585	hazardous. landfill
Italy	2004	71,814	
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 (Langoya)
United Kingdom[1]	2000	78,125	hazardous landfill

4.3.2.3 Stabilisation Processes

The high expenses for a sustainable final disposal of boiler and filter ashes were 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 14 tries to categorise the various treatment options.

Table 14 Procedures for treatment of boiler and filter ashes

Principle	*Process*	
Solidification/ Stabilisation	without additives cement based systems waste pozzolanic systems chemical stabilisation organic additives or matrix	(Bamberg Model) (Portland cement, alinite) (coal fly ash) (sulphides, TMT 15™) (bitumen)
Thermal treatment	PCDD/F destruction sintering fusion vitrification	(Hagenmaier drum) (mineral respeciation) (melting without additives) (melting with additives)
Combined process	acid extraction + sintering	(3R Process)
	stabilisation with $FeSO_4$, oxidation, sintering	(Ferrox Process)

Without going into detail it seems evident that solidification or stabilisation does not alter the toxic inventory of the material. The established transformation or diffusion barrier does only last for a limited time. Two processes are 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 neutralisation [Reimann 1990], and the Swiss filter ash cement stabilisation after washing [Tobler 1989].

Thermal treatment can be performed at moderate temperatures in the so-called Hagenmaier Drum at 400 °C to destroy dioxins [Hagenmaier 1987]. Another option is vitrification at high temperatures (>1300 °C) to produce glassy products. Vitrification is mainly favoured in Japan as is the case for the 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 by far not compensated by the potential to recover metals. That is why such processes – 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) with a thermal treatment of the compacted extraction residues in the combustion chamber [Vogg 1984]. If this process is applied the filter and boiler ashes disappear. A scheme of the process is shown in Fig. 15. The technical demonstration revealed that the grate ashes from a 3R Process which contain the leached filter ashes show excellent and not changed leaching properties of heavy metals and that the PCDD/F are almost totally destroyed [Vehlow 1990].

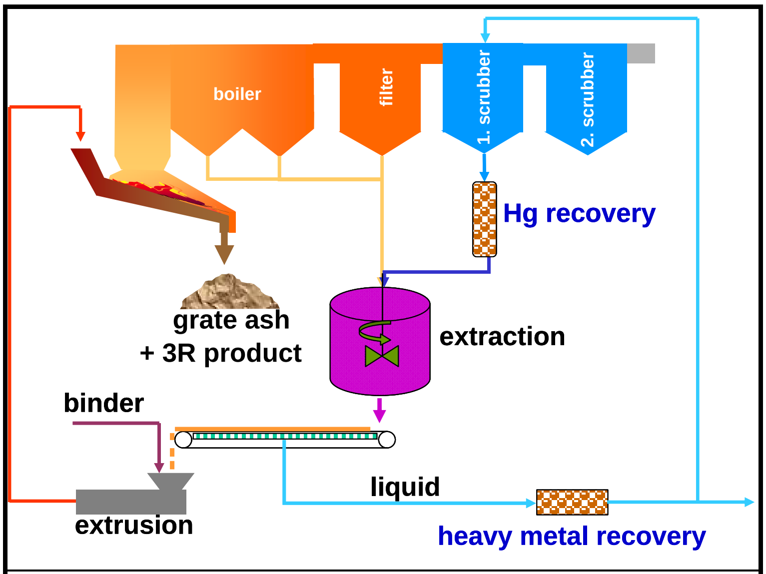

Fig. 15 Scheme of the 3R Process

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 have the quality to be landfilled or they can for quality improvement be fed back into the combustion chamber for further thermal treatment. 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]

4.3.3 Residues from Gas Cleaning

4.3.3.1 Chemical Characterisation and Disposal Practice

The residues from wet gas cleaning without water discharge and those from dry or semi-dry APC systems carry high levels of soluble salts, especially of alkali and earth-alkali chlorides or sulphates. Due to the high solubility a safe disposal can only be guarantied on special and expensive disposal sites. 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 to recover NaCl [Karger 1990], HCl [Kürzinger 1989], Cl_2 [Volkman 1991], or gypsum have been tested. 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. Today e.g. in Germany only few MSWI plants produce HCl [Menke 1999]. All other processes did not make it to the market due to unfavourable economy.

A different - and finally very cheap - way of disposal of filter ashes (and APC residues) is practiced in Germany where authorities enforce the backfilling of cavities in old mines. Salt caverns are already being filled by semi-dry flue gas cleaning residues from MSWI in big bags [Plomer 1995]. This strategy - which is even accepted as 'utilisation' - may be justified with the similar chemical as well as physical properties of the original salt and the disposed residues. However, for likewise activities in old coal mines this argument can hardly be used.

4.4 Economy of Residue Management

Regarding residue management practice in Europe the strategies vary from country to country. Considering the quality of the above described residue streams it is obvious that there is no single best solution solving all problems. As has been mentioned above already, the easiest residue stream to decide upon its final destination is the bottom ash. It is either utilised or it is disposed of on a landfill. In each case a ferrous and non-ferrous scrap removal is mandatory and at least the ferrous separation is done in almost all waste incineration plants.

If landfilling of the bottom ashes is envisaged it can be estimated that the expenses for the necessary pre-treatment – ferrous and non-ferrous scrap removal are approximately covered by the income from the separated metals. In this case the only cost is the gate fee at the landfill. Landfill fees are rather high in some countries and they are expected to increase with time. Furthermore, a number of countries impose a landfill tax on all material going to such sites in order to encourage all kinds of waste reduction and recycling and to keep especially reactive waste away from disposal sites. Actual landfill fees and landfill taxes are compiled for selected countries in Table 15.

Table 15 Landfill fee and landfill tax in €/Mg municipal solid waste [CEWEP 2006]

Country	***Landfill fee average***	***Landfill fee range***	***Landfill tax***
Austria		60 - 130	87
Belgium			58.73[1]/61.82[2]/123.63[3]
Denmark		6.85 – 40.7	50.49
Finland			23
France		60 - 80	7.32 - 9.15
Germany	110	50 - 200	0
Netherlands		110 - 130	84.73
Poland			0
Sweden		50 - 100	47
United Kingdom			29.91[4]

[1] with gas collection,
[2] without gas collection,
[3] landfill without license,
[4] increasing by € 4.27 per year

For utilisation a much more complex pre-treatment including aging is required (compare chapter 4.3.1.4). Data from 1996 state 10 €/Mg of costs for this treatment at Hamburg waste incineration plants [Schumacher 1996]. The MSWI Amsterdam publishes newer data of approx. 50 €/Mg for their bottom ash pre-treatment [City of Amsterdam 2005]. The treated ashes are typically delivered to construction companies for free. Comparing the expenses for pre-treatment with those for landfilling it is obvious that there is a strong economic driver to utilise as much bottom ashes as possible.

For further treatment like fusion as performed in Japan costs of some 100 – 200 €/Mg have to be calculated without getting a product of real economic value. Hence for European conditions such further treatment makes no sense.

The situation is different for filter ashes and APC residues. These are hazardous residues which need to go to special – and typically expensive – disposal sites, but they represent a small fraction of the waste stream entering an incineration plant only. In this case even complex treatment technologies for detoxification and inertisation may pay.

Costs of various filter ash treatment options have been estimated on the basis of published data in Table 16 [Vehlow 1997]. Again, as in the case of bottom ash treatment, the costs of technical processes should be comparable in most industrialised countries whereas the disposal fees will change from country to country. Although theses cost data are rather old it is expected that the relation between the different processes is still reflecting the situation of today.

The table reveals that the specific costs of the technical measures are rather high, but due to the small residue streams the expenses per ton of waste are low and similar for all disposal strategies. Hence the economy will not be the decisive factor for the selection of a specific process and local conditions like access to adequate disposal sites will be more important.

Table 16 Cost estimates for land filling and treatment of filter ashes [Vehlow 1997]

	€/Mg of filter ash	***€/Mg of MSW***
Disposal on special landfill	200	3
Utilisation in salt mines	100	1.5
Cement solidification(1)	25	0.5
Stabilisation(1)	80	2
Solidification+stabilisation(1)	120	2
3R Process	120	2
Fusion/vitrification	180	3

(1) *disposal costs not included*

Since the mass flow and properties of residues from gas cleaning depend on the applied strategy, it seems not useful to discuss their specific disposal or treatment costs. Hence the attempt has been made in the above referenced publication to compare the costs of the respective flue gas cleaning strategies [Vehlow 1997]. The at that time obtained data are compiled in Table 17.

Table 17 Cost estimates for land filling and treatment of scrubbing residues [Vehlow 1997]

Process	***€/Mg of MSW***
Dry sorption	36
Dry sorption without residue disposal	23
Dry sorption with utilisation for backfilling of caverns	32
Semi-dry sorption	29
Wet scrubbing with waste water discharge	25
Wet scrubbing with spray dryer	28
Wet scrubbing with external evaporation	29
Wet scrubbing with HCl/gypsum production	35

Like in the case of the filter ashes the economy of the various options does not differ significantly and again local conditions will be decisive for the most adequate strategy. In Germany the underground 'utilisation' looks economically promising. The gate fee has meanwhile dropped down in some mines to approx. 40 - 70 € per ton of material. As a consequence dry scrubbing processes may be promoted which is in contradiction to the legislative demand for residue minimization. If the strategy gains wide application, however, it will change the management of residues from APC systems in future at least in Germany, where a great number of old mines is waiting to be filled.

4.5 Conclusions for Waste Incineration Residues

Waste incineration is a well established process in many countries and the properties of the residues from this process are also well known. There is a good understanding how to produce high quality bottom ashes which have a high potential for utilisation as building materials. This application, however, is often criticised and addressed as 'under cover disposal'. Switzerland, e.g., does not longer apply utilisation of bottom ashes in road construction and requires landfilling for this residue.

The real critical residues are those from gas cleaning due to their inventory of organic micropollutants, heavy metals and soluble salts. For the latter ones no convincing disposal option aside from final storage in salt mines can be thought of. The salt problem is a difficult one since it is strongly depending on the applied gas cleaning method.

A number of stabilisation and treatment processes including the recovery of species out of these materials have been developed but none has been implemented in full scale due to economic constraints. In this respect it might be useful to investigate treatment processes of gas cleaning residues including macro-economical aspects. There is reason to speculate that even recovery processes which are not profitable for private companies might point out economically useful if future and long-term costs which have to be covered of the society, e.g. for rehabilitation of contaminated sites, are taken into account.

5 Co-incineration and Co-gasification

5.1 Energy from Solid Recovered Fuels

Besides so called dedicated Waste-to-Energy solutions another approach i.e. co-incineration or gasification of Solid Recovered Fuels (SRF) has been introduced to European market. The idea is to prepare fuel to such a quality that it can compete in the market with other commercial fuels, i.e. in applications with high efficiency. As it is well known co-incineration or co-gasification are regarded to fall under the Waste Incineration Directive, so SRF may only be used by installations complying with the emission limit values set by this directive.

The technology applied for co-incineration is mainly combustion in fluidised bed or in grate systems. The industrial sectors range from the power sector to industrial furnaces and cement kilns.

Co-gasification of SRF is yet a rare technology. An example is one plant in Finland where the gasification is performed in a fluidised bed gasifier and where the syngas is fed without any pretreatment directly into a coal fired power plant. A scheme of the process is depicted in the left graph of Fig. 16. Another gasification process for packaging waste is schematically shown in the right graph of the same figure.

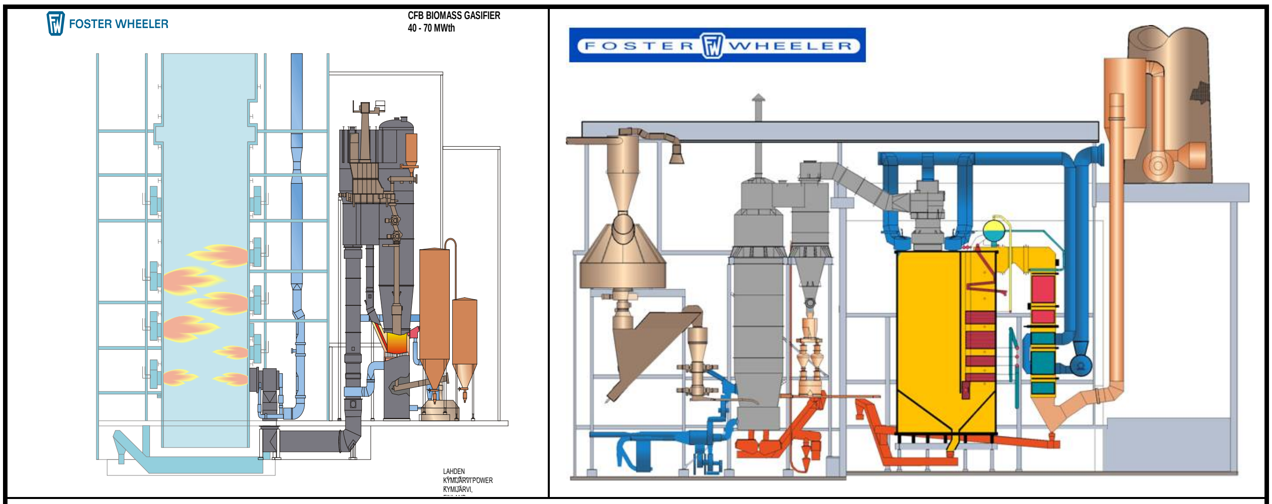

Fig. 16 Co-gasification of SRF in a coal fired power station (left, [Energia Suomessa 2004]), gasification of packaging waste with Al-recovery (right top, Ecogas Process, [Nieminen 2005])

Co-incineration of SRF requires a supply of pre-treated and homogenised waste upgraded to a *fuel* quality that can be traded amongst producers and users of SRF. This implies specifications that are included in commercial transactions for SRF. For combustible wastes not suitable for environmentally sound recycling, such appropriate specifications for their production are under preparation to be included in European Standards.

SRFs are composed of a variety of materials of which some although recyclable may have been made available in such a form that recycling is not environmentally sound. On the one hand, materials collected and/or sorted and prepared into a recyclable form should not be considered as SRFs. On the other hand, recyclable materials should not be excluded from SRFs because such an exclusion could lead to disposal of these materials.

In some countries, e.g. Germany, the production of SRF and similar fuels derived from waste fractions has been increased during the last years, promoted by political will and public opposition against waste incineration. Especially for materials originating from mixed municipal solid waste the quality of the feed varies in wide ranges and the material finds no market in utility boilers or industrial furnaces. That is why a number of specific combustion plants with implemented air pollution control systems have been built and a decent number of such plants with a total capacity of 2.4 Tg/a is actually in the design phase [Radde 2006]. These plants accept SRF, biomass, and also contaminated fuels such as wood from the construction and demolition sector. The plants are either fluidised beds, but during the last time also to a great extent grate systems.

5.2 Classification Principles of SRF (CEN Report)

The classification system, the classes and the specifications that are proposed should help the authorities in writing the permits, be a help for the final user to understand easily what has to be taken into account when dealing with SRF and should increase the positive perception of the public on the use of SRF by saving of natural resources. For example about 50% of the primary fuel consumption of cement kilns and a substantial share of hard coal and lignite for power production could be substituted by waste. The potential for European Solid Recovered Fuels in 2005 is estimated at more than 10 Mt/a, which corresponds to a CO_2-reduction of more than 10 Million tons annually. (In this figure only the biogenic fraction and C/H ratio were considered. The reduction due to less emission of methane from landfills would be a factor ~3 of this). Proposed classification system for SRF is given in Table 18.

Table 18 Classification system for solid recovered fuels

Classification property	*Statistical measure*	*unit*	*Classes*				
			1	*2*	*3*	*4*	*5*
Net calorific value (NCV)	mean	MJ/kg	≥25	≥20	≥15	≥10	≥3
Chlorine (Cl)	mean	%	≤0.2	≤0.6	≤1.0	≤1.5	≤3
Mercury (Hg)	median 80th perc.	mg/MJ	≤0.02 ≤0.04	≤0.03 ≤0.06	≤0.08 ≤0.16	≤0.15 ≤0.30	≤0.50 ≤1.00

5.3 Utilisation of SRF in the European Union

In Europe, during the last ten years, energy policy targets and waste management legislation gave an impetus to the usage of waste derived fuels based on non hazardous wastes. These fuels, having an average content of 50 - 60% on biogenics, may contribute considerably to the reduction of CO_2 emission and the doubling of the share of renewable energy. Moreover, due to liberalisation and need for cost reduction, industry is interested in less expensive homogenous substitute fuels of a specified quality.

At present, the main end-users are the cement and lime industry. However, the market chances in the potential bigger market of the power generation sector are increasing. Total MSW (municipal solid waste) production in EU-15 is estimated to be around 160 - 170 Tg/y [UBA 2001], of which about 18% (29 - 30.5 Tg) are incinerated. The current best estimate of the quantity of solid recovered fuels consumed in Europe is about 1.4 Tg/y, as set out in Table 19 [GUA 2001]. There is no good information about the total amount of actually produced SRF respectively fuel produced from waste fractions in the EU. Germany alone has installed a capacity for the production of such fuel of approx. 6 Tg/a of waste which alone would exceed the above given number for the EU. However, it is assumed that less than 4 Tg/a are really used due to technical problems, but also due to a lack in market for the product. To solve this problem there is a number of dedicated combustion plants for SRF and biomass – mainly for residues from the construction and demolition sector - in design with a capacity of approx. 2.4 Tg/a

Table 19 Quantity of solid recovered fuels produced and consumed in European States, year 2000 (in brackets data of year 2002, when available)

Country	*Production*		*Consumption*		*- Export /Import +*		*Note*
	Gg/y	*toe/y*	*Gg/y*	*toe/y*	*Gg/y*	*toe/y*	*% CK*
Austria	100	50,000	100	50,000			7
Belgium	<100	<50,000	<100	<50,000	n.a.	n.a.	(100)
Denmark	0	0	0	0			
Finland	170	58,000	170	58,000	n.a.	n.a.	0
France	0	0	0	0			
Germany	500 (650)	250,000 (325,000)	500 (650)	250,000 (325,000)	n.a.	n.a.	85
Greece	0	0	0	0			
Iceland	0	0	0	0			
Ireland	0	0	0	0			

Country	***Production***		***Consumption***		***- Export /Import +***		***Note***
	Gg/y	***toe/y***	***Gg/y***	***toe/y***	***Gg/y***	***toe/y***	***% CK***
Italy	<200 (250)	<100,000 (125,000)	<200 (250)	<100,000 (125,000)	n.a.	n.a.	
Luxembourg	0	0	0	0			
Netherlands	250 (350)	100,000	15	6,000	-145	60,000	20
Norway	1)		1)				
Portugal	0	0	0	0			
Spain	n.a.	n.a.	n.a.	n.a.			
Sweden	1)		1)		+500 2)		
United Kingdom	60 (100)	30,000 (50,000)	60 (100)	30,000 (50,000)	n.a.	n.a.	
Total	1.380						

Notes: toe/y =1 Mg oil equivalent per year (It is assumed that solid recovered fuel has a calorific value of 21 MJ/kg, although it is lower in Finland and the Netherlands, and oil has a calorific value of 42 MJ/kg); % CK = % of consumption that occurs in cement kilns. The figures in this table are only indicative as they do not correspond to the same harmonised definition throughout the European Union.

1) There is no overall statistic for Sweden or Norway because this fuel is used in ordinary heat/power plants and in waste incinerators without a demand for detailed specifications. Data for Sweden (2001) are: waste incineration plants for district heating 856.000 Mg/a and power plants for district heating 455.000 Mg/a.

2) No exact figures exist, but approximate figures give 500 Gg of waste which was imported in 1999; 90% consisted of wood, paper, plastic and rubber.

5.4 Ash Quality in Conventional Biomass Installations and from Co-incineration of Biomass with SRF

Co-incineration of SRF in Finland is mainly performed at industrial power stations together with peat and biomass fuels. These installations are usually FB-units with quite high operation temperatures. In the following Table 20 results are shown for three different co-incineration plants burning different amounts of SRF. Some peak values, when compared with coal and peat ashes are found in copper, and zinc concentrations. These peak values were related to SRF qualities produced from dry waste fractions from households, slightly increased values were found with SRF produced from construction wood waste.

Table 20 Bed ash and bottom ash properties from three different co-incineration units from Finland. Plant A used 12 % SRF from household and commercial sources, main fuel was forest residues. Plant B used 20 % SRF from commercial waste main fuel was peat. Plant C used about 20 % SRF from different sources like demolition wood, industrial waste, main fuel was solid biofuels, dried sludge and peat (adopted from [Ranta 2002])

	Bed ash from SRF co-incineration			***Fly ashes from SRF co-incineration***		
	Plant A	***Plant B***	***Plant C***	***Plant A***	***Plant B***	***Plant C***
Antimony (Sb)	27			94		-
Arsenic (As)	21	<30	<30	51	<30	<50
Cadmium (Cd)	0.05	<10	<10	15	<10	<10
Cobalt (Co)	12	41	19	32	26	21
Chromium (Cr)	120	22	48	230	63	100
Copper (Cu)	1200	29	120	2200	120	180
Lead (Pb)	55	<40	<40	790	55	91
Manganese (Mn)	1900	810	2800	5000	1700	7300
Molybdenum (Mo)	10	<5	<5	35	8	7
Nickel (Ni)	15	11	13	53	38	42
Selenium (Se)	<10	-	-	<10	-	-
Zinc (Zn)	1100	550	680	3300	380	1400
Thallium (Tl)	<3	-	-	<3	-	-
Tin (Sn)	28	3.1	-	80	9.6	-
Vanadium (V)	36	23	12	100	56	32

5.5 Ashes from Co-gasification of SRF

Co-gasification of SRF in Finland is performed on one site at the moment at the Kymijärvi power plant in Lahti (compare Fig. 16). Gas from SRF gasification in a fluidised bed is substituting about 15 % of coal in pulverized coal firing. Ash from gasification is not separately collected in this case but mixed with main ash stream. In the studies no marked changes were noticed with regard to ash quality. Of course this depends on SRF quality and amount used.

About the quality of ashes from mono-combustion of SRF as practised in some plants in Germany already no information could be obtained. These ashes will in their composition strongly depend on the quality of the fuel which is in many cases not well controlled as has been outlined already.

5.6 Biomass/Waste Gasification Ash Management

Ash disposal cost for biomass or waste gasification process may however have significant impact on the feasibility of biomass/waste gasification based energy production. Typically a fluidised bed gasifier produces two main ash streams namely bottom ash and fly ash. Bottom or reactor ash is more or less oxidised and resembles conventional fuel ashes from combustion processes. Fly ash (filter dust) of woody material in particular might contain high concentrations (30-40 %) of unburned carbon and harmful compounds restricting further utilisation, or normal disposal. In an EU research program [Nieminen 2006a] three different methods of gasification ash management were studied and developed.

Table 21 Estimates of the ash management cost levels for alternative methods and routes for biomass/waste gasification fly ash

Treatment method/route Fly ashes	Ash management cost; €/t Low – Mean – High	Products of the method
Landfilling at a special site, 0-case	150	None
Use as fuel without treatment	0	Low grade fuel
Granulation and use as fuel	17....24....31	Low grade fuel
Washing and use as fuel	14....20....29	Low grade fuel
Combustion of clean ash in integrated CFB, use as construction material	21....29....39	Secondary construction material + energy
Combustion of clean ash in integrated CFB + granulation, use as forest fertiliser	38…53…70	Low grade fertiliser + energy
Combustion of clean ash in integrated BFB, use as construction material	28....40....55	Secondary construction material + energy
Washing + combustion in integrated CFB, use as construction material	35…49…68	Secondary construction material + energy
Combustion of clean ash in stand-alone CFB, use as construction material	22....31....42	Secondary construction material + energy
Combustion of contaminated ash in stand-alone CFB, use in construction	38....54....72	Secondary construction material + energy
Combustion of clean ash in stand-alone BFB, use as construction material	29....43....58	Secondary construction material + energy
Combustion of contaminated ash in stand-alone BFB, use in construction	45....65....89	Secondary construction material + energy
Oxidising sintering of clean ash, use as aggregate	34....61....94	Aggregate
Oxidising sintering of contaminated low chloride ash, use as aggregate	79....130....179	Aggregate
Washing + oxidising sintering of contaminated ash, use as aggregate	93…150…208	Aggregate
Oxidising smelting, use as aggregate	203....274....351	Aggregate

- Thermal treatment (separate combustion) of gasification ashes. The question of market demand on this type of fuel remains uncertain, but relatively clean carbon-rich ashes could be utilised in industrial furnaces like cement and light weight aggregate kilns.
- Fly ash oxidation process integrated to a gasifier which can reduce unburnt carbon level in ash down to acceptable level for disposal or utilisation. This operation may in some cases be limited by plant availability.
- Conditioning of fly ash trough different washing, agglomeration and thermal sintering processes is always possible but most expensive solution. In many cases side stream management is also increasing the overall cost.

In Table 21 estimated costs of different fly ash handling technologies are summarised. If landfilling cost is assumed to 150 €/Mg it becomes a major cost item for a gasifier plant and thus upgrading options are a realistic solution.

With specific SRF materials it is possible to manage ashes and at the same time recycle materials. This is done at Corenso plant in Finland (Nieminen 2005). Aluminium is a result of the ECOGAS process, in which the plastic and aluminium particles left from liquid packages after the fibre has been recovered for cardboard manufacturing, are blown into a gasifier. In the high temperature of the burner the plastic is turned into energy and aluminium is recovered for further use.

Another interesting gasification ash for material recovery could be automobile shredder residue (SRF) ash which may contain economically interesting amounts of metals (Nieminen 2006b).

6 Pyrolysis of Biomass and Waste

6.1 Pyrolysis of Waste

Pyrolysis is performed in one place in Germany - in Burgau, Bavaria - since 1984 as mono-treatment of waste. The plant has a small throughput of 36000 Mg/a of municipal solid waste which is pyrolysed at a temperature of 500 – 600 °C, the gas is after removal of coarse fly ashes in a cyclone directly burnt in a combustion chamber. The drum is heated by hot combustion flue gases extracted downstream of the combustion chamber [Fichtel 1987]. A scheme of process is seen in the top left graph in Fig. 17.

The solid residue from the pyrolysis process, a kind of coke, is deposited in a German salt mine, attempts to treat it or to use it as base material for charcoal production have not been made.

A combination of drum pyrolysis and coal fired power plant is the ConTherm process. Two lines for rotary drum pyrolysis which started operation in 2004. The plant comprises two lines with a capacity of 50000 Mg of waste derived fuel each [Hauk 2004]. The pyrolysis coke .

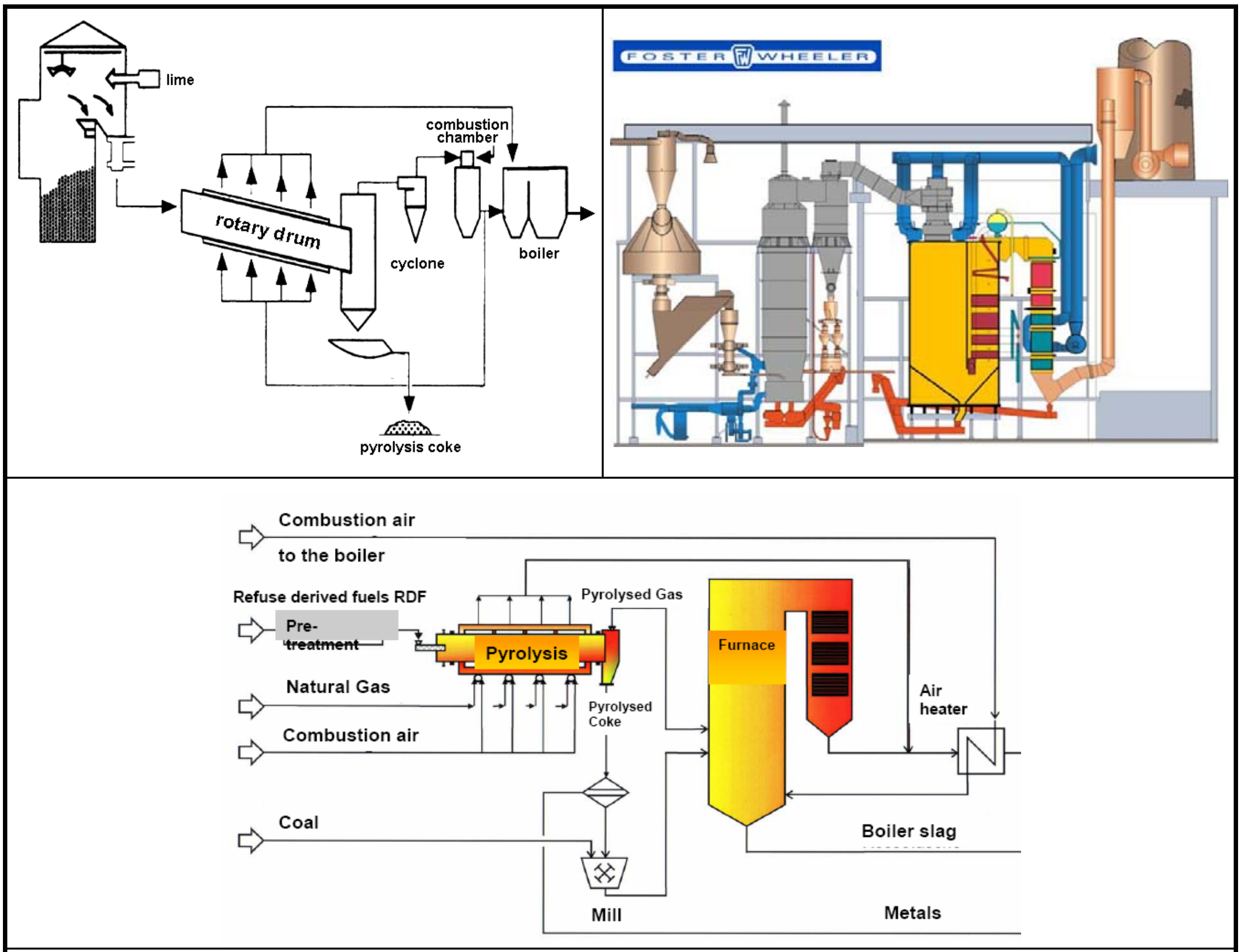

Fig. 17 Pyrolysis plant for municipal solid waste (top left, [Fichtel 1987]), integrated flash pyrolysis of SRF (top right, ITP Process [Sipilä 1999]), integrated rotary drum pyrolysis for SRF (bottom, ConTherm Process [Hauk 2004])

Flash-pyrolysis of waste or SRF is also aimed to be an integrated process where non-liquid parts of pyrolysis products are used in a main furnace to produce part of the energy needed for pyrolysis. A scheme of such process is depicted in the top right graph of Fig. 17. In this concept ashes are mixed with the ashes of main fuel and when considering utilisation of such ashes quality control of the fuel will be of high importance.

6.2 Fast Pyrolysis of Biomass

6.2.1 Introduction

Biomass pyrolysis is the thermal decomposition of biomass occurring in the absence of oxygen. The products of this decomposition consist of liquids, gases and charcoal otherwise called char. The product distribution depends on the process conditions. Table 22 compiles typical product yields of different pyrolsis processes of wood. Lower temperatures and longer vapour residence times favour the production of char. High temperatures and longer residence times increase biomass conversion to gas, and moderate temperatures (ca. 500°C) and short vapour residence time (<2 s) are optimum for producing liquids (75%). The latter case is known as fast pyrolysis [Bridgewater 1994]. Fast pyrolysis char sequesters almost all the original alkali content of the biomass and much of the chlorine [Jensen 2001]. It is usually recovered from two cyclones in series, although a little work has been carried out using a hot vapour filter. The first cyclone collects the majority of the char in particulate form, whereas the second cyclone collects the remaining char in powder form. Since the char yield is typically 12 %wt on dry biomass, starting with 1%wt ash results in a char with about 8% wt ash since nearly all the ash reports to the char.

Fresh char is pyrophoric, which constitutes a potential handling hazard. Therefore, it must either be cooled down in an inert atmosphere before handling and even then remains pyrophoric for days or weeks. It has a volatiles content of ca. 22% as determined by thermogravimetric analysis between 50 and 950°C under nitrogen. It can be utilised as a char by-product and exported or it can be used within the fast pyrolysis unit as a source of energy for providing the process heat. In this latter case, the ash content of the char needs careful management to avoid fouling.

Table 22 Typical product yields (dry wood basis) obtained by different modes of pyrolysis of wood

Mode	***Conditions***	***Liquid***	***Char***	***Gas***
Fast	moderate temperature, around 500C, short hot vapour residence time ~ 1 s	75%	12%	13%
Intermediate	moderate temperature , around 500C, moderate hot vapour residence time ~ 10-20 s	50%	20%	30%
Slow (carbonisation)	low temperature, around 400C, very long residence time	30%	35%	35%
Gasification	high temperature, around 800C, long residence times	5%	10%	85%

This study covers potential uses of char and ash, which are not integrated in the pyrolysis process. Although a range of commercial charcoal uses exists, no markets have been established for char produced by fast pyrolysis of biomass.

6.2.2 Effect of Feedstock Ash on Fast Pyrolysis Product Distribution

Literature data on the pyrolysis of a range of biomass feedstocks indicate that char yield depends on the ash content of the feedstock. As the ash content increases, the yield of organic liquid decreases and the yields of char and gas (on a dry ash free basis) increase (see Table 23). It has been suggested that biomass with high ash content often contains significant amount of alkali metal cations such as potassium and sodium which lead to catalytic cracking of the pyrolysis liquids in the vapour phase affecting the product distribution by reducing the liquid yield and increasing the gas yield. Alkali earth metals such as calcium and magnesium are also thought to behave as catalysts although their effect is not considered as significant as that of potassium and sodium (particularly at temperatures below 600ºC). High phosphorous is associated with high char yields, because phosphates when used as fire retardants promote the production of a char layer during the pyrolysis phase of combustion [LaVan 1990]. Work correlating the ash content and composition of the feedstock with the product distribution has been recently performed at Aston University [Coulson 2006]. Some of the results are presented in Table 24 and Table 25.

Table 23 Pyrolysis yield data for a range of feedstocks and authors

Feedstock	***T °C***	***Yields wt% dry feedstock basis***							***Ref***
		Ash	***Gas***	***Total liquids***	***Organic liquid***	***Water***	***Char***	***Closure***	
Poplar sawdust	504	0.46	11.00	76.90	66.20	10.70	11.80	99.70	[Scott 1982]
Pine (wood)	514	0.48	15.47	72.15	59.69	12.46	9.67	97.29	[Hague 1998a]
Spruce sawdust	500	0.5	11.00	78.10	66.50	11.60	12.20	101.30	[Scott 1982]
Hybrid Poplar	500	1.2	15.69	62.96	58.00	4.96	14.00	92.64	[Agblevor 1996]
Pine (bark)	505	1.94	14.32	49.98	39.92	10.06	28.60	92.90	[Hague 1998b]
Miscanthus	465	3.16	16.16	64.37	56.51	7.88	16.79	97.33	[Hague 1998b]
Sugar cane bagasse	500	3.9	11.60	68.70	61.40	7.30	18.80	99.10	[Palm 1993]
Sunflower hulls	500	4	19.50	56.10	46.30	9.80	23.20	98.80	[Piskorz 1992]
Switchgrass	500	4.6	10.90	66.46	nd	nd	21.60	98.96	[Agblevor 1996]
Corn Stover	500	5	15.89	63.05	55.47	7.58	15.90	94.85	[Agblevor 1996]
Rape straw	474	5.18	18.85	62.12	51.19	10.93	14.78	95.74	[Hague 1998b]
Rape meal	483	7.68	13.06	62.53	51.03	11.50	18.61	94.20	[Hague 1998b]
Sweet Sorghum bagasse	510	9.2	11.65	69.39	58.79	10.60	13.35	94.39	[Palm 1993]
Wheat chaff	515	22.5	15.90	66.70	51.00	15.70	17.60	100.20	[Piskorz 1992]

nd: not determined

Table 24 Pyrolysis yield data for grasses [Coulson 2006]

					Yields wt% dry feedstock basis					
Feedstock	***Pyrolysis Temperature °C***	***Ash content wt% d.b.***	***Total alkali metal content****	***Total alkali earth metal content*****	***Gas***	***Total liquids***	***Organic liquid***	***Water of reaction***	***Char***	***Closure wt% d.b.***
Miscanthus (leached)	504	1.725	0.12	0.19	12.9	69.1	60.1	9.0	11.7	93.8
Switchgrass	517	4.25	0.63	0.42	16.4	59.1	45.3	13.8	16.1	91.6
Cynara stem/branch	442	4.36	0.73	0.63	16.4	55.8	42.3	13.5	20.3	92.5
Arundo	460	4.14	0.55	0.21	15.4	59.1	45.9	13.2	20.7	95.3

*K, Na measured by ICP AES, ** Ca, Mg measured by ICP AES*

Table 25 Inorganic composition of pyrolysis feedstocks and ash content [Coulson 2006]

	Metals content by ICP-AES, wt% dry biomass								
Feedstock	***Na***	***K***	***Ca***	***Mg***	***Cl***	***P***	***Total alkali metals***	***Total alkali/alkali earth metals***	***Ash content***
Arundo	0.004	0.55	0.125	0.08	0.34	0.095	0.554	0.759	4.14
Arundo (washed)	0.008	0.29	0.08	0.04	<0.1	0.05	0.298	0.418	2.75
Miscanthus (leached)	0.005	0.12	0.125	0.065	<0.1	0.004	0.125	0.315	1.73
Cardoon stem/branch	0.21	0.52	0.565	0.065	0.495	0.045	0.73	1.36	4.36
Switchgrass	0.28	0.35	0.26	0.16	0.49	nd	0.63	1.05	4.25
Switchgrass (leached)	0.001	0.075	0.475	0.16	0.265	nd	0.076	0.711	4.06

nd: not determined

The overall yield of organic liquids reduces as the quantity of catalytically active alkali (and possibly alkali-earth) metal species present in the feedstock increases and the yields of gas and reaction water increase. A very low organic liquid yield of 42.3 wt% on a dry feedstock basis was obtained for cardoon with high alkali and alkali earth metal contents, whereas low metal content rain leached miscanthus exhibited much higher yield (60.1% dry feedstock basis). The ash composition data show that high ash content alone is not a guarantee of high alkali metal content (Table 25). Switchgrass (leached) had only 0.076 wt% alkali metals with an ash content of 4.06%. This has been attributed to significant quantities of inert inorganics such as silica in the structure of switchgrass, which strengthen and waterproof the outer layer of the stems to make them resistant to wind, rain and standing water. Therefore, it is important not to make assumptions on the alkali metal content of a feedstock based only on its ash content.

6.2.3 Ash Recycling

Char combustion at the pyrolysis site that is carried out to provide the required heat for the process results in phosphorous as described in chapter 6.2.2. Consequently, it could be transported back to the land to be used as a fertiliser, thus recycling the micro-nutrients and minimising the need for additional fertilisation while ensuring sustainability. Another possibility is mixing the ash with water (ash is partially soluble in water) to provide a liquid fertiliser. Both types of fertilisers could be marketed as renewable products with a green tag. Recycling of the char not only recycles the nutrients but the char also acts as a soil conditioner.

Bottom ash from municipal waste incinerators is currently recycled in England as aggregate (over 40%, i.e. over 200,000 tonnes p.a. by 2000). For example, over the last five years, between 25,000 and 62,000 tonnes per annum of the total ash produced by the Tyseley Energy from Waste Plant in Birmingham is taken to a nearby Ash Reprocessing Plant where the ash has been recycled into products used in the building and road/pathway construction industries [Tyseley Energy from Waste Plant 2006]. The recycling of this ash minimises the use of landfill space and reduces the use of primary aggregates. Bottom ash can safely be recycled as secondary aggregate, because dioxin levels are similar to those typically found in urban soils, according to a study conducted by the Environment Agency in 2002 [Environment Agency 2002]. Similarly, the ash resulting from char combustion could also be recycled as secondary aggregate and be employed in road construction and concrete manufacture, although there is concern about the high levels of alkali and its effect on aggregate performance. The main uses of secondary aggregates are presented in Table 26.

Table 26 Applications and uses of recycled secondary aggregates [Greenspec 2006]

Application	***Examples***
Concrete	Ready mixed concrete
Manufactured concrete products	Wide range of products. Examples include concrete blocks, kerbs, pipes, slabs
Geotechnical applications / civil engineering	Fill
Roads, pavements, car parks and hardstanding	Asphalt-bound and hydraulically bound mixtures

There are other possibilities, such as whole char recycling which has other advantages and is discussed in the next section.

6.3 Potential Uses of Charcoal from Biomass Carbonisation

6.3.1 Introduction

In developing countries charcoal from biomass carbonisation (slow pyrolysis) is the principal domestic fuel as it can be stored and transported more easily than solid biomass, which often degrades too rapidly in tropical climates. In industrial countries it is used similarly as fuel in open-air barbecues. Charcoal has a range of other applications [FAO 1985]. In the chemical industry it is used in the manufacture of carbon disulfide, sodium cyanide and carbides. In metallurgy it is used in smelting and sintering iron ores, production of ferro-silicon and pure silicon, case hardening of steel (by packing the steel in charcoal dust) and as a purification agent in smelting non-ferrous metals. Charcoal has strong reducing properties. When heated with metallic ores containing oxides and sulphides, the carbon combines readily with oxygen and sulphur, facilitating metal extraction. Brazil's charcoal based iron industry is considered the biggest in the world. Six million tonnes of charcoal are produced every year for use in heavy industry, such as steel and alloy production [[World Energy Council 2006]. Charcoal-iron industries also exist in Argentina and Malaysia [FAO 1985].

Charcoal is utilised in the cement industry as a fuel, in pigments, in pharmaceuticals for controlling infections of the digestive tract and as a gas generator in carbonation of soft drinks. Poultry and animal feeds are sometimes supplemented with charcoal fines to control certain diseases. Moreover, charcoal is used in horticulture and in activated carbon production [FAO 1985]. The last two applications are discussed in more detail in the following sections.

In theory there is no reason why char produced by fast pyrolysis of biomass could not replace charcoal in all the applications mentioned above. Char produced below 500°C retains carboxylic acid groups, which bind ammonia exceptionally well. When treated with ammonia it forms a hydrated ammonia charcoal, which has been found to be a good scrubbing agent for removing SO_x and NO_x from fossil fuel combustion streams as well as reducing CO_2 emissions. The resulting products (i.e. ammonium bicarbonate, ammonium sulphate and ammonium nitrate) are excellent fertilisers [New Hampshire 2005].

6.3.2 Horticulture

Charcoal has been used in traditional agricultural practices as well as in modern horticulture. At present there is strong evidence about the beneficial properties of charcoal for sustainable soil management. Charcoal has an extremely high affinity to nutrients. It is much more effective in retaining most nutrients and keeping them available to plants than other organic matter such as common leaf litter, compost or manure. This is also the case for phosphorus which is not retained by usual soil organic matter. In addition, charcoal displays a much higher persistence in soil than any other form of organic matter that is commonly applied to soil. Therefore, all associated benefits with respect to nutrient retention and soil fertility are longer lasting than with alternative management [Lehmann 2006a.

Research on the Amazonian Dark Earths has demonstrated the importance of charcoal for the surprisingly sustainable high fertility and high organic matter contents of these soils locally known as Terra Preta de Indio [Lehmann 2006a]. Applications of charcoal to soil has shown to considerably improve crop yields and maintain more stable soil organic matter over longer periods of time than commonly feasible by additions of mulches and manures. Degraded soils can be restored and losses of nutrients can be reduced as seen from experimentation at various sites in South America and Eastern Africa [Lehmann 2006a]. It is purchased at a considerable premium by Japan for improving golf courses.

Additions of charcoal to soil have shown definite increases in the availability of potassium, phosphorous and zinc, and to a lesser extent calcium and copper, as well as in total nitrogen concentrations. Both cation exchange capacity (CEC) and pH are also frequently increased through such additions, by up to 40% of initial CEC and one pH unit respectively. Higher nutrient availability for plants is the result of both the direct nutrient additions by the charcoal and greater nutrient retention due to higher CEC, but it can also be an effect of changes in soil microbial dynamics [Glaser 2002, Lehmann 2006b].

The response function is additionally dependent on the properties of charcoal, soil properties (greater response occurs on nutrient deficient, sandy soils), concurrent nutrient and organic matter additions and plant species. Additions of inorganic or organic fertilisers are usually essential for high productivity and increase the positive response of the char amendment. However, the relative effect of the char addition may not be as high as for unfertilised crops. Long-term studies with charcoal applications are needed to evaluate their effects on sustained soil fertility and nutrient dynamics [Glaser 2002, Lehmann 2006b].

Char produced by fast pyrolysis of biomass, in particular grasses that have higher alkali and alkali-earth metal content than wood (see chapter 6.2.2), could be also used in horticulture instead of charcoal from biomass carbonisation (slow pyrolysis). Important opportunities lie in the combination of char soil management with energy production via fast pyrolysis of biomass.

6.3.3 Activated Carbon Production

Although char makes an excellent fuel, it is the lowest value use of the material. Activation produces a higher value char product. There are two main methods of producing activated carbon, chemical activation and gaseous activation. Chemical activation involves mixing an inorganic chemical compound with the carbonaceous raw material and the most widely used activating agents are phosphoric acid and zinc chloride. Gaseous activation uses steam and carbon dioxide.

Activated carbon has a vast range of applications. It is used as a filtering material for liquids and gases. For example in drinking water purification, waste water treatment plants, purification of exhaust emissions, reduction of toxic and harmful vapour levels in air [FAO 1985]. It has also been found to be useful in removing mercury from the flue gas stream of a fossil fuel combustor [New Hampshire 2005]. Decolourisation of sugar cane and beet solutions, vitamin solutions and pharmaceuticals and high fructose syrup are other important uses. Other applications include cigarette filters, catalysts for chemical processes, support for platinum and palladium catalysts, food additives, additives in rubber tyres, evaporation control systems and evaporative air coolers [FAO 1985].

It has been established that fast pyrolysis char has high potential as a precursor for activated carbon. Results from the University of Saskatchewan has shown a 66-fold increase in the BET surface area of char (10 m^2/g before activation) with a relatively high yield (>38 wt %), low ash content (≤ 7 wt %) and suitable percentage of microporous and mesoporous area [Azargohar 2005]. No details of the feedstock were reported. Another study from the Iowa State University has demonstrated the production of activated carbon from oat hulls with optimal surface area (>500 m^2/g) with steam activation times of 90 min or longer. The same researchers reported that corn stover is not likely to be a good candidate for activated carbon production [Fan 2004]. Ensyn has shown interest in the production of activated carbon from fast pyrolysis char and was involved in a relevant project [Government of Canada Climate Change 2004].

Char produced by fast pyrolysis of agricultural residues or grasses has a higher content of alkali metals and alkali earth metals compared to char produced by fast pyrolysis of wood. Consequently if it is going to be used as precursor for activated carbon, the reduction of its alkali and alkali earth metal content might be beneficial. Two possible scenarios are presented below.

6.3.3.1 Biomass washing

The work conducted at Aston University showed that crops subjected to rain leaching by overwintering exhibited much lower alkali metals content than those harvested promptly at the end of the growing season (Table 23). Since fast pyrolysis char sequesters the original alkali content of the biomass, char from rain leached crops will have much lower alkali metals content than char from non-leached crops. Washing tests showed that washing had the same effect on the metals content with rain leaching. Since natural rain leaching to reduce the content of soluble alkali metals cannot be relied upon for all temporal harvesting windows and geographic locations, the economic feasibility of a separate controllable washing process reducing the metals content of the feedstock should be evaluated. Up to date there is relatively little information published on biomass washing. Only agricultural waste straws have been considered in any detail for the purpose of reducing ash, metals and chlorine in combustion applications.

6.3.3.2 Char washing

One of the advantages of the char wash process compared to the biomass wash process is that a much smaller mass of solid material has to be washed. Biomass char extraction has not been investigated in detail, while some straw leaching investigations have been carried out. A laboratory study on the extraction of straw derived char showed that most of the chlorine and potassium could easily be washed out of the straw [Jensen 2001]. 35–58% of the char potassium was dissolved very fast, followed by a secondary slow potassium release that was strongly influenced by particle size, water temperature, char type and water potassium chloride content. The residual 5–10% of the char potassium remained in the char and could not be removed with pure water. Therefore, if a potassium removal of less than 90% is acceptable, char wash may be better than straw wash. The feasibility of both options should be assessed before any option is selected. Elemental analysis of unwashed and washed char showed an extraction of sulphur, potassium and chlorine, while almost all hydrogen, carbon and nitrogen were retained in the char.

6.3.3.3 Waste Water Disposal

The cost of washing and then subsequently drying the biomass to the low moisture content required for fast pyrolysis (10%) is likely to be prohibitive if performed at the conversion plant. However, washing may become both cheaper and beneficial to the sustainability of the whole biomass to energy chain if performed at or close to the farm. The wash water could potentially be utilised for irrigation, directly recycling the soluble nutrients possibly aiding the maintenance of soil condition and hence reducing the cost and environmental impact of the use of commercial fertilisers.

A similarly large amount of waste water containing potassium, chlorine, sulphate and carbonate will be generated by the char extraction process. It could be utilised as a raw material for the production of fertilisers by vacuum-evaporation or reverse osmosis. The economic feasibility of this route should be evaluated.

6.3.4 Potential Utilisation of Charcoal

Char generated via fast pyrolysis of biomass could be pelletised and used as a fuel in barbecues, ovens and boilers or to provide the required heat in the pyrolysis process. Moreover, there is a range of other potential uses. The origin of the char (biomass feedstock) influences its ash content and composition and as a result plays an important role in identifying the best possible use. Char produced via fast pyrolysis of wood (very low ash content, low alkali metals content) might be best suited for use in metallurgy and in activated carbon production. On the other hand char produced via fast pyrolysis of agricultural residues and grasses, due to its higher ash and alkali metals content, might be more suitable for use in horticulture as a soil conditioner and fertiliser. Otherwise the char or the biomass feedstock before getting pyrolysed could be washed in order to lower its alkali metals content and then be used for activated carbon production, whereas the waste water could be employed for irrigation or fertiliser production. Studies should be undertaken to assess the technical and economic feasibility of these char utilisation routes. Nevertheless higher added value uses of char are expected to have a positive economic impact on the pyrolysis process.

7 Anaerobic Digestion

7.1 Technology

7.1.1 Application in Agriculture

Anaerobic digestion has a long tradition for biogas production of organic waste from agriculture. This application has during the last years strongly been promoted in some countries, especially in Germany, Austria and Sweden were power derived from biogas is subsidised.

Austria operated in 2005 approx. 130 biogas facilities, another 120 were in the design or building phase. (Pötsch 2005). In 2004 some 150000 m^3 of organic substances have been treated by this technology. The main input material with 62 % was manure, approx. 25 % were residues, and another 8.5 % were energy crops [Pötsch 2004].

In Germany the number of biogas plants in the agricultural sector has been increased from approx. 100 in 1990 to some 3400 in 2006 with an installed electricity capacity of 850 MW. The potential of energy recovery from agriculture residue by biogas production in Germany is estimated to approx. 12 TWh/a of power plus 35 TWh/a of heat from manure only. An additional 23 TWh/a of power and 33 TWh/a of heat could be derived from energy crops [Weiland 2006].

Anaerobic digestion is typically performed as a one-stage process. Two different process types are used: wet digestion with 8 – 10 % of solid matter in the digester and the dry process with >30 % of solid matter. New facilities prefer by far the wet process. A scheme of a single stage wet process is shown in Fig. 18.

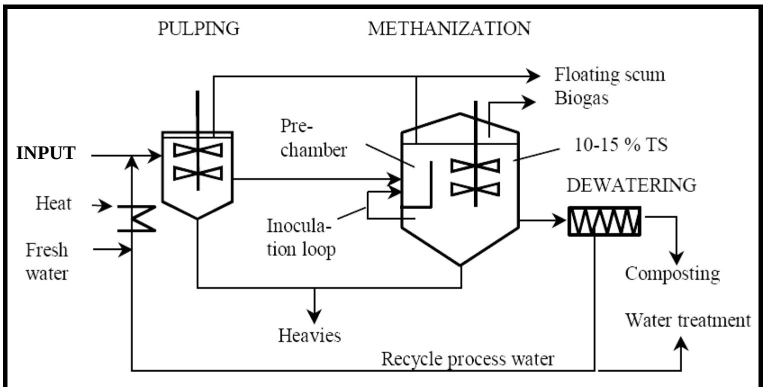

Fig. 18 Scheme of a single stage wet digestion process [Vandevivere 2005]

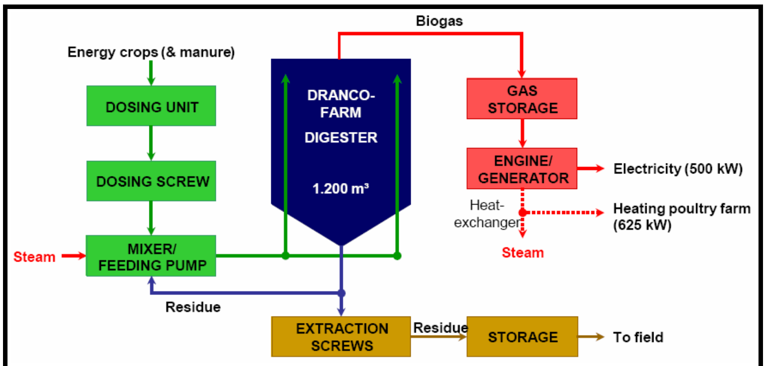

Fig. 19 Dranco-Farm dry digestion process [Weiland 2006]

The dry process has the advantage of small reactor volume and it is mainly utilised for energy crop gasification. As an example the flow diagram of a dry process which is especially adapted to this feed is shown in Fig. 19. In this process the biomass moves vertically down the digester without any mixing. As the graph points out the solid residues of the process are stored and used as fertilizer.

7.1.2 Application in Waste Management

The most practiced and oldest application of anaerobic digestion is the stabilisation of sludge from waste water purification. In so-called 'fouling towers' the carbon inventory is mainly converted into methane which serves as energy source. In solid waste management strategies, however, this technology plays for the time being an only minor role. Few small digestion plants treat source separated organic waste fractions. The problem is the quality of the feed material which should be free from plastics and inert materials. Biogas is typically used in gas engines, partially together with landfill gas. The potential for power generated by biogas from organic municipal solid waste is estimated to reach 1.2 TWh/a [Weiland 2006]. A typical application of anaerobic digestion for source separated organic fraction of municipal solid waste in the city of Karlsruhe, Germany, is shown in Fig. 20.

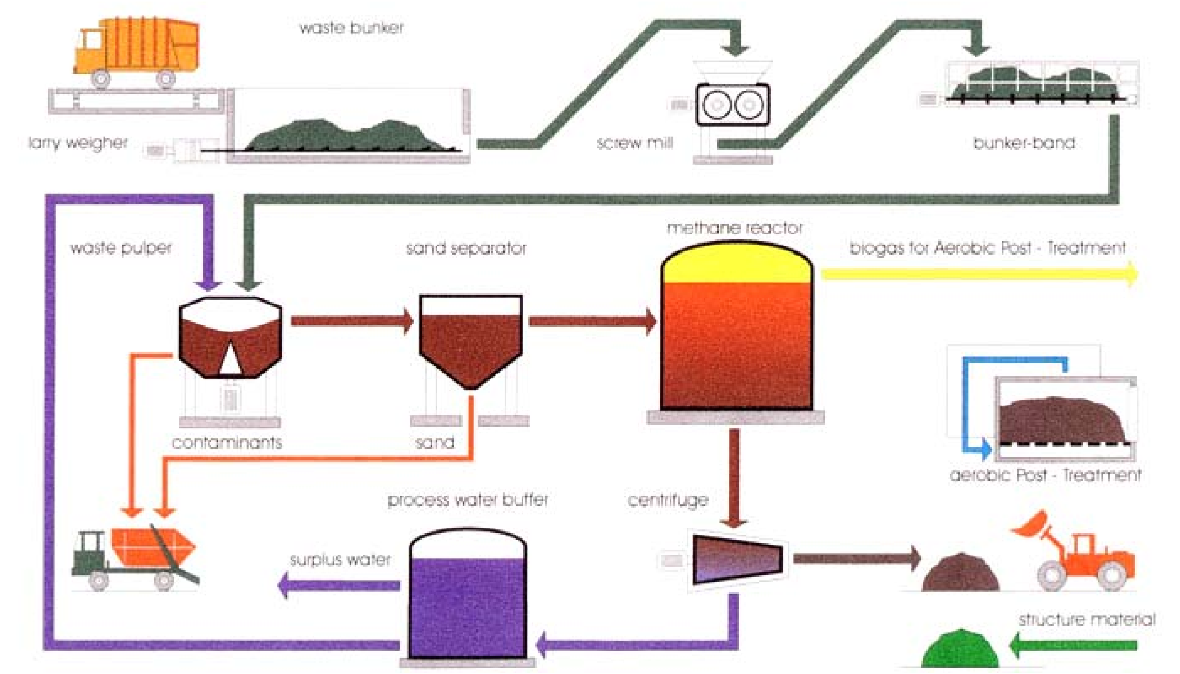

Fig. 20 Anaerobic digestion plant in Karlsruhe, Germany

7.2 Residue Quality and Management

The residues from anaerobic digestion can be classified in different ways according to their origin. Residue from pure manure fermentation is called biogas manure and is regarded as clean and high in nutrients. Residues from digestion of manure and/or agricultural residues may carry higher levels of pollutants. Residues from treatment or co-treatment of organic waste fractions have to be looked upon critically in view of their pollutant inventory.

Due to the fact that the main feed material for anaerobic digestion comes from the agricultural sector it is not surprising that also the main application of the residues is – either directly or after composting - as fertiliser in agriculture. In view of this strategy main quality parameters of these residues are the acidity/alkalinity and the inventory of components which have a nutrient potential. Data from two Austrian long term monitoring programs [Reinhofer 2006] are compiled in Table 27. The monitored digestion plants were Hartberg which treated organic waste fractions and St. Stefan/R which used pure agricultural feed materials and co-substrates.

The table contains also typical data for the same parameters as taken by the same authors from a literature revue and complemented with their own analytical results.

Table 27 Analytical data of digestion residues from the Hartberg and St. Stefan/R digestion plants and typical data taken from literature [Reinhofer 2006]

	Hartberg	***St. Stefan/R***	***typical data***
pH	7.4 ± 0.8	8.3 ± 0.1	7.9
dry matter [%]	2.1 ± 1.4	4.9 ± 1.8	4.1
organic fraction [% d.m.]	63.7 ± 17.4	60.3 ± 10.8	65
bioavailable organic fraction [% d.m.]	64.3 ± 67.1	40.1 ± 10.8	47.7
total N [% d.m.]	14.6 ± 9.1	13.5 ± 4.8	7.3
NH_4 N [% d.m.]	11.0 ± 7.8	10.2 ± 3.4	6.8
PO_4 P [% d.m.]	1.8 ± 0.9	3.1 ± 0. 4	0.7
K [% d.m.]	0.3 ± 0.2	0. 7 ± 0.3	5.4

The obtained data show a broad scattering during the test period. The variation of the averaged data from both facilities is for many parameters not significant. The pH of the Hartberg residues is much higher than that of the St. Stefan ones which implies a higher risk of nitrogen losses especially when brought to the acre at elevated temperatures due to evaporation of NH_3. For both plants the nitrogen and the phosphorous content was much higher and the potassium content much lower than the typical data.

Unfortunately heavy metals have not been analysed in these tests but there are limited data available in literature. These are compiled in Table 27 together with standards for fertilisers, compost and other materials used in agriculture [Reinhofer 2006]. The EU Directive 91/2092/EEC sets limits for ecological agriculture, Austria has a regulation for fertilisers and for compost of three quality classes which serve different utilisation scenarios.

Table 28 Data on heavy metal concentrations in digestion residues and EU and Austrian standards for fertilisers and compost (concentrations in mg/kg [Reinhofer 2006])

	literature data	***EU Directive 91/2092/EEC***	***freight in g/ha (2 years)***	***AU fertiliser regulation (2004)***	***Austrian compost regulation quality class***		
					A+	A	B
Cr	12.5	70	600	100	70	70	250
Ni	20	25	400	60	25	60	100
Cu	88	70	700	-	70	150	500
Zn	365	200	3000	-	200	500	1800
Cd	0.6	0,7	10	1	0,7	1	3,0
Hg	0.8	0,4	10	1	0,4	0,7	3
Pb	18.7	45	600	150	45	120	200

The table indicates that for Cu, Zn, and Hg the averaged literature data exceed the EU and the identical Austrian limits for compost class A+. The literature data for Ni and Cd are rather close to these limits. Such findings indicate that a distribution of residues from anaerobic digestion on arable land has to be looked upon critically, especially if waste materials are treated.

Several processes for treatment and de-contamination of digestion residues have been proposed. These comprise various composting processes, separation of nutrients like nitrogen or phosphorous and also of heavy metals. There is not much knowledge about the efficiency and the economy of the single processes and there is also not much information available, which processes find to what extent application in agriculture or waste management.

8 Conclusions and Outlook

The review of the quality and of disposal or utilisation options for residues from thermal processes for waste and biomass indicates partly a rather good knowledge, partly needs for more in-depth information.

Residues from waste incineration have been subject to intense research programs for many years and it can be concluded that the quality of bottom ashes has meanwhile a high standard and that the measures to maintain and control this standard are well understood and widely applied. The question whether an utilisation as secondary building material is accepted or not depends on the definition of acceptable economic impact and is more a political and societal decision than a technical one.

For filter ashes and gas cleaning residues the situation is more complex. Their quality is known: due to their high inventory of heavy metals and organic micro-pollutants they are classified as hazardous waste which means they require specific measures for their safe long-term disposal. In case of residues from the chemical gas cleaning stages there is a distinct difference in quality concerning the residues from wet dry gas cleaning with liquid effluents and from those processes which end up with a high salt load. Wet scrubbing requires water purification and results in a final neutralisation residue containing mainly metal hydroxides the main obstacle in the solid residues from effluent evaporation or dry scrubbing is the high amount of soluble salts. For soluble salts no convincing disposal option aside from final storage in salt mines can be thought of. The salt problem is a difficult one since it depends strongly on the applied gas cleaning method. Unfortunately the water authorities in a number of countries, e.g. in Germany, restrict the discharge of effluents from waste incineration plants into sewers.

A number of stabilisation and treatment processes for filter ashes and gas cleaning residues including the recovery of species out of these materials have been developed but none has been implemented in full scale due to economic constraints. In this respect it might be useful to investigate treatment processes of gas cleaning residues including macro-economical aspects. There is reason to speculate that even recovery processes which are not profitable for private companies might point out economically useful if future and long-term costs which have to be covered of the society, e.g. for rehabilitation of contaminated sites, are taken into account.

The quality of residues from co-combustion of SRF or other waste derived fuels are less well investigated. Their quality as well as that of residues from combustion of contaminated biomass is mainly depending on the quality of the fuel. The inventory of critical ingredients in fuel produced from waste or waste fractions, especially of halogens and heavy metals, is often rather high and shows typically a wide range of variation. A reliable quality control for such fuels is very difficult, especially if they originate from mixed municipal solid waste.

Also little information is available for residues from gasification of biomass since only few data have been published. The main residue may have a potential for utilisation, however, the published data indicate that additional post-process treatment is necessary to reach the required properties. Such extra treatment will make any application scenario too expensive. Other residues can – like gas cleaning residues from waste incineration – be inertised in order to meet the criteria for the access to cheaper landfills than those for hazardous waste.

A similar conclusion can be drawn for the quality and management of residues from pyrolysis or carbonisation of biomass. A high potential of application of such charcoal is theoretically possible but the ecological compatibility of some of the proposed scenarios has not yet been shown. An open question is also the potential of such residues for the recovery of ingredients with fertiliser capabilities like potassium of phosphorous.

Limited sound information, too, was found for residues from anaerobic digestion of agricultural and other biomass and organic waste fractions. There are two main issues concerning their environmental compatibility: the potential pollution in case materials originated from waste is treated respectively co-treated and the inventory of nutrients in case 'clean' biomass from the agricultural sector only was used. Published data indicate the risk of too high pollutant concentration in a number of analysed residues which endangers their typical utilisation as fertilisers in agriculture. There are also proposals for treatment technologies in order either to separate pollutants or nutrients, however, not much information is available about their efficiency and their application in real systems.

A final conclusion can be drawn that there is need for further research on long-term reliable management strategies, especially for all types of residues from gas cleaning in all processes. Additionally the residues from co-combustion of waste and coal, from combustion of SRF, from gasification and pyrolysis, as well as from fermentation of biogenic matter need more detailed investigation. The challenge in all residue management scenarios - especially if these residues derive from waste or contaminated fuels - is the definition of sinks for pollutants. This task has not only a scientific and technical aspect, essential prerequisites for long-term sound and aftercare-free solutions are also socio-economic effects and the public acceptance.

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