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Characterization of fly ashes from biomass combustion with focus on their utilization

Dissertation

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Dipl.-Ing. Dr.techn. Christof Lanzerstorfer

Supervisor:

Univ.-Prof. Dipl.-Ing. Dr.techn. Tobias Pröll

University of Natural Resources and Life Sciences, Vienna; Institute for Chemical and Energy Engineering

Reviewers:

Univ.-Prof. Dipl.-Ing. Dr.techn. Christoph Pfeifer

University of Natural Resources and Life Sciences, Vienna; Institute for Chemical and Energy Engineering

Professor M.Sc. Ph.D. Britt-Marie Steenari

Chalmers University of Technology, Gothenburg, Sweden

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Abstract

Fly ashes from several biomass combustion plants using various types of biomass as fuel have been investigated in several studies. In three studies the main focus was on the chemical composition and the physical properties of the fly ashes. In another study the flowability of fly ashes from the combustion of forest residues was investigated in detail. The dependence of the concentration of various components on the particle size was investigated for one fly-ash. A two-stage leaching process for the removal of heavy metals from the fly ash was tested on bench scale.

In the literature little data on the physical properties of fly ashes from biomass combustion is available. The measured physical properties provide an improved basis for the design of fly ash handling and storage equipment. The results showed that for reliable flowability results shear tests are required. The more easy-to-determine flow indicator angle of repose over-estimated the flowability of the fly ashes in several cases. The particle size was identified as the parameter with the highest influence on the flowability of the fly ashes.

In the cyclone fly ash of a forest residue combustion plant, for many components a dependence of the concentration on the particle size was found. Some heavy metals (Bi, Cd, Cu, Hg, Pb and Zn) and nutrients (K and NO_3^-) were enriched in the smaller size fractions while others were depleted (Fe, Al, Si, Ti, As, Ba and V). For several other components no distinct dependence of the concentration on the particle size was found.

In most fly ashes from the combustion of forest residues one or more heavy metal concentrations were above the limit concentrations for use as a soil conditioner for forest and agricultural land. Thus, treatment of these fly ashes for the reduction of the heavy metal content would be required. In contrast, the fly ashes from the combustion of straw and *Miscanthus* were only slightly contaminated with heavy metals and can be used as a soil conditioner without pre-treatment.

For reduction of the heavy metal content of biomass combustion fly ashes a two-stage leaching process was investigated. The test showed the potential of this process to reduce the heavy metal concentrations while keeping the losses of the nutrients within an acceptable range.

The application potential of biomass combustion fly ashes for construction materials seems to be quite limited. Considering the chloride content of the various biomass combustion fly ashes, only for cyclone fly ash from wood combustion might this be a feasible option.

Keywords: biomass combustion, fly ash, utilization, characterization

Kurzfassung

Flugaschen aus mehreren Verbrennungsanlagen welche unterschiedliche Biomasse als Brennstoff einsetzten, wurde in mehreren Studien untersucht. In drei Studien lag der Schwerpunkt auf der chemischen Zusammensetzung und den physikalischen Eigenschaften der Flugaschen. In einer weiteren Studie wurde die Fließfähigkeit von Flugaschen aus der Verbrennung von Waldhackgut genauer untersucht. Die Abhängigkeit der Konzentration von verschiedenen Stoffen von der Korngröße wurde für eine Flugasche untersucht. Weiters wurde ein zweistufiger Laugungsprozess zur Entfernung von Schwermetallen aus der Flugasche in einem größeren Laborversuch getestet.

In der Fachliteratur sind nur wenige Daten über die physikalischen Eigenschaften von Biomasseflugasche vorhanden. Die in den Studien gemessenen Daten stellen daher eine verbreiterte Basis für die Auslegung von Förder- und Lagereinrichtungen für Flugasche zur Verfügung. Die Ergebnisse zeigten auch, dass belastbare Ergebnisse zur Fließfähigkeit von Flugaschen nur mittels Scherversuchen erhalten werden können. Mit der Messung des Schüttwinkels, der oft als Indikator für die Fließfähigkeit verwendet wird, wurde in mehreren Fällen die Fließfähigkeit überschätzt. Als der Parameter mit dem größten Einfluss auf die Fließfähigkeit wurde die Partikelgröße identifiziert.

Anhand einer Zyklonasche einer Waldhackgutverbrennungsanlage wurde die Abhängigkeit der Konzentration verschiedenster Komponenten von der Partikelgröße gezeigt. Mehrere Schwermetalle (Bi, Cd, Cu, Hg, Pb und Zn) und Nährstoffe (K und NO_3^-) waren in den Feinfraktionen angereichert während andere Komponenten (Fe, Al, Si, Ti, As, Ba und V) abgereichert waren. Für eine Reihe von weiteren Komponenten wurde keine ausgeprägte Abhängigkeit festgestellt.

Bei den meisten Flugaschen aus der Verbrennung von Waldhackgut war die Konzentration eines oder mehrerer Schwermetalle über dem Grenzwert für die Ausbringung auf land- und forstwirtschaftlich genutzten Flächen. Daher wäre für eine Ausbringung eine Behandlung dieser Asche zur Verringerung der Schwermetallkonzentrationen erforderlich. Im Gegensatz dazu waren die Flugaschen aus der Verbrennung von Stroh und *Miscanthus* nur geringfügig mit Schwermetallen belastet. Diese können daher ohne Vorbehandlung ausgebracht werden.

Ein zweistufiger Laugungsprozess zur Reduktion des Schwermetallgehalts von Biomasse-flugaschen wurde untersucht. Die Ergebnisse bestätigten das Potential des Verfahrens, den Schwermetallgehalt bei gleichzeitig akzeptablen Verlusten an Nährstoffen zu reduzieren.

Die Möglichkeiten zur Verwendung von Biomasseverbrennungsflugaschen in Baustoffen scheinen sehr limitiert. Unter Berücksichtigung des Chloridgehalts der verschiedenen

Biomasseverbrennungsflugaschen könnte dies nur für Zyklonasche aus der Verbrennung von Waldhackgute eine sinnvolle Option zu sein.

Schlüsselwörter: Biomasseverbrennung, Flugasche, Verwertung, Charakterisierung

List of included peer-reviewed papers

This thesis was written as a cumulative thesis. Therefore, the core parts of this work consist of the following scientific publications in peer-revewed journals:

Lanzerstorfer C. (2014). Chemical and physical characterization of cyclone fly ashes from five grate-fired biomass combustion plants. Carpathian Journal of Earth and Environmental Sciences 9(4): 129-135.

Lanzerstorfer C. (2015a). Chemical composition and physical properties of filter fly ashes from eight grate-fired biomass combustion plants. Journal of Environmental Sciences 30: 191-197. DOI:10.1016/j.jes.2014.08.021

Lanzerstorfer C. (2015b). Cyclone fly ash from a grate-fired biomass combustion plant: dependence of the concentration of various components on the particle size. Fuel Processing Technology 131: 382-388. DOI:10.1016/j.fuproc.2014.12.010

Lanzerstorfer C, Kröppl M. (2015). Bench scale two stage heavy metal leaching test with fly ash from woody biomass combustion. Environmental Engineering and Management Journal (accepted).

Lanzerstorfer C. (2016a). Chemical composition and properties of ashes from combustion plants using Miscanthus as fuel. Journal of Environmental Sciences (accepted).

Lanzerstorfer C. (2016b). Characterization of the flowability of fly ashes from grate-fired biomass combustion. Fuel Processing Technology (accepted). DOI:10.1016/j.fuproc.2016.05.020

Content

1 Introduction

1.1. General

The limited availability of fossil fuels and concerns about climate change caused by the carbon dioxide emissions from fossil fuel combustion have given rise to combustion of woody biomass for heat and power generation (European Biomass Association, 2013). Biomass combustion is considered to have almost no impact on the carbon dioxide content of the atmosphere because the emissions produced during combustion are compensated by the carbon dioxide fixed in the biomass during its growth.

One disadvantage of biomass combustion is the production of a considerable amount of ash, a bulk solid material with a broad range of particle sizes. Depending on the type of combustion process and the off-gas cleaning system, different ash fractions result from the combustion as residues. Bottom ash, the coarser ash fraction, is discharged from the firing grate (grate-fired combustion) or removed from the fluidized bed (in fluidized bed combustion). The finer ash fractions (fly ash) leave the combustion zone together with the flue gas. This fly ash usually accounts for one quarter of the total amount of ash (Van Loo and Koppejan, 2008). The fly ash has to be separated from the flue gas in a dust collector. In order to comply with low dust emission limits (< 20 mg/m³ (STP)), an electrostatic precipitator (ESP) or a fabric filter has to be used as a fly ash separator. The collection efficiency of cyclones is limited, especially for fine particles. Single stage dust collection by a cyclone is only sufficient for biomass combustion plants with a higher dust emission limit. However, cyclones are often used as pre-separators in two-stage de-dusting systems. If the coarser dust is collected in a pre-separator the filter fly ash separated in the second de-dusting stage accounts for 2 – 10% of the total amount of ash (Narodoslawsky and Obernberger, 1996).

The separated fly ashes have to be discharged from the dust separators and conveyed to closed storage in dust silos or containers. In several plants the cyclone fly ash is directly mixed with the bottom ash and discharged as mixed ash. Figure 1 shows a simplified process flow diagram of a plant design with two stage de-dusting of the off-gas.

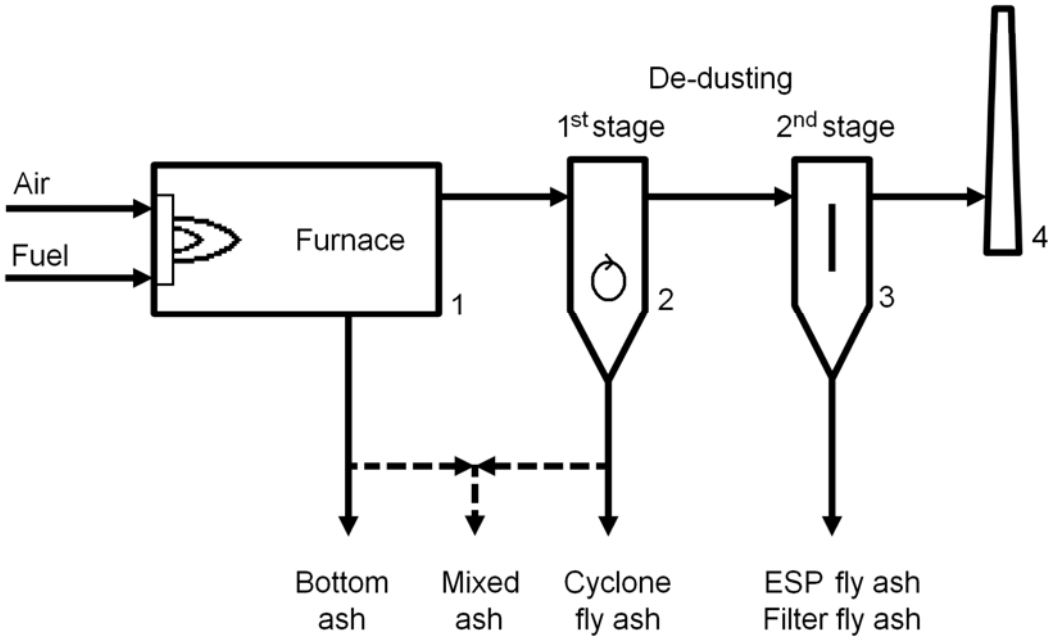


Figure 1. Simplified process flow diagram (1: furnace; 2: cyclone; 3: ESP or filter; 4: stack)

1.2. Utilization of biomass combustion fly ashes

For the utilization of fly ash from biomass combustion two main uses are discussed in the literature (Melotti et al., 2013; Haglund, 2008; Niu et al., 2016):

1. Utilization for construction materials,
2. Use as a soil conditioner for forest and agricultural land.

For the use of biomass combustion fly ashes in these applications the chemical composition and the physical properties of the fly ashes are important. Optionally, the fly ashes can be be treated before use.

The chemical composition of biomass combustion fly ashes has been investigated widely. Data are available, for example, in Steenari and Lindqvist (1997), Steenari et al., (1999), Hansen et al., (2001), Van Loo and Koppejan (2008), Rönkkömäki et al. (2008), Pöykiö et al. (2009a,b), Dahl et al. (2009), Ingerslev et al. (2011), Singh et al. (2011), Melotti et al. (2013) and Sano et al. (2013).

The requirement for treatment of the fly ash before its use depends on the chemical composition of the ash. For example, if the concentration of certain heavy metals is above the limit concentration the ash may not be used as soil conditioner. In that case a leaching process that removes these heavy metals could be applied.

Information about the physical properties of biomass combustion fly ash is surprisingly rare. Van Loo and Koppejan (2008) reported values for the particle density and the bulk density of different biomass combustion fly ashes. Results from particle size distribution measurements are available in Lind et al. (1999). Data about the flow properties of fly ash from biomass combustion were not found in a review of the literature.

The storage capacity of dust silos depends greatly on the bulk density of the material and the angle of repose, provided there is no special equipment installed in the silo for the distribution of the feed material. Knowledge of the flow properties of the ash is necessary to effectively design fly ash storage silos, hoppers of fly ash collection equipment and other ash handling equipment so that no flow problems occur (Schulze, 2008). If the outlet opening of a silo is too small, a stable arch can form above the outlet and stop the flow. Especially very fine materials can form cohesive arches as a result of the compressive strength caused by consolidation and inter-particle adhesive forces. Another possible source of problems is funnel flow, which can be caused by a hopper wall which is too shallow or too rough. In this case the dust cannot slide down the hopper walls. Thus, stagnant zones build up and the material flow is limited to a flow zone above the outlet opening. The dust in these stagnant zones can consolidate with time to such an extent that it will not be able to flow out after the flow zone has emptied (Schulze, 2008).

1.2.1 Utilization for construction materials

For the incorporation of biomass combustion fly ashes in new cement formulations it is necessary to control the carbon, chloride and sulphate content of the employed biomass combustion fly ashes (Rajamma et al., 2010). The unsatisfactory chemical composition of raw biomass combustion fly ash represents a limitation for their reuse as filler/partial sand replacement material in concrete. Due to their high content of chlorides and sulphates, raw biomass combustion fly ashes may be reused only for unreinforced concrete and no requirements category (low-quality concrete) (Berra et al. 2015). Biomass-coal co-firing and blending of pure wood fly ash and coal fly ash produces fly ashes with concrete-utilization properties that lie within the range of pure coal fly ashes. The data also indicate that pure wood fly ash is less suitable for concrete application than coal, co-fired or blended fly ash (Wang et al. 2008). Additionally, several existing standards exclude the use of biomass combustion fly ash in cement (Niu et al. 2016).

1.2.2 Use as soil conditioner for forest and agricultural land

The recycling of biomass ashes to the forest soil is proposed to help to close the nutrient cycles for the soil where the biomass was grown (Hallenbarter et al., 2002; Moilanen et al., 2002; von Wilpert, 2002; von Wilpert et al., 2014).

In Austria only bottom ash and cyclone fly ash from the combustion of chemically untreated biomass can be utilized as soil conditioner on agricultural land and forests if the concentrations of pollutants are below the limit concentrations (Bundesministerium für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft, 2011). Filter fly ash is not allowed to be utilized in that way because the concentrations of several volatile heavy metals are highest in this fine ash fraction. Therefore, excluding the filter fly ash from recirculation to the soil where the biomass has grown provides a sink for these elements. In other European countries the conditions for biomass combustion fly ash utilization are different. The limit concentrations for some Scandinavian countries are summarized in Table 1.

Table 1. Concentration limits for heavy metals and boron for utilisation of ash from biomass combustion as a soil conditioner in forests and agriculture; in mg/kg d.w.

	Austrian guideline[1] (BMLFUW, 2011)		Finland cited in Nurmesniemi et al. (2012)	Sweden cited in Emilsson (2006)	Denmark cited in Haglund (2008)	Lithuania cited in Stupak et al. (2008)
	A	B				
As	20	20	40	30	-	30
Cd	5	8	25	30	5 / 15[2]	30
Cu	200	250	700	400	-	400
Pb	100	200	150	300	120	300
Zn	1200	1500	4500	7000	-	7000
Cr	150	250	300	100	100	100
Ni	150	200	150	70	30 / 60[3]	70
V	-	-	-	70	-	70
B	-	-	-	500	-	500
Hg	-	-	1.0	3	0.8	3

[1] if the concentrations are below limits according to A, no soil analysis is required

[2] left Cd limit for straw ash, right Cd limit for wood ash

[3] between 30 and 60 mg/kg a reduced ash quantity can be applied

1.3. Treatment of biomass combustion fly ashes

From the literature it is well known that heavy metal concentrations are increased in fine ash fractions (Steenari and Lindqvist, 1997; Narodolawsky and Obernberger, 1996; Fedje et al., 2010; Dahl et al., 2009). However, this is not the case for all heavy metals. The reason for accumulation of some heavy metals in fine ash fractions is condensation and adsorption of their volatile compounds on the surface of the fly ash during cooling of the flue gas or reaction with fly ash components (Lind et al. 1999; Valmari et al. 1998).

Several processes for the reduction of heavy metals or chloride and sulphate in fly ash are mentioned in the literature. These processes can be classified as follows:

- thermal treatment for volatilisation and subsequent collection of components
- hydrometallurgical treatment (leaching)
- fractionated dedusting of the off-gas, and
- mechanical/electromechanical fly ash separation processes (e.g. classification, ...).

Thermal treatment for volatilisation and subsequent collection of components

Thermal treatment of fly ash at high temperature for removal of heavy metals has been investigated for biomass ash (Dahl and Oberberger, 1998; Dahl, 2000; Fraissler et al., 2009) and other ash types (Nowak et al., 2010). Decontamination of the ashes down to the limit values for utilization as a soil conditioner in forests is possible. However, these processes are quite costly because of the high temperatures required. Due to the complexity of such a process, this would be feasible only for bigger installations.

Hydrometallurgical treatment (leaching)

Hydrometallurgical processes for decontamination of biomass combustion fly ash are described in the literature (Steenari et al., 1999b; Mellbo et al., 2008; Pedersen 2003; Perdersen et al. 2003). High removal rates for Cd and Zn can be realised at low pH-values of the leaching solution but at the same time most of the nutrients (K, Ca, Mg) are also dissolved. The generation of liquid waste containing heavy metals, which has to be treated afterwards, is disadvantageous, too. Due to the complexity of hydrometallurgical processes the application is feasible only for bigger installations.

Fractionated de-dusting of the off-gas

Fractionated de-dusting of the off-gas is often applied in biomass combustion plants. In a first separation stage, typically a cyclone, coarse fly ash which is less contaminated by heavy

metals is collected from the flue gas. A fabric filter, or an electrostatic precipitator installed as a second de-dusting stage, collects the fine fly ash fraction. The contamination of the cyclone fly ash can even be reduced by the operation of the cyclone at a higher temperature (Ljung and Nordin, 1997). However, the parameters for the fractionation are influenced by the combustion plant operation (flue gas volume flow) and cannot easily be adjusted during plant operation.

Mechanical/electromechanical fly ash separation processes (e.g. classification, ...)

A different approach for fractionated fly ash collection is described in Ovara et al. (2006), where fly ash from the different electric fields of the electrostatic precipitator was collected and analysed separately. As expected, the mean particle size of the collected dust decreased from the first field of the electrostatic precipitator to the third field, whereas the concentration of cadmium increased. Magnetic separation experiments with coal fly ash as described in Kukier et al. (2003) showed no significant enrichment for arsenic, neither in the magnetic nor in the non-magnetic fraction. In Lacher (2007) an air classifier was used to separate the fly ash into a coarse fraction which is less heavy metal contaminated and a fine fraction which is enriched in heavy metals.

1.4. Aim of this work

The aims of the studies included in this thesis were, firstly, the characterization of biomass combustion fly ashes with respect to their chemical composition and their physical properties with the main focus on the properties which are not available or available only to a limited esxtent in the literature, e.g. the flowability of the fly ash. Secondly, the enrichment of heavy metals in the finest fly ash fractions was investigated and third, a two stage leaching process was studied for the leaching of fly ashes that exceed the heavy metal limits for soil conditioners.

2 Materials and methods

2.1. Materials

All fly ash samples investigated in the various studies of this thesis were taken from grate-fired combustion plants using solid biomass as fuel. Table 2 gives an overview of the plants from where the fly ash samples originated. The fly ash samples were taken from the dust discharge of the respective dust separators. Most fly ashes investigated were from the combustion of forest residues with the main fraction being softwood. Some fly ashes from the combustion of wheat straw and *Miscanthus* were also investigated. One fly ash sample was from the combustion of a residue from palm oil production (empty fruit bunches, EFB).

Table 2. Overview of biomas combustion plants supplying fly ash samples (the dust separator where the fly ash samples were taken in the respective study is printed in black; other possibly installed dust separators are printed in grey)

	Thermal capacity in MW_{th}	Off-gas cleaning system		Combusted biomass
		1st stage	2nd stage	
Fly ash samples in Lanzerstorfer C. (2014)				
Plant A	0.6	Single cyclone	-	Wood chips, forest residue, 60% softwood
Plant B[3]	1.1	Single cyclone	-	Wood chips, forest residue, 60% softwood
Plant C[1]	5.0	Multi-cyclone	ESP	Wood chips, forest residue, 80% softwood
Plant D	4.0	Multi-cyclone	-	Residue from palm oil production (empty fruit bunches)
Plant E[2]	2.2	Single cyclone	Fabric filter	Wheat straw
Fly ash samples in Lanzerstorfer C. (2015a)				
Plant A	8.0	Multi-cyclone	ESP	Wood chips from forest residue > 90%; sawdust and bark < 10%
Plant B[1]	5.0	Multi-cyclone	ESP	Wood chips from forest residue, 80% softwood, 20% hardwood
Plant C	10	Multi-cyclone	ESP	Wood chips from forest residue, 80% softwood (spruce), 20% hardwood (beech, oak and birch)
Plant D[4]	10	Multi-cyclone	ESP	Wood chips from forest residue, 90% softwood (spruce), 10% hardwood (beech, oak and birch)
Plant E	50	Multi-cyclone	ESP	Rubber tree: 95% wood chips and 5% bark
Plant F	2.0	Multi-cyclone	Fabric filter	90% Wood chips from forest residue and 10% horse dung
Plant G[2]	2.2	Single cyclone	Fabric filter	Wheat straw, chuffed
Plant H	45	-	Fabric filter	Wheat straw, disintegrated bales
Fly ash samples in Lanzerstorfer C. (2015b)				
Plant	0.55	Single cyclone	-	Wood chips, forest residue, 60% softwood
Lanzerstorfer C, Kröppl M. (2015)				
Plant[1]	5.0	Multi-cyclone	ESP	Wood chips, forest residue, 80% softwood

[1,2,3,4] Fly ashes from the same biomass combustion plant

Table 2 (continued)

	Thermal capacity in MW_{th}	Off-gas cleaning system		Combusted biomass
		1st stage	2nd stage	
Fly ash samples in Lanzerstorfer C. (2016a)				
Plant A	0.40	Single cyclone	-	*Miscanthus*
Plant B	0,75	Single cyclone	-	*Miscanthus*
Fly ash samples in Lanzerstorfer C. (2016b)				
A	0.5	Baffle separator	-	Wood chips, forest residue
B	0.5	Baffle separator	-	Wood chips, forest residue
C	1.0	Multi-cyclone	-	Wood chips, forest residue
D[3]	1.1	Single cyclone	-	Wood chips, forest residue
E	3.0	Multi-cyclone	-	Wood chips, forest residue
F	3.0	Multi-cyclone	-	Wood chips, forest residue
G	1.5	Multi-cyclone	ESP	Wood chips, forest residue
H	2.0	Multi-cyclone	ESP	Wood chips, forest residue
J	2.0	Multi-cyclone	ESP	Wood chips, forest residue
K	2.0	Multi-cyclone	ESP	Wood chips, forest residue
L	3.0	Multi-cyclone	ESP	Wood chips, forest residue
M	3.5	Multi-cyclone	ESP	Wood chips, forest residue
N	4.0	Multi-cyclone	ESP	Wood chips, forest residue
O[4]	10	Multi-cyclone	ESP	Wood chips, forest residue
P	10	Multi-cyclone	ESP	Wood chips, forest residue
Q	25	Multi-cyclone	ESP	Wood chips, forest residue

[1,2,3,4] Fly ashes from the same biomass combustion plant

2.2. Methods

In this chapter, an overview over the methods used in the various studies for this thesis is given.

2.2.1 Characterization of physical properties

The particle size distribution of the samples was measured using a laser diffraction instrument with dry sample dispersion from Sympatec, type HELOS/RODOS. The particle size distribution of coarse material was determined using the laboratory sieve shaker from Fritsch, type ANALYSETTE 3 PRO with sieves from 8 mm to 500 µm. The undersize material (< 500 µm) was analyzed using the laser diffraction instrument.

The spread of the distribution was calculated as the quotient of x_{90} and x_{10} (Rumpf, 1990).

Microscopic images of particles were taken with a Motic SMZ-168 microscope.

The particle density $\rho_{particle}$ was determined according to EN ISO 8130-3 (European Committee for Standardization, 2011) using a liquid displacement pyknometer. The capacity of the pyknometer used was approximately 100 cm^3 and n-heptane was used for displacement of the air.

The bulk density ρ_{bulk} of the samples was measured according to EN ISO 60 (European Committee for Standardization, 1999) using a 100 cm^3 measuring cylinder.

The voidage of the bulk fly ash was calculated as $1-\rho_{bulk}/\rho_{particle}$.

The angle of repose was determined according to ISO 4324 (International Organization for Standardization, 1977) calculating the base angle of the material cone.

The yield locus for the dust samples was determined using an RST-XS ring shear tester from Schulze. The volume of the shear cell is 30 cm^3. In order to perform a shear test, the dust sample is loaded vertically at a normal stress and then a shear deformation is applied to the sample by moving the top plate at a constant rotation velocity which results in a horizontal shear stress in the sample. To measure a point of a yield locus two steps are necessary. In the pre-shear step, the sample is consolidated and the point of steady-state flow is determined with a pair of values for the normal stress σ and the shear stress τ. In the second step, a point of the yield limit is determined at a reduced normal stress. The corresponding pair of values for the normal stress and the shear stress at a point of incipient flow is one point of the yield limit. By repetition of the procedure the whole yield locus is determined. The bulk density is determined from the mass of the dust sample and its volume which is

calculated from the measured height of the sample in the shear cell. A Mohr stress circle can be drawn which is tangential to the yield locus and runs through the point of steady-state flow can be drawn. The slope of a tangent to this stress circle which runs through the origin of the σ-τ-diagram represents the effective angle of internal friction (Schulze, 2008).

The wall yield locus for the dust samples was also determined with the ring shear tester using a wall shear cell. In this shear cell the bottom ring is formed by a sample of the wall material which was structural steel S235JR (1.0038). For a shear test, the dust sample is loaded vertically at a normal stress and then moved relative to the wall material surface at a constant rotation velocity. To measure a point of a wall yield locus, corresponding pairs of values for the normal stress and the shear stress are determined. The slope of a straight line running through the origin of the σ-τ-diagram and a point of the wall yield locus is the kinematic angle of wall friction (Schulze, 2008).

2.2.2 Characterization of flowability

An indication of the flowability of bulk solids and powders can be derived from the Hausner ratio (Hausner, 1967) and from Carr´s compressibility (Carr, 1965), which are both calculated from the bulk density and the tapped bulk density (Stanley-Wood, 2008). However, in advanced bulk solids technology shear testers are used for the measurement of flow properties (Jenike, 1970). On the basis of such measurements a reliable design of bulk solids handling and storage equipment is possible.

The ratio ff_c of the consolidation stress σ_1 to the unconfined yield strength σ_c gives a quantitative characterization of the flowability of a granular material (Schulze, 1996).The consolidation stress is equal to the major principal stress of the Mohr stress circle which is tangential to the yield locus and runs through the point of steady-state flow. The unconfined yield strength results from the stress circle which is tangential to the yield locus and runs through the origin (Jenike, 1970). The larger the ff_c is, the better a granular material flows. The flowability usually depends on the consolidation stress. For most materials a better flowability will be obtained at a greater consolidation stress. This can be visualized best in a diagram showing the unconfined yield strength dependent upon the consolidation stress when the diagram also includes lines of constant ff_c ratio (Schulze, 1996). The change in flowability is better visible in the diagram with the logarithmically scaled axis because constant flowability results in a line which is parallel to the grid (Lanzerstorfer, 2016d).

2.2.3 Determination of the chemical composition

The moisture content of the ash samples was determined gravimetrically. The samples were dried at 105°C for one hour. Alternatively, the moisture content of the dust samples was

determined with an OHAUS, type MB 45 moisture analyser. The samples were dried at 105°C until the weight of the sample was constant.

The carbon content (TC) was determined with a Elementar Analysensysteme LiquiTOC system with a Solids Material extension. By combustion with air the carbon is transformed into CO_2 which is subsequently analysed.

For the determination of the concentration of metals, sulphate, and phosphate the solid samples were dissolved by aqua regia digestion according to ISO 11466 (International Organization for Standardization, 1995) prior to analysis.

The metals were measured by inductively-coupled plasma optical emission spectroscopy (ICP-OES). For the analysis an ICP-OES system Ultima 2 from Horiba Jobin Yvon was used.

The concentration of alkali and earth alkali metals, sulphate and phosphate was measured by ion chromatography (IC) using a Dionex ICS-1000 system.

Chloride and nitrate were determined by IC in an aqueous leachate of the solid samples.

2.2.4 Included measurements were performed by external laboratories

Microscopic images of particles from the various particles were taken with a scanning electron microscope TESCAN, type VEGA LM. Further information about the chemical composition of the particle surface was obtained in combination with energy dispersive X-ray spectroscopy (SEM-EDX).

The concentration of mercury was measured using cold vapour atomic absorption spectrometry (CV-AAS).

The concentration of Si was analysed gravimetrically according to ISO 934 (International Organization for Standardization, 1994)

2.2.5 Leaching experiments

The fly ash mixture was dosed by a vibration feeder into 5 dm^3 plastic beakers containing tap water until the chosen L/S ratio was reached. The slurry in the beakers was stirred using an overhead stirrer IKA RW20 with a three-bladed propeller stirrer. After leaching the liquid was separated from the insoluble material by vacuum filtration. The water used for cleaning and for flushing the filter cake was added to the filtrate.

In the second leaching step the filter cake from the first leaching stage was mixed with tap water in a plastic container. Concentrated hydrochloric acid was added to the caustic

suspension until the chosen pH was reached. The slurry in the container was stirred for some time. After that the liquid was separated from the insoluble material by vacuum filtration.

For the production of the solid mixtures for agglomeration an Erweka AR 403/SW 1/S plough-share drum mixer was used. For pelletizing an Erweka AR 403/AR 402 GTE pelletizer was used. The produced pellets were collected in a crystallizing dish and subsequently dried in the free laboratory atmosphere.

For the precipitation of the leached heavy metals the waste water was stirred in a plastic container while sodium hydroxide solution was added until a pH of 10 was reached. The precipitate was filtered off by vacuum filtration. Samples were taken from the filtrate for chemical analysis.

The stability of the pelletized ash was tested by a shatter test including a repeated free fall of the samples in a 150 mm plastic tube from a height of 2 m onto a steel plate. The particle size distribution of a sample of about 200 g of pelletized ash was determined before and after the sample had fallen ten times from the top of the tube onto the steel plate at the bottom.

2.2.6 Air classification experiments

A laboratory classifier 100 MZR from Hosokawa Alpine was used for sequential dry classification of the fly ash sample. In the first classification step the finest size fraction, Particle Class 1, was separated from the bulk and collected at the outlet of the classifier. The remaining coarse fraction was used as feed material in the second classification step, in which the classifier was operated at reduced speed to shift the cut size diameter of the classification to a coarser particle size. In this classification step the material was split into Particle Class 2 and a new coarse fraction. This procedure was repeated. A detailed description of such a sequential classification process can be found in Lanzerstorfer and Kröppl (2014).

3 Results and discussion

3.1. Chemical composition

The chemical composition of first stage de-dusting (cyclone) fly ash (Lanzerstorfer, 2014) and of second stage de-dusting (ESP and filter) fly ash (Lanzerstorfer, 2015a) from the combustion of wood and straw was investigated. In another study the composition of ashes from the combustion of *Miscanthus* was investigated (Lanzerstorfer, 2016a). The average heavy metal concentrations of fly ashes from the combustion of various biomass fuels separated into first and second stage de-dusting fly ashes are summarized in Table 3. The main findings from these studies were:

- Fly ash from the combustion of straw and palm oil production residues were in compliance, even with the most stringent limits, for use as soil conditioner.
- In the fly ash and in the mixed bottom and fly ash from *Miscanthus* combustion the heavy metals concentrations were also below these limits.
- Most fly ashes from the combustion of woody biomass exceeded the Austrian limits for use as soil conditioner.
- In wood combustion fly ashes the most volatile heavy metals As, Hg, Pb and Zn were significantly higher in the fly ash from second stage de-dusting but this effect was less significant for Cd.
- In the fly ash from straw combustion K was present at a very high concentration, while in the fly ashes from the combustion of woody biomass the concentrations of Ca and Mg were higher.

It appears that the heavy metal concentrations are higher in the fly ashes from the combustion of fuels from perennial plants (wood, *Miscanthus*) compared to those from the combustion of annual plants (straw) or fruit residues (empty fruit bunches (EFB)). Additionally, the concentrations of the volatile heavy metals are higher in the fly ashes from wood combustion compared to combustion of *Miscanthus*. It can be assumed that the average time of growth of the combusted wood was higher than the few years of growth of the combusted *Miscanthus.* Thus, there is a tendency that the heavy metals content of fly ash from biomas combustion is higher the longer the combusted biomass has grown. This suggests the idea of an accumulation of heavy metals during plant growth. However, the different types of fuel plants and different soil conditions could also have caused or contributed to this observation.

Table 3. Average concentrations of heavy metals and boron in mg/kg d.w. and Cl^- in g/kg d.w

	1st stage fly ash			2nd stage fly ash	
	Wood[1]	*Miscanthus*[1]	Straw and EFB[1]	Wood[1]	Straw[1]
n	3	1	2	6	2
As	12±3	6	13±6	30±17	8±2
B	559±21	193	63±59	298±192	60±61
Ba	320±66	848	146±157	234±154	152±169
Bi	136±5	-	53±69	131±63	26±26
Cd	59±43	7	2±1	47±37	6±4
Co	43±6	16	< 25	33±6	29±6
Cr	46±18	90	18±6	64±30	15±11
Cu	44±8	90	< 5	113±68	< 5
Hg	0.2±0.1	-	0.1±0.1	1.2±1.6	0.4±0.1
Mo	47±27	43	< 5	23±15	25±29
Ni	35±11	45	10±7	20±12	< 5
Pb	165±78	57	26±1	396±302	< 20
Sb	12±3	28	18±11	10±1	< 10
Sr	517±127	366	106±13	342±179	40±21
V	42±2	101	34±13	22±14	11±2
Zn	3,110±1,470	785	172±37	8,490±7,220	282±62
Cl^-	9.9±0.9	19	74±68	72±84	208±66

[1] Average ± standard deviation; for samples with a concentration below the detection limit in the calculation of the average and the standard deviation the detection limit was used

3.2. Physical properties

The physical properties of first stage de-dusting (cyclone) fly ash (Lanzerstorfer, 2014) and of second stage de-dusting (ESP and filter) fly ash (Lanzerstorfer, 2015a) were investigated. Additionally, the properties of ashes from the combustion of *Miscanthus* were investigated (Lanzerstorfer, 2016a). The main findings from the studies were:

- The density of fly ash from straw combustion was significantly lower.
- The bulk density was higher for the cyclone fly ashes.
- The flowability of the fly ashes was worse for finer ashes.

- The finest fly ash originating from a straw combustion plant without a pre-separator showed a differing characteristic: while the mass median diameter was much smaller the flowability of this fly ash according to the angle of repose was considerably better. This behaviour could be attributed to the formation of small agglomerates by the fly ash. These agglomerates rolle down the slope of the cone thus reducing the angle of repose.

For fly ashes from the combustion of forest residues the bulk density correlate quite well with the mass median diameter, the correlation coefficient is 0.85 (Figure 2). This is not the case for the coarse cyclone fly ashes from the combustion of straw and *Miscanthus*. For the fly ash from straw combustion this could be attributed to a certain content of large and longish particles which are presumably remainders of incompletely combusted straw stalks.

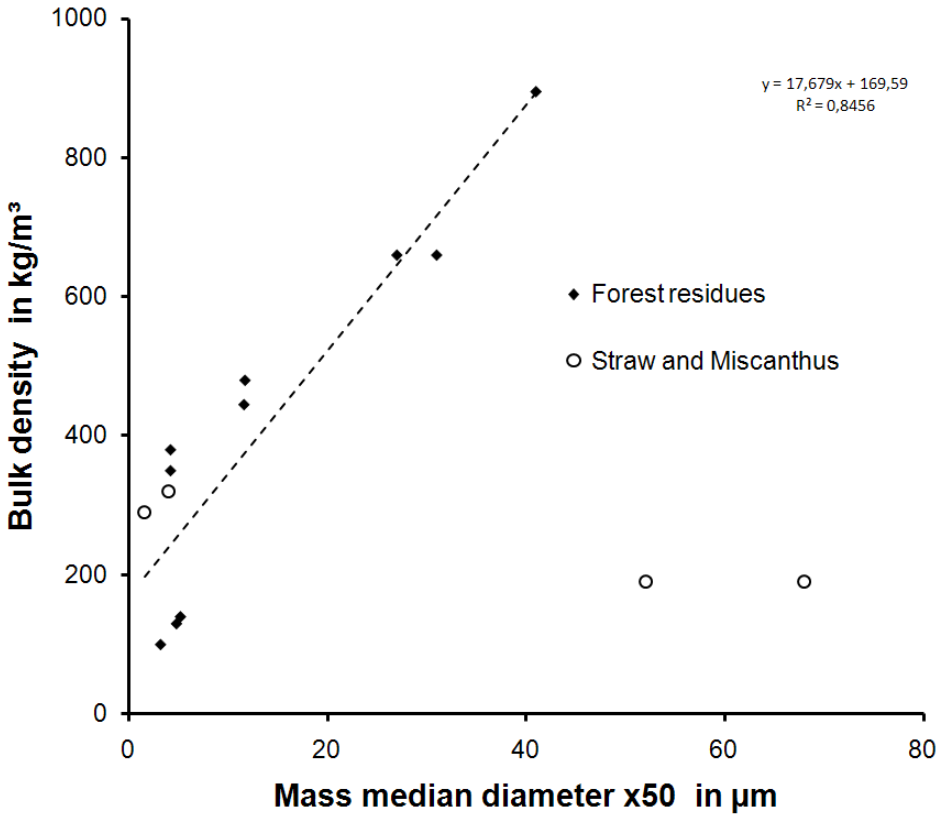
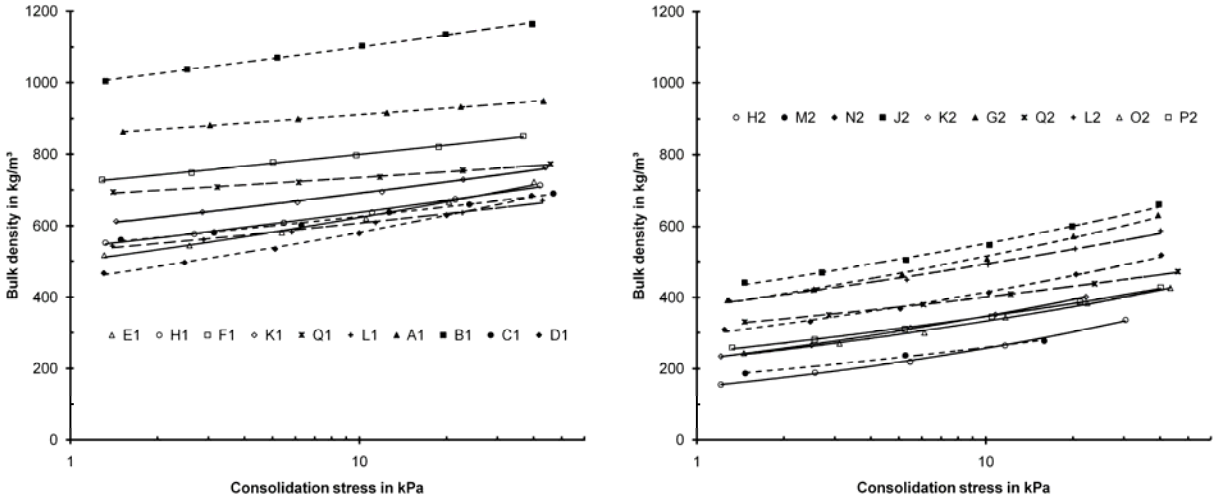


Figure 2. Bulk density of the fly ashes as a function of the particle size

3.3. Flowability of biomass combustion fly ash

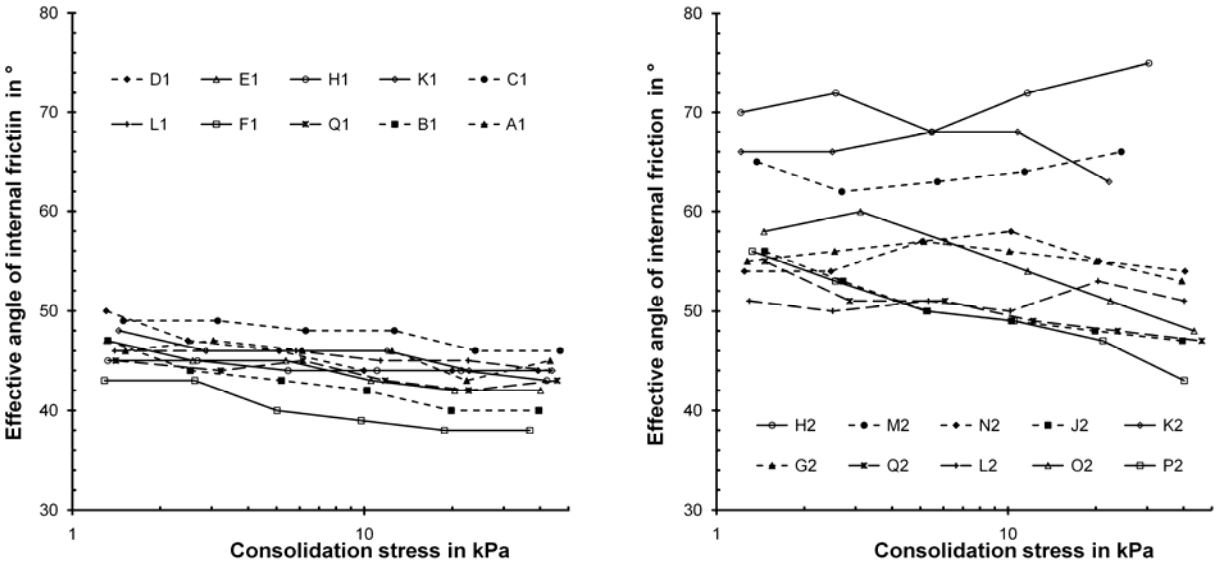
The flowability of 20 fly ashes from the combustion of woody biomass was investigated in detail (Lanzerstorfer, 2016b). The shear test revealed a significant difference between the

first stage fly ashes (cyclone fly ashes) and the second stage fly ashes (ESP fly ashes). In Figure 3, Figure 4 and Figure 5 the bulk desities, the effective angles of internal friction and the wall friction angles are shown, respectively. The sample codes are identical to those used in Lanzerstorfer (2016b). Generally, the bulk density is lower for second stage fly ashes and the value of the effective angle of internal friction and of the wall friction angle is higher.



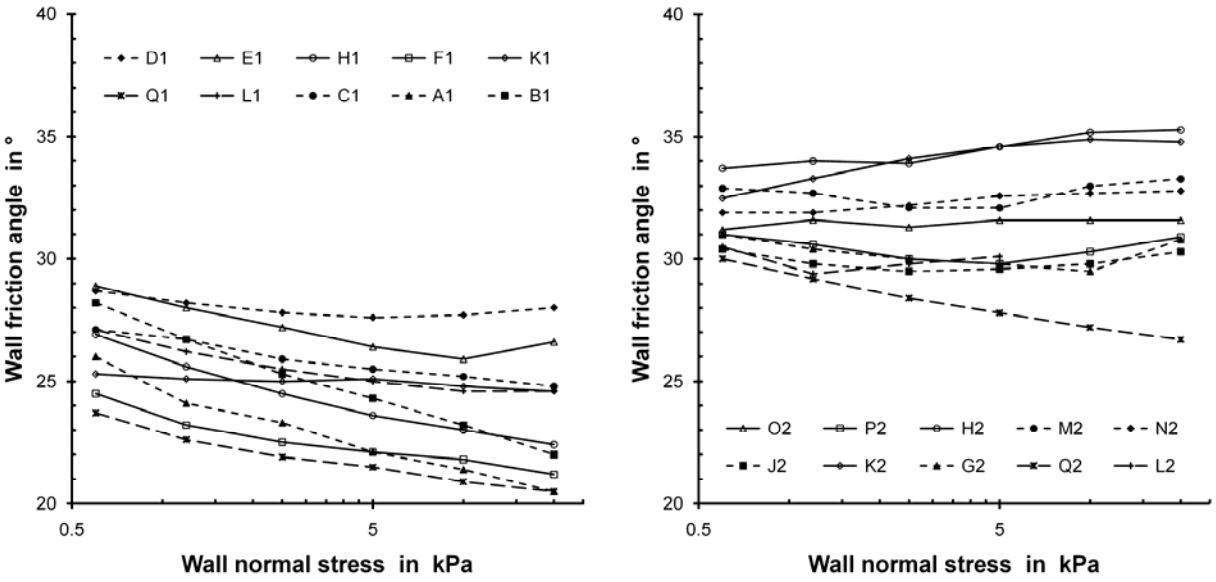
First-stage dust separators Second-stage dust separators

Figure 3. Bulk density of the fly ashes as a function of the consolidation stress



First-stage fly ashes Second-stage fly ashes

Figure 4. Effective angle of internal friction as a function of the consolidation stress



First-stage fly ashes Second-stage fly ashes

Figure 5. Wall friction angle as a function of the wall normal stress

The main findings in this study were:

- The flowability category of the coarser first-stage fly ashes was cohesive to easy-flowing, while for the second-stage fly ashes the flowability category was very cohesive to cohesive.
- A good correlation was found between the flowability of the fly ashes and the mass median diameter of their particle size distribution.
- The correlation of the flowability with the bulk density or with the angle of repose was less significant and no correlation was found with the other parameters investigated.
- Also the effective angle of internal friction, the wall friction angle and the bulk density can be expressed as a function of the mass median diameter.

Thus, the particle size is the most important parameter for the flowability of the fly ashes. The results for the flowability based on the flowability indicator angle of repose obtained in earlier studies (Lanzerstorfer, 2014; Lanzerstorfer, 2015a) are not representative. The flow indicator over-estimated the flowability of the fly ashes in several cases. For reliable flowability results shear tests are required.

3.4. Two stage leaching process

In a bench scale two stage leaching process for the treatment of fly ash that exceeds heavy metal limit values for utilization as soil conditioner ash agglomerates were produced that were below the limit concentrations for utilization on agricultural and forest land (Lanzerstorfer and Kröppl, 2015). The main findings of this experiment were:

- The loss of nutrients caused by the treatment was about 10% for Ca and 8% for K in case of use of the dried K-concentrate in the agglomeration step.
- The addition of 15% hydrated lime in the agglomeration step showed a very positive effect in the reduction of the fines content in the product and on the mechanical stability of the agglomerates.
- The particle size distribution of the agglomerates produced in the drum mixer was a bit wider compared to those produced on the pelletizing disc but the stability of the agglomerates was nearly the same. Therefore, mixing and agglomeration in one aggregate should be considered in the further development of the process.
- The mass of the precipitate from the waste water treatment was about 10% of the mass of the fly ash. Thus, the mass of residue requiring disposal in landfill sites was reduced substantially.
- The heavy metal concentrations in the treated discharge water were significantly lower than typical limit values for waste water.

3.5. Air classification

A cyclone fly ash which exceeded the limits for use as a soil conditioner was split into size fractions using an air classifier (Lanzerstorfer, 2015b). The composition of the various size fractions was analyzed. The main fresults of this study were:

- For many components the normalised concentration is a function of the particle size.
- The concentration of K and of the anions Cl^-, NO_3^- and SO_4^{2-} was increased in the fine particle classes and decreased in the coarse particle classes.
- For the metals Fe, Al, Si and Ti the size dependence was opposite, the concentration was lower in the fine particle classes and higher in the coarse particle classes.
- The concentration of the nutrients Ca, Mg, Na and PO_4^{3-} and the TC content were nearly independent of the particle size.
- The concentration of the heavy metals Bi, Cd, Cu, Hg, Pb and Zn was higher in the fine particle classes.

- For As, Ba and V the concentration was higher in the coarse particle classes.
- For B, Co, Mn, Sb and Sr no distinct dependence of the concentration on the particle size was found.
- For Cr, Ni and Mo also the concentration in the fine particle classes was higher than in the coarse particle classes. However, the behaviour of these components cannot be evaluated because of the high recovery rate caused by the erosion of some classifier material mentioned above (Lanzerstorfer, 2015c).

3.6. Implications on the utilization of biomass combustion fly ashes

Generally, the flowability of the fly ashes decreased with smaller particle size. Therefore, from the point of view of ash handling, the separation of the fly ash in a single stage de-dusting unit would be preferable. In such systems the coarser first-stage fly ash and the fine grained second stage fly ash would be separated together. Thus, the very cohesive second-stage fly ash would be avoided.

3.6.1 Utilization for construction materials

Considering the chloride content of the various biomass combustion fly ashes, only cyclone fly ash from wood combustion seems to be a feasible material. All other fly ashes contain higher amounts of chloride. Leaching of the chlorides with water to remove the chlorides could be an alternative. However, in this case the oxides get hydrated and the material would have to be used as feed material to the cement production process instead of partly substituting the cement. Because of the high chloride concentrations in the other fly ashes air classification does not seem to be a feasible alternative for the reduction of the chloride content. The chloride enrichment in the fine fraction and the chloride depletion in the coarse fraction were not that sufficient in the air classification process.

3.6.2 Use as a soil conditioner for forest and agricultural land

The use ob fly ash from the combustion of straw or Miscanthus as a soil conditioner for forest and agricultural land is highly recommendable because of the nutrient content of the fly ashes and the compliance with the strictest heavy metals limits. Alternatively, straw combustion fly ash could even be used as a secondary raw material for potassium fertilizer production because of its high potassium content.

Most fly ashes from wood combustion contained one or more heavy metals in a concentration above the limit concentrations for use as a soil conditioner for forest and agricultural land. The investigated two-stage leaching process showed the potential for reducing the heavy metal concentrations with acceptable losses of the nutrients. Air classification could be applied to reduce the amount of fly ash which has to be treated by the leaching process.

4 Summary and outlook

Various fly ashes from biomass combustion plants have been investigated with respect to their chemical composition and their physical properties. Especially for the physical properties of fly ashes from biomass combustion and the chemical composition of fly ash from combustion plants using *Miscanthus* as fuel only few data were available in the literature.

The measured physical properties now provide a basis for the design of fly ash handling and storage equipment. To obtain reliable flowability results for fly ashes shear tests are required because the flow indicator angle of repose over-estimated the flowability of the fly ashes in several cases. The particle size was identified as the most important property which influences the flowability of the fly ashes.

For a cyclone fly ash from a combustion plant using forest residues as fuel a dependence of the concentration of many components on the particle size was found. Several components were enriched in the smaller particle size fractions (e.g. K, Cl^-, NO_3^-, SO_4^{2-}, Bi, Cd, Cu, Hg, Pb and Zn) while others are enriched in the coarse fractions (Fe, Al, Si, Ti, As, Ba and V). For other components no distinct dependence of the concentration on the particle size was found (Ca, Mg, Na, PO_4^{3-}, TC, B, Co, Mn, Sb and Sr). Further investigations on different types of fly ash are recommended to study this effect.

Fly ashes from the combustion of straw and *Miscanthus* are only slightly contaminated with heavy metals and can be used as a soil conditioner for forest and agricultural land without pre-treatment. In contrast, for most fly ashes from the wood combustion plants investigated the concentrations of some heavy metal were above the limit concentreations. Thus, treatment of these fly ashes for the reduction of the heavy metal content would be requied. The two-stage leaching process investigated showed the potential of reducing the heavy metal concentrations at acceptable losses of the nutrients. The next step required would be a pilot test of this process.

The utilization of biomass combustion fly ashes for construction materials seem to be limited especially by the high chloride content of most biomass combustion fly ashes. Considering the chloride content of the various biomass combustion fly ashes, only cyclone fly ash from wood combustion might be a feasible material for this utilization.

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6 Included papers

6.1. Paper 1

Lanzerstorfer C. (2015a). Chemical composition and physical properties of filter fly ashes from eight grate-fired biomass combustion plants. Journal of Environmental Sciences 30: 191-197. DOI:10.1016/j.jes.2014.08.021

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Chemical composition and physical properties of filter fly ashes from eight grate-fired biomass combustion plants

Christof Lanzerstorfer

School of Engineering and Environmental Sciences, University of Applied Sciences Upper Austria, Stelzhamerstraße 23, A-4600 Wels Austria

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Physical properties

ABSTRACT

For the handling, treatment and utilization of fly ash from biomass combustion its chemical composition and physical properties are important. In this study eight filter fly ashes from different grate-fired biomass combustion plants were investigated. In fly ash from straw combustion high concentrations of (K) were found, whereas in the fly ash from wood combustion the concentrations of Ca and Mg were higher. The average concentration of PO_4^{3-} was similar in both types of fly ashes. In all wood fly ashes some measured heavy metal concentrations were above the limits for utilization. The straw fly ashes were much less contaminated and can be utilized. For wood fly ash most parameters showed little variation, except from one fly ash where the dust pre-separator is in poor condition. The average values were: mass median diameter 4.3±0.8 μm, spread of particle size distribution 19±11, particle density 2620±80 kg/m^3 and angle of repose 50°±1°. The density of the straw fly ashes is lower (2260±80 kg/m^3) and the spread of the size distribution is higher (72±24). For one straw combustion fly ash the values of the mass median diameter and the angle of repose were similar to the values of wood combustion fly ash, for the other straw fly ash the values differed considerably. While the particle size of this fly ash was much smaller, surprisingly the angle of repose was also lower. This can be attributed to the formation of small agglomerates in this fly ash, which were not disintegrated without a certain stress.

Introduction

Due to the limited availability of fossil fuels and concerns about climate change caused by the carbon dioxide emissions from fossil fuel combustion, the combustion of biomass for heat and power generation is rising continuously (European Biomass Association, 2013). The combustion of biomass is considered to be nearly carbon dioxide neutral because the carbon dioxide emissions produced during combustion are almost compensated by the carbon dioxide fixed in the biomass while it grows.

In the combustion process the inorganic constituents of the biomass remain as ash. The finer ash particles leave the combustion zone together with the off-gas as fly ash. Before the discharge of the off-gas the fly ash has to be separated. In order to comply with low dust emission limits at standard pressure and temperature (STP) (<20 mg/m^3 (STP)), a fabric filter or an electrostatic precipitator (EP) has to be used for the separation of the fly ash. Upstream of these separators a pre-separator, *e.g.*, a cyclone is usually installed. If the coarser dust is collected in a pre-separator the filter fly ash accounts for 2%-10% of the total amount of ash (Narodoslawsky and Obernberger, 1996).

The filter fly ash is a bulk material with a small grain size that has to be handled, treated and utilized or disposed of at landfill sites. For the decision about the further fate of the fly ash the chemical composition is essential. The physical properties are relevant for the design of the handling and storage facilities.

In Austria only bottom ash and cyclone fly ash from the combustion of chemically untreated biomass can be utilized as a

E-mail address: c.lanzerstorfer@fh-wels.at.

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soil conditioner on agricultural land and forests if the concentrations of pollutants are below the limit concentrations (Bundesministerium für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft, 2011). Filter fly ash is not allowed to be used in that way because the concentrations of volatile heavy metals are highest in this fine ash fraction. Therefore, excluding the filter fly ash from recirculation to the soil where the biomass has grown provides a sink for these elements. In other European countries the conditions for biomass fly ash utilization are different. The limit concentrations for some Scandinavian countries and Lithuania are summarized in Table 1.

For the design of the storage bins and other ash handling equipment physical properties of the fly ash like the bulk density and the angle of repose are important. The angle of repose can also be used for an approximate categorization of the flowability of the material.

In the literature some data are available for the chemical composition of biomass filter fly ashes. In several studies (Dahl et al., 2009; Singh et al., 2011; Melotti et al., 2013; Sano et al., 2013) data of fly ashes from the combustion of woody biomass and mustard stalks collected in EPs have been reported. As there was no pre-separator installed in the combustion plants where the samples were collected, the particle size distribution of the investigated fly ash samples was rather coarse. In two of these studies the mass median diameter of the fly ash is reported to be 100 and 60 μm. Some data of second stage filter fly ash are available in van Loo and Koppejan (2008). Sander and Andrén (1997), Hansen et al. (2001) and Aguiar del Toro et al. (2009) reported on the chemical composition of fly ash from straw combustion. However, no information is given on the type and arrangement of dust separators where the fly ash samples were collected. Generally, one can say that in the published studies, the type and number of the analyzed components vary a lot and that in no work the broad spectrum of components from the nutrients to the heavy metals is covered.

Data on the physical properties of fly ash from biomass combustion are very rare. In van Loo and Koppejan (2008) data for the density and the bulk density of filter fly ashes are reported.

The aim of this study was to characterize filter fly ashes from the combustion of wood and straw with respect to their chemical composition and their physical properties. It was particularly intended to provide a complete set of physical properties and chemical composition data for each fly ash sample because the published literature usually focuses only on certain parameters of the samples investigated. All fly ashes from the combustion of woody biomass were taken from the second stage of two-stage dust separation systems. Of the fly ash samples from straw combustion plants, only one is from a plant where a pre-separator is installed, the other is from the off-gas filter of a single-stage system.

Table 1 – Heavy metal concentration limits for utilization of ash from biomass combustion as a soil conditioner in forests and agriculture (unit: mg/kg dw).

	Finland [a]	Sweden [b]	Lithuania [c]
As	40	30	30
B		500	500
Cd	25	30	30
Cr	300	100	100
Cu	700	400	400
Hg	1.0	3	3
Ni	150	70	70
Pb	150	300	300
V		70	70
Zn	4500	7000	700

dw: dry weight.
[a] Data source is from Nurmesniemi et al., 2012.
[b] Data source is from Emilsson, 2006.
[c] Data source is from Stupak et al., 2008.

1. Materials and methods

1.1. Material

Fly ash from eight grate-fired biomass combustion plants was collected for this study. The samples were taken from the dust discharge of the final dedusting system which was either an electrostatic precipitator (EP) or a fabric filter. An overview of the thermal capacities of the combustion plants, the type of dust separator installed and the combusted biomass is given in Table 2. In all plants for the combustion of woody biomass (from plant A to plant F) a pre-separator, usually a cyclone, is installed upstream of the final dust separator from which the samples were taken. The arrangement is the same in plant G, whereas in plant H no pre-separator is installed upstream of the dust filter. In plant F some hydrated lime is added to the off-gas before it enters the separator. The volume of each fly ash sample of approximately 2 dm^3 was collected. The sample volumes were reduced to a volume suitable for the various laboratory tests using sample dividers which were applied repeatedly (Retsch PT100, Quantachrome Micro Riffler).

1.2. Chemical analysis

All chemical analyses of the fly ashes were measured in duplicate. In the results the average values are presented. The moisture content was measured gravimetrically. The samples were dried at 105°C for 1 hr. The carbon content (TC) was determined with a LiquiTOC system from Elementar Analysensysteme, Hanau, Germany. By combustion with air the carbon is transformed into CO_2 which is subsequently analyzed.

The solid fly ash samples were dissolved by aqua regia digestion (International Organization for Standardization, 1995) prior to analysis of the concentration of metals, sulfate and phosphate. The concentration of most metals was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES) using an Ultima 2 from Horiba Jobin Yvon, Bensheim, Germany. The concentration of mercury was measured using cold vapor atomic absorption spectrometry (CV-AAS) according to EN ISO 12846 (European Committee for Standardization, 2012). The concentration of alkali and earth alkali metals, sulfate and phosphate was measured by ion chromatography (IC) using a Dionex (Sunnyvale, Carlifornia, USA) ICS-1000 system. For analysis of cations the set-up was: analytical column IonPac® CS12A 4 × 250 mm; suppressor: CSRS® 300, 4 mm; eluent: 20 mmol methanesulfonic acid, flow rate 1.0 mL/min. For the measurements of anions the set-up was: analytical column IonPac® AS14A 4 × 250 mm; suppressor: ASRS® 300, 4 mm; eluent: 8.0 mmol sodium carbonate/1.0 mmol sodium hydrogen carbonate; flow rate 1.0 mL/min.

The chloride and nitrate concentration of a solid sample cannot be analyzed after digestion by aqua regia. As nearly all chlorides and nitrates are highly soluble in water, the concentration of chloride and nitrate of a sample can be

Table 2 – Biomass combustion fly ashes investigated.

	Thermal capacity in MWth	Type of separator	Combustion temperature (typical)	Combusted biomass (approximate composition)
Plant A	8.0	EP	950°C	Wood chips from forest residue > 90%; sawdust and bark < 10%
Plant B	5.0	EP	900°C	Wood chips from forest residue, 80% softwood, 20% hardwood
Plant C	10	EP	830°C	Wood chips from forest residue, 80% softwood (spruce), 20% hardwood (beech, oak and birch)
Plant D	10	EP	900°C	Wood chips from forest residue, 90% softwood (spruce), 10% hardwood (beech, oak and birch)
Plant E	50	EP	n.a.	Rubber tree: 95% wood chips and 5% bark
Plant F	2.0	Fabric filter	850°C	90% wood chips from forest residue and 10% horse dung
Plant G	2.2	Fabric filter	680°C	Wheat straw, chuffed
Plant H	45	Fabric filter	1200°C	Wheat straw, disintegrated bales

n.a.: not available; EP: electrostatic precipitator.

determined in an aqueous leachate. Approximately 2 g of a sample was leached in 200 mL of deionized water for 1 hr. To aid the leaching process the samples were placed in an ultrasonic bath. After leaching the remaining solids were separated by filtration. The concentration of chloride and nitrate was also measured by IC.

1.3. *Measurement of physical properties*

The particle size distribution of the samples was measured using a laser diffraction instrument with dry sample dispersion from Sympatec (Clausthal-Zellerfeld, Germany), type HELOS/RODOS. The spread of the distribution was calculated as the quotient of x_{90} and x_{10} (Rumpf, 1990). For sieving of the fly ash a laboratory sieve shaker from Fritsch (Idar-Oberstein, Germany), type ANALYSETTE 3 PRO was used.

The particle density was determined according to EN ISO 8130-3 (European Committee for Standardization, 2011). This method is based on a determination of the mass and the volume of a test portion using a liquid displacement pyknometer. The capacity of the pyknometer used was approximately 100 cm^3 and n-heptane (density: 0.681 g/cm^3) was used for displacement of the air. The bulk density of the samples was measured according to EN ISO 60 (European Committee for Standardization, 1999). Sample powder stored in the funnel (120 cm^3) flows by gravity into the coaxial 100 cm^3 measuring cylinder when the bottom cover of the funnel is removed. The excess material is removed by drawing a straightedge blade across the top of the measuring cylinder. The voidage of the bulk fly ash was calculated as $1 - \rho_{bulk}/\rho_{particle}$.

The angle of repose was determined according to ISO 4324 (International Organization for Standardization, 1977). A cone of material is obtained by passing the powder through a special funnel placed at a fixed height above a completely flat and level plate. The base angle of the cone can be calculated from the diameter of the base plate and the height of the cone. The angle of repose can be used as an indicator to categorize the flowability of powders. The flowability categories according to the United States Pharmacopeial Convention USP 29-NF24 (as Stanley-Wood, 2008, p. 29) are "excellent/very free flow" for an angle of repose of 25°–30°, "good/free flow" for 31°–35°, "fair" for 36°–40°, "passable" for 41°–45°, "poor/cohesive" for 46°–55°, "very poor/very cohesive" for 56°–65° and "very very poor/non-flow" if the angle of repose is greater than 66°.

2. Results and discussion

2.1. *Chemical composition*

The total carbon (TC) concentration and the nutrient concentrations in the fly ash are summarized in Table 3. For these components, the average relative standard deviation calculated from the duplicate measurements was 4.8%. The TC content of the fly ash characterizes the completeness of the combustion in the furnace: the lower the TC concentration the better the combustion process. The measured values for the fly ashes from wood chips combustion were in the published range (van Loo and Koppejan, 2008) except for the fly ash from plant F, where some horse dung was added to the fuel. A great difference was found in the TC content of the two straw combustion fly ashes. This difference was also visible in the color of the fly ashes. The fly ash from plant G is black whereas the color of the fly ash of plant H is white to light gray. Presumably, this difference can be explained by the large difference in the combustion temperature between the two plants. Generally, the higher TC values were found in the fly ashes from the smaller combustion plants.

The concentrations of the various components in the fly ash samples show considerable variation, the relative standard deviation is typically in the range of 25% to 100%. However, this was also found by other researchers investigating fly ashes from different wood or straw combustion plants (Sano et al., 2013; van Loo and Koppejan, 2008). The nutrient contents (K, Ca, Mg, PO_4^{3-}) of both fly ash types are in the published concentration range. The average nutrient concentrations differ between the two ash types. K was present at very high concentration in the straw fly ashes whereas the concentrations of Ca and Mg were higher in the fly ashes from woody biomass. The highest Ca concentration was found in the fly ash from plant F but this is not surprising because in this plant some lime is added to the flue gas. The contents of

Table 3 – Concentrations of nutrients and other main components in the fly ashes (all concentrations except the humidity based on dry weight).

	Fly ash A	Fly ash B	Fly ash C	Fly ash D	Fly ash E	Fly ash F	Wood combustion fly ash [a]	Fly ash G	Fly ash H	Straw combustion fly ash [a]
Humidity (%)	0.7	1.4	1.7	3.1	0.6	1.5	1.5 ± 0.9	3.3	0.7	2.0 ± 1.8
TC (%)	2.9	1.5	2.7	4.4	2.4	9.2	4.1 ± 2.9	12.3	1.4	6.9 ± 7.7
Cl^- (g/kg)	6.2	34.4	25.0	236.7	74.6	52.3	72 ± 84	161.0	254.2	208 ± 66
NO_3^- (g/kg)	0.1	0.6	0.1	0.4	2.2	0.0	0.6 ± 0.9	0.3	1.7	1.0 ± 1.0
PO_4^{3-} (g/kg)	21.1	20.5	39.5	25.5	24.9	13.4	24 ± 9	28.9	15.9	22 ± 9
SO_4^{2-} (g/kg)	23.9	288	128	63.0	47.2	77.1	105 ± 96	184	66.3	125 ± 96
Na (g/kg)	3.3	8.0	4.8	47.0	26.7	5.1	16 ± 18	7.4	4.9	6 ± 2
K (g/kg)	47.2	311	192	177	148	118	165 ± 88	570	407	488 ± 115
Mg (g/kg)	12.7	4.7	30.0	11.6	17.5	3.7	13 ± 10	0.4	7.7	4 ± 5
Ca (g/kg)	158	59.3	231	125	281	316 [b]	171 ± 87 [b]	5.4	32.8	19 ± 19
Al (g/kg)	19.1	2.1	8.4	7.2	4.6	1.3	7 ± 6	1.4	0.01	0.7 ± 1.0
Fe (g/kg)	13.2	3.2	8.6	10.4	4.1	1.9	7 ± 5	1.5	0.7	1.1 ± 0.6
Mn (g/kg)	8.4	4.1	14.6	6.8	2.9	1.0	6 ± 5	0.1	0.04	0.1 ± 0.1

[a] Average ± standard deviation.
[b] In plant F some lime is added to the flue gas; therefore the Ca concentration of the fly ash of plant F was not considered in the calculation of the average.

the metals Al, Fe and Mn in the fly ash are also considerably higher in the wood ash compared to straw ash.

The average concentration of PO_4^{3-} was similar in both fly ash types and the concentration of NO_3^- was very low in all fly ash samples. Although nitrogen is present in wood (0.1%–0.5%) and in straw (0.4%–0.6%) at similar concentrations than Ca (0.3%–0.7% in wood and 0.3%–0.5% in straw) (Hartmann, 2009) almost no nitrogen is present in the ash. This can be explained by the fact that nearly all nitrogen contained in solid fuel leaves the combustion as NOx (Glarborg et al., 2003).

The concentrations of heavy metals and other minor components are summarized in Table 4. For these components, the average relative standard deviation calculated from the duplicate measurements was 12%. For the various fly ash samples the variation of the heavy metals concentrations is quite high, the relative standard deviation is typically in the range of 25% to more than 100%. However, the variation of heavy metals concentrations was even higher in the wood ash samples investigated by Sano et al. (2013).

For most heavy metals, the measured concentrations in the ash from wood combustion are lower compared to the results published by van Loo and Koppejan (2008) whereas for As, V and Hg the results are very similar. The concentrations in ash from the combustion of wood pellets are lower for As, Cd, Pb and Zn and higher for Ba, Sr, Cr and Ni (Sano et al., 2013). The heavy metal concentrations reported by Singh et al. (2011) are for a fly

Table 4 – Concentrations of heavy metals and other minor components in the fly ashes (unit: mg/kg dw).

	Fly ash A	Fly ash B	Fly ash C	Fly ash D	Fly ash E	Fly ash F	Wood combustion fly ash [a]	Fly ash G	Fly ash H	Straw combustion fly ash [a]
As	19	**36**	27	**62**	15	19	30 ± 17	7	10	8 ± 2
B	263	221	**671**	292	227	114	298 ± 192	17	103	60 ± 61
Ba	484	91	191	136	357	144	234 ± 154	271	33	152 ± 169
Bi	95	237	124	167	59	104	131 ± 63	8	45	26 ± 26
Cd	19	**105**	**41**	**77**	9	**32**	47 ± 37	3	8	6 ± 4
Co	39	39	<25	<25	34	34	33 ± 6	<25	33	29 ± 6
Cr	92	76	87	70	15	41	64 ± 30	22	7	15 ± 11
Cu	11	140	145	156	<5	<5	113 ± 68	<5	<5	<5
Hg	0.8	0.1	**1.7**	**4.2**	<0.05	0.1	1.2 ± 1.6	0.3	0.4	0.4 ± 0.1
Mo	24	43	<5	<5	27	32	23 ± 15	<5	46	25 ± 29
Ni	31	23	27	4	31	6	20 ± 12	<5	<5	<5
Pb	**352**	**602**	**250**	**892**	53	**228**	396 ± 302	<20	<20	<20
Sb	10	12	<10	<10	10	11	10 ± 1	<10	<10	<10
Sr	284	242	641	283	461	141	342 ± 179	55	25	40 ± 21
V	36	38	<10	<10	30	10	22 ± 14	<10	13	11 ± 2
Zn	**3670**	**19000**	**7990**	**15400**	567	4380	8490 ± 7220	238	325	282 ± 62

dw: dry weight.
Bold values indicate significance at the values exceed the limit concentrations for utilization of the fly ash as a soil conditioner in at least one of the countries listed in Table 1.
[a] Average ± standard deviation; for samples with a concentration below the detection limit in the calculation of the average and the standard deviation the detection limit was used.

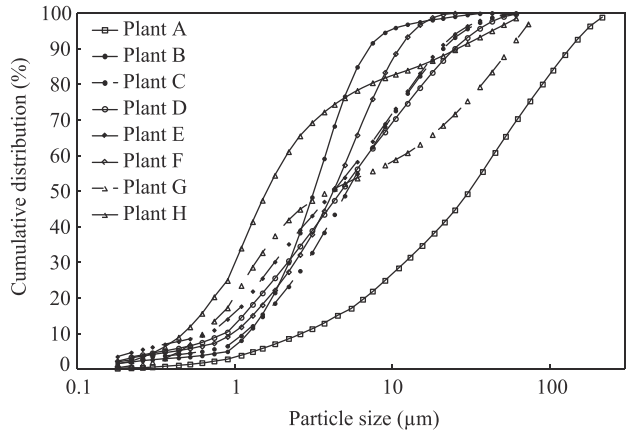

Fig. 1 – Particle size distribution of the fly ashes.

ash from the combustion of mustard stalks, which might explain the much lower concentrations compared to the present study. For the fly ash from straw combustion, the measured concentrations for Cd, Cu, Pb and Zn are a bit below the published range (Sander and Andrén, 1997; Hansen et al., 2001; Aguiar del Toro et al., 2009) whereas the concentrations for Cr and Ni are within the range.

Generally, the average heavy metal concentrations are much lower in the fly ash from straw combustion. Only for Co and Mo are the average concentrations the same for both types of fly ashes. The composition of the fly ash from plant F where 10% horse dung is added to the woody biomass fuel showed no significant differences to the composition of the fly ashes from the other wood combustion plants.

No fly ash from wood combustion is below all the limit concentrations of any county according to Table 1 except the fly ash from plant E in which rubber tree wood is used as fuel. In none of the other fly ashes from wood combustion all heavy metal concentrations are below the limit concentrations of any of the countries. In Table 4 all values exceeding the limit concentrations for utilization of the fly ashes as a soil conditioner in at least one of the countries are printed in bold type. The most critical heavy metals with respect to limit violation are Cd, Pb and Zn, and to a lesser extent Hg and As. The heavy metal concentrations in the straw combustion fly ashes are below the limit concentrations given in Table 1.

2.2. *Physical properties*

The particle size distributions of the fly ashes are shown in Fig. 1. It is evident that there is a considerable difference between the particle size distribution of fly ashes from wood combustion and fly ashes from straw combustion (plants G and H). The size distributions of wood fly ashes are S-shaped and the curves are close together for most of the ashes investigated. Only the fly ash from plant A is much coarser. The mass median diameter of this fly ash is nearly as high as those reported for fly ashes from wood combustion collected in a filter or EP without a pre-separator (Singh et al., 2011; Melotti et al., 2013). The coarse particle size of fly ash A can be explained by the poor conditions of the cyclone pre-separator installed at this plant. When this fly ash is excluded from the calculation the average mass median diameter for the fly ashes from wood combustion is 4.3 ± 0.8 μm. The mass median diameters of the fly ashes and the other physical properties are summarized in Table 5.

The size distribution of the fly ashes from straw combustion is bimodal. This results in a double S-shaped curve of the cumulative distribution. Although no pre-separator is installed in plant H the particle size distribution of this fly ash is the finest. This might be partially explained by the high quality of the combustion in plant H indicated by the very low TC content of the fly ash.

The average spread of the size distribution of the fly ashes from wood combustion excluding fly ash A, is 19 ± 11. Due to the coarse fractions in fly ash A the spread of this fly ash is about three times as high. The spread of the straw combustion fly ashes is also much higher (72 ± 24).

The density of the fly ashes varies between about 2200 and 2750 kg/m^3. The lower values were found for the fly ashes from straw combustion, its density is 2260 ± 80 kg/m^3. The density of fly ash from wood chips combustion is 2620 ± 80 kg/m^3. A reasonable explanation for the lower density of the fly ash from straw combustion is by its high content of potassium chloride, which has a relatively low density of 1.988 kg/dm^3 (Lide, 2002).

The bulk density varies within a considerable range. Fly ash A shows the highest value of 660 kg/m^3. The reason for the high bulk density is most probably the coarse and broad particle size distribution which results in a better flowability of the fly ash. The bulk density of the other fly ashes from wood chips combustion varies from 100 to 380 kg/m^3. For the fly ash from straw combustion the bulk density was about 300 kg/m^3. The results of the density measurements correspond well with the density data reported by van Loo and Koppejan (2008). For the bulk density of fly ash from straw combustion the measured values are twice as high as the published values. However, the type of combustion system was different in this case (van Loo and Koppejan, 2008). For filter fly ash from wood combustion no data for the bulk density were found in the literature. For the voidage there is no significant difference between the fly ashes from wood combustion of from straw combustion. However, the voidage of the coarse fly ash from plant A was lower. The average

Table 5 – Physical properties of the fly ashes.

	Fly ash A	Fly ash B	Fly ash C	Fly ash D	Fly ash E	Fly ash F	Fly ash G	Fly ash H
Mass median diameter d_{50} (μm)	31	3.2	5.2	4.8	4.2	4.2	4.0	1.6
Spread of the size distribution	51	6	18	29	30	11	89	55
Density (kg/m^3)	2570	2610	2720	2740	2570	2540	2210	2320
Bulk density (kg/m^3)	660	100	140	130	380	350	320	290
Voidage	0.74	0.96	0.95	0.95	0.85	0.86	0.86	0.88
Angle of repose (degree)	50	49	49	50	52	50	50	43

value of the voidage of the fly ashes without fly ash from plant A was 0.90 ± 0.05.

The angles of repose of the fly ashes from wood combustion are in a very narrow range from 49° to 52°, the average is 50° ± 1°. The corresponding flowability category is "poor/cohesive". Also the fly ash from plant A which is much coarser than the other fly ashes shows no better flowability. The angle of repose of one fly ash from straw combustion (plant G) is similar to those of the fly ashes from wood combustion. Surprisingly, the angle of repose of the finest fly ash (plant H) is lower and the corresponding flowability category is "passable". This can be explained by a visible tendency of this fly ash to build micro-agglomerates. For the investigation of this effect, samples of the fly ashes were sieved on a 200 μm sieve. The amplitude was 2 mm and the sieving time was 2 min. According to the measured particle size distributions (Fig. 1) practically all fly ash material should pass through the 200 μm sieve. For the fly ashes A to G the oversize fraction which did not pass through the 200 μm sieve was in the range of 3% to 10%. For fly ash H this fraction was about 50%. This oversize fraction consists of small agglomerates which did not disintegrate during the sieving procedure. However, the particle size distribution of the particles which build these agglomerates is nearly the same as the particle size distribution of the fly ash.

3. Conclusions

The average nutrient concentrations differ between the two ash types. In the fly ash from straw combustion, K is present at a very high concentration. In the fly ashes from the combustion of woody biomass the concentrations of Ca and Mg are higher. The average concentration of PO_4^{3-} is similar in both fly ash types and the concentration of NO_3^- is very low in all fly ash samples.

In the filter fly ash from woody biomass combustion a higher concentration of heavy metals can be found whereas in the fly ash from the combustion of straw the heavy metal concentrations are typically much lower. All fly ashes from wood combustion except fly ash E exceed the Scandinavian limits for the utilization of the ash as a soil conditioner. The heavy metal concentrations in the straw combustion fly ashes are below the limit concentrations. Only the Cd concentration in the fly ash from plant H is higher than the respective limit in Denmark, which is the lowest limit for Cd.

The TC concentration, which is an indicator for the quality of the combustion, was generally higher in the fly ashes from the smaller combustion plants.

For several physical properties of fly ash from wood combustion, especially the mass median diameter, the spread of the particle size distribution, the particle density, the voidage and the angle of repose only little variation was found for the fly ash from different combustion plants. An exception was the fly ash from a plant where the pre-separator was in very poor conditions which resulted in a coarser particle size and a higher bulk density. For the bulk density the range of the variation was higher.

For the fly ash from straw combustion the particle density is lower and the spread of the size distribution is considerably higher. For one fly ash from straw combustion the other measured properties were quite similar to those of the fly ashes from wood combustion. The other fly ash originating from a straw combustion plant without a pre-separator showed a different characteristic. While the mass median diameter was much smaller the flowability of this fly ash was considerably better. This can be attributed to the formation of small agglomerates which are not disintegrated unless a certain shear force is exerted on these agglomerates.

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6.2. Paper 2

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Chemical composition and properties of ashes from combustion plants using *Miscanthus* as fuel

Ashes from *Miscanthus* combustion

Christof Lanzerstorfer[1*]

[1]School of Engineering/Environmental Sciences, University of Applied Sciences Upper Austria, Stelzhamerstraße 23, A-4600 Wels, Austria

* Corresponding author: E-mail: c.lanzerstorfer@fh-wels.at

Abstract

Miscanthus giganteus is one of the energy crops being considered to show the potential for a substantial contribution to sustainable energy production. In the literature there is only little data available about the chemical composition of ashes from the combustion of *Miscanthus* and practically no data about their physical properties. However, for handling, treatment and utilization of the ashes this information is important. In this study ashes from two biomass combustion plants using *Miscanthus* as fuel were investigated. The density of the ashes was 2,230±35 kg/m³, which was similar to the density of ashes from straw combustion. Also the bulk densities were close to those reported for straw ashes. The flowability of the ashes was a little worse than the flowability of ashes from wood combustion. The measured heavy metal concentrations were below the usual limits for utilization of the ashes as soil conditioner. The concentrations in the bottom ash were similar to those reported for ash from forest residue combustion plants. In comparison with cyclone fly ashes from forest residue combustion the measured heavy metal concentrations in the cyclone fly ash were considerably lower. Cl^-, S and Zn were enriched in the cyclone fly ash which is also known for ashes from wood combustion. In comparison with literature data obtained from *Miscanthus* plant material the concentrations of K, Cl^- and S were lower. This can be attributed to the fact that the finest fly ash is not collected by the cyclone de-dusting system of the *Miscanthus* combustion plants.

Key words: biomass combustion; *Miscanthus*; ash composition; ash properties;

Introduction

Concerns about climate change caused by the carbon dioxide emissions from the combustion of fossil fuels lead to a continuous rise in the combustion of biomass for heat and power generation (European Biomass Association, 2013). The combustion of biomass is considered to be almost carbon dioxide neutral because the carbon dioxide emissions produced during the combustion process are almost offset by the carbon dioxide fixed by photosynthesis during the growth of the biomass. Besides forest and agricultural residues energy crops are also used as fuels in biomass combustion plants. *Miscanthus giganteus* is one of the energy crops being considered to show the potential for a substantial contribution to sustainable energy production (Lewandowsky et al., 2003). In Europe the area of agricultural land where *Miscanthus* was grown in 2011 was approximately 20,000 ha (European Biomass Association, 2013). In 2014, the acreage of *Miscanthus* in Austria was 1,180 ha (Statistik Austria, 2015) with the main production areas being in Upper and Lower Austria. The yield of dry biomass depends on the soil quality, the water supply and the temperature. In upper Austria, the yield on good soil is in the range of 15-22 t dry mass per hectare (Frühwirth and Liebhard, 2006).

In the combustion of *Miscanthus* the inorganic constituents remain as ash. Most of the ash is discharged as bottom ash but some of the ash leaves the combustion zone together with the off-gas as fly ash. The amount of produced fly ash depends on the combustion conditions and the type of combustion process. In biomass combustion the fly ash typically accounts for about one quarter of the total amount of ash (van Loo and Koppejan, 2008). In smaller size combustion plants the fly ash is collected in a single de-dusting stage by a cyclone or a multi-cyclone. The collected cyclone fly ash is usually discharged from the combustion process together with the bottom ash as mixed ash. The total ash content of *Miscanthus* is reported to be in the range of 2.0% – 3.5% (European Biomass Association, 2013). Similar values were reported by Baxter et al. (2012) and Michel et al. (2012) for the ash content of samples from the whole plant.

In many countries ashes from the combustion of chemically untreated biomass are utilized as soil conditioner on agricultural land and forests if the concentrations of pollutants are below the limit relevant concentrations. The recycling of biomass ashes to the soil is proposed to help to close the nutrient cycles for the soil where the biomass was grown (von Wilpert et al., 2014). Country-specific limit concentrations for heavy metals can be found in the literature (Bundesministerium für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft, 2011; Emilsson, 2006; Nurmesniemi et al., 2012).

The ashes from the combustion processes are bulk materials that have to be handled, stored, treated and utilized or disposed of at landfill sites. The chemical composition of ashes is essential in determining its ulilization. For its use as a soil conditioner the country-specific limits are decisive. The physical ash properties like the bulk density and the flowability are important parameters for the design of the handling and storage facilities (Schulze, 2008).

In the literature there is only little data available for the chemical composition of ashes from the combustion of *Miscanthus*. Baxter et al. (2012) and Michel et al. (2012) reported the concentrations of main ash components in ashes produced by combustion of small samples of *Miscanthus* in a muffle furnace at 550°C for 3h and 400°C for 8h, respectively. The ash content and concentration data for main ash components and some heavy metals for *Miscanthus* plants are available in Obernberger et al. (2006). From this data the expected content of the components in the ash can be calculated. No data was found in the literature for the physical properties of ashes from the combustion of *Miscanthus*.

The aim of this study was to characterize bottom ash and cyclone fly ash from the combustion of *Miscanthus* in full scale combustion plants with respect to their chemical composition and their physical properties.

1 Materials and methods

1.1 Material

The ashes investigated in this study were collected from two grate-fired biomass combustion plants using *Miscanthus giganteus* as fuel. The thermal capacity of plant A and plant B was 400 KW_{th} and 750 KW_{th}, respectively. The biomass for the two combustion plants was grown in Lower Austria (250 m a.s.l.) and Upper Austria (350 m a.s.l.), respectively. In April, the culm material was harvested leaving the leafs out on the soil. The material was chopped and stored under open air roof. In both plants the combustion temperature measured about 1 m above the combustion grate was approximately 600°C. Each plant was equipped with a cyclone for the de-dusting of the combustion off-gas. Ash samples of 1 dm^3 were collected at the ash discharge systems. From plant A only a combined bottom ash and cyclone fly ash sample could be obtained, whereas, in plant B the bottom ash and the cyclone fly ash were collected separately. The volume of the ash samples was reduced to a volume suitable for the various laboratory tests using sample dividers which were applied repeatedly (Haver&Boecker HAVER RT and Quantachrome Micro Riffler).

1.2 Analytical methods

The moisture content of the dust samples was determined with an OHAUS, type MB 45 moisture analyser. The dust samples were dried at 105°C until the weight of the sample was constant. The particle size distribution of the ash samples was determined using a Fritsch ANALYSETTE 3 PRO laboratory sieve shaker with sieves from 10 mm to 500 µm. The undersize material of the 500 µm sieve was analysed using a Sympatec, type HELOS/RODOS laser diffraction instrument with dry sample dispersion. The calibration of the instrument was verified with a SiC-P600'06 standard from Sympatec. The target value for the mass median diameter x_{50} is 25.59 µm and the acceptable range is 24.82 µm to 26.36 µm. The measured value for the x_{50} was 25.64 µm.

The density of the ashes ρ_S (particle density) was determined according to EN ISO 8130-3 (European Committee for Standardization, 2011). The mass and the volume of a test portion of ash was determined using a 100 cm³ liquid displacement pyknometer. N-heptane (density: 0.681 g/cm³) was used for the displacement of the air. The bulk density ρ_B of the ash samples was determined according to EN ISO 60 (European Committee for Standardization, 1999). For the measurement 120 cm³ of the powder stored in a funnel flow by gravity into the coaxial 100 cm³ measuring cylinder. The volume of the certified measuring cylinder is 100±0.5 cm³ and the precision of the balance was ±0.01 g. The excess material is removed by drawing a straight blade across the top of the cylinder. The voidage was calculated as $1 - \rho_B / \rho_S$.

The angle of repose can be used as a flowability indicator for bulk solids and powders. It was measured according to ISO 4324 (International Organization for Standardization, 1977). For the measurement a cone of material is obtained by passing the powder through a special funnel placed at a fixed height above a completely flat and level circular plate. The base angle of the cone is calculated from the diameter of the base plate and the height of the cone. The reproducibility of the measurements was ± 1°.

The yield locus for the ash samples was determined using a Schulze RST-XS ring shear tester with a 30 cm³ shear cell. The test procedure was conducted in accordance with ASTM D 6773 (2008) at four values of the normal stress (600 Pa, 2,000 Pa, 6,000 Pa and 20,000 Pa). A quantitative characterization of the flowability of a bulk solid is possible with the factor ff_c which is calculated as the ratio of the consolidation stress σ_1 and the unconfined yield strength σ_c. The flow category can be in the range from not flowing with $ff_c < 1$ to free flowing with $ff_c > 10$ (Schulze, 2008). Other results obtained in the shear test are the effective angle of internal friction and the bulk density, both as a function of the stress. The kinematic angle of

wall friction with structural steel S235JR (1.0038) was determined using a shear cell where the bottom ring was formed by a sample of this material. Details on the performance of a shear tests can be found elsewhere (Lanzerstorfer, 2015a). The calibration of the shear tester was verified at a normal stress of 3,000 Pa at pre-shear using the certified reference material BCR-116 from the Community Bureau of Reference (Limestone Powder), which was also used in a round robin test on ring shear testers (Schulze, 2011). The measured values of the shear stress were in the range of the reported mean shear stress $\tau m \pm 0.6$ times the reported standard deviation s.

All chemical analyses were determined by testing each sample in duplicate. In the results the average values are presented. The average relative standard deviation calculated from the duplicate measurements was 5.6%. For the determination of the concentration of metals and sulphate in the ashes the solid samples were dissolved by aqua regia digestion according to ISO 11466 (International Organization for Standardization, 1995) prior to analysis. For determination of the Cl^- and NO_3^- concentration the ash samples were leached in deionized water. The concentrations of Na, K, Ca, Mg, Cl^-, NO_3^-, PO_4^{3-} and SO_4^{2-} were measured by ion chromatography (Dionex ICS-1000 system). The other metals were measured by inductively-coupled plasma optical emission spectroscopy (Horiba Jobin Yvon Ultima 2 system). The details of the analytical methods can be found elsewhere (Lanzerstorfer 2015b). The concentration of Si was analysed gravimetrically according to ISO 439 (International Organization for Standardization, 1994). The total carbon (TC) content of the dusts was determined using an Elementar Analysensysteme LiquiTOC system with a solids material extension. By combustion with air organic and inorganic carbon is transformed into CO_2 which is subsequently analysed.

2 Results and discussion

2.1 Physical properties

The particle size distributions of the ashes are shown in **Fig. 1**. For the finer fraction the distributions are very similar for all three ashes. On the coarse end the size distributions of the bottom ash and the mixed ash extend to particle sizes of several mm while the maximum particle size of the cyclone fly ash is approximately 300 µm. The mass median diameters of the fly ashes and the other physical properties are summarized in **Table 1**. In contrast to cyclone fly ash from forest residue combustion plants the cyclone fly ash was somewhat coarser (Lanzerstorfer, 2014a, 2014b).

The density of the *Miscanthus* ashes varied in a small range. The average density of the ashes was 2,230 ± 35 kg/m³. This is considerably lower than the density of ashes from forest residue combustion but similar to the density of ashes from straw combustion (van Loo and Koppejan, 2008). The bulk density of the cyclone fly ash was also much lower than the bulk density of the bottom ash and the mixed ash. It was in the range of the bulk density reported for cyclone fly ash from straw combustion while the bulk density of the bottom ash was between those reported for wood ash and for straw ash (van Loo and Koppejan, 2008). As a result of the low bulk density the voidage of the cyclone fly ash was much higher.

Fig. 2 shows the dependence of the bulk density of the ashes on the consolidation stress measured in the shear tests. The density of all ashes increased with the increasing consolidation stress. When the axis for the consolidation stress is in the logarithmic scale the measured values for the density almost follow a straight line. In the diagram also the values for the bulk density measured according to EN ISO 60 [16] are shown at a consolidation stress of 1.0 kPa. These values fit quite well to the density function.

Table 1 Physical properties of the ashes

		A_{mixed}	B_{bottom}	$B_{cyclone}$
Moisture	%	0.8	0.9	3.7
Density	kg/m³	2,270	2,230	2,200
Bulk density	kg/m³	780	580	190
Mass median diameter d_{50}	µm	86	123	52
Voidage	-	0.66	0.73	0.91
Angle of repose	°	49	48	52

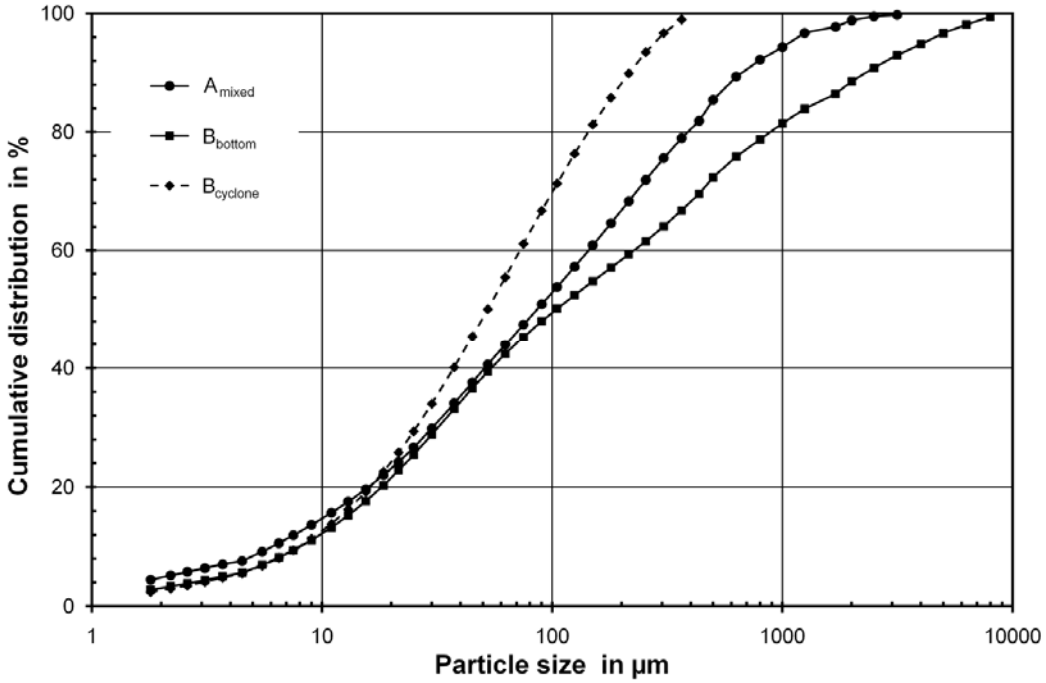

Fig. 1 Particle size distribution of the ashes

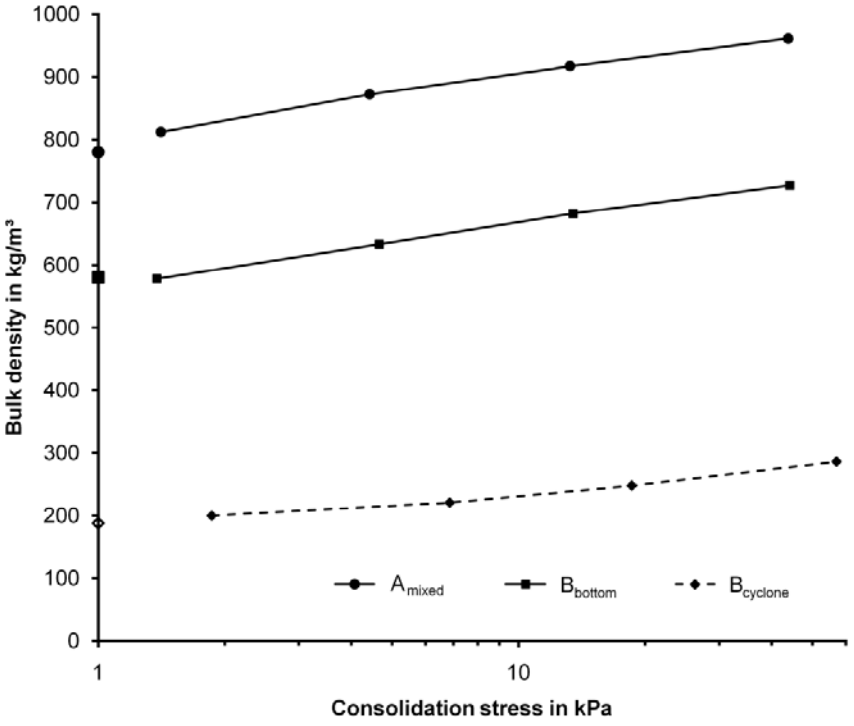

Fig. 2 Bulk density of the ashes as a function of the consolidation stress

The angles of repose were in a small range from 48° to 52°. Therefore, the corresponding flowability category is “poor/cohesive” for all three ashes (Stanley-Wood, 2008). The value of the angle of repose for the cyclone fly ash is similar to those of fly ashes

from the combustion of other biomass (Lanzerstorfer, 2015b) while the value for the bottom ash is much higher than those reported for the bottom ash from forest residue combustion (Lanzerstorfer 2014b). Similar results for the flowability characterization were obtained in the shear tests. The results for the flowability are shown in the left of **Fig. 3**. The flowability improves with increasing stress. When both axes are in the logarithmic scale the measured values for the ff_c almost follow a straight line. For the lower values of the consolidation stress the flowability ff_c was in the range from 2 to 4. This corresponds with a flowability category of “cohesive” (Schulze, 2008).

At higher values of the consolidation stress the flowability of the bottom ash and the mixed ash improved to “easy flowing”, thus reaching nearly the flowability reported for forest residue combustion bottom ash (Lanzerstorfer, 2014b). The flowability behaviour of the cyclone fly ash was similar to those reported for cyclone fly ash from forest residue combustion, only the ff_c was somewhat lower (Lanzerstorfer, 2014b).

In the right of **Fig. 3** the effective angles of internal friction and the wall friction angles are shown as a function of the normal stress. Generally, the effective angle of internal friction was higher for the cyclone fly ash. For all ashes, the effective angle of internal friction decreased with increasing normal stress. For the wall friction angles similar observations were made: with increasing wall normal stress the wall friction angles decrease. But in contrast to the effective angles of internal friction the wall friction angles for the cyclone fly ash were a bit lower than for the bottom ash and the mixed ash.

In summary, it can be noted that the flow relevant properties of the ashes from *Miscanthus* combustion are quite similar to those from combustion even though the particle size and the values for density showed noticeably differences. Thus, the design of dust handling and storage equipment for *Miscanthus* combustion plants can be the same as for the wide spread wood combustion plants.

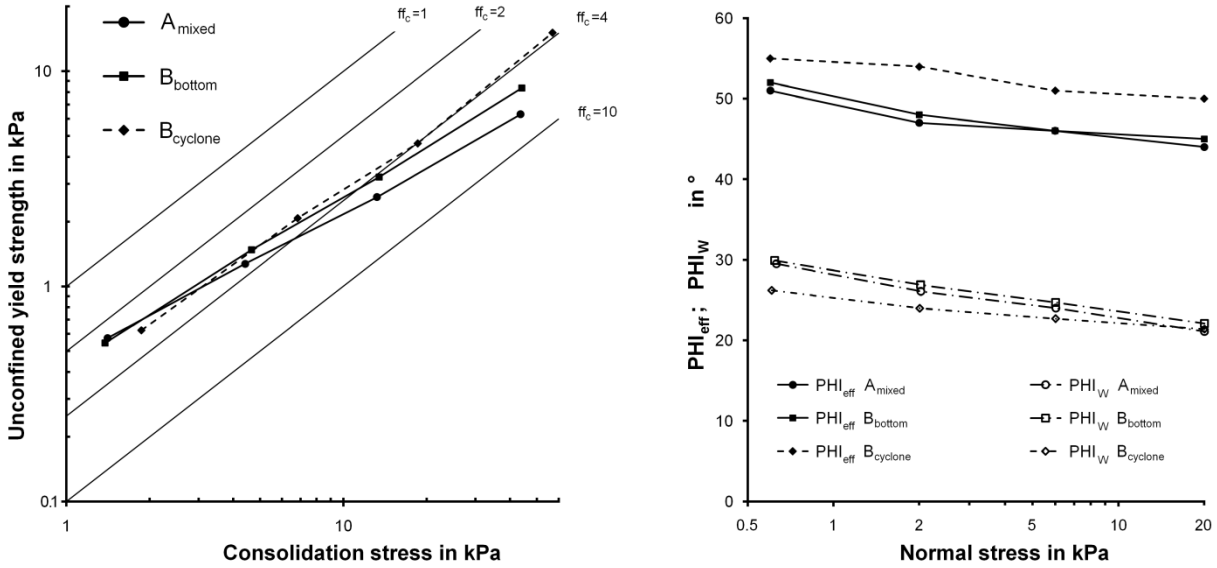

Fig. 3 Flowability of the ashes as a function of the consolidation stress (left) and effective angle of internal friction and wall friction angle (right)

2.2 Chemical composition

The total carbon (TC) content and the concentrations of the main ash forming components are summarized in **Table 2**. There was still some TC in the bottom ash and the mixed ash. This was also reflected in the dark grey to black colour of these ashes. In the cyclone fly ash the TC content was significantly higher. The value of 12.6% is much higher than in typical cyclone fly ash from forest residue combustion plants but in the same range as reported for a small straw combustion plant (Lanzerstorfer, 2014a).

Another significant difference between the cyclone fly ash and the bottom ash was found in the Cl^- concentrations. It was about ten times higher in the cyclone fly ash compared to the bottom ash. The same effect but less pronounced was found for S. This can be explained by the higher volatility of Cl^- and S components. A similar difference is also found in the ashes from forest residue combustion (Pöykiö et al., 2009).

Considering the fact that the mixed ash from plant A is a mixture with bottom ash as the major component and cyclone fly ash as the minor component the overall composition the ashes from plant A and B do not differ very much. Increased concentrations of the ash from plant A were found for Ca, Mg and S while in the ash from plant B the Al and Si content was higher.

Although the N content of the whole *Miscanthus* plant is approximately 0.7% (Obernberger et al., 2006) practically no NO_3^- was found in the ash samples. This means that practically all N contained in the plant material leaves the combustion process in the gaseous phase.

In ashes produced in laboratory analysis from *Miscanthus* plant material the concentrations of K, Cl^- and S were considerably higher (Baxter et al., 2012; Michel et al., 2012; Obernberger et al., 2006). This difference might be explained by the fact that the finest fly ash fraction is not collected by the cyclone of the de-dusting system in the *Miscanthus* combustion plant while K, Cl^- and S are especially enriched in the finest fractions of the fly ash from biomass combustion (Lanzerstorfer, 2011, 2015c). Therefore, the bottom ash and the cyclone fly ash are depleted in these components.

Table 2 Concentrations of main components in the ashes (all concentrations in g/kg based on dry weight)

	A_{mixed}	B_{bottom}	$B_{cyclone}$	Baxter et al. (2012)[1]	Michel et al. (2012) [1]	Obernberger et al. (2006)[2]
TC	22.8	14.4	126			
Cl^-	3.25	1.92	19.9	72	37	50
NO_3^-	0.1	0.1	0.2			
P_2O_5	16.1	11.5	12.5	40	33	40
SO_3	18.7	5.0	19.4	37		125
Na_2O	0.64	0.40	0.43	5	1	
K_2O	115	107	92.0	283	378	251
Al_2O_3	14.9	41.2	91.1	3		
BaO	0.96	0.95	1.16			
CaO	100	33.3	37.7	63	59	92
Fe_2O_3	30.3	25.9	61.0	2		4
MgO	42.9	13.9	17.3	59	28	36
MnO	8.83	1.39	2.36			
SiO_2	599	719	509	393	467	
SrO	0.58	0.43	0.46			
TiO_2	0.85	1.03	2.45			
Sum	975	977	993			

[1] Calculated average of reported values
[2] Calculated from reported ash content and concentration data for the plant

The concentrations of heavy metals and other minor ash components are summarized in Table 3. The measured heavy metal concentrations were below the usual limits for ash utilization as soil conditioner (Bundesministerium für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft, 2011; Emilsson, 2006; Nurmesniemi et al., 2012).

The concentrations of the heavy metals in the bottom ash and in the mixed ash were in a similar range as reported for the concentrations in bottom ash from forest residue combustion plants. Thus, the concentrations were somewhat higher than in the bottom ash from straw combustion (van Loo and Koppejan, 2008). The heavy metals concentrations in the cyclone fly ash were a little higher than in the bottom ash and the mixed ash. Only for Zn significant enrichment was found in the cyclone fly ash. In comparison with cyclone fly ashes from forest residue combustion the measured heavy metal concentrations were considerably lower, but still somewhat higher than the concentrations found in cyclone fly ash from straw combustion (Lanzerstorfer 2104a; van Loo and Koppejan, 2008).

Thus, recycling of the ashes including the fly ashes from *Miscanthus* combustion to the soil is highly recommendable in contrast to the fly ashes from wood combustion plant, which has to be excluded from recycling in many cases because of exceeding some heavy metals limit concentrations.

Table 3 Concentrations of heavy metals and other minor components in the ashes (all concentrations in mg/kg based on dry weight)

	A_{mixed}	B_{bottom}	$B_{cyclone}$	Obernberger et al. (2006)[1]
As	3	13	6	5
B	220	99	193	
Cd	5	2	7	3
Co	8	8	16	
Cr	82	41	90	25
Cu	158	51	90	50
Mo	35	37	43	
Ni	45	23	45	50
Pb	41	35	57	50
Sb	10	10	28	
V	46	48	101	
Zn	659	105	785	250

[1] Calculated from reported ash content and concentration data for the plant

3 Conclusions

The investigation of ashes from combustion plants using *Miscanthus* as fuel revealed some differences and some similarities in the properties of the ashes compared to the well investigated ashes from forest residue combustion and straw combustion.

The particle size of the bottom ash and the mixed ash was in a typical range but the cyclone fly ash was somewhat coarser than cyclone fly ash from forest residue combustion.

The densities of the ashes from *Miscanthus* combustion were similar to those reported for straw ashes and, therefore, significantly lower than the densities of ashes from wood combustion. The measured bulk densities for the bottom ash and the mixed ash were between those reported for wood ash and for straw ash and the bulk density of the cyclone ash was close to that of cyclone fly ash from straw combustion.

The angles of repose for the three ashes were all close to 50°, the corresponding flowability category is “poor/cohesive”. This value compares well with the angle of repose of other biomass combustion fly ash but is significantly higher than reported for bottom ash from forest residue combustion. Similar results for the flowability characterization were obtained in the shear tests. The flowability of all ashes improved with increasing stress, especially the flowability of the bottom ash and the mixed ash.

In the bottom ash and the mixed ash there was still some TC content, but in the cyclone fly ash the TC content was significantly higher. The value of 12.6% is much higher than in typical cyclone fly ash from forest residue combustion plants but it was in the same range as found for a small straw combustion plant (Lanzerstorfer, 2014a).

The Cl^- and the S concentration in the cyclone fly ash were considerably higher compared to the bottom ash. The same effect is known for the ashes from wood combustion.

The overall composition the ashes from plant A and B do not differ very much. Increased concentrations of the ash from plant A were found for Ca, Mg and S while in the ash from plant B the Al and Si content was higher.

The literature values obtained from ashes produced in the laboratory from *Miscanthus* plant material show considerably higher concentrations of K, Cl^- and S. This difference might be explained by the fact that the finest fly ash was not collected by the cyclone of the de-dusting system in the *Miscanthus* combustion plant and K, Cl^- and S are especially enriched in the finest fractions of the fly ashes from biomass combustion.

The measured heavy metal concentrations were below the usual limits for utilization as soil conditioner. The concentrations in the bottom ash and in the mixed ash were similar to those reported for bottom ash from forest residue combustion plants. In the cyclone fly ash the heavy metals concentrations were a bit higher, but only for Zn a significant enrichment was found in the cyclone fly ash. In comparison with cyclone fly ashes from forest residue combustion the measured heavy metal concentrations were considerably lower.

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6.3. Paper 3

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CHEMICAL AND PHYSICAL CHARACTERIZATION OF CYCLONE FLY ASHES FROM FIVE GRATE-FIRED BIOMASS COMBUSTION PLANTS

Christof LANZERSTORFER

School of Engineering/Environmental Sciences, University of Applied Sciences Upper Austria, Stelzhamerstraße 23, A-4600 Wels, Austria, e-mail: c.lanzerstorfer@fh-wels.at

Abstract: The fly ash leaves the combustion zone with the off-gas and is separated from the off-gas by dust separators. For the handling and treatment of fly ash its chemical composition and physical properties are important. Fly ashes from biomass combustion slightly contaminated with heavy metal can be utilized as a soil conditioner, thus closing the nutrient cycles for the soil where the biomass was grown. In this study five cyclone fly ashes from grate-fired bio mass combustion plants were investigated. Most of the fly ashes showed poor flowability, especially the fly ashes with small particle size. The flowability of the fly ash from straw combustion was also poor although this fly ash is rather coarse. This is probably caused by longish remainders of incompletely combusted straw stalks in this fly ash. All fly ashes contain valuable nutrients for the soil. However, in all fly ash samples from wood chip combustion the measured concentrations of Cd and Zn were above the limit concentration. Therefore, these fly ashes cannot be used as soil conditioners. The fly ashes from straw combustion and from palm oil residue combustion were much less contaminated by heavy metals and can be utilized as soil conditioner.

Keywords: biomass combustion, cyclone fly ash, nutrients, heavy metals, physical properties

1. INTRODUCTION

Limited availability of fossil fuels and concerns about climate change caused by the carbon dioxide emissions from fossil fuel combustion cause a continuous rise in combustion of biomass for heat and power generation (European Biomass Association, 2013). Biomass combustion is considered to be almost carbon dioxide neutral because the emissions produced during combustion are offset by the carbon dioxide fixed in the biomass during its growth.

The inorganic constituents from the combusted biomass remain as ash. Some of the ash leaves the combustion zone together with the off-gas as so called fly ash. The amount of fly ash produced depends on the kind of biomass combusted and the type of combustion process. The fly ash usually accounts for about one quarter of the total amount of ash (van Loo & Koppejan, 2008). The fly ash has to be separated from the flue gas in a dust collector. Single stage dust collection by a cyclone or by multi-cyclones is only sufficient for biomass combustion plants which have a higher dust emission limit because of the limited collection efficiency of cyclones, especially for fine particles. In order to comply with low dust emission limits (<20mg/m³ (STP)), a fabric filter or an electrostatic precipitator (EP) is often installed downstream of the cyclone.

The fly ash collected in the cyclones is a bulk material that has to be handled, treated and utilized or disposed of at landfill sites. For the decision about the further fate of the fly ash the chemical composition is essential. In Austria bottom ash and cyclone fly ash from the combustion of chemically untreated biomass can be utilized as soil conditioner on agricultural land and forests if the concentrations of pollutants are below the limit concentrations (Bundes-ministerium für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft, 2011). The recycling of biomass ashes to the forest soil is proposed to help to close the nutrient cycles for the soil where the biomass was grown (Hallenbarter et al., 2002; Moilanen et al., 2002; von Wilpert et al., 2014). In other European countries the limit concentrations for biomass fly ash utilization can be different. The limit concentrations for Austria and for Scandinavian countries are summarized in table 1.

For the design of the storage bins and other fly ash handling equipment the physical properties of the ash are important. For example, in the calculation of the storage capacity of bins the bulk density of the fly ash and its angle of repose are required. The angle of repose can also be used for a rough categorization of the flowability of the material (Stanley-Wood, 2008).

In the literature only few data are available for biomass cyclone fly ashes. Some data on the chemical composition of cyclone fly ashes were reported by Hansen et al., (2001), Ingerslev et al., (2011), Pöykiö et al., (2009), Rönkkömäki et al., (2008) and van Loo & Koppejan (2008). Data of the density of cyclone fly ash were published by van Loo & Koppejan (2008).

The aim of this study was to characterize cyclone fly ashes from five different grate-fired biomass combustion plants. For this purpose the chemical composition of the fly ashes was analyzed and several physical properties were measured. Additionally the suitability of the different cyclone fly ashes as soil conditioner was verified with respect to the Austrian and Scandinavian limits.

2. MATERIAL AND METHODS

2.1. Materials

Cyclone fly ashes from five grate-fired biomass combustion plants were collected for this study. An overview of the thermal capacities of the plants, the type of cyclone installed and the combusted biomass is given in table 2. The fly ash samples of approximately 2dm³ were collected at the discharge system of the dust collectors. The volume of the ash samples was reduced to a volume suitable for the various laboratory tests using sample dividers which were applied repeatedly (Retsch PT100, Quantachrome Micro Riffler).

2.2. Methods

The moisture content of the ash samples was determined gravimetrically. The samples were dried at 105°C for one hour. The particle size distribution was measured using a Sympatec, type HELOS/RODOS laser diffraction instrument with dry sample dispersion. The density (particle density) was determined according to ÖNORM EN ISO 8130-3 (Österreichisches Normungsinstitut, 2011).

Table 1. Heavy metal concentration limits for utilisation of ash from biomass combustion as a soil conditioner in forests and agriculture; in mg/kg d.w.

	Austrian guideline[1] (Bundesministerium für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft, 2011)		Finland cited in Nurmesniemi et al. (2012)	Sweden cited in Emilsson (2006)	Denmark cited in Haglund (2008)
	A	B			
As	20	20	40	30	
Cd	5	8	25	30	5 / 15[2]
Cr	150	250	300	100	100
Cu	200	250	700	400	
Ni	150	200	150	70	30 / 60[3]
Pb	100	200	150	300	120
Zn	1200	1500	4500	7000	
V				70	
B				500	
Hg			1.0	3	0.8

[1] if the concentrations are below limits according to A, no soil analysis is required
[2] left Cd limit for straw ash, right Cd limit for wood ash
[3] dosage limit for values between 30–60 mg/kg

Table 2. Biomass combustion fly ashes investigated

	Thermal capacity in MW_{th}	Type of cyclone	Combusted biomass
Plant A	0.6	Single cyclone	Wood chips, forest residue, 60% softwood
Plant B	1.1	Single cyclone	Wood chips, forest residue, 60% softwood
Plant C	5.0	Multi-cyclone	Wood chips, forest residue, 80% softwood
Plant D	4.0	Multi-cyclone	Residue from palm oil production (empty fruit bunches)
Plant E	2.2	Single cyclone	Wheat straw

This method is based on a determination of the mass and the volume of a test portion using a liquid displacement pyknometer. The capacity of the pyknometers used was approximately 105cm³ and n-heptane (density: 0.681g/cm³) was used for displacement of the air. The bulk density of the samples was determined according to ÖNORM EN ISO 60 (Österreichisches Normungsinstitut, 1999). The measurement is carried out in the following way: the powder stored in the funnel (120cm³) flows by gravity into the coaxial 100cm³ measuring cylinder when the bottom cover of the funnel is removed. The excess material is removed by drawing a straightedge blade across the top of the vessel.

The angle of repose was determined according to DIN ISO 4324 (Deutsches Institut für Normung, 1983). The measurement is carried out in the following way: a cone of material is obtained by passing a given volume of the powder through a special funnel placed at a fixed height above a completely flat and level plate. The base angle of the cone is calculated from the diameter of the base plate and the height of the cone. The angle of repose can be used as a flowability indicator to categorize the flowability of bulk solids and powders. The categories according to the United States Pharmacopeial Convention USP 29-NF24 (as cited in Stanley-Wood, 2008) are “excellent” for an angle of repose of 25°-30°, “good/free flow” for 31°-35°, “fair” for 36°-40°, “passable” for 41°-45°, “poor/cohesive” for 46°-55°, “very poor/very cohesive” for 56°-65° and “very very poor/ non-flow” if the angle of repose is greater than 66°.

All chemical analyses were determined by testing each sample in duplicate. In the results the average values are presented. The carbon content (TC) was determined with a LiquiTOC system from Elementar Analysensysteme. By combustion with air the carbon is transformed into CO_2 which is subsequently analysed. For the determination of the concentration of metals, sulphur and phosphor in the fly ash the solid samples were dissolved by aqua regia digestion (International Organization for Standardization, 1995) prior to analysis. The metals were measured by inductively coupled plasma optical emission spectroscopy (ICP-OES). For the analysis an ICP-OES system Ultima 2 from Horiba Jobin Yvon was used. The concentration of mercury was analysed using cold vapour atomic absorption spectrometry (CV-AAS) according DIN EN ISO 12846 (Deutsches Institut für Normung, 2010). The concentration of alkali and earth alkali metals, sulphate and phosphate was measured by ion chromatography (IC), (Dionex ICS-1000 system; cations: analytical column IonPac® CS12A 4x250mm; eluent: 20mM methanesulfonic acid, flow rate 1.0ml/min; anions: analytical column IonPac® AS14A 4x250mm; eluent: 8.0mM sodium carbonate / 1.0mM sodium hydrogen carbonate; flow rate 1.0ml/min).

Chloride and nitrate cannot be analysed after digestion by aqua regia. However, nearly all components containing these ions are highly soluble in water. Therefore, for the determination of the chloride and nitrate concentration in the samples, approximately 2grams of a sample were leached in 200ml of deionized water for one hour. To aid the leaching process the samples were placed in an ultrasonic bath. After leaching the remaining solids were separated by filtration. The concentration of chloride and nitrate was measured by IC.

3. RESULTS AND DISCUSSION

The fly ash particle size distributions are shown in figure 1. It is obvious that there are considerable differences between the cyclone fly ash samples investigated. All fly ashes from wood chip combustion (plant A, B and C) show a similar course of the size distribution curve.

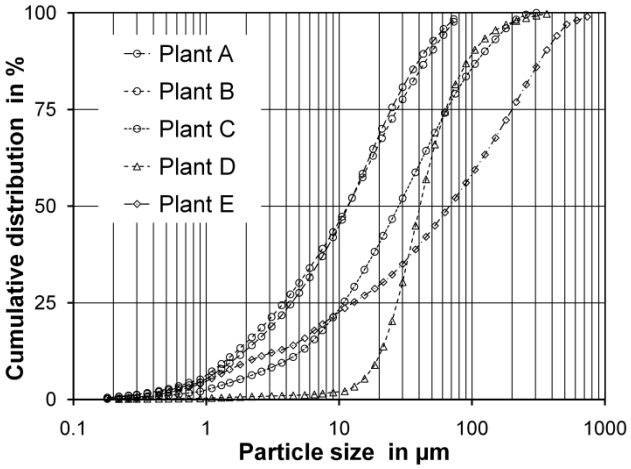

Figure 1. Particle size distribution of various cyclone fly ashes.

However, the size distribution of the fly ash from plant C is a little coarser. The spread of the distribution, defined as the quotient of x_{95} and x_5 (Rumpf, 1990) ranges from 61 to 98. The other fly ashes are coarser and the shape of their size distribution function is different. Fly ash D has a very narrow particle size distribution whereas fly ash E has a wide size distribution. The mass median diameters and the spreads of the size distribution of the various fly ash samples are summarized in table 3.

The results for further physical parameters are also shown in table 3. The humidity of most fly ash samples was far below 1%. In the straw combustion

fly ash the water content was a bit higher.

The density of the fly ashes varies between 2270 kg/m³ and 2800 kg/m³. The higher values were found for the fly ashes from wood chips combustion whereas the lowest value was measured for the fly ash from straw combustion. The bulk density of the fly ashes varies within a wide range. The lowest value of 190 kg/m³ was found for the straw combustion fly ash while the fly ash from the palm oil residue combustion reaches a bulk density of about 900 kg/m³. The results of the density measurements for fly ash from wood chips and straw combustion correspond well with the data presented by van Loo & Koppejan (2008).

The angle of repose is in the range of 35° to 53°. The corresponding flowability categories are "good/free flow" for the fly ash from plant D and "poor/cohesive" for all other fly ashes. In figure 2 the ratio of the bulk density to the density is shown as a function of the angle of repose. The worse the flowability of the material expressed in the form of the angle of repose, the lower is the ratio of bulk density to density. This can be explained by the reduced ability of poorly flowing material to fill gaps between the particles. For a free flowing material with a typical porosity of 0.4 the ratio of bulk density to density would be 0.6. The fly ash from wood chips combustion showed a tendentiously higher ratio than the fly ash from other biomass.

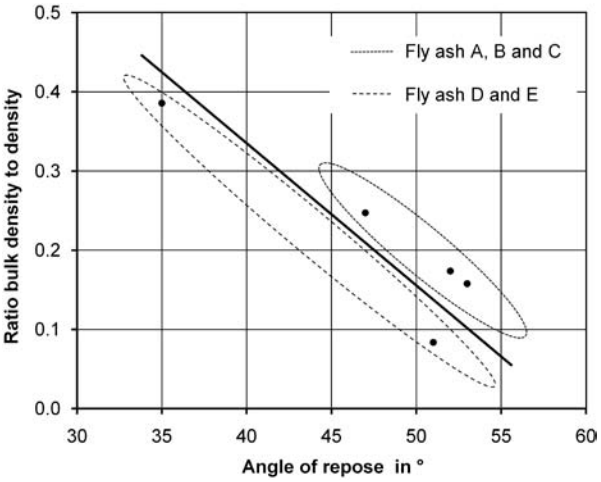

Figure 2. Density ratio versus angle of repose

The good flowability of fly ash D results from its relatively large particle size, the small spread of the size distribution and the close to spherical particle shape (Fig. 3).

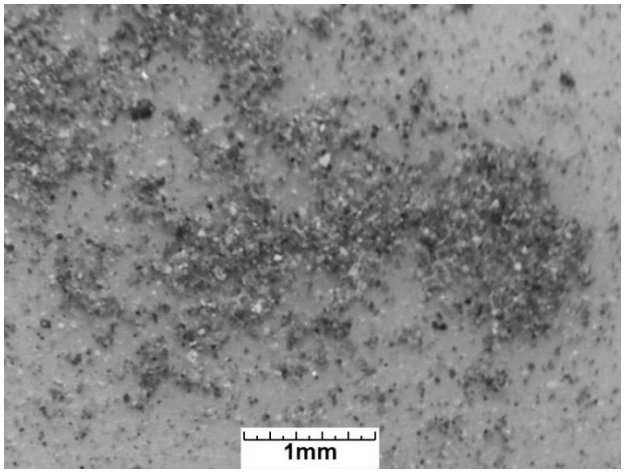

Figure 3. Microscopic image of the fly ash from plant D

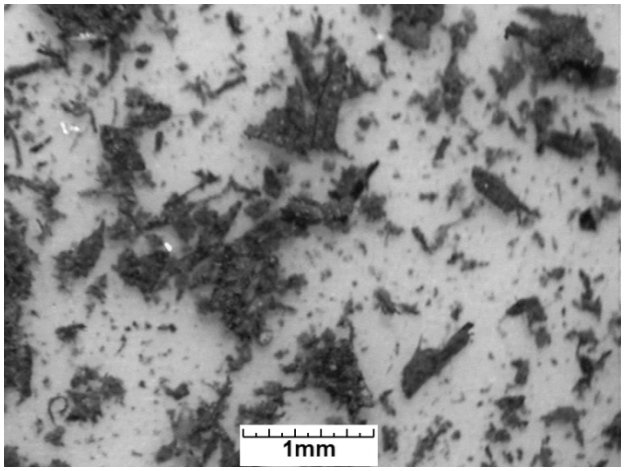

Figure 4. Microscopic image of the fly ash from plant E

The average particle size of the fly ash from plant E is even larger, however, the spread of the size distribution is wide and the bigger particles are far from being spherical (Fig. 4). It has to be mentioned that these large particles are over-represented by number in the shown image. The bigger particles are presumably remainders of incompletely combusted straw stalks.

Table 3. Physical properties of the cyclone fly ashes

		Fly ash A	Fly ash B	Fly ash C	Fly ash D	Fly ash E
Humidity	%	0.6	0.5	0.4	0.4	3.3
Density	kg/m³	2750	2800	2670	2320	2270
Bulk density	kg/m³	480	445	660	895	190
Mass median diameter d_{50}	µm	11.7	11.6	27	41	68
Spread of the size distribution	-	61	73	98	10	440
Angle of repose	°	52	53	47	35	51

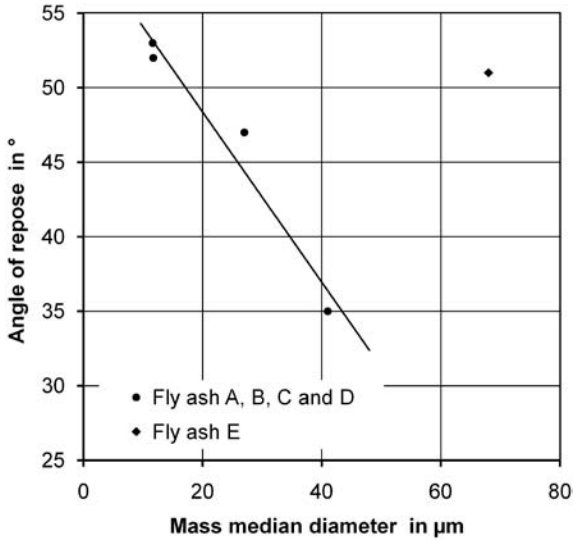

Figure 5. Angle of repose versus mass median diameter

The total carbon (TC) content of the oversize material obtained by sieving the fly ash with a 200µm sieve was 21%, which is nearly twice the average TC content of the fly ash. The effect of these irregular, longish particles can also be seen in a diagram where the angle of repose is shown as a function of the particle size (Fig. 5).

For the fly ashes A to D a good correlation between the angle of repose and the mass median diameter was found. Deviating from this correlation the angle of repose of fly ash E is comparatively much too high.

The results of the chemical analysis are summarized in table 4. The total carbon content of the fly ash characterizes the completeness of the combustion in the furnace. The average value for the fly ashes from wood chips combustion is 2.0±0.5%. This is in the range of the published values (van Loo & Koppejan, 2008). In the straw combustion fly ash sample the total carbon content was much higher (13.1 %).

For the utilization of the cyclone fly ash as a soil conditioner two items are important: a high content of nutrients, especially Ca, Mg, K, P and N, and heavy metal concentrations below the limit concentrations. The average concentration of Ca, Mg and PO_4^{3-} in the fly ash from wood chips combustion was 255±16g/kg, 16.6±1.6g/kg and 51±5g/kg, respectively.

Table 4 Chemical composition of the cyclone fly ashes (all concentrations based on dry weight); measured values exceeding the Austrian limit concentration for utilization of the fly ash as soil conditioner are printed in bold type

		Fly ash A	Fly ash B	Fly ash C	Fly ash D	Fly ash E
TC	%	1.8	1.7	2.7	1.7	13.1
Cl^-	g/kg	10.7	8.9	10.2	26	122
NO_3^-	g/kg	0.6	0.2	0.7	0.6	0.3
PO_4^{3-}	g/kg	54	55	46	36	22
SO_4^{2-}	g/kg	72	60	84	28	47
Na	g/kg	1.6	1.7	2.8	0.6	2.2
K	g/kg	89	88	88	103	275
Mg	g/kg	15	18	16	10	9.2
Ca	g/kg	255	271	240	191	39
Al	g/kg	6.8	7.9	11.8	9.0	1.5
Fe	g/kg	5.1	5.8	12.2	11.8	9.6
Mn	g/kg	10.1	10.8	12.3	0.4	0.2
As	mg/kg	9	11	15	17	8
B	mg/kg	546	547	583	105	21
Ba	mg/kg	355	360	244	35	257
Bi	mg/kg	132	141	135	101	4
Cd	mg/kg	**38**	**30**	**108**	1	2
Co	mg/kg	39	39	50	< 25	< 25
Cr	mg/kg	33	39	67	13	22
Cu	mg/kg	35	51	47	< 5	< 5
Hg	mg/kg	0.22	0.23	0.13	< 0.05	0.21
Mo	mg/kg	78	31	33	< 5	< 5
Ni	mg/kg	27	30	48	15	< 5
Pb	mg/kg	157	92	247	27	< 25
Sb	mg/kg	15	12	10	10	< 25
Sr	mg/kg	428	460	663	115	97
V	mg/kg	43	40	43	43	< 25
Zn	mg/kg	**2560**	**2000**	**4780**	198	145

In the straw fly ash the concentration of Ca especially is much lower and also the PO_4^{3-} concentration is less than half. On the other hand, the K concentration in straw fly ash is 275g/kg, which is about three times the concentration measured for the wood chips fly ash. The nutrient content of the fly ash from the palm oil residue combustion is between that of the fly ash from wood combustion and that of the fly ash from straw combustion. The concentration of NO_3^- is very low in all fly ash samples.

The measured concentrations of the nutrients in fly ash from wood chips combustion compare quite well with the data reported by Hansen et al. (2001), Ingerslev et al. (2011), Pöykiö et al., (2009) and van Loo & Koppejan (2008). In the fly ash from straw combustion the concentration of K was more than twice the concentration reported by van Loo & Koppejan (2008), whereas the concentrations of the other nutrients did not differ that much.

There is a higher concentration of most heavy in the fly ash samples from wood combustion (plant A, B and C) compared to the fly ashes from straw and palm oil residue combustion. In all three ash samples from wood combustion the Cd concentration is above the Austrian limit concentration and also above the limit concentrations in Finland and Denmark, which are substantially higher than the Austrian limit. For Sweden the limit for Cd is still higher but even there only the fly ash sample from plant B would fulfil the requirements. In the fly ashes from straw and palm oil residue combustion the Cd concentration is very low. The Zn concentrations of the wood fly ashes are also above the Austrian limit. However, only the fly ash from plant C exceeds the Finnish limit and no fly ash exceeds the Swedish limit. All other heavy metal concentrations are below the given limits.

For the concentrations of the heavy metals in cyclone fly ash from wood chips combustion considerable differences are found in the published studies. The values measured in this study are in the range of the published values. The measured heavy metals concentrations for the straw combustion ash fit very well with the data published by van Loo & Koppejan (2008).

Thus, none of the investigated fly ashes from wood combustion can be utilized as soil conditioner but have to go into landfills or must be treated to reduce the concentrations of Cd and Zn. The fly ash from straw combustion and the fly ash from palm oil residue are much less contaminated by heavy metals and therefore can be utilized as soil conditioner.

4. CONCLUSIONS

Five cyclone fly ashes from grate-fired biomass combustion plants were investigated. The three fly ashes from wood chips combustion are quite similar in physical properties and in chemical composition. The fly ash from palm oil residue combustion and the fly ash from straw combustion are quite different. Most of the fly ashes exhibit poor flowability. The angle of repose increases with decreasing particle size. An exception from this correlation is shown by the fly ash from straw combustion which is probably caused by the longish remainders of incompletely combusted straw stalks.

All fly ashes contain valuable nutrients for the soil, especially K, Ca, Mg and PO_4^{3-}. However, the concentration of the various nutrients depends on the type of biomass combusted. In the fly ash from wood chips combustion the measured concentrations of Cd and Zn were above the limit concentration. Therefore, these fly ashes cannot be used as soil conditioners. The fly ashes from straw and from palm oil residue combustion were much less contaminated with heavy metals and therefore can be utilized as soil conditioner.

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6.4. Paper 4

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Cyclone fly ash from a grate-fired biomass combustion plant: Dependence of the concentration of various components on the particle size

Christof Lanzerstorfer

School of Engineering/Environmental Sciences, University of Applied Sciences Upper Austria, Stelzhamerstraße 23, A-4600 Wels, Austria

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Particle size

ABSTRACT

In this study cyclone fly ash from a grate-fired combustion plant using forest residues as fuel was split into particle size classes with mass median diameters of 2.0 μm, 4.3 μm, 9.1 μm, 18 μm and 43 μm by use of an air classifier. The particle classes were analysed for total carbon, Na, K, Mg, Ca, Sr, Ba, Ti, V, Cr, Mo, Mn, Fe, Si, Co, Ni, Cu, Zn, Cd, Hg, B, Al, Pb, As, Sb, Bi, Cl^-, NO_3^-, PO_4^{3-} and SO_4^{2-} and the size dependence of the concentrations c was modelled using the relation $c \sim 1/d^N$. For several components a considerable dependence of the concentration on the particle size was observed. Increasing concentration with decreasing particle size was found for K, Bi, Cd, Cu, Hg, Pb, Zn and for Cl^-, NO_3^- and SO_4^{2-}. The metals Al, As, Ba, Fe, Si, Ti and V showed the opposite behaviour. Other components, including TC, Ca, Mg, PO_4^{3-}, Na and Mn showed no size-dependence. Investigation of single particles by scanning electron microscope in combination with energy-dispersive X-ray spectroscopy revealed that the analysed concentrations are representative for the particle classes only, the composition of single particles in a particle class can deviate considerably.

1. Introduction

Concerns about climate change caused by the carbon dioxide emissions from the combustion of fossil fuels cause a continuous rise in the combustion of biomass for heat and power generation [1]. Biomass is considered to be an almost carbon dioxide neutral fuel because the carbon dioxide emissions produced during its combustion are compensated by the carbon dioxide fixed in the biomass while it grows. In the combustion process most of the inorganic constituents of the biomass remain as ash. The finer ash fraction leaves the combustion zone as so called fly ash together with the off-gas. The amount of fly ash produced depends on the kind of biomass combusted. Also the type of combustion process influences the fly ash production. The fly ash is separated from the off-gas in dust separators like cyclones, electrostatic precipitators or fabric filters. Because of the limited collection efficiency of cyclones single stage dust collection by a cyclone is only sufficient for biomass combustion plants with higher dust emission limits. In order to comply with low dust emission limits two-stage off-gas cleaning systems are often applied where an electrostatic precipitator or a fabric filter is installed downstream of the cyclone. In grate-fired biomass combustion the cyclone fly ash accounts for 10%–35% of the total amount of ash produced [2].

For the decision about the further use of the ash the chemical composition is essential. In Austria cyclone fly ash as well as bottom ash from the combustion of chemically untreated biomass can be utilized as soil conditioner on agricultural land and forest soil if the concentrations of several heavy metals are below the limit concentrations, whereas it is not allowed to use filter fly ash that way because in the finer fly ash usually the heavy metal concentrations are higher [3]. The recycling of biomass ashes on the forest soil is proposed to help to close the nutrient cycles for the soil where the biomass was grown [4,5]. In Scandinavian countries fly ash from biomass combustion is also recycled on the soil. However, the heavy metal limit concentrations vary from country to country [6,7]. Another way proposed for the utilization of biomass fly ash is its use in cement-based material [8]. Biomass fly ash can be used to replace some cement in cement-based mortars. However it is necessary to control the carbon, chloride and sulphate content of the employed biomass fly ashes.

The chemical composition of fly ash from grate-fired biomass combustion has been investigated in some studies, e.g. [9–13]. In several other studies the fly ash investigated originated from other combustion systems like fluidized bed systems or the combustion system is not really specified [14–17]. But there is not very much information available on the dependence of the composition of the fly ash on the particle size. The distribution of heavy metals in the four size fractions of a cyclone fly ash originating from a grate-fired boiler combusting forest residue was investigated in one study [18]. In this study a vibrating sieve shaker was used to split the fly ash into the particle classes 250–500 μm, 125–250 μm, 75–125 μm and <75 μm. Because of the equipment used the separation was limited to the coarse size cuts. In two other studies the size dependence of the composition of fly ash from fluidized-bed combustion of biomass was investigated. In both studies a vibrating sieve shaker was used for size fractionation. Another study investigated the distribution of heavy metals and other components in three size

E-mail address: c.lanzerstorfer@fh-wels.at.

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Table 1
Data of the particle classes produced.

Dust particle class	Mass fraction in %	Mass median diameter d_{50} in μm
Loss	7.0	–
1	9.9	1.93
2	15.8	4.25
3	20.1	9.07
4	31.5	17.8
5	15.7	43.3

fractions of the fly ash from a bubbling fluidized-bed combustor burning eucalyptus and pine bark [19]. The mass median diameter of the fly ash investigated was 34 μm. The size classes produced were 200–500 μm, 50–200 μm and 20–50 μm. A third study investigated fly ash from a fluidized-bed boiler that combusts forest residues [20]. The particle classes produced by sieving were 125–250 μm, 74–125 μm and <74 μm. In all three studies only a limited number of components were analysed in the various size fractions produced.

The distribution of Cd in various size fractions was studied for a fly ash from a circulating fluidized bed boiler using willow wood chips as fuel [21]. In a series of different separation steps — dry sieving at 45 μm, wet sieving at 25 μm after suspension of the solids in water and subsequently sedimentation with a cut size of 5 μm to separate the finer fraction of biomass fly ashes into size classes. The size class <5 μm was separated into two size classes, 0 - 2.5 μm and 2.5 - 5 μm, in a centrifugal SPLITT fractionation cell. Besides the complexity of the procedure the water required for this process can dissolve various components thereby reducing the concentration of these components in the fly ash. In another study cyclone fly ash from a grate-fired biomass combustion plant using bark as fuel was separated into five size fractions by wet sieving in acetone and analysed them for Cd and Zn. The size fractions were >60 μm, 40–60 μm, 20–40 μm, 5–20 μm and <5 μm.

In some studies cascade impactors were used to determine the distribution of some components directly in the size fractions of the fly ash [23,24]. These studies focus especially on the submicron particle size range. Only in one study an air classifier was used to split a biomass fly ash sample into size classes for analysis of the size dependent distribution of some components [25]. The advantage of an air classifier is its capacity of dry fractionation of fine-grained material at small cut size.

The aim of this study was to investigate the size-dependence of a broad range of components (alkali, alkali earth and heavy metals, anions and total carbon (TC)) in fly ash from a grate-fired biomass combustion plant. For this purpose a cyclone fly ash sample was split into several size fractions using a laboratory air classifier. The chemical composition of the fly ash and the particle classes produced were analysed and the dependence of the concentration, c, on the particle size, d, was described by a simple relation $c \sim 1/d^N$ according to [26].

2. Material and methods

2.1. Materials

The cyclone fly ash sample investigated in this study was collected from a grate-fired biomass combustion plant. The combusted biomass was wood chips and forest residue in a mixture of hardwood and softwood with an estimated fraction of softwood of about 60%. The thermal capacity of the plant is 550 kW. The combustion temperature in the furnace was about 900 °C. A fly ash sample of approximately 2 dm^3 was collected at the discharge system of the cyclone. In a first step, the contents of the dust container into which the dust is discharged from the cyclone, were homogenized manually. In a second step, dust samples of about 200 cm^3 each were taken with a sample blade at ten different, randomly selected locations in the dust container and filled into the sample container. As the dust container was emptied the last time one week before the sample was taken, the collected fly ash sample is a one week average. In the laboratory the volume of the collected ash sample was reduced to a volume suitable for the various laboratory tests using sample dividers (Haver & Boecker HAVER RT, Quantachrome Micro Riffler). The sample dividers were applied repeatedly.

2.2. Methods

A laboratory classifier 100 MZR from Hosokawa Alpine was used for sequential dry classification of the fly ash sample. In the first classification step the finest size fraction, particle class 1, was separated from the bulk and collected at the outlet of the classifier. The remaining coarse fraction was used as feed material in the second classification step, in which the classifier was operated at reduced speed to shift the cut size diameter of the classification to a coarser particle size. In this classification step the material was split into particle class 2 and a new coarse fraction. This procedure was repeated twice. The selected speed of the classifier in the four classification runs was 21,300 rpm, 11,200 rpm, 5900 rpm and 3000 rpm.

The particle size distribution of the samples was measured using a Sympatec, type HELOS/RODOS laser diffraction instrument with dry sample dispersion. Microscopic images of particles from the various particle classes were taken with a scanning electron microscope TESCAN, type VEGA LM. Further information about the chemical composition of the particle surface was obtained in combination with energy dispersive X-ray spectroscopy (SEM-EDX).

All chemical analyses were determined by testing each sample in duplicate. In the results the average values are presented. The total carbon (TC) content was determined with a LiquiTOC system from Elementar Analysensysteme. The concentration of most metals (Al, As, B, Ba, Bi, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Sr, Ti, V and Zn) was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES) using an Ultima 2 instrument from Horiba Jobin Yvon. The samples were dissolved by an aqua regia digestion procedure according to ISO 11466 [27]. The concentration of mercury was measured using cold vapour atomic absorption spectrometry (CV-AAS). For analyses of Na, K, Ca, Mg, Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-} ion chromatography was used (Dionex ICS-1000). For the determination of the Cl^- and NO_3^- contents the samples were leached with water instead of the digestion by aqua regia. The concentration of Si was analysed gravimetrically according to ISO 934 [28].

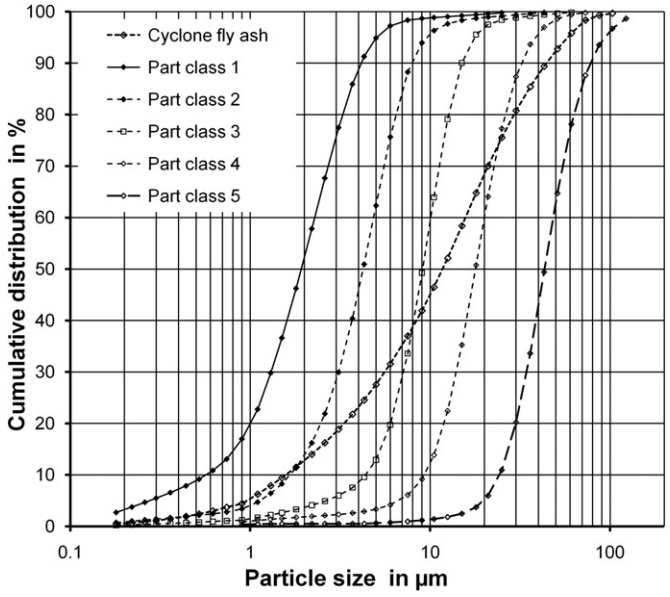

Fig. 1. Particle size distribution of the cyclone fly ash and the dust particle classes produced.

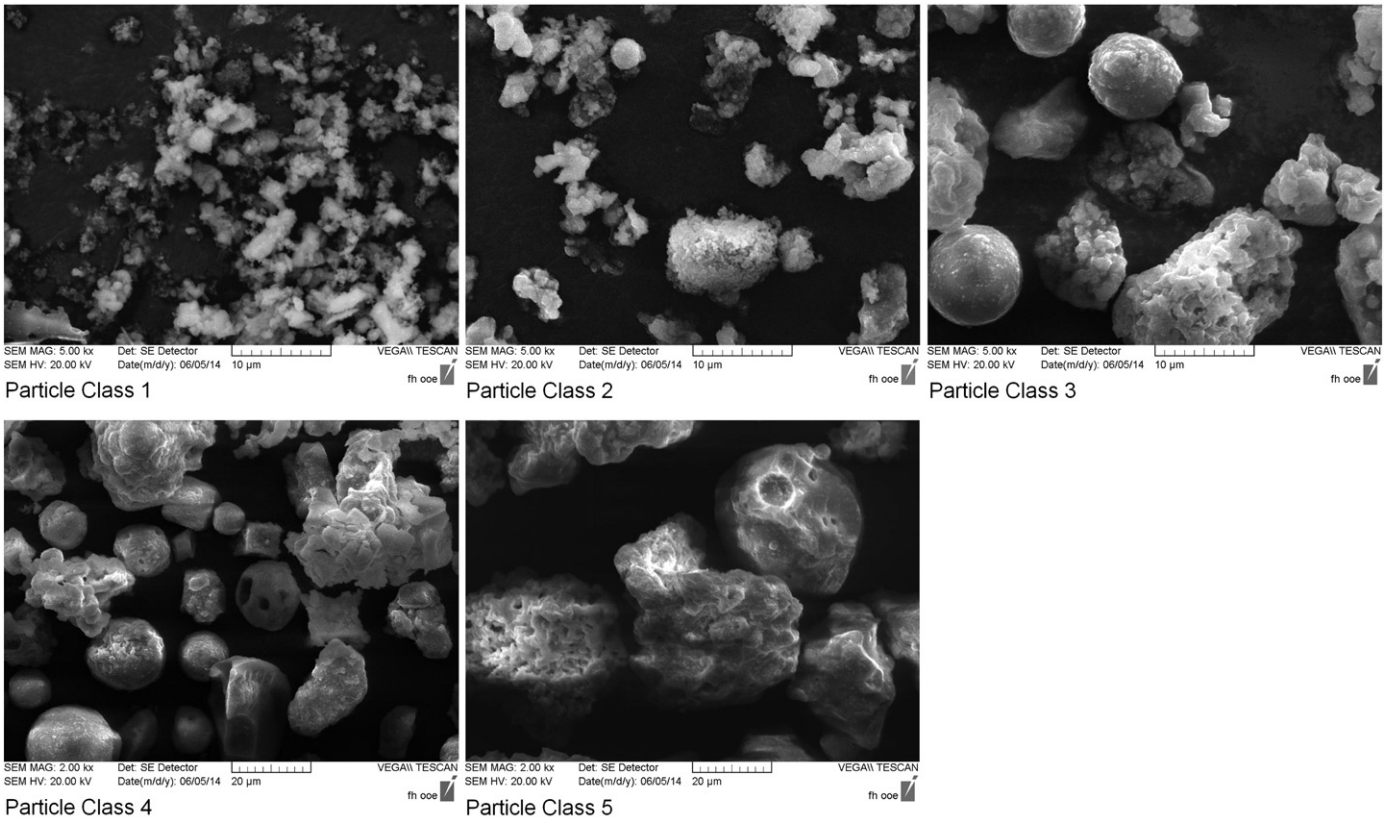

Fig. 2. Scanning electron microscope images of particles from the various particle classes produced.

2.3. Calculation

The normalised concentration $C_{i,j}$ of the various components i in the particle class j is defined by Eq. (1):

$$C_{i,j} = \frac{c_{m,i,j}}{c_{m,i,0}} \quad (1)$$

where $c_{m,i,0}$ is the mass concentration of component i in the cyclone fly ash and $c_{m,i,j}$ is the mass concentration of the component in this particle class.

The dependence of the concentration of material deposited onto particles can be described thus: $c \sim 1/d^N$ [26]. The exponent N results from the mechanism of condensation or reaction of the components on the particles. The mass median diameter d_{50} was used as the characteristic particle size of the particle classes produced. When the mass concentration of the component in the filter dust is incorporated into the constant K, the function for the normalised concentration of a component can be expressed by Eq. (2):

$$C_{i,j}(d_{50}) = K_i \cdot \frac{1}{\left(d_{50,j}\right)^{N_i}} \quad (2)$$

The exponent and the constant for each component can be obtained by linear regression of the calculated normalised concentrations.

3. Results and discussion

3.1. Particle size of the cyclone fly ash and the ash fractions produced

The mass fraction and the characteristic particle sizes for the five dust particle classes produced are summarized in Table 1. The mass fraction of the loss in the first classification run caused by the limited collection efficiency of the fine fraction collector was 7.0%. No characteristic particle size can be determined for the loss. However, it is obvious that it is smaller than for particle class 1. The particle size distributions of the cyclone fly ash and the five dust particle classes produced are shown in Fig. 1.

Scanning electron microscope (SEM) images of particles from the various particle classes are shown in Fig. 2. The size of the particles shown corresponds well with the mass median diameter of the respective particle class. The shape of the particles varied within a wide range from solid spheres to agglomerates consisting of squared or rounded particles. The SEM-EDX spectra also revealed that the chemical composition at the surface of the particles is different. In Fig. 3 SEM-EDX spectra of three particles with different shapes from particle class 3 are shown.

The spectrum of the spherical particle (Spectrum 1) shows mainly Ca, Si, O, and P with smaller amounts of Mg, Mn, Fe and Al. The spectrum of the agglomerate (Spectrum 2) consists of K, S and O suggesting the compound K_2SO_4. The spectrum also shows minor amounts of Cl, Na and Zn. The angular particle (Spectrum 3) consists mainly of Ca, S and O with small amounts of K, Cl and Mg. These results demonstrate that the chemical analysis of the material of a particle class only represents an average composition but the composition of individual particles can differ substantially.

3.2. Chemical analysis of the cyclone fly ash and the ash fractions produced

The chemical analysis of the fly ash and the particle classes produced are shown in Table 2. In the particle classes the analysed concentrations of Cr, Mo and Ni are not representative because their recovery rate in the classification was 4.14, 1.85 and 4.20, respectively. The high recovery rate which is much above the theoretical value of 1.0 indicates

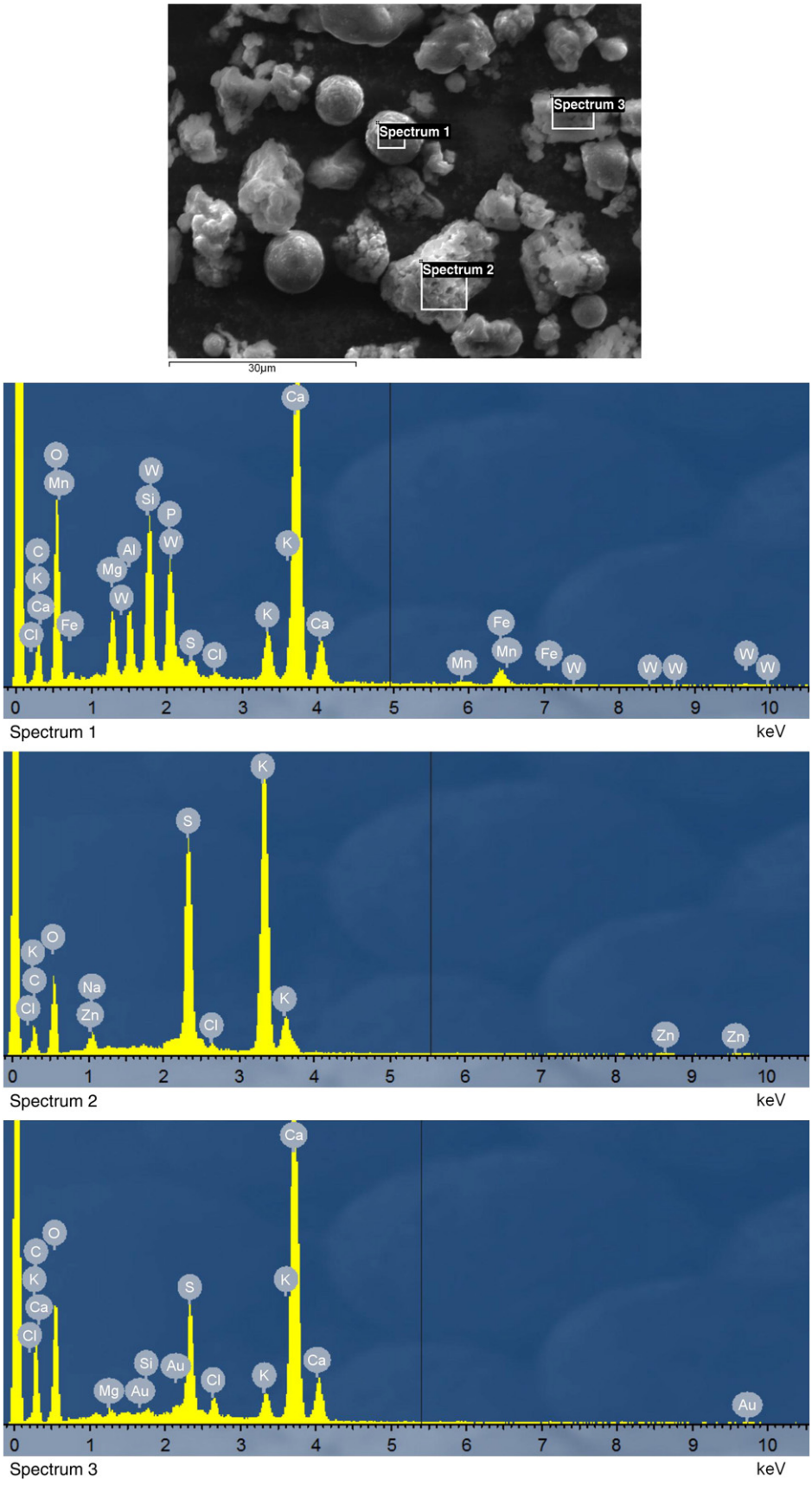

Fig. 3. Scanning electron microscope image and SEM-EDX spectra of particles from particle class 3.

Table 2
Chemical composition of the cyclone fly ash.

	Concentration in mg/kg based on dry weight						Recovery rate in the classification procedure	Exponent N	R^2
	Cyclone fly ash	Particle class 1	Particle class 2	Particle class 3	Particle class 4	Particle class 5			
TC	19,000	17,000	22,000	24,000	20,000	13,000	1.04	0.088	0.20
Cl^-	10,670	23,900	15,400	11,700	7630	1820	1.08	0.773	0.90
NO_3^-	650	1290	1060	710	320	<d.l.	0.99	0.610	0.90
PO_4^{3-}	35,000	19,900	34,300	37,900	33,600	32,000	0.92	−0.121	0.34
SO_4^{2-}	80,000	173,000	105,000	74,800	51,800	29,000	1.02	0.561	0.996
Al	7390	1340	2860	5230	9340	13,200	0.91	−0.750	0.98
As	27	14	18	19	28	34	0.86	−0.284	0.96
B	574	558	781	691	508	360	1.00	0.171	0.48
Ba	380	250	216	405	438	716	1.08	−0.368	0.87
Bi	132	202	189	138	100	80	1.03	0.324	0.96
Ca	255,000	201,000	261,000	294,000	251,000	186,000	0.95	0.027	0.02
Cd	41	68	66	46	27	10	1.02	0.620	0.88
Co	4	2	5	4	4	4	0.96	−0.105	0.20
Cr	36	264	270	129	77	76	4.18	–	–
Cu	146	206	212	158	112	92	1.03	0.294	0.92
Fe	5700	2540	3730	4650	7200	9810	1.01	−0.438	0.99
Hg	0.22	0.46	0.40	0.28	0.05	0.05	1.00	0.840	0.83
K	86,000	175,000	101,000	68,400	48,700	41,100	0.94	0.472	0.96
Mg	20,300	16,100	24,500	22,900	18,600	17,700	0.98	−0.010	0.01
Mn	11,000	7070	11,400	11,800	11,600	9690	0.96	−0.083	0.22
Mo	10	33	31	19	12	10	1.85	–	–
Na	1900	2300	1690	2430	2010	1930	1.09	0.024	0.04
Ni	22	165	162	81	51	54	4.20	–	–
Pb	179	281	219	157	95	47	0.84	0.579	0.96
Sb	11	10	10	11	10	11	0.95	−0.026	0.62
Si	62,600	7480	16,600	33,900	89,300	165,000	1.03	−1024	0.99
Sr	453	357	526	520	439	396	0.99	−0.004	0.00
Ti	448	54	139	285	612	848	0.93	−0.908	0.97
V	14	6	10	13	20	23	1.09	−0.413	0.96
Zn	3030	5680	4190	2820	1690	1150	0.96	0.536	0.99

that the sample has got contaminated in the classification procedure. It is already known that samples can become contaminated with some Cr, Ni and Mo by erosion of stainless steel material from the classifier [29]. For Fe this contamination can be disregarded because the Fe content of the fly ash is more than a hundred times higher than the content of Cr, Ni and Mo. Therefore, the relative concentration increase for Fe caused by the erosion of classifier material is much smaller.

For most of the other components analysed, the recovery was ± 10%. Only for As and Pb was the loss somewhat higher, 14% and 16%, respectively. For the calculation of the recovery the composition of the loss fraction was assumed to be the same as the composition of particle class 1.

The ratio of the Cd and the Zn concentrations in the finest particle class to the concentration in the coarsest particle class of about 5 and 7 is quite similar to the results reported in [22]. In [21] the fly ash from biomass combustion the ratio for Cd was also in a similar range. For other components no size dependence of the concentration is available for this size range.

For the coarse size range with the coarsest particle class of 250–500 μm and the finest particle class (<75 μm) a similar ratio of the concentrations of Cd and Zn in the finest particle class to the concentration in the coarsest particle class was found [18]. But also for Ba and V in the finest particle class an enrichment of comparable range was reported which is in contrast to the depletion of these components in the finer particle classes found in this study. For Pb no dependence of the concentration on the particle size was found in [18] whereas in this study the enrichment of Pb in the finer particle classes was very similar to those of Zn and Cd.

In [19] increasing concentrations with decreasing particle size were found for all components analysed but Hg. This might be explained by the high content of undissolved impure silica which accounted for 57% in the finest particle class and 86% in the coarsest particle class. The source for this high silica content is not specified but could be produced by erosion of bed material. Thus components which are not enriched in the fly ash mixture excluding silica would be present at a threefold concentration in the finest particle class compared to the coarsest particle class.

In [20] increased concentrations in the finest particle class were found for Zn, Ba, V and As but the concentrations of Cd and Co were particle size independent. While for Zn and Co the behaviour was similar in this study, the results for the other components were different.

In Fig. 4 the normalised concentrations of the analysed nutrients Ca, Mg, K and Na, of the anions Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-}, of the metals Al, Fe, Si and Ti and the TC are shown in dependence of the mass median diameter of the dust particle classes. The same depiction for the heavy metals is shown in Fig. 5. It can be seen that for many components the normalised concentration is a function of the particle size. On the left the elements are shown which are enriched in the smaller particle size classes whereas the elements which are depleted in these size classes are represented on the right. In the middle the elements without a pronounced dependence of the concentration on the particle size are shown.

The exponent N for each component was obtained by linear regression of the calculated normalised concentrations. A positive exponent indicates that the element is enriched in the smaller particle classes while a negative exponent stands for the contrary. When the exponent is close to zero, no significant size dependence of the concentration was observed. The resulting exponents are also summarized in Table 2. For all components with a distinct dependence of the concentration on the particle size (absolute value of $N > 0.2$) the correlation coefficient was higher than 0.83. In case the slope of the regression line is close to zero the correlation coefficient does not provide usable results.

The concentration of K and of the anions Cl^-, NO_3^- and SO_4^{2-} was increased in the fine particle classes and decreased in the coarse particle classes. Components volatile in the combustion process can recondense on the fly as particles or react with the fly ash when the off-gas cools down. These processes take place on the surface of the fly ash particles. Because of the higher specific surface of the smaller particles volatile components are enriched in the fine fractions of the fly ash. A more detailed description of the mechanism of the

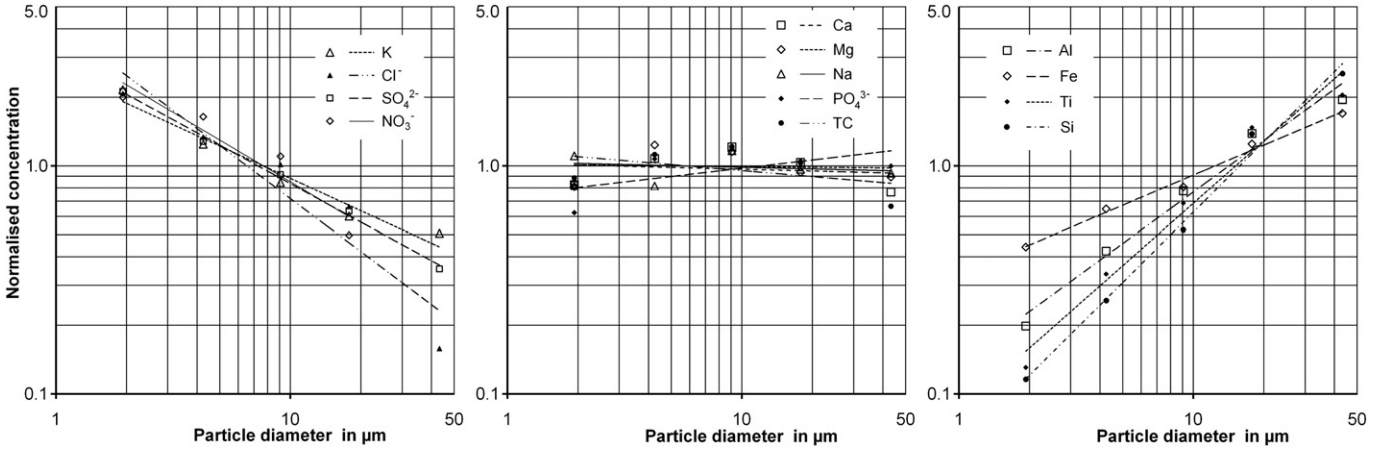

Fig. 4. Normalised concentration of Ca, Mg, K, Na, Cl^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, Al, Fe, Si, Ti and TC as a function of the mass median diameter of the particle class.

enrichment of volatile components can be found in the literature [24,26]. For the metals Fe, Al, Si and Ti the size dependence was opposite, the concentration was lower in the fine particle classes and higher in the coarse particle classes. The concentration of the nutrients Ca, Mg, Na and PO_4^{3-} and the TC content were nearly independent of the particle size.

When the main components (Mg, Ca, Si, Al, Fe, Mn, Na, K, S, P) are calculated as oxides and Cl^- and TC are added, the fraction of the sum of these components on the total mass is 75% to 80%. The inclusion of the minor components does not increase this fraction substantially. The gap to 100% might be caused by the reaction of the oxides contained in the fly ash with the water vapour of the off-gas present in the dust container. Other contributions to this gap could be some crystal water, e.g. with the sulphates or that a part of the carbon is present as carbonate.

The concentration of the heavy metals Bi, Cd, Cu, Hg, Pb and Zn was higher in the fine particle classes whereas for As, Ba and V the opposite effect was observed. For B, Co, Mn, Sb and Sr no distinct dependence of the concentration on the particle size was found.

For Cr, Ni and Mo also the concentration in the fine particle classes was higher than in the coarse particle classes. However, the behaviour of these components cannot be evaluated because of the high recovery rate caused by the erosion of some classifier material mentioned above.

The largest dependence on the grain size which is visible at the highest absolute values of the exponent was observed for concentrations of Ti, Hg, Cl^- and Al with values for the exponent of −0.91, 0.84, 0.77 and −0.75, respectively.

The exponents found for Ca, Cd, Co and Mg compare well with the results derived from the data published in [25] whereas exponents for Cu, K, Pb and Zn were a bit smaller [30]. For As the size dependence found in this study was opposite to the published result.

4. Conclusions

The size dependence of the composition of a cyclone fly ash from a grate-fired biomass combustion plant was investigated. For several components no distinct size dependence of the concentration was found. This is true for TC, PO_4^{3-}, Na, Mn, B, Co, Sb and Sr. Also the main components Ca and Mg showed this behaviour with the exception of the finest particle class where the concentration was much lower. Its lower concentration can be explained at least partially by the dilution caused by the high enrichment of K and SO_4^{2-} in the finest particle class combined with the high absolute content of these components. A considerable increase in the concentration with decreasing particle size was found for K, for the heavy metals Bi, Cd, Cu, Hg, Pb and Zn and for Cl^-, NO_3^- and SO_4^{2-}. The metals Al, As, Ba, Fe, Si, Ti and V showed the opposite behaviour with lower concentrations in the fine particle classes.

Investigation of single particles by SEM-EDX revealed that the analysed concentrations are representative for the particle classes only, the composition of single particles in a particle class can deviate considerably.

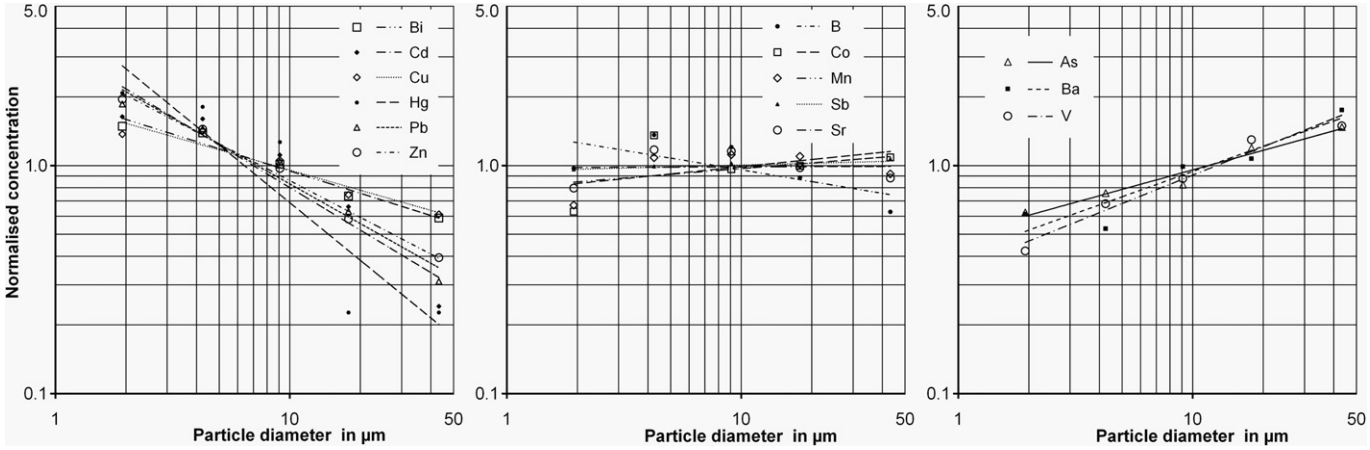

Fig. 5. Normalised concentration of various heavy metals as a function of the mass median diameter of the particle class.

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6.5. Paper 5

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"Gheorghe Asachi" Technical University of Iasi, Romania

BENCH SCALE TWO STAGE HEAVY METAL LEACHING TEST WITH FLY ASH FROM WOODY BIOMASS COMBUSTION

Christof Lanzerstorfer*, Michaela Kröppl

School of Engineering/Environmental Sciences, University of Applied Sciences Upper Austria, Stelzhamerstraße 23, Wels, A-4600, Austria

Abstract

In this paper a two stage bench scale leaching procedure is used to assess the heavy metals release from a wood-based fly ash of a 5.0 MW_{th} grate-fired boiler. In the first step mostly K was leached with water. In the subsequent acid leaching step heavy metals were leached at a pH of 3. The remaining solids were agglomerated together with the bottom ash and the dried K-concentrate from the first leaching step whereas the filtrate was treated before discharge. In the agglomerates produced the heavy metal concentrations were below the limit concentrations for utilization. The loss of nutrients caused by the treatment was about 10% for Ca and for K 8%. The addition of 15% hydrated lime in the agglomeration step showed a very positive effect on the reduction of the fines contained in the product and on the mechanical stability of the agglomerates. The mass of the precipitate from the waste water treatment was about 10% of the mass of the fly ash. Thus, the mass of residue requiring disposal in landfill sites was reduced substantially. The heavy metal concentrations in the treated discharge water were significantly lower than typical limit values for waste water. This paper also presents the current heavy metal limit values for ash used as a soil conditioner in forestry and agriculture in Austria, Finland, Sweden, Denmark and Lithuania.

Key words: ash, biomass, heavy metals, leaching, waste

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*Author to whom all correspondence should be addressed: e-mail: c.lanzerstorfer@fh-wels.at; Phone: +43 50804 43220; Fax.: +43 50804 943220

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1. Introduction

The limited availability of fossil fuels and concerns about climate change caused by the carbon dioxide emissions from fossil fuel combustion give rise to the combustion of woody biomass (AEBIOM, 2013). Depending on the type of combustion process and the off-gas cleaning system different ash fractions result from the combustion as residues. Bottom ash, the coarse ash fraction, is discharged from the firing grate (grate fired combustion) or removed from the fluidized bed (in fluidized bed combustion). Fly ash, the fine ash fraction, leaves the combustion zone together with the flue gas and is collected from the flue gas in a dust collector, e.g. a cyclone, a fabric filter or an electrostatic precipitator (EP). In some plants a cyclone is applied as a pre-separator upstream of a fabric filter or an EP.

Biomass ash as well as biomass fly ash contain valuable nutrients like potassium and calcium which can be returned to the forest soil to avoid nutrient insufficiencies and increase plant growth (Hallenbarter et al., 2002; Moilanen et al., 2002). For the spreading of ash on forest soil some kind of stabilisation of the ash is required to avoid dust emissions during the spreading process and a rapid increase of the soil pH (Steenari and Lindqvist, 1997). Several methods for processing ashes into spreadable products are available (Emilsson, 2006; Holmberg et al., 2003; Orava et al 2006; Mahmoudkhani et al., 2007; Sarenbo et al., 2009). Because of the formation of less soluble compounds such as calcite the dissolution of granulated ash is considerably delayed compared to untreated wood ash (Holmberg and Claesson, 2001; Steenari et al., 1999a). From an economic point of view pelletization and granulation are superior to the self-hardening process (Rasmusson et al., 2013).

However, the utilisation of biomass ash as soil conditioner is limited by the admissible input of the various heavy metals to the soil. The legal limits of various countries for utilisation of biomass ash as a soil conditioner in forests or agriculture are shown in Table 1. In bottom ash the concentrations of heavy metals are usually below the limits (Dahl et al., 2009, 2010; Nurmesniemi et al., 2012; Pitman, 2006; Steenari and Lindqvist, 1997) but in some cases exceeding concentrations for Cr are reported (Ingerslev et al., 2011; Pöykiö et al., 2009). In biomass fly ash, depending on the kind of biomass and the applicable limits, the critical heavy metals are usually Cd, As, Zn and Pb (Lanzerstorfer, 2014, 2015; Nurmesniemi et al., 2012; Stahl and Dorsch, 2008).

If the recycling of any biomass ash to the soil is prohibited because of the high contamination with heavy metals this ash has to be disposed of by landfilling, but this is quite cost intensive and valuable nutrients get lost for the soil.

Table 1. Heavy metal concentration limits for utilisation of ash from biomass combustion as a soil conditioner in forests and agriculture; in mg/kg d.w.

	Austrian guideline[1] (BMLFUW, 2011)		***Finland cited in Nurmesniemi et al. (2012)***	***Sweden cited in Emilsson (2006)***	***Denmark cited in Haglund (2008)***	***Lithuania cited in Stupak et al. (2008)***
	A	B				
As	20	20	40	30		30
Cd	5	8	25	30	5 / 15[2]	30
Cu	200	250	700	400		400
Pb	100	200	150	300	120	300
Zn	1200	1500	4500	7000		7000
Cr	150	250	300	100	100	100
Ni	150	200	150	70	30 / 60[3]	70
V				70		70
B				500		500
Hg			1.0	3	0.8	3

[1] *if the concentrations are below limits according to A, no soil analysis is required*
[2] *left Cd limit for straw ash, right Cd limit for wood ash*
[3] *between 30 and 60 mg/kg a reduced ash quantity can be applied*

Actually, in Austria the utilisation of the finest fly ash fraction collected in fabric filters or EPs is not permitted and the mixing of ash fractions is only permitted if the concentrations in all fractions are below the limits according category B (BMLFUW, 2011). However, if the cyclone ash has to be decontaminated before utilization because of exceeding the limits, a combined treatment of all fly ashes including the finest fraction seems feasible. If the concentrations in the treated fly ash are below the limits according A, the mixing of the treated fly ash with the bottom ash would be permitted. Thus, a single homogenous product for soil conditioning would be available.

Thermal treatment of biomass fly ashes at high temperature for the removal of heavy metals has been investigated (Dahl and Obernberger, 1998; Dahl, 2000). Decontamination of the ashes down to the limit values for utilisation as a soil conditioner in forests is possible. However, these processes would be quite costly because of the high temperatures required.

Various hydrometallurgical leaching experiments for the decontamination of biomass fly ash are described in the literature (Hansen et al., 2001; Pedersen, 2003; Pedersen et al., 2003; Pirker et al., 1998). High removal rates for Cd can be realised at low pH-values in the leaching solution (Hansen et al., 2001). However, at low pH also part of the nutrients (K and Ca) is dissolved. Therefore, in some experiments a first leaching step using water prior to extraction of the heavy metals to remove soluble salts has been used (Pedersen, 2003). The

potassium-rich solution produced in this process could probably be utilized in the fertilizer industry.

For an economically feasible leaching process a low leaching agent to ash ratio (L/S) is desirable because a high L/S ratio would result in larger equipment size and higher consumption rates of chemicals. Reported values for L/S range from 1.0 to 6.7 (Pedersen, 2003) up to 40 (Pirker et al., 1998).

The above leaching experiments were carried out on a small scale in a laboratory where only a few grams of fly ash were treated. In the experiments the process step of the removal of heavy metals was investigated but no subsequent step to turn the remaining ash into a useable product. However, in order to be able to spread the ash on soil without extensive dusting the material has to be agglomerated. The agglomerates also have to withstand handling to a certain extent.

The aim of this study is to investigate the whole process chain of a two-stage leaching process for heavy metal contaminated biomass fly ash for the removal of heavy metals from the first leaching step to the final production of agglomerates and the treatment of the liquid effluent in a bench scale test. This leaching process investigated aims to allow the recycling of the remaining ash in an agglomerated form on the soil whereby the majority of the nutrients should remain in the product. To be able to produce agglomerates for testing a few kilograms of fly ash have to be processed. The concentrations of heavy metals in the agglomerates produced are analysed and compared with the Austrian concentration limits for utilization as a soil conditioner. Also the recovery of nutrients is calculated and the stability of the agglomerates tested.

2. Experimental

2.1. The leaching process investigated

In Fig. 1 a simplified process scheme of the two-stage leaching process is shown. In the first leaching step (vessel 1) potassium is leached together with other water-soluble salts from the ashes by using tap water. In a solid-liquid separation step (vacuum filter 2 with vacuum system 3) the clear solution is separated from the insoluble solids. The solids are treated in a second leaching step (vessel 4) with an acid. Depending on the pH-value, the heavy metals get dissolved. In a further solid-liquid separation step (vacuum filter 5 with vacuum system 6) the heavy metal containing solution is separated from the remaining solids. These solids can then be agglomerated along with the bottom ash. A binding material like

lime can be used to improve the mechanical strength of the granular product which can be used as a soil conditioner in forestry or agriculture.

The potassium-containing solution from the first leaching stage can be directly utilized elsewhere or it can be used in the agglomeration step after the evaporation of most of the water. The waste water from the second leaching stage containing the leached heavy metals has to be treated before discharge e.g. by precipitation of the heavy metals with sodium hydroxide at a pH of 9 to 10.

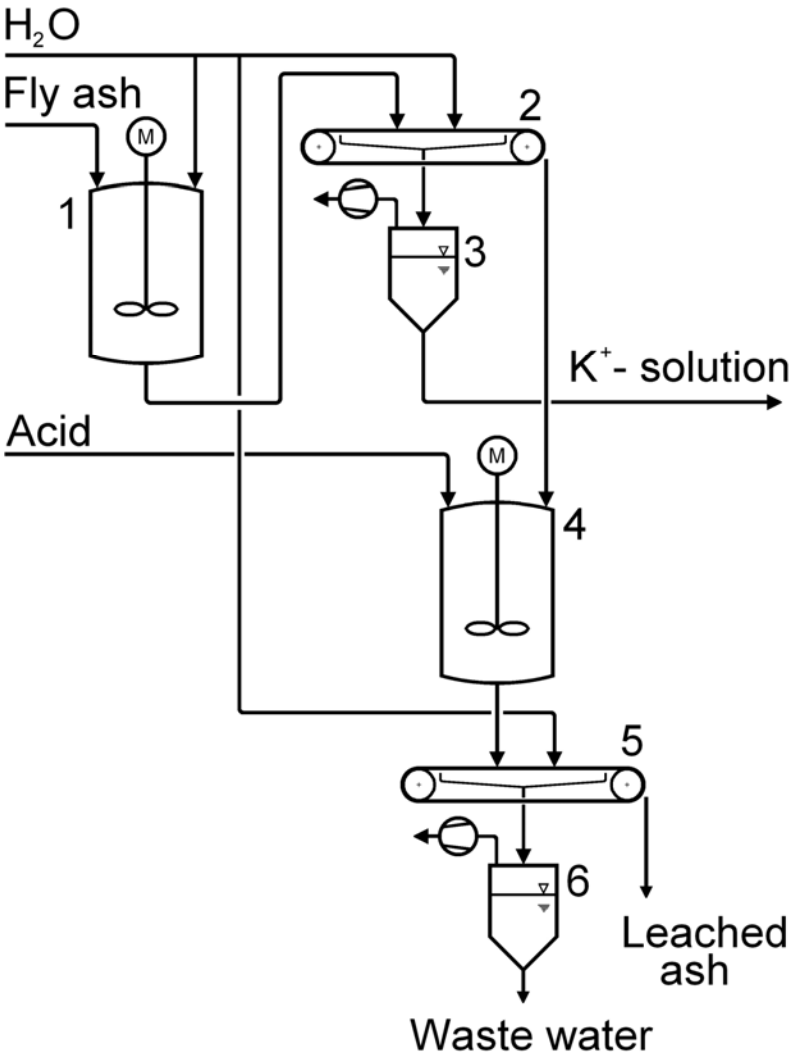

Fig. 1. Simplified process flow diagram of the two-staged leaching process

2.2. Ash sample

The ash samples were taken from a 5.0 MW_{th} grate-fired district heating plant. This plant is equipped with a two-stage system for dust collection consisting of a cyclone and an EP installed in series. The biomass used for combustion is wood chips from a forest in a

mixture of softwood and hardwood with about 80% softwood. The ratio of cyclone ash to EP ash is approximately 3 to 1. A sample of approximately 10 dm³ was taken from each fly ash at the discharge system of the dust collectors. Additionally, a bottom ash sample was collected. The oversize fraction of the bottom ash (> 10 mm) which accounted for 8.5% of the mass was removed by sieving.

Cyclone ash and EP ash were mixed in the ratio of 3 to 1 in several batches in an Erweka AR 403/ SW 1/S plough-share drum mixer with a maximum working volume of 3.5 dm³. The speed of the mixer was 300 rpm and a mixing time of 5 min was selected. In total, about 3.5 kg of the fly ash mixture were produced. This amount of processed ash was chosen to have enough leached ash for the final agglomeration tests.

2.3. Leaching

Based on pre-tests, an L/S ratio of 2.0 was chosen for the first leaching step. The fly ash mixture, split into two batches, was dosed by a vibration feeder into two 5 dm^3 plastic beakers containing tap water until the chosen L/S ratio was reached. Tap water was used for leaching because it would also be used in an industrial implementation of the process. The concentrations of the relevant ions in the tap water are: Cl^- 6.1 mg/dm³; NO_3^- 8.4 mg/dm³; SO_4^{2-} 6.9 mg/dm³; Na 4.8 mg/dm³; K 1.0 mg/dm³; Mg 13 mg/dm³; Ca 69 mg/dm³. The slurry in the beakers was stirred using overhead stirrers IKA RW20 with a three-bladed propeller stirrer with a diameter of 100 mm at 180 rpm. After 30 minutes the liquid was separated from the insoluble material by vacuum filtration. As the diameter of the available suction filter was only 125 mm, the slurry was split into eight parts which were filtered separately. For cleaning the stirrer and the beaker 0.4 dm³ tap water was used, which is equivalent to an L/S of 0.15. The diluted slurry produced was added to the filtration batches in equal portions. The filter cake was flushed with tap water four times. The amount of water for each flushing was equivalent to an L/S of 0.5. From each filter cake three small samples were taken for analysis. All samples were combined to one sample for the determination of the average dry matter content of the filter cake. The filtrates and the flushing waters from all filtration batches were combined and homogenized before a sample was taken for chemical analysis.

In the second leaching step the filter cake from the first leaching stage was mixed with tap water in a plastic container. Based on some pre-tests and literature data (Hansen et al., 2001) a pH of 3.0 was chosen for acid leaching. Concentrated hydrochloric acid was added to the caustic suspension until the chosen pH was reached. The slurry in the container was stirred by using an overhead stirrer IKA RW20 with a three-bladed propeller stirrer with a

diameter of 100 mm at 180 rpm. After 30 minutes the liquid was separated from the insoluble material by vacuum filtration. The filtration velocity was very slow, therefore, only 0.6 dm^3 of the suspension were filtered in each batch. Each filter cake was flushed with 0.2 dm^3 tap water. All the filter cakes as well as the filtrates were combined and homogenized before samples were taken.

2.4. Agglomeration

For the production of the solid mixtures for agglomeration an Erweka AR 403/SW 1/S plough-share drum mixer was used. The speed of the mixer was 300 rpm and a mixing time of 5 min was selected. In one case this mixer was also used for agglomeration at a reduced speed of 60 rpm. For pelletizing an Erweka AR 403/AR 402 GTE pelletizer was used. The diameter of the pelletizing disc was 400 mm, the inclination of the disc was 55°, and the disc was operated at 170 rpm. In some tests water was added manually with a spray bottle.

The produced pellets were collected in a crystallizing dish and subsequently dried in the free laboratory atmosphere.

Three different types of solid products were produced. For the first product (A) filter cake from the second leaching stage was mixed in the drum mixer with bottom ash in a ratio which corresponds to the occurrence of the different ash fractions in the biomass combustion plant supplying the ash samples. Subsequently, the homogenized material was dosed onto the pelletizing disc. Water was added during pelletizing.

For the second product (B) and the third product (C) a basic mixture which was identical to the mixture for product A was produced in a first step. In a second step dried K-concentrate from the first leaching stage was added to the mixture in a ratio which corresponds to the actual ratio of produced filter cake to produced concentrate. To improve the strength of the agglomerates some hydrated lime was added in a third step. Product B was agglomerated using the pelletizing disc while adding some water, whereas product C was granulated in the drum mixer at a reduced speed of 30 rpm.

2.5. Waste water treatment

For the precipitation of the leached heavy metals the waste water was stirred in a plastic container while a 4 mol/dm^3 sodium hydroxide solution was added until a pH of 10 was reached. An overhead stirrer IKA RW20 with a three-bladed propeller stirrer with a diameter of 100 mm was used. The speed was 100 rpm. After 30 minutes the precipitate was

filtered off by vacuum filtration. Samples were taken from the filtrate for chemical analysis and the mass of the heavy metal filter cake was determined gravimetrically.

2.6. Chemical analysis and measurements

The pellet samples and the bottom ash sample were milled in a Retsch mixer mill MM301 with agate grinding tools prior to analysis. For the chemical analysis the solid samples were dissolved by aqua regia digestion (ISO 11466, 1995). The concentration of the heavy metals (As, Cd, Cr, Cu, Ni, Pb and Zn) in the ash samples and in the leaching solutions was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES) with a Horiba Jobin Yvon Ultima 2. The concentration of the nutrients (K and Ca) was analysed by ion chromatography (IC) with a Dionex ICS-1000.

For pH-measurements a Mettler Toledo Seven Multi pH meter was used. The dry matter content of the filter cake was determined with a Sartorius infrared moisture analyser MA35M at 105°C.

The oversize fraction of the bottom ash sample (> 10 mm) was separated prior to the size analysis by using a 10 mm sieve. The particle size distribution of the pelletized ash and the bottom ash was determined by using a laboratory sieve shaker (Fritsch ANALYSETTE 3 PRO) with sieves from 8 mm to 200 µm. The particle size distribution of the fly ash samples was measured by using a laser diffraction instrument with dry sample dispersion from Sympatec, type HELOS/RODOS. Prior to the measurement the fly ash samples were sieved at 400 µm by using the laboratory sieve shaker to remove the oversize fraction.

The bulk density of the fly ash was measured according to ÖNORM EN ISO 60 (1999), the bulk density of the bottom ash and the pelletized ash samples was measured according to ÖNORM ISO 697 (1999).

The stability of the pelletized ash was tested through a fall test including a repeated free fall of the samples in a 150 mm plastic tube from a height of 2 m onto a steel plate. The particle size distribution of a sample of about 200 g of pelletized ash was determined before and after the sample had fallen ten times from the top of the tube onto the steel plate at the bottom.

3. Results and discussion

3.1. Characterization of the ashes used

The compositions of the ashes are summarized in Table 2. The concentrations of the heavy metals are in the published range (van Loo and Koppejan, 2008). The heavy metal

concentrations in the bottom ash (fraction < 10 mm) were below the Austrian limits for use as soil conditioner (BMLFUW, 2011). In the cyclone ash the concentrations of Cd, Pb and Zn were above the limit concentrations for utilization. Therefore, it would not be legal to recycle the cyclone ash on the soil. In the EP ash the concentrations for As, Cd, Pb and Zn exceeded the limits. The EP ash is also above the limits of all other countries shown in Table 1. The cyclone ash might be acceptable in some countries, e.g. Lithuania.

Table 2. Composition of the ash samples (values above Austrian limit concentration in italics)

	Bottom ash (fraction < 10 mm)	***Cyclone ash***	***EP ash***
Heavy metals in mg/kg ash d.w.			
As	5	20	*36*
Cd	1	*30*	*105*
Cr	41	67	76
Cu	93	47	140
Ni	34	48	23
Pb	15	*250*	*600*
Zn	254	*4780*	*19000*
Nutrients in g/kg ash d.w.			
K	59	81	258
Ca	280	240	59

d.w. dry weight

The mass median diameter (MMD) was 3.5 µm for the EP ash and 30 µm for the cyclone ash. The bottom ash is coarse, its MMD was about 400 µm. The bulk density of the EP ash, the cyclone ash and the bottom ash was 75 kg/m³, 660 kg/m³ and 1130 kg/m³, respectively.

3.2. First leaching step

Divided into two batches, 3.21 kg of ash mixture were treated. The amount of the filtrate including the flushing water was 11.4 dm³ and the mass of the wet filter cake was 4.58 kg. The dry matter content of the filter cake was 60%. A water equivalent to an L/S of 0.57 remained in the filter cake, which is a bit more than the water of the last flushing (L/S of 0.5). About 14% of the mass of the ash mixture got dissolved in the first leaching step.

The filtrate of the first leaching step was rich in K (18.5 g/dm³) because a high fraction of K was found in the solution (46%), whereas only a small fraction of Ca was dissolved. The pH of the leachate was about 12. This corresponds well with leaching experiments with fly

ash from the combustion of wood with an L/S of 16 and a leaching time of 24 hours, in which a fraction of about 77% of K was removed from the fly ash, whereas the fraction of leached Ca was about 15% (Steenari et al., 1999b). From the analysed heavy metals only Cr and Cu were dissolved to a noticeable extent, whereas the critical elements (As, Cd, Pb and Zn) were not dissolved. Therefore, recycling the dried leachate in the agglomeration step would not transfer a significant amount of those heavy metals to the product.

From the combined filtrate and flushing water a concentrate was produced by the evaporation of the water. This material was added to the solid mixture in some agglomeration experiments.

3.3. Second leaching step

The filter cake from the first leaching step was mixed with tap water. Subsequently the pH-value of the suspension was adjusted to 3.0 by adding concentrated HCl. The mass of the wet filter cake was 3.58 kg with a dry matter content of 47%. Therefore, about 32% of the mass of the ash mixture got dissolved in this leaching step. The amount of the filtrate including the flushing water was 10.6 dm^3.

In the filtrate of the second leaching step the Ca concentration was 29 g/dm^3, about 50% of the Ca of the fly ash was dissolved in this step. Also some K was dissolved in this step (about 20%) as well as a substantial fraction of the heavy metals contained in the fly ash with the exception of Cr, Ni and Pb was dissolved.

Table 3. Leaching of heavy metals

	Fraction of component leached from the fly ash in the first leaching step in %[1]	***Fraction of component leached from the fly ash in the second leaching step in %[1]***
As	< d.l.	100
Cd	1	73
Cr	38	29
Cu	15	105
Ni	7	19
Pb	< d.l.	27
Zn	1	73

< d.l. concentration in the leachate below detection limit

[1] Fraction of component leached = (1 - Concentration in product / Concentration in feed) * 100%

The difference to 100% is the fraction of the components contained in the fly ash which remains in the filter cake and therefore is also contained in the final product. When the dried leachate from the first leaching step is added in the agglomeration step the contained components are also found in the product. Values above 100% result from the analytical inaccuracy.

3.4. Treatment of discharge water

After the heavy metal precipitation with NaOH at a pH of 10 the precipitate was separated by filtration. The concentrations of Cd, Cu, Pb and Zn in the filtrate were 9 µg/dm³, 37 µg/dm³, 10 µg/dm³ and 83 µg/dm³, respectively. The concentrations of As, Cr and Ni were below the detection limits (< 50 µg/dm³). The concentrations in the cleaned discharge water were far below the limit concentrations for discharge water from gas cleaning systems used by Decostere et al., (2009)

The precipitate from the waste water treatment was about 10% of the total mass of the fly ash treated. The fraction of the heavy metals in the precipitate was nearly the same as leached in the second leaching step because of the very low content of these components in the treated discharge water. Safe disposal of the precipitate in appropriate landfills would be mandatory in the case of industrial application of the process.

3.5. Agglomerated ash

For product (A) 500 g of filter cake from the second leaching stage were mixed with 1350 g of bottom ash. During pelletizing 52 g of water were added. For product (B) and (C) the basic mixture was identical. The added amount of dried K-concentrate was 60 g and the added amount of hydrated lime was 115 g. During pelletizing of product B about 40.5 g of water were added.

The concentration of K in product A was 66 g/kg, in products B and C it was higher (74 g/kg) because of the addition of the dried K-concentrate from the first leaching stage. For the second type of product the loss of K was about 8%, whereas for product A the total loss of K was 18%. The Ca concentration was 230 g/kg and did not differ much between the two product types. The increase of the Ca concentration caused by the hydrated lime addition was partly compensated by the addition of the K-concentrate. The total loss of Ca was about 10%. The concentration of Ca in the products is in the same range as in a biomass ash granule product studied by Mellbo et al. (2008).

The average concentrations of the heavy metals in the product are shown in Table 4. All concentrations are below the Austrian limits for utilization. Also the calculated heavy metal concentrations of a mixture of the bottom ash and the untreated fly ashes are shown. For such a mixture the concentrations of Cd and Zn would be above the limit concentrations. The calculated reduction rates were highest for Cd and Zn and a bit lower for As and Cu. The removal rate of Pb was substantially lower and Cr and Ni were not removed by the leaching process.

Table 4. Heavy metal concentration of the product in mg/kg product d.w. (values above Austrian limit concentration are printed in italics)

	Ash pellets	***Mixed ashes (bottom ash, cyclone ash and EP ash) without leaching***	***Reduction rate in %***
As	9	17	48
Cd	4	*13*	69
Cr	49	48	-2
Cu	43	87	51
Ni	34	36	5
Pb	72	95	24
Zn	745	*2270*	67

The agglomerated ash samples were stored in open air laboratory conditions for four weeks. Then the particle size distribution of the agglomerated ash samples was measured. The MMD of product A was the smallest with 1300 µm. Presumably because of the addition of fine hydrated lime the MMD was higher for product B (2450 µm) and product C (1980 µm). Compared to product B product C shows a wider particle size distribution. This results from the different agglomeration techniques. As expected the product produced by a pelletizing disc showed a more uniform size distribution compared to the product granulated in the mixer (Pietsch, 2002). After the falling test the MMD of product A was 980 µm, which corresponds to a reduction of the MMD of about 25%. Both other agglomerates showed higher strength in the falling test, the MMD after the falling test was 2150 µm and 1870 µm for product B and C, respectively. The reduction of the MMD caused in the falling tests was only 12% for product B and 6% for product C. The particle size distributions of the agglomerated ash samples before and after the falling tests are shown in Fig. 2.

The bulk density of products A, B and C was 520 kg/m³, 610 kg/m³ and 550 kg/m³, respectively. The smaller the fractions of fines in the products the higher was the bulk density. Thus, a lower fraction of fines also reduces the required storage volume.

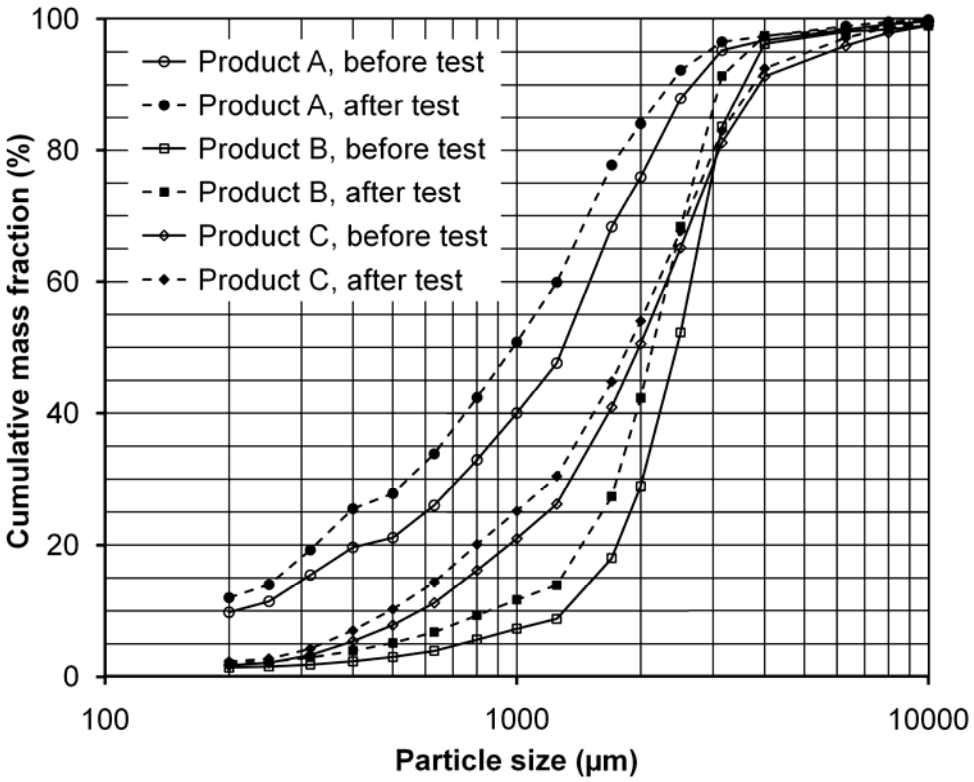

Fig. 2. Particle size distribution of agglomerates before and after falling test

4. Conclusions

A two stage leaching process for the treatment of fly ash from woody biomass combustion which exceeds heavy metal limit values for utilization on soils was investigated in a bench scale experiment. In the agglomerates produced the heavy metal concentrations were below the limit concentrations for utilization on agricultural and forest land. The loss of nutrients caused by the treatment was about 10% for Ca and 8% for K in the case that the dried K-concentrate was used in the agglomeration step.

The addition of 15% hydrated lime in the agglomeration step showed a very positive effect in the reduction of the fines content in the product and on the mechanical stability of the agglomerates. The particle size distribution of the agglomerates produced in the drum mixer was a bit wider compared to those produced on the pelletizing disc but the stability of the agglomerates was nearly the same. Therefore, mixing and agglomeration in one aggregate should be considered in the further development of the process.

The mass of the precipitate from the waste water treatment was about 10% of the mass of the fly ash. Thus, the mass of residue requiring disposal in landfill sites would be reduced substantially. The heavy metal concentrations in the treated discharge water were significantly lower than typical limit values for waste water.

Starting points for a further optimization of the process in the future are for example the use of flushing water which contains less dissolved ions than leaching water in the treatment of the next batch. This would reduce the amount of water which has to be evaporated for K recycling as well as reduce the amount of waste water which has to be treated.

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6.6. Paper 6

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Characterization of the flowability of fly ashes from grate-fired combustion of forest residues

Christof Lanzerstorfer*

Highlights

- Flowability of fly ash from grate-fired forest residue combustion was investigated
- The flowability correlates well with the particle mass median diameter
- Also other parameters (bulk density, friction angles) depend on the particle size

Abstract

Data about the flowability of fly ashes are important for the design of hoppers of fly ash collection equipment and fly ash storage silos. Fly ashes from sixteen grate-fired combustion plants (first-stage and second-stage de-dusting fly ash) were examined for flow relevant properties. The flowability category of the coarser first-stage fly ashes was cohesive to easy-flowing, while for the second-stage fly ashes the flowability category was very cohesive to cohesive. A good correlation was found between the flowability of the fly ashes and the mass median diameter of their particle size distribution. The correlation of the flowability with the bulk density or with the angle of repose was less significant. No correlation was found with the other parameters investigated. Moreover, the effective angle of internal friction, the wall friction angle and bulk density can be expressed as a function of the mass median diameter. Thus, the particle size is the most important parameter for the flowability of the fly ashes.

Keywords: fly ash, size distribution, flowability

* Corresponding author. Tel.: +43 50804 43220; fax.: +43 50804 943220

E-mail address: christof.lanzerstorfer@fh-wels.at

1. Introduction

Concerns about climate change caused by the carbon dioxide emissions from fossil fuel combustion have given rise to combustion of biomass for heat and power generation [1]. Biomass combustion is considered to have almost no impact on carbon dioxide emissions because the carbon dioxide emissions produced in the combustion process are compensated by the carbon dioxide fixed during growth of the biomass. In Austria nearly 80% of the biomass-based energy is derived from wood [2]. Forest residues, saw mill residues and bark account for approximately half of this energy. For small and medium size combustion systems grate-fired combustion is usually applied [3].

Combustion of biomass generates a considerable amount of ash which consists of the inorganic matter contained in the biomass plus a small fraction of unburnt carbon and organic matter. While most of the ash from grate-fired combustion is discharged as bottom ash (75-90%), the fine fraction of the ash leaves the combustion zone as fly ash together with the flue gas [4]. The fly ash has to be separated from the flue gas in a dust collector. In order to comply with low dust emission limits, usually electrostatic precipitators (ESPs) are used as fly ash collectors. The collection efficiency of inertial separators, like cyclones, is limited, especially for fine particles. Dust collection by a cyclone is sufficient for smaller biomass combustion plants only because of higher dust emission limits. However, a cyclone is often used as a pre-separator upstream of the ESP in two-stage dust collection systems.

The chemical composition of biomass fly ashes has been investigated widely [4-13], but data of the physical properties of fly ash are rare. Values for the particle density and the bulk density of different biomass fly ashes have been reported [5-7]. Some results from particle size distribution measurements are also available [8,9,14], but only few data are available for the flow properties of fly ash from biomass combustion [14]. Results for the angle of repose for various fly ashes from biomass combustion are available in [6,7], which can be used as an indicator for the flowability characterization [15]. However, for the dusts from various other industrial de-dusting systems it has been shown that the angle of repose and other easy-to-determine flow indicators often overestimate the flowability of the fine-grained dusts [16-18].

Knowledge of the flow properties of fly ash is required for proper design of fly ash storage silos, hoppers of fly ash collection installations and other fly ash handling equipment so that no flow problems occur [19]. For the design calculations, the flow function (unconfined yield strength σ_c as a function of the consolidation stress σ_1), the effective angle of internal friction φ_e, the wall friction angle φ_w and bulk density ρ_b, as a function of the consolidation stress, are required [19-21]. These properties can be measured using a shear tester.

The aim of this study is to characterize the flowability of fly ashes from grate-fired forest residue combustion plants. Fly ash samples collected from several combustion plants were tested using a ring shear tester. Additionally, the particle size distribution and other properties of the fly ashes: the humidity, the bulk density, the angle of repose and the total carbon content, as a measure of the quality of the combustion, were determined. Thus, the influence of various parameters on the behaviour of the fly ashes can be investigated.

2. Methods

2.1 Sample collection and sample preparation

Fly ash samples from sixteen grate-fired biomass combustion plants were collected for this study. In all combustion plants forest residues were used as the main fuel. In some plants a small fraction of sawmill residues and bark was used additionally. The thermal capacities of the plants and the type of off-gas cleaning system installed are summarized in Table 1. From plants with a two-stage off-gas cleaning system fly ash samples were collected from both stages, if possible. However, in several plants the fly ash from the cyclone pre-separator is not discharged separately but discharged together with the bottom ash. Fly ash samples of approximately 2 dm^3 were collected at the discharge outlet of the dust collectors. The volume of the ash samples was reduced to a volume suitable for the various laboratory tests using sample dividers which were applied repeatedly (Haver RT 12.5, Quantachrome Micro Riffler).

Table 1 List of fly ashes investigated

Plant	Thermal capacity in MW_{th}	Off-gas de-dusting system	
		First stage	Second stage
Single stage de-dusting system			
A	0.5	Baffle separator	-
B	0.5	Baffle separator	-
C	1.0	Multi-cyclone	-
D	1.1	Cyclone	-
E	3.0	Multi-cyclone	-
F	3.0	Multi-cyclone	-
Two-stage de-dusting system			
G	1.5	Multi-cyclone; no sample available	ESP
H	2.0	Multi-cyclone	ESP
J	2.0	Multi-cyclone; no sample available	ESP
K	2.0	Multi-cyclone	ESP
L	3.0	Multi-cyclone	ESP
M	3.5	Multi-cyclone; no sample available	ESP
N	4.0	Multi-cyclone; no sample available	ESP
O	10	Multi-cyclone; no sample available	ESP
P	10	Multi-cyclone; no sample available	ESP
Q	25	Multi-cyclone	ESP

2.2 Measurement procedures

The moisture content of the fly ash samples was determined gravimetrically. The samples were dried at 105°C for one hour.

The total carbon (TC) content of the fly ashes was measured using an Elementar Analysensysteme LiquiTOC system with a solids material extension. By combustion with air all carbon is transformed into CO_2, which is subsequently analyzed. The system was calibrated using a soil standard from Elementar Analysensysteme with 4.1% TOC/TC.

The particle size distribution of the fly ashes was determined using a laser diffraction instrument with dry sample dispersion from Sympatec, type HELOS/RODOS. The calibration of the instrument was verified with a SiC-P600’06 standard from Sympatec. The target value

for the mass median diameter x_{50} is 25.59 µm and the acceptable range is 24.82 µm to 26.36 µm. The measured value for the x_{50} was 25.62 µm.

The spread of the particle size distribution was calculated as the quotient of x_{90} and x_{10} [22]. The x_{10} is the particle size with 10% of the mass of the material consisting of particles smaller than this size and 90% of the mass of the material consisting of larger particles. The x_{90} is defined in a similar way.

The bulk density of the fly ash samples was determined according to ÖNORM EN ISO 60 [23]. For such a measurement the bottom cover of the funnel is removed which lets 120 cm^3 of powder stored in the funnel flow by gravity into the coaxial measuring cylinder. The volume of the certified measuring cylinder is 100±0.5 cm^3. The excess material is removed by drawing a straightedge blade across the top of the vessel.

The yield locus for the fly ash samples was determined using a RST-XS Schulze ring shear tester with a 30 cm^3 shear cell. For a shear test the fly ash sample is loaded vertically via the cover of the shear cell at a certain normal stress, then a shear deformation is applied to the fly ash sample by moving the shear cell at a constant velocity resulting in a horizontal shear stress in the sample. Each point of a yield locus is measured in two steps. In the first step, the pre-shear step, the sample is consolidated. Here the point of steady-state flow with the pair of values for the normal stress σ, the shear stress τ and the bulk density are determined. In the second step, a point of the yield limit is measured at a reduced normal stress. The corresponding pair of values for the normal stress and the shear stress at a point of incipient flow is one point of the yield limit. The whole yield locus is determined by repetition of the procedure. A Mohr stress circle, which runs through the point of steady-state flow and is tangential to the yield locus, can then be drawn. The slope of a tangent to this stress circle which runs through the origin of the σ-τ-diagram represents the effective angle of internal friction [19]. The test procedure was conducted at six values of the normal stress (600 Pa, 1,200 Pa, 2,500 Pa, 5,000 Pa, 10,000 Pa and 20,000 Pa) as described.

The calibration of the shear tester was verified at a normal stress of 3,000 Pa at pre-shear using the certified reference material BCR-116 from the Community Bureau of Reference

(Limestone Powder), which was also used in a round robin test on ring shear testers [24]. The measured values of the shear stress were in the range of the reported mean shear stress $\tau_m \pm 0.6$ times the reported standard deviation s.

The wall yield locus for the fly ash samples was determined using a RST-XS Schulze ring shear tester with a wall friction shear cell. In this cell the bottom ring is formed by a sample of the wall material which was structural steel S235JR (1.0038). For a shear test, the fly ash sample is loaded vertically at a certain normal stress and is then moved in relation to the wall material surface at a constant velocity. To measure a point of the wall yield locus corresponding pairs of values for the normal stress and the shear stress are determined. Wall friction angle measurements were performed at six values of the wall normal stress (600 Pa, 1,200 Pa, 2,500 Pa, 5,000 Pa, 10,000 Pa and 20,000 Pa). The kinematic angle of wall friction is the slope of a straight line running through the origin of the σ-τ-diagram and a point of the wall yield locus [19].

2.3 Numerical characterization of flowability

A quantitative characterization of the flowability of a bulk solid is possible by the flowability ff_c which is the ratio of consolidation stress σ_1 to unconfined yield strength σ_c [25]. The consolidation stress is equal to the major principal stress of the Mohr stress circle which runs through the point of steady-state flow and is tangential to the yield locus. The unconfined yield strength results from the stress circle that runs through the origin and is tangential to the yield locus [20]. The higher ff_c is, the better a bulk solid flows. The usual classification to define flow behaviour is: not flowing: $ff_c < 1$; very cohesive: $1 < ff_c < 2$; cohesive: $2 < ff_c < 4$; easy-flowing: $4 < ff_c < 10$, and: free-flowing: $10 < ff_c$ [25].

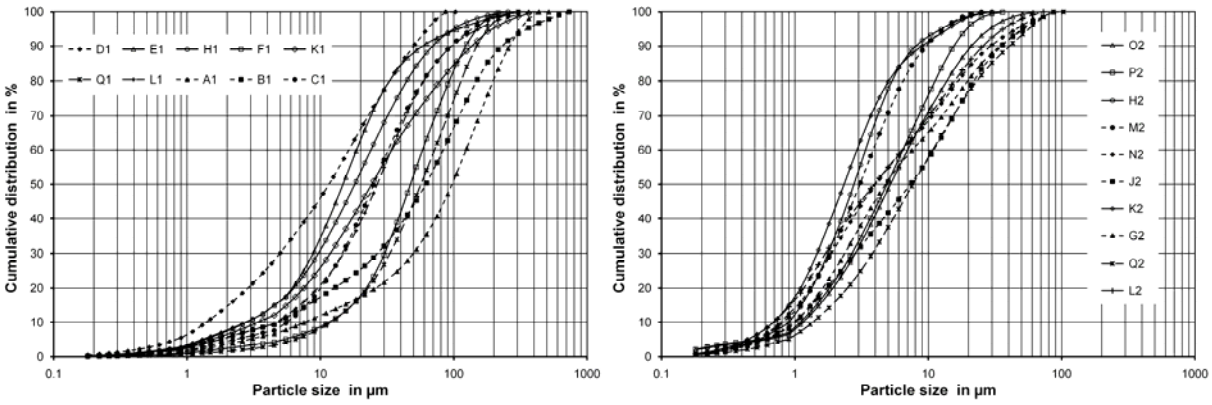
The flowability of a bulk solid depends on the consolidation stress. For most bulk solids better flowability will be obtained at a greater consolidation stress. Due to this dependence it is not possible to describe the flowability of a bulk solid with only one numerical value. A good visualization of the flowability can be given in a diagram with logarithmic scaled axes

showing the unconfined yield strength dependent upon the consolidation stress, when the diagram also includes lines of constant ff_c ratio [26].

3. Results

3.1 Fly ash particle size distributions

The particle size distributions of the first-stage and the second-stage fly ashes are summarized in Fig. 1. The mass median diameters of the fly ashes varied in a wide range (Table 2). The first-stage fly ashes were generally coarser. For the fly ashes separated by a baffle separator the mass median diameter was 62 µm and 97 µm, whereas the mass median diameter of fly ashes separated by cyclones was in the range of 12 µm to 60 µm. The mass median diameters of the second-stage fly ashes lay in the range of 2 µm to 8 µm.



First-stage fly ashes Second-stage fly ashes

Fig. 1 Particle size distribution of the fly ashes

3.2 Fly ashes properties

The spread of the size distribution, the humidity, the TC, the angle of repose and the bulk density of the fly ash samples from the first-stage and second-stage dust separators are summarized in Table 2. The humidity of the fly ash samples was generally low. The values were somewhat lower for the coarser first-stage fly ashes. The TC varied between 9.8 and 113 g/kg. However, there was no significant difference between the first-stage and the second-stage fly ashes. The bulk density varied between 100 and 1010 kg/m³. The average

bulk density of the first-stage fly ashes was nearly three times the average bulk density of the second-stage fly ashes. The average spread of the particle size distribution was similar for both groups of fly ashes. Surprisingly, this was also true for the angle of repose although the particle size of the second-stage fly ashes was much smaller.

The bulk density of the fly ashes correlated well with the particle size. This relationship, shown in Fig. 2, can be expressed by the equation $\rho_b = 213 \cdot \ln(x_{50}) - 88$. The correlation coefficient was 0.91.

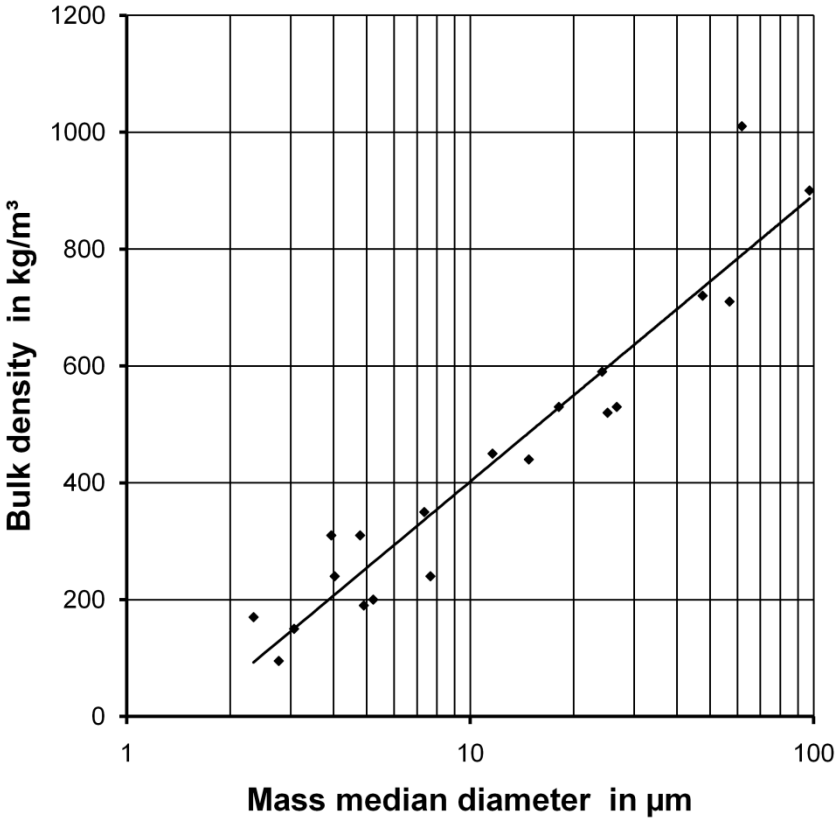


Figure 2 Bulk density as a function of the mass median diameter of the fly ash particles

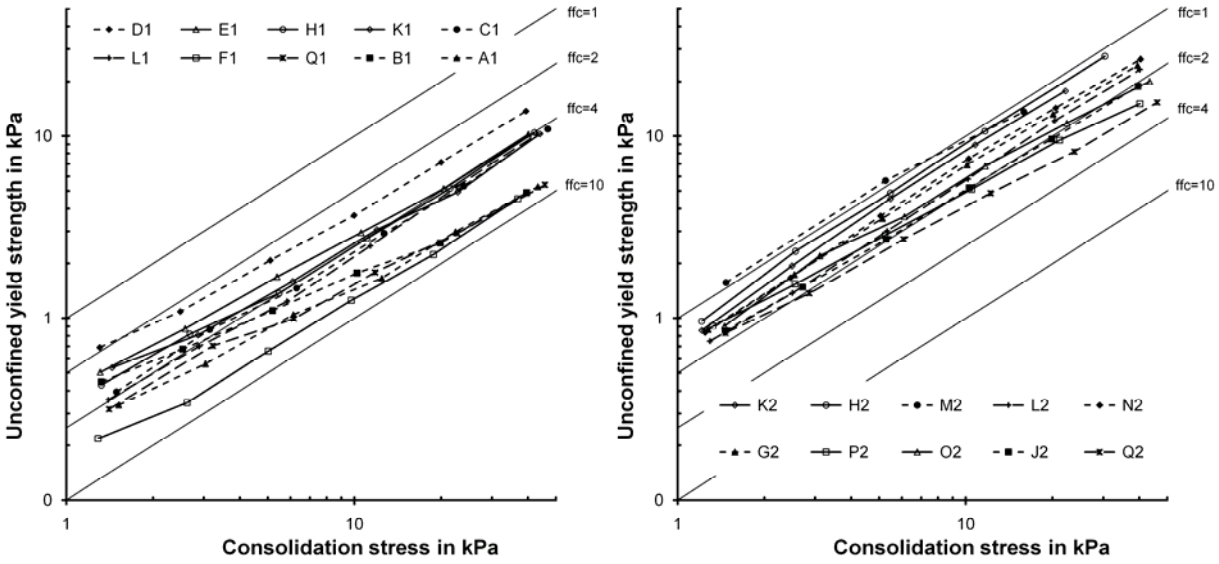
Table 2. Characteristic data of the fly ashes

Fly ash	Mass median diameter in µm	Humidity in %	TC in g/kg	Bulk density in kg/m³	Spread of the particle size distribution	Angle of repose in °	Average effective angle of internal friction in °	Average wall friction angle in °
First-stage fly ashes								
A1	97	1.0	32.6	900	35	39	45.5 ± 1.4	22.9 ± 2.0
B1	62	0.9	37.6	1010	46	44	42.7 ± 2.7	25.0 ± 2.3
C1	25	1.0	43.2	520	18	44	47.7 ± 1.4	25.9 ± 0.9
D1	11.6	0.4	17.0	450	36	53	45.8 ± 2.4	28.0 ± 0.4
E1	14.8	1.3	17.7	440	21	48	44.0 ± 2.0	27.2 ± 1.1
H1	18.1	0.7	41.9	530	25	47	44.2 ± 0.8	24.3 ± 1.7
F1	48	0.4	9.8	720	11	35	40.2 ± 2.3	22.6 ± 1.2
K1	24	0.8	57.7	590	40	43	45.7 ± 1.5	25.0 ± 0.2
L1	27	1.3	30.8	530	25	42	45.3 ± 0.8	25.5 ± 1.0
Q1	57	0.5	36.4	710	12	36	43.7 ± 1.2	21.9 ± 1.2
Average	38	0.8	32	640	27	43	44.5	24.8
Second-stage fly ashes								
G2	4.8	1.2	28.8	310	34	45	55.3 ± 1.4	30.3 ± 0.6
H2	2.8	1.9	13.6	100	9	40	71.4 ± 2.6	34.5 ± 0.7
J2	7.4	0.6	33.2	350	35	49	50.5 ± 3.4	29.9 ± 0.4
K2	2.3	2.1	70.5	170	13	43	66.2 ± 2.0	34.0 ± 1.0
L2	3.9	1.2	19.7	310	37	47	51.0 ± 1.1	30.0 ± 0.5
M2	3.1	1.5	13.7	150	11	44	64.0 ± 1.6	32.7 ± 0.5

N2	4.0	1.0	30.2	240	36	47	55.3 ± 1.8	32.4 ± 0.4
O2	5.2	1.7	26,9	200	18	49	54.7 ± 4.5	31.5 ± 0.2
P2	4.9	1.9	35.0	190	14	52	49.7 ± 4.5	30.4 ± 0.5
Q2	7.7	3.5	113	240	30	48	50.2 ± 2.9	28.2 ± 1.2
Average	4.6	1.7	38	230	24	46	56.8	31.4

3.3 Fly ash flow properties

The results for the flowability of the fly ashes are shown in Fig. 3. Generally, the flowability of the fly ashes improved slightly at higher values of the consolidation stress. The flowability category of the first-stage fly ashes was cohesive to easy-flowing, while for the second-stage fly ashes it was very cohesive to cohesive. For the second-stage fly ashes with the smallest particle size (H2, K2 and M2) no measurement results at the highest normal stress (20 kPa) were obtained. This was due to a strong slip-stick effect which was not observed at a normal stress of 5 kPa or lower. At 10 kPa a slight slip-stick effect was observed that did not disturb the measurement. For the coarser second-stage fly ashes and for the first-stage fly ashes no slip-stick effect was observed.



First-stage fly ashes Second-stage fly ashes

Fig. 3 Dependence of the flowability on the consolidation stress

Solely for the mass median diameter of the fly ashes was a good correlation with the flowability discovered, whereas for other parameters investigated (spread of the size distribution, humidity, TC, angle of repose) no noticeable correlation could be established. The correlation of the flowability at a normal stress of 5 kPa with the mass median diameter is depicted in Fig. 4. The relationship can be expressed by the equation $ff_c = 0.715 \cdot x_{50}^{0,551}$. The

correlation coefficient for this relation was 0.96. As the bulk density correlates with the mass median diameter, a correlation between the flowability and the bulk density can also be found. However, the correlation coefficient for this relationship is less pronounced.

For the flowability and the angle of repose a reasonable linear correlation emerged only when the fly ashes with a mass median diameter of less than 4.9 µm were excluded (correlation coefficient: 0.82). For the finer grained fly ashes the angle of repose was nearly as small as for the coarsest fly ashes. The smaller angle of repose for these fine fly ashes can be explained by the formation of agglomerates which were observed rolling down the slope of the formed cone, thus reducing the angle of repose. This effect has already been reported for other fine-grained dusts from off-gas cleaning systems [26].

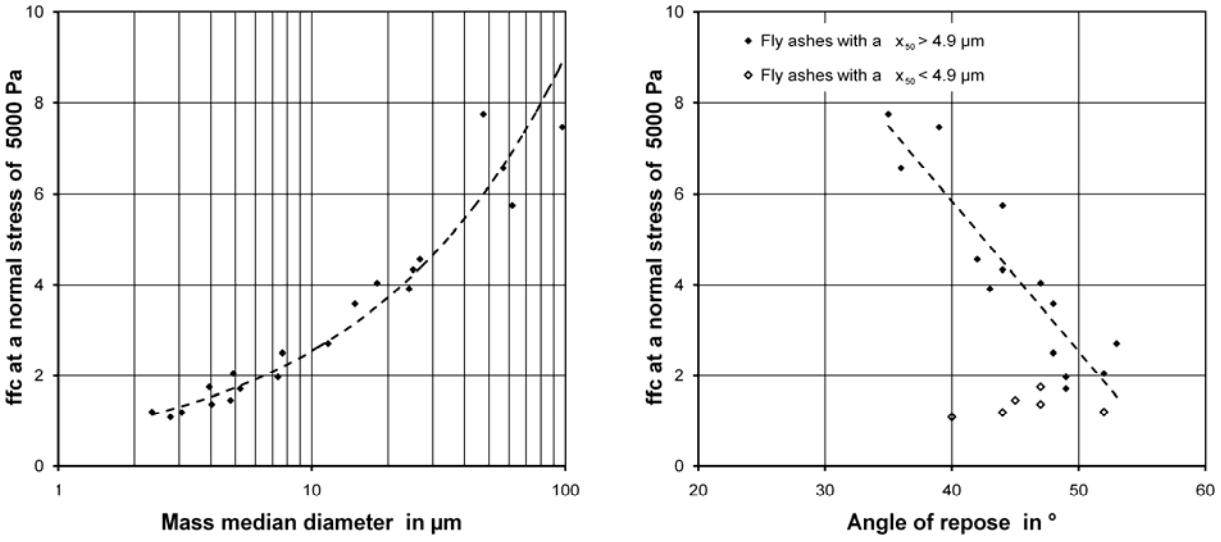


Fig. 4 Flowability ff_c as a function of the mass median diameter of the fly ash particles (left side) and as a function of the angle of repose (right side)

The bulk density increases with higher values of the consolidation stress. The dependence of the bulk density on the consolidation stress can be approximated by equations of the type $\rho_b = B \cdot \sigma_1^c$. The results for the constants B and c and the correlation coefficients are summarized in Table 3. All correlation coefficients were higher than 0.99.

Table 3. Characteristic data of the approximation functions

Fly ash	B	c	r^2
First-stage fly ashes			
A1	854	0.0283	0.999
B1	994	0.0440	0.998
C1	545	0.0607	0.994
D1	449	0.1130	0.998
E1	498	0.0975	0.995
H1	539	0.0733	0.997
F1	718	0.0467	0.997
K1	597	0.0638	0.997
L1	528	0.0611	0.991
Q1	684	0.0309	0.994
Second-stage fly ashes			
G2	372	0.1412	0.995
H2	149	0.2351	0.998
J2	415	0.1231	0.995
K2	225	0.1867	0.999
L2	376	0.1179	0.994
M2	117	0.1633	0.994
N2	292	0.1525	0.995
O2	225	0.1700	0.997
P2	245	0.1497	0.994
Q2	315	0.1043	0.999

The values of the exponent c correlated well with the particle size: the coarser the particles, the lower the exponent c was. This relationship, shown in Fig. 5, can be expressed by the equation $c = 0.328 \cdot x_{50}^{-0,522}$. The correlation coefficient was 0.94.

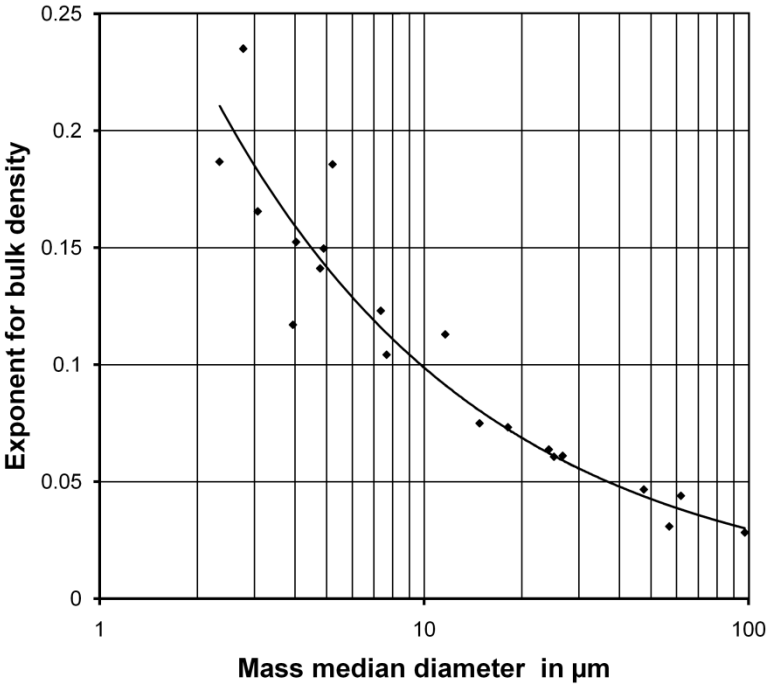


Fig. 5 Exponent of the density function as a function of the mass median diameter of the fly ash particles

The average effective angles of internal friction of the ash samples are shown in Table 2 together with their standard deviation. For the first-stage fly ashes the effective angle of internal friction lay in the range of 40° to 50°; the average value for these fly ashes was 44.5°. For all first-stage fly ashes the values of the effective angle of internal friction slightly decreased at higher levels of consolidation stress. For the second-stage fly ashes the values of the effective angle of internal friction were considerably higher, especially for the finest fly ashes. For these fine fly ashes the values fluctuated, while for the somewhat coarser second-stage fly ashes the values also decreased at higher consolidation stress. The average value for the effective angle of internal friction of the second-stage fly ashes was 56.8°.

The average wall friction angles of the fly ashes with the structural steel S235JR are also summarized in Table 2. The average wall friction angles of the first-stage fly ashes were in the range of 22° to 28°, whereas for the second-stage fly ashes the values were in the range of 28° to 35°. For the second-stage fly ashes the wall friction angles were almost independent of the wall normal stress, while for most first-stage fly ashes the wall friction angles were lower for higher values of the wall normal stress.

The average effective angle of internal friction and the average wall friction angle, as a function of the mass median diameter, are shown in Fig. 6. Both friction angles were lower for the coarser fly ashes. As can be seen on the right side of Fig. 6, the average wall friction angles correlated well with the mass median diameters of the fly ash samples. The relation can be expressed by the equation $\varphi_W = 37.0 \cdot x_{50}^{-0,116}$. The correlation coefficient was 0.91. The relation between the average effective angle of internal friction and the mass median diameter cannot be accurately described by the simple function of the type $\varphi_e = a \cdot x_{50}^{k}$, depicted in Fig. 6, which resulted in a poor correlation coefficient of 0.70. For the mathematically more complex relation $\varphi_e = 56.2 \cdot \ln\left(2 \cdot \ln\left(x_{50}\right)\right)^{-0.361}$ the correlation coefficient was 0.87.

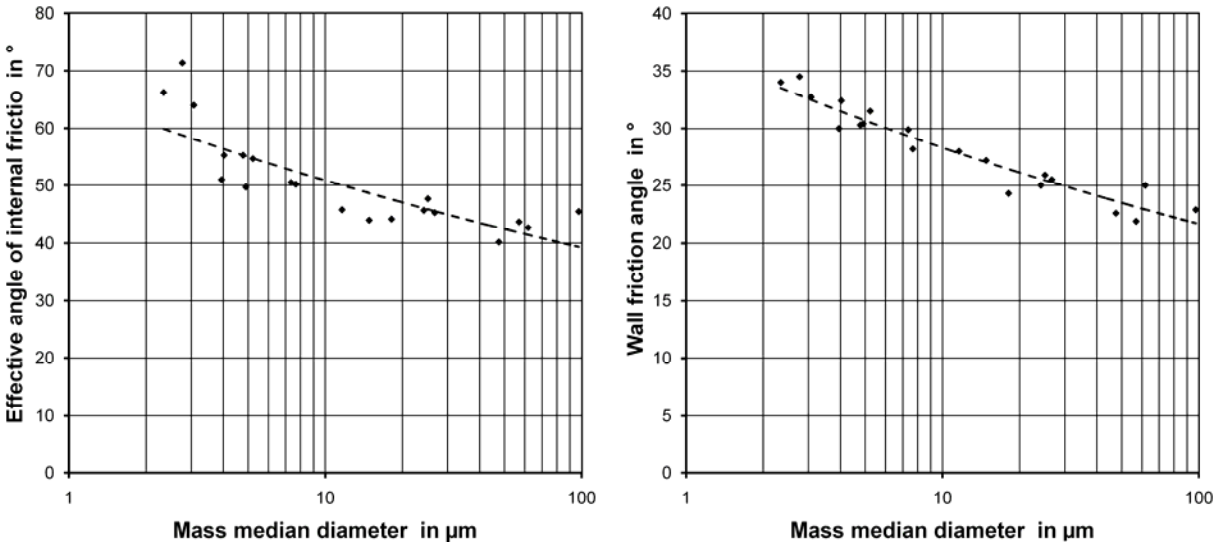


Fig. 6 Average effective angle of internal friction and average wall friction angle as a function of the mass median diameter of the fly ash

There was also some correlation of the average effective angle of internal friction and average wall friction angle with the bulk density. However, the coefficients for this correlation were not so satisfactory.

4. Conclusions

The particle size of fly ashes from grate-fired combustion of forest residues can vary in a wide range; the mass median diameters of the size distributions lay in the range of approximately 2 – 100 µm. As expected, the fly ashes from first-stage dust separators were coarser, while the mass median diameter of second-stage fly ashes was generally less than 10 µm.

The flowability of the first-stage fly ashes was cohesive to easy-flowing, whereas for the second-stage fly ashes it was very cohesive to cohesive. The flowability of the fly ashes correlated fairly precisely with the mass median diameter of the ash particles, although a noticeable correlation with the angle of repose was only found for the coarser fly ashes with a mass median diameter of > 4.9 µm.

The bulk density of the fly ashes also correlated with the mass median diameter. Therefore, a correlation was discovered between the flowability and the bulk density as well. However, the correlation coefficient for this interdependence was far lower. For the other parameters determined, the humidity, the TC and the spread of the size distribution no correlation with the flowability was found.

Furthermore, other parameters relevant for the design calculations, the effective angle of internal friction, the wall friction angle and the bulk density as a function of the consolidation stress can be stated as a function of the mass median diameter.

Thus, the particle size, expressed by the mass median diameter of the size distribution, is the most important parameter for the flowability of the fly ashes.

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