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

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### 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<sub>th</sub> 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.

*Keywords:* ash, biomass, heavy metals, leaching, waste

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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 (Farias et al., 2017; 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; Mahmoudkhani et al., 2007; Orava et al., 2006; Sarenbo et al., 2009). Because of the formation of less soluble compounds such as calcite the

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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 utilization 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 utilization 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.

Actually, in Austria the utilization 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 utilization 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 carried out 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.

**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.

	<i>Austrian guideline<sup>1</sup> (BMLFUW, 2011)</i>		<i>Finland cited in Nurmesniemi et al. (2012)</i>	<i>Sweden cited in Emilsson (2006)</i>	<i>Denmark cited in Haglund (2008)</i>	<i>Lithuania cited in Stupak et al. (2008)</i>
	<i>A</i>	<i>B</i>				
As	20	20	40	30		30
Cd	5	8	25	30	5 / 15 <sup>2</sup>	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 <sup>3</sup>	70
V				70		70
B				500		500
Hg			1.0	3	0.8	3

Note: <sup>1</sup> if the concentrations are below limits according to A, no soil analysis is required;

<sup>2</sup> left Cd limit for straw ash, right Cd limit for wood ash;

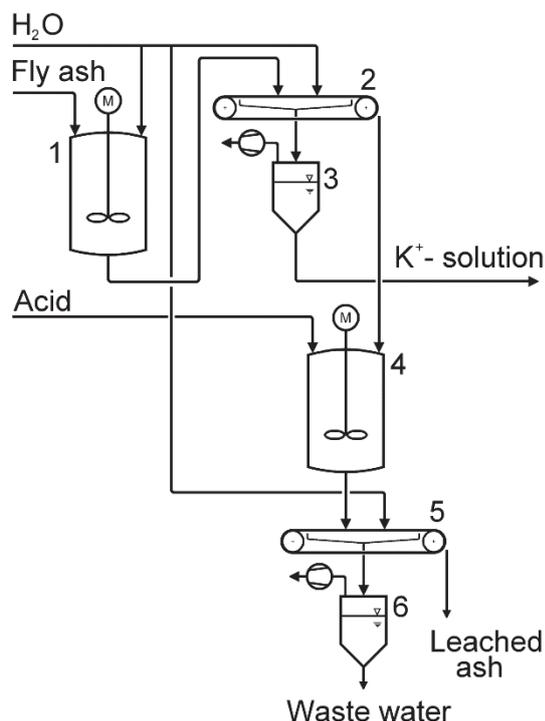
<sup>3</sup> between 30 and 60 mg/kg a reduced ash quantity can be applied.

The concentrations of heavy metals in the agglomerates produced are analyzed 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.



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

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.

### 2.2. Ash sample

The ash samples were taken from a 5.0 MW<sub>th</sub> 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 dm<sup>3</sup> 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 dm<sup>3</sup>. 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<sup>3</sup> 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<sup>-</sup> 6.1 mg/dm<sup>3</sup>; NO<sub>3</sub><sup>-</sup> 8.4 mg/dm<sup>3</sup>; SO<sub>4</sub><sup>2-</sup> 6.9 mg/dm<sup>3</sup>; Na 4.8 mg/dm<sup>3</sup>; K 1.0 mg/dm<sup>3</sup>; Mg 13 mg/dm<sup>3</sup>; Ca 69 mg/dm<sup>3</sup>. 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 dm<sup>3</sup> 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<sup>3</sup> of the suspension were filtered in each batch. Each filter cake was flushed with 0.2 dm<sup>3</sup> 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<sup>3</sup> 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 analyzed 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 analyzer 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 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.

### 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. 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/m<sup>3</sup>, 660 kg/m<sup>3</sup> and 1130 kg/m<sup>3</sup>, 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 dm<sup>3</sup> 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/dm<sup>3</sup>) 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 analyzed 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<sup>3</sup>.

In the filtrate of the second leaching step the Ca concentration was 29 g/dm<sup>3</sup>, 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 as shown in Table 3.

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

	<i>Bottom ash (fraction &lt; 10 mm)</i>	<i>Cyclone ash</i>	<i>EP ash</i>
<i>Heavy metals in mg/kg ash d.w.</i>			
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
<i>Nutrients in g/kg ash d.w.</i>			
K	59	81	258
Ca	280	240	59

Note: d.w. dry weight

**Table 3.** Leaching of heavy metals

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

Note: < d.l. concentration in the leachate below detection limit;

<sup>1</sup> 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  $\mu\text{g}/\text{dm}^3$ , 37  $\mu\text{g}/\text{dm}^3$ , 10  $\mu\text{g}/\text{dm}^3$  and 83  $\mu\text{g}/\text{dm}^3$ , respectively. The concentrations of As, Cr and Ni were below the detection limits ( $< 50 \mu\text{g}/\text{dm}^3$ ). 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.

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  $\mu\text{m}$ . Presumably because of the addition of fine hydrated lime the MMD was higher for product B (2450  $\mu\text{m}$ ) and product C (1980  $\mu\text{m}$ ). 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  $\mu\text{m}$ , 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  $\mu\text{m}$  and 1870  $\mu\text{m}$  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  $\text{kg}/\text{m}^3$ , 610  $\text{kg}/\text{m}^3$  and 550  $\text{kg}/\text{m}^3$ , 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.

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

	<i>Ash pellets</i>	<i>Mixed ashes (bottom ash, cyclone ash and EP ash) without leaching</i>	<i>Reduction rate in %</i>
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

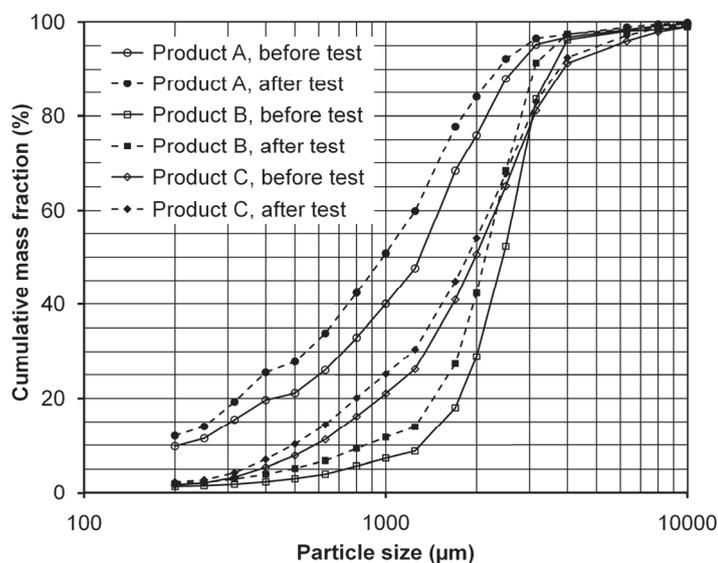


Fig. 2. Particle size distribution of agglomerates before and after falling test

#### 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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#### References

- AEBIOM, (2013), European Bioenergy Outlook 2013, Statistical Report, European Biomass Association, Brussels, On line at: <http://www.aebiom.org/wp-content/uploads/2015/10/Statistical-report-article.pdf>.
- BMLFUW, (2011), Guideline for the utilization of biomass ashes on agricultural and forest land (in German), Bundesministerium für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft, Wien, Austria.
- Dahl J., Obernberger I., (1998), *Thermodynamic and Experimental Investigations on the Possibilities of Heavy Metal Recovery from Contaminated Biomass Ashes by Thermal Treatment*, Proc. 10th Europ. Conf. and Technology Exhibition: Biomass for Energy and Industry, Würzburg, Germany.
- Dahl J., (2000), *Chemistry and behaviour of environmentally relevant metals in biomass combustion and thermal ash treatment processes*, PhD Thesis, Institute of Chemical Engineering, University of Technology Graz, Austria.
- Dahl O., Nurmesniemi H., Pöykiö R., Watkins G., (2009), Comparison of the characteristics of bottom ash and fly ash from a medium-size (32 MW) municipal district heating plant incinerating forest residues and peat in a fluidized-bed boiler, *Fuel Processing Technology*, **90**, 871-878.
- Dahl O., Nurmesniemi H., Pöykiö R., Watkins G., (2010), Heavy metal concentrations in bottom ash and fly ash fractions from a large-sized (246 MW) fluidized bed boiler with respect to their Finnish forest fertilizer limit values, *Fuel Processing Technology*, **91**, 1634-1639.
- Decostere B., Hogie J., Dejangs P., Van Hulle S.W.H., (2009), Removal of heavy metals occurring in the washing water of flue gas purification, *Chemical Engineering Journal*, **150**, 196-203.
- Emilsson S., (2006), *International Handbook – From Extraction of Forest Fuels to Ash Recycling*, Swedish Forest Agency, Stockholm, Sweden.
- Farias R.D., Garcia C.M., Palomino T.C., Andreola F., Lancellotti I., Barbieri L., (2017), Valorization of agro-industrial wastes in lightweight aggregates for

- agronomic use: preliminary study, *Environmental Engineering and Management Journal*, **16**, 1691-1699.
- Haglund N., (2008), Guideline for classification of ash from solid biofuels and peat utilized for recycling and fertilizing in forestry and agriculture, NT Technical report 613, Nordic Innovation Centre, Oslo, Norway, On line at: <http://www.nordtest.info/index.php/technical-reports/item/guideline-for-classification-classification-of-ash-from-solid-biofuels-and-peat-utilised-for-recycling-and-fertilizing-in-forestry-and-agriculture-nt-tr-613.html>.
- Hallenbarter D., Landolt W., Bucher J.B., Schütz J.-P., (2002), Effects of wood ash and liquid fertilization on the nutritional status and growth of Norway Spruce (*Picea abies* (L.) Karst.), (in German), *Forstwissenschaftliches Centralblatt*, **121**, 240-249.
- Hansen H.K., Pedersen A.J., Ottosen L.M., Villumsen A., (2001), Speciation and mobility of cadmium in straw and wood combustion fly ash, *Chemosphere*, **45**, 123-128.
- Holmberg S.L., Claesson T., (2001), Mineralogy of granulated wood ash from a heating plant in Kalmar, Sweden, *Environmental Geology*, **40**, 820-828.
- Holmberg S.L., Claesson T., Abul-Mihl M., Steenari B.-M., (2003), Drying of granulated wood ash by flue gas from saw dust and natural gas combustion, *Resources, Conservation and Recycling*, **38**, 301-316.
- Ingerslev M., Skov S., Sevel L., Pedersen L.B., (2011), Element budgets of forest biomass combustion and ash fertilization – A Danish case-study, *Biomass and Bioenergy*, **35**, 2697-2704.
- ISO 11466, (1995), Soil quality – Extraction of trace elements soluble in aqua regia, International Organization for Standardization, Genève, Switzerland.
- Orava H., Kuopanportti H., Tontti T., (2006), *Disc Pelletization of Wood Ash from a Pulp Mill to be Used as a Forest Fertilizer*, Proc. 5th Int. Conf. for Conveying and Handling of Particulate Solids, Sorrento, 16.6.
- Lanzerstorfer C., (2014), Chemical and physical characterization of five cyclone fly ashes from grate-fired biomass combustion, *Carpathian Journal of Earth and Environmental Sciences*, **9**, 129-135.
- Lanzerstorfer C., (2015), Chemical composition and physical properties of filter fly ashes from eight grate-fired biomass combustion plants, *Journal of Environmental Sciences*, **30**, 191-197.
- Mahmoudkhani M., Richards T., Theliander H., (2007), Sustainable use of biofuel by recycling ash to forests: treatment of biofuel ash, *Environmental Science and Technology*, **41**, 4118-4123.
- Mellbo P., Sarenbo S., Stålnacke O., Claesson T., (2008), Leaching of wood ash products aimed for spreading in forest floors – Influence of method and L/S ratio, *Waste Management*, **28**, 2235-2244.
- Moilanen M., Silfverberg K., Hokkanen T.J., (2002), Effects of wood-ash on the tree growth, vegetation and substrate quality of a drained mire: a case study, *Forrest Ecology and Management*, **171**, 321-338.
- Nurmesniemi H., Mäkelä M., Pöykiö R., Manskinen K., Dahl O., (2012), Comparison of the forest fertilizer properties of ash fractions from two power plants of pulp and paper mills incinerating biomass-based fuels, *Fuel Processing Technology*, **104**, 1-6.
- ÖNORM ISO 697, (1986), Surface active agents: washing powders; determination of apparent density; method by measuring the mass of a given volume, (in German), Österreichisches Normungsinstitut, Wien, Austria.
- ÖNORM EN ISO 60, (1999), Plastics – Determination of apparent density of material that can be poured from a specified funnel, (in German), Österreichisches Normungsinstitut, Wien, Austria.
- Pedersen A.J., (2003), Characterization and electro-dialytic treatment of wood combustion fly ash for the removal of cadmium, *Biomass and Bioenergy*, **25**, 447-458.
- Pedersen A.J., Ottosen L.M., Villumsen A., (2003), Electro-dialytic removal of heavy metals from different fly ashes – Influence of heavy metal speciation in the ashes, *Journal of Hazardous Materials*, **B100**, 65-78.
- Pietsch W., (2002), *Agglomeration Processes: Phenomena, Technologies, Equipment*, Wiley-VCH, Weinheim.
- Pirker K., Braunegg G., Reisenhofer E., Oberberger I., (1998), *Heavy Metal Recovery from Contaminated Biomass Ashes by Chemical Leaching and Biosorption*, In: *Ash and Particulate Emissions from Biomass Combustion*, Oberberger I. (Ed.), Institute of Chemical Engineering, Technical University Graz, 191-212.
- Pitman R.M., (2006), Wood ash use in forestry – a review of the environmental impacts, *Forestry*, **79**, 563-588.
- Pöykiö R., Rönkkömäki H., Nurmesniemi H., Perämäki P., Popov K., Välimäki I., Tuomi T., (2009), Chemical and physical properties of cyclone fly ash from the grate-fired boiler incinerating forest residues at a small municipal district heating plant (6 MW), *Journal of Hazardous Materials*, **162**, 1059-1064.
- Rasmusson H., Sarenbo S., Claesson T., (2013), Ash products and their economic profitability, *The Open Waste Management Journal*, **6**, 1-5.
- Sarenbo S., Mellbo P., Stålnacke O., Claesson T., (2009), Reactivity and leaching of wood ash pellets dehydrated by hot air and flue gas, *The Open Waste Management Journal*, **2**, 47-54.
- Stahl E., Dorsch P., (2008), Quality and utilization possibilities of wood ash from untreated wood, (in German), *Umweltwissenschaften und Schadstoff-Forschung*, **20**, 290-298.
- Steenari B.-M., Lindqvist O., (1997), Stabilisation of biofuel ashes for recycling to forest soil, *Biomass and Bioenergy*, **13**, 39-50.
- Steenari B.-M., Karlsson L.G., Lindqvist O., (1999a), Evaluation of the leaching characteristics of wood ash and the influence of ash agglomeration, *Biomass and Bioenergy*, **16**, 119-136.
- Steenari B.-M., Schelander S., Lindqvist O., (1999b), Chemical and leaching characteristics of ash from combustion of coal, peat and wood in a 12 MW CFB – a comparative study, *Fuel*, **78**, 249-258.
- Stupak I., Asikainen A., Röser C., Pasanen K., (2008), *Review of Recommendations for Forest Energy Harvesting and Wood Ash Recycling*, In: *Sustainable Use of Forest Biomass for Energy*, Röser D., Asikainen A., Raulund-Rasmusen K., Stupak I., (Eds.), Springer, Dordrecht, 155-196.
- van Loo S., Koppejan J., (2008), *The Handbook of Biomass Combustion and Co-firing*, Earthscan, London.