Characterization of Poultry Litter Ash in View of Its Valorization

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Abstract

The overall aim of this research was to evaluate the valorization potential of the poultry litter ash produced in the biomass power plant of BMC Moerdijk (the Netherlands), since the ash contains phosphorus (P) and potassium (K), which are both essential nutrients. As a first step, the ash was characterized by means of chemical analysis. Ash collected in the superheater section of the boiler had the highest P concentration (10.6%). Furthermore, the P concentration in the ash decreased as it was collected further downstream in the boiler and flue gas cleaning part of the installation. K showed an opposite concentration trend, that is, its concentration was the lowest in the superheater ash (9.4%) and increased to 15.5% in the electrostatic precipitator ash. Based on the results of the chemical analysis, different valorization options could be considered. Although poultry litter ash has the same heavy metal/P ratio as poultry litter and is free of pathogens and toxic organic substances, its recycling as a P/K fertilizer is hindered by legal constraints. Furthermore, the use of the ash in/as animal feed is not straightforward because of its origin (animal feces) and waste status. Besides P and K, other ash elements such as calcium, silicon, magnesium, iron and aluminum can also be valorized, for example by using the ash as building material or in cement production. However, in these applications the high P and K concentration of the ash can be a technical obstacle rather than a benefit. In this regard, it can be interesting to separate the fertilizer elements, that is, P and K, from the rest of the ash by means of for example a wet chemical extraction after which the remaining solid residue better meets the composition requirements for building material or raw material for cement production.

Graphic Abstract

Keywords Phosphorus · Potassium · Poultry litter ash · Recycling · Valorization

Statement of Novelty

The present study is the first of its kind to provide a comprehensive overview of valorization pathways for poultry litter ash, based on its chemical characterization.

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Introduction

Phosphorus (P), in nature mainly occurring as phosphate (PO_4^{3-}), is an essential micronutrient for all living organisms. To compensate for P uptake by crops, globally 17.8 million tons of P is annually used in agriculture and this P is mostly extracted from phosphate rock, a non-renewable resource [1–3]. Experts estimate that the demand for P containing fertilizers will double by 2050 compared to 2012. This increasing demand can be explained by the increasing world population, the improving quality of life in developing countries and the growing requirement for feed and food and hence fertilizers [3, 4]. Consequently, the phosphate rock demand will outrun the supply within the next 25 to 30 years and experts estimate that the global phosphate rock reserves will be depleted within 50 to 100 years [2, 3, 5]. The European Union considers both P and phosphate rock as one of the 27 critical raw materials because of their strategic importance and the economic dependence on a limited number of non-European suppliers (mainly China, Morocco and the United States) [3, 6]. Therefore, to meet future P demands, it is important to recover P from alternative sources.

Ash, as a by-product of the incineration of P rich residues such as wastewater treatment sludge, animal manure or animal by-products, is most promising for P recovery because of its high P and low moisture content [2, 7–10]. For example, the poultry litter ash from the biomass power plant considered in this work contains on average 5.5% P (12.7% P_2O_5) [11], which is much higher compared to, for instance, liquid waste streams such as wastewater and urine that only contain 0.0005 to 0.035% P [12, 13]. Since this poultry litter ash also contains on average 9.9% of the essential micronutrient potassium (K) (11.9% K_2O) [11], it is an interesting (source for) fertilizer (production). However, this poultry litter ash also contains some heavy metals originating from the poultry litter, mainly copper (Cu) and zinc (Zn) (respectively, about 400 and 1800 mg/kg dry matter (DM) [11]), which might pose a regulatory problem for direct application as fertilizer, depending on local legislation.

Furthermore, Blake and Hess investigated the suitability of poultry litter ash as a feed supplement for broiler chickens and concluded that this is an alternative way to valorize the P and calcium (Ca) in the ash [14]. However, besides P and Ca, also trace elements such as Cu and Zn can be valorized this way, by directly reintroducing them in the feed cycle. Indeed, Cu and Zn are trace elements essential for important biochemical functions and necessary for maintaining health of humans and animals throughout life [15–17]. Hence, they are often added to diets in quantities higher than what is necessary to fulfil the nutritional requirements [16, 17].

Besides P and K, the poultry litter ash considered in this work also contains on average 18.1% Ca, 6.8% silicon (Si),

3.1% magnesium (Mg), 0.5% iron (Fe) and 0.4% aluminum (Al) [11] and has therefore an interesting potential for use as building material or in cement production [18]. Some possible applications are use as loose construction aggregates, as replacement for sand, gravel or cement in construction material, as raw material in cement production or as feedstock for ceramic materials production. However, it should be noted that each of these options desires specific ash properties [19].

The overall aim of this research was to evaluate the valorization potential of the poultry litter ash produced by the biomass power plant of BMC Moerdijk (the Netherlands). In a first step, the different ash streams that are generated in the installation were characterized by means of sieving tests and chemical analysis. In a second step, the obtained elemental composition of the different ash streams and size fractions was compared with legal limit values and desirable concentrations for their use as fertilizer, in/as animal feed, as building material or in cement production.

Materials and Methods

Poultry Litter Combustion Installation and Ash Sampling

The biomass power plant of BMC located in Moerdijk, the Netherlands, annually generates 291,000 MWh of electricity by incinerating about 420,000 tons of poultry litter in a fluidized bed furnace producing 60,000 tons of poultry litter ash. The installation consists of a fluidized bed, an energy recovery unit (hereafter referred to as boiler) and a flue gas cleaning unit [8]. The ash streams considered in this work were representatively sampled at five different points in the installation as indicated in Fig. 1: (1) bed ash, collected at the bottom of the fluidized bed (26% of total ash mass produced); boiler ash, more specifically (2) SH ash, collected at the bottom of the superheater (6%) and (3) ECO ash, collected at the bottom of the economizer (5%); (4) ESP ash, collected at the bottom of the electrostatic precipitator (58%); (5) bag ash, collected at the bottom of the Turbosorp® and baghouse filter (5%).

In the fluidized bed, hot air is blown through the sand layer to control the bed temperature at 750 °C and to cause the sand to behave like a boiling liquid. Kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) is added in the fluidized bed to prevent agglomeration of K rich low melting point salts on the furnace walls. The poultry litter ash is fed on top of the fluidized sand bed, thoroughly mixes with the fluidizing air and combusts. In the post-combustion zone, secondary air is introduced raising the temperature to 1000 °C to assure complete burnout [8]. The residence time of at least two seconds at minimum 850 °C (Directive 2000/76/EC [20]) guarantees

Fig. 1 Graphical representation of the poultry litter combustion installation of BMC Moerdijk. The blue ovals indicate the sample points of the five different ash streams

the complete removal of pathogens and toxic organic pollutants [8, 11]. The *bed ash* drops through the furnace bed and is collected under the fluidized bed (see Fig. 1). This ash stream contains most of the sand and in fact consists of spherical coated sand particles. Lighter ash particles are entrained from the bed with the flue gas and are retained as dust in the boiler and in the flue gas cleaning installation.

The *SH ash*, collected at the bottom of the superheater (see Fig. 1), consists mainly of particles entrained from the fluidized bed and of fly ash that is formed by condensation and solidification of evaporated salts. The “shot cleaning system” feeds metal balls at the top of the economizer to remove dust that has deposited on these boiler section surfaces. The metal balls hit the walls and the tubes of the boiler on their way down, removing deposited ash particles that are collected together with the finer ash particles from the flue gas at the bottom of the economizer, resulting in *ECO ash* (see Fig. 1).

After the flue gas has passed the steam boiler, it enters the flue gas cleaning unit (electrostatic precipitator, Turbosorp[®], baghouse filter and selective catalytic reduction DeNO_x). The electrostatic precipitator removes 95% of the dust particles still present in the flue gas; the ash collected at the bottom is referred to as *ESP ash* (see Fig. 1). In the Turbosorp[®] reactor, lime (Ca(OH)₂) is added to neutralize the acid gasses (HCl, SO₂) in the flue

gas. In the baghouse filter, the reaction products and the non-reacted lime particles are separated from the flue gas by means of long filter bags. The ash collected at the bottom of the Turbosorp[®] and the baghouse filter is further referred to as *bag ash* (see Fig. 1). Finally, in the selective catalytic reduction DeNO_x, the nitrogen oxides in the flue gas are converted to harmless nitrogen and water, by addition of ammonia over a catalyst [8].

The bed, ECO and ESP ash were sampled in week 12–13 (2017), whereas the bag ash was sampled in week 12–13 and 17–20 (2017), and the SH ash in week 18 (2017). The mixed ash, which is the combination of bed, SH, ECO, ESP and bag ash with a mass ratio 26:6:5:58:5, was sampled in week 16–19 (2017). About 500 ml of each ash stream was sampled once a day and mixed thoroughly with the samples collected on the other days in the indicated periods. The resulting pooled ash samples analyzed in this work are thus well-blended samples that are representative of the solid residues of the poultry litter incineration process. However, from previous analytical results [11] it is clear that the ash composition can rather change over time, which is primarily related to the variation in poultry litter composition between different suppliers (e.g. poultry litter from broiler and layer chickens) and over the year (seasonal variation).

181 Ash Sieving

182 To obtain an indication of the particle size distribu-
 183 tion, bed and ECO ash were sieved into different parti-
 184 cle size fractions with a Fritsch Vibratory Sieve Shaker
 185 Analysette 3 for 10 min at amplitude 30%. Six samples
 186 of about 200 g of bed ash were each sieved over six piled
 187 up sieves with a mesh size of 0.125, 0.5, 0.71, 1, 2 and
 188 4 mm, respectively. Three samples of about 30 g of ECO
 189 ash were each sieved over five piled up sieves with a mesh
 190 size of 63, 125, 250, 315 and 400 μm , respectively. The
 191 sieve mesh sizes were selected in such a way that the mass
 192 of the ash remaining on the coarsest sieve and in the pan
 193 at the bottom was less than 15% of the total ash mass. SH,
 194 ESP and bag ash were not sieved because they consisted
 195 of fine powders that did not show a significant difference
 196 in particle size.

197 Chemical Ash Analysis

198 The ash particle fractions obtained after sieving and the
 199 entire ash streams, that is, the ash streams as received
 200 prior to sieving, were crushed and digested with a com-
 201 bination of aqua regia and hydrofluoric acid (HF). The
 202 method used in this paper was based on CMA/2/II/A.3
 203 [21], which is based on the European standard EN
 204 13656:2002 “Characterization of waste—Microwave
 205 assisted digestion with hydrofluoric (HF), nitric (HNO_3),
 206 and hydrochloric (HCl) acid mixture for subsequent deter-
 207 mination of elements” [22]. VITO (an independent Flem-
 208 ish research organization in the field of cleantech and
 209 sustainable development) applied the method as described
 210 in CMA/2/II.A.3 on bottom and fly ash and concluded
 211 that this method yielded results comparable to alternative
 212 destruction methods [23, 24]. However, in this work an
 213 ultrasonic bath was used instead of microwave assisted
 214 digestion because the former allowed more complete dis-
 215 solution of silicates in the specific ash stream studied in
 216 this work. A well-sealed 100 ml HDPE digestion bottle
 217 with 500 mg of dry ash, 8 ml aqua regia and 3 ml HF
 218 was placed in an ultrasonic bath (Branson 3510) for 24 h.
 219 Next, the bottle was cooled for 1 h and the content was
 220 transferred to a 100 ml PP volumetric flask containing
 221 about 2.8 g boric acid and diluted to the mark. This solu-
 222 tion was further filtered over a syringe filter (0.45 μm),
 223 diluted and analyzed for P, K, Ca, Mg, sodium (Na), sul-
 224 fur (S), Si, Al, cadmium (Cd), chromium (Cr), Cu, Fe,
 225 manganese (Mn), molybdenum (Mo), nickel (Ni), lead
 226 (Pb), titanium (Ti) and Zn by Inductively Coupled Plasma
 227 Optical Emission Spectroscopy (ICP-OES) (Varian 720-
 228 ES ICP-OES). No glassware was used for digestion and
 229 dilution.

Solubility of P and K

The P and K solubility in water, neutral ammonium cit-
 rate and 2% citric acid were determined for bed, SH, ECO,
 ESP, bag and mixed ash, based on the European regulation
 2003/2003 relating to fertilizers [25]. For the determination
 of the solubility in water and 2% citric acid, a well-sealed
 50 ml PP falcon tube (HDPE flat cap) with 300 mg of dry ash
 and respectively, 30 ml demineralized water (18.2 M Ω .cm,
 Millipore Direct-Q 3 UV) or 30 ml 2% citric acid (20 g/l) at
 room temperature was placed horizontally on a reciprocating
 shaker (Heidolph Promax 2020) for 30 min at maximum
 speed (400 rpm). For the determination of the solubility in
 neutral ammonium citrate, a well-sealed 100 ml HDPE bot-
 tle with 500 mg of dry ash and 50 ml neutral ammonium
 citrate (169 g citric acid/l; make neutral solution (pH 7.0)
 by adding 25% ammonium hydroxide) was placed in a water
 bath thermostatically controlled at 65 °C and equipped with
 a suitable stirrer (Julabo SW22) for 1 h at maximum speed
 (200 rpm). Next, the HDPE bottle was immediately cooled
 in an ice bath to ambient temperature. All obtained solutions
 were filtered over a syringe filter (0.45 μm), diluted and ana-
 lyzed for P and K by ICP-OES (Varian 720-ES ICP-OES).

Leaching Experiments

Batch leaching experiments were conducted based on
 CMA/2/II/A.12 [26], which is based on the European
 standard EN 12457-4:2002 “Characterization of waste—
 Leaching—Compliance test for leaching of granular waste
 materials and sludges—Part 4: One stage batch test at a
 liquid to solid ratio of 10 l/kg for materials with particle
 size below 10 mm (without or with size reduction)” [27]. A
 well-sealed 100 ml HDPE bottle with 9 g of untreated dry
 ash and 90 ml demineralized water (18.2 M Ω cm, Millipore
 Direct-Q 3 UV) was placed horizontally on a reciprocating
 shaker (Heidolph Promax 2020) for 24 h at maximum speed
 (400 rpm). Next, the ashes were filtered over a syringe filter
 (0.45 μm). ICP-OES (arsenic (As), barium (Ba), Cd, cobalt
 (Co), Cr, Cu, Mo, Ni, Pb, antimony (Sb), selenium (Se), tin
 (Sn), vanadium (V) and Zn), Ion Chromatography (chlo-
 rides (Cl^-) and sulfates (SO_4^{2-})) and Ion Selective Electrode
 (fluorides (F^-)) were used to determine the concentration
 of the elements of interest in the remaining solution. Batch
 leaching tests were used for practical reasons; however, the
 leaching results have to be validated in a legally prescribed
 column test for correct comparison with the legal leaching
 limit values.

Statistical Analysis

All experiments (i.e. ash sieving, chemical ash analysis,
 solubility of P and K and leaching experiments), were

Fig. 2 Average retained mass fraction (%) in each sieve. The error bars indicate plus and minus one standard deviation. **a** Bed ash (n=6); **b** ECO ash (n=3)

Fig. 3 Different particle size fractions for bed ash (mm)

Fig. 4 Different particle size fractions for ECO ash (µm)

performed in triplicate, except for bed ash sieving which was performed in sextuplicate. Average values and standard deviations were determined to assess statistical significance of trends and differences.

Results and Discussion

Ash Sieving

The particle size distribution of the bed ash (Fig. 2a) and ECO ash (Fig. 2b) shows a more or less Gaussian (normal) distribution with an average particle size of 1 mm and 125 µm, respectively. About 73% of the bed ash particles has a size between 0.71 and 2 mm and about 78% of the ECO ash particles has a size between 63 and 315 µm.

The different observed particles and particle size fractions of the bed and ECO ash (Figs. 3 and 4) can be linked to the operation of the fluidized bed and the economizer section of the boiler, respectively. The bed ash particles consist on the one hand of sand particles, which are initially already about 0.7 mm and are coated in the fluidized bed [28], further increasing their size, and on the other hand of unreacted, white kaolinite particles and fine dust (see Fig. 3). The ECO ash, however, consists of both larger deposits of

ash particles removed from the walls and tubes of the boiler by the shot cleaning system, and of finer fly ash particles retained directly from the flue gas passing the boiler (see Fig. 4).

Chemical Ash Analysis

Tables 1 and 2 give the elementary composition of the bed, SH, ECO, ESP, bag and mixed ash and of the sieved bed and ECO ash size fractions, whereas Figs. 5 and 6 give a graphical representation of their P, K and Si concentration. As already mentioned in “Ash Sieving”, SH, ESP and bag ash were not sieved because they consisted of fine powders that did not show a significant difference in particle size.

The lower P concentration in the bed ash (5.0%) (see Fig. 5) can be explained by the high Si concentration (9.2%) due to the presence of sand used in the fluidized bed. Indeed, the bed ash consists of sand particles originally of about 0.7 mm that are coated in the combustion process by deposition of salts from the fuel. The bed ash coating has a high P concentration [28, 29], whilst the sand core contains almost no P and is “diluting” the P in the bed ash. For the bed ash (see Fig. 6), there is no real distinction of the P concentration

Table 1 Average concentration $\pm$ standard deviation of P, K, Ca, Mg, Na, S, Si, Al, Cd, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Ti and Zn in the bed, SH, ECO, ESP, bag and mixed ash (% of DM and mg/kg DM); n = 3

	Bed ash	SH ash	ECO ash	ESP ash	Bag ash	Mixed ash
P (% of DM)	5.0 ± 0.03	10.6 ± 0.11	8.9 ± 0.10	6.4 ± 0.06	2.3 ± 0.32	6.0 ± 0.08
K (% of DM)	9.4 ± 0.07	11.1 ± 0.06	11.5 ± 0.07	15.5 ± 1.32	14.3 ± 1.55	12.5 ± 0.30
Ca (% of DM)	20.2 ± 0.10	19.3 ± 0.11	20.1 ± 0.22	12.4 ± 0.08	20.6 ± 1.60	18.2 ± 0.36
Mg (% of DM)	2.6 ± 0.03	6.2 ± 0.06	5.2 ± 0.04	3.5 ± 0.01	1.2 ± 0.15	3.0 ± 0.56
Na (% of DM)	2.7 ± 0.02	2.6 ± 0.02	3.4 ± 0.01	3.6 ± 0.02	1.6 ± 0.12	1.9 ± 0.02
S (% of DM)	3.1 ± 0.02	1.7 ± 0.05	1.8 ± 0.02	6.0 ± 0.05	4.8 ± 0.48	3.1 ± 0.03
Si (% of DM)	9.2 ± 0.39	4.0 ± 0.03	5.6 ± 0.05	2.8 ± 0.04	1.4 ± 0.12	6.8 ± 0.27
Al (mg/kg DM)	6642 ± 113	7799 ± 84	9306 ± 69	5671 ± 42	2494 ± 69	5021 ± 187
Cd (mg/kg DM)	<2	3.5 ± 0.2	2.7 ± 0.2	4.9 ± 0.3	3.1 ± 0.07	2.1 ± 0.02
Cr (mg/kg DM)	15.9 ± 0.5	29.7 ± 1.6	29.2 ± 0.8	31.2 ± 0.8	16.1 ± 0.6	18.7 ± 0.2
Cu (mg/kg DM)	391 ± 6	741 ± 49	568 ± 31	698 ± 36	353 ± 8	435 ± 6
Fe (mg/kg DM)	4423 ± 204	6787 ± 85	8168 ± 326	4444 ± 53	2216 ± 32	4284 ± 205
Mn (mg/kg DM)	1595 ± 20	3594 ± 15	3076 ± 47	2090 ± 17	761 ± 16	1939 ± 16
Mo (mg/kg DM)	15.0 ± 0.5	24.1 ± 1.1	19.9 ± 1.0	33.5 ± 2.4	22.8 ± 0.7	18.0 ± 0.1
Ni (mg/kg DM)	23.1 ± 0.6	46.4 ± 2.5	36.6 ± 1.0	33.7 ± 3.0	10.9 ± 0.3	25.2 ± 0.5
Pb (mg/kg DM)	<2	8.0 ± 0.9	5.2 ± 0.1	13.6 ± 0.7	10.1 ± 0.5	4.5 ± 1.0
Ti (mg/kg DM)	226 ± 6	464 ± 27	514 ± 24	342 ± 22	121 ± 3	241 ± 1
Zn (mg/kg DM)	985 ± 32	2226 ± 99	1755 ± 68	2591 ± 205	1150 ± 19	1497 ± 39

as function of the particle size. Although the P concentration in the 0.5–1 mm fraction is slightly lower than in the other bed ash size fractions. This lower P concentration is because Si is more present in particles of about 0.7 mm and hence “diluting” the P in this particle size fraction, whereas the particles smaller than 0.7 mm consist of broken off coating particles that are again richer in P.

Figure 5 also shows that the SH ash (10.6% P) and ECO ash (8.9% P) have the highest P concentration, followed by the ESP ash (6.4% P). Since P is not volatilized upon the combustion [7, 30, 31] of poultry litter, the high P concentration in the SH and ECO ash can be explained by the presence of small particles that, in the fluidized bed, were broken off the P rich coating around the sand grains by erosion and that were subsequently entrained with the flue gas. The relative amount of this sand “coating particles” that have a higher P and lower Si concentration than the bed ash, decreases the

further downstream the ash is collected in the flue gas part of the installation (boiler + flue gas cleaning) whereas the relative amount of P poor fine fly ash particles increases. This explains why the average P concentration of the ash decreases throughout the boiler and flue gas cleaning part of the installation and is sustained by the similar decrease in the Si concentration (see Fig. 5). In the ECO ash, the smaller particles (< 250 μ m) (see Fig. 6) have the highest P concentration, indicating that these particles indirectly originate from the fluidized bed, possibly by intermediate deposition on the walls and tubes with subsequent removal and size reduction by the “shot cleaning system”.

The P concentration in the bag ash is the lowest (2.3%), which can be related to the relative high amount of P poor fly ash and the high Ca concentration (20.6%), indicating a high proportion of lime and lime reaction products, “diluting” the overall P.

Table 2 Average concentration $\pm$ standard deviation of P, K, Ca, Mg, Na, S, Si, Al, Cd, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Ti and Zn in the sieved bed and ECO ash fractions (% of DM and mg/kg DM); n = 3

	Bed ash										ECO ash									
	> 4 mm	2–4 mm	1–2 mm	0.71–1 mm	0.5–0.71 mm	0.125–0.5 mm	< 0.125 mm	> 400 μ m	315–400 μ m	250–315 μ m	125–250 μ m	63–125 μ m	< 63 μ m							
P (% of DM)	5.4 $\pm$ 0.07	6.0 $\pm$ 0.11	5.9 $\pm$ 0.08	5.0 $\pm$ 0.02	3.7 $\pm$ 0.04	5.4 $\pm$ 0.01	5.7 $\pm$ 0.06	5.2 $\pm$ 0.04	6.5 $\pm$ 0.05	7.8 $\pm$ 0.07	9.4 $\pm$ 0.01	9.9 $\pm$ 0.10	9.2 $\pm$ 0.06							
K (% of DM)	10.0 $\pm$ 0.06	9.5 $\pm$ 0.01	9.8 $\pm$ 0.06	9.4 $\pm$ 0.11	8.1 $\pm$ 0.07	7.0 $\pm$ 0.16	8.0 $\pm$ 0.07	14.4 $\pm$ 0.36	10.2 $\pm$ 0.14	10.1 $\pm$ 0.23	10.9 $\pm$ 0.15	11.6 $\pm$ 0.16	13.3 $\pm$ 0.12							
Ca (% of DM)	14.0 $\pm$ 0.13	22.8 $\pm$ 0.25	23.9 $\pm$ 0.40	17.0 $\pm$ 0.19	12.9 $\pm$ 0.10	24.6 $\pm$ 1.10	28.5 $\pm$ 0.35	20.3 $\pm$ 0.26	23.2 $\pm$ 0.04	21.4 $\pm$ 0.22	19.8 $\pm$ 0.13	19.4 $\pm$ 0.19	18.1 $\pm$ 0.14							
Mg (% of DM)	2.8 $\pm$ 0.05	3.0 $\pm$ 0.02	2.9 $\pm$ 0.05	2.4 $\pm$ 0.01	1.8 $\pm$ 0.04	2.9 $\pm$ 0.01	3.0 $\pm$ 0.03	3.0 $\pm$ 0.03	3.8 $\pm$ 0.02	4.5 $\pm$ 0.05	5.4 $\pm$ 0.02	5.6 $\pm$ 0.06	5.3 $\pm$ 0.05							
Na (% of DM)	2.8 $\pm$ 0.01	2.7 $\pm$ 0.01	2.7 $\pm$ 0.01	2.7 $\pm$ 0.004	2.6 $\pm$ 0.02	2.6 $\pm$ 0.01	2.9 $\pm$ 0.01	3.1 $\pm$ 0.02	3.1 $\pm$ 0.01	3.2 $\pm$ 0.04	3.4 $\pm$ 0.02	3.5 $\pm$ 0.04	3.5 $\pm$ 0.03							
S (% of DM)	3.4 $\pm$ 0.03	3.4 $\pm$ 0.03	3.5 $\pm$ 0.05	3.1 $\pm$ 0.05	2.3 $\pm$ 0.03	1.7 $\pm$ 0.05	2.4 $\pm$ 0.03	3.9 $\pm$ 0.07	1.8 $\pm$ 0.01	1.8 $\pm$ 0.42	1.4 $\pm$ 0.03	1.8 $\pm$ 0.04	2.7 $\pm$ 0.02							
Si (% of DM)	14.8 $\pm$ 0.45	7.0 $\pm$ 0.13	5.8 $\pm$ 0.21	12.8 $\pm$ 0.38	19.0 $\pm$ 0.12	9.1 $\pm$ 0.75	3.6 $\pm$ 0.22	5.0 $\pm$ 0.02	6.5 $\pm$ 0.10	7.7 $\pm$ 1.45	5.9 $\pm$ 0.08	4.7 $\pm$ 0.01	3.7 $\pm$ 0.07							
Al (mg/kg DM)	5548 $\pm$ 32	5535 $\pm$ 144	5224 $\pm$ 79	7393 $\pm$ 134	10,686 $\pm$ 23	7923 $\pm$ 512	6168 $\pm$ 58	9757 $\pm$ 141	11,838 $\pm$ 318	13,147 $\pm$ 2348	9454 $\pm$ 19	7867 $\pm$ 127	7532 $\pm$ 67							
Cd (mg/kg DM)	< 2	< 2	< 2	< 2	< 2	< 2	< 2	4.3 $\pm$ 0.7	2.4 $\pm$ 0.07	2.4 $\pm$ 0.04	2.6 $\pm$ 0.06	3.3 $\pm$ 0.2	5.0 $\pm$ 0.2							
Cr (mg/kg DM)	18.8 $\pm$ 1.0	21.2 $\pm$ 0.4	17.7 $\pm$ 0.6	15.5 $\pm$ 0.1	15.5 $\pm$ 1.6	21.3 $\pm$ 4.9	22.1 $\pm$ 0.6	37.1 $\pm$ 12.3	24.8 $\pm$ 1.6	29.4 $\pm$ 1.8	33.5 $\pm$ 3.5	37.6 $\pm$ 3.0	41.5 $\pm$ 3.4							
Cu (mg/kg DM)	384 $\pm$ 13	458 $\pm$ 9	444 $\pm$ 7	417 $\pm$ 9	331 $\pm$ 9	305 $\pm$ 57	483 $\pm$ 11	603 $\pm$ 35	482 $\pm$ 4	546 $\pm$ 12	622 $\pm$ 27	637 $\pm$ 32	714 $\pm$ 35							
Fe (mg/kg DM)	4365 $\pm$ 83	4422 $\pm$ 34	4331 $\pm$ 102	4260 $\pm$ 89	4285 $\pm$ 84	6368 $\pm$ 580	4323 $\pm$ 65	9026 $\pm$ 103	6426 $\pm$ 663	8552 $\pm$ 1876	7718 $\pm$ 85	8511 $\pm$ 102	9300 $\pm$ 57							
Mn (mg/kg DM)	1686 $\pm$ 32	1943 $\pm$ 40	1940 $\pm$ 49	1601 $\pm$ 36	1135 $\pm$ 17	1598 $\pm$ 197	1470 $\pm$ 10	1830 $\pm$ 20	2244 $\pm$ 18	2734 $\pm$ 38	3236 $\pm$ 24	3251 $\pm$ 28	2920 $\pm$ 22							
Mo (mg/kg DM)	15.1 $\pm$ 0.9	16.4 $\pm$ 0.1	16.3 $\pm$ 0.6	14.3 $\pm$ 0.2	10.9 $\pm$ 0.4	11.8 $\pm$ 0.1	16.0 $\pm$ 0.3	31.7 $\pm$ 3.9	19.8 $\pm$ 0.6	21.6 $\pm$ 0.5	22.5 $\pm$ 0.8	21.2 $\pm$ 1.4	22.7 $\pm$ 1.9							
Ni (mg/kg DM)	25.3 $\pm$ 0.8	27.6 $\pm$ 0.1	26.2 $\pm$ 0.7	21.5 $\pm$ 1.7	17.7 $\pm$ 1.4	26.8 $\pm$ 9.8	30.5 $\pm$ 2.5	39.1 $\pm$ 15.5	28.7 $\pm$ 0.8	34.9 $\pm$ 1.8	39.5 $\pm$ 2.6	44.2 $\pm$ 3.2	50.7 $\pm$ 2.7							
Pb (mg/kg DM)	48.4 $\pm$ 2.0	8.4 $\pm$ 1.0	2.5 $\pm$ 0.1	8.4 $\pm$ 1.0	7.1 $\pm$ 1.0	< 2	< 2	56.9 $\pm$ 2.4	2.8 $\pm$ 0.3	1.9 $\pm$ 0.2	2.7 $\pm$ 0.8	4.8 $\pm$ 0.8	12.5 $\pm$ 0.6							
Ti (mg/kg DM)	236 $\pm$ 9	242 $\pm$ 10	245 $\pm$ 8	261 $\pm$ 4	293 $\pm$ 11	290 $\pm$ 9	297 $\pm$ 4	408 $\pm$ 15	478 $\pm$ 4	567 $\pm$ 25	564 $\pm$ 28	639 $\pm$ 33	557 $\pm$ 20							
Zn (mg/kg DM)	1020 $\pm$ 28	1200 $\pm$ 14	1158 $\pm$ 28	969 $\pm$ 18	749 $\pm$ 38	876 $\pm$ 26	885 $\pm$ 45	2971 $\pm$ 62	1403 $\pm$ 40	1320 $\pm$ 11	1341 $\pm$ 69	1683 $\pm$ 116	3784 $\pm$ 7

Fig. 5 P, K and Si concentration in the bed, SH, ECO, ESP and bag ash (% of DM). The data points indicate the average concentration in the three replicates. Standard deviations are given in Table 1. Filled rectangle P; filled circle K; filled triangle Si

Figure 5 further shows that ESP ash has the highest K concentration (15.5%), followed by bag ash (14.3%), ECO ash (11.5%), SH ash (11.1%) and bed ash (9.4%). K shows an opposite concentration trend compared to P. This can be explained by the fact that, in general, K is an element that upon combustion easily forms salts, such as potassium chloride (KCl), that are volatilized at the prevailing temperatures [32]. Therefore, K is typically present in higher concentrations in the fly ash. The further down the ash is collected in the flue gas part of the installation, the higher is the relative amount of fly ash in the ash, the higher is also the K concentration. As is the case for P, the lower K concentration in the bag ash than in the ESP ash can be related to the presence of lime and lime reaction products, “diluting” the K in the K rich fly ash fraction of the bag ash. For K, it is difficult to relate the particle size to the concentration.

Taking into account the mass rate of each stream, the highest amount of P and K are present in the ESP ash (2230 tons of P/year and 5380 tons of K/year), followed by the bed ash (780 tons of P/year and 1460 tons of K/year).

However, this is quite logic because they cover about 58% and 26% of the total ash stream, respectively.

Possible Valorization Applications of the Different Ash Streams

Direct Application of Ash as Fertilizer

The poultry litter ash is a potentially interesting fertilizer since it contains P and K, both essential nutrients, in compounds that show a good bioavailability in pot and field tests conducted for the specific ash investigated in this paper [33–37]. Furthermore, the ash is free of pathogens and organic toxic substances such as pharmaceuticals [8, 11], and its heavy metal/P ratio is the same as in poultry litter, only the ash is more concentrated [8]. However, recycling poultry litter ash and in this way closing the P and K cycle, is subject to legislation on the use of waste materials as fertilizer.

Table 3 gives the P and K solubility in water, neutral ammonium citrate and 2% citric acid for bed, SH, ECO, ESP, bag and mixed ash. The differences in P and K solubility between the different poultry litter ash streams shows that some streams are, in the frame of the European regulation 2003/2003, more interesting for use as a fertilizer. Table 3 shows for instance that the P solubility is increasing the further downstream the ash is collected in the flue gas part of the installation (boiler + flue gas cleaning), and has hence an increasing potential for use in agriculture. However, according to Fig. 5, the P concentration in the ash is decreasing the further downstream the ash is collected in the flue gas part of the installation, so the ash streams with the highest P solubility have the lowest P concentration. Based on the K solubility in water (see Table 3), SH and ECO ash have a lower agricultural value, whereas ESP and bag ash have in general the highest agricultural value for K, which is also

Fig. 6 P, K and Si concentration in the sieved bed and ECO ash fractions (% of DM). The data points indicate the average concentration in the three replicates. Standard deviations are given in Table 2. Filled rectangle P; filled circle K; filled triangle Si

Table 3 Average water, neutral ammonium citrate and 2% citric acid solubility $\pm$ standard deviation of P and K in the bed, SH, ECO, ESP, bag and mixed ash (% of P total; % of K total); n=3

	Bed ash	SH ash	ECO ash	ESP ash	Bag ash	Mixed ash
Water (% of P total)	<0.2	<0.1	<0.1	<0.2	<2.3	<0.2
Neutral ammonium citrate (% of P total)	14.8 ± 0.5	67.3 ± 4.1	74.6 ± 1.5	74.2 ± 4.9	83.8 ± 7.9	58.0 ± 1.8
2% citric acid (% of P total)	46.5 ± 0.4	78.0 ± 1.5	81.8 ± 1.1	92.8 ± 2.3	89.2 ± 4.3	72.7 ± 1.9
Water (% of K total)	73.6 ± 1.5	36.5 ± 0.3	34.4 ± 0.6	77.4 ± 7.0	87.5 ± 3.0	66.6 ± 1.8
Neutral ammonium citrate (% of K total)	81.3 ± 3.3	81.3 ± 3.5	80.9 ± 1.3	92.6 ± 12.2	95.9 ± 1.8	91.2 ± 4.0
2% citric acid (% of K total)	86.2 ± 2.1	94.3 ± 1.7	87.2 ± 1.0	100.0 ± 9.0	96.7 ± 1.8	92.1 ± 3.9

confirmed by data on the solubility in neutral ammonium citrate and 2% citric acid. Yet, the P solubility in water and neutral ammonium citrate of the mixed poultry litter ash (see Table 3) is relatively low compared to the P solubility of commonly used P commercial fertilizers such as triple super phosphate ($\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$) (> 90% water soluble P; $\pm 95\%$ neutral ammonium citrate soluble P [38, 39]). Hence, as also found by Komiyama et al. for other litter ash, immediate available P for plants is not expected [10]. Furthermore, the K solubility in water of the mixed poultry litter ash (see Table 3) is also relatively low compared to for example potassium chloride ($\pm 100\%$ water soluble K [40]), a commonly used K fertilizer. However, P and K solubility in water, neutral ammonium citrate and 2% citric acid are not always representative for the fertilizing value. Pot and field tests give a better indication of the real bioavailability of fertilizers. For that reason, Ehlert and Nelemans, Delhay and Bourié investigated the agricultural value of poultry litter ash produced by the biomass power plant of BMC Moerdijk in pot and field tests [33–37]. They indicated that hydrated poultry litter ash shows a similar P and K efficacy compared to the reference mineral fertilizers triple superphosphate, dicalcium phosphate (CaHPO_4), potassium chloride and potassium sulfate (K_2SO_4) [33–37], even if its P and K solubility in water and neutral ammonium citrate, and hence the bioavailability according to the European regulation 2003/2003, was totally different.

To further evaluate the valorization potential of the different (sieved) ash streams as a fertilizer, the heavy metal concentrations given in Tables 1 and 2 are, as a first benchmark, compared to the limit values laid down in the Flemish legislation for the use of waste streams as fertilizer (VLAREMA, Annex 2.3.1, 2012 [41]). The Flemish limits were selected because they were at the time of the experiments one of the most stringent in Europe, so this first comparison represents a worst case scenario. It can be concluded that the Cu and Zn concentration in all the ash streams (see Table 1) are two to three times higher than the 2012 VLAREMA limits (375 and 900 mg/kg DM, respectively [41]). Hence, this

impedes the direct application of the individual ash streams and consequently also of the entire mixed ash stream as a fertilizer in Flanders. According to Table 1, the Cd, Cr, Ni and Pb concentration in all ash streams comply with the 2012 VLAREMA limit values (Cd 6 mg/kg DM; Cr 250 mg/kg DM; Ni 50 mg/kg DM; Pb 300 mg/kg DM [41]). Other heavy metals regulated in VLAREMA are As (150 mg/kg DM) and mercury (Hg) (5 mg/kg DM) [41]. These heavy metals are not considered in this work, however, previous analytical results over a period of two years (2013–2014, n=58) indicate that the mixed poultry litter ash contains on average less than 3 mg As/kg DM and less than 0.05 mg Hg/kg DM [11] and thus comply with the 2012 VLAREMA limit values. As mentioned before, it should be noted here that the ash composition can rather change over time, which is primarily related to the variation in poultry litter composition between different suppliers and over the year. When looking at the sieved ash streams (see Table 2), all fractions comply with the 2012 VLAREMA limit values for Cd, Cr, Ni and Pb, but only the (combination of the) bed ash fractions <0.71 mm respects the 2012 VLAREMA limits for Cu and Zn. These fractions, however, only represent 3.2% of the total ash mass that is generated, corresponding to 1900 tons/year, and their combined P concentration is limited to 4.3%.

There is, however, a big difference in legal limit values for the use of poultry litter ash, or more general of waste materials as fertilizer, in the different European member states. For example, the maximum admissible concentration for Zn in poultry litter ash is 2063 mg/kg DM in the UK (UK poultry litter ash quality protocol [42]), compared to for instance 900 mg/kg DM in Flanders (VLAREMA, 2012 [41]), while there is no fixed limit for Zn in France (Anses – Dossier no 2012-0393 [43]). In addition, the 2012 VLAREMA legislation, which is used as a worst case benchmark in this work, was adapted in March 2018: the limit values for Cu and Zn were increased to 800 and 1500 mg/kg DM, respectively [44]. Hence, the bed, bag and mixed poultry litter ash analyzed in this work, now comply with the legislation for direct use as a fertilizer on Flemish fields. However, for the mixed

poultry litter ash, the Zn concentration analyzed in this work (1497 mg/kg DM) is lower than the average concentration in ash samples previously sampled over a period of two years (1800 mg/kg DM, 2013–2014, $n = 58$ [11]).

From the discussion above, it can be concluded that it depends on local legislation in place whether the poultry litter ash can be directly applied as fertilizer. This clearly demonstrates the need for a uniform European legislation as being prepared by the European Commission's STRUBIAS working group. It should also be noted that there are no legal concentration limits for heavy metals, more specifically Cu and Zn, in conventional fertilizers and in manure used as a fertilizer. Although the absolute heavy metal concentration is higher in poultry litter ash than in poultry litter, by applying the same amount of P with these two 'fertilizers', also the same amount of heavy metals is applied to the soil [8]. Furthermore, legislation often only considers absolute concentrations of heavy metals instead of dosage. Most European member states give absolute concentration limits, whereas the Dutch regulation, for example, gives dosage limits per kg of nutrient (Uitvoeringsbesluit Meststoffenwet, Annex II [45]). This way, the legislation in the Netherlands indirectly takes into account the amount of fertilizer that will be put on the land as well as the actual quantity of heavy metals that is brought into the environment. The Flemish legislation used as a benchmark in this work gives both concentration and dosage limits (VLAREMA [41, 44]). In this regard, the poultry litter ash analyzed in this work fully complies with the dosing limits for Cu and Zn (mass/area) in the Flemish legislation, but as already explained, not necessarily with the concentration limits. This can be explained by the fact that the concentration limits set by VLAREMA are based on the dosage of waste streams of which typically 2 ton/ha can be applied to not exceed the maximum dosage limits for P set in the Flemish Manure Decree [46, 47]. However, since mixed poultry litter ash is more concentrated in P compared to most other waste streams used as fertilizer, only maximum 1 ton/ha of mixed poultry litter ash can be applied to not exceed the dosage limits for P [47]. Taking into account the maximum dosage of poultry litter ash per hectare in Flanders, the maximum allowable Cu and Zn concentration would be 1600 and 3000 mg/kg DM to comply with the dosage limits of 1600 and 3000 g/ha/year (VLAREMA, 2018 [44]). Hence, indicating that mixed poultry litter ash containing on average 400 mg Cu/kg DM and 1800 mg Zn/kg DM [11] can be used as a fertilizer on Flemish soil without causing damage to the environment.

In order to successfully market the poultry litter ash as a fertilizer, the ash not only has to meet the legal limit values, but also has to fulfil a demand. Data from Eurostat on the gross nitrogen (N) and P balance (2014) [48] shows that in most European member states there is a positive P balance, that is, more P is supplied to the soil than is taken

up by the plants. However, Bulgaria, the Czech Republic, Estonia, Germany, Italy, Hungary, Romania and Slovakia have a negative P balance, whereas the N balance is positive (except for Romania). This makes the ash of BMC Moerdijk, which is rich in P but poor in N, an interesting alternative for phosphate rock based fertilizers for these member states. Germany has the highest market potential as in 2014, the net P balance was about minus 61,200 tons of P, followed by Bulgaria (− 30,400 tons of P), Romania (− 27,400 tons of P), Slovakia (− 16,000 tons of P), the Czech Republic (− 13,700 tons of P), Hungary (− 12,300 tons of P), Italy (− 11,500 tons of P) and Estonia (− 6800 tons of P) [48]. In comparison, the ash annually produced by BMC Moerdijk contains about 3600 tons of P.

Use of Ash in/as Animal Feed

The use of poultry litter ash in/as animal feed is considered here as an alternative P valorization pathway. This because it would close the P cycle in a more direct way, perfectly fitting in the idea of a circular economy. Furthermore, as already discussed in the introduction, not only can P be valorized by using the ash (as supplement) in for example poultry feed, but also trace elements such as Cu and Zn by directly reintroducing them in the feed cycle.

Regulation (EC) No 1069/2009 [49] is the main regulation on the use of animal by-products in, amongst others, animal feed. This regulation divides animal by-products into three categories and only animal by-products from category 3 such as heads of poultry, pig bristles, feathers, eggs from terrestrial animals, etc. may be used for feeding farmed animals other than fur animals. Hence, feces such as poultry litter and also their derived products including poultry litter ash, are excluded for the use in or as animal feed [49]. Furthermore, according to Commission Regulation (EU) No 142/2011 (Annex III, Chapter I, Section 3) [50], poultry litter ash can also be considered as a waste product instead of an animal by-product implying that it falls under the waste legislation. Given these legal restrictions, the use of poultry litter ash in animal feed is considered here purely hypothetical. Besides, an intermediate ash treatment may be necessary to produce a material suitable for use in/as animal feed, which can then reach the end-of-waste status if it complies with the legal requirements for use in/as animal feed.

Based on the chemical characterization and previous analytical results [11] and regardless of the status of the ash (waste or animal by-product), it can be concluded that: (1) mixed poultry litter ash (see Table 1) meets the legal limit values (Directive 2002/32/EC [51]) for the *undesirable heavy metals* Pb, Hg and Cd for use in/as animal feed, and (2) the As concentration in the ash has to be determined with a lower detection limit to confirm compliance. However, to be used in animal feed, the poultry litter ash also

has to comply with the limit values for all other *undesirable substances* in directive 2002/32/EC (Annex I) (e.g. nitrogen compounds, mycotoxins, inherent plant toxins, organic chlorine compounds, dioxins and PCB's and harmful botanical impurities) [51]. However, because legislation prohibits the use of feces in or as animal feed, regardless of the concentration of undesirable substances, no detailed analysis was performed for all undesirable substances mentioned above. Nonetheless, previous analysis already indicated that no anti-biotic residues nor micro-biological residues could be detected in the ash and the total amount of dioxins was on average 1.46 ng I-TEQ/kg [11]. Furthermore, at this moment, there is no added value for carrying out more analyses on the undesirable substances.

Maximum concentrations of *trace elements* (Co, Cu, Fe, Mn and Zn) in animal feed are regulated by Commission Regulation (EC) No 1334/2003 [52]. By comparing these maximum allowable concentrations of trace elements with the concentrations in the mixed poultry litter ash (see Table 1), it can be concluded that the ash exceeds the legal limit values and is not suitable for use as pure animal feed. However, assuming that the end-of-waste status is received for use in/as animal feed, the poultry litter ash can be mixed with other, complementary animal feed streams to obtain a balanced feed mix that meets the limit values for trace elements. Based on the trace element concentrations in the mixed ash stream (see Table 1) and the limit values for trace elements in poultry feed [52], the maximum share of poultry litter ash in poultry feed is 6.5%. This means that the 60,000 ton poultry litter ash yearly produced has to be mixed with at least 860,000 ton of other animal feed components (with about 0 mg/kg of trace elements, mainly Cu, Mn and Zn). This results in about 920,000 ton of poultry feed based on poultry litter ash, which is lower than the 3.2 million ton of poultry feed that is yearly consumed in the Netherlands [53]. Therefore, if the end-of-waste status is received for use in/as animal feed, in principle, all the ash produced in the installation of BMC Moerdijk could be valorized in poultry feed. This calculation gives only a hypothetical idea of potential mass streams, since also the speciation (i.e. the chemical form in which the element is present) of the trace elements has to be considered. The trace elements are for instance not necessarily present in the same chemical form in the poultry litter ash than in the animal feed. Given the relatively low concentration of these metals in the ash (see Table 1) their speciation could, however, not be determined by for instance X-ray diffraction analysis.

In addition to the legal restrictions on the use of poultry litter ash in animal feed, the availability of P in the ash is also important. The P solubility in 2% citric acid provides an indication to the level of P available (increasing solubility in 2% citric acid is linearly related to an increasing absorption coefficient) [54]. Table 3 shows that the P solubility in 2%

citric acid of the mixed poultry litter ash was 72.7% of total P, which is slightly lower than for most phosphates used in animal feed such as monosodium phosphate (NaH_2PO_4), disodium phosphate (Na_2HPO_4), monoammonium phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$), monocalcium phosphate ($\text{Ca}(\text{H}_2\text{PO}_4)_2$), etc., which all have a P solubility of more than 95% in 2% citric acid [54].

Use of Ash as Building Material

Besides P and K, other ash elements such as Ca, Si, Mg, Fe and Al can also be valorized, for example by using the ash as building material. To use a waste product as a building material, it has to meet, depending on legislation in place, either only leaching limits such as for example set in the Dutch legislation (Regeling bodemkwaliteit, Annex A [55]) or both concentration and leaching limits such as for example set in the Flemish legislation (VLAREMA, Annex 2.3.2. [41]). Comparing the ash composition given in Table 1 with the concentration limit values for heavy metals in the VLAREMA legislation, it can be concluded that the Cu and Zn concentration in all the ash streams are two to three times higher than the limits (375 and 1250 mg/kg DM, respectively [41]). Hence, this impedes the direct application of the individual ash streams and consequently also of the entire mixed ash stream as a building material in Flanders. Also for the sieved ash streams (see Table 2), the Cu and Zn concentration in all fractions are two to four times higher than the limits, except for the (combination of the) bed ash fractions < 0.71 mm. These fractions, however, only represent 3.2% of the total ash mass that is generated.

The results of batch leaching experiments on the mixed ash stream are given in Table 4, since it is this ash stream that is most relevant for use as building material. The leaching of Cr, Mo, Se, Sn, Zn, chlorides and sulfates is higher than the limit values in the Flemish and Dutch legislation. Hence, from a leaching point of view, the mixed ash cannot be used as a building material as such. However, as for untreated poultry litter ash, untreated bottom ash of waste incineration (WtE bottom ash) does often also not directly meet the leaching limits. It is therefore common practice to treat this WtE bottom ash by sieving, washing, carbonation, mild heat treatment, addition of mineral additives and aging. These operations remove certain heavy metals, sulfates and chlorides whereas non-rinsed heavy metals are stabilized in the ashes [19, 56–59]. Based on a comparison of the elemental composition of untreated WtE bottom ash [56, 57] and the untreated mixed poultry litter ash, it seems highly likely that poultry litter ash will satisfy legal limit leaching values for use as a building material in Flanders or the Netherlands after conventional WtE bottom ash treatment.

Besides concentration and leaching limits, the particle size distribution of the mixed poultry litter ash is also a point

Table 4 Average leaching $\pm$ standard deviation of regulated elements (Flemish and Dutch legislation) for mixed poultry litter ash (batch leaching test); $n = 3$

	Leaching (mg/kg DM)
As	< 0.2
Ba	7.0 ± 0.2
Cd	< 0.02
Co	< 0.02
Cr	2.8 ± 0.04
Cu	0.3 ± 0.01
Mo	12.2 ± 0.1
Ni	< 0.2
Pb	< 0.2
Sb	0.2 ± 0.03
Se	3.3 ± 0.04
Sn	0.6 ± 0.02
V	0.3 ± 0.003
Zn	5.8 ± 0.3
Cl ⁻	$27,063 \pm 468$
F ⁻	1.9 ± 0.2
SO ₄ ²⁻	$84,139 \pm 688$

Fig. 7 Ternary CaO, SiO₂ and Al₂O₃ + Fe₂O₃ diagram for cement clinker and the ash constituents of different raw materials and fuels (Used by permission of Umweltbundesamt, from Bolwerk et al. [61]); the mixed poultry litter ash composition is indicated by the blue point in the ternary diagram

of attention for its use as a building material. The mixed ash stream contains a higher proportion of fine particles compared to conventional WtE bottom ash because it also contains the finer SH, ECO, ESP and bag ash. Conventional WtE bottom ash treatment separates particles < 0.1 mm as a sludge fraction that is landfilled [58]. Basically, this means that from a particle size point of view, the bed ash has the highest potential as building material and a preliminary sieving of the mixed ash stream may be necessary to make its valorization as building material economically feasible.

WtE bottom ash can also, after treatment, be used as a replacement for sand in for example concrete applications. In this regard, the high P concentration in the poultry litter ash might be problematic because it can negatively interfere with the hydration of cement. P compounds are indeed reported in the literature to be retarders of cement hydration. They can strongly delay the setting time leading to a slower build-up of strength in the concrete, whereas hardening can be greatly lowered at least at early age [60].

Use of Ash in Cement Production

The Ca, Si, Fe and Al in the poultry litter ash can also be valorized by using the ash as a raw material in cement production in two possible ways: (1) as a raw material for clinker production, then it is added together with the other raw materials in the rotary kiln, and (2) as a raw material for cement, then it is mixed with grounded clinker as is already the case for fly ashes from other thermal processes [18].

A comparison of the elemental composition of the mixed poultry litter ash with the composition of raw materials for cement clinker production indicates that it can be interesting

to use the mixed ash as a raw material for clinker production as it provides valuable elements in a good ratio. Figure 7 gives the ternary diagram (CaO, SiO₂ and Fe₂O₃ + Al₂O₃) for cement clinker and the ash constituents of different raw materials and fuels [18, 61]. From the mixed poultry litter ash composition (indicated by the blue point in Fig. 7), it can be concluded that the ratio of the main components (Ca, Si, Al and Fe) in the mixed poultry litter ash corresponds well to the ratio of these components in cement clinker. However, the possible obstacles for using poultry litter ash in cement production are the high P, K and S concentration. Furthermore, the Zn, Cu and Mn concentrations are ten to hundred times higher in the mixed ash than in the conventional raw materials of cement.

According to Oye and King Lam et al., a high P content in cement clinker (due to use of incineration ash with a high P content), will affect the hydraulic properties of the cement. Higher amounts of P in cement clinker will lead to stabilization of the belite (Ca₂SiO₄) phase during burning of the cement clinker, which is then suppressing the formation of alite (Ca₃SiO₅), the main hydraulic phase, in the final cement. Hence, a lower amount of alite in the final cement leads to an increase in setting time of the cement (drying/hardening) and likewise to a slower build-up of strength in the concrete [62, 63].

The high K concentration in the poultry litter ash and in the clinker produced thereof may negatively influence the alkali-silica reaction that takes place between the highly alkaline (K, Na) solution in the concrete pores and the

amorphous silica phase in the cement and/or in other concrete constituents when cement is mixed with water. Reaction of alkali with Si forms an alkali-silica reaction gel, which then in the presence of moisture swells and increases in volume due to further water absorption. This swelling leads to stress development and potentially cracking of the concrete or causes a significant movement of concrete components, which leads to critical structural problems [62, 64, 65]. However, when poultry litter ash is used in geopolymer cement production, where alkali aluminosilicate materials are created by alkali activation of a silicate source [66–69], the high alkali content in poultry litter ash can be an advantage. K rich biomass ash can be used as an alternative alkali activator instead of alkali activators with a high environmental impact, such as sodium hydroxide (NaOH) solutions, commonly used in geopolymer cement production [66]. Preliminary tests were conducted to explore the potential of the poultry litter ash in geopolymer cement production. These tests indicated that partial replacement of blast furnace slag, commonly used as alkali activator in geopolymer cement production, by poultry litter ESP ash results in a faster compressive strength development of the concrete product, which is a promising effect. Furthermore, poultry litter bed ash was used to partially replace sand in geopolymer cement concrete and also here the compressive strength development was promising. However, further research on the use of poultry litter ash for geopolymer cement production, including the effect on cracking and workability, is still necessary.

Furthermore, S can also cause problems when the poultry litter ash is used in cement applications. The so called “sulfate attack” causes loss of adhesion of the cement hydration product, extensive cracking and expansion due to formation and expansion of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$) [70].

Wet Chemical Extraction

Of all the considered application options, P only remains in the food cycle if the ash is used as a fertilizer or in/as animal feed and not if it is used as building material or in cement production. However, as mentioned before, this is mainly hindered by the legislation on the use of waste materials as fertilizer or in/as animal feed. Hence, another option to increase the valorization potential of the poultry litter ash is to separate the fertilizer elements, that is, P and K, from the rest of the ash so that they remain in circulation and are not dissipated in for instance building materials. The most straightforward option to do so is a wet extraction with subsequent precipitation of the extracted P and possibly K in a pure form with a high market value. This is a process similar to the one used for P production from phosphate rock (e.g. patent US 8425872 B2 from Ecophos [71]) or for P recovery from sewage sludge ash or biomass ash as investigated,

amongst others, by Xu et al., Atienza-Martinez et al., Fang et al., Hong et al., Darwish et al., Ottosen et al., Donatello et al., Cohen and Kaikake et al. [2, 4, 7, 29, 72–76]. However, since incineration ash is a more complex matrix than phosphate rock and the specific composition and mineralogy of poultry litter ash differ from for example sewage sludge ash and other biomass ash, the acid extraction method for phosphate rock or other types of incineration ash cannot be transferred to poultry litter ash as such. Indeed, the type of acid used for P extraction, its concentration and the purification procedure depend on the specific composition of the parent material (P content, heavy metal concentrations, mineralogy, etc.) (see e.g. [2, 4, 7, 29, 72–76]). Hence, emphasizing the need for a specific P extraction and P recovery method.

The extraction should be optimized in such a way that heavy metals interfering with the use of the ash as fertilizer, in/as animal feed, as building material or as raw material for cement production (e.g. Cu, Mn and Zn) are co-extracted but precipitated separately from the P and K. Ideally, the heavy metals are precipitated as a compound that can be easily valorized by secondary metal refiners, whereas the solid residue of the ash remaining after extraction can be more easily applied as building material or as raw material in cement production.

Conclusions

In this paper, it is shown that the ash collected in the SH section of the steam boiler has the highest P content and this P content is decreasing the further downstream ash is collected in the flue gas part of the installation, whereas K shows an opposite concentration trend.

The poultry litter ash is a good fertilizer since it contains P and K, both essential nutrients, in compounds that show a good bioavailability. However, even if the ash is free of pathogens and toxic organic substances, and its heavy metal/P ratio is the same as in poultry litter, the recycling of P and K from poultry litter ash is hindered by the lack of a uniform European legislation on the use of waste materials as fertilizer, taking into account dosage rather than concentration.

Since poultry litter ash is considered as a waste product instead of an animal by-product, its use in/as animal feed is not straightforward. Furthermore, the availability of P in the ash is slightly lower compared to commonly used P compounds in animal feed. Yet, poultry litter ash contains besides P also trace elements (e.g. Cu and Zn) in a high concentration. Therefore, it could provide as well a circular source of these elements by adding it to other animal feed components, given that their speciation in the poultry litter ash corresponds to that in animal feed. Purely hypothetically, taking into account the concentration of the trace elements in

the poultry litter ash and the limit concentrations in poultry feed, the maximum share of poultry litter ash in poultry feed would be 6.5%.

Other elements such as Ca, Si, Mg, Fe and Al are present in the poultry litter ash in a good concentration ratio for the use of the ash as building material or in cement production. However, contradictory enough, the high P and K concentration in the ash can be a technical obstacle. A promising novel application to be further explored is the use of the poultry ash in geopolymers cement production where it can (partially) replace the necessary alkali activator.

Of all the considered application options, P only remains in the food cycle if the ash is used as a fertilizer or in/as animal feed and not if it is used as building material or in cement production. P recovery from alternative sources is important because phosphate rock is depleting and P is an essential micronutrient for all living organisms. In this regard, it can be interesting to separate the fertilizer elements, that is, P and K, from the rest of the ash by doing for example a wet chemical extraction so that the P remains in the cycle, whereas the solid residue of the ash remaining after extraction can be more easily applied as building material or as raw material for cement production.

It should, however, be noted that the discussion in this paper is rather technical, since in practice, economic and environmental aspects will also influence the valorization potential.

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