Characterisation of poultry litter ash in view of its valorisation

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Keywords: poultry litter ash, characterisation, valorisation, recycling
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Abstract

The overall aim of this research was to evaluate the valorisation potential of the poultry litter ash produced in the biomass power plant of BMC Moerdijk (the Netherlands). This poultry litter ash contains phosphorus (P) and potassium (K), both essential nutrients. Chemical characterisation showed that ash collected in the superheater part of the boiler had the highest P concentration (10.6%). Furthermore, the P concentration decreased as the ash was collected further downstream in the boiler and flue gas cleaning part of the installation. K showed an opposite concentration trend, i.e. its concentration was the lowest in the superheater ash (9.4%) and increased to 15.5% in the electrostatic precipitator ash. However, even if 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. Besides P and K, also other ash elements such as calcium, silicon, magnesium and aluminium can be valorised e.g. by using the ash as building material or in cement. However, in these applications the high P and K concentration of the ash can rather be a technical obstacle than a benefit. In that regard, it could be interesting to separate the fertilizer elements, i.e. P and K from the rest of the ash by means of e.g. a wet chemical extraction after which the remaining solid residue better meets the composition requirements for building material or raw material for cement.

1. 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]. Experts estimate that the demand for P containing fertilizers will double by 2050 compared to 2012. This 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 [2, 3]. As a consequence, 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, 4]. The European Union (EU) considers phosphate rock as one of the 27 critical raw materials because of its strategic importance and the economic dependence on a limited number of non-EU suppliers (e.g. mainly China, Morocco, and the United States) [2, 5]. 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 wastes 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 [6, 7, 8]. For example, the poultry litter ash from the biomass power plant considered in this work contains on average 6.1% P (14.1% P_2O_5). Since this poultry litter ash also contains on average 10.9% of the essential micronutrient potassium (K) (13.2% K_2O), it is an interesting (source for) fertilizer (production) [personal communication, BMC Moerdijk]. This poultry litter ash also contains some heavy metals originating from the poultry litter, mainly copper (Cu) and zinc (Zn) (respectively about 400 and 2 000 mg/kg dry matter (DM) [personal communication, BMC Moerdijk]), which might pose a regulatory problem for direct application as fertilizer, depending on local legislation. It should however be noted that Cu and Zn are trace minerals essential for important biochemical functions and necessary for maintaining health of humans and animals throughout life [9].

Besides P and K, the poultry litter ash considered in this work also contains on average 20% calcium (Ca), 6.8% silicon (Si), 3.4% magnesium (Mg) and 0.4% aluminium (Al) [personal communication, BMC Moerdijk] and has therefore an interesting potential for use as building material or in cement production [10].

The overall aim of this research was to evaluate the valorisation potential of the poultry litter ash produced by the biomass power plant of BMC Moerdijk (the Netherlands). In a firsts step, the different ash streams that are generated in the installation were characterised 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 in/as fertilizer, as building material or in cement production.

2. Materials and methods

2.1. *Poultry litter combustion installation*

The biomass power plant of BMC located in Moerdijk, the Netherlands, generates 285 000 MWh of electricity annually by incinerating about 430 000 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 from the fluidized bed (26% of total ash mass produced); boiler ash, more specifically (2) SH ash, collected from the superheater (6%) and (3) ECO ash, collected from the economizer (5%); (4) ESP ash, collected from the electrostatic precipitator (58%) and (5) bag ash, collected from the Turbosorp® and baghouse filter (5%) [Personal communication, BMC Moerdijk].

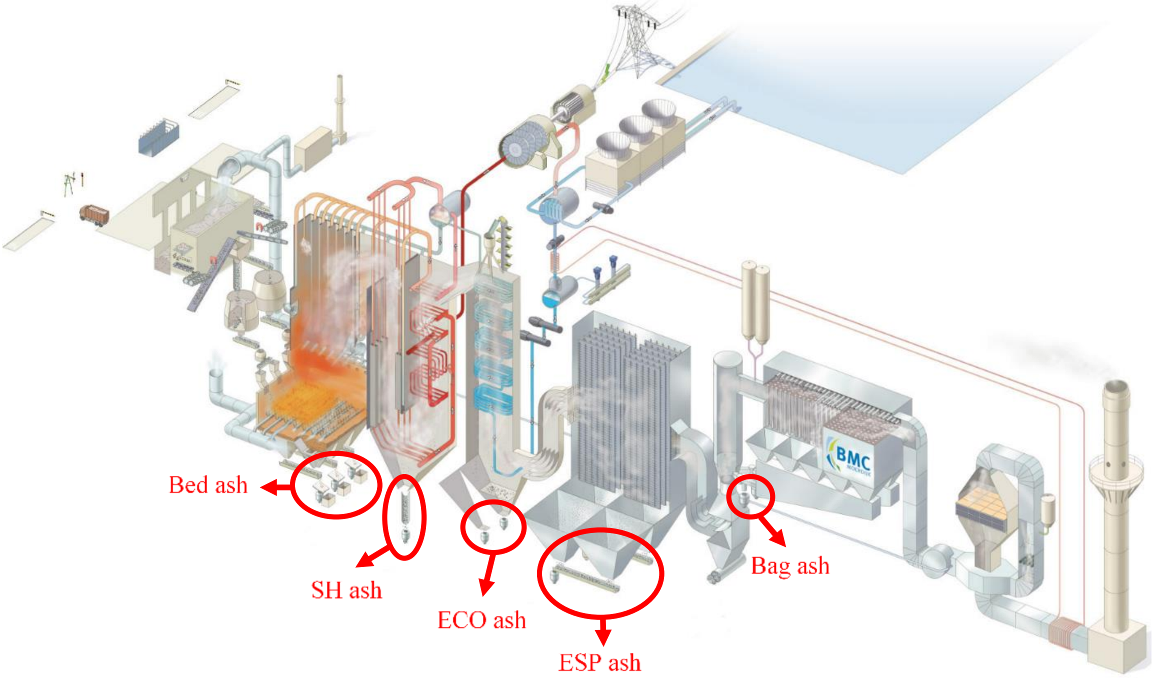


Fig. 1 Graphical representation of the poultry litter combustion installation of BMC Moerdijk [8]. The red ovals indicate the sample points of the five different ash streams.

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 ($Al_2Si_2O_5(OH)_4$) 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 burn out [8]. The residence time of at least two seconds at minimum 850°C (Directive 2000/76/EC) guarantees the complete removal of pathogens and toxic organic pollutants. 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. In fact, the bed ash consists of spherical coated sand particles. Lighter ash particles not dropping through the furnace bed are entrained as dust with the flue gas and are retained in the boiler and in the flue gas cleaning installation [Personal communication, BMC Moerdijk].

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” in the economizer feeds metal balls at the top of the economizer to remove dust that has deposited on this boiler section surfaces. These 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) [Personal communication, BMC Moerdijk].

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 DeNOx). 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 neutralise the acid gasses (HCl, SO_2) in the flue gas. In the baghouse filter, the salts formed by lime addition 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 DeNOx, 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 of the other days in the indicated periods. The ash samples analysed in this work are thus well-blended samples that are representative of the incineration process's solid residues. However, from previous analytical results 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, i.e. different types of poultry litter, e.g. broiler and layer chickens, and over the year (seasonal variation) [Personal communication, BMC Moerdijk].

2.2. Ash sieving

Bed and ECO ash were sieved into different particle size fractions with a Fritsch Vibratory Sieve Shaker Analysette 3 for 10 minutes at amplitude 30%. About 200 g of bed ash (six sieve tests) or 30 g of ECO ash (three sieve tests) was sieved each time. The other ash streams were not sieved because they consisted of fine powders that did not show a significant difference is particle size.

2.3. Chemical ash analysis

After sieving, all fractions and the entire ash streams i.e. the ash streams as received prior to sieving, were crushed and destructed in triplicate with a combination of aqua regia and hydrogen fluoride (HF) (according to CMA/2/II/A.3). A well-sealed HDPE destruction bottle with 500 mg dry ash sample, 8 ml aqua regia and 3 ml HF was placed in an ultrasonic bath (Branson 3510) for 24 hours. Next, the bottle was cooled for 1 hour and the content was transferred to a 100 ml PP volumetric flask with about 2.8 g boric acid and diluted to the mark. These solutions were further filtered over a syringe filter (0.45 µm), diluted and analysed for P, K, Ca, Mg, sodium (Na), sulphur (S), Si, Al, cadmium (Cd), chromium (Cr), Cu, iron (Fe), manganese (Mn), molybdenum (Mo), nickel (Ni), lead (Pb), selenium (Se), titanium (Ti) and Zn by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) (Varian 720-ES ICP-OES). No glassware was used during destruction and dilution.

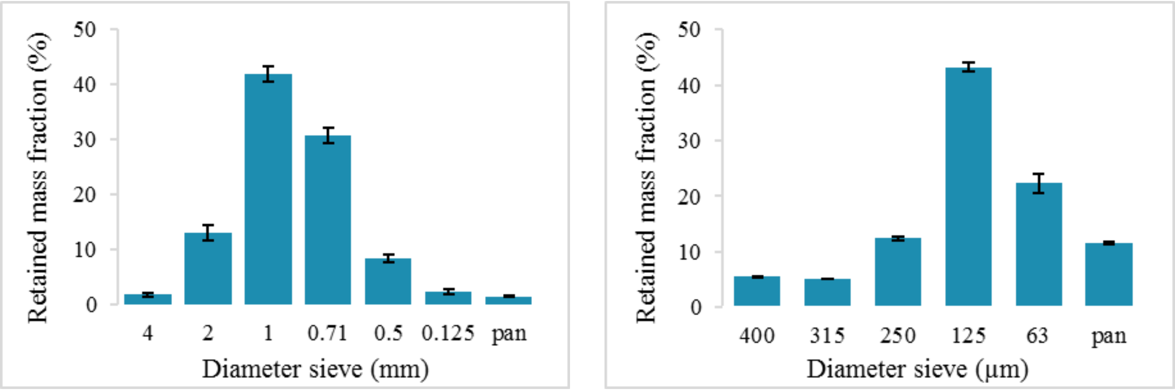
2.4. Leaching experiments

Batch leaching experiments (according to CMA/2/II/A.12 and CMA/2/II/A.19) were conducted in triplicate in closed containers. A well-sealed HDPE bottle with 9 g of untreated dry ashes and 90 ml MiliQ water was placed horizontally on a reciprocating shaker (Heidolph Promax 2020) for 24 hours at maximum speed (400 rpm). Next, the ashes were left to settle for 15 minutes and 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), Se, tin (Sn), vanadium (V) and Zn), Ion Chromatography (chlorides (Cl^-) and sulphates (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 leaching limit values.

3. Results and discussion

3.1. Ash sieving

The particle size distribution of the bed (Fig. 2 (a)) and ECO ash (Fig. 2 (b)) showed a more or less Gaussian (normal) distribution with an average particle size of 1 mm and 125 µm, respectively. About 70% of the bed ash particles has a size between 2 and 0.71 mm and about 75% of the ECO ash particles has a size between 315 and 63 µm.



(a) (b)

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).

The different observed particles and particle size fractions (Fig. 3 and Fig. 4) could 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 grey coated sand particles, which are initially already about 0.7 mm and are coated in the fluidized bed, further increasing their size, and on the other hand of unreacted, white kaolinite particles and fine dust. The ECO ash however, consists of both larger deposited 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.

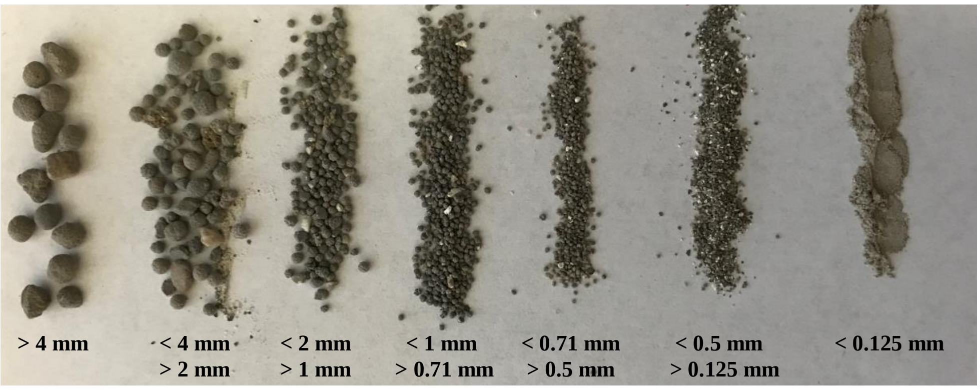


Fig. 3 Different particle size fractions for bed ash.

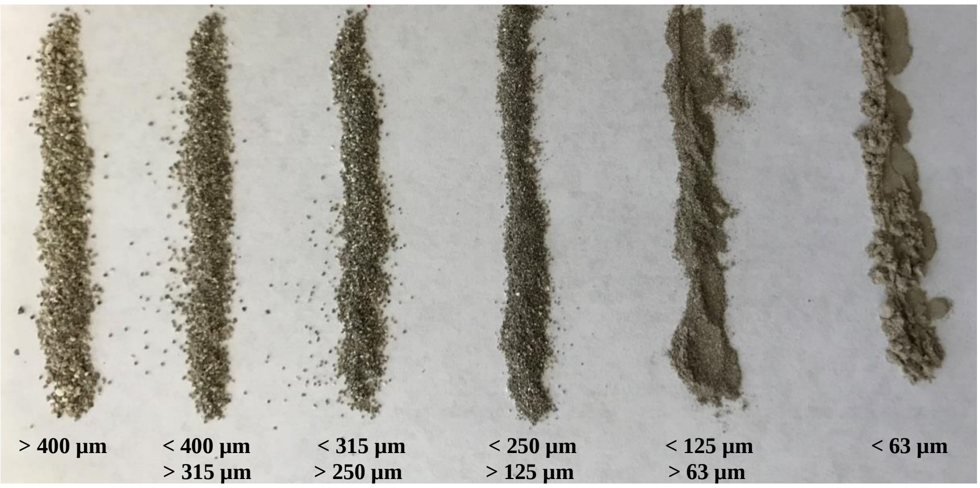


Fig. 4 Different particle size fractions for ECO ash.

3.2. Chemical ash analysis

Table 1 and Table 2 give the elementary composition of the different ash streams and of the sieved bed and ECO ash size fractions, whereas Fig. 5 and Fig. 6 give a graphical representation of their P, K and Si concentration. SH, ESP and bag ash were not sieved because they consisted of fine powders that did not show a significant difference is particle size.

Table 1 Average concentration (μ) of P, K, Ca, Mg, Na, S, Si, Al, Cd, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Se, Ti and Zn in the ash streams and in the mixed ash (% of DM and mg/kg DM); standard deviation (σ); n = 3.

			Bed ash	**SH ash**	**ECO ash**	**ESP ash**	**Bag ash**	**Mixed ash**
P	**μ**	**(% of DM)**	5.0	10.6	8.9	6.4	2.3	6.0
	σ	**(% of DM)**	0.02	0.09	0.08	0.05	0.2	0.07
K	**μ**	**(% of DM)**	9.4	11.1	11.5	15.5	14.3	12.5
	σ	**(% of DM)**	0.06	0.06	0.07	1.3	1.1	0.2
Ca	**μ**	**(% of DM)**	20.2	19.3	20.1	12.4	20.6	18.2
	σ	**(% of DM)**	0.08	0.09	0.2	0.07	1.1	0.3
Mg	**μ**	**(% of DM)**	2.6	6.2	5.2	3.5	1.2	3.0
	σ	**(% of DM)**	0.02	0.05	0.03	0.01	0.1	0.5
Na	**μ**	**(% of DM)**	2.7	2.6	3.4	3.6	1.6	1.9
	σ	**(% of DM)**	0.02	0.02	0.01	0.02	0.09	0.02
S	**μ**	**(% of DM)**	3.1	1.7	1.8	6.0	4.8	3.1
	σ	**(% of DM)**	0.02	0.04	0.02	0.04	0.3	0.02
Si	**μ**	**(% of DM)**	9.2	4.0	5.6	2.8	1.4	6.8
	σ	**(% of DM)**	0.3	0.02	0.04	0.03	0.09	0.2
Al	**μ**	**(mg/kg DM)**	6 642	7 799	9 306	5 671	2 494	5 021
	σ	**(mg/kg DM)**	92	68	56	34	49	153
Cd	**μ**	**(mg/kg DM)**	< 2	3.5	2.7	4.9	3.1	2.1
	σ	**(mg/kg DM)**		0.2	0.2	0.2	0.05	0.02
Cr	**μ**	**(mg/kg DM)**	16	30	29	31	16	19
	σ	**(mg/kg DM)**	0.4	1.3	0.6	0.6	0.4	0.2
Cu	**μ**	**(mg/kg DM)**	391	741	568	698	353	435
	σ	**(mg/kg DM)**	5	40	25	30	6	5
Fe	**μ**	**(mg/kg DM)**	4 423	6 787	8 168	4 444	2 216	4 284
	σ	**(mg/kg DM)**	167	69	266	43	23	167
Mn	**μ**	**(mg/kg DM)**	1 595	3 594	3 076	2 090	761	1 939
	σ	**(mg/kg DM)**	20	15	47	17	12	13
Mo	**μ**	**(mg/kg DM)**	15	24	20	33	23	18
	σ	**(mg/kg DM)**	0.4	0.9	0.8	1.9	0.5	0.1
Ni	**μ**	**(mg/kg DM)**	23	46	37	34	11	25
	σ	**(mg/kg DM)**	0.5	2.0	0.8	2.5	0.2	0.4
Pb	**μ**	**(mg/kg DM)**	< 2	8.0	5.2	14	10	4.5
	σ	**(mg/kg DM)**		0.7	0.1	0.5	0.4	0.8
Se	**μ**	**(mg/kg DM)**	< 2	5.7	7.7	15	8.2	4.7
	σ	**(mg/kg DM)**		1.3	0.8	1.2	0.5	1.3
Ti	**μ**	**(mg/kg DM)**	226	464	514	342	121	241
	σ	(mg/kg DM)	5	22	20	18	2	1
Zn	**μ**	**(mg/kg DM)**	985	2 226	1 755	2 591	1 150	1 497
	σ	**(mg/kg DM)**	26	81	55	167	14	32

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

			Bed ash							**ECO ash**					
			> 4 mm	**< 4 mm > 2 mm**	**< 2 mm > 1 mm**	**< 1 mm > 0.71 mm**	**< 0.71 mm > 0.5 mm**	**< 0.5 mm > 0.125 mm**	**< 0.125 mm**	**> 400 µm**	**< 400 µm > 315 µm**	**< 315 µm > 250 µm**	**< 250 µm > 125 µm**	**< 125 µm > 63 µm**	**< 63 µm**
P	**µ**	**(% of DM)**	5.4	6.0	5.9	5.0	3.7	5.4	5.7	5.2	6.5	7.8	9.4	9.9	9.2
	σ	**(% of DM)**	0.06	0.09	0.06	0.02	0.04	0.01	0.05	0.03	0.04	0.06	0.01	0.08	0.05
K	**µ**	**(% of DM)**	10.0	9.5	9.8	9.4	8.1	7.0	8.0	14.4	10.2	10.1	10.9	11.6	13.3
	σ	**(% of DM)**	0.05	0.01	0.05	0.09	0.06	0.1	0.05	0.3	0.1	0.2	0.1	0.1	0.1
Ca	**µ**	**(% of DM)**	14.0	22.8	23.9	17.0	12.9	24.6	28.5	20.3	23.2	21.4	19.8	19.4	18.1
	σ	**(% of DM)**	0.1	0.2	0.3	0.2	0.08	0.9	0.3	0.2	0.04	0.2	0.1	0.2	0.1
Mg	**µ**	**(% of DM)**	2.8	3.0	2.9	2.4	1.8	2.9	3.0	3.0	3.8	4.5	5.4	5.6	5.3
	σ	**(% of DM)**	0.04	0.02	0.04	0.01	0.03	0.01	0.03	0.02	0.01	0.04	0.02	0.05	0.04
Na	**µ**	**(% of DM)**	2.8	2.7	2.7	2.7	2.6	2.6	2.9	3.1	3.1	3.2	3.4	3.5	3.5
	σ	**(% of DM)**	0.01	0.005	0.01	0.003	0.02	0.01	0.01	0.01	0.01	0.03	0.02	0.04	0.03
S	**µ**	**(% of DM)**	3.4	3.4	3.5	3.1	2.3	1.7	2.4	3.9	1.8	1.8	1.4	1.8	2.7
	σ	**(% of DM)**	0.03	0.03	0.04	0.04	0.02	0.04	0.02	0.06	0.01	0.3	0.03	0.03	0.01
Si	**µ**	**(% of DM)**	14.8	7.0	5.8	12.8	19.0	9.1	3.6	5.0	6.5	7.7	5.9	4.7	3.7
	σ	**(% of DM)**	0.4	0.1	0.2	0.3	0.1	0.6	0.2	0.01	0.08	1.2	0.06	0.01	0.06
Al	**µ**	**(mg/kg DM)**	5 548	5 535	5 224	7 393	10 686	7 923	6 168	9 757	11 838	13 147	9 454	7 867	7 532
	σ	**(mg/kg DM)**	26	117	65	109	19	418	48	115	260	1917	15	104	55
Cd	**µ**	**(mg/kg DM)**	< 2	< 2	< 2	< 2	< 2	< 2	< 2	4.3	2.4	2.4	2.6	3.3	5.0
	σ	**(mg/kg DM)**								0.6	0.06	0.03	0.05	0.2	0.2
Cr	**µ**	**(mg/kg DM)**	19	21	18	15	15	21	22	37	25	29	33	38	41
	σ	**(mg/kg DM)**	0.9	0.3	0.5	0.1	1.3	4.0	0.5	10	1.3	1.5	2.9	2.4	2.8
Cu	**µ**	**(mg/kg DM)**	384	458	444	417	331	305	483	603	482	546	622	637	714
	σ	**(mg/kg DM)**	11	7	5	8	7	47	9	29	3	10	22	26	29
Fe	**µ**	**(mg/kg DM)**	4 365	4 422	4 331	4 260	4 285	6 368	4 323	14 822	6 426	8 552	7 718	8 511	9 300
	σ	**(mg/kg DM)**	68	28	83	73	69	473	53	8197	541	1531	69	83	46
Mn	**µ**	**(mg/kg DM)**	1 686	1 943	1 940	1 601	1 135	1 598	1 470	1 830	2 244	2 734	3 236	3 251	2 920
	σ	**(mg/kg DM)**	32	40	49	36	17	197	10	20	18	38	24	28	22
Mo	**µ**	**(mg/kg DM)**	15	16	16	14	11	12	16	32	20	22	22	21	23
	σ	**(mg/kg DM)**	0.7	0.08	0.5	0.1	0.3	0.05	0.2	3.2	0.5	0.4	0.6	1.1	1.5
Ni	**µ**	**(mg/kg DM)**	25	28	26	21	18	27	30	39	29	35	39	44	51
	σ	**(mg/kg DM)**	0.6	0.1	0.6	1.4	1.1	8.0	2.1	13	0.6	1.5	2.1	2.6	2.2
Pb	**µ**	**(mg/kg DM)**	48	8	2.5	8	7	< 2	< 2	57	2.8	1.9	2.7	4.8	12
	σ	**(mg/kg DM)**	1.6	0.8	0.1	0.8	0.8			1.9	0.3	0.2	0.7	0.6	0.4
Se	**µ**	**(mg/kg DM)**	2.0	< 2	2.7	< 2	< 2	< 2	< 2	22	10	9	8	11	18
	σ	**(mg/kg DM)**	1.3		0.7					0.7	0.6	0.8	0.8	0.7	1.0
Ti	**µ**	**(mg/kg DM)**	236	242	245	261	293	290	297	408	478	567	564	639	557
	σ	**(mg/kg DM)**	7	8	6	4	9	7	3	12	3	20	22	27	16
Zn	**µ**	**(mg/kg DM)**	1 020	1 200	1 158	969	749	876	885	2 971	1 403	1 320	1 341	1 683	3 784
	σ	**(mg/kg DM)**	23	11	23	15	31	22	37	51	33	9	56	95	6

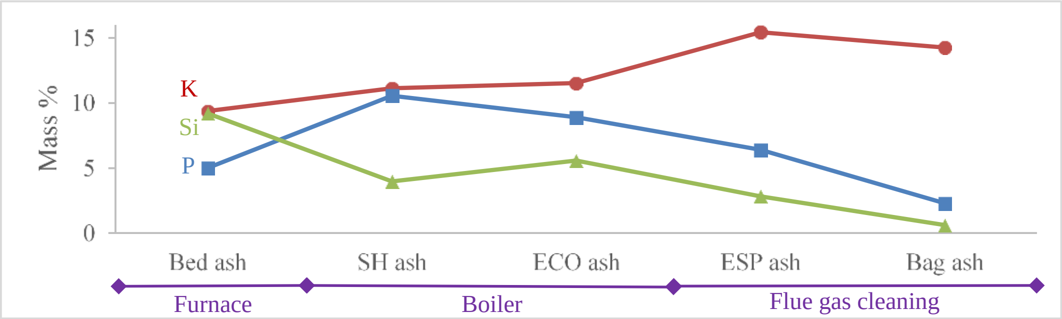


Fig. 5 P, K and Si concentration in the different ash streams (% of DM). Data of the dots indicate the average concentration in the three replicates. The standard deviation is given in Table 1. ■ P; ● K; ▲ Si.

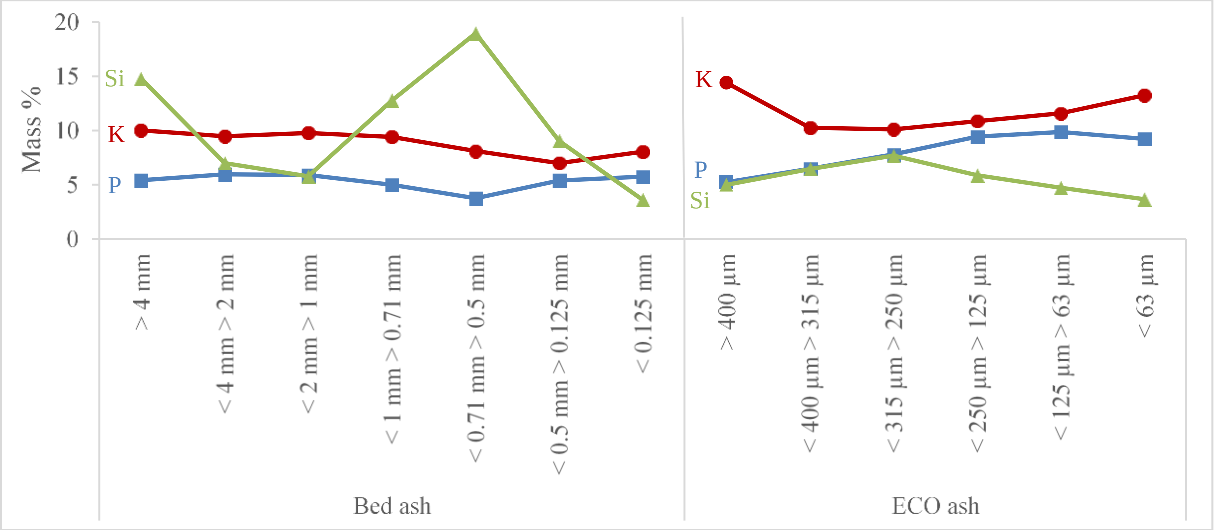


Fig. 6 P, K and Si concentration in the sieved bed and ECO ash fractions (% of DM). Data of the dots indicate the average concentration in the three replicates. The standard deviation is given in Table 2. ■ P; ● K; ▲ Si.

Fig. 5 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 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 P rich relatively coarse "coating particles" 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 increases. This is sustained by the similar decrease of the Si concentration. In the ECO ash, the smaller particles (< 250 µm) (Fig. 6) have the highest P concentration, indicating that also these smaller particles originate from the fluidized bed, possibly indirectly i.e. by intermediate deposition on the walls and tubes with subsequent removal by the shot cleaning system.

The lower P concentration in the bed ash (5.0%) (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, whilst the sand core contains almost no P and is "diluting" the P in the bed ash. For the bed ash, there is no real distinction of the P concentration as function of the particle size, although the P concentration in the < 1 mm > 0.5 mm fraction is slightly lower than in the other bed ash size fractions, this because Si is more present in particles of about 0.7 mm, 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.

The P concentration in the bag ash is the lowest (2.3%), which can be explained by the relative 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 P.

Fig. 5 also 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 e.g. KCl that are volatilized at the prevailing temperatures. 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 was the case for P, the lower K concentration in the bag ash than in the ESP ash can be explained by the high Ca concentration, "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. However, for the bed ash, the larger particle sizes appear to have slightly higher K concentrations. This is probably due to the kaolinite dosage in the fluidized bed to prevent agglomeration of K rich low melting point salts on the furnace walls. Under ideal conditions, K will bind with Al-silicates and will probably remain in the bigger particle ash fractions.

Taking into account the mass rate of each stream, the highest amount of P and K are present in the ESP ash (2 230 tons of P/year and 5 380 tons of K/year), followed by the bed ash (780 tons of P/year and 1 460 tons of K/year), which is quite logic because they cover about 58% and 26% of the total ash stream.

3.3. *Possible valorisation applications of the different ash streams*

3.3.1. Direct application as fertilizer

The poultry litter ash is a good fertilizer since it contains P and K, both essential nutrients, in compounds that show a good bioavailability in pot and field tests [11]. Furthermore, the ash is free of pathogens and organic toxic substances such as pharmaceuticals, and its heavy metal/P ratio is the same as in poultry litter, only the ash is more concentrated [8]. However, recycling of P and K from poultry litter ash and this way closing the nutrient cycle, is hindered by the legislation on the use of waste materials as fertilizer.

To evaluate the direct valorisation potential of the different (sieved) ash streams as a fertilizer, the heavy metal concentrations determined by means of the elemental analyses were, 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 [12]), which were at the time of the experiments one of the most stringent in Europe. It could be concluded that the Cu and Zn concentration in all the ash streams are two to four times higher than the 2012 VLAREMA limits (375 and 900 mg/kg DM, respectively [12]) and thus impeded 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 and Table 2, the Cd, Cr, Ni and Pb concentration in all (sieved) ash streams complied 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 [12]). Other heavy metals regulated in VLAREMA are As (150 mg/kg DM) and Hg (5 mg/kg DM) [12]. These heavy metals were not considered in this work, however, previous analytical results over a period of 2 years (2013 – 2014, n = 58) indicated that the mixed poultry litter ash contains on average < 3 ± 0.35 mg As/kg DM and < 0.05 ± 0.01 mg Hg/kg DM [Personal communication, BMC Moerdijk] and thus complied with the 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, only the (combination of the) bed ash fractions < 0.71 mm respected the 2012 VLAREMA limits for Zn and Cu. These fractions however only represent 3.2% of the total ash mass that is generated, corresponding to 1 900 tons/year, and their combined P concentration is limited to 4.3%.

It should however be noted that there is 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, according to the UK poultry litter ash quality protocol [13], compared to e.g. 900 mg/kg DM in Flanders (VLAREMA, annex 2.3.1, 2012 [12]), while there is no fixed limit for Zn in France [14]. Also, the VLAREMA legislation, which was used as a 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 [15]. Hence, the bed, bag and mixed poultry litter ash analysed 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 analysed in this work (1 497 mg/kg DM) is in general lower than the average concentration obtained from previous analytical results over a period of 2 years (2 000 mg/kg DM [personal communication, BMC Moerdijk]). So a first observation is that whether the poultry litter ash can be directly applied as fertilizer, depends on local legislation in place, which clearly demonstrates the need for a uniform European legislation as being prepared by the European Commission’s STRUBIAS working group. A second finding is that legislation often only considers absolute concentrations of heavy metals instead of dosage. Most European member states give absolute concentration limits, whereas the Dutch regulation gives dosage limits per kg of nutrient (Uitvoeringsbesluit Meststoffenwet, annex II [16]). This way, the legislation in the Netherlands indirectly takes into account the amount of fertilizer that will be put on the land and this way also takes into account 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 [12, 15]). A third finding is that there are no legal concentration limits for heavy metals 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]. In this regard, the poultry litter ash analysed in this work fully complies with the dosing limits for Cu and Zn (mass/area) in the Flemish legislation, but as already explained, not with the concentration limits (VLAREMA [12, 15]). This can be explained by the fact that the concentration limits set by VLAREMA are based on the dosage of waste streams reusable as fertilizer of which typically 2 ton/ha has to be applied to meet the maximum dosage limits for P set in the Flemish Manure Decree [17, 18]. However, since mixed poultry litter ash is more concentrated in P than most other waste streams reusable as fertilizer, only maximum 1 ton/ha of mixed poultry litter ash has to be applied to meet the dosage limits for P [18]. Taking into account the maximum dosage of poultry litter ash per hectare in Flanders, the maximum allowable Zn concentration would be 3000 mg/kg DM to comply with the dosage limit of 3000 g/ha/year (VLAREMA, 2018 [15]), hence indicating that mixed poultry litter ash containing on average 2000 mg Zn/kg DM [Personal communication, BMC Moerdijk] could 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, not only the ash 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) [19] shows that in most European member states there is a positive P balance, i.e. more P is supplied to the soil than is taken up by the plants and hence the demand for P fertilizers is likely to be low. However, Bulgaria, the Czech Republic, Estonia, Italy, Hungary, Romania and Slovakia have a negative P balance, whereas the N balance is positive (except for Bulgaria). This makes the ash from BMC Moerdijk, which is rich in P but poor in N, an interesting additional fertilizer for these member states. Bulgaria has the highest market potential, in 2014, the net P balance was about - 30 400 tons of P, followed by Romania (- 27 400 tons of P), Hungary (- 12 300 tons of P), Italy (- 11 500 tons of P), Estonia (- 6 800 tons of P), Slovakia (- 4 800 tons of P) and the Czech Republic (- 2 100 tons of P) [19]. In comparison, the ash annually produced by BMC Moerdijk contains about 3 660 tons of P.

3.3.2. Use of ash as building material

Besides P and K, also other ash elements such as Ca, Si, Mg and Al can be valorised e.g. by using the ash as building material. For use of waste products as a building material, both concentration and leaching limits for heavy metals, chlorides, sulphates and fluorides have to be met e.g. according to Flemish (VLAREMA, annex 2.3.2. [12]) and Dutch legislation (Regeling bodemkwaliteit, annex A [20]). As for its application as fertilizer, it can be concluded that the Cu and Zn concentration in all the ash streams are two to three times higher than the VLAREMA limits (which are 375 and 1250 mg/kg DM, respectively [12]) and thus impeded the direct application of the individual ash streams and consequently also of the entire mixed ash stream as a building material in Flanders. The results of batch leaching experiments on the mixed ash stream are given in Table 3, 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 sulphates was 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, also untreated bottom ash of waste incineration (WtE bottom ash) often does not directly meet the leaching limits. It is therefore customary to treat this WtE bottom ash by sieving, washing and possibly aging. These operations remove certain heavy metals, sulphates and chlorides whereas non-rinsed heavy metals are stabilized in the ashes [21, 22, 23]. Based on a comparison of the elemental composition of untreated WtE bottom ash [21, 22] and the untreated mixed poultry litter ash, it seems highly likely that poultry litter ash will satisfy legal limit values for use as a building material in Flanders or the Netherlands after conventional WtE bottom ash treatment.

Table 3 Average leaching ± standard deviation of regulated elements (Flemish and Dutch legislation) from 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 ± 468
F^-	1.9 ± 0.2
SO_4^{2-}	84 139 ± 688

Besides leaching, also the particle size distribution of the mixed poultry litter ash is a point of attention for its use as a building material. The mixed ash stream contains a higher proportion of fine particles than conventional WtE bottom ash because it also contains the finer SH, ECO, ESP and bag ash. Conventional bottom ash treatment separates particles < 0.1 mm as a sludge fraction that has to be landfilled [23]. 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 valorisation as building material economically feasible.

WtE bottom ash can also, after treatment, be used as a replacement for sand in e.g. 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. The setting time of concrete can be strongly delayed leading to a slower build-up of strength in the concrete, whereas hardening can be greatly lowered at least at early age [24].

3.3.3. Use of ash in cement production

The Ca, Si and Al in the poultry litter ash can also be valorised 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.

A comparison of the elemental composition of the mixed poultry litter ash with the composition of raw materials for cement clinker production indicated 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. Fig. 7 gives the ternary diagram (CaO, SiO_2 and Fe_2O_3 + Al_2O_3) for cement clinker and the ash constituents of different raw materials and fuels [10]. From the mixed poultry litter ash composition (indicated by the red point in Fig. 7), it can be concluded that the ratio of the main components 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.

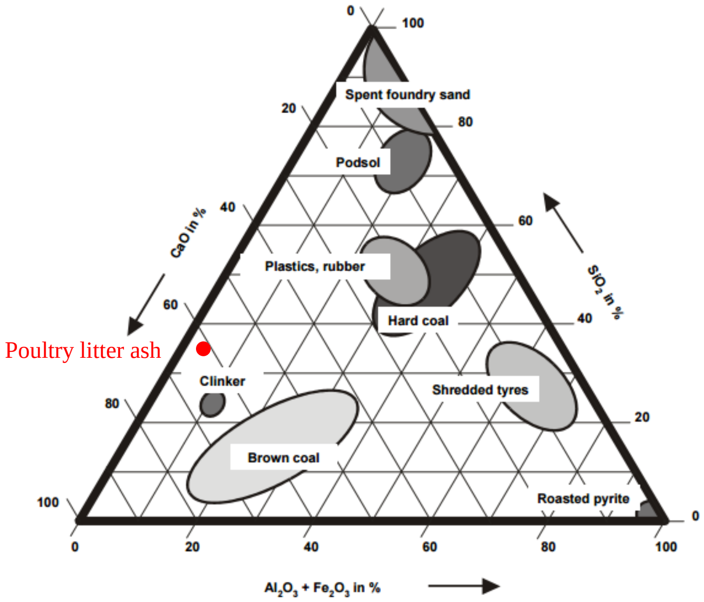


Fig. 7 Ternary CaO, SiO_2 and Al_2O_3 + Fe_2O_3 diagram for cement clinker and the ash constituents of different raw materials and fuels [10]. The mixed poultry litter ash composition is indicated by the red point in the ternary diagram.

According to Lam et al. (2010) and Oye (2012), a high P content in cement clinker (due to use of incineration ash with a high P content), will affect the hydraulic properties of cement. Higher amounts of P in cement clinker will lead to stabilisation of the Ca_2SiO_4 phase during burning of the cement clinker, which is then suppressing the formation of Ca_3SiO_5 in the final cement, which is the main hydraulic phase. Hence, a lower amount of Ca_3SiO_5 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 [25, 26].

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 [25, 27, 28]. However, when poultry litter ash is used in geopolymer cement production, where alkali aluminosilicate materials are created by alkali activation of a Si source, the high alkali content in poultry litter ash can be an advantage. Peys et al. (2016) investigated e.g. the use of K rich biomass ashes as activators in metakaolin-based inorganic polymers (geopolymers). The K rich biomass in their research was used as an environmentally friendly alternative for e.g. sodium hydroxide (NaOH) solutions, commonly used as alkali activator in geopolymer cement production [29].

Besides P and K, also S can cause problems when the poultry litter ash is used in cement applications. The so called "sulphate attack" causes loss of adhesion of the cement hydration product, extensive cracking, and expansion due to formation and expansion of gypsum ($CaSO_4.2H_2O$) and ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O$) [30].

3.3.4. Wet chemical extraction

Of all the considered application options, P only remains in the food cycle if the ash is used as a fertilizer, however, as mentioned before, this is mainly hindered by the legislation on the use of waste materials as fertilizer. Hence, another option to increase the valorisation potential of the poultry litter ash is to separate the fertilizer elements, i.e. P and K from the rest of the ash. The most straightforward option to do so is a wet extraction with subsequent precipitation of the extracted P and eventually K in a pure form with a high market value, which is a process similar to the one used for P production from phosphate rock. The extraction should be optimized in such a way that heavy metals interfering with the use of the ash as fertilizer, 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 can be precipitated as a compound that can be easily valorised by secondary metal refiners, whereas the solid residue of the ash remaining after extraction can be easily applied as building material or as raw material in cement production.

4. Conclusions

In this paper, it was 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 showed 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 legislation on the use of waste materials as fertilizer. Valorisation of other ash elements such as Ca, Si, Mg and Al by using the ash as building material or in cement production can rather be hindered by the high P and K concentration that form a possible technical obstacle for those applications. However, of all the considered application options, P only remains in the food cycle if the ash is used as a fertilizer. P recovery from alternative sources is important because phosphate rock is depleting and P is an essential micronutrient for all living organisms. In that regard, it could be interesting to separate the fertilizer elements, i.e. P and K from the rest of the ash by doing e.g. a wet chemical extraction whereas the solid residue of the ash remaining after extraction can be easily applied as building material or as raw material for cement production.

Acknowledgements

This study was financially supported by BMC Moerdijk (Industrial park M349, Middenweg 36a, 4782 PM Moerdijk, The Netherlands). Further, the FWO is acknowledged, as Lorien Luyckx is a SB PhD fellow at Fonds Wetenschappelijk Onderzoek Vlaanderen (FWO) (project number 1S08418N).

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