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Research article

Transformation of inorganic matter in poultry litter during fluidised bed gasification

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ABSTRACT

This work investigates the transformation, release and fate of inorganic matter during fluidised bed gasification of poultry litter and also poultry litter mixed with limestone as an additive. The poultry litter, the cyclone and bed ash were characterised by means of chemical fractionation analysis, as well as X-ray diffraction. Concurrently, the release of inorganic species during gasification of the feedstock was measured in separate laboratory experiments using molecular beam mass spectrometry. In addition, FactSage was used to predict the formation of gaseous species and the composition of solid residues from gasification under equilibrium conditions. On average, the cyclone ash accounts for 4.6 wt% and the bed ash 12.4 wt% of the total poultry litter fed into the reactor. All phosphorous (P) was present in the cyclone ash as stable phosphates, while potassium (K) in both cyclone and bed ash was mainly present as H_2O leachable KCl, organically associated and stable phosphates and silicates. Furthermore, an assessment was made against the appropriate criteria, whether the ashes from gasification can be categorised as component materials for EU fertiliser products.

1. Introduction

The global livestock industry is the largest anthropogenic land user, employing 1.3 billion people and accounting for 40–50% of agricultural GDP, providing one-third of humanity's protein intake [1]. The emissions from livestock production represent 14.5% of total anthropogenic greenhouse gas (GHG) emissions amounting to 7.1 $GtCO_2eq/yr$ [2]. Between 2020 and 2029 global livestock production is expected to expand by 14% with poultry the fastest growing meat accounting for about half of the projected increase in total meat output. Its short production cycle allows producers to respond quickly to market signals, while also allowing for rapid improvements in genetics, animal health and feeding practices [3]. The poultry sector generates a large quantity of litter, which is a mixture of bedding material, waste feed, dead birds, broken eggs and chicken feathers. The amount produced varies from country to country but ranges from 1.5 to 5.7 kg of litter/bird over the production cycle [4].

Poultry litter is primarily recycled by direct land application as a source of nutrients (N, K and P) for agricultural crops [5]. However, due to the geographical dislocation of animal feed production from animal production, intensive poultry farming has given rise to excessive local application of manure based nutrients at levels beyond that which sustainably can be used on arable land [6] causing excessive soil fertilisation leading to environmental issues [7,8]. Compared with other animal manures, poultry litter has a relatively low moisture content and therefore is one of the most suitable manures for thermal processes, such as combustion, pyrolysis or gasification in order to recover energy as well as nutrients [4,8–11]. Combustion remains the most advanced and widely applied technology with commercial scale incinerators of poultry litter currently used for heat and electricity production and ash recovery in the UK, the USA and The Netherlands [8,12]. Research on poultry litter combustion and co-combustion continues to facilitate further improvements [13–16].

Unlike combustion, gasification of poultry litter has been limited to research facilities [17–19] and small-scale testing applications [20,21]. In gasification, a sub-stoichiometric amount of oxygen is used for partial oxidation, leading to a smaller final volume of flue gas requiring cleaning compared to combustion [22]. Arena et al. carried out fluidised

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bed gasification of chicken manure and concluded that the hot producer gas could be used directly in a specially designed burner [17,23]. Experimental studies on poultry litter gasification to date have focused mainly on the effect of process conditions on producer gas composition and carbon conversion efficiency.

Poultry litter has a high ash content which is useful as a source of plant nutrients but on the other hand can cause technological problems such as a) agglomeration and b) deposition during thermal treatment. When the concentration of low melting temperature ash forming elements (K, Na) dominates over higher melting elements (Ca, Mg) as in the case of poultry litter, it gives rise to ash melting and agglomeration in fluidised bed reactors [24,25]. These issues have been reported both in fluidised bed combustion [26–28] and gasification [17,21]. Blending poultry litter with limestone has been shown to supress such problems [18]. Limestone provides calcium which (a) reacts with phosphorus forming a high melting temperature calcium phosphate as well as (b) forms a Ca-rich layer over K-rich silicate melt on the silica particles surface then enhanced diffusion of Ca^{2+} in the melt and subsequent substitution of K^{+} ions with Ca^{2+} leads to formation of solid Ca-silicates with higher melting temperature [28–30]. Mixing of poultry litter with other feedstock has also been proposed to mitigate agglomeration issues during gasification [19,28].

There are several studies that investigate the properties of ash from poultry litter combustion [28,31], including its direct application as a P source for agricultural crops [32], application as a hydrated ash [33] as well as recovery of the P by elution/extraction [34,35]. Previous studies reported that poultry litter ash contains P and K chemical species that show good bioavailability during pot and field tests [36]. However, application of poultry litter ash as a fertiliser is highly dependent on local regulations in place in EU member states. For example direct recycling of poultry litter ash as a P/K fertiliser is forbidden in Flanders region, because it contains high concentration of Zn and Cu [31]. Zn and Cu are a typical supplement in poultry diet which affect bird's growth performance [37]. A recent study shows that the P in ash from poultry litter combustion was mainly present as a K-Ca-P-rich amorphous phase, with some crystalline compounds such as apatite and whitlockite [28]. To the authors knowledge there is no report which examined properties of ash from the gasification of poultry litter.

K, Na, Zn, and Pb can be partly released into the gas phase during combustion or gasification and form aerosols which may condense on cooler surfaces of the combustion/gasification units and form deposits, inhibiting heat transfer, and causing corrosion and fouling issues [26,38–40]. Among the various compounds found in ash, K has the highest impact on aerosol formation, since it is usually found in higher concentrations than other elements [26]. A recent study by Dong et al. [41] reported that the partitioning of ash forming matter between the gaseous phase and solid fraction depends on the reaction atmosphere i.e. reductive or oxidative. In an oxidising atmosphere the sulphur for instance forms K_2SO_4, while under reducing conditions sulphur was reported to be in the gaseous phase [42,43]. Release of aerosols forming elements was measured for the combustion of poultry litter [15] but such information has not been reported for gasification processes.

The objective of this study is to provide some fundamental understanding of how operating conditions (temperature and equivalence ratio (ER)) and limestone addition affect the transformation, release and fate of inorganic matter and the final composition of the cyclone ash during the fluidised bed gasification of poultry litter. We compared the chemical composition of bed and cyclone ash using chemical fractionation analysis (CFA) and X-ray diffraction (XRD). The ash compositions were evaluated against the criteria in the revised EU fertiliser regulations, in order to determine their suitability as component nutrient materials for fertiliser [44]. In this study, we have mainly focused on the fate of P as well as K, Na, S and Cl. The gaseous inorganic species in the hot gas were identified by means of molecular beam mass spectrometry (MBMS) measurements. The release of gaseous species as well as the composition of the condensed phases formed during the process was predicted by FactSage calculations.

2. Experimental methodology

2.1. Materials

The poultry litter used in this study was collected from a poultry farm in The Netherlands. Considering the heterogeneous nature of the feedstock [4,9], it was partially dried and sieved to a particle size in the range of 0.7–2.8 mm. A detailed description of the analytical techniques used to measure the properties of the feedstock are reported elsewhere [18]. During preliminary gasification experiment using poultry litter alone, the bed agglomeration/defluidisation occurred at a gasifier temperature of 750 °C [18]. Consequently, as a mitigation strategy, limestone was added to avoid defluidisation and agglomeration issues at higher temperature. To maintain the Ca/P molar ratio over 2, the limestone addition level was set to 8 wt%. The gasification experiments were conducted using either a mixture of poultry litter (92 wt%) and limestone (8 wt%) or poultry litter alone. The limestone used in this study was supplied by Rheinkalk GmbH (Brilon, Germany) with particle size in the range 0.9–1.2 mm. XRD analysis of the limestone using the Rietveld refinement showed a mixture of 95 wt% calcite and 5 wt% dolomite (as shown in the supplementary material Table S-1 and Fig. S-10). A batch of fresh silica sand (1.2 kg) with a mean particle size of 0.31 mm (range 0.25–0.50 mm) was used as the bed material for each experiment. After each gasification experiment, the elutriated char and fine ash particles (cyclone ash) were collected in the cyclone and retained for analysis. At the end of the experiment, the mixture of bed material, unconverted carbon in the bed (char), ash and limestone, (referred to as bed ash) were removed from the reactor for analysis. Both materials were stored in sealed containers. The median particle sizes D10, D50 and D90 of cyclone ash samples were in the range 3.5–10.1 μm, 42.7–54.9 μm, 138–172 μm, respectively (Malvern Mastersizer 3000 with the Aero S).

The elemental properties of poultry litter feedstock, cyclone and bed ash are presented in Table 1 (refer to Table 2 for process conditions regarding limestone addition). The mass of solids remaining after gasification (the cyclone ash and the bed ash) account for <20 wt% of the total poultry litter fed into the reactor. The cyclone ash collected in the cyclone accounts for 0.8 to 6.0 wt% (lower value at the highest temperature) and the bed ash between 10.5 and 14.7 wt% of feedstock used in the tests. The carbon content of the cyclone ashes varied between 12 and 22 wt% while that of the bed ash is much lower, 7.71 wt% for poultry litter gasification and 1.8 wt% for poultry litter blended with limestone. Chlorine content in the cyclone ash is 0.77 wt% when poultry litter was not blended with limestone. This value dropped significantly when the poultry litter was blended with the limestone to between 0.06 and 0.27 wt%.

2.2. Gasification experiments

The gasification experiments were conducted within the EU FP7 BRISK project using a lab scale air blown bubbling fluidised bed reactor with a 5 kW_{th} capacity at the Energy Research Centre of The Netherlands, now part of The Netherlands Organisation of Applied Research TNO (ECN part of TNO). A detailed description of the experimental procedures and measurements techniques can be found in [18] whereas, the summary of operating conditions and vol% of selected gas compounds in the product gas is presented in Table 2. Each gasification experiment lasts about an hour. The test numbers in Table 2 correspond to those in reference [18], which provides complementary results of gasification experiments. It is worth noting that the hydrochloric acid (HCl) content was measured only once a day (test 3 and 10), whereas COS and H_2S were measured continuously at 4 min intervals using an online micro gas chromatograph (Varian, CP-4900).

Table 1
Ultimate properties of poultry litter feedstock, bed and cyclone ash.

	Poultry litter	Poultry litter + limestone	Cyclone ash					Bed ash	
Test number	–	–	2	5	9	10	14	2 and 3	5–8
	wt%, dry basis								
Moisture content (a.r.)	22.10	20.33	–	–	–	–	–	–	–
Ash content	17.54	26.41	71.45	71.21	71.97	79.54	82.83	86.23	94.96
Carbon	45.11	43.16	22.93	20.57	20.16	15.15	12.25	7.71	1.80
Hydrogen	5.30	4.88	0.38	0.37	0.32	0.25	0.23	0.21	0.15
Nitrogen	5.34	4.92	1.40	1.27	1.16	0.96	0.61	0.32	0.01
Sulphur	0.74	0.69	1.35	1.69	1.64	1.27	1.44	0.31	0.23
Chlorine	0.58	0.53	0.77	0.06	0.27	0.26	–	–	–
Oxygen (by difference)	25.39	19.42	1.72	4.83	4.48	2.57	2.64	5.21	2.86
Dry and ash free basis									
H/C	–	–	0.20	0.22	0.19	0.20	0.22	0.33	0.99

a.r. – as received.

Table 2
Summary of operating conditions for gasification tests at ECN part of TNO and the measured content of selected gas compounds in the product gas [18].

Test number*	2	3	5	9	10	11	14
Feedstock type	Poultry litter		Poultry litter with limestone				
Poultry litter feed rate, kg/h (a.r.)	0.66		0.49	0.61			0.57
Limestone (kg/h)	0.0		0.04	0.05			0.05
Total feed rate (kg/h)	0.66		0.53	0.66			0.62
Bed temperature of gasifier (T_g)**, °C	700		700	750			800
Equivalence ratio, ER (−)	0.22	0.30	0.29	0.23	0.28	0.33	0.30
Air flow rate, (dm^3/min)	7.2	10	7	7	8.5	10	8.5
Nitrogen flow rate, (dm^3/min)	4.8	2	5	5	3.5	2	3.5
Fluidising medium flow rate, dm^3/min	12	12	12	12	12	12	12
Superficial gas velocity based on the total product gas yield, m/s (T_g)	0.24	0.24	0.22	0.24	0.23	0.23	0.24
Mass of cyclone ash as % of total poultry litter fed	5.6		5.8	6.0			0.8
Mass of bed ash as % of total poultry litter fed	12.6		11.7	10.5			14.7
Content of selected gases in the product gas							
H_2S, (% v/v)	0.062	0.057	0.042	0.023	0.030	0.028	0.023
COS, (% v/v)	0.004	0.003	0.002	0.001	0.001	0.001	0.001
HCl, (% v/v)	–	0.0013	–	–	0.0009	–	–

* Test number from [18].

** The reactor temperatures were measured by thermocouples.

2.3. Chemical fractionation analysis of poultry litter, cyclone and bed ash

The poultry litter, cyclone and bed ash samples were analysed by CFA. The CFA method is described in detail by Zevenhoven et al. [45], Pettersson et al. [46] and Lynch [47], therefore, only a brief description is provided here. The poultry litter, cyclone and bed ash were consecutively washed in water, 1 M NH_4Ac (ammonium acetate solution) and 1 M HCl (hydrochloric acid solution). The leachates were analysed for Si, K, Na, Mg, Ca, Al, Mo, Ni, Cd, Cr, Cu, Pb and Se by atomic absorption spectrometry (AAS) (Varian Spectra AA-220), for P using inductive coupled plasma atomic emission spectroscopy (ICP-OES) (Agilent 5100 ICP-OES fitted with an SPS4 auto-sampler) and for Cl and S using ion chromatography. Selective leaching of the poultry litter in solutions of increasing "aggressiveness" gives information of the chemical form of the ash-forming matter in the fuel. The water soluble elements are present in the form of salts; elements eluted by ammonium acetate are organically associated (bound to the carbonaceous material) as well as some calcium carbonate and acid soluble elements present predominantly as carbonates or sulphates [45,46]. Generally, the ash-forming elements, those leached out by water and NH_4Ac are considered to be volatile species, whereas species leached by HCl are considered the non-volatile ash-forming elements found in the raw material [24,46,48,49]. Note, that in this study the solid residue remaining after leaching tests was not analysed. It was reported that most of Si is typically left in the residue [45,46]. Lynch [47] reported that for poultry litter 17% of Fe, 7% of Al and Mn, and 1–2% Mg, K, P, and Ca remained in the residue after leaching with H_2O, NH_4Ac and HCl. The same elements were in the residue after leaching cyclone ash samples. Jordan et al. [48], on the other hand observed for cane bagasse that after CFA 50% of Si, Al and S, 30% of Ca and Fe, 20% of Mg and Mn, and 10% of K left in the residue.

2.4. Content of ash forming elements

Inorganic constituents in poultry litter and cyclone ash samples were measured using AAS and ICP-OES after nitric acid, hydrogen peroxide and hydrofluoric acid (HNO_3-H_2O_2-HF) digestion in a microwave oven according to BS EN 15290:2011. Before digestion, the poultry litter and cyclone ash were ashed at 550 °C.

The concentration of ash forming elements in poultry litter, poultry litter mixed with limestone and cyclone ash are presented in Table 3. The data presented in Table 3 shows that K is the most abundant alkali metal in poultry litter, with other main ash forming elements consisting of Si, Ca, P, Al, S, Mg and Na, some of which are considered as plant macronutrients. Aerosol formation strongly depends upon the amount of K released from the fuel [50], and the sum of K, Na, Zn and Pb of 18,690 mg/kg is an indicator of high aerosol emissions from poultry litter during its gasification.

It was anticipated that the mixture of poultry litter with limestone would have a high propensity for the formation of Ca-P compounds (Ca/P molar ratio of 4.77) as previously shown by [28,51]. The surplus Ca reduced the release of S species, by forming CaS, which was confirmed in the experimental campaign (Table 2) as well as in previous work [52].

The most abundant compound in cyclone ash samples is Ca, irrespective of whether poultry litter is mixed with limestone or not,

Table 3
Concentration of ash forming elements in poultry litter and cyclone ash samples.

Test number			2	3	5	9	10	11	14
Elements	Poultry litter	Poultry litter + limestone	Cyclone ash	Cyclone ash	Cyclone ash	Cyclone ash	Cyclone ash	Cyclone ash	Cyclone ash
	mg/kg dry basis								
Si	11,863	10,672	72,528	71,003	63,452	67,146	64,948	62,891	62,049
Ca	9922	48,215	110,362	108,036	104,943	111,053	107,357	104,033	102,608
K	20,901	18,803	101,898	102,032	91,527	84,948	99,342	98,674	95,620
Mg	2655	3049	56,845	57,204	60,274	59,117	61,921	61,918	65,425
Na	2662	2395	42,256	47,243	45,993	39,443	42,913	44,246	39,704
P	8685	7813	88,275	77,477	76,033	81,044	93,502	86,959	94,465
Fe	525	472	6888	7016	7173	7168	7079	7575	8444
Ti	47	43	531	478	505	535	517	501	494
Al	883	795	9816	9609	9334	9877	9554	13,115	9127
Cu	104	94	1673	1767	1580	1813	1416	1459	1430
Mn	323	291	2352	2362	2215	2490	2563	2368	2652
Zn	398	358	112	116	76	61	67	69	60
$S_{inorganic}$	3104	2793	–	–	–	–	–	–	–
Cd	15	14	31	32	29	31	31	25	30
Cr	3	3	411	311	296	372	205	222	245
Mo	90	80	113	124	214	10	267	242	225
Ni	27	25	225	153	175	224	141	181	500
Pb	32	29	529	670	732	884	526	458	667
Se	551	495	1738	1700	2752	1766	1960	2248	2564

followed by K, P and Mg. Total K is between 85 and 100 g/kg and total P is between 76 and 94 g/kg. Although, cyclone ash was enriched in macro and micronutrients, trace elements were also present and exceeded the upper acceptable application limit set by the UK Quality Protocol for Poultry Litter Ash (Se, Cd, Cr, Hg, Mo, Pb, Cu, Ni) [53] which restricts its direct use as an agricultural P-K fertiliser [54].

2.5. X-ray diffraction

The crystalline constituents of the cyclone ash were characterised using an Empyrean X-ray diffractometer (Malvern Panalytical, The Netherlands) in para-focusing Bragg-Brentano geometry (setup: Cu LFF tube operated at 40 kV and 40 mA, BBHD-mirror with 0.4° divergence, 0.04 rad soller slits, PIXcel3D detector in 1D mode). The samples were placed on a background-free Si single crystal sample holder. The phase analyses were done in the HighScore software package Version 4.8 (Malvern Panalytical, The Netherlands) and the ICDD PDF-2 database 2004 (International Centre for Diffraction Data, USA). For Rietveld refinement the profile analysis software TOPAS Version 6 (Bruker AXS GmbH, Germany) was used. Crystal structures were obtained from the ICSD (Inorganic Crystal Structure Database, FIZ Karsruhe, Germany).

2.6. Molecular beam mass spectrometry

The initial release of inorganic species during the pyrolysis stage of initial gasification was investigated in a lab-scale gasification reactor coupled to a molecular beam mass spectrometer (MBMS) for in situ hot gas analysis. The setup is briefly described here as a full description can be found elsewhere [55]. The gasification experiments were carried out in an electrically heated furnace with a high-density alumina reactor tube. The temperature in the reaction zone was kept at 700 or 800 °C to match the temperatures of the fluidised bed reactor. The reaction atmosphere consisted of 85 vol% He (to increase resolution in the MBMS) and 15 vol% CO_2 (to simulate gasification conditions). To investigate the influence of steam, 10 vol% water vapour was included in respective experiments. The total gas flow was set to 4 L/min for all experiments. The end of the alumina reactor was coupled directly to the MBMS to sample the high-temperature gasification products without quenching, ensuring an in-situ high temperature gas analysis. A total of 50 mg of poultry litter was gasified in a single run. For some experiments, the poultry litter was mixed with 100 mg silica sand (as bed material) and/or 4 mg limestone. A total of 6 samples were measured, and the results were averaged to ensure the reliability of the results. Quantification of the mass-to-charge spectra for the sulphur species $^{34}H_2S^+$, $^{60}COS^+$ and $^{64}SO_2^+$, the alkali species $^{39}K^+/NaO^+$ and $^{74}KCl^+$ and the phosphorous species $^{62}P_2^+$ and $^{63}PO_2^+$ was achieved by normalisation to the $^{44}CO_2^{2+}$ base level signal.

2.7. Thermodynamic calculations

Thermodynamic calculations were performed using the computational package FactSage 8.0 [56]. The new oxide database called GTOx developed by Forschungszentrum Jülich and GTT-Technologies [57,58] combined with the commercial database SGPS [59] for pure gaseous and H-, Cl-containing solid/liquid stoichiometric substances have been used in the present work. The equilibrium calculations were conducted under defined conditions (chemical composition of a system, temperature, pressure). All available phase relations and transformations were considered for the calculation: the minimisation of Gibbs free energy approach was used to find the equilibrium state of the system. All constituents presented in Table S-2 were used as the input parameters for FactSage calculations. The compositions of the corresponding fuel are based on the elemental composition (Table 1), the ash composition analysis (Table 3) and the feeding rate (0.66 kg/h for poultry litter and 0.61 kg/h for poultry litter with limestone (Table 2)). The amount of oxygen has been calculated according to the fluidised bed gasification conditions (ER = 0.3, Table 2). The calculations are performed for the temperature range from 500 to 1100 °C. The results presented in this study were obtained under equilibrium conditions where kinetic effects are not taken into account. All phases from the databases (GTOx and SGPS) including gaseous phase, stoichiometric compounds, solid and liquid solutions were considered.

Equilibrium calculations were conducted for the cyclone ash collected after gasification in the temperature range from 700 to 800 °C at ERs of 0.23, 0.28, 0.29 and 0.3, using ash compositions provided in (Table S-2), whereas a certain amount of oxygen was added to enable the transformation of all elements into their corresponding oxidised form (SiO_2, Al_2O_3, etc.). The gas phase was excluded from the calculations and only residual solid inorganic phases being considered depending on temperature.

3. Results and discussion

3.1. Leaching of poultry litter, bed and cyclone ash

Results of CFA of poultry litter are presented in Fig. 1 (a and b). About 80% of Cl and S, 75% of Na, 60% of K, 50% of Mg, 26% of P and 10% of Ca were leached by water from the original poultry litter which is in line with the findings of Lynch [47]. Na, K, Mg are nutrients in the poultry diet typically added as chlorides [60,61], while Ca is a typical supplement added as a calcium phosphate [62]. Some of minor elements (concentration < 500 mg/kg) were also leached by water such as Mo as well as a small fraction of Mn, Ni, Cu, Se and Cd. Ammonium acetate leaching releases organically bound ions. For poultry litter these were primarily Si, K, Mg, Na. Cl and S but also a small portion of P, Ca, Se, Mn and Ni. About 20% of K was organically bound confirming results from Lynch et al. [47]. Hydrochloric acid dissolves most of the poorly soluble inorganic salts, carbonates and sulphates. In poultry litter 100% of Al and Cr, 99% of Zn, 88% of Mn, 85% of Ca, 62% of P and 45% of Si was leached with HCl. Lynch [47] reported similar trends for Ca and Mn however, the authors also reported that a fraction of Al was leached by water and ammonium acetate.

Speciation of P in poultry litter in this study (26% water leached, 12% ammonium acetate leached and 62% HCl leached) is in line with findings of other researchers [63,64] who reported that the majority of P in poultry litter was in stable HCl leached form (Ca associated, apatite P) but also a high portion was water leached. In contrast, Ghanim et al. [65] observed that 50% of total P was water soluble and only 6.2% was organic P (associated with organic matter and amorphous Al/Fe oxides, non-apatite P).

The speciation of the elements between the bed ash and the cyclone ash was evaluated to investigate the retention of elements by bed ash and the transformation of elements from soluble to a more stable form. A comparison of CFA of the bed ash and the cyclone ash from two gasification tests is presented in Fig. 2. The gasification tests were carried out at 700 °C. When poultry litter alone was gasified, the bed ash accounted for 12.6 wt% and cyclone ash of 5.9 wt% of the total fuel fed. Moreover, when a mixture of poultry litter and limestone was gasified the bed ash accounted for 11.7 wt% and cyclone ash of 5.8 wt% of the total fuel fed. It is apparent, that more Ca and Si were bound in the bed ash than in the cyclone ash. All of the Al, Si, over 80% of Ca and Mg and 10% of S was present in the bed ash as stable compounds (HCl leached). Almost all P was present in the cyclone ash as stable compounds (HCl leached). A much higher fraction of the K and Na present in the bed ash was more stable (HCl leached) than that of the cyclone ash. A significant fraction of K and Na remained organically bound in both bed and cyclone ash. The organically bound elements are associated with not fully converted char. The fraction of organically bound Ca, Mg, Si was higher in bed ash when from poultry litter was gasified without limestone addition. The

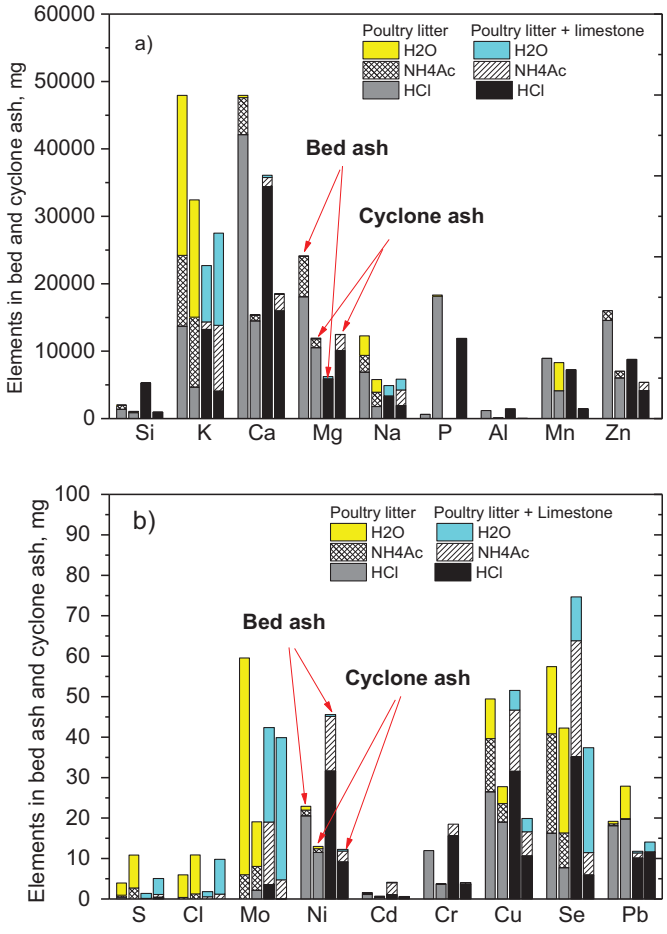

Fig. 2. Comparison of CFA of bed and cyclone ash for gasification at 700 °C without (feeding rate 0.66 kg/h) and with limestone (feeding rate 0.53 kg/h): a) major elements, b) minor elements. To each element in the figure, four columns are assigned, of which columns 1 and 3 correspond to bed ash while 2 and 4 to cyclone ash.

water leached portion of K and Na can be associated either with unconverted organic matter or alkali condensed with the small char/ash particles. It was clear that more Cl and S were bound in the cyclone ash than in the bed ash. Over 90% of Cl and 80% of S was water leached from the cyclone ash.

Minor elements like Ni, Cr, Cu, Cd, and Se were mainly retained in the bed ash. The amount of Pb in the cyclone ash was slightly higher compared to that in the bed ash. Mo was distributed equally between the

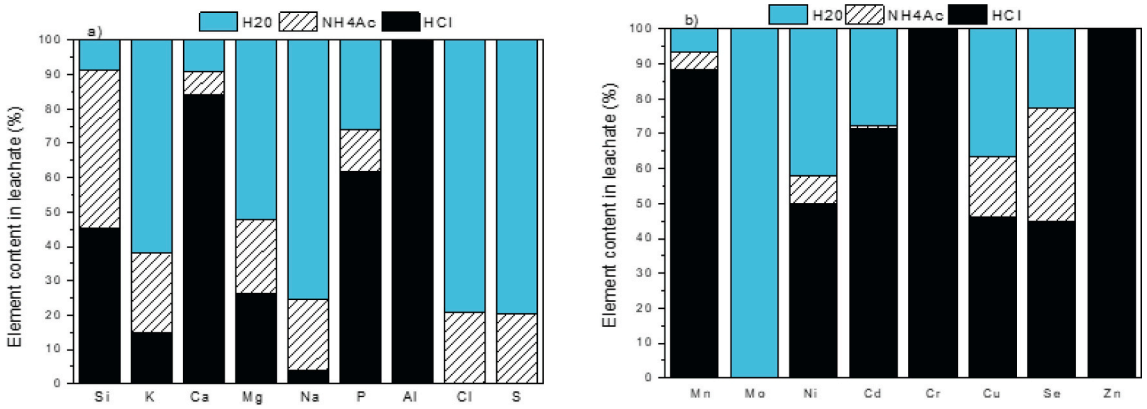

Fig. 1. Chemical fractionation of poultry litter: a) major elements, b) minor elements.

cyclone and the bed ash when poultry litter was gasified with limestone whereas it was much higher in the bed compared to the cyclone ash for gasification of poultry litter on its own. The fraction of water-soluble Se and Pb was much higher in the cyclone ash compared to the bed ash, which may indicate condensation of Se and Pb containing compounds on the cyclone ash particles. The very high volatility of Se and Pb under gasification conditions and condensation of Se and Pb containing species during the cooling stage have been reported [66].

The overall retention of elements in the bed ash and the cyclone ash are comparable to the results obtained for fluidised bed combustion of poultry litter [67] except for Pb where in contrast to combustion, a higher quantity was observed for gasification cyclone ash relative to bed ash. A similar partitioning of Pb was reported from fluidised bed thermal treatment of municipal solid waste in a reducing atmosphere but the exact opposite partitioning was seen for Ni, Cu and Cr [41].

Results from the CFA of cyclone ash obtained at different gasification temperatures and ER are presented in Fig. 3 and in the supplementary material Figs. S-1 and S-2. No obvious trend was seen for the distribution of elements between water, NH_4Ac and HCl within cyclone ashes for gasification between 700 and 800 °C, except transformation into stable compounds. After gasification most of Mg (74–93%) was transformed into stable compounds while the remaining Mg was organically bound. A portion of Ca was also transformed into stable compounds which resulted in an increase in the HCl leached fraction from 84% in poultry litter to 92% in cyclone ash. A similar trend was observed for P, virtually all P in cyclone ash was HCl leached. These findings are in line with

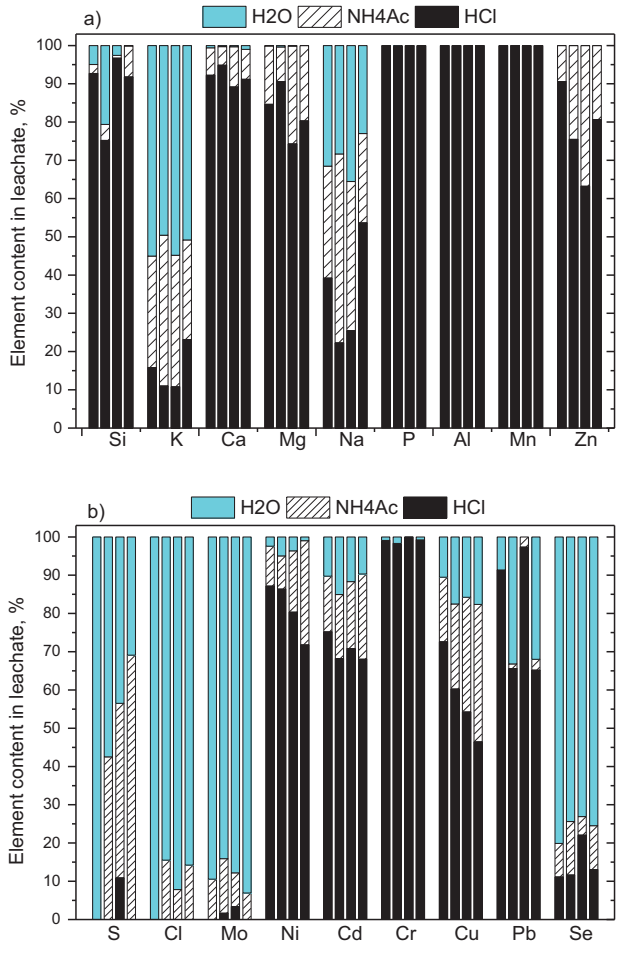

Fig. 3. Chemical fractionation of the ash-forming matter in cyclone ash air gasification with limestone addition, each bar represents a different process conditions starting from the left: (700, ER = 0.29), (750, ER = 0.28), (750, ER = 0.33), (800, ER = 0.25–30); a) major elements, b) minor elements.

observations for sewage sludge by Qian et al. [68], who reported that high temperature (>700 °C) thermal treatment promotes the formation of stable, insoluble Ca, Mg − P compounds while the proportion of water soluble and organic P decreases [65]. On the other hand for K, 48–56% remained water leachable after the gasification with 30–39% comprising of organically bound K within the residual char/carbon matrix which is in agreement with observations by Jensen et al. [69] for char from straw pyrolysis. Na exhibited similar behaviour. The amount of Na in the cyclone ash was about half that of K (Table 3), of which 25–41% was water leached and 29–49% ammonium acetate leached. Regarding Cl, the water leached fraction of 85–92% represented an increase over the original poultry litter while the NH_4Ac leached component of 8–15% was lower. The opposite trend was observed for S, the water leached fraction of 30–57% was lower while the NH_4Ac leached of 42–69% was higher than in original poultry litter. Most of minor elements are mainly HCl leached except Se (77–88%) and Mo (96–100%), and very small quantities of Cu, Pb, Cd and Ni, which were water or NH_4Ac leached. The presence of water-soluble compounds in cyclone ash suggests that although K, Na, Cl, Se, Mo, Pb and Cu are released to the gas phase during gasification and they condensed into the ash fraction.

In general, the results of CFA for the major elements in gasification cyclone ash are comparable to cyclone ash from combustion [47] except for K and Na. In contrast to gasification, much higher fractions of K (40 vs. 13%) and Na (70 vs. 25%) were found as stable compounds (HCl leached). However, in the combustion tests [47], ash was also collected in bag filters, where the fraction of volatile K (water and NH_4Ac leached) was double than that reported in the cyclone and the fractions of stable compounds were comparable to gasification cyclone ash.

A comparison between cyclone ash from gasification of poultry litter with and without limestone addition at 700 °C (Figs. S-1 and S-2 in supplemental material) did not show significant differences for the majority of the major elements, except for Ca, which gave about 20% higher concentration at ER values of 0.29 and 0.35. Regarding the minor elements, the fraction of water leached Se and Mo in cyclone ash, was higher when poultry litter was mixed with limestone.

3.2. X-ray diffraction

The XRD reflections of all cyclone ash samples were similar, indicating heat treatment temperature and ERs had no significant influence on ash morphology during gasification, as reported in Fig. S-3 (in supplementary material). The XRD results showed that cyclone ash samples exhibit reflections from crystalline quartz, calcite, sylvite (KCl), periclase (MgO), oldhamite (CaS), apatite ($Ca_5(PO_4)_3OH$), $KNaCa_2(PO_4)_2$ and whitlockite ($Ca_3(PO_4)_2$), (Figs. S-4-9 in supplementary material). The whitlockite phase was not detected in the cyclone ash from gasification at 750 °C using an ER of 0.33 with limestone addition. Moreover, the XRD analysis of both cyclone ash samples from 700 and 750 °C using ERs of 0.3 and 0.33 without and with limestone addition showed that oldhamite is present in minor amounts. The XRD reflections of the original poultry litter showed the presence of quartz (SiO_2), calcite ($CaCO_3$) and a crystalline pattern corresponding to cellulose [70], as shown in Fig. S-11.

The Rietveld refinement was conducted to quantify the compounds which are present in the cyclone ash sample. The results suggest the formation of a $KNaCa_2(PO_4)_2$ phase in all cyclone ash samples, as reported in Table 4. The wt% values reported in Table 4 represent semi-quantitative ratios of the identified crystalline phases. The results show that the calcite in all cyclone ash samples originates from the poultry litter (Fig. S-11 in supplementary material), as significant amounts of calcite were found in samples from gasification at 700 °C using an ER of 0.3 without limestone addition. This study also shows that the addition of limestone in a gasifier only slightly influences the composition of the cyclone ash from different temperatures and ERs. Not all peaks in the XRD were attributed to identified species. As these peaks

Table 4
Results of Rietveld analysis on XRD data of fly ash samples from gasification at 700, 750 and 800 °C using ERs of 0.3, 0.29, 0.23, 0.28 and 0.33 (quantification in wt%, refined unit cell volume V_{uc} and lattice parameters).

Phase		700 °C	700 °C	750 °C	750 °C	750 °C	800 °C
		0.3	0.29	0.23	0.28	0.33	0.30
		Without limestone	With limestone	With limestone	With limestone	With limestone	With limestone
$Ca_3(PO_4)_2$, whitlockite (trigonal, R3c)	wt%	19	32	40	23	0	38
	V_{uc} (Å^3)	3463.1	3458.7	3457.4	3462.5		3456.9
	a (Å)	10.384	10.380	10.380	10.385		10.379
	c (Å)	37.049	37.064	37.056	37.068		37.057
α-$NaKCa_2(PO_4)_2$ (trigonal, P-3 m1)	wt%	37	10	11	24	26	14
	V_{uc} (Å^3)	187.8	185.8	185.9	187.6	190.3	186.3
	a (Å)	5.441	5.417	5.420	5.437	5.465	5.424
	c (Å)	7.327	7.311	7.308	7.331	7.360	7.314
$Ca_5(PO_4)_3(OH)$, apatite (hexagonal, P63/m)	wt%	13	16	13	17	41	13
	V_{uc} (Å^3)	531.1	532.2	533	532.9	530.4	533.7
	a (Å)	9.430	9.442	9.450	9.450	9.418	9.461
	c (Å)	6.898	6.893	6.892	6.891	6.905	6.885
KCl, sylvite (cubic, Fm-3 m)	wt%	10	12	12	13	11	11
	V_{uc} (Å^3)	249.5	249.3	249.5	249.5	249.7	249.4
	a (Å)	6.295	6.294	6.295	6.295	6.297	6.295
$CaCO_3$, calcite (trigonal, R-3c)	wt%	8	19	13	13	8	16
	V_{uc} (Å^3)	367.5	367.3	367.6	367.3	367.3	367.9
	a (Å)	4.986	4.987	4.989	4.989	4.987	4.991
	c (Å)	17.067	17.05	17.056	17.042	17.054	17.056
SiO_2, quartz (trigonal, P3221 lattice parameters not refined)	wt%	2	4	4	2	0.5	2
	V_{uc} (Å^3)	112.9	112.9	112.9	112.9	112.9	112.9
	a (Å)	4.912	4.912	4.912	4.912	4.912	4.912
	c (Å)	5.404	5.404	5.404	5.404	5.404	5.404
MgO, periclase (cubic, Fm-3 m)	wt%	9	7	8	8	11	6
	V_{uc} (Å^3)	74.96	75.03	75.06	75.08	75.15	75.13
	a (Å)	4.217	4.218	4.218	4.219	4.220	4.220
CaS, oldhamite (cubic, Fm-3 m)	wt%	1.3				2.3	
	V_{uc} (Å^3)	184.9				184.9	
	a (Å)	5.697				5.697	

were very minor it is considered unlikely their identification will show any significant differences between the different cyclone ashes.

The XRD results showed that the calcium-based species such as calcite, oldhamite, apatite and whitlockite were the dominating phases in the temperature range from 700 to 800 °C at all ERs. Calcium, being an important dietary nutrient for the poultry [60], is expected to be present in a crystalline structure in the cyclone ash samples, based on previous reports [71,72].

In general, the XRD results show that the same crystalline compounds (apatite, whitlockite, $KNaCa_2(PO_4)_2$ and periclase) were present in the cyclone ash from gasification and ashes collected down-stream of the fluidised bed combustor [26], with exception of oldhamite (CaS) which was found only in gasification cyclone ash and K_2SO_4 found only in ash samples from combustion. This finding is also in line with observations by Kaknics [42]. A recent study [28] on combustion of chicken litter reported the presence of P in amorphous compounds in addition to crystalline compounds such as whitlockite, apatite and $Ca_9MgK(PO_4)_7$.

3.3. Molecular beam mass spectrometry

The association of inorganic elements in fuels and ashes influence not only their leachability but also their volatility. The release and subsequent condensation and/or reaction of volatile species determine the chemical and mineral composition of residual ashes and it is therefore important to understand the transformation mechanisms of inorganic constituents. To complement the characterisation of the condensed phases, the initial release of gas phase species was investigated by MBMS. It should be noted that these batch-type measurements were not designed to simulate the conditions in a fluidised bed with its intense mixing of all phases, but rather to gain some understanding of the relevant release mechanisms during pyrolysis and early stage gasification. Furthermore, fast reactions between fuel constituents and released species with additives (limestone) and bed material (silica sand) can be qualitatively identified by the experimental setup used as previous investigations reveal [73,74].

3.3.1. Qualitative results of the MBMS measurements

The release of all considered species started immediately after insertion of the sample into the furnace indicated by the drop of the intensity of $^{44}CO_2^{2+}$ (m/z 22), except for the experiments with addition of steam, where a short delay was observed (Figs. S-12 and S-13 in supplementary material). The duration of release is slightly shorter at 800 °C than at 700 °C due to faster kinetics. Sulphur is released as H_2S and COS, as well as SO_2. Due to the short residence time in the flow channel reactor, any SO_2 released is not reduced in the gas phase as would happen in a fluidised bed and therefore is always detected in such release experiments [55]. Furthermore, the gas atmosphere containing CO_2 (and H_2O) used in the present experiments is not sufficiently oxidising to oxidise major parts of H_2S after release. Under equilibrium conditions the concentration of SO_2 would be orders of magnitude lower than that of H_2S. Therefore, the detected SO_2 is considered a primary

release form of sulphur. However, the release of SO_2 is an indication that some sulphatic sulphur is present in poultry litter or formed inside the fuel during pyrolysis, which is reduced to sulphidic sulphur during fluidised bed gasification. Alkalis are released as chlorides $^{74}KCl^+$ and $^{39}K^+$ as fragment of KCl, and hydroxides $^{39}NaO^+$ as a fragment of NaOH. Phosphorous is detected as elemental phosphorous $^{62}P_2^+$ and phosphorous oxide as $^{63}PO_2^+$. It should be noted that due to clustering and fragmentation inside the MBMS the exact same species will not necessarily be detected as calculated. Zn was not released or only in very low amount. Since $^{64}SO^{2+}$ overlaps the main isotope $^{64}Zn^+$, the intensities of the other isotopes at *m/z* 66, 67, and 68 were considered, none of which were significant compared to the background signal.

3.3.2. Semi-quantitative results of the MBMS measurement

The averaged normalised peak area of the species released is depicted in Fig. 4.

The release of sulphur species is much higher in the presence of steam than without steam. The release behaviour of sulphur can be observed during the gasification of coal, and steam injection normally accelerates the release of several species [75]. The same effect is observed for HCl. The additions of silica sand and limestone have no clear effect during the relatively short contact time between released species and additives in the batch-type flow-channel reactor experiments. Due to the high volatility of these species, the effect of temperature is negligible in the narrow temperature range applied. In the case of alkali species, the addition of steam causes a shift from chlorides to hydroxides according to Eq. (1), as can be seen from the low intensity of $^{74}KCl^+$ and the relatively high intensity of $^{39}K^+/NaO^+$, which are likely fragments of the respective hydroxides.

$$\mathrm{AlkCl\ (g) + H_2O\ (g) \rightarrow AlkOH\ (g) + HCl\ (g)\ (with\ Alk = Na, K)} \quad (1)$$

The addition of silica sand causes a slight decrease in alkali release due to the formation of alkali silicates. An increase of gasification temperature from 700 °C to 800 °C causes a slight increase of alkali release due to higher volatility of alkali salts at higher temperatures. There is no obvious trend found for the release of P species. However, the release of both, elemental and oxidic P is relatively low as can be seen from the low signal intensity. Release of P during devolatilisation step of single-particle biomass gasification was observed by other researchers [76].

3.4. Thermodynamic calculations with FactSage

3.4.1. Gasification of poultry litter

Equilibrium calculations were conducted to predict the formation of inorganic phases during the gasification of poultry litter and in the mixture of poultry litter with limestone depending on temperature. The elemental compositions of the corresponding fuels (poultry litter and poultry litter with limestone) presented in Table S-2 were used in thermodynamic equilibrium calculations.

The minor inorganic phases including the slag phase are shown in Fig. 5 with respect to the temperature. The slag represents the oxide melt containing pure oxides and binary and ternary species (e.g. phosphates, silicates). The main phases such as the gas phase and the unreacted carbon (Fig. S-14) were excluded from Fig. 5 to improve the identification of the minor phases. The slag phase was calculated to form at temperatures above 680 °C, while carbon was predicted to be completely converted above 700 °C.

Among the silicates, several phases e.g. nepheline (NEKS), wollastonite (WOLL), garnet (GARN), olivine (OLIV), melilite (MELM) and calcium phosphate-silicate (C2SP) were predicted by the FactSage calculations (Fig. 5). A sulphide phase with formula (Ca, Mg, Mn, Fe)(S) was identified in the calculation of the poultry litter with limestone, in which calcium predominates (marked as CaS(s) in Fig. 5b). Olivine undergoes conversion at 850 °C to C2SP, and both phases mostly comprise of Ca_2SiO_4 with small amounts of other dissolved constituents (Mg, Al).

The calculations also indicated the presence of several P-containing phases. Potassium pyrophosphates ($K_4P_2O_7$) are calculated to predominate at low temperatures for poultry litter (Fig. 5a) while for poultry litter with limestone, the potassium orthophosphates are stable (Fig. 5b). There are two solution phases, K_3PL and K_3PM based on the low and medium temperature modification of K_3PO_4, respectively. The general solution formula $(K_2O)_1(P_2O_5)_1(K_2O,CaO,K_2CaO_2,MgO,$

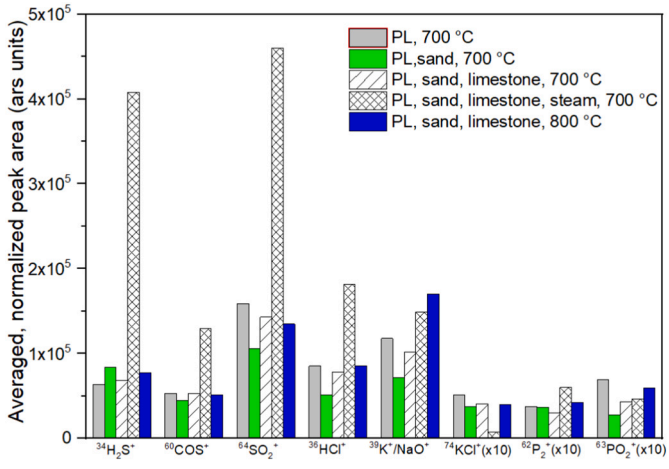

Fig. 4. Averaged, normalised peak area of several species released during gasification of poultry litter using MBMS instrument.

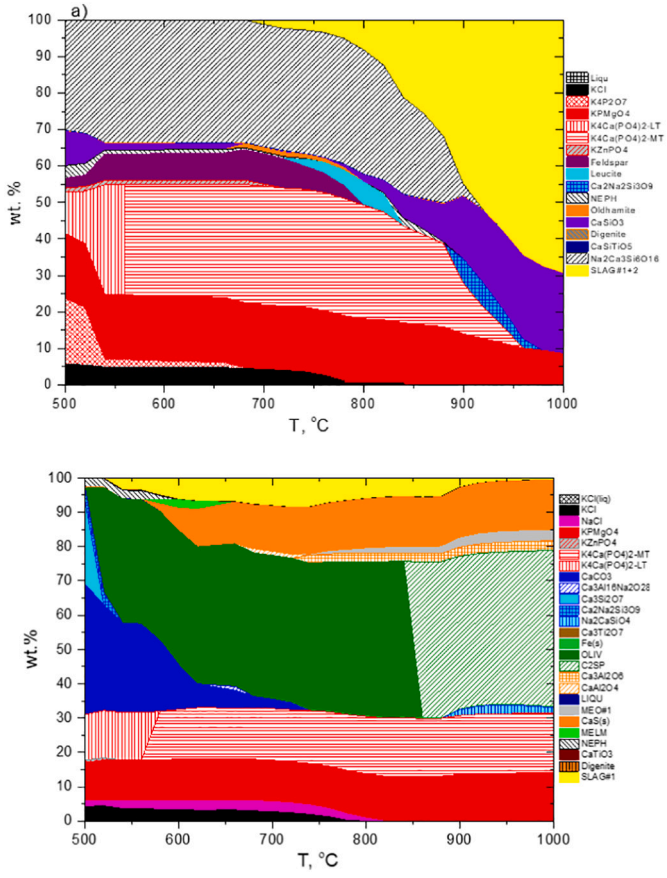

Fig. 5. Output results of FactSage calculations of (a) poultry litter and (b) mixture of poultry litter and limestone: transformation of inorganic condensed phases (stoichiometric compounds, solid solutions and slag) under gasification conditions (ER = 0.3).

$K_2MgO_2)_1$ allows prediction of the solubility between potassium orthophosphate and the mixed phosphate (K, Ca). These phases are named after their most abundant component, $K_4Ca(PO_4)_2$ (Fig. 5). $K_4Ca(PO_4)_2$-LT was calculated to transform to $K_4Ca(PO_4)_2$-MT above 580 °C. The predicted transformation of P was also observed during thermal treatment of sewage sludge [68]. Another P-containing compound is the mixed orthophosphate ($KPMgO_4$), which is calculated to be stable in the whole temperature range considered (Fig. 5). Moreover, calcium carbonate is predicted to be stable at lower temperature for the mixture of poultry litter with limestone in agreement with the presence of excess $CaCO_3$. Fig. 5 (a, b) show other phases (stoichiometric compounds and solutions) present in a poultry litter during gasification in significantly smaller concentrations (leucite, feldspar, $Ca_2Na_2Si_3O_9$, KCl, etc.).

The FactSage calculations presented in Fig. 5 and Fig. S-14, do not distinguish between the bed ash and the cyclone ash.

Lynch et al. [26] carried out thermodynamic calculations (using FactSage v6.1) for combustion of poultry litter in air, the author predicted only hydroxyapatite ($Ca_5(PO_4)_3OH$) and whitlockite ($Ca_3(PO_4)_2$ as P-containing inorganic phases. The discrepancies between these calculations and the present data are explained by non-coincidence of chemical compositions and the process conditions used. Moreover, the properties of the databases used (their completeness and self-consistence) impacts on the results. In the present calculations, the database used [57] was extended in terms of the phosphorous-containing phases [77]. Ternary systems containing alkali and earth-alkali phosphates have recently been included into the GTOx database, while this data set was likely to have been incomplete in the database FToxid used by Lynch.

Equilibrium calculations of poultry litter gasification (Fig. 6a and b) predicted the formation of gaseous KCl, K_2Cl_2, NaCl and Na_2Cl_2 at temperatures above 620 °C, while the formation of KOH, NaOH and elemental K and Na were observed at temperatures higher than 800 °C confirming previous research finding for other biomasses [69,78,79]. The concentration of KOH, NaOH, K and Na were below 0.001 mol% and were excluded from Fig. 6b. Zn(g) was predicted to form at temperatures higher than 950 °C, but its content was below 0.0006 mol%, therefore it was excluded from Fig. 6b. When poultry litter was blended with limestone higher concentration of K_2Cl_2, Na_2Cl_2, KOH, NaOH and elemental K and Na was predicted (Fig. 6d). Zn(g) was predicted to vaporise at temperatures higher than 700 °C.

In general, the current FactSage calculations show that KCl, K_2Cl_2, NaCl were the main gaseous alkali containing compounds in gasification, that is similar to the case of combustion of poultry litter [26]. One significant difference between the two processes was the formation of small quantities of K_2SO_4 in combustion and KOH, K, NaOH and Na in gasification. Similarly, sulphur containing compounds SO_2, SO_3 and K_2SO_4 were predicted for combustion whereas H_2S, COS, and HS are predicted for gasification. The concentration of S_2, H_2S_2, SO and SO_2 as predicted by calculations were below 0.0001 mol% and were excluded from Fig. 6b and further discussion. The concentration of HCl was predicted to decrease during combustion from 600 to 900 °C while in gasification, its concentration was fairly constant within the applied temperature range with or without limestone.

3.4.2. *Partitioning of S, Cl, K, Na and Zn between different phases*

A distribution of S, Cl, K, Na and Zn between the solid, liquid and gas phases from FactSage calculations as a function of temperature is presented in Fig. 7 and Fig. S-15 (in supplementary material). The results show the weight percent of the element input for the calculations. Note, that the calculations do not distinguish between the bed and cyclone ash. For gasification of poultry litter less than 5% of the S was in the solid phase ((Ca, Mn, Fe)(S)) which above 800 °C, was converted into liquid

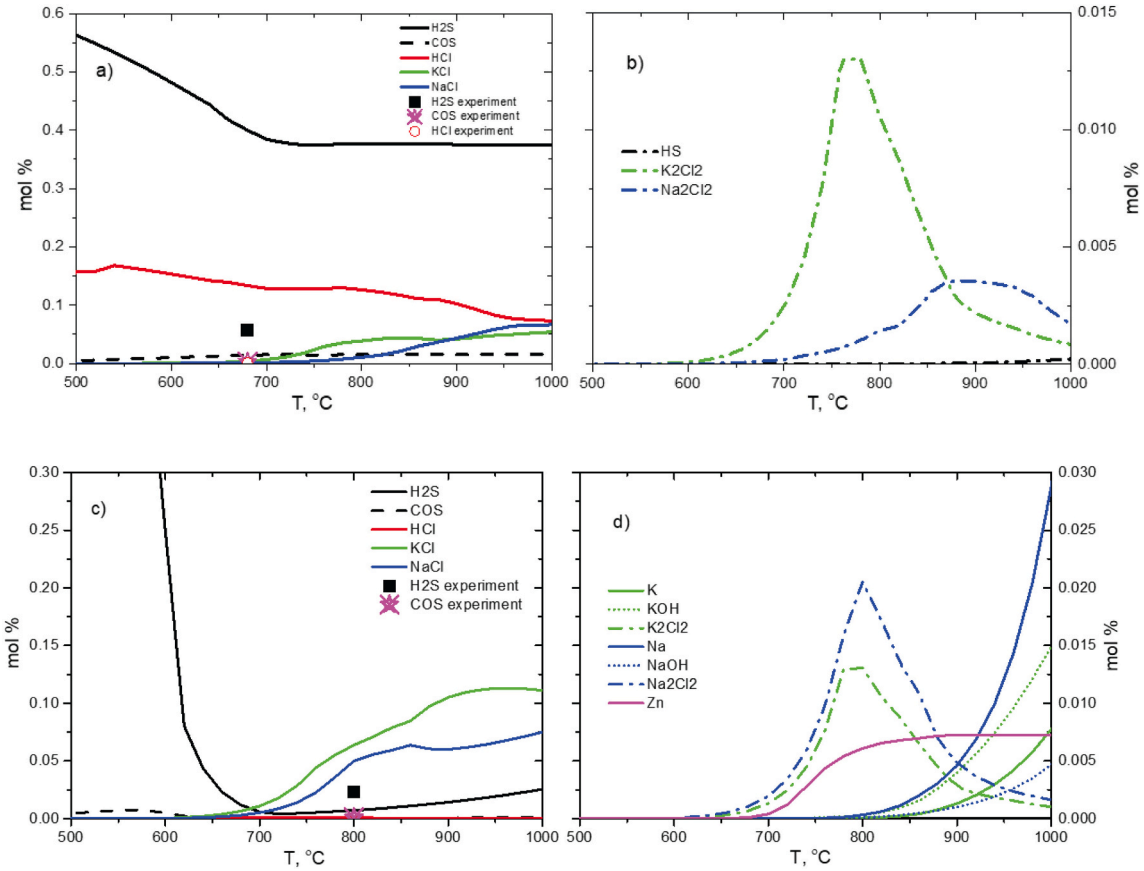

Fig. 6. Output results of FactSage calculation using GTOx database of gasification of (a and b) poultry litter and (c and d) poultry litter with limestone: minor gas species.

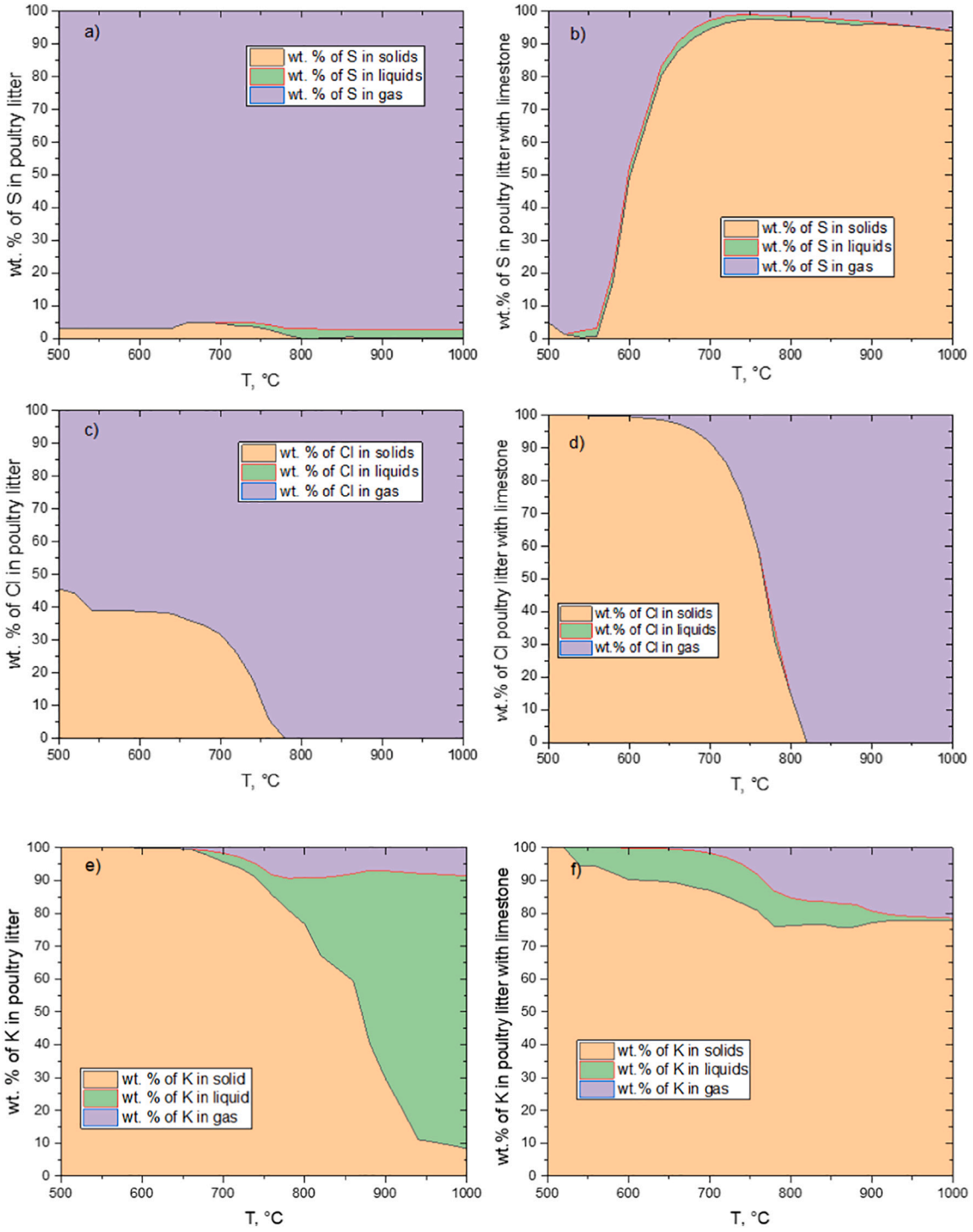

Fig. 7. The calculated distribution of S, Cl and K between solid, liquid and gas phases: poultry litter (a, c and e) and poultry litter with limestone (b, d and f) gasification at ER = 0.3.

phases while sulphur essentially remains in the gas phase. Addition of limestone on the other hand led to the fixation of S in solid phases (Fig. 5b) (CaS(s), digenite) at gasification temperatures >600 °C. Only about 3% of S was calculated to be in the gas phase.

At 700 °C 35% of the Cl was still in the solid phase (alkali chlorides) but it was completely volatilised during the gasification of poultry litter above 770 °C. When poultry litter was mixed with limestone below 700 °C most of the Cl reacted to form solid compounds, (Fig. 5b). At 750 °C around 20% of the Cl was in the gas phase and above 800 °C Cl was completely in the gas phase.

For gasification of poultry litter at 800 °C a majority of the K was predicted to be in the solid phases, mostly $K_4Ca(PO_4)_2$ and $KPMgO_4$ (Fig. 5a), 14% was in liquid phase (Slag) and 9% in the gas phase. Limestone addition reduced the amount of K in the liquid phase (8% at 800 °C) but increased it in the gas (15% at 800 °C). The predicted solid phases containing K were the same as for gasification of poultry litter (Fig. 5b).

The predicted distribution of Na was similar to that of K containing compounds (Fig. S-15 in supplementary material). For gasification of poultry litter at 800 °C a majority of the Na was predicted to be in the

solid phase as $Na_2Ca_3Si_6O_{16}$ (Fig. 5a), 10% in the gas phase and 3% was in liquid phase. For poultry litter with limestone at temperatures above 800 °C Na was predicted to be mainly in the gas (50%) and liquid phase (30%). However, above 900 °C Na_2CaSiO_4 was predicted to precipitate (Fig. 5b).

For the gasification of poultry litter between 700 and 800 °C all Zn was predicted to be in the liquid phase (slag) (Fig. S-15c). For poultry litter with limestone Zn remained mainly in the slag (at temperatures above 700 °C), but the predicted amount in the gas phase increased steadily and reached 74% at 800 °C (Fig. S-15d).

3.4.3. Cyclone ash from gasification of poultry litter

The inorganic phases in the cyclone ash from gasification of poultry litter with limestone were predicted using the equilibrium calculations and compared with the XRD results. The results are presented in Figs. 8 and 9 and in the supplemental material (Figs. S-16 and S-17). The main phases are the mixed alkali-earth-alkali phosphates ($KMgPO_4$, $Na_4Mg(PO_4)_2$), carbonates ($CaCO_3$, $CaNa_2(CO_3)$), silicates (e.g. nepheline, wollastonite, NC2S3). The latest phase is solid solution based on $Na_2Ca_2Si_3O_{12}$. The alkali aluminosilicates were calculated to be more stable than SiO_2 as shown on XRD. The composition of the cyclone ash changed with temperature. The fraction of $Na_4Mg(PO_4)_2$ increased from 2 to 8 wt% while $CaCO_3$ decreased from 16 to 12 wt%, with an increase of gasification temperature from 700 to 800 °C.

Salts (sulphates, hydrophosphates and chlorides) were also considered by calculations, but were not predicted, at least in significant amounts with the exception of NaCl which was predicted at less than 0.01 wt% (Fig. 8). The predicted amount of KCl is lower than that detected by XRD. Comparing the calculations and XRD data shows that the relative amount of $CaCO_3$ measured by XRD (Table 4) for cyclone ash samples obtained at different process conditions corresponds well with FactSage calculations. The largest amount of $CaCO_3$ was calculated for the cyclone ash from gasification of poultry litter with limestone at 700 °C and ER = 0.29 (Fig. 8), in line with the XRD results. The maximal amount of the predicted $CaCO_3$ (Figs. 9, S-16, S-17) correlates with the XRD results with the difference that $CaCO_3$ was predicted to decomposed at 700–800 °C under equilibrium conditions.

The phase composition calculated differs from that detected by XRD. The reason is that we do not have identical conditions during calculations and in the real system; the calculation considers the equilibrium state only; the incompleteness of the database could also be a contributory factor.

3.5. Transformation, release, and fate of inorganic species

Some interesting properties of poultry litter were revealed by CFA;

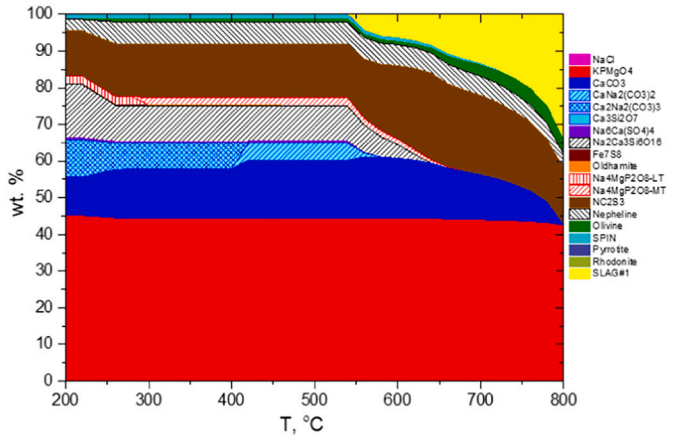

Fig. 8. Output results of FactSage calculation for cyclone ash after gasification of poultry litter with limestone at 700 °C and ER = 0.29.

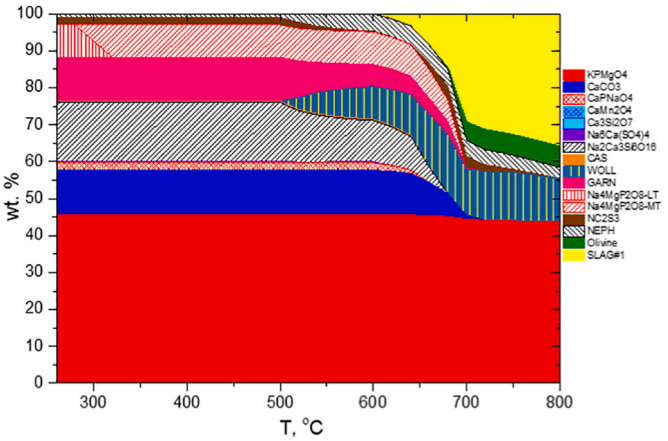

Fig. 9. Output results of FactSage calculation for cyclone ash after gasification of poultry litter with limestone at 800 °C and ER = 0.3.

38 wt% of the major ash forming compounds are present as water-soluble salts, 16 wt% as organically bound ions (NH_4Ac leached) and the remaining 46 wt% as stable compounds (HCl leached). Similar to other thermal treatment processes, e.g. hydrothermal carbonisation [65] and pyrolysis [80], during gasification of poultry litter with or without limestone both the water and NH_4Ac leached portions of the major ash forming elements were transformed into stable HCl leachable compounds. A more detailed discussion about transformation of P and some very volatile elements S, Cl, K, and Na is provided in sections below.

3.5.1. Fate of S in gasification

According to the CFA 80% of S in poultry litter is water soluble and the remainder is organically associated, thus available for volatilisation. The propensity of S for volatilisation was observed in MBMS measurements that showed an immediate release of H_2S, COS and SO_2. FactSage calculations for poultry litter predicted over 95% of S in the gas phase, with H_2S dominating over the whole temperature range (Fig. 6a). The concentration of H_2S measured during fluidised bed gasification experiments (Table 2, Fig. 6a) was lower than predicted by calculations while the amount of COS was in line with experimental values (Fig. 6a). For the gasification of poultry litter with limestone (Fig. 6c) H_2S concentration drops sharply at temperature above 650 °C due to sulfidation of limestone, as reported previously [81,82]. The same trend was observed for COS. Only about 3% of S was predicted to be present as gaseous species at 800 °C (Fig. 7b). The calculated concentrations of H_2S and COS correspond closely with experimental results (Table 2, Fig. 6c). The effect of limestone addition on the release of H_2S and COS was not detected/shown by MBMS (Fig. 4) indicating that longer residence times typical for fluidised bed reactors are necessary for the reaction between sulphur species and limestone. The residues after gasification, irrespective of process condition, contain S in water soluble and organically associated form (Figs. 2a, 3a and S-1 in supplementary material).

3.5.2. Fate of Cl in gasification

Like S, the majority of Cl in poultry litter is water soluble (80%) and the reminder organically bound (20%) and thus available for volatilisation. The susceptibility of Cl for volatilisation was also observed in MBMS measurements that showed an immediate release of HCl and KCl. FactSage calculations for poultry litter predicted 55% release of Cl at temperature below 500 °C, and complete volatilisation above 750 °C (Fig. 7c). HCl is the dominant chlorine species over the entire temperature range (Fig. 6c) but its . concentration measured during gasification experiments (Table 2) was lower than that predicted by FactSage calculations. Other Cl containing species predicted to form were alkali chlorides. For the gasification of poultry litter with limestone complete

volatilisation of Cl above 800 °C was predicted, however the calculated concentration of HCl was an order of magnitude lower but alkali chlorides were higher than when gasifying poultry litter alone (Fig. 6c and d). The effect of limestone on the release of HCl was not detected by MBMS measurements.

More of Cl was retained in the cyclone than in bed ash, mostly as water soluble compounds as confirmed by CFA (Figs. 3b and S-2 in supplementary material), XRD (Table 4) and calculations (Figs. 5a and b, Figs. 8 and 9). A Similar observation regarding Cl release was reported by Björkman and Strömberg while pyrolysing and gasifying biomass at 200–900 °C [83].

3.5.3. Fate of K and Na in gasification

K, as the most abundant alkali metal in poultry litter (Table 3), is mainly present in water soluble (60%) and organically bound form (20%). MBMS measurements showed an immediate but relatively low release of KCl indicated by low signal intensity. Generally, Cl is known for its carrier function for the release of K [84,85]. The K release is also influenced by Al and Si which are known for their alkali metal sorption properties [86–88]. A low molar ratio of Al/Si of 0.07 for poultry litter indicate low alkali metal sorption capability and high release of K. According to calculations for poultry litter the release of K started at gasification temperatures higher than 620 °C and at 800 °C 9% of K was in the gas phase (Fig. 7e). KCl and K_2Cl_2 were the main species predicted to form (Fig. 6a and b). When poultry litter was mixed with limestone more K was predicted to be released in the gaseous phase; at 800 °C 15% of K (Fig. 7f). The concentrations of KCl and K_2Cl_2 were higher compared to poultry litter (Fig. 6c and d). In the residues after gasification, irrespective of process conditions, a significant fraction of K remained organically bound but the water soluble fraction (50%) dominates (Figs. 2a, 3a and S-1 in supplementary material), mostly as KCl whose presence was confirmed by XRD (Table 4) and calculations (Fig. 5a and b). The predicted release of K is in a good agreement, with observations by Hedayati et al. [76] who reported 4–17% release of K at 800 °C for gasification of agricultural residues. Moreover, main release of K was observed at the char conversion stage.

Like K, Na in poultry litter is mainly present in water soluble (75%) and organically bound forms (20%) (Fig. 1). An immediate release of NaOH was measured by MBMS. FactSage predicted the release of Na at gasification temperature higher than 620 °C and at 800 °C 10% of Na was in the gas phase (Fig. S-15 in supplementary material). NaCl and Na_2Cl_2 were the main species predicted to be formed (Fig. 6a and b). When poultry litter was mixed with limestone 30% of Na was predicted to be released in the gaseous phase; at 800 °C (Fig. S-15). In both, the bed and cyclone ash (Figs. 2a and 3a), as a result of re-condensation on char particles the water-soluble fraction of Na was at 30%.

3.5.4. Fate of P in gasification

According to CFA results all reactive forms of P in poultry litter (26% as water-soluble compounds 14% as organically associated ions, (Fig. 1a)) were transformed during gasification into stable compounds (only 1–2% is water leached in cyclone and bed ash) (Figs. 2a, 3a and S-1 in supplementary material). MBMS measurements showed elemental phosphorus and phosphorus oxide (Fig. 4), released as a result of decomposition of organic matter as intermediates which may be taking part in reactions to finally form stable solid compounds. Since the measured intensity of the phosphorus species is low, these reactions seem to be relatively fast. Single step FactSage calculations did not predict the formation of any stable P containing gaseous compounds. The relatively small release of P is in good agreement with the release observed during gasification of agricultural residues, mainly at the devolatilisation stage [76].

From the mass balance calculation, it is evident that the distribution of P between the bed and cyclone ash depends on gasification temperature. At 700 and 750 °C more P was retained in the cyclone ash than in the bed ash, 70 and 84% of total P, respectively. The yield of cyclone ash was similar at both temperatures (5.8 and 6.0 wt% of feedstock used in the tests). The lowest amount of P in cyclone ash was observed at 800 °C, 42% of the total P fed into the gasifier. At these process conditions the yield of cyclone ash was also the lowest (0.8 wt%) while the yield of bed ash the highest (14.5 wt%). A possible explanation for this observation is that, for gasification of poultry litter with limestone, there is an excess of Ca in the reactor and the P species released during the devolatilisation at temperature of 800 °C react rapidly with available Ca to form stable Ca-P compounds, which are than mostly retained in the bed ash.

Apatite ($Ca_5(PO_4)_3OH$), $KNaCa_2(PO_4)_2$ and whitlockite ($Ca_3(PO_4)_2$) were the crystalline compounds in the cyclone ash as detected by XRD (Table 4, Figs. S-3 to S-9). For comparison at similar gasification conditions, the mixed alkali-alkaline earth phosphates ($KMgPO_4$, $K_4Ca(PO)_4$ and $K_4P_2O_7$) were calculated under equilibrium conditions (XRD vs calculations: poultry litter Table 4, column 3 and Fig. 5a; poultry litter with limestone Table 4, column 8 and Fig. 5b). Calcium was found to be integrated in the condensed phases as silicates, carbonates, sulphide, and phosphates. The complex orthophosphate, $KNaCa_2(PO_4)_2$) found by XRD, was not predicted by calculations, because it was not included in the thermodynamic database. It should be noted, that it is most likely that amorphous phases containing P are present in the cyclone ash, as was observed for combustion ash [28]. The presence of amorphous $KMgPO_4$ was also reported for gasification of agricultural residues [76]. In the thermodynamic calculations only crystalline phases can be predicted. However, according to the model used for the thermodynamic description of the melt phase, the predicted slag consists of various components (silicates, oxides, phosphates, etc.). Assuming that the slag phase can be considered as an amorphous phase, the predominant species can be determined. Thus, $K_4P_2O_7$, $KMgPO_4$, $KZnPO_4$ were found as main P-containing species in the slag phase by calculations.

3.6. Utilisation of ashes

According to the technical report for new fertilising materials under the Fertilising Products Regulation (2019/1009) [44], EU fertilising products may contain materials obtained through the thermochemical conversion under oxygen-limiting conditions (e.g. gasification). The cyclone and bed ash from the gasification of poultry litter could be categorised as a component material for EU fertiliser products provided, they meet certain criteria. The cyclone ash under investigation meets two of these criteria, the molar ratio of H/C content (assuming that all C content in poultry litter is organic) <0.7 and a Cl content $<3\%$ (Table 1). However, the Cr, Mo, and Se content in the cyclone ash (in the range from 252 to 426 mg/kg, 117–276 mg/kg and 1762–2855 mg/kg on a dry matter basis, respectively) exceeds the specified limits of selected metals and metalloids as proposed in STRUBIAS (243 mg/kg, 52 mg/kg and 108 mg/kg, respectively). When poultry litter is gasified with limestone the molar ratio of H/C for bed ash is above 0.7 (Table 1). Therefore, the bed ash from gasification of poultry litter with limestone cannot be considered as a component material for fertiliser [44].

Although the content of total P in cyclone ashes is between 76 and 96 g/kg, the water soluble P accounts for only for 0.1–2% of the total P and does not meet threshold for STRUBIAS product function category materials which requires a minimum of 25% water soluble P [44]. The XRD results for the cyclone ash samples exhibits reflection from crystalline apatite, whitlockite and $KNaCa_2(PO_4)_2$. Apatite is largely unavailable to plants in the short time span relevant for annual crops [89]. Whitlockite has previously been investigated and showed promising results in plant growth experiments [90]. Therefore, further research is required to investigate whether P in cyclone ash from poultry litter gasification is plant available or rather more suitable for P extraction.

4. Conclusion

The fluidised bed gasification of poultry litter (operated at 700, 750, 800 °C and ERs in the range of 0.22–0.3) facilitated the transformation

of water-soluble and organically associated portion of the inorganic matter containing ash forming elements into HCl leached compounds. Regarding the transformation of P, K, Na, S and Cl, the elements of the main interest in this study, following conclusions are drawn:

- P in cyclone and bed ash was present as HCl leached phosphates, irrespective of process conditions. However, the distribution of P between the cyclone and bed ash seems to be affected by gasification temperature. The experiments suggest that limestone addition impacts the composition of cyclone ash less than the temperature. Apatite ($Ca_5(PO_4)_3OH$), $KNaCa_2(PO_4)_2$ and whitlockite ($Ca_3(PO_4)_2$) were the crystalline compounds in cyclone ash as detected by XRD.
- K in cyclone and bed ash was present mainly in water-soluble form (48–56%) but also as organically associated (30–39%) within the residual char/carbon matrix for all process conditions. At gasification temperature of 800 °C 9% and 15% of K was predicted to be released as stable gas species for poultry litter and poultry litter with limestone, respectively.
- Na in cyclone and bed ash was more or less evenly distributed between the HCl leached, organically associated and water-soluble forms. According to predictions by the thermodynamic calculations at 800 °C 10% and 50% of Na is released as stable gas species for gasification of poultry litter, and poultry litter with limestone, respectively.
- There was more S present in cyclone ash than in bed ash with 30–60% as water-soluble and 40–70% as organically associated S.
- Cl was recaptured on cyclone and bed ash particles mainly as water-soluble compounds for all process conditions.

While it has been found that the cyclone and bed ash from gasification of poultry litter do not meet the requirements for component materials for fertiliser products as set out in STRUBIAS report, there is nevertheless the potential that mixing poultry litter ash with other feedstock to provide a cost-efficient solution or recycled fertiliser components. Therefore, further research is required to investigate whether P in cyclone ash from poultry litter gasification is plant available or rather more suitable for P extraction.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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