COATING AND MELT INDUCED AGGLOMERATION IN A POULTRY LITTER FIRED FLUIDIZED BED COMBUSTOR

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ABSTRACT

The combustion of poultry litter, which is rich in phosphorus, in a fluidized bed combustor (FBC) is associated with agglomeration problems, which can lead to bed defluidization and consequent shutdown of the installation. Whereas earlier research indicated coating induced agglomeration as the dominant mechanism for bed material agglomeration, it is shown experimentally in this paper that both coating and melt induced agglomeration occur. Coating induced agglomeration mainly takes place at the walls of the FBC, in the freeboard above the fluidized bed, where at the prevailing temperature the bed particles are partially molten and hence agglomerate. In the ash, P_2O_5 forms together with CaO thermodynamically stable $Ca_3(PO_4)_2$, thus reducing the amount of calcium silicates in the ash. This results in K/Ca silicate mixtures with lower melting points. On the other hand, in-bed agglomeration is caused by thermodynamically unstable, low melting HPO_4^{2-} and $H_2PO_4^-$ salts present in the fuel. In the

23 hot FBC these salts may melt, may cause bed particles to stick together and may subsequently
24 react with Ca salts from the bed ash, forming a solid bridge of the stable $\text{Ca}_3(\text{PO}_4)_2$ between
25 multiple particles.

26 **KEYWORDS**

27 Fluidized bed combustion; Agglomeration; Poultry litter; Thermodynamic; Coating induced;
28 Melt induced

29

30 **HIGHLIGHTS**

- 31 • Coating induced agglomeration not due to K phosphates, but due to K silicates
- 32 • Melt induced agglomeration due to H_2PO_4^- and HPO_4^{2-} salts in the fuel
- 33 • Wall agglomeration corresponds to coating induced mechanism
- 34 • In-bed agglomeration corresponds to melt induced mechanism

35

1. INTRODUCTION

Intensive livestock breeding is in many regions responsible for the imbalance between supply and demand for fertilizers in agriculture. The excessive supply of e.g. cattle manure, applied to agricultural land, may lead to nutrient saturation and eutrophication problems. This over-application of manure is counteracted by e.g. the EU Nitrates Directive [1] and other national or international legislation.

Legislation limiting the use of animal manure for land fertilization urges the development of alternative treatment options, such as recycling into animal feed, biogas production, composting and combustion [2,3]. As there is a growing demand for sustainable energy production, energetic valorization of manure is becoming more and more subject to research [4-6], and is already applied in full scale installations. The low moisture content in combination with the high organic carbon concentration of e.g. poultry litter results in relatively high heating values, which allows this biomass to be combusted in a fluidized bed combustor [7].

The fluidized bed combustor (FBC) of BMC Moerdijk in the Netherlands is one of the first power plants fired with poultry litter, a combination of poultry manure and bedding material of the sheds. The produced ash (bottom ash, boiler ash and air pollution control residue combined) is rich in P, K and Ca. It is exported to be processed into inorganic soil amendment.

The high concentration of P and K in the ash increases however the risk for bed particle agglomeration, which leads to defluidization resulting in unforeseen shutdown of the installation. Hence, the availability of the installation of BMC Moerdijk is somewhat limited (75 % to 93 % for the period 2009-2012), compared to the availability of for instance a coal fired power plant. Given the temperature of the fluidized bed (750 °C to 765 °C),

agglomeration problems might be attributed to the melting of alkali silicates [4,8,9] and of alkali and alkaline earth phosphates [10-12].

In earlier research on agglomeration during combustion and gasification of biomass, Visser et al. [13] introduced the concepts of “coating induced agglomeration” (where a coating layer deposits on the bed particles that may partially melt and cause agglomeration) and “melt induced agglomeration” (i.e. agglomeration of bed particles caused by liquid bridges of molten ash particles), based on the composition of inter-particle regions of agglomerated samples. However, to our knowledge, all subsequent research was based on the concept of coating induced agglomeration, as attempts were made to explain agglomeration by the equilibrium phase composition of the bed material (mostly sand particles coated with ash) and resulting melt phase [4,8,14,15]. Brus et al. [16] explicitly called coating induced agglomeration the dominant agglomeration mechanism.

Melt induced agglomeration therefore rather appeared a concept, than experimentally evidenced. In our research on agglomeration at the FBC installation of BMC Moerdijk, we observed experimentally that two mechanisms can clearly be distinguished when poultry litter is combusted. In both mechanisms melt formation is responsible for agglomeration, though coating induced agglomeration results from the melting of thermodynamically stable compounds in the bed ash, i.e. the bed material (silica sand) coated with fuel ash, after thermodynamic equilibrium was reached. On the other hand, melt-induced agglomeration is caused by low-melting salts present in the fuel that melt, form a liquid bridge between bed ash particles, and only then react with the ash particles to achieve thermodynamic equilibrium. In that case, the agglomeration occurs before thermodynamic equilibrium is reached.

In this paper, both coating and melt induced agglomeration in the poultry litter fired FBC of BMC Moerdijk are discussed. Thermodynamic calculations were performed to estimate the

speciation of the four main ash forming elements, Ca, K, P and Si. Phase diagrams were then used to detect species that may cause coating induced agglomeration. Melt induced agglomeration is observed based on the composition of the poultry litter, containing low melting salts, forming a liquid bridge between bed ash particles, and only then reacting to reach the thermodynamic equilibrium composition of the bed ash.

2. MATERIALS AND METHODS

2.1 Installation

The installation of BMC Moerdijk (the Netherlands), with a capacity of 37 MW of electricity, includes a bubbling fluidized bed combustor (BFBC), followed by an energy recovery section and a flue gas cleaning section. The installation processes 1200 t/d of wet poultry litter, transported from approximately 600 poultry farmers all over the Netherlands [17], producing approximately 165 t/d of ash, of which 66.3 t/d is bed ash. The ash, rich in K and P, is used as a resource for the production of inorganic fertilizer. 23.3 t/d of silica sand (approx. 80% between 0.55 mm and 0.90 mm) is continuously injected into the FBC as fresh bed material. The bed ash (i.e. silica sand coated with poultry litter ash) is not recirculated, but continuously extracted at a low rate at the bottom of the bed via extraction hoppers and a conveyor screw.

The BFBC operates at a bed temperature of 750 °C to 765 °C, with an average pressure drop over the bed of 13 kPa. Above the bed, in the freeboard, secondary air is injected and the temperature may exceed 1 000 °C. In the installation, both in-bed agglomeration, and severe agglomeration to the wall in the freeboard occur occasionally. When the wall agglomerates have grown significantly, they may fall into the fluidized bed, disturbing the fluidization and potentially causing complete defluidization.

2.2 Elemental analysis

105 bed ash samples (i.e. sand particles coated with ash, sampled at the conveyor screw below the extraction hoppers at regular times over a period of approximately 24 months) and 53 agglomerates (sampled after a shutdown) from the FBC of BMC Moerdijk were analyzed. The samples were each dissolved in aqua regia. K, Na and Mg were analyzed using atomic absorption spectrometry, according to NEN 7436; the P concentration was determined according to NEN 7435; Ca was analyzed with ICP-MS. The chloride and sulfate content of the samples were determined spectrophotometrically according to NEN-EN-ISO 15682 and NEN-ISO 22743, respectively. Because the analyses were mainly performed for process control reasons, chloride, sulfate and Na were not analyzed in all of the samples.

Si was not analyzed, but it can be estimated from literature and operational data. Most of the Si in the bed ash comes from the added silica sand. From the 66.3 t/d of bottom ash that is produced in the FBC of BMC, 23.3 t/d was added as silica sand bed material. As discussed by Billen et al. [8], it is not straightforward to determine which fraction of the SiO_2 in the bed ash effectively takes part in the reactions. Moreover, it is reported earlier that the mass fraction of SiO_2 in the poultry litter ash itself (laboratory ashed fuel, without silica sand bed particles) is very low, only 2.8 % [18]. Based on the amount of silica sand added to the bed as fresh bed material, the mass fraction of SiO_2 in the bed ash is estimated at 35 %.

2.3 Equilibrium calculations

Thermodynamic equilibrium calculations were performed using FactSage [19] in order to estimate the speciation of the four major ash forming elements, Ca, K, P and Si.

Thermodynamic data for several compounds were used from Sandström and Boström [20] ($\text{K}_4\text{P}_2\text{O}_7$), Sandström et al. [21] (KPO_3 , K_3PO_4), Sandström et al. [22] ($\text{Ca}(\text{PO}_3)_2$, $\text{Ca}_2\text{P}_2\text{O}_7$, $\text{Ca}_3(\text{PO}_4)_2$), Allendorf and Spear [23] (K_2O , K_2SiO_3 , $\text{K}_2\text{Si}_2\text{O}_5$, $\text{K}_2\text{Si}_4\text{O}_9$), Holland and Powell

130 [24] (SiO_2 , CaSiO_3 , $\text{Ca}_3\text{Si}_2\text{O}_7$, Ca_2SiO_4), Haas et al. [25] (CaO) and Jung and Hudon [26]
131 (P_2O_5).

132 When the speciation of Ca, K, P and Si in the bed ash or agglomerates is known, the
133 composition can be plotted in the relevant phase diagrams, in this case of the $\text{CaO-K}_2\text{O-P}_2\text{O}_5$
134 and $\text{CaO-K}_2\text{O-SiO}_2$ systems. As explained by Billen et al. [8], not the total oxide
135 concentrations should be plotted, but e.g. for the $\text{CaO-K}_2\text{O-SiO}_2$ system only the fraction of
136 the oxides that has not reacted to phosphates. For the $\text{CaO-K}_2\text{O-P}_2\text{O}_5$ system only the fraction
137 of the oxides that has not reacted to silicates should be taken into account. Indeed, Ca that has
138 already reacted to e.g. $\text{Ca}_3(\text{PO}_4)_2$, can no longer contribute to formation of stable Ca silicates
139 (that increase the melting point of the K/Ca silicate mixture) and this fraction should therefore
140 be omitted from the $\text{CaO-K}_2\text{O-SiO}_2$ phase diagram. The phase diagram of $\text{CaO-K}_2\text{O-SiO}_2$ is
141 shown in Figure 1, with an indication of the areas with solidus temperatures lower than 1 000
142 °C (temperature in the freeboard of the FBC of BMC Moerdijk) and lower than 800 °C (bed
143 temperature of the FBC of BMC Moerdijk), respectively. It appears from this phase diagram
144 that ash rich in K silicates has low melting temperatures.

145

146 Figure 1 – Ternary phase diagram of CaO-K₂O-SiO₂, with an indication of the areas with
 147 solidus temperatures lower than 1 000 °C (solid lines) and lower than 800 °C (dashed lines).
 148 Adopted from [27].

149 In Section 3.1 will be shown that, analogously to other biomass types [8], in poultry litter ash
 150 no K phosphates are formed, only Ca phosphates. Therefore the phase diagram of CaO-K₂O-
 151 P₂O₅ is not shown here.

152 2.4 Agglomeration experiments

153 In order to experimentally evaluate the effect on agglomeration of an increase in
 154 concentration of each of the four main ash forming elements separately, experiments were
 155 performed in a muffle furnace. 0 g, 0.2 g, 0.4 g, 0.6 g, 0.8 g or 1 g of CaO, K₂O, P₂O₅ or SiO₂
 156 was added to 5 g of non-agglomerated bed ash sampled at the FBC of BMC Moerdijk. The
 157 non-agglomerated bed ash was first crushed and mixed in order to obtain a homogeneous
 158 powder. CaO and SiO₂ were added in oxide form, K₂O was added as K₂CO₃ and P₂O₅ was

159 added as $\text{NH}_4\text{H}_2\text{PO}_4$. Preliminary gravimetric analysis showed that K_2CO_3 decomposes in
 160 K_2O and CO_2 , and $\text{NH}_4\text{H}_2\text{PO}_4$ decomposes in NH_3 , H_2O and P_2O_5 , after heating together with
 161 bed ash at minimum 650 °C. Amounts of $\text{NH}_4\text{H}_2\text{PO}_4$ and K_2CO_3 corresponding to 0 g, 0.2 g,
 162 0.4 g, 0.6 g, 0.8 g or 1 g of K_2O and P_2O_5 were added.

163 The mixtures were placed in a porcelain crucible and heated for 1 h in a muffle furnace at 650
 164 °C to 950 °C ($\Delta = 50$ °C). To simulate only the addition of P_2O_5 and to exclude the possible
 165 agglomeration effects of $\text{NH}_4\text{H}_2\text{PO}_4$, the mixtures to which this compound was added were
 166 re-grinded after heating and reheated for 1 h. After cooling of the mixtures, the level of
 167 agglomeration was determined based on the force that had to be applied to break the
 168 “agglomerates”, as was done by e.g. Öhman et al. [28] and Lindström et al. [29]. The
 169 agglomeration levels are here adapted to the characteristics of the bed ash from poultry litter
 170 combustion. The applied forces and bending moment are estimated semi-quantitatively, by
 171 measuring the force applied during manual testing.

172 Level 0 – no adhesion of particles

173 Level 1 – powder-like adhesion of particles, undone by shaking of the crucible that contains
 174 the mixture

175 Level 2 – agglomerates, broken by compressive force of at most ca. 10 N

176 Level 3 – agglomerates, broken by compressive force between ca. 10 N and ca. 100 N

177 Level 4 – agglomerates, non-breakable by compressive force (at most ca. 100 N), but broken
 178 by application of a bending moment

179 Level 5 – agglomerates, non-breakable by bending moment of at most ca. 1 N·m

180 The effect of $\text{NH}_4\text{H}_2\text{PO}_4$ on agglomeration was also investigated, as was the effect of similar
 181 phosphate salts such as KH_2PO_4 and NaH_2PO_4 . 1 g of each of these salts was added to 5 g of
 182 bed ash. The resulting mixture was heated at several temperatures above 650 °C.

3. RESULTS

3.1 Composition of bed ash and agglomerates

The average concentration of the main ash forming elements (except Si) in normal bed ash and in agglomerated ash (sampled during a shutdown) is shown in Figure 2. The error bars represent the standard deviation of the samples. Examples of agglomerate samples are shown in Figure 6a and 6b. Figure 2 confirms that the four main ash elements are Si, the mass fraction of which was estimated at 16 % (corresponding to 35 % of SiO_2 , see Section 2.2), Ca, K and P. As a sufficiently large amount of melt phase must be present to cause agglomeration of bed particles [12], only the effects of these four elements in the ash are discussed here.

It appears from Figure 2 that the P concentration in the agglomerated ash on the average exceeds the P concentration of non-agglomerated bed ash. Also, the average concentration of K is slightly higher in the agglomerates, whereas the average Ca concentration is somewhat lower in the agglomerates, compared to the non-agglomerated bed ash. These results seem to confirm the conclusions of Lindström et al. [29], who claimed that the melt formation in P rich ash can be attributed to low melting alkali, in this case K, phosphates.

198

199 Figure 2 – Concentration of the main ash forming elements in non-agglomerated bed ash and
 200 agglomerated ash. The number of analyzed samples per element is indicated below the
 201 horizontal axis. The error bars represent the standard deviation of the results for the
 202 considered elements in the different samples.

203 Thermodynamic equilibrium calculations were performed, in order to estimate the speciation
 204 of the four main ash forming elements in the investigated samples. These calculations show
 205 that in general Ca phosphates are more stable than Ca silicates and K phosphates, and K
 206 silicates are more stable than K phosphates and Ca silicates. A similar thermodynamic
 207 analysis was performed for other fuel types by Billen et al. [8]. The results allow to plot the
 208 Ca/K silicate and Ca/K phosphate concentrations in the diagrams of the CaO-K₂O-SiO₂ and
 209 CaO-K₂O-P₂O₅ system, respectively.

210 In none of the samples K phosphates were formed at 726.85 °C. In all of the analyzed bed ash
 211 samples, Ca₃(PO₄)₂ was the only phosphate formed according to the calculations. In some of
 212 the agglomerated samples also Ca₂P₂O₇ or Ca(PO₃)₂ was formed. Of these three compounds,

213 $\text{Ca}(\text{PO}_3)_2$ has the lowest melting temperature, i.e. 983 °C [8]. The higher the CaO content of
214 these phosphates, the higher their melting temperature. It seems therefore that only in some
215 cases, where $\text{Ca}(\text{PO}_3)_2$ was formed due to a low Ca concentration, deposition of phosphates
216 molten at the temperature of the freeboard (approximately 1 000 °C), may cause
217 agglomeration to the wall.

218 In Figure 3, a plot of CaO, K_2O and SiO_2 concentrations in the ternary diagram, shows that
219 the composition of agglomerated ash samples differs from that of normal bed ash. In general,
220 the ratio of K silicates to Ca silicates is higher in the agglomerated ash than in the normal bed
221 ash. In general, K silicates are responsible for lower melting points, whereas Ca silicates
222 increase the melting point of the mixture. Many agglomerated ash samples have either a low
223 Ca concentration or a high P concentration, hindering the formation of Ca silicates. The
224 reason why a high P concentration can cause agglomeration is thus not the melting of low
225 melting alkali phosphates [29], but rather the formation of thermodynamically more stable Ca
226 phosphates instead of Ca silicates. This results in the formation of low melting K silicates that
227 melt at typical bed temperatures (800 °C).

Figure 3 – Ternary composition [mass fraction in %] diagram of the silicates of K and Ca, for both normal bed ash and agglomerated ash samples. The solid contour line and dashed contour line delimits the same areas as in Figure 1.

3.2 Coating induced agglomeration

Coating induced agglomeration was observed during a first series of experiments. Coating induced agglomeration, according to Visser et al. [13], is the presence of a partially molten coating layer on bed particles, causing these particles to stick together. It was shown earlier that agglomeration according to this mechanism occurs after reaching chemical equilibrium within the bed particles, taken into account diffusion limitations [9].

Addition of CaO, K₂O, P₂O₅ or SiO₂ changes the composition and hence also the agglomeration level of normal bed ash. When larger amounts of molten phase are present in the ash, more agglomeration is to be expected. The effect separately adding each of the four oxides to the agglomeration level of the ash at different temperatures, is shown in Figure 4.

The addition of CaO generally reduced the agglomeration level of the ash; P_2O_5 and K_2O addition increased the agglomeration level. SiO_2 only slightly increased the agglomeration level. Examples of agglomerated bed ash samples are shown in Figure 6c.

From thermodynamic calculations, similar to those of section 3.1, it was concluded that in the blank bed ash, without additions, P_2O_5 was always present as $Ca_3(PO_4)_2$. As this is assumed the Ca phosphate with the highest Ca/P ratio formed (thermodynamic data for Ca phosphates with more CaO were not found in the literature), the addition of more CaO results in the formation of Ca silicates, e.g. $CaSiO_3$ or Ca_2SiO_4 [8]. K_2O on the other hand, reacts with SiO_2 to form K_2SiO_3 , $K_2Si_2O_5$ or $K_2Si_4O_9$. This is also shown in Figure 5, where the thermodynamically calculated concentration of Ca and K silicates in the blank bed ash sample (without addition of the four oxides) is indicated as point B. The addition of CaO, K_2O , P_2O_5 and SiO_2 to the bed ash causes the composition of the ash to diverge from point B, in the directions given by the points represented by “Ca”, “K”, “P” and “Si”, respectively.

As expected, CaO addition to the bed ash effectively reduces the agglomeration level, because of the formation of Ca silicates, that increase the melting point of the silicate mixture. Both K_2O and P_2O_5 addition increase the agglomeration level of the bed ash. Addition of K_2O increases the concentration of K silicates and hence reduces the melting points of the silicate mixture. The increasing agglomeration level for increasing P_2O_5 concentration can be explained by the reaction of P_2O_5 with Ca silicate, forming $Ca_3(PO_4)_2$. CaO is therefore removed from the CaO- K_2O - SiO_2 system, lowering the melting point of the silicate mixture. This change of the composition as a consequence of P_2O_5 addition is indicated by the letters “P” in Figure 5, and its effect on the melting point of the silicates can be seen in Figure 1. The addition of SiO_2 has a less pronounced effect.

265

266 Figure 4 – Effect of the addition of (salts of) CaO, K₂O, P₂O₅ and SiO₂ on the agglomeration

267 level of normal bed ash at temperatures of 650 °C to 950 °C.

Figure 5 – Change of the composition of the bed ash sample upon addition of CaO, K₂O, P₂O₅ and SiO₂ in the ternary silicate diagram. The increase of the amount of oxide (represented by Ca, K, P, Si) added caused the composition to diverge from the blank sample (B).

3.3 Melt induced agglomeration

During the coating induced agglomeration experiments, P₂O₅ was added as the instable salt NH₄H₂PO₄, which decomposes at high temperatures, releasing NH₃ and H₂O. However, before decomposition, NH₄H₂PO₄ melts and this caused the bed ash particles to stick together following the melt induced mechanism of agglomeration (Section 1) as noticed during the experiments discussed in Section 3.2. The fact that melting and decomposition occur almost simultaneously was confirmed by Abdel-Kader et al. [30].

Poultry litter generally has a pH of 8-9, so when water is vaporized upon heating, phosphate generally precipitates as hydrogen or dihydrogen phosphate salts. Indeed, Toor et al. [31], He

et al. [32] and Sato et al. [33] showed that in poultry litter, phosphorus is mainly present as $\text{Na}_2/\text{K}_2 \text{HPO}_4^{2-}$ or CaHPO_4 . As is the case for $\text{NH}_4\text{H}_2\text{PO}_4$, these phosphate salts melt at very low temperatures, before they decompose with release of H_2O and might thus also cause melt induced agglomeration of bed ash.

Similar to the agglomeration caused by $\text{NH}_4\text{H}_2\text{PO}_4$ addition, also addition of NaH_2PO_4 and KH_2PO_4 to bed ash samples caused the samples to agglomerate severely at elevated temperatures ($> 650^\circ\text{C}$) during heating experiments. Figure 6d shows a picture of bed ash samples to which KH_2PO_4 was added after heating at 650°C for 1 h. The resulting agglomerate is very porous, due to the release of water vapor, and its structure and color are remarkably similar to that of the agglomerates found in the sand bed of the installation (Figure 6b). The agglomeration mechanism can be described based on reactions (1-3). The suffix ‘-BA’ means that CaO or $\text{Ca}_3(\text{PO}_4)_2$ is part of or bound to the bed ash.

Reactions (1-3) show that liquid salts stick to one or multiple bed particles, and can in this way form a liquid bridge. Because the bed ash contains a high amount of CaO , present in a form that is thermodynamically less stable than $\text{Ca}_3(\text{PO}_4)_2$, the molten phosphates can react with this CaO , forming the most stable phosphate, $\text{Ca}_3(\text{PO}_4)_2$. This $\text{Ca}_3(\text{PO}_4)_2$ remains solid at temperatures up to 1500°C , which are not reached in the installation, so the bridge between particles solidifies, resulting in hard agglomerates. Agglomeration of the particles and

305 solidification of the liquid bridges due to chemical reactions occurs very rapidly, explaining
306 the obtained porous agglomerates during the heating experiments (Figure 6d).

307 The mechanism described above indicates why melt induced agglomeration is also called
308 'heterogeneous agglomeration' [9]. Indeed, it is not the melting of the bed particles
309 themselves that causes agglomeration, but rather the melting of a salt present in the fuel ash,
310 before reaching chemical equilibrium at the bed temperature.

311
312 Figure 6 – Samples from the FBC of BMC Moerdijk of (a) a wall agglomerate and (b) an in-
313 bed agglomerate, and samples from the lab experiments with (c) equilibrium agglomeration
314 and (d) non-equilibrium agglomeration. The 1 euro cent coin is shown for scale comparison.

315 4. DISCUSSION

316 As mentioned in section 2.1, for the poultry litter fired in the FBC of BMC Moerdijk, two
317 types of agglomeration can be distinguished: wall agglomeration and in-bed agglomeration.

Wall agglomeration occurs in the freeboard to the inclined wall above the bed (as indicated in Figure 7), designed in such way that the flue gas velocity is decreased and a splash zone, a boundary between the bed particles and the freeboard, is created. Because secondary air is introduced above the fluidized bed, complete burnout of volatilized substances takes place, resulting in temperatures in the freeboard exceeding 1 000 °C. As can be seen from the coating induced agglomeration experiments (Figure 4 and Figure 5), the high temperature of the freeboard causes melt formation in ash with a high P_2O_5 or K_2O concentration. This melt causes particles to stick to the inclined wall, when they fall down due to the reduced flue gas velocity.

Figure 7 – Schematic representation of wall agglomeration and in-bed agglomeration in the FBC of BMC Moerdijk.

A typical wall agglomerate sample from freeboard in the FBC of BMC Moerdijk is shown in Figure 6a. It has a heterogeneous morphology and is composed of layers with varying colors. This indicates the deposition of partially molten ash with different compositions, reflecting the variation in fuel composition. Given this morphology, it is very unlikely that the agglomerate is formed in the fluidized bed. The samples are mostly dense, yet brittle. The morphology of the samples from the coating induced agglomeration experiments (Figure 6c)

is similar to that of the wall agglomerates. This indicates that agglomeration to the wall is caused by coating induced agglomeration, due to a high P concentration in the ash. The high P concentration is responsible for the formation of $\text{Ca}_3(\text{PO}_4)_2$, resulting in lower Ca silicate concentrations and hence silicate mixtures with lower melting points. It is very unlikely that wall agglomeration is caused by the melt induced agglomeration mechanism, as the fuel is introduced in the fluidized bed, and the low melting phosphates (HPO_4^{2-} or H_2PO_4^- salts) are therefore already decomposed before entrained particles reach the freeboard.

From Figure 3 it appears that the samples corresponding to a relatively high Ca concentration, potentially in combination with a low P concentration (resulting in a high Ca silicate concentration), are mainly not agglomerated. This seems contradictory to the findings of Figures 5 and 6. For these sample compositions the solidus temperature is higher than 800 °C, but lower than 1 000 °C, in the CaO-K₂O-SiO₂ ternary phase diagram. The difference between the samples in Figure 3 and the findings from the experiments can be attributed to the fact that addition of K₂O increases the viscosity of Ca silicate glasses, in casu of Ca/K silicate mixtures [34,35]. The resulting highly viscous melt causes agglomeration in stationary conditions (in a muffle furnace, without fluidization), but the higher the viscosity, the lower the agglomeration propensity in a fluidized bed [36,37]. This explains the different agglomeration behavior of non-agglomerated bed ash samples in Figure 3 compared to samples in Figure 5, where compositions in the same region of the CaO-K₂O-SiO₂ phase diagram were agglomerated (samples after K₂O addition).

On the other hand, the morphology of in-bed agglomerate samples (Figure 6b) is similar to the morphology of the samples of melt induced agglomeration experiments (addition of NaH_2PO_4 and KH_2PO_4 , Figure 6d). This effect is especially visible in the colored images. In this case, also an increase of the P concentration enhances the extent of agglomeration, although the cause differs to that of wall agglomeration. Here, as explained in Section 3.3,

mainly CaHPO_4 melts and subsequently reacts with the bed ash. The thermal behavior and effect on melt induced agglomeration are similar for most of the inorganic phosphates present in poultry manure. In contrast to coating induced agglomeration, in the melt induced mechanism a high concentration of Ca in the bed ash does not reduce the extent of agglomeration. This might explain why ash has agglomerated in the FBC of BMC Moerdijk, despite the high concentration of Ca silicates with regard to K silicates (Figure 3).

Experiences from the FBC operators learned that a defluidization mainly occurs when a large agglomerate falls from the wall into the bed, disturbing the air flow from the nozzles, and is therefore caused by the coating induced agglomeration mechanism. Melt induced agglomeration is in general responsible for relatively small agglomerates.

5. CONCLUSIONS

In this paper the occurrence of both coating induced agglomeration and melt induced agglomeration was for the first time experimentally observed for the combustion of poultry litter in an FBC.

Coating induced agglomeration mainly occurs at the wall of the freeboard of the FBC. In contrast to earlier research and despite the high P concentration of poultry litter, low melting alkali phosphates are not the cause of coating induced agglomeration. When the concentration of P is high, with respect to the Ca concentration, the formation of $\text{Ca}_3(\text{PO}_4)_2$ reduces the amount of Ca silicates in the ash, leading to lower melting temperatures of the Ca/K silicate mixture and subsequent agglomeration. Wall agglomeration is therefore attributed to low melting K silicates.

The melt induced mechanism is responsible for in-bed agglomeration in a poultry litter fired FBC. P is mainly present in the poultry litter as inorganic HPO_4^{2-} or H_2PO_4^- salts, which generally have low melting temperatures and a low thermodynamic stability. Introducing the

fuel into the FBC, these HPO_4^{2-} or H_2PO_4^- salts melt and may form liquid bridges between particles. In order to reach thermodynamic equilibrium, $\text{Ca}_3(\text{PO}_4)_2$ is formed after reaction of the HPO_4^{2-} or H_2PO_4^- salts with CaO or Ca salts from the bed ash, resulting in solidification of the inter-particle bridges. It was observed that this melt induced mechanism, resulting in in-bed agglomeration, may occur very fast.

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