Experimental Investigation of Mineral Particle Deposition in the Cement Production Process

Xiaozan Wang, Peter Arendt Jensen, Morten Nedergaard Pedersen, and Hao Wu*

ABSTRACT: This study aims to improve the understanding of the formation and prevention of deposits caused by the introduction of alternative fuels in the cement industry. Experiments were conducted with cement mineral materials in a laboratory-scale entrained flow reactor. To simulate the temperature conditions in a cement calciner, two different deposit probe systems were used: a high probe surface temperature (HPST) deposit system with a probe surface temperature range of 700–1200 °C and a low probe surface temperature (LPST) deposit system with a probe surface temperature range of 500–700 °C. The effects of fed materials (raw meal, hot meal, bypass dust), flue gas temperature (700–1200 °C), deposit probe surface temperature (550–1200 °C), gas velocity (0.9–2.7 m/s), and experimental duration (5–60 min) on the deposit formation rate were investigated. The results revealed that the concentration of KCl in the fed materials has a large influence on deposit formation. In HPST experiments with furnace temperatures ranging from 700 to 1100 °C, the bypass dust has a higher deposition rate than hot and raw meals, due to a large amount of K and Cl (>10 wt %) in the bypass dust, which forms melts and increases the stickiness between impacting particles and deposits. In LPST experiments, the presence of KCl facilitated the deposit formation rate by providing a sticky layer on the deposit probe via condensation, resulting in a higher deposition rate of bypass dust than the raw meal. An increase in gas velocity showed a negative effect on the deposit formation rate due to an increase in rebound. The present study suggests that keeping the calciner wall temperature at 900−1100 °C and a low level of KCl content would effectively reduce the deposit formation, thereby increasing the equipment life and reducing the operating cost during cement production.

1. INTRODUCTION

The cement industry is highly energy-intensive with the global average thermal energy consumption being around 4.2 GJ/ton clinker.1,2 Until recently, most of the energy has been provided by fossil fuel combustion, leading to a high climatic impact. Around 4.1 billion tons of cement was produced in 2020, which contributed to approximately 8% of global CO₂ emissions.3−5 According to a roadmap for CO₂ reduction in the cement sector,6 its direct emissions shall be 24% from the current levels by 2050. Due to the partial CO₂ neutrality and low cost of solid recovered fuel (SRF),7−16 SRF has been increasingly employed in both dedicated-firing and co-firing with fossil fuel in cement kilns and calciners.10−13,14 However, the use of SRF in industrial units has arisen a number of operational issues, as these alternative fuels have different combustion characteristics compared with fossil fuels.12,14,15 The high use of SRF results in the high input of chlorine and alkali metals and increased circulation of chlorine and sulfur amounts, facilitating the formation and growth of mineral particle deposits.16−19

Mineral particle deposition is frequently observed in cement production plants and occurs typically in cyclone preheaters, calciners, and rotary kilns, thereby affecting the production efficiency and stability of operation.20−22 The extent and causes of particle deposition at different locations, on the other hand, differ significantly.23 The buildup forming in preheater cyclones and the cold area of calciner walls (<800 °C) are usually induced by the condensation of inorganic volatile species from the high-temperature flue gas, which provides a sticky film for the formation and growth of mineral particle buildup.17 In the high-temperature areas of the calciner and rotary kiln, ranging from 800 to 1400 °C, the fed mineral particles may melt and stick to the surfaces of the equipment.23 Without regular cleaning, excessive deposition can further accumulate to tens of centimeters in thickness and tons of meters in length,24 leading to equipment erosion, blockage of the flue gas channel, and even unscheduled plant outages.25−27

Several studies have analyzed mature deposits formed in industrial rotary kilns, calciners, and preheaters.28−32 An...
overview of the crystalline phases found in mature deposits formed during cement production and their typical locations are shown in Table 1.

| phases        | formula                                     | location               |
|---------------|---------------------------------------------|------------------------|
| spurrrete     | (2CaO·SiO₂)₂·CaCO₃                         | calciner, lower cyclone, riser, and kiln |
| ellestadite   | Ca₉₀(SiO₄)₃(SO₄)₂Z₂ (where Z = OH, F, Cl) | kiln and riser         |
| sulfo spurrite| (2CaO·SiO₂)₂·CaSO₄                         | kiln cyclone and riser |
| anhydrite     | CaSO₄                                       | kiln, calciner, kiln, and cyclone |
| calcite       | CaCO₃                                       |                        |

Based on the characterization of the deposits from industrial-scale plants, deposit formation, hardening mechanisms, and key parameters influencing deposit formation have been proposed and evaluated. Shi et al. proposed a mechanism describing coating formation, with the support from the characterization of preheater and kiln buildups, showing that the presence of minerals such as KCl, CaSO₄, and 2CaSO₄·K₂SO₄ would act as solid and/or liquid bonds binding raw materials (CaCO₃, and SiO₂) together, which results in the formation of the coating. Eriksson et al. sampled ring deposits from a rotary kiln when the plant was shut down and identified three hardening mechanisms of the deposits, referring to the increased densification of ring deposits, the formation of calcite and spurrrete, and the intrusion of molten fuel ash into the refractory, resulting in a strong attachment of the deposit to the refractory. Belgacem et al. investigated the form and amount of the compounds in different deposit samples from the kiln inlet and proposed that the fluctuating operating temperature and the low calcination degree were the main reasons for the ring formation and growth. Zhou et al. studied the corrosion effect of the deposits rich in alkali salts on the refractory bricks used in the transition zone of a cement rotary kiln. The results showed a constantly changing temperature field and the condensation of alkali salts with a high thermal expansion coefficient led to high thermomechanical stress, subsequently resulting in the structural spalling and deterioration of refractory linings. Furthermore, Pieper et al. investigated the impact of the formed coating deposits on refuse-derived fuel combustion and clinker properties in rotary kilns with CFD simulations. They revealed that the local heavy coating resulted in lower gas temperature and an increase in the free lime content in the clinker.

Despite the significant challenges induced by deposit formation, the existing studies are primarily focused on the characterization of mature deposits in the cement production process. To the authors’ best knowledge, no research work has been performed under well-controlled laboratory conditions to understand quantitatively the deposit formation with different materials and process conditions. An enhanced understanding of deposit formation under conditions relevant to the cement production process, especially the interactions of cement meals with an elevated level of alkali and chlorine species, is required to comprehend the particle deposition phenomenon and explore countermeasures in cement manufacturing using SRF.

Thus, this work aims to increase the knowledge of mineral particle deposition in the cement production process using SRF through well-controlled particle deposition experiments in a lab-scale entrained flow reactor (EFR) imitating the temperature conditions in the cement calciner. The effects of critical factors, such as feed materials, flue gas temperature, deposit probe surface temperature, and gas velocity, on the deposit formation rate were investigated. In addition, the mechanisms of deposition under different conditions were discussed.

2. EXPERIMENTAL SECTION

2.1. Materials. Materials were collected from a cement factory equipped with a five-stage preheater with an in-line calciner and a clinker production capacity of 3800 tons per day. In the calciner, the fuel is a mix of 50% coal and 50% SRF on an energy basis. In the kiln, coal is used as the only fuel. Three materials from the cement factory were used: raw meal (RM), hot meal (HM), and bypass dust (BD), as shown in Figure 1.

RM was the raw material used for cement production, which was collected after the raw mill process and contained mainly CaCO₃, SiO₂, and some minor amounts of Al and Fe. HM was the calcined meal that was collected from the outlet of the bottom stage preheater cyclone. BD was collected from the filter of the bypass system, where the hot gas was extracted from the kiln inlet and mixed with cold air to quench and condense the chloride, thereby removing chlorine from the process. The reason for using the abovementioned three materials in our research was that RM, HM, and BD were present in the calciner, HM was a calcined material that contained some SRF ash, and BD was enriched in alkali and chloride from SRF ash. The detailed elemental compositions shown in Table 2 were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES). Note that the Cl content was determined by ion chromatography (IC), based on the water-soluble content. Furthermore, the concentration of water-soluble K in RM and BD is also provided in Table 2. The amounts of K, S, and Cl in the three materials followed the order of BD > HM > RM. Note that only RM and BD were subjected

![Figure 1. Pictures of the used raw materials: (a) RM, (b) HM, and (c) BD.](https://doi.org/10.1021/acsomea.2c03870)
Three Materials

Table 2. Elemental Composition (Dry Basis) and LOI of the Three Materials

| properties       | RM  | HM  | BD  |
|------------------|-----|-----|-----|
| Si, wt %         | 6.67| 7.67| 7.50|
| Al, wt %         | 1.80| 2.01| 2.70|
| Fe, wt %         | 1.45| 1.68| 1.40|
| Ca, wt %         | 24.20| 38.23| 33.20|
| P, wt %          | 0.03| 0.04| 0.04|
| K, wt %          | 0.69| 1.78| 6.90|
| water-soluble K, wt % | 0.01| 5.10|
| Na, wt %         | 0.10| 0.15| 0.27|
| S, wt %          | 0.16| 0.51| 0.92|
| water-soluble Cl, wt % | 0.02| 6.40|
| LOI, 975 °C, wt % | 35.47| 5.53| 6.56|

Table 3. Main Crystalline Phases in the Three Materials Based on XRD Analysis

| materials | main crystalline phases |
|-----------|------------------------|
| RM        | CaCO₃ and SiO₂         |
| HM        | CaCO₃, CaO, SiO₂, and KCl |
| BD        | SiO₂, CaO, and KCl     |

deposit probe systems was used, as shown in Figure 3. Both systems commonly include a gas supply system, a particle feeding system containing a screw feeder and a vibration table, a water-cooled particle injection probe, an electrically heated gas preheater, an electrically heated vertical SiC reactor tube with a length of 2 m and an inner diameter of 0.08 m, and a water-cooled bottom chamber. A ceramic protection tube with a thickness of 0.009 m was mounted in the outlet of the main furnace to prevent the accumulation of melted deposits on the SiC tube, which caused an inner diameter of 0.062 m in the area of the reactor outlet. Two different deposit probe systems were used in this work. Figure 3a shows the EFR with a high probe surface temperature (HPST) deposit probe system. A SiC tube combined with a 45° inclined ceramic (≥95% Al₂O₃) head, on which the deposit would be formed, was used to mimic the refractory lined wall in a calciner. The probe head was placed into the EFR furnace via an elevator to obtain a probe surface temperature similar to the gas temperature in the reactor. Based on temperature measurements by a thermocouple on the top of the vertical SiC tube, it was confirmed that the probe surface temperature was the same as the heating elements/furnace temperature in the performed experiments. In this work, most experiments were carried out using the HPST deposit system, which is more relevant to industrial cases, where a small temperature difference is expected between the gas and the surface of the refractory lined walls. Furthermore, some experiments were performed to explore the particle deposition behavior when a considerable temperature difference between the probe surface and flue gas was present, simulating the possible existence of local colder surfaces in a cement calciner. This was done using a low probe surface temperature (LPST) deposit probe system, as shown in Figure 3b. The LPST deposit probe system, which was located at 0.15 m below the outlet of the reactor, consisted of a stainless steel tube with a length of 0.15 m and an outer diameter of 0.01 m, embedded with five thermocouples. The probe surface temperature can be adjusted between 500 and 700 °C with the presence of an air-cooled system. The temperature of the flue gas at the steel tube location was measured by a suction pyrometer, typically being 150–320 °C lower than the furnace temperature set-point. The measured temperatures at different experimental conditions are given in the Supporting Information (Figure S4).

In an experiment, the materials were entrained with 15 NL/min feeder gas (both feeder gas and preheater gas are air) and fed into the preheater. Subsequently, the materials along with feeder gas were mixed with various volume flow rates of preheated gas (35–93 NL/min) in the inlet of the main reactor. The particles were transported, heated up, and finally formed a deposit on the ceramic probe/stainless steel tube. The ceramic probe/stainless steel tube was taken out from the bottom/side port after each experiment, and the deposit was collected for further analysis. Furthermore, the deposit formation rate and deposit propensity were introduced to assess the impact of various operational parameters. Equations 1–3 provide the formulas for

![Figure 2. Particle size distribution of RM, HM, and BD with a Malvern Mastersizer 3000 using dry analysis.](image)
calculating the deposit formation rate and deposit propensity.\textsuperscript{37,38}

\[
\text{deposit formation rate} \left[ \frac{g}{m^2 \cdot h} \right] = \frac{\text{weight of collected deposit}[g]}{S_p[m^2] \cdot t[h]} \quad (1)
\]

\[
\text{local particle flux} \left[ \frac{g}{m^2 \cdot h} \right] = \frac{\text{weight of injected materials}[g]}{S_r[m^2] \cdot t[h]} \quad (2)
\]

deposit propensity[\%] = \frac{\text{deposit formation rate}[g/(m^2 \cdot h)]}{\text{local particle flux}[g/(m^2 \cdot h)]} \times 100 \quad (3)

where \( S_p \) is the cross-sectional area of the deposit probe, being 0.0007 and 0.0008 m\(^2\) for the HPST and LPST systems, respectively. \( t \) is the experiment duration. \( S_r \) means the local cross-sectional area of the reactor where the probe was placed, being 0.005 and 0.003 m\(^2\) for the HPST and LPST systems, respectively.

**2.3. Experimental Conditions.** Experiments were conducted in the EFR to study the effects of fed materials, furnace temperature, flue gas temperature, probe surface temperature,
experiment duration, and gas velocity on the deposit formation rate.

For the experiments using the HPST system, the three different materials were tested at 700−1200 °C. A particle feeding rate of 100 g/h was used, with a standard experiment duration of 0.5 h. The gas flow was adjusted to maintain a gas velocity of 0.9 m/s at all temperatures. The corresponding particle flux was 19894 g/m²·h. Additional measurements were performed with HM to investigate the effect of gas flow velocity at a fixed temperature of 1200 °C by adjusting the gas velocity to be in a range of 0.9−2.0 m/s. The detailed experimental matrix can be found in the Supporting Information (Table S1).

When the LPST system was employed, the furnace temperature varied between 1000 and 1400 °C, with the corresponding gas temperature (at the probe) being between 840 and 1080 °C. The experiments were performed with air cooling, keeping the probe temperature at 550 °C, and without air cooling, resulting in a probe temperature between 570 and 740 °C, depending on furnace temperature. The particle feeding rate was maintained at 100 g/h in all experiments, the gas velocity was maintained at 2.67 m/s at the outlet of the reactor at all furnace temperatures, and the experiment duration was 60 min. Experiments were performed with RM, BD, and a mixture consisting of 95 wt % RM and 5 wt % KCl. One set of experiments was performed with BD at a furnace temperature of 1400 °C varying the experiment duration between 5 and 60 min. The detailed experimental matrix can be found in the Supporting Information (Table S2).

2.4. Analytical Methods for Deposits. The collected deposit samples were subjected to XRD analysis (Huber diffractometer, combined with the Search Match 3.1 software package by MDI Livermore, CA and the diffraction database of PDF2−2019) to identify the crystalline phases. Each sample was scanned from 0 to 90° (2θ) for 0.5 h. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was performed to determine the elemental composition of the deposits. For ICP-OES analysis, around 0.25 g of the sample was digested using US EPA 3052 with 6 mL of 65% HNO₃, 2 mL of 30% HCl, and 2 mL of 40% HF. After the digestion samples were complexed with 12 mL of 10% H₃BO₃ and diluted to 50 mL with ultrapure water. Finally, the samples were diluted 10x for analysis. The amount of Cl was determined by ion chromatography (IC), where around 1 g of the sample was mixed in 10 mL of ultrapure water for 24 h for Cl extraction, before analysis. Additionally, around 10 mg of the sample was distributed evenly on a carbon tape sticking on a sample holder for scanning electron microscopy coupled with energy-dispersive spectroscopy (SEM-EDS) to investigate the morphology and elemental distribution of deposit samples.

3. RESULTS AND DISCUSSION

3.1. Results of HPST Experiments. 3.1.1. Effect of Furnace Temperature and Fed Materials on the Deposit Formation Rate. The effects of fed materials and furnace temperature (= flue gas temperature = probe surface temperature) on the deposit formation rate and deposit propensity using the HPST probe are shown in Figure 4. Note that the calculation of the deposit propensity of RM and HM shown in Figure 4b has been corrected by the calcination of CaCO₃. According to a previous study, it was assumed that all of the CaCO₃ particles both in RM and HM were calcined completely when furnace temperature is larger than 900 °C in this work. Furthermore, the hardness of deposit removal was defined and is provided in Table 4. The hardness of the deposits was determined in a qualitative manner using the following definitions:

- Easy: most deposit falls off by turning the probe upside down.
- Moderate: most of the deposit falls off by tapping the probe with a metal spoon.

![Figure 4](https://doi.org/10.1021/acsomega.2c03870)
• Hard: most of the deposit can be removed by scraping with a metal spoon.

It can be seen that with the increase of furnace temperature from 700 to 1200 °C, the deposit formation rate of RM initially showed a similar level at 700 and 800 °C, followed by a significant decrease from 800 to 1000 °C, and ultimately, the deposit formation rate progressively increased with the further increase of furnace temperature from 1000 to 1200 °C. The trend of the deposit formation rate of BD is quite similar to RM in the investigated temperature range; however, the values of BD are always higher than those of RM under the same conditions except at 1200 °C where they are similar. When it comes to HM, the deposit formation rate decreased gradually from 700 to 1000 °C and then increased from 1000 to 1200 °C.

The decomposition of CaCO$_3$ taking place between 850 and 900 °C, 36,41 may explain the observed trend of the RM deposit formation rate. At temperatures where calcination of CaCO$_3$ is not initiated, the influence of furnace temperature is limited, that is why the deposit formation rates at 700 and 800 °C were at a similar level. The following steep decrease from 800 to 1000 °C could be attributed to an increased decomposition degree of CaCO$_3$, which leads to a lower particle flux, as a consequence of the lower deposit formation rate until 1000 °C. A possible reason for deposit formation rate trends of HM and BD in the temperature range of 700–1000 °C could be the presence of KCl, which has a melting point of 770 °C. The maximum deposit formation rate of BD at 800 °C can be explained by the fact that KCl begins to melt, which increases the sticking propensity of impacting particles and deposits. With the further increase in furnace temperature, KCl is increasingly present in the gas phase, which leads to a steep decrease in the BD deposit formation rate from 800 to 1000 °C. In terms of HM, the maximum deposit formation rate was observed at 700 °C after which it gradually decreased until 1000 °C. There are two possible reasons for the decrease: (1) most of the KCl was evaporated with the increased furnace temperature and (2) the increased calcination degree of CaCO$_3$ in HM may also play a role in the lower deposit formation rate.

The trends of the deposit formation rate of the three different materials in the range of 1000–1200 °C were similar, where the melting of the cement meal particles became the dominating factor in the deposit formation process. The presence of eutectic in the CaO–Al$_2$O$_3$–Fe$_2$O$_3$–SiO$_2$ system allowed the cement meal particles to melt and soften at temperatures around 1200 °C. As a result, the deposit formation rates of the three materials increased slightly at 1100 and increased sharply at 1200 °C, where all three materials behaved very similarly. Furthermore, the deposits of the three materials collected at 1200 °C were evaluated to be “Hard”, as shown in Table 4, which indicated the presence of an extensive degree of particle melting. The deposit properties of the three materials overall showed similar trends to the deposition rate. One trend that was more clear from deposition propensity was that RM had higher deposition propensity than HM at 800–900 °C. This may because the density of RM particles was higher than that of HM particles since conversion from CaCO$_3$ to CaO would reduce the particle density and therefore reduce the impaction degree.

The elemental compositions of deposit samples were determined by ICP-OES, as shown in Figures 5–7. Overall, the composition of the deposits represents well the composition of the raw materials (RM, HM, and BD). A common trend is that the amount of Cl is depleted in the deposits compared to the raw materials, most likely due to the evaporation of KCl. This depletion increases with increasing temperatures. For deposits collected at 900 °C or above, the chlorine content in the deposits becomes negligible (<0.1 wt %). The depletion degrees of K and S in deposits are less compared to that of Cl, indicating that most of the K and S exist as species with high thermal stability, such as K$_2$SO$_4$, CaSO$_4$, and potassium silicates. As observed by earlier studies, 34–42 the reaction affinity of volatile elements (Cl, K, Na, Ca, S) in a cement system should follow the following order: (a) chlorine reacts with alkali primarily, forming compounds with an order of KCl, NaCl, and CaCl$_2$; (b) the excess alkali metals may exist as alkali sulfates (K$_2$SO$_4$, Na$_2$SO$_4$), carbonates (K$_2$CO$_3$, Na$_2$CO$_3$), or even hydroxides (KOH, NaOH) or be incorporated in clinker components containing Si, Al, and Ca; and (c) the excess sulfur reacts with CaO, forming CaSO$_4$.

Combined with the analysis results of elemental composition in Figures 5–7, the potassium compounds in the deposit samples that can most likely melt are KCl, K$_2$SO$_4$, and potassium silicate. It has been substantiated that a deposit with a higher percentage of KCl sticks to the probe more easily during the experiment, resulting in a higher deposit formation rate. KCl would facilitate deposit formation via melting at temperatures between 700 and 800 °C when the furnace temperature reached 900 °C; however, most of the KCl evaporated. With the further increase of furnace temperature to 1000 °C, K$_2$SO$_4$, which has a melting temperature of 1067 °C, would take over and have the same effect as KCl, becoming the dominant cause of deposit formation. The reduction of S contents in HM and BD at 1200 °C justifies the evaporation and/or decomposition of K$_2$SO$_4$. 43,44 Figure 5 also illustrates that the concentrations of Cl, K, and S in RM deposit samples were always at a much lower level compared with HM and BD, which could explain the lower deposit formation rate of RM compared to HM and BD at almost all of the investigated furnace temperatures (except HM at 800 °C due to incomplete calcination). As shown in Figures 6 and 7, the concentrations of K, Cl, and S of HM deposits were always lower than those of BD deposits under the same furnace temperature conditions. Hence, in the range of furnace
temperatures from 700 to 1100 °C, the deposit formation rate of BD is higher than that of HM. All of the collected experimental deposit samples were subjected to XRD analysis with the identified crystal phases in each sample shown in Table 5. The detailed XRD spectra are provided in the Supporting Information (Figures S1−S3).

It could be seen that most samples were identified with Ca(OH)$_2$, which is attributed to the moisture absorption during sample cooling and/or storage of samples. KCl was evaporated at 800 °C of HM and 900 °C of BD. Furthermore, the presence of Ca$_2$SiO$_4$ was identified in BD samples from 900 to 1200 °C, and even all of the SiO$_2$ was reacted, forming Ca$_2$SiO$_4$ at 1200 °C.

3.1.2. Effect of Gas Velocity on the Deposit Formation Rate. Figure 8 illustrates the effect of gas velocity on the deposit formation rate and deposit propensity of HM in the range of 0.9 to 2.0 m/s. It can be seen that as the gas velocity increased, the deposit formation rate reduced. A higher gas velocity, and hence a higher particle velocity, increases the likelihood of particles rebounding from the probe surface rather than sticking on it. Additionally, a higher gas velocity can blow off some formed deposits, which only stick lightly on the probe. Both mechanisms would result in a lower deposit formation rate.

3.2. Results of LPST Experiments. 3.2.1. Effect of Fed Materials on the Deposit Formation Rate. Figure 9 depicts the chemical composition of deposit samples with BD in the HPST system. Experiments were conducted with a feeding rate of 100 g/h, a gas velocity of 0.9 m/s, an experiment duration of 30 min, and furnace temperatures ranging from 700 to 1200 °C.
influence of the fed material types on the deposit formation rate and deposit propensity in the LPST experiments, where the probe was kept at a fixed temperature of 550 °C and the gas temperature and feed material type were changed. It can be seen that the deposit formation rate of BD is substantially higher than that of RM in the investigated flue gas temperature range. This is probably due to the much higher concentration of volatile alkali species such as KCl in BD than that in RM. At gas temperatures above 1000 °C, KCl will be present in the gas phase and direct condensation on the deposit probe may take place, generating a sticky surface layer thereby leading to a larger deposit formation rate of BD.

According to the ICP-OES analysis of water-soluble contents of Cl and K in RM and BD given in Table 2, the weight percentages of KCl in RM and BD were determined to be 0.03 and 10.50 wt %, respectively. To validate the influence of the amount of KCl in the fed material, a mixed material of 95 wt % RM and 5 wt % KCl, which is around the average value of the KCl contents in RM and BD, was utilized. In comparison to pure RM, the deposit formation rate increased significantly with the addition of KCl, demonstrating that the presence of KCl plays a key role in the deposit formation process. The deposit formation rate of RM + KCl is lower than that of BD because the amount of KCl added to RM is lower than that of BD. Furthermore, the trends of RM + KCl and BD differ with respect to flue gas temperature. The peaked deposition rate of RM + KCl at around 963 °C implies that there may be other factors influencing the deposit formation rate, such as the amount of the added KCl being larger than the amount of KCl in RM and BD. There are two possible deposition mechanisms of added KCl in the RM mixture: (1) the heterogeneous condensation of gaseous KCl on the probe/deposits, and (2) the incomplete evaporation KCl particles stuck on the probe/deposits. With the increase of furnace temperature from 1000 to 1200 °C, the evaporation effect of KCl becomes more and more significant, hence the first mechanism becomes more dominant. However, with the further increase of furnace temperature until 1400 °C, the temperature gradient between the flue gas and the bottom chamber increased, inducing the nucleation of KCl before it condensed on probe/deposits. The formed KCl aerosol may flow away with streamline, instead of sticking on the probe/deposits, subsequently influencing the overall deposit formation rate. The peak value of the deposit formation rate at 1200 °C furnace temperature (963 °C flue gas temperature) is probably due to the competition and coordination result of two mechanisms. In terms of deposit propensities of applied materials, the overall trends are similar to the deposit formation rate, except for one point at 963 °C, where RM + KCl showed a higher deposit propensity than BD. This is because the higher deposit formation rate at 963 °C as we discussed and the calcination of CaCO₃ causes a light density, thereby reducing the impaction degree.

3.2.2. Effect of Flue Gas Temperature on the Deposit Formation Rate. Figure 9 also reveals that the deposit formation rate of BD increased with rising flue gas temperature, whereas the deposit formation rate of RM was little impacted by flue gas temperature in the examined range. The explanation may be that the higher flue gas temperature causes a high temperature of the outer part of the deposit, leading to a higher fraction of melted KCl in the deposit. Furthermore, a higher temperature gradient between the probe surface and flue gas may promote KCl condensation. Due to the fact that RM contains quite low KCl, the increasing flue gas temperature has little impact on RM deposit formation.

3.2.3. Effect of Probe Surface Temperature on the Deposit Formation Rate. The influence of probe surface temperature on the deposit formation rate and deposit propensity is shown in Figure 10 for RM and BD. Experiments were carried out with and without air cooling of the deposit probe. With air cooling, the probe surface temperature was maintained at 550 °C, whereas without air cooling, the probe surface temperature increased slightly with the increase of flue gas temperature (see the top x-axis). The results show that a higher probe surface temperature (uncooled probe) has a negligible effect on the deposit formation rate and deposit propensity of RM, but it does result in a slightly greater deposit formation rate and deposit
propensity of BD. A higher temperature difference between the probe surface and flue gas theoretically equates to a stronger driving force for thermophoresis and condensation. The experiments, on the other hand, show no significant influence of changed gas temperature in the RM experiments, and opposite results are obtained in the BD experiments, implying that condensation and thermophoresis are not primary mechanisms for deposit formation in the investigated cases. The deposit samples presented in the Supporting Information (Figures S7–S10) show that the amount of deposit on the windward side is much larger than that on the leeward side, which also indicates that the dominant mechanism is inertial impaction. In the BD experiments with varied probe temperatures, a furnace temperature increasing from 1000 to 1100 °C leads to a higher deposit formation rate clearly, which probably is caused by the increased content of KCl in the gas phase. A small increase in the deposit formation rate in the BD experiments with fixed probe temperature is probably caused by the increased melting fraction of KCl (or other salts) in the outer part of the deposit.

3.2.4. Effect of Experiment Duration on the Deposit Formation Rate. Experiments with different durations (5, 7.5, 15, 30, 60 min) when using BD were performed to investigate deposit formation by different mechanisms, and the results are shown in Figure 11.

The deposit formation rate and deposit propensity of 5 and 7.5 min are substantially higher than the succeeding ones. This is likely due to the larger temperature difference between the probe surface and the flue gas in the early stages, indicating a strong driving force for thermophoresis and condensation.
Condensation and thermophoresis at this stage are critical because they create a sticky layer that aids deposit development. As the experiment progresses, the generated deposit on the probe obstructs heat transfer between the flue gas and the steel tube, resulting in a greater deposit surface temperature than that at the probe surface. The driving force of thermophoresis and condensation is diminished, resulting in a slower rate of deposit formation after 15 min. From 15 to 60 min, there is a slight increase in the deposit formation rate. As the deposits grow, the deposit surface temperature increases. This may cause softening of the deposit and an increased deposit melt fraction, promoting further deposit formation. This is in accordance with the results comparing the cooled and uncooled probes (Figure 10c,d), which also shows that increased probe and deposit temperatures accelerate deposit formation.

3.3. Discussion. 3.3.1. Morphology and Mechanisms of Deposition. It is critical to understand the impact of important operational parameters on the deposit formation rate, as well as the contributions of deposition mechanisms.49,50 The basic mechanisms of particle deposition are widely thought to be inertial impaction, thermophoresis, and condensation.51,52 All of the deposit samples in our study were photographed prior to collection, some selected pictures of experimental deposit samples are given in Figure 12 (HPST deposit probe system) and Figure 13 (LPST deposit probe system). Additional pictures of deposit samples can be found in the Supporting Information (Figures S5–S10).

Figure 12 exhibits some selected images of deposit samples obtained with the HPST deposit system, which reveal that all deposits, regardless of materials used, only formed on the windward side, but also on the leeward side, regardless of the materials used. It shows that inertial impaction and thermophoresis both play a role in deposit formation.53 Furthermore, there is always a temperature gradient between the flue gas and the probe surface in all LPST deposit system experiments, and the probe surface temperature is lower than the melting temperature of KCl (770 °C), implying that in the cases where BD was used, condensation of KCl also plays a role during deposit formation. The deposit formed on the leeward side appears finer than the windward deposits, which supports the presence of condensation and thermophoresis. To confirm our hypothesis, the SEM-EDS analysis of selected experimental deposits was performed, with the results presented in Figure 14. The element mapping in Figure 14a is for the case where BD was utilized in the LPST deposit system with a flue gas temperature of 1080 °C and a probe surface temperature of 550 °C. It appears that the K and Cl distributions are overlapping, and the crystal structure of KCl is typical cubic, implying the presence of KCl condensation on the surface of the deposit/deposit probe. Figure 14b demonstrates the microstructure and element mapping in the HPST deposit system with BD at a furnace temperature of 800 °C, where the distributions of K and Cl were roughly the same. However, the crystalline structure of KCl was not cubic, suggesting that KCl in this sample originates from the melting of the original KCl in BD rather than the condensation of gaseous KCl. Finally, in the case of BD utilized with a 1200 °C furnace temperature in the HPST deposit system, no K and Cl were identified, as shown in Figure 14c, implying that all of the KCl evaporated and did not contribute to deposition (also consistent with the ICP-OES analysis).

4. PRACTICAL IMPLICATION

The applied experimental EFR conditions resemble the conditions within cement plants with respect to gas temperatures (700–1400 °C), surface temperatures (550–1200 °C), and chemistry of the applied particles (RM, HM, and BD). However, there are also some important differences: a cement plant using SRF can experience relatively high gas phase concentrations of HCl and SO2 in the calciner and these conditions were not simulated in the present experimental study. Also, the times available for deposit buildup and deposit removal are in real industrial systems much longer than the maximum duration of 1 h used in the present study. Therefore, in an
Figure 13. Selected images of experiment deposits with the LPST deposit system. Experiments were performed with a mean gas velocity of 2.67 m/s, a feeding rate of 100 g/h, a furnace temperature of 1400 °C, a flue gas temperature of 1080 °C, a probe surface temperature of 550 °C, and an experiment duration of 60 min, with different materials: (a) RM, (b) 95% RM + 5% KCl, and (c) BD.

Figure 14. Microstructure and element distribution map of different deposit samples, (a) material: BD, LPST deposit system, flue gas temperature = 1080 °C, probe surface temperature = 550 °C, experiment duration = 1 h; (b) material: BD, HPST deposit system, flue gas temperature = furnace temperature = probe surface temperature = 800 °C, experiment duration = 0.5 h; and (c) material: BD, HPST deposit system, flue gas temperature = furnace temperature = probe surface temperature = 1200 °C, experiment duration = 0.5 h.
industrial-scale calciner, loose deposits typically detach from walls because of turbulent flows, while similar deposits in the EFR system can stay on the inclined deposit probe surface in the relatively stable flow conditions in the EFR. Anyhow, we believe that the EFR experiments provide an improved understanding of how critical deposits are initially formed in cement plants.

The EFR results obtained a broad range of deposit formation rates. From a minimum of around 1000 g/(m$^2$ h) (deposit propensity of 5%) in the LPST system using RM and applying gas temperatures from 850 to 1080 °C and a probe surface temperature of 550 °C up to a maximum of 4000 g/(m$^2$ h) (deposit propensity of 20%) in the HPST system using BD and applying a gas temperature of 800 °C.

4.1. LPST Probe. The LPST simulates conditions where the wall temperature is somewhat lower than the flue gas temperature, which potentially can occur where the cold raw meal mixes with hot gas. In this part of the study, surface temperatures varied in the range of 550–737 °C. Generally, a higher deposit formation rate is observed when the fed material alkali content is increased. An increased probe surface temperature leads most cases to a moderate increase in the deposit formation rate. In the case of the low-alkali-content RM, no influence of changing the probe surface temperature was observed. The mechanisms that contributed to the deposit formation process included impaction, direct condensation, and thermophoresis.

An investigation of the influence of probe residence time on deposit formation indicates that the initial deposit buildup is dominated by direct condensation and thermophoresis, while the later stages of the deposit formation process are dominated by inertial impaction.

The practical implication of this part of the work is that condensation and thermophoresis can be important mechanisms for deposit formation in areas where there is a temperature gradient between the flue gas and the deposit/wall surface. In these areas with cold surfaces, deposits enriched in volatile species (e.g., KCl) and fine particles (e.g., small meal particles) can be formed by thermophoresis/condensation. These deposits may over time develop into hard deposits that are difficult to remove. Furthermore, in a full-scale calciner co-firing with SRF and coal, hard deposits enriched in KCl, CaCO$_3$, and spurrrite are obtained, justifying our above hypothesis.

4.2. HPST Probe. The HPST simulates calciner conditions where the walls are refractory lined and the temperature difference between the wall surface and the gas and particles in the calciner chamber are relatively small.

All of the three materials investigated in the EFR with the HPST show relatively high deposit formation rates at 700 to 800 °C (2000–4000 g/(m$^2$ h)), decreasing to 1000–3000 g/(m$^2$ h) at 1000–1100 °C. We believe that the main cause for this is that the salt species (especially KCl) present in the deposits at relatively low temperatures generate some melt that increases the stickiness of the deposit and therefore increases the deposit formation rate. At higher temperatures (1000 to 1100 °C) most of the salt species are present in the gas phase and do not contribute to the deposit formation process. At the highest surface temperature investigated (1200 °C), the three materials have a similar deposit formation rate of 3000 g/(m$^2$ h) and this is probably mainly caused by the melting of eutectics containing a range of elements (Ca–Al–Fe–Si).

The hardness of the deposits (how difficult they were to remove) was only moderate in most cases. Only at a temperature of 1200 °C, hard deposits were formed with all of the three applied feed types. In a real calciner, the picture may change somewhat. The longer residence time and the higher concentrations of HCl and SO$_2$ could significantly influence the deposit sintering and maturing process. The conditions will probably lead to more hard deposits by sulfation of Ca-rich species and also the formation of more complex species like spurrrite.

In most parts of a cement calciner, the deposit formation process is dominated by impaction. Other mechanisms that may play a significant role in power plant boilers such as direct condensation and thermophoresis are probably not important for most of the places in calciners.

The practical relevance of this study for deposit formation in calciners can be summarized in a few points. It shall be kept in mind that the temperatures in full-scale calcination reactor chambers range from 700 to 1200 °C and that surfaces typically are refractory lined with only a minor temperature fall from the gas and particles to the refractory surface.

- The lowest deposit formation rates are seen at intermediate temperatures (900–1100 °C). Decreasing the temperature to 700 °C actually increases the deposit formation rate. However, it must be foreseen that the sintering of deposits may be more severe at higher temperatures. A local surface temperature of 1200 °C should be avoided if possible, as both the deposit formation rate and the hardness of the deposit are high also for materials with low K/S/Cl content.

- It is clearly observed that materials with high K/Cl/S content that typically appear with high SRF firing lead to increased deposit formation rates. This indicates that keeping especially the K content at a low level will reduce deposit formation in a calciner.

5. CONCLUSIONS

To simulate the buildup formation in cement plants, especially at the conditions prevailing in calciners, mineral particle deposition studies were carried out in a well-controlled high-temperature entrained flow reactor (EFR) coupled with high probe surface temperature (HPST) and low probe surface temperature (LPST) deposit systems, and surface temperatures from 550 up to 1200 °C were investigated. Furthermore, the effects of fed material chemistry, local flue gas temperature (700–1200 °C), experiment duration (5–60 min), and gas velocity (0.9–2.0 m/s) on deposit formation were explored. Three different materials were applied in the experiments to represent particles that can appear in cement plants. Samples were obtained from a cement factory using approximately 50% SRF fuel in a calciner and included a noncalcined raw meal (RM) rich in Ca, Si, and Al but with only trace amounts of K, S, and Cl; a hot meal sample (HM) that was a calcined product containing some ash species from the SRF and therefore had a K content of approximately 2 wt % and Cl and S contents of approximately 1 wt %; and also a bypass dust sample (BD) that had K, Cl, and S contents of 6.90, 5.40, and 0.92 wt %, respectively.

Below are the main findings from the HPST experiments, where inertial impaction is the dominant deposition mechanism due to no temperature difference between the flue gas and the probe surface:

1. At flue gas temperatures of 700–1100 °C, BD has a higher deposition rate and deposition propensity than HM and RM, primarily because BD contains a larger amount of...
KCl and K$_2$SO$_4$, which would melt and increase the stickiness of the impacting particles and/or deposits. The maximum deposition rate is observed at 800 °C, which is 4315 g/(m$^2$-h).

2. At a flue gas temperature of 1200 °C, the three materials have similar deposition rates and the formed deposits are harder to remove, due to the softening/melting of cement particles.

3. Flue gas velocity (0.9—2.0 m/s) showed a negative effect of increased gas velocity on the deposit formation, which is explained by the rebound of particles with high momentum from the probe.

4. Overall, the composition of the deposits represents well the composition of the raw materials. The amount of Cl is depleted in the deposits compared to the raw materials, especially at temperatures above 900 °C, due to evaporation of KCl.

For the LPST experiments, the main findings are as follows:

1. Inertial impaction, condensation, and thermophoresis all contribute to deposition formation, with the latter two playing a more important role in the initial phase (0—7.5 min) of deposit formation.

2. The deposition rate increases in the order of RM, 95% RM + 5% KCl, and BD due to the amount of KCl in each feed material.

3. An increase in flue gas temperature increases the deposition rate of BD but not for RM, due to the small concentration of KCl in RM.

There are still many issues regarding the understanding of the deposit formation processes where further studies are wanted. Especially, the maturation and sintering of deposits need further clarification. The role of longer residence times and high concentrations of HCl and SO$_2$ on cement plant deposit sintering should be studied further.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/10.1021/acsomega.2c03870.

Summary of the XRD analysis of deposit samples of RM, HM, and BD; measurement of flue gas temperature using a suction pyrometer under different temperatures and average gas velocity; experimental matrix using HPST and LPST deposit collecting systems; and summary of the pictures of deposit samples of RM, HM, and BD. (PDF)

**AUTHOR INFORMATION**

**Corresponding Author**

Hao Wu — Department of Chemical and Biochemical Engineering, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark; orcid.org/0000-0003-0462-2491; Email: haw@kt.dtu.dk

**Authors**

Xiaozan Wang — Department of Chemical and Biochemical Engineering, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark

Peter Arendt Jensen — Department of Chemical and Biochemical Engineering, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark; orcid.org/0000-0001-6784-5321

Morten Nedergaard Pedersen — FLSmidth A/S, 2500 Valby, Denmark

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.2c03870

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This project is funded by China Scholarship Council (CSC), and the ProBu—Process Technology for Sustainable Building Materials Production project (grant number: 8055-00014B) funded by Innovation Fund Denmark, FLSmidth A/S, Rockwool International A/S, and Technical University of Denmark.

**REFERENCES**

(1) Tanaka, N. Energy Technology Transitions for Industry; International Energy Agency, 2009. DOI: 10.1787/9789264068612-en.

(2) Pedersen, M. N. Co-Firing of Alternative Fuels in Cement Kiln Burners. PhD thesis, Technical University of Denmark, 2018.

(3) James, F. Reilly. Mineral Commodity Summaries 2021; U.S. Geological Survey, 2021.

(4) Baumert, K. A.; Herzog, T.; Pershing, J. Navigating the Numbers; Billings, H., Ed.; World Resources Institute, 2005.

(5) Andrew, R. M. Global CO2 Emissions from Cement Production, 1928—2018. Earth Syst. Sci. Data 2019, 152, 1—67.

(6) Birol, F. Technology Roadmap - Low Carbon Transition in the Cement Industry; International Energy Agency, 2020. DOI: 10.4324/9781315264783-86.

(7) Arikartane, W. K.; Melaena, M. C.; Tokheim, L.-A. Determination of Biomass Fraction for Partly Renewable Solid Fuels. Energy 2014, 70, 465—472.

(8) Nakhai, M.; Pedersen, M. N.; Wu, H.; Skærup Jensen, L.; Glarborg, P.; Jensen, P. A.; Grøvain, D.; Dam-Johansen, K. Aerodynamic and Physical Characterization of Refuse Derived Fuel. Energy Fuels 2018, 32, 7685—7700.

(9) Vainio, E.; Yrjas, P.; Zevenhoven, M.; Brink, A.; Laurén, T.; Hupa, M.; Kajolminna, T.; Vesala, H. The Fate of Chlorine, Sulfur, and Potassium during Co-Combustion of Bark, Sludge, and Solid Recovered Fuel in an Industrial Scale BFB Boiler. Fuel Process. Technol. 2013, 105, 59—68.

(10) Chatterjee, A.; Sui, T. Alternative Fuels – Effects on Clinker Process and Properties. Cem. Conc. Res. 2019, 123, No. 105777.

(11) Rahman, A.; Rasul, M. G.; Khan, M. M. K.; Sharma, S. Recent Development on the Uses of Alternative Fuels in Cement Manufacturing Process. Fuel 2015, 145, 84—99.

(12) Pedersen, M. N.; Nielsen, M.; Clausen, S.; Jensen, P. A.; Skærup Jensen, L.; Dam-Johansen, K. Imaging of Flames in Cement Kilns to Study the Influence of Different Fuel Types. Energy Fuels 2017, 31, 11424—11438.

(13) Gerassimidou, S.; Velis, C. A.; Williams, P. T.; Castaldi, M. J.; Black, L.; Komilis, D. Chlorine in Waste-Derived Solid Recovered Fuel (SRF), Co-Composted in Cement Kilns: A Systematic Review of Sources, Reactions, Fate and Implications. Crit. Rev. Environ. Sci. Technol. 2021, 51, 140—186.

(14) Grammelis, P.; Basinas, P.; Malliopoulos, A.; Sakellaropoulos, G. Pyrolysis Kinetics and Combustion Characteristics of Waste Recovered Fuels. Fuel 2009, 88, 195—205.

(15) Hernandez-Atonal, F. D.; Ryu, C.; Sharifi, V. N.; Swithenbank, J. Combustion of Refuse-Derived Fuel in a Fluidised Bed. Chem. Eng. Sci. 2007, 62, 627—635.

(16) Domínguez, I. R.; Gómez-Millán, J.; Alvarez, M.; De Aza, S.; Contreras, L.; De Aza, A. H. Build-up Formation and Corrosion of Monolithic Refractories in Cement Kiln Preheaters. J. Eur. Ceram. Soc. 2010, 30, 1879—1885.

(17) Wolfson, R. G.; Kobes, W.; Fine, M. E. Precipitation in NaCl-KCl Mixed Crystals. J. Appl. Phys. 1966, 37, 704—712.
