Utilization of lime-dried sludge for eco-cement clinker production: effects of different feeding points

Haihua Cao, Wei Liu, Jingcheng Xu, Jia Liu, Juwen Huang, Xiangfeng Huang and Guangming Li

ABSTRACT

Co-processing lime-dried sludge (LDS) in cement kilns is an appropriate technique to solve the problem of LDS disposal and promote the sustainable development for cement industry. However, there were limited studies that investigated the effects of feeding points on product quality and cement kiln emissions. In this study, simulated experiments were conducted by dividing the feeding points into high-temperature zones (HTZs) and raw mill (RM). Cement quality and major cement kiln emission characteristics were comprehensively investigated. The results showed that in terms of burnability, compressive strength and microstructure, the optimum co-processing amount of LDS were 9 wt% when feeding at RM, while 6% when feeding at HTZs. Meanwhile, the organic emissions of RM samples were mainly low environmental risk compounds of amides and nitrogenous heterocyclic compounds. Inorganic gaseous pollutions of NOx and SO2, respectively, were 8.11 mg/g DS and 12.89 mg/g DS, compared with 7.61 mg/g DS and 4.44 mg/g DS for HTZs. However, all the cement kiln emissions concentration were still much lower than standard requirements. Overall, RM had a bigger LDS co-processing capacity and higher, but acceptable, cement kiln emissions. Feeding LDS via RM could dispose larger amounts of sludge and provide more alternative materials for cement manufacturing.

Key words | cement kiln, co-processing, emissions, feeding points, lime-dried sludge

INTRODUCTION

Currently, sewage sludge production in China is about 600 Mt DS/y (NBSC 2012), and it is predicted to reach 1,200 Mt DS/y by 2020. Sewage sludge, which may contain pathogenic organisms and pollutants, a variety of toxic metals and high amounts of soluble salts, has a high risk for public health and the environment (Samaras et al. 2008; Zorbas et al. 2011). Still, the potential hazards to public health and the environment could be avoided if the best available technologies are applied for the sludge disposal, which, in turn, allow efficient recycling of the sludge as a raw material or a fuel. Meanwhile, a total of 2,420 Mt of cement were manufactured in 2015 in China, which accounted for approximately 50% of the global annual production (NBSC 2014; Fang et al. 2015). Cement industry is well known as an energy and raw material-intensive industry and generates large amounts of air pollutants (Brown et al. 2014). As of now, cement kilns development policies have been focused on sustainability, which includes the conservation of natural resources by utilizing alternative raw materials, such as sewage sludge (Benhelal et al. 2013).

The hazard to the environment potentially brought with the sewage sludge through pathogenic organisms and pollutants can be completely diminished in well-maintained cement kilns, where high temperature, long residence time, good turbulence and mixing conditions are ensured (Yan et al. 2014). At the same time, high caloric value and appropriate inorganic composition make it possible for utilizing sludge as an alternative raw material and fuel in the cement industry (Li et al. 2013). Taking the above advantages into account, co-processing sewage sludge in a cement kiln has received increasing attention in recent years. The effects of utilizing sludge in cement production on cement quality were studied by Lin et al. and Rodriguez et al. (Lin et al. 2012; Husillos Rodríguez et al. 2013); the
emissions to air were studied by Oh et al. (Oh et al. 2014; Fang et al. 2015; Liu et al. 2015a); and the impact on the environment using life cycle assessment was performed by Liu et al. and Deviatkin et al. (Liu et al. 2015b; Deviatkin et al. 2016).

Still, only limited numbers of studies on the effect of the feeding points of the lime dried sludge (LDS) on the properties of the manufactured cement were published despite a wide utilization of the sludge in China, e.g. in Xiaohongmen and Fangzhuang wastewater treatment plants (WWTPs) in Beijing, the Jizhuangzi WWTP in Tianjing, and the Jiading WWTP in Shanghai. The common feeding points are the main burner at the rotary kiln outlet end, the feed chute at the transition chamber at the rotary kiln inlet end, the precalciner burners to the precalciner, and the feed chute to the precalciner (Hasanbeigi et al. 2012; Li et al. 2013). Feeding of mechanically dewatered sludge (MDS) via the raw mill (RM) at the inlet of the dry scrubber is not appropriate due to the high organic content of MDS, whereas the feeding becomes possible if lime drying is applied to reduce the moisture content of the sewage sludge. However, after lime drying, the properties of sludge changed significantly. With 0.3–0.5 kg CaO/kg DS, low organic matter and low moisture content, LDS has a higher potential to be an alternative material and is possible to be fed via RM (Valderama et al. 2013; Xu et al. 2014; Liu et al. 2015c). Consequently, the potential feeding points of LDS to the cement kilns can be divided into two categories: high-temperature zones (HTZs) and RM as shown in Figure 1.

The conditions of the two feeding points vary significantly. Regardless of the feeding points, two aspects, namely the ‘three ratios’ and the high temperature, should be considered. The ‘three ratios’ determining the quality of the clinker manufactured are silica ratio (SM) values (1.70–2.70), alumina ratio (IM) values (0.90–1.90), and lime saturation (KH) values (0.87–0.96) (Lin et al. 2009; Lin et al. 2012). The ratios are calculated as shown in Equations (1)–(3).

\[
\text{Lime saturation ratio (KH)} = \frac{\text{CaO} - 1.65\text{Al}_2\text{O}_3 - 0.35\text{Fe}_2\text{O}_3}{2.80\text{SiO}_2} \tag{1}
\]

\[
\text{Silica ratio (SM)} = \frac{\text{SiO}_2}{\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3} \tag{2}
\]

\[
\text{Alumina ratio (IM)} = \frac{\text{Al}_2\text{O}_3}{\text{Fe}_2\text{O}_3} \tag{3}
\]

The three ratios can easily be controlled during the feeding and homogenising processes. If the composition of sludge was similar to that of cement raw materials, it could be used as an alternative material in large amounts. If not, then limestone, clay, and ferrous raw materials should be added to ensure a suitable composition. If LDS is introduced via RM, these parameters could be controlled automatically, while introduction via HTZs would not provide the benefit.

Secondly is the high temperature. HTZs with a high temperature (about 800–1,500°C) and a long enough residence time (>2 s) could destroy the organic matters in LDS, and finally generate carbon dioxide (CO₂), sulfur dioxide (SO₂) and nitrogen oxides (NOₓ). Even though the temperature in the RM feeding point is low, the high temperature flue gas will still go through the cement kiln enabling the destruction of any organic compounds. However, the concentration of SO₂ and NOₓ could be different between these two methods (Liu et al. 2015c). In addition, for both feeding at HTZs and RM, co-processing LDS would introduce impurities such as heavy metals and phosphate, which also could affect the quality of cement clinkers and the environment (Staněk & Sulovský 2009; Yang et al. 2014).

In this study, laboratory experiments were conducted to investigate the differences between these two alternative feeding points, namely HTZs and RM. Multiple parameters, such as properties of LDS, differences in the raw meal blends, properties of sintered clinker, and properties of the hydration products, were investigated. The characteristics of cement kiln emission, including organic and inorganic gaseous compounds, were also investigated. The results presented here could be used as a theoretical guide for selecting the appropriate feeding point for LDS to reduce the environmental risks associated with the sludge disposal and to achieve the sustainable development in the cement industry.

**EXPERIMENTAL SECTION**

**Materials**

MDS and LDS samples were collected from Xiaohongmen WWTP in Beijing that employed the anaerobic-anoxic-oxic (A/A/O) process to remove nitrogen and phosphorus from the wastewater. In the oxic zone, nitrification is performed and the nitrate thus produced is recycled to the anoxic zone (internal recycle), where denitrification takes place. The influent and sludge are mixed under anaerobic conditions in the anaerobic zone (external recycle). The
alternate anaerobic/oxic conditions make phosphorus removal efficient. The cement raw material was obtained from Beijing cement plant.

**Experimental procedures**

**Cement clinker production process**

To study the effects of the feeding points on cement quality, simulation experiments were conducted. The chemical compositions of the raw mixes are shown in Table 1. For simulation of feeding at RM, SiO₂, CaCO₃, Al₂O₃, and Fe₂O₃ (analytical reagent) were used to maintain KH = 0.91 ± 0.01, SM = 2.59 ± 0.01, and IM = 1.48 ± 0.01.

To study the HTZs’ feeding point, LDS was pretreated in a muffle furnace for 30 min under 900 °C and then mixed with cement raw materials. And raw mixtures were prepared with absolute alcohol, put into a cylindrical mold, and pressed to \( \varphi 40 \times 5 \) mm slice by applying a pressure of 30 MPa. These slices were then heated to 1,450 °C at a rate of 10 °C/min, after which they were held for 1 h in a furnace, then cooled to room temperature. The resulting clinkers were ground to ASTM 200 mesh together with 3.5 wt.% gypsum, after which the clinker hydration productions were obtained.

**Cement emissions collection and detection process**

The cement kiln emissions experiments were carried out in a laboratory-scale tubular furnace (Figure 2). The feed gas was a synthetic gas mixture (N₂/O₂). For organic gaseous collection, 2.000 ± 0.002 g sludge was heated under the temperatures of 100 °C, 200 °C, 300 °C and 400 °C. Cyclohexane was used as an absorption media during the collection process. For the detection of inorganic gaseous pollutants OPTIMA7 was used (MRU, Germany). The temperature of the tubular furnace raised up from 20 to 1,000 °C at a rate of 20 °C/min. Oxygen content for each feeding points simulation was based on actual operation parameters for co-processing LDS in cement kilns at the Beijing Cement Co. Ltd (Beijing, China). The oxygen contents were 6%, 6% and 2% for RM, HTZ-A and HTZ-B&C, respectively. As HTZ-B and HTZ-C have similar working conditions, the same experiments were conducted to investigate the inorganic gaseous pollutants emission.

**Analysis methods**

The chemical compositions of LDS and cement raw material were confirmed using a wavelength dispersion X-ray fluorescence spectrometer (PW2404, The...
Netherlands), while the content of f-CaO in the clinkers was analyzed by the glycerol-ethanol method (AQSIQ 2008), and the properties of DSC during the heating process (10 °C/min) were determined using a STA 449C Jupiter Synchronous thermal analyzer (Netzsch, Germany). Additionally, the microscopic structural characteristics of the clinkers were examined with a Quanta 200 F ESEM (FEI Company, USA) using an accelerating voltage of 20 kV and a magnification of 1,000.

Clinker crystalline phases were identified using a D8-Advance Diffractometer (Bruker Optics, Germany) in the 2θ range at 10–70° in the step of 0.02°, counting by 4 s per step. The radiation was Cu Kα at a wavelength of 0.1541 nm (40 kV).

Compressive strength tests were carried out according to GB/T17671-1999 (AQSIQ 1999). Mortars were prepared by mixing cement with deionized water at a water-to-cement weight ratio of 0.50 and cement-to-sand ratio of 3, were cast in 40 mm × 40 mm × 160 mm molds, and were vibrated during casting to remove air bubbles. The molded pastes were kept at 20 ± 2 °C and a relative humidity exceeding 90% for 24 h, then the molds were removed. The demolded

Table 1 | Chemical compositions of raw mixtures for HTZs and RM simulation (wt %)

<table>
<thead>
<tr>
<th>Sample names</th>
<th>LDS ratio</th>
<th>LOI*</th>
<th>SiO2</th>
<th>CaO</th>
<th>Al2O3</th>
<th>Fe2O3</th>
<th>P2O5</th>
<th>SO3</th>
<th>Cl</th>
<th>MgO</th>
<th>Na2O</th>
<th>K2O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>0%</td>
<td>27.63</td>
<td>15.65</td>
<td>46.70</td>
<td>3.60</td>
<td>2.43</td>
<td>0.00</td>
<td>0.29</td>
<td>0.23</td>
<td>2.61</td>
<td>0.00</td>
<td>0.52</td>
</tr>
<tr>
<td>HTZs-3</td>
<td>3%</td>
<td>27.77</td>
<td>15.30</td>
<td>46.45</td>
<td>3.54</td>
<td>2.66</td>
<td>0.16</td>
<td>0.46</td>
<td>0.23</td>
<td>2.55</td>
<td>0.01</td>
<td>0.52</td>
</tr>
<tr>
<td>HTZs-6</td>
<td>6%</td>
<td>27.92</td>
<td>14.95</td>
<td>46.20</td>
<td>3.47</td>
<td>2.90</td>
<td>0.32</td>
<td>0.63</td>
<td>0.23</td>
<td>2.50</td>
<td>0.03</td>
<td>0.51</td>
</tr>
<tr>
<td>HTZs-9</td>
<td>9%</td>
<td>28.06</td>
<td>14.60</td>
<td>45.96</td>
<td>3.41</td>
<td>3.13</td>
<td>0.48</td>
<td>0.80</td>
<td>0.23</td>
<td>2.44</td>
<td>0.04</td>
<td>0.51</td>
</tr>
<tr>
<td>HTZs-12</td>
<td>12%</td>
<td>28.21</td>
<td>14.25</td>
<td>45.71</td>
<td>3.34</td>
<td>3.36</td>
<td>0.64</td>
<td>0.97</td>
<td>0.23</td>
<td>2.39</td>
<td>0.06</td>
<td>0.51</td>
</tr>
<tr>
<td>HTZs-15</td>
<td>15%</td>
<td>28.40</td>
<td>13.79</td>
<td>45.38</td>
<td>3.25</td>
<td>3.67</td>
<td>0.85</td>
<td>1.20</td>
<td>0.22</td>
<td>2.31</td>
<td>0.08</td>
<td>0.50</td>
</tr>
<tr>
<td>HTZs-18</td>
<td>18%</td>
<td>28.50</td>
<td>13.55</td>
<td>45.22</td>
<td>3.21</td>
<td>3.83</td>
<td>0.95</td>
<td>1.31</td>
<td>0.22</td>
<td>2.27</td>
<td>0.09</td>
<td>0.50</td>
</tr>
<tr>
<td>RM-3</td>
<td>3%</td>
<td>28.89</td>
<td>15.38</td>
<td>45.90</td>
<td>3.54</td>
<td>2.39</td>
<td>0.16</td>
<td>0.43</td>
<td>0.21</td>
<td>2.31</td>
<td>0.01</td>
<td>0.47</td>
</tr>
<tr>
<td>RM-6</td>
<td>6%</td>
<td>29.70</td>
<td>15.24</td>
<td>45.42</td>
<td>3.51</td>
<td>2.37</td>
<td>0.32</td>
<td>0.57</td>
<td>0.18</td>
<td>1.98</td>
<td>0.03</td>
<td>0.41</td>
</tr>
<tr>
<td>RM-9</td>
<td>9%</td>
<td>30.50</td>
<td>15.11</td>
<td>44.93</td>
<td>3.48</td>
<td>2.35</td>
<td>0.48</td>
<td>0.71</td>
<td>0.16</td>
<td>1.64</td>
<td>0.04</td>
<td>0.35</td>
</tr>
<tr>
<td>RM-12</td>
<td>12%</td>
<td>31.38</td>
<td>14.92</td>
<td>44.48</td>
<td>3.44</td>
<td>2.33</td>
<td>0.64</td>
<td>0.85</td>
<td>0.13</td>
<td>1.30</td>
<td>0.06</td>
<td>0.29</td>
</tr>
<tr>
<td>RM-15</td>
<td>15%</td>
<td>32.25</td>
<td>14.74</td>
<td>44.02</td>
<td>3.39</td>
<td>2.30</td>
<td>0.79</td>
<td>0.99</td>
<td>0.10</td>
<td>0.95</td>
<td>0.07</td>
<td>0.23</td>
</tr>
<tr>
<td>RM-18</td>
<td>18%</td>
<td>33.06</td>
<td>14.60</td>
<td>43.54</td>
<td>3.37</td>
<td>2.28</td>
<td>0.95</td>
<td>1.13</td>
<td>0.08</td>
<td>0.62</td>
<td>0.09</td>
<td>0.17</td>
</tr>
</tbody>
</table>

*LOI: Loss of Ignition at 1,000 °C.

Figure 2 | The schematic diagram of cement emissions experiments.
samples were cured in a water tank at 20 ± 2°C for set times, after which their strengths were measured.

The total organic carbon (TOC) of heated sludge samples was determined using a TOC analyzer (Shimadzu, Japan) and the organic matters in the collected samples were identified using a gas chromatography–mass spectrometer (Thermo Focus DSQ, USA).

RESULTS AND DISCUSSION

Effects on cement quality

Burnability

The free lime (f-CaO) was used to imply the burnability of raw mixtures, which also related to cement setting time, soundness, and compressive strength (Nawaz et al. 2016). The influence of the co-processed amount of LDS on the f-CaO content in cement at different feeding points is shown in Figure 3.

As shown in Figure 3, the f-CaO content of HTZs clinkers declined to 0.19% at the co-processing amount of 6 wt%, after which it rose rapidly with the increase of the LDS co-processing amount. Therefore, a small amount of LDS (<6 wt%) could improve the burnability of clinkers, making them easier to sinter. The reduction of the f-CaO content could be related to the introduction of multiple trace elements present in LDS, such as phosphate and heavy metals, which reduce the eutectic point and accelerate the formation of liquids, consequently decreasing the formation temperature of tricalcium silicate (C₃S). If the amount of co-processed LDS exceeds 6 wt%, the introduction of LDS would reduce the burnability of the clinker. This could be explained by changes in ‘three ratios’. The SM, IM, and KH of HTZs samples are shown in Table 2. Although there was a small decline for SM and IM and a small increase for KH when adding a small amount of LDS, the three ratios were still kept at an appropriate value. As LDS increased, KH first exceeded the appropriate range (0.87–0.96), and then became the limiting parameter of clinker sintering. This was primarily because adding LDS introduced excessive amounts of CaO, which could impact the KH and sintering of clinkers.

Comparing HTZs simulation, RM simulation revealed that the f-CaO content did not show the same trend, but instead increased very slowly with increasing co-processing LDS amount. Based on the above analysis, if introducing sludge from HTZs, LDS would not go through feedback control system of cement kiln, which meant the components of mixture raw materials couldn't be controlled. Therefore, the trace elements and excessive CaO would impact f-CaO. However, introducing LDS via RM revealed that the original feedback control system could ensure the correct ratio of raw material components, thereby avoiding the negative effects of component changes. That is the reason RM samples showed a better performance at high LDS co-processing amounts.

Generally speaking, during feeding of LDS via HTZs, a small amount (<6 wt %) of LDS could improve the burnability of raw mixtures. If feeding LDS via RM, no obvious effect on burnability was observed when the co-processing amount was below 9 wt%.

Compressive strength

The compressive strength of all samples was measured after curing for 3, 7, and 28 days. The results are given in Figure 4. According to the standards for common Portland cement (AQSIQ 2007), the compressive strength of ordinary grade cement (42.5R) should be higher than 22 MPa and

<table>
<thead>
<tr>
<th>Samples names</th>
<th>Control</th>
<th>HTZ-3</th>
<th>HTZ-6</th>
<th>HTZ-9</th>
<th>HTZ-12</th>
<th>HTZ-15</th>
<th>HTZ-18</th>
</tr>
</thead>
<tbody>
<tr>
<td>SM</td>
<td>2.59</td>
<td>2.47</td>
<td>2.35</td>
<td>2.23</td>
<td>2.13</td>
<td>1.99</td>
<td>1.93</td>
</tr>
<tr>
<td>IM</td>
<td>1.48</td>
<td>1.33</td>
<td>1.2</td>
<td>1.09</td>
<td>0.99</td>
<td>0.89</td>
<td>0.84</td>
</tr>
<tr>
<td>KH</td>
<td>0.91</td>
<td>0.93</td>
<td>0.94</td>
<td>0.96</td>
<td>0.98</td>
<td>1</td>
<td>1.02</td>
</tr>
</tbody>
</table>

Figure 3 | f-CaO content in clinkers sintered at different feeding points and co-processing amount.
42.5 MPa when curing for 3 and 28 days, respectively. As shown in Figure 4, the compressive strength of the control samples (the ones without LDS addition) was much higher compared with the requirements for the ordinary grade cement.

The results of the comparison showed that the compressive strength of HZTs-3, HZTs-6, RM-3, RM-6, and RM-9 were higher than the control at all hydration ages. For the rest of the samples, the compressive strength was lower than those of the control samples, and decreased with the increasing of co-processing amount. Specifically, a small amount of LDS was beneficial for the development of compressive strength. As shown in Figure 4, the compressive strength of HTZs-6 reached 93.95 MPa, which was much higher than the control one (78.53 MPa). This result was in accordance with the previous results observed for clinker characteristics. Conversely, HZTs-15 and HZTs-18 had lower compressive strength after curing for 28 days than 7 days, which were also much lower than the values of the control. The changes of compressive strength with different amount of LDS are similar to those of f-CaO measurements in Figure 3. As shown in Figure 4, the f-CaO values of HZTs-15 and HZTs-18 were 0.84% and 1.2%, respectively, which were 3.3 and 4.7 times higher than the control. The high levels of f-CaO in HZTs-15 and HZTs-18 were only partially hydrolyzed after curing for 7 days, which caused a reduction in strength. After curing for 28 days, a great deal of hydration occurred and significantly impaired the compressive strength of the samples. For RM simulation, the negative effects of the introduction of excessive CaO could be almost completely avoided. Thus, there was no strength shrinkage phenomenon for RM samples. Nevertheless, the co-processing amount of LDS should still be stringently controlled because of the additive effects of the trace elements. Overall, controlling an appropriate LDS co-processing amount enabled a high compressive strength of cement clinker for both HZTs and RM. The amounts were suggested to be 6 wt% for HTZs and 9 wt% for RM.

**SEM observation of cement paste**

Microstructures of cement pastes were also investigated through SEM after 3 days of hydration (Figure 5). The major constituents of hydrated cement clinker samples were calcium silicate hydrate (CSH) and calcium hydroxide (CH), which were mainly produced from the reaction between Alite and water. Ettringite (CASH) crystals have also been observed in the pores with CSHs (Luo et al. 2014). As shown in Figure 5, CSH, CH, and CASH were all identified in the cement paste samples, but with differences in densities and shapes.

Hollow shells (Hadley grains) were a prominent feature of HTZs-3 paste, which were typical for C3S microstructures. For RM-3, there were large amounts of CASH crystals, which were short hexagonal prism gels with a length of about 0.25 μm. The sufficient amounts of CSH and CASH could increase friction and bridge the intergrain distances (Ylmén et al. 2009), which is the main reason for the high compressive strength of HTZs-3 and RM-3. However, as the LDS addition increased, the CSH gel decreased obviously, while CH crystal was generated in a large amount. As shown in Figure 5, thin platy CH crystals were seen in high abundance in the HTZs-15 paste. Simultaneously, large plate-like CH crystals were observed.
in RM-15, which may due to the continued CH growth in the vicinity of previously formed CH assemblages. The generation of a large amount of CH crystals was closely related to the amount of f-CaO. Furthermore, the different characteristics at microstructures were in accordance with the changes of compressive strength.

**Effects on cement kiln emissions**

In this study, the emission characteristics of major organic gaseous pollutions, as well as inorganic gaseous pollutions, were studied.

**Organic gaseous pollutions**

Because of all HTZs had a temperature >850 °C and residence time >2 s, and turbulence (Yan et al. 2014), organic matters would be completely incinerated. But for RM, sludge would be heated gradually and organic emissions would be generated during this process. This section mainly focused the organic gaseous pollutants for RM feeding process, and MDS was used to be the control sample. To simulate the sludge-heating process at RM and the cyclone preheater, MDS and LDS were heated from 20 °C to 400 °C at 10 °C/min. The changes of TOC content in sludge (Table 3) and organic compounds released during different temperature phases were shown in Figure 6.

As shown in Table 3, adding lime led to an obvious decrease in TOC content. Indeed, the TOC content in LDS samples was only 22–45% of that in MDS. This was mainly owing to CaO hydration reactions and organic matter degradation (Rodriguez et al. 2012), which reduced the microbial (pathogen) contents, hydrolyzed complex molecules. Lime also could make the organic matter be retained in LDS, which may easily be emitted at a lower temperature. For instance, being heated from 20 °C to 200 °C led to
reductions in TOC of 30% and 40% for MDS and LDS. It meant that if co-processing LDS via RM, most organic matters were released and could be treated by the bag filter. The organic matters would not enter the cyclone preheater and the optimum dioxin generation temperature range could be avoided. Accordingly, LDS could have a lower dioxin risk than MDS.

As shown in Figure 6, the types of MDS and LDS emissions differed greatly. Specifically, the major compounds of the MDS samples were mainly fatty acids and chain alkanes, which accounted for 90.38%, 76.65%, 79.30%, and 61.75% of the total emissions at 0–100 °C, 100–200 °C, 200–300 °C, and 300–400 °C. The major compounds released from LDS were amides and nitrogenous heterocyclic compounds, which accounted for 88.53%, 80.74%, 53.37%, and 54.43% of the aforementioned temperature phases, respectively. The fatty acids released from MDS samples were mainly C12–C16 acids such as lauric acid and palmitic acid, which had a relatively high boiling point and could condense in a bag filter. This likely explained the clogging of the bag filter (personal communication). However, LDS emissions consisted of amides, pyrroles, and pyrazines, which had a lower risk of clogging. The pollutant emissions of aromatic hydrocarbons and phenols for LDS were also much lower than for MDS.

In summary, lime drying could decrease the hazardous effects to the environment during the process of co-combustion sludge in cement kilns. Major organic emissions for LDS co-processing were low environmental risk compounds of amides and nitrogenous heterocycles.

Inorganic gaseous pollutions

The prevalent inorganic gaseous pollutions during LDS co-processing were SO2 and NOx, which not only could cause adverse respiratory effects, but also could form

Table 3 | Chemical compositions, heavy metal concentrations and TOC concentration of different samples

<table>
<thead>
<tr>
<th>Items</th>
<th>Moisture</th>
<th>LOI a</th>
<th>SiO2</th>
<th>CaO</th>
<th>Al2O3</th>
<th>Fe2O3</th>
<th>P2O5</th>
<th>Fe2O5</th>
<th>P2O5</th>
</tr>
</thead>
<tbody>
<tr>
<td>MDS (wt%)</td>
<td>86.63</td>
<td>48.46</td>
<td>6.00</td>
<td>8.20</td>
<td>2.10</td>
<td>15.20</td>
<td>7.90</td>
<td>15.20</td>
<td>7.90</td>
</tr>
<tr>
<td>LDS (wt%)</td>
<td>74.42</td>
<td>52.47</td>
<td>4.02</td>
<td>38.49</td>
<td>1.41</td>
<td>10.18</td>
<td>5.29</td>
<td>10.18</td>
<td>5.29</td>
</tr>
<tr>
<td>Items</td>
<td>Cu</td>
<td>Zn</td>
<td>Ni</td>
<td>Cr</td>
<td>Pb</td>
<td>Cd</td>
<td>As</td>
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</tr>
<tr>
<td>MDS (mg/kgDS)</td>
<td>202.76</td>
<td>523.59</td>
<td>30.33</td>
<td>125.45</td>
<td>41.34</td>
<td>1.21</td>
<td>29.52</td>
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<tr>
<td>LDS (mg/kgDS)</td>
<td>61.91</td>
<td>354.86</td>
<td>10.46</td>
<td>28.56</td>
<td>18.20</td>
<td>0.56</td>
<td>11.64</td>
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<td>Temperatures</td>
<td>20–100 °C</td>
<td>20–200°C</td>
<td>20–300°C</td>
<td>20–400°C</td>
<td>20–400°C</td>
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<td>20–400°C</td>
<td>20–400°C</td>
<td>20–400°C</td>
</tr>
<tr>
<td>MDS samples (%)</td>
<td>40.20</td>
<td>28.49</td>
<td>24.05</td>
<td>9.70</td>
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<tr>
<td>LDS samples (%)</td>
<td>18.42</td>
<td>11.29</td>
<td>5.48</td>
<td>3.44</td>
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</table>

aLOI: Loss on ignition at 1,000 °C.

Figure 6 | Organic emissions of MDS and LDS10 during different temperature phase; AH: aromatic hydrocarbons; NHC: nitrogenous heterocyclic compounds; ONC: other nitrogenous compounds.
sulfate or nitrate fine (small) particles (PM2.5) in the atmosphere.

The characteristics of emissions are shown in Figure 7. It could be found that the curves of SO$_2$ and NO$_X$ had similar variation tendency, but the emission amount differed greatly. For variation tendency, all the samples showed a centralized releases phenomenon for NO$_X$ from 400 to 700 °C, which was similar to Chen’s study (Chen et al. 2015). The SO$_2$ generation presented as two phases: 200 to 400 °C, organic sulfur (such as aliphatic thiols RSH, thioethers RSR', sulfur anthracene RSSR', etc.) and a small amount of pyrite in the accumulation of combustion; 900 to 1,000 °C, the decomposition of sulfate (Jin et al. 2014). The total release quantity could be calculated through the integral calculus between concentration and gas volume. For RM simulation, total emission of NO$_X$ and SO$_2$, respectively, were 8.11 and 12.89 mg/g DS. For HTZs, their average values were 7.61 and 4.44 mg/g DS. The results indicated that HTZ-B and HTZ-C had relative lower NO$_X$ (82% of HTZ-A samples), which had close relative to their low oxygen content condition (2%). Besides, the SO$_2$ emission of RM was more than twice of HTZs. That is mainly because of the raw material used to simulate HTZs co-processing had been sintered for 30 min under 900 °C. That is to say, the predominant solid material was CaO for HTZs simulation rather than CaCO$_3$ for RM simulation. The SO$_2$ absorbed by CaO made HTZs simulation presented lower SO$_2$ emission. To study the effect of higher SO$_2$ emission on cement kiln system, actual operation parameters of Beijing Cement Co. Ltd were used. The cement work had a specialized cement manufacturing line to co-processing sludge, whose production capacity, flue gas volume and desulfurization efficiency respectively were about 3,500 t clinker/d, 300,000 Nm$^3$/h and 99%. Combining the results in this study: co-processing amount of 9% and SO$_2$ emission amount of 12.89 mg/g DS. The concentration of SO$_2$ would increase from about 15.0 mg/m$^3$ to 22.9 mg/m$^3$, which still was much lower than the 100 mg/m$^3$ of standard requirements (AQSIQ 2015). Thus, it could be concluded that feeding LDS from RM had a relative higher but acceptable cement kiln emissions.

CONCLUSION

The co-processing of LDS in cement kilns could reduce the amount of sewage sludge to be managed, minimize the environmental risks associated with the sludge and also make the sludge a suitable raw material. Sludge feeding via HTZs and RM is not generally recommended due to inappropriate technical issues. However, lime drying process altered the properties of LDS make it suitable for feeding via RM.

Under the conditions of the present study, the optimum co-processed amount of LDS while feeding through RM was 9 wt%, which was slightly higher than that of feeding through HTZs-6 wt%. Below the optimum co-processing amounts, all cement products showed good performance. Firstly, the f-CaO content of the samples was <0.33%, which was much lower than the requirement of current regulations in China of <1.5%. Secondly, the samples all showed a high compressive strength and HTZs-6 even reached 78.53 MPa. Thirdly, major hydration constituents (CSH, CH, and CASH) were all identified in hydrated clinkers.

For cement kiln emissions, the results showed that RM had higher, but acceptable, cement kiln emissions compared with HTZs. The major organic emissions of RM simulation
were low environmental risk compounds of amides and nitrogenous heterocyclic compounds. As for inorganic gaseous pollutions, NO$x$ and SO$2$ concentration in the emissions of RM simulation, respectively, were 8.11 mg/g DS and 12.89 mg/g DS, compared with the 7.61 mg/g DS and 4.44 mg/g DS for HTZs. However, all the cement kiln emissions concentrations were still much lower than standard requirements (GB4915-2013).

Therefore, feeding of LDS through RM is recommended where active demand on LDS exists and cement kilns have high-end air pollution techniques. The results have both theoretical significance and practical value for China and other countries with similar conditions.

ACKNOWLEDGEMENT

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REFERENCES


