Pol. J. Environ. Stud. Vol. 25, No. 3 (2016), 959-971
DOI: *10.15244/pjoes/61825*

Original Research

The Property of Lime Sewage Sludge and its Influence on Co-Processing in Cement Kilns

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Received: 5 March 2015
Accepted: 16 February 2016

Abstract

In recent years, co-processing lime-dried sludge (LS) in cement kilns has attracted increasing interest in China. However, there are few published studies focused on the effect of sludge properties. In this study, LS properties and their effects on co-processing in a cement kiln were studied by performing experimental analyses and theoretical calculations. The results indicated that the heating value of municipal sewage sludge (MSS) was decreased with lime dosage. By adding 10% lime, the heating value would be almost halved to 7,198 kJ/kg. Heavy metals in LS are much lower than the limit concentration of the standard. Chlorine and sulfur are about 0.06-0.35% and 0.22-0.56%, respectively, which completely meets the relation requirement. Additionally, adding lime promotes the transformation and decomposition of ammonia and protonated amine proteins, nitrogen, and the generation of pyridine nitrogen. Theoretical calculation results show that the maximum co-processing ratio for RS is 4.5%, which can be increased by increasing the addition of a suitable amount of lime (0-16%). 10% with a 6.5% maximum co-processing ratio is suggested as the optimum lime dosage for co-combustion of LS in cement kilns.

Keywords: lime-dried sludge, sludge properties, cement kiln, lime dosage, co-processing

Introduction

Domestic wastewater capacity in China has maintained a rapid growth trend in recent years, and has reached 125 million m^3/d in 2013 [1]. As the by-product of wastewater treatment, the weight of municipal sewage sludge (MSS) has significantly increased. At present, MSS production is about 6 million tons (measured as dry matter) [2], and this total is predicted to reach 12 million tons [3]. As such, the treatment of sludge is of increasing importance in China.

Dewatering sludge is well known as one of the most difficult and important processes in effective MSS treatment and resource utilization. In China, the long-standing and most frequently used dewatering methods are centrifuges, belt pressures, and filter presses. However, in recent years a lime-drying process has been widely adopted in wastewater treatment plants (WWTPs) in

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China. These include the Xiaohongmen and Fangzhuang WWTPs in Beijing, the Jizhuangzi WWTP in Tianjing, and the Jiading WWTP in Shanghai [4-6]. In addition to the lime being used to improve dewatering performances (frequently about 7% weight percentage), numerous other lime concentrations are being used to achieve better dewatering results with a lime-drying process. A 20% lime dosage by weight has been reported as being necessary to reduce sludge moisture from 80.62% to 60% [7]. Then there is a challenge in the subsequent disposal of lime-dried sludge (LS). Landfilling, incineration, agricultural use, and composting have been China's most frequently used sludge disposal methods [8], with landfilling being the most widely used. However, the problems of odor and landfill leachates have resulted in the adoption of increasingly strict standards [9]. As an alternative, incineration has attracted increasing attention. Sludge incineration technologies can be grouped into two categories: mono-incineration and co-combustion technologies [10]. Due to its lower energy consumption and greenhouse gas emissions, the latter has been growing in popularity in China [11]. As reported in our study, co-combustion of sludge in cement kilns has been gradually adopted in cities such as Beijing, Guangzhou, and Hangzhou. In addition, LS co-processing projects have also been reported [11, 12].

Due to LS co-processing programs still in the initial stage, there are few reports specific to this technology. Fortunately, a few developed countries such as the United States and Japan, as well as a number of countries in the European Union, have more experience with co-processing wastes or raw sludge (RS) in cement kilns [13]. A number of common factors have been identified and should be examined. In particular, consideration should be given to the properties of sludge and its overall suitability for co-processing.

Firstly, the moisture content of sludge can affect its stability and convenience in transport, and its storage and kiln-feeding operations. Furthermore, high moisture content may cause a temperature drop and an increase in the evaporated water in cement kilns, which can cause a reduction in product quality and potential overload for the off-gas cleaning devices. A moisture content of less than 30% has been suggested [13-15]. Secondly, heating value is a decisive parameter in determining the amounts of conventional fuel required in substitutions [14, 16, 17]. It is also inextricably connected with the organic matter and moisture contents. The cement industry requires a heating value of greater than 6,250 kJ/kg [16]. Lastly, it is well known that the ash produced in the sludge combustion process is absorbed by the cement clinker product. Since the chemical composition of the sludge may vary (CaO, SiO_2, Al_2O_3, Fe_2O_3), they may affect cement quality. If the weight percentage of sludge ash is greater than 50% and the volume of raw material in sludge ash is greater than 80%, it can be used as a good alternative material [13-15]. Overall, it cannot be overemphasized that sludge properties have significant effects on co-combustion of sludge in a cement kiln.

In contrast to the sludge produced in developed countries, sludge in China has less organic matter (30-50% compared with 60-70% in developed countries) and higher sand content, due to inefficient wastewater treatment systems and the different lifestyles of its residents [18, 19]. Moreover, after the addition of lime, sludge properties differ with respect to their heating values, chemical compositions, and organic forms. Naturally, these differences affect sludge co-processing, i.e., disposal capacity and gas pollutant emissions. Hence, it is important to study lime sludge properties and its influence on co-processing in cement kilns as this technology is being widely adopted.

This study used the gravimetric method to determine the moisture content and organic matter present in the sludge. The water-solid bond strength was also studied by combining thermal gravimetry analysis (TGA) and differential thermal analysis (DTA) [20]. In addition, chemical composition and heating value of sludge were also investigated, as well as the changes in its organic forms. Lastly, this article calculated the theoretical co-processing capacity and the material flow for co-processing LS in cement kilns based on the sludge properties' results.

Materials and Methods

Sludge Sample and Experimental Procedures

An RS sample was collected from a municipal WWTP in Beijing that employed an anaerobic/anoxic/oxic process to remove nitrogen and phosphorus from the wastewater. Its physicochemical characteristics and elemental analysis were shown in Table 1.

The major experimental procedures were as follows: adding CaO (particle diameter <100 mesh) to the sludge at 5% (sample LS5), 10% (LS10), 15% (LS15), or 20% (LS20) of the mass of the RS; mixing rapidly for 5 min and spreading on trays to dry in natural environment; and sampling sludge properties at 30 min, 0.5 d, 1 d, 3 d, 7 d, 14 d, and 21 d. Besides, some theoretical analysis and calculations were done to study the effect of sludge properties on co-processing.

Table 1. Physicochemical characteristics and elemental analysis of the dewatered sludge.

Item	Proximate analysis ^{a}			Ultimate analysis		
	Moisture	Volatile matter	Ash	C	H	N
Value (wt%)	86.6	60.4	35.8	37.06	5.38	5.07

^{a} The values of ash, volatile matter, C, H, N were in dry mass.

Samples Analysis

Moisture Content

According to the standard of Determination Method for Municipal Sludge in Wastewater Treatment Plant (CJ/T 221-2005)[21], the gravimetric method was used to determine the moisture content in each sludge sample, as calculated by Eq. (1):

$$\omega_1(\%) = \frac{(w_1 - w_2)}{w_1} \times 100 \tag{1}$$

…where w_1 is the mass of the sludge sample (approximately 10 g) and w_2 is the mass after drying in an electric oven at 103-105ºC for 2 h.

Volatile Matter and Ash

The gravimetric method was used to determine the release of volatiles from the sludge samples using Eq. (2).

$$\omega_2(\%) = \frac{(w_2 - w_3)}{w_2} \times 100 \tag{2}$$

…where w_3 is the mass of the sludge sample after two continued prepayment steps: first the sludge was dried in an electric oven for 2 h at 103-105ºC and then it was incinerated in a muffle furnace at 550±50ºC for 1 h.

The quantity of ash in the sample was calculated using Eq. (3).

$$\omega_3(\%) = 1 - \omega_2(\%) \tag{3}$$

Elemental Analysis

Samples were vacuum freeze-dried (Scientz-10N) for 24 h at 65 Pa with a cold trap temperature of -50ºC and material temperature of -25°C. Before elemental analysis, the dry samples were ground to powders (<200 mesh), and then the C, H, and N contents were determined using a Vario EL III elemental analyzer (Germany).

Water-Solid Bond Strength

Using the method recommended by Chen [20], the continuous moisture distribution in waste-activated sludge was calculated by combining TGA and DTA (Q600 SDT).

Chemical Composition

The chemical composition of the sludge samples and raw meal were confirmed using a wavelength dispersion X-ray fluorescence spectrometer (XRF) (PW2404), and pretreatment of vacuum freeze-dried also needed as previous.

Heavy Metal

Heavy metal concentration: The heavy metal concentrations in the samples were confirmed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Agilent720ES). The samples were crushed and the heavy metals were extracted by acid ($HF:HClO_4:HNO_3$ = 2:1:1) in a closed microwave digestion instrument (Milestone ETHOS1).

Heating Value

The dry matter heating value in freeze-dried sludge samples were determined using an oxygen bomb calorimeter (IKAC5000). Moreover, the higher heating value (HHV) and lower heating value (LHV) of the samples were calculated using Eqs. (4-5), respectively:

$$\mathrm{HHV} = (1 - \omega_1(\%)) \times \text{dry matter heating value} \tag{4}$$

$$\mathrm{LHV} = \mathrm{HHV} - (\omega_1(\%) \times c \times (373 - T) + \omega_1(\%) \times H_v) \tag{5}$$

… where c is the specific heat of water (4.2 kJ/kg), T is room temperature (298 K), and H_v is the evaporation heat of water (2,260 KJ/Kg).

Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra of the sludge samples were obtained using an FTIR spectrophotometer (Nicolet 5700). Before analysis the wet samples were freeze-dried. Each lyophilized sample was placed on a gold mirror and analyzed using reflection mode in the wave number range 400-4,000 cm^{-1}.

X-ray Photoelectron Spectroscopy (XPS)

Nitrogen speciation of the freeze-dried samples was investigated by XPS with an Axis Ultra DLD (Kratos Analytical). A monochromatic Al Kα X-ray source (1,486.6 eV) was used. In addition, the software package XPS peak 4.1 was used to fit the XPS peaks.

Results

Effect of Lime on Sludge Moisture Content and Water-Solid Bond Strength

Moisture content is very important for a sludge co-processing system. On one hand, moisture content of sludge could decide the sludge-adding pattern. Sludge with high moisture content (close to liquid) should use a special pump, while low-moisture-content sludge (close to solid) is usually best on a chain plate conveyor. On the other hand, high moisture content may affect the heat balance in a cement kiln [22]. Sludge with high moisture

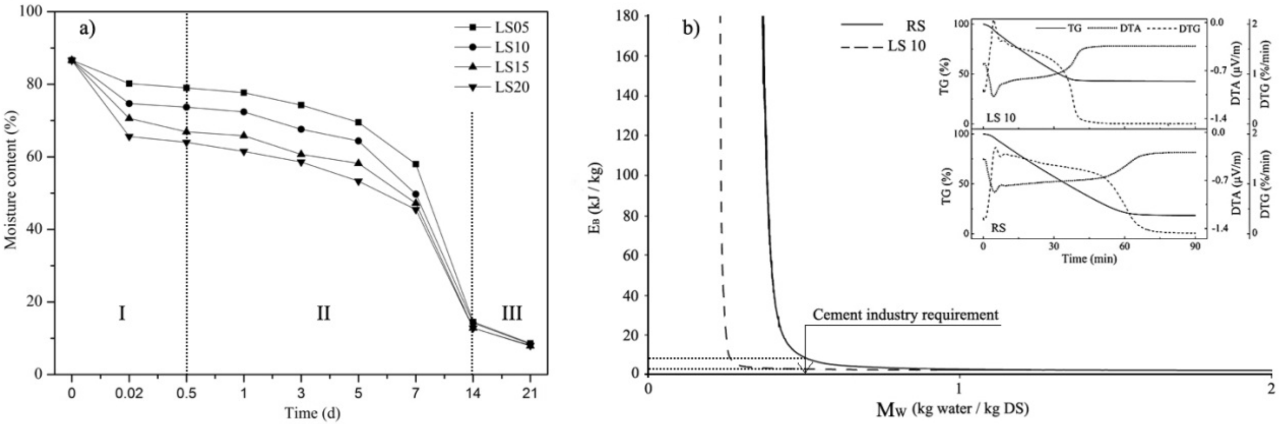


Fig. 1. Effect of lime on sludge moisture content and water-solid bond strength: a) moisture content decreased with time for different lime dosages in LS; b) bond strength versus residue moisture plot for RS and LS10.

content would consume a large amount of energy to water evaporating, and the sludge with lower moisture content could save part of the fuel. As such, moisture content is one of the limiting parameters during co-processing in a cement kiln. Unlike RS, the moisture content of LS has a noticeable relationship with the lime dosage and drying time. Moisture contents in different LS samples were monitored and the water-solid bond strengths of RS and LS10 also were compared, as shown in Fig. 1.

As shown in Fig. 1a, the sludge lime drying process could be separated into three stages: (I) hydration of quicklime, (II) natural air drying, and (III) stabilization. In the first stage, the addition of CaO rapidly increased the ratio of dry matter in sludge samples and its hydration exothermic reaction created a high temperature condition to evaporate the water in the sludge. As a result, the moisture content significantly decreased, and this decrease was positively correlated with lime dosage. Normally, this stage occurred in the mixer, where lime was vigorously mixed with rotary blades. Then the well-mixed sludge was spread out in WWTP to dry naturally, namely by entering the second stage of the drying process. The moisture content continuously decreased at this stage, with an accelerated decrease after three days of drying. At this point, almost all the interstitial water had been removed, leaving the sludge particles exposed to the air. Therefore, specific surface area of sludge samples increased and the water in the sludge evaporated quickly. This evaporation continuously affected the moisture content in stage II. In addition, it was noted that the moisture content could drop below 60% when adding sufficient lime (dosage >10%) and drying for seven days. During the stabilization stage, LS was naturally dried for 14 days. The moisture contents for all experimental conditions were below 20% (mainly comprising surface water and bound water). Thus, a high dewatering efficiency was achieved.

The relationship between water-solid bond strength and residue moisture in the combined TGA and DTA [20] and the results are illustrated in Fig. 1b. Notably, when the residue moisture content was high (greater than 1 kg water·kg DS^{-1}), the bond strength was essentially zero. This high-moisture content exhibited almost the same energy level as bulk water, which meant it was free water in the sludge. However, when the residue moisture content was less than 1 kg water·kg DS^{-1}, the bond strength significantly increased, and continued to increase as the residue moisture content continued to decrease. After adding lime, the bond strength was significantly reduced. As shown in Fig. 1b, when Mw was 0.53 kg water·kg DS^{-1} (35% moisture content), LS had a much weaker bond strength than RS. Therefore, the addition of lime can improve the dewatering efficiency. This is because the lime hydration reaction uses not only the interstitial water but also some portion of the surface water and bound water.

In short, the lower moisture content and weaker water-solid bond strength in LS may have an active effect on the heating balance of cement kilns and the thermal drying process during co-combustion.

Effect of Lime on Inorganic Composition

Effect of Lime on Chemical Composition

The chemical composition of the raw material plays an important role while co processing sludge in a cement kiln. During cement production, these compositions are strictly controlled to a certain range. If the composition of sludge is similar to raw meal cement particles, it could be used as an alternative material in large amounts. If not, then limestone, clay, and ferrous raw materials should be added to guarantee a suitable composition, which means that the sludge should be added from raw mill, and be heated in a cyclone preheater and precalciner before entering the cement kiln. If raw mill is chosen to be the MSS feed point, some problems arise that will affect cement production, such as odorous matter emissions, bag filter overload, dioxin risk, and energy waste. Therefore, a careful investigation of the effect of lime on the composition of sludge is essential with respect to co-processing LS in

Table 2. Chemical compositions of cement raw materials and sludge samples (wt %).

Samples	LOI [a]	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	P_2O_5
RS	65.26	6.09	3.22	5.74	6.09	0.98	6.02
LS5	55.03	4.05	1.65	2.54	41.05	1.49	2.88
LS10	48.80	2.08	1.43	2.26	61.75	1.09	2.09
LS15	42.84	1.85	1.29	1.60	75.15	0.93	1.89
LS20	35.58	1.90	1.28	1.40	88.72	1.10	1.69

[a] LOI: Loss on ignition at 1,000ºC.

cement kilns. XRF was used to determine the chemical compositions of different sludge samples, and the results are shown in Table 2.

From the data in Table 2 it can be found that RS has a high sand content. This may be explained by the low efficiency of the rotational flow grit chamber and incomplete wastewater treatment system processes. Moreover, high ferric salt and phosphorus contents are characteristic of RS. This is because chemical phosphorus removal techniques have been widely applied in WWTPs in recent years in China. Phosphorus can be removed from waste water by forming an iron phosphate precipitate, which may have caused phosphorus enrichment in the excess sludge. In addition, CaO is widely used as an amendment during the mechanical dewatering of sludge; hence, there is also a high CaO content in RS. In general, due to its similar composition with cement material, RS can be used as an alternative material in cement manufacturing [16].

The composition of LS samples is significantly different than that of RS. The weight percentage of CaO increases with the lime dosage, while other components significantly decrease – as is clearly shown in Fig. 2, which depicts the composition of RS as being similar to ferrous raw material, but different from that of raw meal. This means that other materials should be supplemented to guarantee a suitable composition when using RS to produce cement clinker. The addition of lime greatly changed the $CaO–SiO_2–R_2O_3$. In Fig. 2 we see that chemical composition of LS became more similar to raw meal with the increasing lime dosage. In addition, the main replacement for the raw material (CaO) from LS was $Ca(OH)_2$ because its decomposition energy (57.86 kJ/mol) was far less than that of $CaCO_3$ (178.50 kJ/mol) in raw materials. Consequently, this helped conserve the energy required for $CaCO_3$ decomposition [23].

Effect of Lime on Heavy Metal

To ensure clinker quality and reduce pollution emissions, the heavy metal of cement raw material must be monitored and controlled during cement production. For co-processing LS in a cement kiln, heavy metals in sludge as well as mixed raw materials were detected in this work. The results of heavy metal concentrations are shown in Table 3. As shown in Table 3, the heavy metal concentrations were on a low level, which ranged between 1 mg/kg to 130 mg/kg, except for Zn. That's mainly because the sludge was collected from a domestic sewage treatment plant with fewer sources of heavy metal. In addition, heavy metal concentration decreased with the increasing lime dosage. For LS10, the heavy metal could be decreased to only half of RS, which could greatly reduce the risk. It is worth noting that all samples and all kinds of heavy metal were much lower than the requirement (Cd<45 mg/kg, Cr<1,500 mg/kg, Pb <1,500 mg/kg, and Zn<10,000 mg/kg) of "Code for design of sludge co-processing in cement kiln" (GB 50757-2010) [24], indicating that LS was suitable for co-processing in a cement kiln in the aspect of heavy metal.

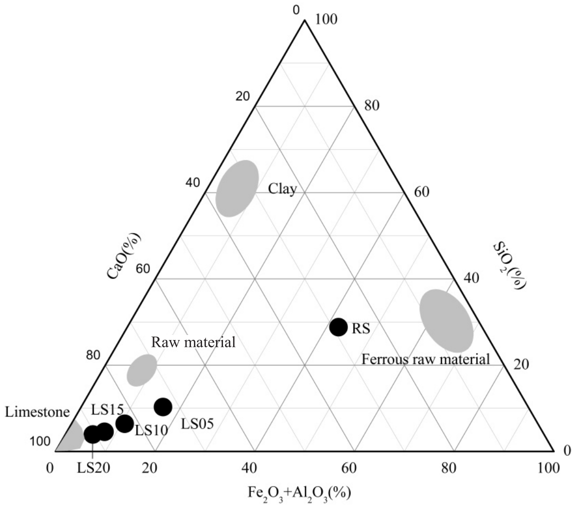


Fig. 2. Chemical composition of ash from sludge samples, clay, raw material, limestone, and ferrous materials in a ternary diagram of $CaO–SiO_2–R_2O_3$.

Effect of Lime on Chlorine and Sulfur

According to the report published by Berkeley Lab [25], chlorine can cause accelerated corrosion of the facility and affect the overall quality of cement and concrete. The concentrations should not be greater than 0.7%. Besides,

Table 3. Heavy metal concentrations of different lime-dried sludge (mg/kg).

Samples	As	Cd	Cr	Cu	Ni	Pb	Zn
RS	26.39	1.07	86.65	125.37	28.69	30.15	717.17
LS05	13.79	0.70	31.86	70.27	11.14	17.36	700.56
LS10	11.64	0.56	28.56	61.91	10.46	18.20	354.86
LS15	10.52	0.55	23.58	53.56	8.93	15.63	384.45
LS20	8.45	0.48	20.97	46.54	7.50	15.08	315.50

Table 4. The effect of lime on chlorine and sulfur (wt %).

Samples	RS	LS05	LS10	LS15	LS20
Cl	0.35	0.29	0.11	0.06	ND
S	0.56	0.48	0.34	0.23	0.22

high concentrations of sulfur may lead to crusting at the cyclone preheater and calciner. Its concentration should be limited, and the common portland cement standard (GB/T 175-2007) [26] requires that sulfur be lower than 3.5%.

The contents of chlorine and sulfur were detected by X-ray fluorescence (PW2404) and a Vario EL III elemental analyzer, respectively. The results are shown in Table 4. Chlorine of all LS samples was lower than 0.3%, which completely meets the requirement. Sulfur concentration of RS was 0.56%, which was much lower than the requirement. What's more, the concentration decreased with the increase of lime. Thus, low chlorine and sulfur of lime-dried sewage sludge should have little effect on co-processing.

Effect of Lime on Organic Matter and Heating Value

For co-combustion of sludge in cement kilns, sludge from WWTPs must be pretreated to reduce the water content. Using waste heat from cement kilns has been recommended to dry the sludge [22]. Furthermore, organic matter can help significantly control pollution odor during the thermal drying process. The heating value, which impacts the heat balance in cement kilns, has a close relationship with organic matter. Hence, the effect of lime on both organic matter and heating value is an important consideration in co-processing.

Fig. 3a shows the regulation of change for organic matter during the stabilization process. As seen in Fig. 3a, organic matter greatly decreases in stage I, while it remains almost unchanged in stages II and III. There are two reasons for the drop during stage I. The first is that the addition of lime increasing the solid content, hence the ratio of organic matter naturally decreases. The second reason is that the hydration reaction created a high-temperature and highly alkaline environment, which may have promoted the volatility and transformation of the organic matter, thus reducing its weight ratio. The increased solids content by the addition of lime is the main reason; its effect on the weight percentage of the organic matter was double that caused by the hydration reaction. However, during stages II and III, the loss of hydrolysis heat over time and the volatility of the organic matter ended, and the growth of the microorganism was prevented due to the highly alkaline environment [27]. Thus, the organic matter content was stable.

In this study, heating value of the sludge samples were also measured, as it was a key parameter in co-processing and was positively correlated with organic matter. As shown in Fig. 3b, the dry matter heating value of RS was 15908 kJ/kg, which was slightly higher than the Chinese average value 11,850 kJ/kg [28], and roughly equal to that of inferior coal (<18,800 kJ/kg). From Fig. 3b, it can be seen that the organic matter and heating value of dry matter decreases as the lime dosage increases. More importantly, the heating value of the dry matter showed a linear correlation with the organic matter. It is well known that LHV, considering the evaporation heat of water, can directly reflect the effect of the heating value on the heat balance in cement kilns. Hence, LHV of the sludge samples was calculated based on their moisture content and dry-matter heating values. The results showed that LHV of RS was -98.2 J/kg, indicating that these conditions were not only unprofitable but also detrimental to the heating balance in the cement kilns. However, the use of lime drying can avoid this negative effect. For example, LHV and HHV of LS10 after drying for seven days were 2,585 kJ/kg and 7,198 kJ/kg, respectively. Co-combustion of LS10 in cement kiln would not impact the heat balance.

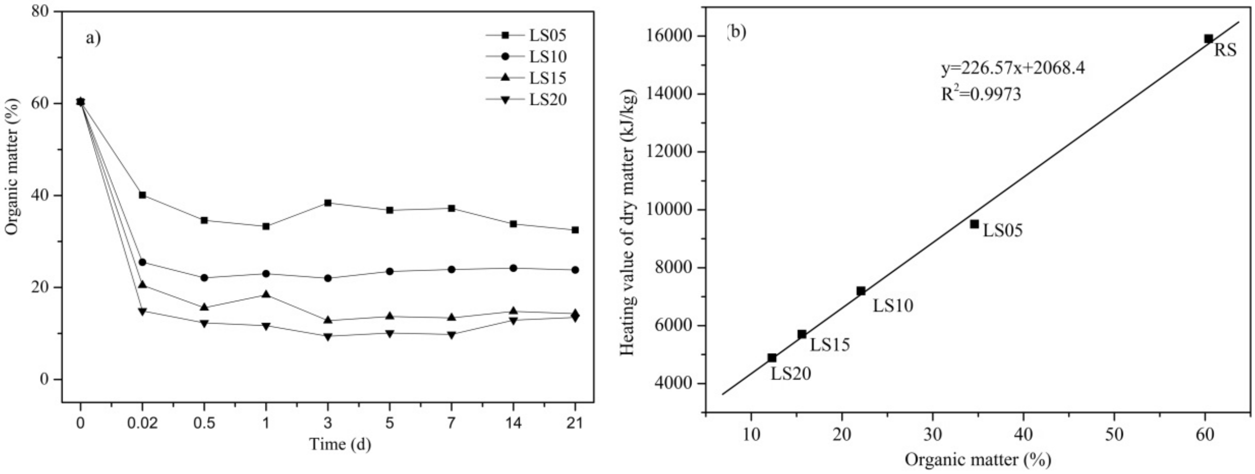


Fig. 3. Effect of lime on organic matter and the heating value: a) regulation of the change in organic matter content for different LS samples; b) relationship between the organic matter content and heating value of dry matter.

However, it is worth noting that the heating value of sewage sludge should be at least 11,000 kJ/kg or more for European cement factories (some cement industry requirements are 13,000 or 15,000 kJ/kg). Compared with the European standard, heating value requirement of the cement industry in China is relatively low. The reason is that the sludge of China has less organic matter (30-50% compared with 60-70% in European) and cannot reach the heating value requirement of using sludge as conventional fuel for European cement factories. Thus, LS could be more appropriately used as cement raw material owing to its large amount of active compositions such as CaO, SiO_2, Al_2O_3, and Fe_2O_3.

Effect of Lime on Organic Matter Form

Because of the noticeable relationship between the form of the organic matter in sludge and the emission of gas pollutants during co-processing, XPS and FTIR to study the organic forms in both RS and LS samples. Figs 4 and 5 show the results of the FTIR and XPS spectra (using RS and LS10 as examples), respectively. In addition, the relative content of different functional groups was identified based on the XPS fitting results by XPS peak 4.1.

FTIR spectra of the sludge samples using previously published data [29, 30]. From Fig. 4 it can be seen that RS contained various organic species, including alkyl compounds, oxyacid hydroxyl acid and its derivatives, ketone, alcohol, and phenol. The lime-stabilized sludge, however, showed four obvious differences. The first was a sharp and strong band at 3,643 cm^{-1}, which was attributed to the O-H stretch vibrations of $Ca(OH)_2$ – the hydration products of CaO. The second difference was the absorbance at 874 cm^{-1}, which became stronger with increases in the lime dosage. And this band to CO_3^{2-} in $CaCO_3$, which had been generated by the reaction . The third difference occurred between 1,550 cm^{-1} and 1,300 cm^{-1}. The strong bands around 1,540 cm^{-1} (amide II band) and 1,455 cm^{-1} (aliphatic C-H stretching and bending) overlapped and became a broad absorption band as lime dosage increased. This was mainly caused by the hydrolysis of protein, which involves the breaking of the complex protein chains, resulting in a decrease of –CO–NH_2 compounds [31]; hence, the weight ratio of the alkane compounds was naturally high. Lastly, the absorbance at 800-700 cm^{-1} became weaker due to the transformation and decomposition of aromatic compounds. The weight decrease of aromatic compounds was active to pollution control during the sludge drying process for co-processing in a cement kiln.

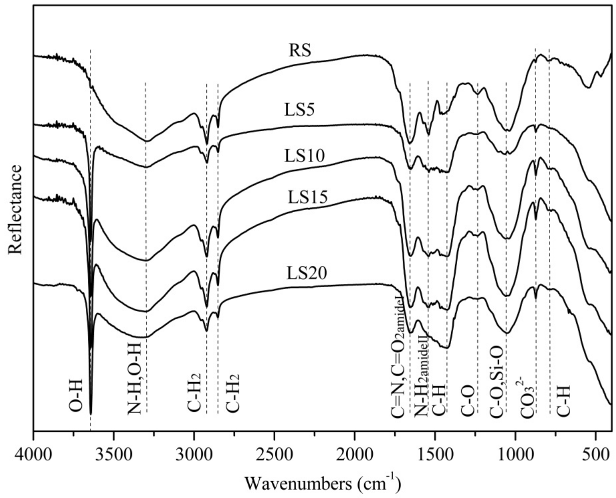


Fig. 4. FTIR spectra of different lime-conditioned sludge samples after being stabilized for 12 h.

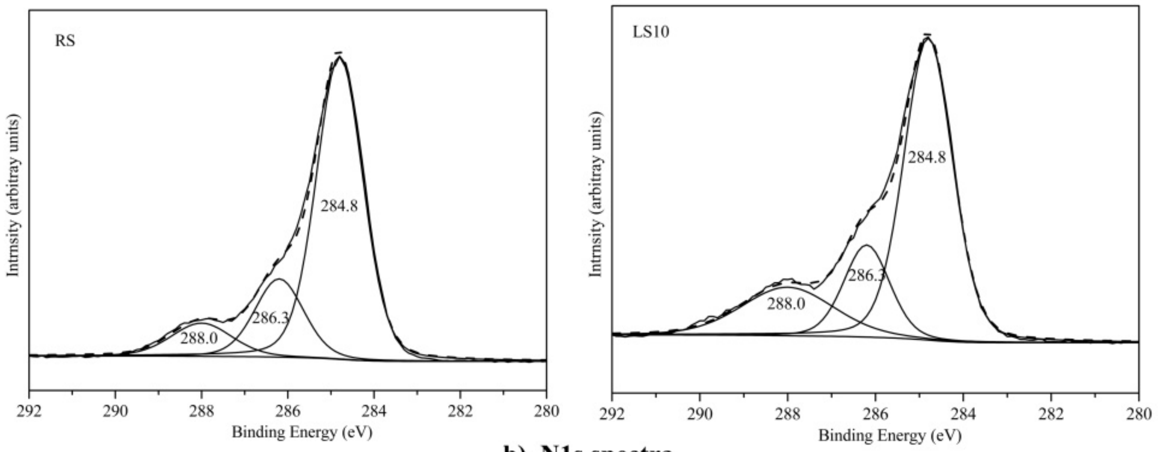
As previously mentioned, XPS was used to analyze the relative content of the different functional groups, and these results are shown in Fig. 5 and Table 5.

As shown in Fig. 5 and Table 5, C–C and C–H were the predominant carbon chemical bonds for RS, and account for the 70% peak area ratio at the C 1s peak. Therefore, it could be identified that the primary carbonic compounds in sludge samples were aliphatic compounds. These findings were also in accord with the FTIR results. In addition, the addition of lime resulted in a marked increase in the relative contents of the C=O and O–C–O compounds. This may be explained by the fact that the nucleophilic addition and dehydration reaction occurred under high-pH and high-temperature conditions.

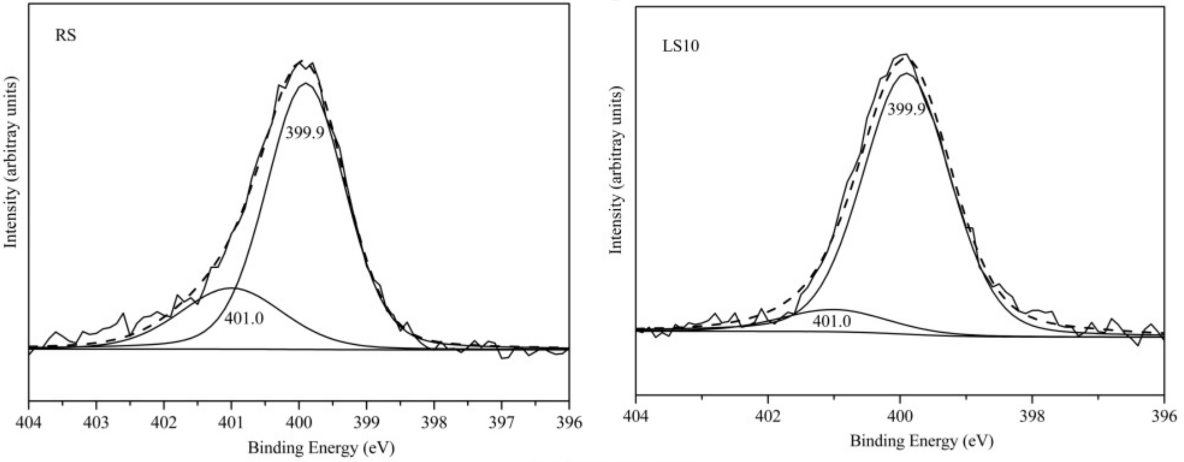
From the O 1s peak, it could be seen that there were few oxides in RS samples. In other words, oxygen in RS mainly existed in the form of organic O. Note that –COOH in RS occupied about 20% of the peak area. In addition, according to the binding energy changes at 530.7 eV and 533.5 eV, the addition of lime not only increased the O in the $Ca(OH)_2$ but also transformed the O in the –COOH to inorganic oxides. Moreover, the O in the O–H group decreased after the addition of lime, perhaps due to the conversion and decomposition of the alcohols and phenols.

In this study, three types of nitrogen were distinguished by XPS [31-33]: Py–N (398.8 eV), Pr–N (399.9 eV), and Q–N (401.0 eV). Py–N corresponds to pyridinic nitrogen. Pr–N corresponds to pyrrolic nitrogen and to pyridinic nitrogen in association with its oxygen functionality, and mainly referred to protein nitrogen. N–Q represents the nitrogen that substituted the carbon in the aromatic graphene structure, leading to slightly more positively charged nitrogen, resembling the quaternary nitrogen in ammonium ions. As shown in Table 5, before lime stabilization, Pr–N accounted for 77.05% of the peak area ratio, and Q–N percentage was 22.95%. In addition, there was almost no Py–N. However, the addition of lime changed the nature of the nitrogen distribution: N–H significantly decreased, the peak area ratios of N–O and C–N increased, and Py–N compounds were generated. These results were mainly due to the high-temperature and highly alkaline environment. Under these conditions, most of the N–H reacted with the O–H to generate NH_3, and ultimately was emitted to the air. Although during the protein hydrolysis process, the chain of amino acids broke,

a) C1s spectra



b) N1s spectra



c) O1s spectra

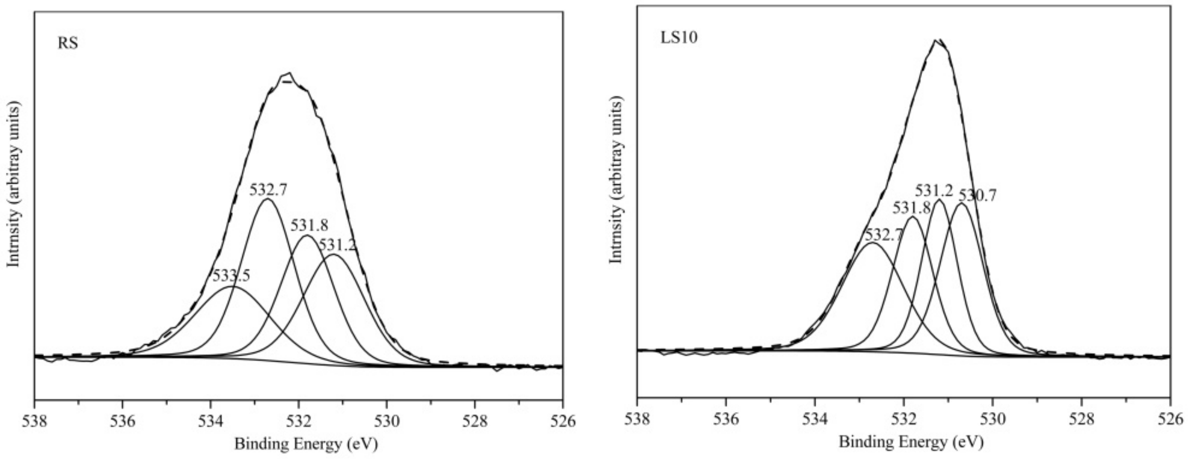


Fig. 5. XPS spectra of RS and LS10 samples after being dried for 12 h: a) C1s spectra, b) N1s spectra, c) O1s spectra.

N–O and C–N remained in the amide or amine. Moreover, the decrease in N–H resulted in an increase in the relative ratio of N–O and C–N. Moreover, pyridinic compounds such as the cyano aromatic compounds may have formed in two different ways: from the dehydrogenation of the amino group present in the proteins and from the addition of nitrogen radicals to the light aromatic hydrocarbons [34].

Note that all these changes could not occur in the absence of CaO. The presence of CaO also meant that typical Ca 2p XPS spectra could also be fitted, and these results are shown in Fig. 6.

The two peaks in the Ca 2p spectrum were assigned to $Ca2p_{3/2}$ and $Ca2p_{1/2}$, respectively [35, 36]. From Fig. 6 it can be seen that the RS core level appeared at 347.50 eV (1.45) and 351.10 eV(1.88) binding energies, respectively, while those for LS10 appear at 346.70 eV (1.57) and 350.30 eV (1.52), respectively. In other words, LS had a lower core level binding energy than RS. This also suggested that the electron density around calcium atoms

Table 5. Relative contents at different binding energy (after peak fitting).

Element	Binding energy/eV	Chemical state	RS	LS05	LS10	LS15	LS20
C	284.8	C–C,C–H	70.78	62.95	63.02	59.16	64.24
	286.2	C–O,C–N	19.16	18.16	17.97	18.36	19.64
	288.0	C=O,O–C–O	10.06	18.89	19.01	22.47	16.11
O	530.7	O in oxides	0.00	33.76	26.98	5.80	42.71
	531.2	O–H	24.68	18.17	22.71	19.34	13.16
	531.8	O=C	24.71	22.26	22.62	30.00	18.19
	532.7	C–O–H,C–O–C,C=O	31.01	25.80	27.69	44.86	25.94
	533.5	–COOH	19.59	0.00	0.00	0.00	0.00
N	398.8	=N–	0.00	7.93	6.37	5.33	10.70
	399.9	N–O,C–N	77.05	92.07	84.91	83.67	84.20
	401.0	N–H	22.95	0.00	8.72	11.00	5.11

in the surface zone was relatively higher in LS [36], which means that Ca probably played an adsorption-bridging role during stabilization. In particular, $Ca(OH)_2$ may have reacted with amino acids to generate organic chelate and clathrate compounds, such as the synthesis of calcium glutamate [37].

Discussion of Results

Effect of Sludge Properties on Co-Processing Capacity

As stated above, the addition of lime had little effect on heavy metal, chlorine, and sulfur, but it had a marked effect on moisture content, heating value, organic forms, and chemical composition. Among the properties, chemical composition would clearly affect the co-processing capacity.

In China, the composition parameters of Chinese cement clinkers have typically been controlled at silica ratio (SM) values of around 1.70-2.70, alumina ratio (IM) values of around 0.90-1.90, and lime saturation (KH) values of around 0.87-0.96 [38, 39]. The compositional parameters in the cement chemistry are determined by Eqs. (6-8).

$$\text{Lime saturation ratio} \quad KH = \frac{CaO - 1.65Al_2O_3 - 0.35Fe_2O_3}{2.80SiO_2} \tag{6}$$

$$\text{Silica ratio} \quad SM = \frac{SiO_2}{Al_2O_3 + Fe_2O_3} \tag{7}$$

$$\text{Alumina ratio} \quad IM = \frac{Al_2O_3}{Fe_2O_3} \tag{8}$$

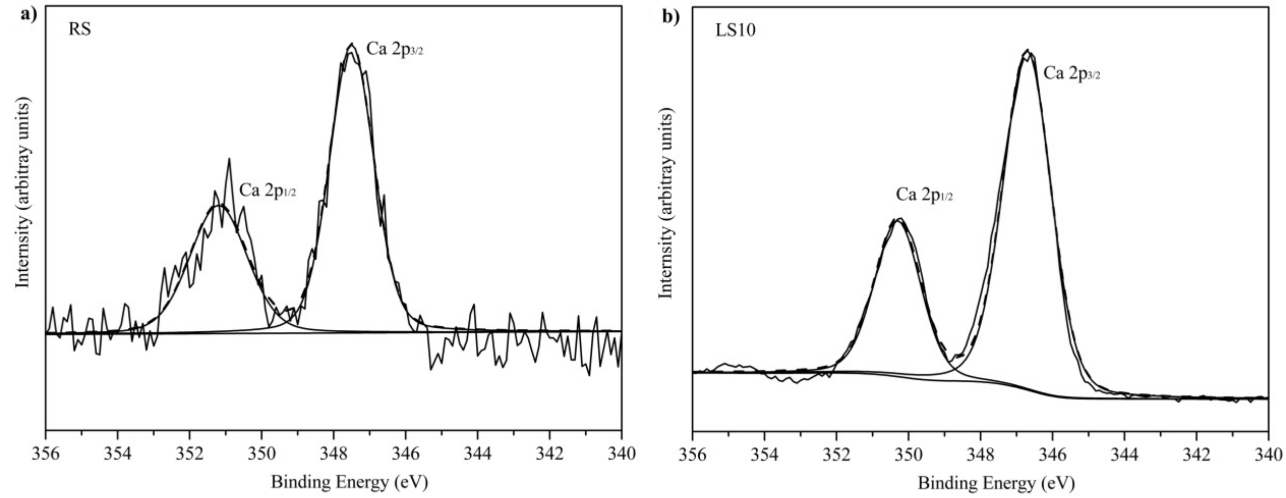


Fig. 6. Ca 2p XPS spectra of RS and LS10: a) raw sludge without CaO and b) raw sludge with 10 wt % CaO.

As clearly indicated by previous results, sludge co-processing can change the composition of the cement clinkers. Furthermore, the effect is increased with the sludge disposal amount. The maximum co-processing ratio would occur when the composition was not being controlled. Thus, by maintaining the composition at KH = 0.90±0.05, SM = 2.50±0.10, IM = 1.50±0.10, based on the data in Table 2, the maximum co-processing ratio can be calculated. Using RS and LS10 as examples, the maximum co-processing ratio was determined based on the results shown in Fig. 7. As illustrated in Fig. 7, SR was the limiting parameter because of the high silt concentration in RS. However, KH was first uncontrolled after the addition of LS. Notably, the co-processing ratio increased from 4.5% to 6.5%. Thus, lime stabilization was proved to enhance the sludge co-processing capacity. As previously discussed, this has been attributed to the adjustment function of lime. However, if this was the case, the co-processing ratio for LS still should not increase above 6.5%. If it did, KH of the cement clinker would rapidly increase and the excess CaO would generate f-CaO, which would degrade the strength of the cement.

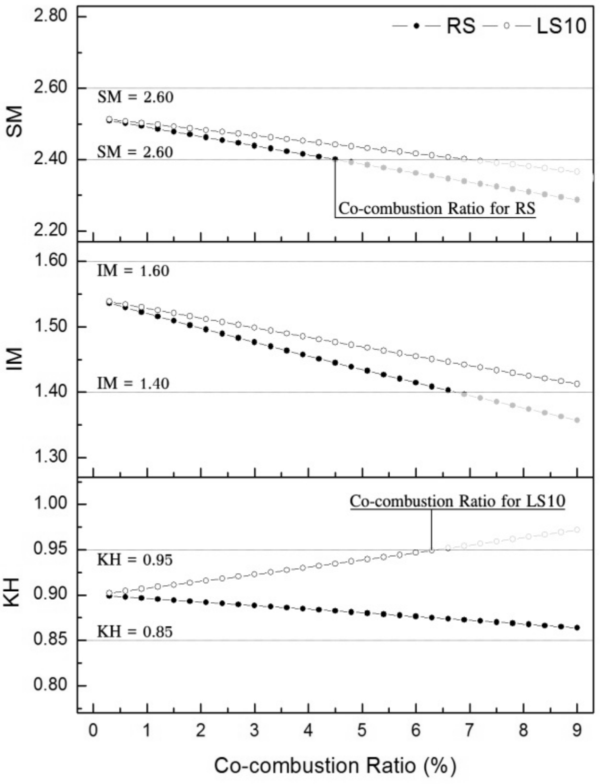


Fig. 7. Effect of the sludge co-processing ratio on clinker composition.

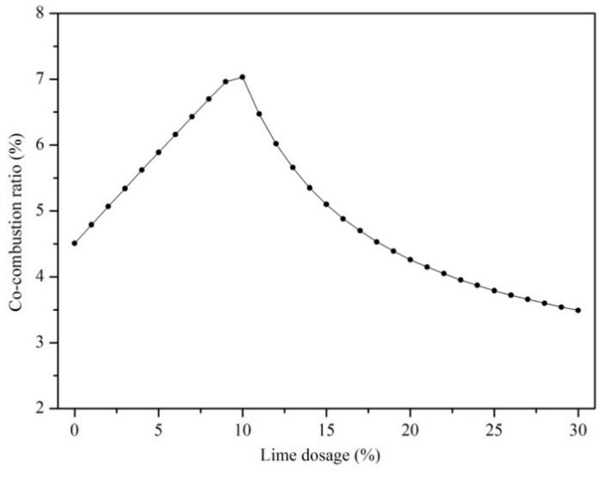


Fig. 8. Theoretical maximum co-processing ratios for different lime sludge samples.

Some theoretical calculations also were performed to study the maximum co-processing ratios for different LS samples. It is well known that the temperature in cement kilns can reach 1,500ºC, after which all the calcium in sludge is in the form of CaO. Thus, the theoretical calculations for the lime-drying process were simplified by adding CaO to the sludge ash. The relationship between lime dosage and the maximum co-processing ratios were determined. As shown in Fig. 8, the maximum co-processing ratios for RS and LS10 were 4.5% and 7.0%, respectively, which were basically the same as the actual calculated values. It also could be concluded that a small amount of lime could play an important active role in improving sludge co-processing ratios. However, the lime dosage should be no higher than 10%, otherwise the co-processing capacity would decrease. In short, 10% lime showed the highest ratio and is suggested as the optimum lime dosage. As stated above, the heating value of LS10 was 7,200 kJ/kg (>6,250 kJ/kg), and the useful composition in ash was 44.47% (>40%). Thus, the properties of LS10 meet industry requirements [13, 16]. In short, 10% is suggested as the optimum lime dosage for co-processing LS in cement kilns.

Analysis of Material Flow for Co-combustion of LS in Cement Kilns

Based on the results in section 2, Fig. 9 shows the material flow for co-processing LS in cement kilns.

For co-processing sludge in cement kilns, moisture content and chemical composition are the limiting factors. As shown in Fig. 9, dewatering sludge to a moisture content of 30% for RS and LS10 required 81.6 g and 64.5 g of water during the thermal process, respectively. In addition, LS had a higher (about 1.25) drying capacity for the same dry conditions. From Fig. 9 it also could be seen that the condensate of LS had a lower organic compound content. As discussed above, the addition of lime promoted the transformation and emission of the organic compounds. In particular, the organic sources decreased, and the organic chelate and clathrate compounds generated during the lime stabilization process had higher boiling points. Thus, there were few materials to be compensated in the condensing tower. In short, LS had a smaller condensed water yield as well as a lower pollution load, which were

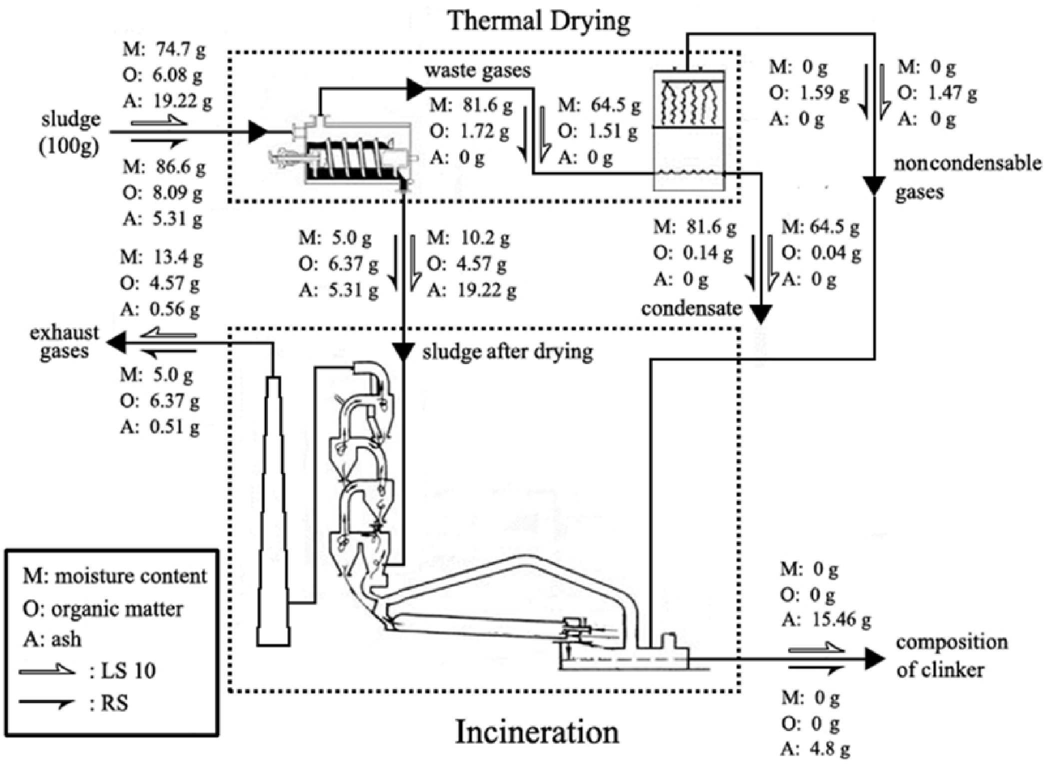


Fig. 9. Material flows for co-processing sludge in cement kiln; materials in gases were calculated by the weight difference method.

conducive for condensed water treatment and gas-phase pollution control.

As also shown in Fig. 9, compared with RS, LS had a lower amount of organic matter transformed to exhaust gases. Combined with previously shown results, LS may also have lower CO_2 and NOx emissions. This is due to the different carbon and nitrogen contents entering the cement kiln, as well as the different nitrogen forms. After adding lime, macromolecule nitrogen-containing compounds resolve into light compounds and NH_3 [34], mainly caused by the decrease in Q–N. In addition, because of nitrogenized reactions, Py–N increased. In particular, the addition of lime resulted in a decrease of $–NH_2$-containing compounds, and an increase in acid amides (–CONH) and nitrogen-containing heterocyclic compounds. In general, the addition of lime caused Q–N to decrease, and Pr–N and Py–N to increase. Furthermore, in the study by Kambara [40], it was believed that the dominant factors controlling NO_x emissions were the amount of volatile nitrogen and the $[NH_3]/[HCN]$ ratio. These NH_3 yields can be replaced by the weight percentage of Q–N. HCN yields are the sum of the weight percentages of Pr–N and Py–N. Thus, adding lime can lead to a lower $[NH_3]/[HCN]$ ratio in sludge and co-processing LS in cement kilns may result in lower NO_x emissions than with RS.

Conclusions

In this study, the effect of lime on moisture content, chemical composition, organic matter, and heating value of sludge was investigated. Based on the results, influences on the co-processing ratio and the material flow during co-processing sludge in cement kilns were also discussed. The main conclusions are as follows.

The addition of lime significantly reduced the moisture content and water-solid bond strength in sludge samples. The moisture content was less than 60% and LHV was greater than 1,900 kJ/kg for all LS samples dried for seven days.

In contrast to RS, LS had a composition more similar to cement raw material. Adding LS changed the relative content of SiO_2, CaO, Fe_2O_3, and Al_2O_3 in cement raw meal, which improved the sludge co-processing capacity in the cement kiln. Heavy metal, chlorine, and sulfur content of LS are on low level and could completely meet the relation requirement.

Different lime dosages to the sludge had different effects on the maximum sludge co-processing ratio. For lime dosage between 0% and 10%, CaO played a role in adjusting the chemical composition, and a higher sludge co-processing capacity could be achieved. However, when the lime dosage was above 10%, a negative effect of the microelements dominated and the maximum sludge co-processing ratio decreased. Lime dosage of 10% is suggested as being the optimum dosage for co-processing LS in cement kilns, and the sludge addition ratio should not be greater than 6.5%.

Adding lime enhanced gas pollution control during co-processing. The aromatic compounds are decreased, and thus positively affect the environment rotation. The addition of lime also promoted the decomposition and transformation of Q–N and the generation of Py–N. Compared with RS, co-processing LS may also achieve lower NO_x emissions.

Acknowledgements

This study was supported by the National Major Science and Technology Project of Water Pollution Control and Management, China (Grant No. 2010ZX07319-001-02).

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