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Short Communication

In-Situ Oxygen Measurement by a YSZ Oxygen Sensor During Sewage Sludge Combustion

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Combustion experiments with in-situ oxygen measurement were performed to evaluate the impacts of oxygen alteration on the incineration of dried sewage sludge. Consequently, temperature was linked to the sludge combustion process, and the effects were mainly shown in the reaction rate of sludge combustion, EMF and θ curves, where the combustion temperature of 800 ℃ decreased much more rapidly than that of 600 ℃, and the combustion process reached a final stable state much faster when a high temperature was adopted than when a low temperature was adopted. The oxygen concentration was an important factor for the combustion of sewage sludge since it significantly influenced the oxidation rates of the organic compounds in the sludge samples. However, the amount of oxygen consumption was not affected by the oxygen concentration if the sludge was well combusted; it directly proportionally changed with the change in sludge amount. This relationship can be potentially used to evaluate the pollution levels in solid wastes, such as sewage sludge, which will be very interesting and worthy of further investigation. Organic carbon in organic compounds was converted into inorganic carbon during the sludge combustion process and resulted in almost 100% of TOC removal. Probably due to the coalescence of the produced phosphorus oxide with non-flammable inorganic substances, the TP levels were much higher than the TOC, TN, TS and TCl levels in the ashes. For the extensive thermal disposal of sewage sludge, measures must be taken to mitigate the potential risk of gaseous toxic emissions produced by these treatments.

Keywords: combustion; sewage sludge; oxygen concentration; sensor; in-situ measurement

1. INTRODUCTION

Inorganic and toxic components in wastewaters form sludge during treatment. The quantity of sewage sludge to be handled has significantly increased due to the upgrade and expansion of wastewater treatment plants, which has become an important environmental issue [1]. Meanwhile, conventional methods (e.g., landfilling, agricultural recycling and disposal to sea) are restricted for the consideration of sustainable development. As a result, combustion, co-combustion, pyrolysis and other thermal disposal of sludge have been widely investigated with the advantages of quantitative reduction and resource recovery, which has resulted in the consideration of potential options for sewage sludge treatment and drawn increased attention [1, 12].

Various combustors were studied and developed for the thermal disposal of sewage sludge and its blends. Multiple hearth, fluidized bed and smelting furnaces were adopted in sewage sludge combustion and its co-combustion with coals and municipal solid wastes [2]. Using a bubbling fluidized bed combustor, the co-combustion of sewage sludge and biomass was improved under oxygen-enriched condition [3]. The oxy-fuel co-combustion of waste sludge and biomass with flue gas recirculation was investigated using a 30-kW circulating fluidized bed, and the results indicated that the combustion reaction was accelerated, the ignition time was shortened by increasing the oxygen ratio, and the oxygen injection rate was optimized with the consideration of stable and economic operation [4-5]. By combining a pressurized fluidized bed combustor and a turbocharger driven by flue gas, a new sewage sludge incinerator was designed, and the operational data for the combustion characteristics of sewage sludge were obtained. With this incinerator, CO, NO_x, and N_2O emissions in the flue gas were less than half of those of a conventional plant; meanwhile, both energy recovery and low environmental impact could be simultaneously realized [6]. To reduce the generation and emission of pollutants, particularly the near zero emission of carbon dioxide during the waste incineration process, a new type of high-intensity combustion technology, oxy-fuel combustion technology, was adopted to design a waste-to-energy incineration power plant in China [7]. The pyrolysis of three types of municipal sewage sludges was performed using a slowly heating and gas sweeping fixed-bed reactor; the gas and oxygen-containing liquid yields correlated with both temperature and volatile matter contents in the sludges [8].

Through the investigation of thermochemical processes of sewage sludge, dehydration, devolatilization, char combustion, and secondary devolatilization were proposed as the reaction mechanism and kinetic model [9]. The activation energy for the combustion of sewage sludge char was estimated to be 130-144 kJ/mol, and the kinetics were controlled by the oxygen transfer processes, including the mass transfer of oxygen to the external surface of the burning char particle, diffusion of oxygen from the external surface into the porous matrix to the surfaces of grains, and diffusion of oxygen into the microporous grains, where a reaction occurs with the carbon char [10]. Oxygen substantially influenced the sewage sludge decomposition [11]: when the oxygen concentration increased from 20 to 80 vol.%, the apparent activation energy increased from 52.30 to 123.16 kJ/mol for the combustion of paper mill sludge in oxygen-enriched air, and the reaction orders of all runs were approximately 1 [12]. Direct combustion of sewage sludge resulted in the presence of water vapor, which reduced the NO_x concentration in the flue gas for low O_2 contents (≤30 vol.%) in the combustion agent but increased the NO_x emission for high O_2 contents (≥40 vol.%); however, excessive water vapor in the combustion atmosphere would promote the formation of some reduced gases [13].

Co-combustion of sewage sludge blend was supposed as an alternative method to improve the thermal performance of the mono-combustion treatment. A series of consecutive first-order reactions was considered for the co-combustion of coal-sewage sludge blend, and no interactions among the components were detected. In the lower-temperature region, the blend reactivity was similar to that of sludge, while in the higher-temperature region, it was similar to that of coal [14]. Blends of sewage sludge with coal gangue and coal had almost identical thermogravimetry profiles under different oxygen concentrations, and the activation energy was 51.2-164.4 kJ mol^{-1}, which depended on the heating rates [15]. Co-combustion of sewage sludge and coffee grounds showed that the comprehensive combustion index strongly depended on the oxygen concentration, and the activation energy increased in response to the increase in oxygen concentration [16]. Co-combustion of waste-water sludge with coal in large power stations was quite popular in Europe, but due to the generation of nitric oxides and sulphur oxides in the combustion process, and since the removal of these components from flue gas needs expensive installations [17], the ratio of sludge in the fuel; processing parameters, such as the air supply, oxygen control, dust emission, and flue-gas volume; and other components should be carefully considered for further popularization of sewage sludge co-combustion.

Based on the thermochemical characteristics of sewage sludge, pyrolysis was suggested for both massive reduction and resource recovery. Gaseous products of municipal sludge pyrolysis under atmospheres of different N_2/CO_2 ratios indicated that the release of volatiles was enhanced, a large amount of CO_2 and NH_3 was generated due to the existence of moisture [18], and the behavior associated to an aerobic process was observed during the pyrolysis of sewage sludge, which was different from combustion disposal [19]. The possibility of oxide reduction reactions in ash was found in the pyrolysis of an anaerobically digested sludge, and the yields of char, H_2O, CO_2, CO, CH_4, H_2 and organic liquids were fitted to a cubic function of temperature [20]. The combustion of sewage sludge can be considered an oxidative pyrolysis, where the decomposition process is accelerated by the presence of oxygen [21]. The mass loss of sewage sludge in both pyrolyzing and oxidizing conditions was substantially affected by the oxygen concentration: it was related to a volatilization process at low temperature and was due to the slow char oxidation at higher temperature, and the activation energy highly depended on the processing extent of oxidative pyrolysis, which indicated a complex multi-step mechanism [22-23].

Thermal disposal of sewage sludge with oxygen-enriched air combustion systems has been employed in some developed countries (e.g. Japan and Germany). The effects of the oxygen concentration on the mono- or co-combustion of sewage sludge were evaluated in a pilot-scale study [11] or even actual industry studies [2], but reports about the kinetic mechanism and reactional characteristics of sludge degradation in an oxygen-enriched atmosphere are rare, especially concerning the in-situ measurement of oxygen contents; this issue is what motivates this work. The increasing trend for the production of sewage sludge has made it necessary to evaluate thermal disposal alternatives such as pyrolysis, combustion and co-combustion [20]. In these processes, the oxygen concentration substantially influences the effects and efficiency of the disposal of sewage sludge since it determines both reaction mechanisms and final products. Due to the urgency of developing appropriate thermal routines with great treatment capacity and negligible environmental concerns, the combustion of sewage sludge with oxygen in-situ measurement was conducted in this work, which is useful for the combustor design and helpful to study the thermal degradation mechanism of sewage sludge in oxygen-enriched atmospheres.

2. EXPERIMENT

2.1 Experimental facility

The experimental facility in this study is schematically presented in Fig. 1. It had a combustion system with a YSZ oxygen sensor. Solid waste (sewage sludge) was combusted in an Al_2O_3 boat in the combustion chamber in the middle of a furnace. The combustion chamber had an atmosphere determined and controlled by the passing of a gaseous mixture, which was prepared from pure gases, and was directly heated to the combustion temperature using electricity. The volume of the combustion chamber was 5.2 L, which resulted in a total gas volume of 5.2 L.

In-situ measurements of the oxygen partial pressure in the combustion chamber were conducted by the equipped tube-shaped YSZ oxygen sensor with its reference electrode exposed to a flowing gaseous mixture with known oxygen concentration. During each combustion experiment, the oxygen sensor fixed at the medium of the chamber was exposed to the combustion gas, which was prepared by diluting a parent gas (pure O_2) with another balance gas. Gold electrodes worked as both sensing and reference electrodes of the oxygen sensor, which were taken out by two Au wires (diameter of 0.2 mm) through the Al_2O_3 tube and contacted with the high-resolution voltmeter 34410A for electro-motive force (EMF) measurement. The combustion experiment was progressing until a steady state obtained by the YSZ oxygen sensor. The temperature in the combustion chamber was given by a K-type (NiCr-NiAl) thermocouple near the sensing electrode of the oxygen sensor. The pressure in the combustion chamber was obtained by a pressure gauge connected to the gas inlet tube of the chamber. All electronic signals were recorded using a personal computer via a data logger.

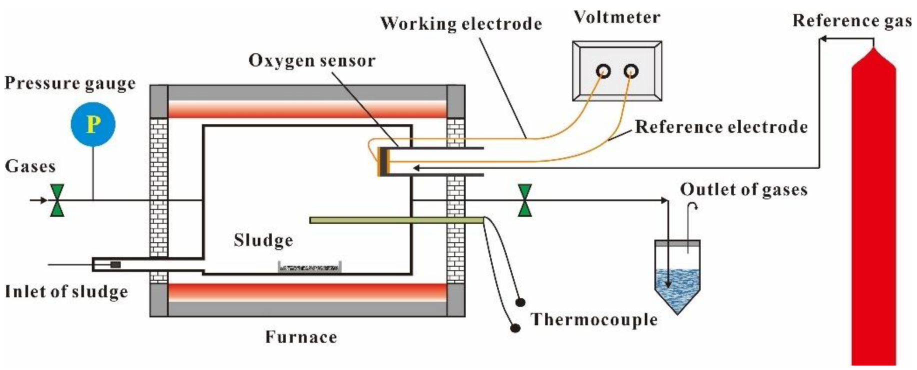


Figure 1. Experimental setup for the combustion of sewage sludge with in-situ oxygen measurement

2.2 Experimental materials

To reduce the effects of moisture on the combustion process, dried sewage sludge was used in this work, and it was prepared by drying the active sewage sludge at 105 ℃ for 8 h, which was supplied by Xiao Jiahe Wastewater Treatment Plant (Chongqing, China). Properties of the dried sewage sludge were obtained by direct analysis of this sample, and the results are presented in Table 1. Here, the total carbon (TC) and total inorganic carbon (TIC) were determined using an Analytic Jena Multi N/C 3100

Analyzer (Germany). The nitrogen content in the dried sewage sludge was determined using an Elementar vario El cube (Germany); the phosphate, sulfate and chloride contents were determined by ion chromatography (ICS 1100, American) after a digestion pretreatment. The ash content of the dried sludge was determined by recording the weight of the remaining portion of the sample after it had been burned in a muffle furnace at 575 °C for 8 h [1].

Table 1. Properties of dried sewage sludge

Total carbon (TC) (mg/g)	123.72
Total organic carbon (TOC) (mg/g)	103.31
Total nitrogen (TN) (mg/g)	24.62
Total phosphate (TP) (mg/g)	9.87
Total sulfate (TS) (mg/g)	3.55
Total chloride (TCl) (mg/g)	6.17
Ash content (% w/w)	45.14

2.3 Experimental procedures

Table 2. Combustion experiments of sewage sludge with oxygen in-situ measurements

Entry	Temperature (℃)	Sewage sludge amount (g)	Combustion gas		Reference gas
			Oxygen concentration (%)	Balance gas	Oxygen concentration (%)
1	600	1.0	75	N_2	0.2
2	700	1.0	75	N_2	0.2
3	800	1.0	75	N_2	0.2
4	700	2.0	75	N_2	0.2
5	700	3.0	75	N_2	0.2
6	700	1.0	60	N_2	0.2
7	700	1.0	45	N_2	0.2
8	700	1.0	30	N_2	0.2
9	700	1.0	15	N_2	0.2
10	700	1.0	60	He	0.2
11	700	1.0	60	CO_2	0.2

A certain amount of dried sewage sludge was weighed and placed as a thin film on the bottom of a clean Al_2O_3 boat for sufficient exposure to the combustion atmosphere. Before sewage sludge feeding, the combustion chamber was electrically heated by the furnace, and the prepared combustion gas was slowly passing through it. Once the temperature reached the setup value, the inlet and outlet valves of the combustion gas were closed. After this stationary state was maintained for several minutes, the Al_2O_3 boat containing the sludge sample was very quickly fed into the combustion chamber by a piston. During the combustion process, the oxygen partial pressure in the combustion chamber was in-situ measured by the equipped YSZ oxygen sensor. When the experiment was completed, the combustor was cooled, and the ash was taken out and directly analyzed.

Two groups of experiments were conducted in this work to investigate the combustion of sewage sludge (Table 2). The first group aimed to study the effects of the temperature (Entries 1-3) and sludge amount (Entries 2, 4-5) on the combustion process. The second group focused on studying the combustion gas, including the effects of the oxygen concentration (Entries 2, 6-9) and balance gas (Entries 2, 10-11) on the combustion of sludge.

2.4 Experimental method

The YSZ oxygen sensor with gold sensing and reference electrodes in this study is written as

O_2(Combustion chamber), Au | YSZ | Au, O_2(Reference gas) (1)

Before feeding sewage sludge into the combustor, the electro-motive force (EMF) of the oxygen sensor E_0 represents the oxygen partial pressure of the combustion gas $(P_{O_2})_0$.

$$E_0(\text{Oxygen sensor}) = \frac{RT}{4F}\ln\frac{(P_{O_2})_0}{(P_{O_2})_r} \quad (2)$$

Using formula (2), oxygen partial pressure of the reference gas $(P_{O_2})_r$ can be obtained as shown in formula (3).

$$\ln(P_{O_2})_r = \ln(P_{O_2})_0 - \frac{4F}{RT}E_0 \quad (3)$$

When the sewage sludge sample was quickly fed into the combustor, the combustion of the sludge began, and the oxygen partial pressure in the combustion chamber at any time $(P_{O_2})_t$ could be represented by the corresponding E_t in formula (4). In formula (4), k_tT is the actual temperature in the combustion chamber, which was determined by the thermocouple, k_t is the alteration rate of temperature caused by the combustion of sludge, which was an exothermal reaction.

$$E_t(\text{oxygen sensor}) = \frac{R(k_tT)}{4F}\ln\frac{(P_{O_2})_t}{(P_{O_2})_r} \quad (4)$$

According to Table 2, a reference gas with the same oxygen concentration was used in each experiment, so formula (5) was obtained based on formulas (3) and (4).

$$\ln\frac{(P_{O_2})_t}{(P_{O_2})_0} = \frac{4F(E_t - k_tE_0)}{R(k_tT)} \quad (5)$$

If θ is defined as the ratio of oxygen amount at any time in the combustion chamber to that before sewage sludge feeding, formula (6) is obtained.

$$\theta = \frac{k_p(P_{O_2})_t}{(P_{O_2})_0} = k_p\exp[\frac{4F(E_t - k_tE_0)}{R(k_tT)}] \quad (6)$$

The pressure in the combustion chamber constantly increased with the progress of sludge combustion because gaseous products of the combustion reaction were kept in the combustor until it was cooled. The rate of change of the pressure in the combustor was reflected by k_p, which was determined by the pressure gauge in Fig. 1. Based on formula (6), the ratio of oxygen consumption at any time during the process of sludge combustion is obtained as shown in formula (7).

$$\Delta\theta = 1 - \frac{k_p(P_{O_2})_t}{(P_{O_2})_0} = 1 - k_p\exp[\frac{4F(E_t - k_tE_0)}{R(k_tT)}] \quad (7)$$

The total oxygen amount in the combustion chamber before feeding the sludge sample into it can be directly obtained by the oxygen concentration and volume of the combustion gas. According to formulas (6) and (7), the amount of oxygen consumption at any time during the combustion experiment can be compute; thus, combustion processes of sewage sludge can be investigated.

3. RESULTS AND DISCUSSION

3.1 Combustion of sewage sludge under different conditions

Fig. 2 shows the effects of temperature on the combustion of sewage sludge. According to Fig. 2A, the oxygen sensor exhibited similar EMF curves when the same amount of sludge was combusted at 600 ℃, 700 ℃, 800 ℃. As previously mentioned, prior to sewage sludge feeding, the combustion chamber was maintained at a notably stationary state for several minutes. The oxygen concentration at this prior state was irrelevant to the combustion reaction, which can be conveniently calculated using formula (2), and the obtained value for each entry was consistent with the adopted value of 75%. This consistency strongly indicates the feasibility of oxygen in-situ measurement in this sewage sludge combustion system by a YSZ oxygen sensor.

When the sewage sludge sample was quickly fed into the combustion chamber after the short prior state, the oxidative reaction of the sludge started and resulted in the rapid decrease in oxygen content in the combustor. This alteration was evidenced by the fast-changing EMF curves since the input of sludge samples. With further oxidation of sludge as time went on, each EMF curve tended to a slowly decreasing speed and finally attained a relatively stationary state, which implies a stable oxygen content in the combustor due to the completion of sludge oxidation. The decrease in oxygen content in the combustor caused by the sludge combustion was also manifested by the value of θ (Fig. 2B), which was defined as the ratio of oxygen amount at any time to that at the prior state. In Fig. 2B, the corresponding θ curves evolved from almost 100% to different stable values. According to formula (6), at the prior state of each experiment, oxygen was not consumed at all because the combustion did not begin. As a result, approximately identical ratios of 100% were observed in this prior stage.

Based on thermodynamic fundamentals, the amount of gaseous substance reciprocally changes with temperature. In this set of experiments (Entries 1, 2 and 3), the mole of the combustion gas decreased with increasing temperature because of the fixed gas volume in the combustor. Accordingly, the total oxygen amount in the combustor decreased in inverse proportion with the increase in temperature. As a result, θ had different values at the final stable state in each curve. Using formula (7), $\Delta\theta$ can be obtained at any time during the progress of sludge combustion. Using $\Delta\theta$ at the final stable state in each entry and considering the inverse proportional relationship between the total oxygen amount and the combustion temperature, very similar amounts of oxygen consumption for each entry were obtained and are shown in Fig. 3. These results were consistent with the processing conditions for the oxidation of sewage sludge. In this set of experiments (Entries 1, 2 and 3), identical amounts of dried sewage sludge with relatively identical components were fully combusted in the combustor. Consequently, a consistent amount of oxygen was demanded for each entry.

According to formulas (2)-(7), temperature was an important parameter related to the EMF value of the oxygen sensor, which might cause different prior EMF levels (E_0) when different combustion temperatures were adopted. If ΔE is defined as the difference in EMF value between the prior state and the final stable state, it increases with increasing temperature as implied in Fig. 2A. Combined with the above explanation of the EMF and θ alteration from the prior state to the final stable state, temperature affected the sludge combustion reaction, but it did not alter the amount of oxygen consumption in this set of experiments. The effects of temperature is mainly shown where the combustion reaction rate of sewage sludge, EMF and θ curves with the combustion temperature of 800 ℃ decreased much rapidly than that of 600 ℃. Although the sewage sludge sample could be well combusted with the three experimental temperatures, the combustion process reached the final stable state much faster when a higher temperature was adopted.

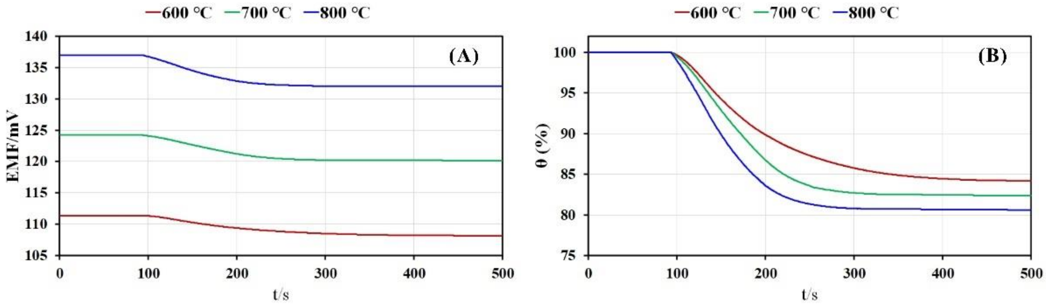


Figure 2. Combustion of sewage sludge at different temperatures (A: Electro-motive force detected by the oxygen sensor; B: θ values calculated by formula (6))

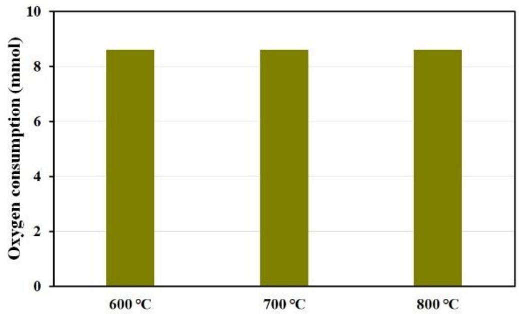


Figure 3. Amount of oxygen consumption for the combustion of sewage sludge at different temperatures

The combustion reaction of dried sewage sludge was mainly caused by the oxidation of organic substances that it contained. To further understand the relationship between the sludge amount and the corresponding oxygen consumption, two other experiments (Entries 4 and 5) were conducted, where the times of combusted sewage sludge were compared with Entry 2, and the results are shown in Fig. 4. In Fig. 4A, since the same combustion gas was used in each entry, very stable and almost identical EMF levels for the prior states were observed. However, with the increase in sewage sludge amount, the EMF curves decreased, which might be attributed to more oxygen being consumed to oxidize the additional organic compounds caused by the increased sludge amount. It was interesting that ΔE (defined as the difference in EMF between the prior state and the final stable state) did not proportionally behave while the sludge amount increased from 1.0 g to 2.0 g and 3.0 g. The results indicate that there is no simple linear relationship between EMF value and oxygen content in the combustor, which can be explained by formulas (2) and (3). However, the corresponding values of θ in Fig. 4B showed proportional alterations with the change in sludge amount.

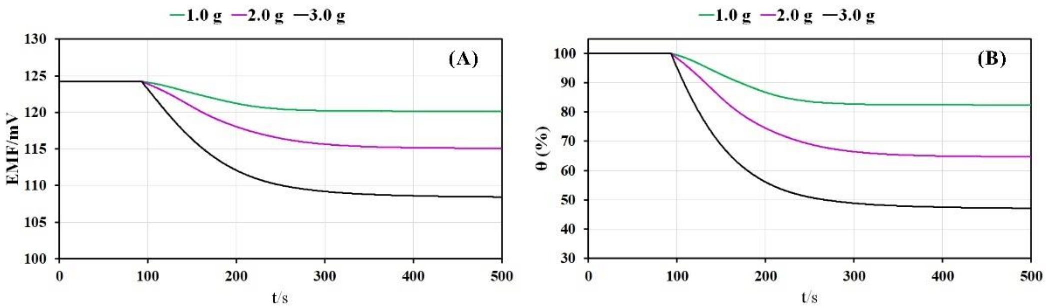


Figure 4. Different amounts of sewage sludge were combusted at 700 ℃ (A: Electro-motive force detected by the oxygen sensor; B: θ values calculated by formula (6))

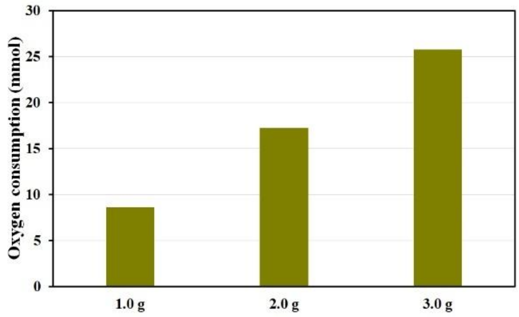


Figure 5. Amount of oxygen consumption for the combustion of sewage sludge with different amounts at 700 ℃

Using the Δθ values obtained by formula (7), the amount of oxygen consumption for each entry was calculated and is shown in Fig. 5. In Fig. 5, the amount of oxygen consumption increases with direct proportion to the increase in sludge amount. These results indicate that the components were well distributed in the dried sewage sludge samples, and the sludges were well combusted in the experiments. Combined with Fig. 3, the oxygen consumption mainly depended on the amount of sewage sludge. As analyzed above, oxygen was consumed to oxidize the organic substances in the sludge, so the amount of organic substances (named TOC_1) can be calculated by the corresponding values of oxygen consumption. The obtained TOC_1 was consistent with the TOC value in Table 1. These results imply that the directly proportional relationship between oxygen consumption and sludge amount can be potentially used to evaluate the pollution levels of solid wastes such as sewage sludge, and it will be very interesting and worthy of further investigation.

3.2 Effects of the combustion gas on the sewage sludge combustion

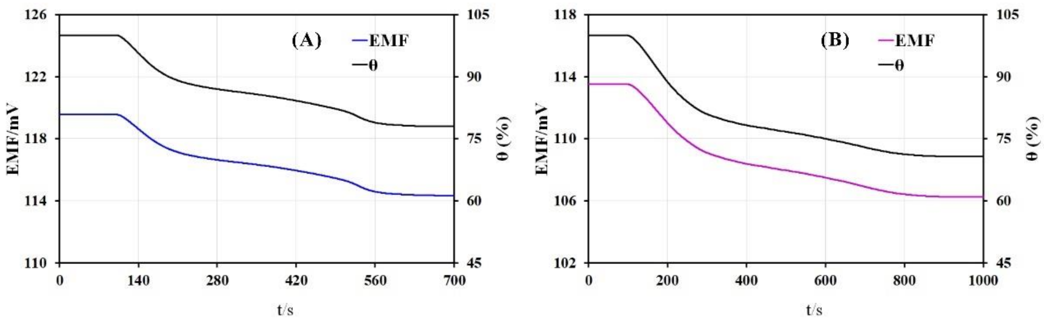
Sewage sludge oxidation occurred in the combustion chamber with a certain volume (5.2 L) of gas in it. As a consequence, the total oxygen amount in the combustor was determined by the oxygen concentration of combustion gas. Fig. 6 presents the experimental results of sewage sludge combustion in atmospheres with different oxygen concentrations. In Fig. 6, since sludge samples were fed into the combustor, EMF curves decreased and finally tended to a relatively stable state because of the end of combustion reaction. Unlike Fig. 2A and Fig. 4A, a plateau appeared in Fig. 6 and separated each EMF curve into three parts. The first part started when the sludge sample was fed into the combustor until appearance of the plateau, when each EMF curve rapidly decreased. The second part was the plateau stage with slowly decreasing EMF as the combustion reaction continued. The third part followed the plateau, where each EMF curve recovered the rapid decreasing rate and gradually tended to the final stable state, which implied the end of combustion. Correspondingly, the θ curves exhibited similar behaviors in Fig. 6.

The change in EMF and θ curves originated from the change in oxygen content in the combustor. The three parts in both curves probably indicate three stages for the combustion reaction. In this study, after several minutes of the prior state, the sludge sample was quickly fed into the combustion chamber, and the organic compounds on the surface of the sludge particles in contact with the surrounding oxygen were immediately oxidized. As a consequence, oxygen amount in the combustor decreased drastically, which might cause the rapidly decreasing EMF and θ values in the first stage. With the rapid sludge oxidation in this first stage, the gaseous products entered the gaseous phase, whereas the solid products and unreacted mineral compounds accumulated on the surface of sludge particle. This build-up hindered the mass transfer of oxygen into the interior part of the particles, further oxidation was restricted, and the oxygen amount in the combustor decreased slowly, which might cause the appearance of a plateau in the EMF and θ curves as shown in Fig. 6. Dennis [10] also reported that oxygen transfer processes strongly restricted the combustion kinetics of sewage sludge. During the plateau stage, organic substances in the interior part of the sludge particles slowly oxidized due to the suppressed oxygen transfer process. Probably since the gaseous products constantly went out of the building obstacles in this plateau stage, the restriction of the build-up disappeared after a long oxidation reaction time. As a result, the mass transfer of oxygen from the external surface of the burning particles into the porous matrix to the surfaces of interior grains was recovered, and further oxidation of the interior organic compounds rapidly occurred. This was the third stage, where oxygen amount decreased with a faster rate than that in the plateau stage. With the continuous sludge combustion, the remained organic compounds in the interior part decreased, which caused the amount of oxygen consumption to gradually decrease, so the oxygen content in the combustor slowly changed until it eventually tended to a relatively stable state, which indicates the end of the combustion.

In this set of experiments, the same amount (1.0 g) of dried sewage sludge was adopted each time, which indicates that the same amount of oxygen is required if the sludge samples are fully combusted. Probably because of the decreased oxygen concentration in the combustor, the oxygen mass transfer was substantially restricted, which made the combustion take much more time to reach the final stable state. The increased ΔE and $\Delta\theta$ with the decrease in oxygen concentration in Fig. 6 can be explained by the increased difference in oxygen concentration between the combustor and the reference gas; formulas (4) and (6) also show these results. The amounts of oxygen consumption for this set of experiments (Entries 2, 6, 7, 8 and 9) were calculated based on $\Delta\theta$ and the corresponding oxygen concentration and are shown in Fig. 7. According to Fig. 7, each entry consumed an almost identical amount of oxygen for the combustion, although different oxygen concentrations were used, and the values are consistent with those in Figs. 3 and 5. These results indicate that the oxygen concentration is an important factor for the combustion of sewage sludge, since it significantly influences the oxidation rates of the sludge samples. However, the amount of oxygen consumption was not affected by the oxygen concentration, and it was mainly determined by the amount of sludge combusted in each entry. Combined with the experimental results at different temperatures, the efficient combustion of sewage sludge is proposed in an atmosphere with a reasonable oxygen concentration and at a relatively high temperature.

Probably due to the large amount of oxygen in the combustor as high-oxygen-content combustion gas (75%) was adopted, the oxidation reaction of organic substances and mass transfer processes of oxygen were significantly promoted, and the impact of the oxygen mass transfer was not noticeable, which caused the absence of plateaus in the EMF and θ curves of Entry 2 in Fig. 2. The oxygen concentration was reported by many other studies as an important factor for sewage sludge combustion. Based on the study of combustion reaction of two types of sludge, Zhang [24] reported that the major mineral compounds in sludge (calcium oxide, phosphorus oxide and aluminosilicate) mainly underwent coalescence to form large molten agglomerates or condensed particles at low oxygen contents, and increasing the oxygen content mitigated the diffusion resistance in the ash layer and improved the combustion reaction of sludge. With the study of the burning process of sewage sludge in O_2/CO_2 atmosphere, Niu [25] reported that the average comprehensive combustion indices in the $40\%O_2/60\%CO_2$ atmosphere were approximately 2 times more than that in the $21\%O_2/79\%CO_2$ atmosphere [26]. Furthermore, combustion rates of petrochemical wastewater sludge in air (O_2/N_2) and oxy-fuel (O_2/CO_2) atmospheres increased with the increase in O_2 concentration [27]. By increasing the oxygen concentration from 20% to 70%, the combustion performance of the blend of sewage sludge and water hyacinth was improved, and the mass loss rate increased [28]. The combustion of municipal solid waste in south China showed that a high oxygen concentration significantly improved the combustion characteristics [29].

Oxygen was balanced by another gas to prepare the combustion gas in this work. Fig. 8 shows the effects of balance gas on the combustion experiments (Entry 2, 10 and 11). Since identical oxygen concentrations and equal amounts of sewage sludge were adopted in each entry, very close EMF levels were observed at the prior state and final stable state. As a consequence, almost the same amount of oxygen was consumed in each entry. Probably due to the inertness of nitrogen and helium gas, EMF and θ curves of Entry 2 behaved similarly with that of Entry 10. In Entry 11, carbon dioxide worked as the balance gas and the main product of the combustion reaction, so some different changes in the EMF and θ curves were observed.



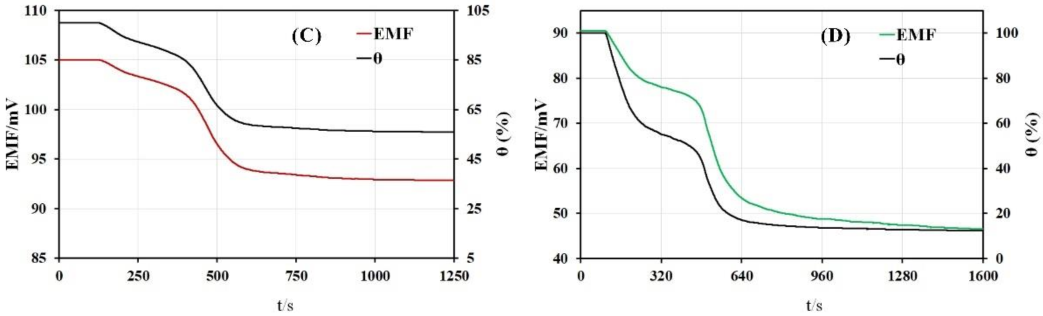


Figure 6. Combustion of sewage sludge with different oxygen concentrations at 700 ℃ (A: 60%; B: 45%; C: 30%; D: 15%)

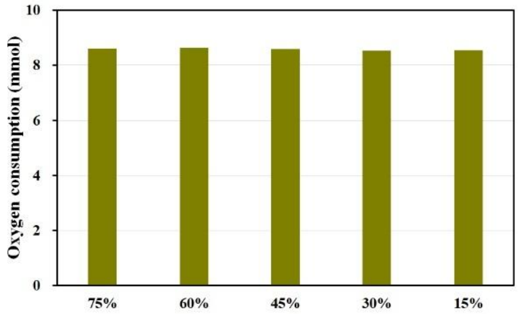


Figure 7. Amount of oxygen consumption for the combustion of sewage sludge with different oxygen concentrations at 700 ℃ (Entry 2: 75%; Entry 6: 60%; Entry 7: 45%; Entry 8: 30%; Entry 9: 15%)

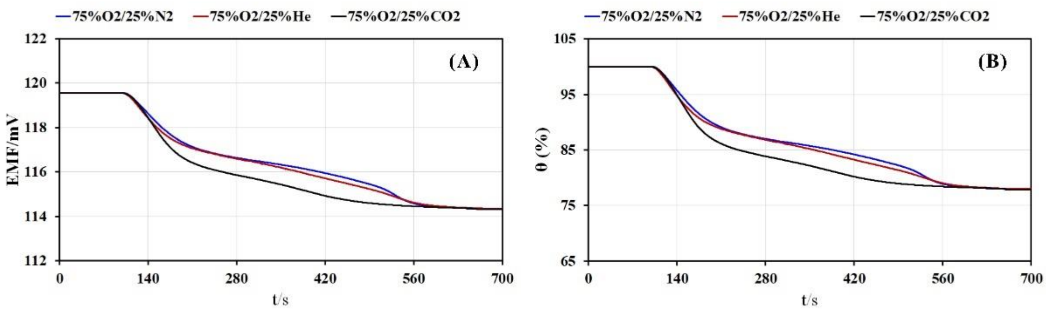


Figure 8. Effects of the balance gas on the combustion of sewage sludge (A: Electro-motive force detected by the oxygen sensor; B: θ values calculated by formula (6)) (Entry 6: 75%O_2/25%N_2; Entry 10: 75%O_2/25%He; Entry 11: 75%O_2/25%CO_2)

The oxidation reaction did not consume the carbon dioxide gas, but it participated in the opposite process as the combustion reaction evolved. Probably because the negative process was much slower than the positive process under this condition with a relatively high oxygen concentration, noticeable alteration was not observed for the oxygen consumption in each entry. Zhuo [30] studied the co-combustion of textile dyeing sludge and coal in N_2/O_2 and CO_2/O_2 atmospheres and reported that there were negative effects in the CO_2/O_2 atmosphere under low oxygen concentrations, but with oxygen concentration increased to 60%, the negative effects declined. Niu [25] reported that due to the impacts of carbon dioxide, the burning process of sewage sludge in the 30%O_2/70%CO_2 atmosphere was very similar to that in air, and the combustion performance was improved with increasing oxygen contents even in O_2/CO_2 atmospheres. Chen [27] also reported that the combustion rates and performance indices of petrochemical wastewater sludge in air (O_2/N_2) and oxy-fuel (O_2/CO_2) atmospheres improved with increasing oxygen concentration.

3.3 Characteristics of the combustion ash of sewage sludge

In this work, the ash after sludge combustion with different oxygen concentrations was removed and analyzed to further understand the oxidation process; the results are shown in Fig. 9. In Fig. 9A, each entry had similar ash content, and the values were consistent with that in Table 1. Thus, the combustion experiments behaved similarly with the ash content analysis for the dried sewage sludge, where sludge was combusted in air for 8 h. Meanwhile, almost 100% of TOC removals were observed in Fig. 9B. These results indicate that organic carbon in the organic compounds convert to inorganic carbon during the combustion of sewage sludge, and the produced CO_2 gas enters the gaseous phase.

According to Fig. 9B, the gaseous products caused by the conversion of N, P, S and Cl elements during the combustion also tended to enter into the gaseous phase, so the total contents of these elements (TN, TP, TS and TCl) in the ash were lower than that in Table 1. Probably due to the coalescence of the produced phosphorus oxide with non-flammable inorganic substances, the TP levels were much higher than TOC, TN, TS and TCl in the ashes. Zhang [24] studied the combustion of two types of sludge and reported that the major mineral compounds in sludge mainly underwent coalescence to form large molten agglomerates. Batch combustion emissions of sludge were influenced by varying oxygen concentrations; when the oxygen concentration increased, the average SO_2 and NO_x concentrations also increased [31].

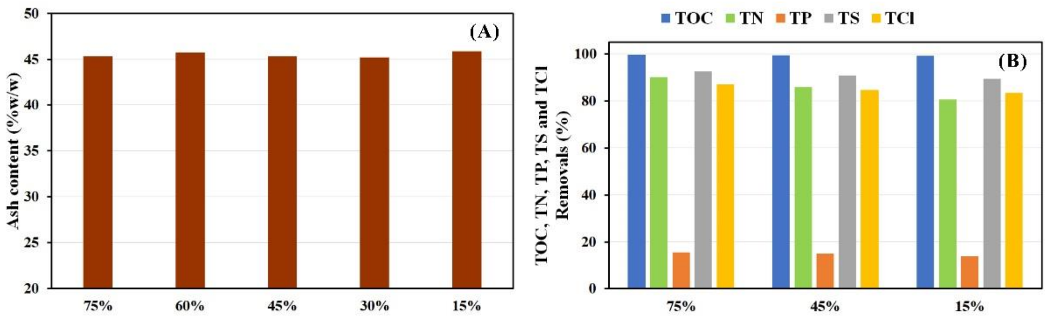


Figure 9. Characteristics of the ash after combustion of sewage sludge with different oxygen concentrations (A: Ash contents for the sludge combustion; B: Removals of TOC, TN, TP, TS and TCl for the sludge combustion) (Entry 2: 75%; Entry 6: 60%; Entry 7: 45%; Entry 8: 30%; Entry 9: 15%)

A combustion technique called moderate or intense low oxygen dilution was applied to the combustion of dried sludge to reduce NO_x emissions, and the experimental results showed that the fuel and air flow patterns were an important factor in maintaining stable combustion, and the horizontal cyclone combustor demonstrated excellent performance in reducing NO_x emissions for the combustion of dried sludge [32]. Thermal disposal of sewage sludge has the advantages of quantitative reduction and resources recovery. However, before extensively using it to dispose the rapidly increasing sewage sludge, measures must be taken to mitigate the potential risk of gaseous toxic emissions produced by these treatments.

4. CONCLUSION

Combustion experiments with in-situ oxygen measurement were performed to evaluate the impacts of oxygen alteration on the incineration of dried sewage sludge. Consequently, temperature was linked to the sludge combustion process; the effects were mainly shown in the reaction rate of sludge combustion, EMF and θ curves, where a combustion temperature of 800 ℃ decreased much more rapidly than that of 600 ℃, and the combustion process reached a final stable state much faster when a high temperature was adopted than when a low temperature was adopted. The oxygen concentration was an important factor for the combustion of sewage sludge; it significantly influenced the oxidation rates of the sludge samples. However, the amount of oxygen consumption was not affected by the oxygen concentration if the sludge was well combusted, and it directly proportionally changed with the change in sludge amount. This relationship can be potentially used to evaluate the pollution levels of solid wastes like sewage sludge, which will be very interesting and worthy of further investigation. Organic carbon in the organic compounds converted into inorganic carbon during the combustion of sewage sludge and resulted in almost 100% of TOC removal. Probably due to the coalescence of the produced phosphorus oxide with non-flammable inorganic substances, TP levels were much higher than TOC, TN, TS and TCl levels in the ashes. For the extensive thermal disposal of sewage sludge, measures must be taken to mitigate the potential risk of gaseous toxic emissions produced by these treatments.

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