Morphology of Burned Ultra-low Density Fiberboards

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The synergistic effect of two fire retardants, a Si-Al compound and chlorinated paraffin, was tested on ultra-low density fiberboards (ULDFs). To further understand the mechanism of fire retardancy, morphologies of unburned and burned ULDFs were studied using a scanning electron microscope with energy dispersive spectroscopy. It was found that as the volume of the burned ULDFs shrank, some crevices appeared. In addition, less fly ash formed on the top of specimens, and more bottom ashes remained in the original framework, with a clear network of structure built by the fibers. Carbon was almost absent in the fly ash; however, the weight ratio of C in the bottom ashes reached the maximum (> 43%) of the composition. Oxygen, Al, and Si appeared to have varying weight ratios for different ashes. Oxygen content increased with increasing Si and Al contents. Furthermore, Cl sharply decreased to less than 1% after combustion. Therefore, upon combustion, it was found that almost all of the substances in ULDFs, except for the Si-Al compound, were pyrolyzed to volatile carbon oxides and Cl compounds, especially the fly ash and lightweight C compounds.

Keywords: Burned ultra-low density fiberboards (ULDFs); Morphology; Scanning electron microscopy; Energy dispersive spectroscopy

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INTRODUCTION

Energy consumption in the construction industry accounts for 20 to 40% of the total energy consumption in the EU (Pérez-Lombard *et al*. 2008). To improve energy efficiency, scientists have designed passive houses and developed several kinds of insulation materials. Those insulation materials have a wide variety of uses and save building energy consumption by 70 to 90% (Isover 2012). Today, plastic foams and mineral wool are commonly used as the insulation materials. These materials accounted for a 95% market share of all insulation materials. Examples of plastic foams mainly include polystyrene foam, polyurethane foam, polyisocyanurate foam, urea-formaldehyde foam, and phenolic foam. Mineral wool covers rock wool and glass wool (Jelle 2011). However, there are some concerns about environmental sustainability, renewability of raw materials, and energy consumption during manufacturing. Therefore, scientists have been looking for substitutes for insulation materials in recent years (Korjenic *et al.* 2011).

Cellulose fiber (Frenette *et al.* 1996; Cervin *et al.* 2013), hemp, wood chips, wood fibers (Rowell *et al.* 1995; Kawasaki *et al.* 1998), and kenaf (Xu *et al.* 2004; Xie *et al.* 2015) are all used as raw materials to produce bio-based insulation. Ultra-low density fiberboards (ULDFs) are one type of bio-based insulation material. The ULDFs are produced using chemical pulp, mechanical pulp, recycled newspaper, and carton boxes as the raw materials; inorganic substances enhance the physical and mechanical properties; and a mixture of polymer vinyl acetate (PVAc) and starch compose the glue that holds the raw materials together. Sodium dodecyl benzene sulfonate (SDBS) is used as a surfactant to disperse the fibers and produce a lightweight material. Under controlled manufacturing conditions, ULDFs have an ultra-low density of 10 to 90 kg/m^3, a low thermal conductivity of 0.026 to 0.038 W/m·K, a sound absorption coefficient of 0.61 to 0.73, and favorable fire resistance properties (Xie *et al.* 2012).

Ultra-low density fiberboards have been studied for more than 10 years. The manufacturing process, foaming mechanism, and application of ULDFs have been reported in previous research (Xie *et al.* 2004, 2008). The studies on mechanical properties have also been conducted to verify the amount and types of inorganic fillers used (Lin *et al.* 2013; Chen *et al.* 2015b). In addition, Liu (2013) studied the fire properties of ULDFs and determined that chlorinated paraffin and Si-Al compounds work better simultaneously than when used individually. Therefore, chlorinated paraffin and Si-Al compound had a synergistic effect on the fire resistance properties of wood fiber. In addition, the synergistic effect reduced the amount of heat, smoke, and off-gases, such as CO and CO_2. Likewise, with an increase in Si-Al compounds, fire resistance of ULDFs was further improved (Niu *et al.* 2014).

However, the studies mentioned above mainly concentrated on the changes in the processing parameters, and improvement of the physical and mechanical properties. Few studies have focused on improving the mechanism of the properties of ULDFs. Interestingly enough, the fire resistance mechanism of plant fiber or cellulose fiber under the synergistic effect of Si-Al compounds and chlorinated paraffin have not been reported until now. The mechanism is very crucial to understanding how to protect loose fibers from fire, and to determine how to modulate the manufacturing process of fiber-based porous materials. Therefore, the objective of this paper is to provide a foundation to further advance the understanding of the mechanism of fire properties of ULDFs. In doing so, the morphology of unburned and burned ULDFs was analyzed using a scanning electron microscope with energy dispersive spectroscopy.

EXPERIMENTAL

Materials

Recycled kraft pulp (spruce-pine-fir, Tembec Inc., Canada), mechanical pulp (*Pinus massoniana*, China), waste carton box (China), and waste newspaper (China) was used as the raw materials for the ULDFs. Then, 500 mL or 900 mL of Si-Al compound, as the two experimental levels, were added into the foaming system and mixed together with the fibers. The manufacturing process of the ULDFs was conducted according to Niu *et al.* (2014). Next, the ULDFs were burned using a cone calorimeter (Fire Testing Technology Ltd., UK) at 780 °C and a heat flux of 50 kW/m^2, in accordance with the ISO 5660-1 (2002) standard. Then, fly ash (upper ash), resulting from complete combustion, and bottom ash, resulting from incomplete combustion, were obtained. The two types of ash, along with unburned ULDFs, were used as the specimens for the morphology characterization.

Methods

Unburned ULDFs were photographed. A scanning electron microscope (SEM, Jeol JSM-6460, USA) with energy dispersive spectroscopy (EDS, Oxford Instruments, UK) was used to visualize the micromorphology of the unburned and burned specimens, the distribution of fibers, and the weight ratios of the main elements in the burned specimens; however, the fly ash with 500 mL of Si-Al compound was not included (1-fly ash). The preparing and testing processes were completed using similar procedures to Niu *et al.* (2014). The mapping was performed using an acceleration voltage of 25 kV, a current of 8 μA, and a working distance of 12 mm. The 1-fly ash was tested using an extreme high resolution scanning electron microscope (XHR-SEM, FEI Magellan-400, USA) with an EDS (equipped with X-Max 80 silicon drift detector), under the conditions: acceleration voltage of 10 kV, current of 0.2 nA, and working distance of 5.1 mm. An optical microscope (DSX-100, Olympus, Japan) was used to observe the connection between Si-Al compounds and the fibers.

RESULTS AND DISCUSSION

Unburned ULDFs

Kraft pulp, mechanical pulp, carton boxes, and newspaper were used as the raw materials to produce ULDFs in this study. Independent of material type, the structural composition, the interaction between fibers, and the fire properties were similar. Figure 1 presents the appearance, structure, and micromorphology of the ULDFs for each type of the raw material.

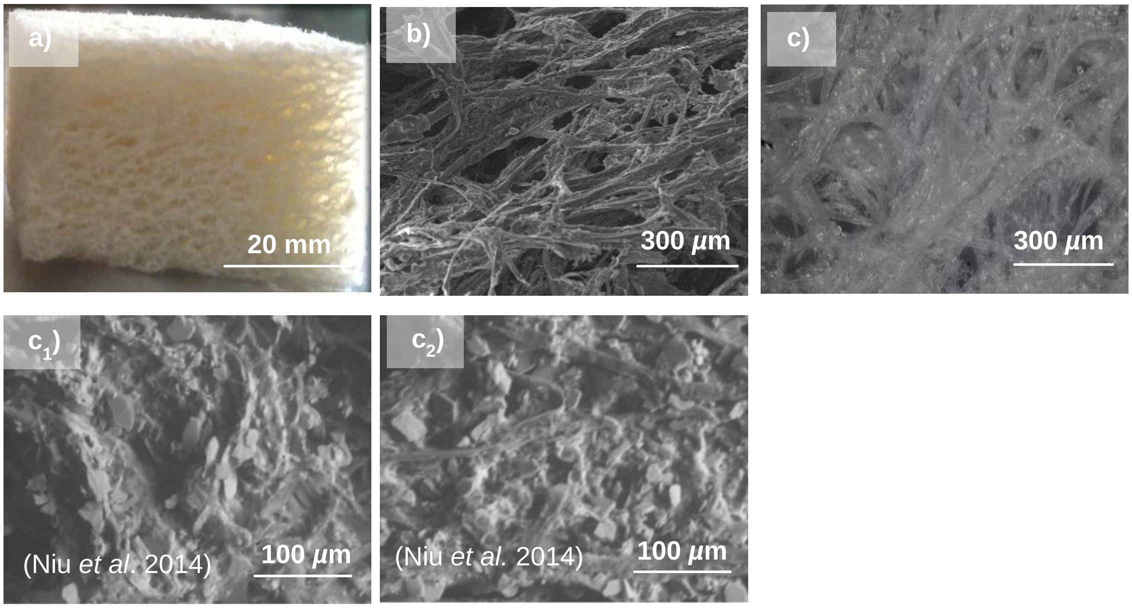


Fig. 1. The morphology of the ultra-low density fiberboards (ULDFs); a) the macromorphology of the ULDF without the Si-Al compound viewed using a common camera; b) the micromorphology of the ULDF without the Si-AL compounds from SEM; c) the micromorphology of the ULDF with the Si-Al compounds from an optical microscope; c_1) and c_2) show the micromorphology of the ULDF with 500 mL and 900 mL of Si-Al compounds from SEM, respectively.

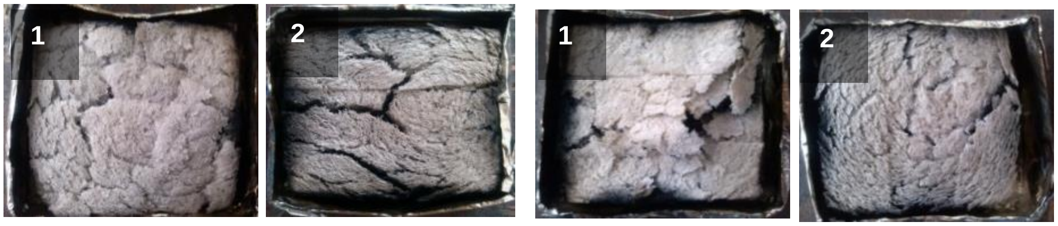
The surface tension of the foaming agent and the mechanical stirring caused the air in the aqueous mixture to disperse through the fibers and expand the volume of the mixture.

Finally, ULDFs were formed that contained a three-dimensional network of fibers (Fig. 1a, b). The porous structure enabled ULDFs to have favorable insulation properties for sound and heat resistance. Furthermore, the junctions between the fibers were connected using charged glue (a mixture of polymer vinyl acetate and starch). This made ULDFs have a certain mechanical strength and resist collapse under the gravitational forces. When the fire retardants were added to the liquid mixture, interactions with the fibers occurred. The fire retardants distributed evenly on the surface of the fibers (Niu *et al.* 2014), providing protection from burning and having a glassy appearance (Fig. 1c). In addition, the fire retardants occupied the opening holes where air could be trapped, as shown in Fig. 1c$_1$ and c$_2$. This improved the fire resistance properties, according to the results from the cone calorimeter and mechanical strength tests (Liu 2013). Meanwhile, the bulk density of ULDFs increased to approximately twice the original density (Xie *et al.* 2012; Niu *et al.* 2014). It was concluded from images c$_1$ and c$_2$, that the additions of 500 mL and 900 mL Si-Al compounds were enough to wrap the exposed fibers. Results suggested that by increasing the amount of Si-Al compound added, the fire resistance and mechanical strength of the ULDFs would be greater.

Burned ULDFs by a Cone Calorimeter

Figure 2 shows the appearance of burned ULDFs using kraft pulp, mechanical pulp, carton boxes, and newspaper as the raw materials, and 500 mL or 900 mL of Si-Al compounds added.

Kraft pulp **Mechanical pulp**



Carton box **Newspaper**

Fig. 2. The morphology of the burned ultra-low density fiberboards (ULDFs) by cone calorimetry at 780 °C. The labeling scheme, 1 and 2, represents the 500 mL or 900 mL amount of Si-Al compounds added, respectively. The size of each specimen was 100×100 mm before combustion.

Carbon, from the carbonized fibers, may have been responsible for maintaining the framework of unburned fibers by retaining their original shape, so that the burned specimens were still present. The volume of those fibers shrank, and some crevices appeared after the combustion process. Fly ash (on the upper layer) was grey and dispersive because of complete combustion in the presence of oxygen; however, bottom ash (on the under layer) was black and integral because of incomplete combustion. In comparison with the specimens containing 500 mL of the Si-Al compounds, the specimens with 900 mL of the Si-Al compounds contained less fly ash. This result suggested that increasing the proportion of Si-Al compounds improved the inhibition effect of combustion. This was in agreement with the results of the fire properties from the Cone Calorimeter. In an example using burned newspaper with 500 mL and 900 mL Si-Al compounds, the micromorphology and distribution of the elements C, O, Al, and Si, as well as the micromorphology of burned specimens are shown in Fig. 3.

From the micromorphology analysis of the burned specimens, the fly ash material was fragmented, lamellar, and lightweight; however, the bottom ash specimens were integral, reticular, and similar to the original structure of the fibers (Fig. 3). As the addition of Si-Al compounds increased, the integrity of the fiber frame for the bottom ash was better. According to the EDS profiles, the elemental C in fly ashes was minimal, especially in the 1-fly ash containing less Si-Al compounds (Fig. 3). This result may have occurred because it reacted with O in the air and mainly generated CO_2 on the surface of the specimens. On the other hand, the C in the bottom ashes was visible and well-regulated. Furthermore, it distributed on the surface of fibers, and its morphology was similar to that of the original fibers. It is possible that C mainly originated from the fibers and was retained in the fibers even after combustion. When considering the weight loss (62% to 71%) (Niu *et al.* 2014) and the brittleness of the burned samples, fibers from the bottom ashes were carbonized, and their molecular structure was destroyed independent of the amount of Si-Al compounds added. However, in fibers without fire retardants, ULDFs will transform into fly ash with less than or equal to 100% of the bottom ashes left after combustion. Therefore, the carbonization of ULDFs was likely attributed to the Si-Al compounds. On the other hand, the glue, alkyl ketene dimer emulsion (AKD), and surfactants offered additional sources of C, all of which were decomposed into carbon oxides and hydroxides when exposed to high temperatures.

The element, O, was derived from each component in the ULDFs. However, it was only present in Si-Al compounds when pyrolysis and/or carbonization occurred in the fibers, glue, and AKD. The elemental O was evident and evenly distributed in the ashes after the combustion in the EDS profiles. The morphology was more similar to the morphology of Si and Al, which suggested that it existed in the form of the Si and Al oxides, and the structures of Si and Al oxides were stable at high temperature (780 °C).

According to the sources of Si and Al, the two types of oxides formed resulted from hydrolysis products of Si-Al compounds charged into an acidic foaming mixture (pH value of 5 to 6). Aluminum and Si oxides were products of aluminum sulfate and sodium silicate, respectively. It should be noted that sodium silicate was also one of the main components in the wood ashes (Etiégni and Campbell 1991) from burned fibers. The Si and Al oxides, measured on the nanoscale level, were individually absorbed on the surface of the fibers (Niu *et al.* 2014), or were incorporated into the fiber's cell wall (Chen *et al.* 2015a). In addition, compound-compound interactions can generate a thin film (Al_2O_3-SiO_2), covering the surface of fibers (Chen *et al.* 2015a). In comparison with Si, Al spots were larger and more concentrated, especially in the EDS profiles of bottom ashes. It was suggested that the result were caused by the agglomeration of Al or Si-Al oxides. The agglomeration of Si-Al oxides on the surface of fibers would significantly impact the fire properties of the ULDFs. The weight ratios of the four elements and Cl from chlorinated paraffin are listed in Table 1.

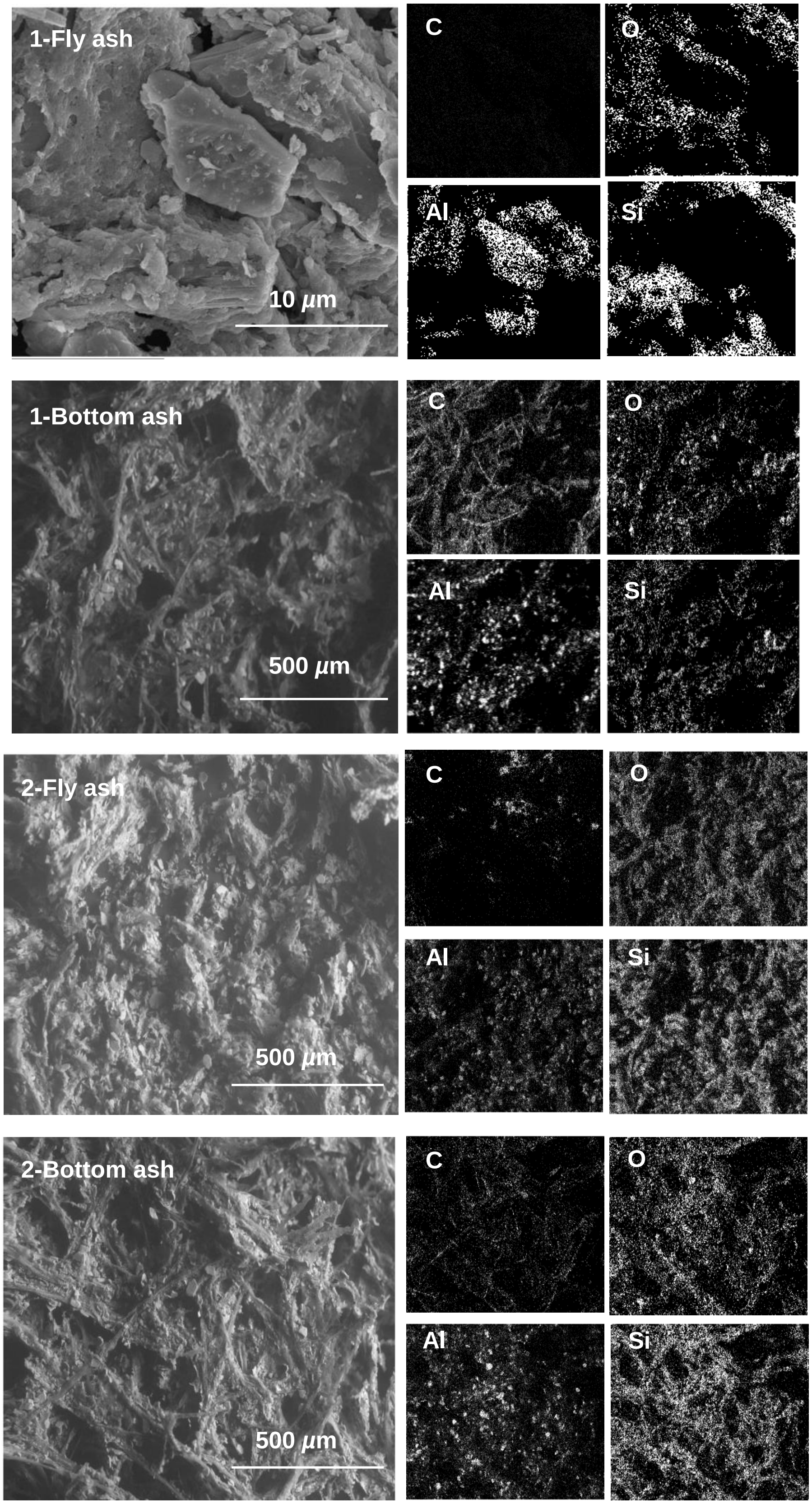


Fig. 3. The micromorphology and the elemental distribution of fly ash and bottom ash by SEM-EDS (Jeol JSM-6460). 1-fly ash that was tested by FEI Magellan-400. The labeling scheme, 1 and 2, denotes 500 mL or 900 mL Si-Al compounds, respectively.

Table 1. Weight Ratios of the Main Elements in ULDFs Pre- and Post-Combustion

Elements	Weight Ratio (%)					
	1-Fly Ash	1-Bottom Ash	1-Pre-Combustion (Niu *et al.* 2014)	2-Fly Ash	2-Bottom Ash	2-Pre-Combustion (Niu *et al.* 2014)
C	—	55.52	8.21	—	43.19	6.16
O	59.93	29.48	52.43	52.11	38.09	57.57
Al	23.85	8.35	11.04	20.09	7.77	14.95
Si	12.79	4.81	4.33	22.92	9.78	6.75
Cl	0.29	0.59	22.16	0.98	0.32	13.52
Total	96.87	98.75	98.17	96.10	99.15	98.95

1 and 2 stand for 500 mL or 900 mL of Si-Al compounds, respectively

Carbon, O, Al, Si, and Cl were the five main elements in ULDFs. The sum of their weight ratios equaled more than 96% of the total weight ratio of all the elements. Before combustion, O was the most common element; its weight ratio was more than 52.4%. Second were Cl and Al with weight ratios ranging from 11.0% to 22.2%. The weight ratios of C and Si were less, and ranged from 4.3% to 8.2%. When the amount of Si-Al compounds added was increased from 500 mL to 900 mL, the percentage of O, Al, and Si increased, and C and Cl decreased.

Combustion at high temperatures resulted in several significant changes to the elements studied. For example, in fly ashes, complete combustion resulted in increasing the weight ratios of O, Al, and Si; however the weight ratio of Cl sharply decreased less than 1%, and C nearly disappeared. In bottom ashes, the weight ratio of C increased to a maximum, and O, Al, Si, and Cl subsequently decreased. Therefore, the results in Table 1 suggested that all other compounds in ULDFs, with the exception of Si-Al compounds, such as fibers, glue, AKD, surfactant, and chlorinated paraffin, were pyrolyzed at 780 °C. The surface of ULDFs was completely pyrolyzed and generated volatile oxides of C, H, and Cl in the presence of an adequate oxygen supply. The inner layer of ULDFs was also degraded and carbonized to form lightweight C, volatile Cl compounds, and C oxide gasses. Therefore, more elemental carbon and less Cl compounds were left in the bottom ashes.

As shown in Table 1, the weight ratios of Si and Al in the bottom ashes component were apparently lower than those in the fly ashes. Actually, the weight ratios of Si and Al did not notably change because Si-Al compounds were more resistant to high-temperatures and possessed a stable chemical structure (Lu *et al.* 2008; Liu 2010), Therefore, the decrease of the weight ratios were mainly attributed to the increases of other elements. On the contrary, bottom ashes had stronger IR absorbance at 1000 cm^{-1} to 400 cm^{-1}, stronger diffraction intensity, and more diffraction peaks during the 2θ from 10° to 60° (Niu *et al.* 2015). Therefore, it is possible that more Si and Al oxides were generated in the bottom ashes during combustion because of the crystalline structure rearrangement of the Si-Al compounds.

When Si-Al compounds increased from 500 mL to 900 mL, the weight ratio of Si increased and Al decreased, especially for the fly ash (Table 1). In theory, both Si and Al should comprise more of the weight ratio with an increase of Si-Al compounds. Therefore, the results were probably affected by changes of other elements. The sum of Si and Al may have increased in the two ashes, with the increase of Si-Al compounds occurring in conjunction with the effects of other elements. The addition of more Si-Al compounds in the burned specimens may provide a possible explanation as to why the specimens with 900 mL Si-Al compounds acquired more favorable fire retardant properties.

CONCLUSIONS

1. The volume of the burned specimens obviously shrank and some crevices appeared. Less fly ash was left in the specimens, and more bottom ash retained in the original fiber framework, especially for the specimens with more Si-Al compounds.
2. The fibers disappeared in the fly ash but retained their original morphology in the bottom ashes. Carbon was almost invisible in fly ashes, however was well-regulated in the bottom ashes. The morphology of O was more similar to that of Si and Al. In comparison with Si, the Al spots were larger and more concentrated, especially in the EDS profiles of the bottom ashes.
3. The total weight ratios of C, O, Al, Si, and Cl were greater than 96% of the total specimen. Carbon comprised the largest percent of the bottom ashes (> 43%). The weight ratios of O, Ai, and Si appeared to have corresponding changes in different ashes. Increases in oxygen content corresponded with increases of Si and Al content. In all cases, Cl sharply decreased to less than 1% after combustion.
4. Other components, except for the Si-Al compounds in ULDFs, such as fibers, chlorinated paraffin, AKD, glue, and surfactant were pyrolyzed to volatile carbon oxides on the surface, and lightweight C comprising the majority of the bottom ashes after combustion. Chlorinated paraffin was almost completely degraded to volatile Cl compounds, *i.e*., HCl. Moreover, Si-Al compounds remained in the ashes in the form of Si and Al oxides when exposed to high temperature.

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