Influence of heating on the weight loss and mineral phase in MSWI ash: LOI of incineration ash

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Abstract. Loss on ignition (LOI) is a very common method for estimating the volatile species in solid sample. Normally, the measurement of LOI can be convenient and accurate, but for municipal solid waste incineration (MSWI) ash, the process may become intricate due to the complexity of the sample. In the incineration ash, there exist various phases, such as mineral, metal, organic and glass. The reaction and transformation of some materials during heating will influence the measurement. 5 incineration ash samples were selected and tested in this study. LOI content was basically measured at high (850° C) and relatively low (440° C) temperatures. The comparison between these two measurements showed a large difference. X-ray diffraction (XRD) and thermal analysis (TG-DTA) were carried out to investigate the mineral changes and weight losses with different ignition temperatures. The mineralogical analysis suggests that the decomposition of hydrate and carbonate phases cannot be neglected for LOI measurement of incineration. A long-time heating under relatively lower temperature (400~450°C) compared with soil sample measurement (≥500°C) was recommended by this study.

1. Introduction
Loss on ignition is widely used to evaluate the organic and volatile matter content in solid sample [1, 2]. A lot of work has been done to optimize the procedure and get more accurate LOI result [3], but there is rare research or literature about the LOI measurement on incineration ash sample. Incineration ash is produced from high-temperature treatment (850~1000° C), while the ignition temperature of LOI is normally lower than that, but the LOI of incineration ash still has practical value because it is a gross measure of the relative burnout of the combustor where the incineration ash was produced [4]. It is often to observe something combustible like small pieces of woods or even paper in incineration ash, which indicate the combustion processes are not completely thorough. The main reason is that during incineration, the temperature inside the combustor is not average and some low-temperature spots would preserve those unburned wastes. So an unbiased index is needed to evaluate the incineration process and the condition of the combustor. LOI measurement, as an inexpensive and simple procedure, is very suitable for this purpose.

But the measurement of LOI on incineration ash sample can be intricate because the composition of incineration ash is complex. Depending on the measurement condition, organic, volatile, hydrate, carbonate and sulphate components in incineration ash can all contribute to the final LOI value [5]. In some cases, the LOI results measured under different circumstances can have big gaps. So it is important to adopt proper measurement condition for different purposes. On the other hand, for the studies on incineration ash, LOI can also be a useful tool. In the field of soil science, there has already been some work about using LOI to estimate certain contents [6]. Because each kind of material has its
distinct temperature range of decomposition, referring to the weight losses with temperature we can roughly estimate what and how much of them may exist in the ash sample.

This paper focused on the effect of temperature on the LOI. TG-DTA and XRD were used as the main analytical methods. 5 different ash samples were picked and examined. The temperatures with obvious weight losses were selected by running TG-DTA onto the samples. Then XRD was used to determine the mineral phase changes related to the weight losses. In the end, a temperature-mineral decomposition diagram was made to help decide the optimal LOI measurement conditions.

2. Materials and methods

2.1 Sample Selection and Preparation
The MSWI ash samples used in the research were from 3 sources with different generation backgrounds. They were simply referred as No.1 to No.5. The sample No.1 and No.2 were newly produced ash from a real incineration plant. No.1 was air cooled, while No. 2 was water quenched after combustion. Sample No.3 was a 2-year stored ash from another incineration plant. No.4 and No.5 were generated by a pilot incinerator. No.4 was fly ash and No.5 was bottom ash. They were both air cooled after formation.

Before the experiment, big particles were removed from the samples by letting the samples pass through a 4.75 mm mesh. The remains were oven dried (105°C overnight) to remove free water. Then all the samples were homogenized by a mechanic mill. The bulk composition was analyzed by utilizing XRF.

2.2 Weight Loss with Temperature
TG-DTA was used in the experiment to get the relationship between weight loss and temperature. Around 30mg of ash sample was taken for each round. Al₂O₃ was used as the inert control. The sample heating chamber was connected with atmosphere directly. The temperature of chamber gradually rose from 25°C to 1400°C by an increment of 10°C per minute.

2.3 Mineral Change and Temperature
With the relationship between weight loss and temperature provided by TG-DTA, several temperatures were selected and let the ash samples exposed to for 2 hours in muffle furnace. Before and after the ignitions, the samples were analyzed by XRD. Through comparison of the XRD profiles, the mineral phase changes could be identified.

3. Results and discussion

3.1 Characterization of the ash samples
The bulk chemical composition of the ash samples was presented by Table 1. The 4 bottom ash samples (No.1, 2, 3, 4) were found to be calcium and silicate based materials with various other elements. Besides CaO and SiO₂, Al₂O₃ and Fe₂O₃ were also dominating components. TiO₂, P₂O₅, MgO, Na₂O and Cl had average contents above 1 wt%, which were considered as major constituents. The others including all the heavy metals were counted as minor (0.1~1 wt %) and trace (<0.1 wt %) constituents. As the only one fly ash sample, No.5 showed a totally different property from the others. It was a calcium based material also had relatively high contents of chloride and zinc. Sample No.4 and No.5 were generated from the same combustion process. The comparison between these two samples revealed that Cl, S, K, Zn and Pb were more concentrated in the fly ash.
Table 1. Bulk chemical composition of the incineration ash samples from different sources

|          | No.1   | No.2   | No.3   | No.4   | No.5   |
|----------|--------|--------|--------|--------|--------|
| SiO₂ (wt.%) | 30.64  | 21.99  | 23.52  | 29.57  | 2.02   |
| Al₂O₃      | 10.68  | 12.03  | 11.09  | 10.74  | 0.58   |
| Fe₂O₃      | 13.01  | 11.14  | 4.95   | 4.13   | 0.77   |
| CaO        | 33.18  | 39.4   | 37.28  | 42.85  | 58.95  |
| TiO₂       | 1.3    | 1.41   | 2      | 1.29   | 0.11   |
| MnO        | 0.08   | 0.09   | 0.1    | 0.13   | 0.02   |
| P₂O₅       | 4.14   | 3.31   | 3.15   | 3.55   | 0.29   |
| MgO        | 2.44   | 2.29   | 2.77   | 2.53   | 2.13   |
| Na₂O       | 2.08   | 1.75   | 2.53   | 2.11   | 3.94   |
| K₂O        | 0.53   | 0.47   | 0.92   | 1.46   | 4.66   |
| Cl         | 0.88   | 1.33   | 3.75   | 0.37   | 18.75  |
| S          | 0.17   | 0.39   | 0.59   | 0.61   | 2.06   |
| Zn (ppm)   | 2707   | 3526   | 2413   | 926    | 7472   |
| Cu         | 1912   | 1641   | 1453   | 411    | 391    |
| Pb         | 326    | 576    | 1997   | 69     | 2721   |
| Cr         | 332    | 332    | 300    | 414    | 64     |
| Ni         | 75     | 88     | 84     | 86     | 38     |
| Ba         | 1126   | 939    | 1108   | 981    | 28     |
| Sn         | 122    | 141    | 126    | 69     | 173    |
| Sr         | 424    | 342    | 441    | 362    | 313    |
| As         | 2      | 2      | 18     | 0      | 18     |
| Cd         | 91     | 95     | 87     | 110    | 258    |

3.2 LOI measured at 440°C and 850°C

Table 2 revealed the great influence of temperature on LOI results. The ignition temperatures were chosen as 440°C and 850°C. The heating process lasted for 4 hour to make all possible reactions complete. It was found that water quenched samples (No.2 and No.3) had much higher weight losses than air cooled ones (No.1 and No.4). For sample No.1 and No.2, they were from the same source and had similar chemical composition (see in Table 1). The extra weight loss of water quenched sample must come from the hydrated contents like portlandite losing their structural water [5]. Fly ash sample (No.5) also had a relatively high LOI. Especially under the temperature of 850°C, almost 20% of total weight was lost during ignition. The volatile contents in fly ash must have contributed to the big weight loss. The gaps of LOI results measured under 440°C and 850°C were considerably big, especially for sample No.1 and No.4. The low LOI values of these two bottom ash samples at 440°C indicated very complete burnout of the combustion process, so the possibility that there might remain some combustible or volatile materials could be ruled out. The decomposition of mineral materials like hydrates or carbonates was the main reason for the additional weight loss at 850°C.

Table 2. LOI values of the incineration samples measured at 440°C and 850°C

|          | No.1   | No.2   | No.3   | No.4   | No.5   |
|----------|--------|--------|--------|--------|--------|
| SiO₂     | 30.64  | 21.99  | 23.52  | 29.57  | 2.02   |
| Al₂O₃    | 10.68  | 12.03  | 11.09  | 10.74  | 0.58   |

3.3 TG-DTA analysis
There are two curves in the TG-DTA profile (see Figure 1). The blue DTA curve recorded the temperature and heat flow associated with thermal transitions in the sample. The downside peak stood for endothermic process. Despite of the beginning stage and the melting process after 1200°C, there were no very obvious exothermic (upside) peak and only several small endothermic peaks being observed. The flat DTA curve from 400°C~1200°C meant no dramatic physical or chemical reactions like burning had occurred in this range.

The black TG curve stood for the weight change of the sample. Continuous weight losses were observed for all the samples. It is worth to note that the weight loss of water quenched samples (No.2 and No.3) started from the very beginning of the measurement, while the air cooled samples had relatively stable stage until temperature reached 400°C. From 400°C, a cliff of TG curve appeared except for sample No.3.

Besides weight loss, there also existed a small endothermic peak in this area (more obvious for sample No.1). Hydrate materials adsorbing heat and losing their structural water loss could explain the phenomena. From 500°C to 600°C, there was another stable stage except for No.3. From around 600°C, another big weight loss occurred. The drop ended at around 650°C. From 1200°C, vitrification began. The ash samples melt and transformed into glass phase.

For the next step of the research, 450°C and 650°C were selected to determine what mineral phase change contributed to the weight losses. Ignition temperature of 850°C was also carried out to get the highest LOI value before ash sample being vitrificated. For water quenched samples, 400°C was also chosen to investigate the cause of weight loss at relatively low temperature condition.

Figure 1. The TG-DTA analysis results of 5 incineration ash samples

3.4 Mineral phase changes with ignition

Table 3 showed the mineral materials contained in the ash samples. Calcite and quartz were the major mineral phases existing in almost all samples. Gehlenite, portlandite and anorthite also had considerable contents. For water quenched samples, hydrocalumite was found. This mineral was formed during hydration with coexistence of chloride.
### Table 3. The thermal constituents in the incineration ash samples

| No.1                  | No.2                     | No.3                  | No.4                  | No.5                  |
|-----------------------|--------------------------|-----------------------|-----------------------|-----------------------|
| Calcite (CaCO₃)       | Calcite                  | Calcite               | Calcite               | Calcite               |
| Quartz (SiO₂)         | Quartz                   | Quartz                | Quartz                | Portlandite           |
| Portlandite (Ca(OH)₂) | Portlandite              | Halite (NaCl)         | Lime (CaO)            | Halite                |
| Hematitie (Fe₂O₃)     | Hematitie                | Hematitie             | Anorthite             | Sylvite (KCl)         |
| Gehlenite (Ca₂Al₂SiO₇)| Gehlenite                | Gehlenite             | Gehlenite             | Arcanite (K₂SO₄)      |
| Anorthite ((Ca,Na)(Si,Al)₄O₈) | Anorthite               | Hydrocalimite         |                       |                       |
| Anhydrite (CaSO₄)     | (Ca₂Al(OH)₆[Cl₁₋x(OH)x] 3(H₂O)) |                       |                       |                       |

Figure 2 showed the mineral phase change of sample No.1 after being exposed to different ignition temperatures for 2 hours. Through comparison with the original profile, portlandite was found to be decomposed at the ignition temperature of 450°C. The peak of calcite decreased at 650°C and totally disappeared at 850°C. The thermal decomposition of them would cause weight loss as it was showed by TG-DTA profile (Figure 1). Besides the decomposition of certain minerals, there were also some newly formed phases identified by XRD: Mayenite (Ca₁₂Al₁₄O₃₃) and larnite (Ca₂SiO₄) appeared after the sample being ignited at 650°C and 850°C.

![XRD profiles of No.1 sample with different treatment conditions.](image-url)

**Figure 2.** XRD profiles of No.1 sample with different treatment conditions. (Port, portlandite; Qtz, quartz; Anh, anhydrite; Cal, calcite; Geh, gehlenite; Hem, hematite; May, mayenite; Larn, larnite).
Same analysis was carried out upon all the other samples. The results were presented by Table 4. Hydrocalumite disappeared under 400°C. Compared with other hydrates, it was less thermal durable and lost structural water at relatively low temperature, which explained the early-stage weight loss of water quenched in Figure 1. After hydrocalumite, portlandite was decomposed at 450–500°C. It also lost structural water and contribute to LOI. Calcite and anhydrite were decomposed after temperature reached 600°C. They would release gases like CO₂ or SO₂. But not all the reactions would contribute to LOI value. Like lime in sample No.4, which was found disappeared at 650°C, it transformed into another mineral phase and would not be counted in the weight loss.

**Table 4. Effect of heating temperature (2h) on the mineral phase of the incineration ash samples**

| Decomposed minerals | Temperature (°C) | Sample |
|---------------------|-----------------|--------|
| Hydrocalumite*      | ~400            | No.2, No.3 |
| Portlandite*        | 450–500         | No.1, No.2 |
| Calcite*            | 600–700         | All the samples |
| Anhydrite*          | 600–850         | No.1 |
| Lime                | 650             | No.4 |

| Newly formed minerals | Temperature (°C) | Sample |
|-----------------------|-----------------|--------|
| Calcium silicate (CaO·SiO₄) | 850            | No.1, No.2, No.4 |
| Calcium aluminate (CaO·Al₂O₃) | 850            | No.1, No.2 |
| Lime                  | 650             | No.5 |

* indicates the decomposition of these minerals would contribute to weight loss.

Table 4 also presents the newly formed minerals in the processes. It needed to be noted that except for larnite and mayenite, most of the new minerals were calcium-silicate or -aluminate based materials with other ions like chloride or phosphate bound. In No.5, lime was generated through the decomposition of calcite and portlandite. Because there was no much silicate or aluminum contained in this sample, it could preserve rather than turning into other form.

**4 Conclusions**

The LOI value of incineration ash was highly depended on the measurement condition, especially the ignition temperature being used. The decomposition of carbonate and hydrate minerals would become the major source of weight loss if ignition temperature became higher than 600°C. For water quenched ash sample, it might need to be even lower. So ignition temperature of 400°C to 450°C was recommended by this study, and the influence of heating time will be evaluated in the future work.

For mineral phase study, it was found that hydrates’ decomposition temperature was around 450°C, but for some thermally unstable materials, the decomposition of them could occur under even lower condition. Calcite would start to decompose when temperature reached 600°C. For anhydrite, its decomposition temperature was found to be 650°C in this research.

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