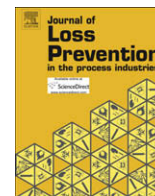




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Heat accumulations and fire accidents of waste piles

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ABSTRACT

In order to prevent fires from waste storages and piles, heat generation and accumulation mechanism of waste piles were investigated by calorimetric and chemiluminescence (CL) studies. As measurement samples, we used refuse-derived fuel (RDF), car shredder dust (SD), and model materials such as papers and plastics. A primary heat generation and a heat accumulation were evaluated by using some calorimeters such as DSC (Mettler Toledo, Schweiz), ARC (Columbia Scientific Ind., USA) and C80 (Setaram, France). Self-ignition temperature was also evaluated by using HP-TG/DTA (Rigaku, Japan). However, these values of wastes vary with respect to each sample due to the heterogeneity of the wastes. For instance, the self-ignition temperature of SD was 154–186 °C and that of RDF was 174–224 °C. In this study, we chose the lowest value from the safety point of view. The results of ARC measurement indicated that the heat accumulation by self-heating started from 83 °C for RDF, and from 96 °C for SD, and the heat accumulation under adiabatic condition gave self-ignition eventually. We also studied the oxidation of them in the low temperature region (between room temperature and 130 °C) using CL analyzer (Tohoku Electronic Ind., Japan). The experimental data showed that RDF containing oxidized polymer and some organic peroxides initiated autoxidation reaction in the low temperature region.

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1. Introduction

In Japan, huge amounts of wastes are generated every year and they are partially forced to pile or store everywhere to avoid incineration treatment with dioxin emissions and also due to lack of disposal sites. In such piles and storages, heat accumulations often occur and cause serious fire accidents. Such fires could not be extinguished easily and generate many kinds of harmful gases for a long term, because such a smoldering combustion is maintained inside of the piles. And recently, these kinds of fire accidents have been increasing. For example, the explosion of the storage tank of RDF power plant in Mie Prefecture killed two fire fighters in Aug. 2003 (Special Committee for Investigation on the Accident of Refuse Derived Fuel Power Plant in Mie Prefecture Japan, 2003), and the fire at the industrial waste landfill in Nagasaki Prefecture in Feb. 2004 that burned for thirteen months and dioxin and other hazardous materials were released (Nagasaki Shimbunsha, 2005). In order to prevent these kinds of fires from the waste piles, it is

important to know about heat generation and accumulation mechanisms, and to discuss the hazard evaluation methods of heat accumulations.

Many studies have investigated the heat accumulation of easily oxidizable materials such as coal, polypropylene or unsaturated fatty acid (Nelson, 1989; Wang, Dlugogorski, & Kennedy, 2003). In these materials, heat generation mainly carried out by autoxidation, and heat accumulation of them during its oxidation is understood by the thermal ignition theory based on the balance between heat generation rate and heat release rate. In the case of waste piles, the factor of heat generation and release is complicated. It was reported that water contents of RDF contribute for heat generation around room temperature (Fu, Li, & Koseki, 2005). Besides, it is considered that fermentation promoted this heat generation (Sakka, Kimura, & Sakka, 2006; Yasuhara, 2004). And many studies about oxidative hazard of RDF indicate that RDF exothermic process starts above 130 °C (Fu et al., 2005; Fu, Koseki, & Iwata, 2006). However, the mechanism of self-ignition from primary heat generation by microorganism via heat accumulation by autoxidation has not yet been clarified. In this study, heat generation and heat accumulation mechanism of stored wastes were investigated by applying the chemical safety evaluation methods to the waste materials such as calorimetric and CL studies in order to prevent the fire accidents of waste piles.

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Table 1
Compositions of RDF.

Papers, textiles, etc.	Plastics, rubbers, etc.	Woods, splits, straws, etc.	Garbage, dust, etc.	Nonflammable materials
30–60 wt%	10–30 wt%	1–10 wt%	8–40 wt%	1–6 wt%

2. Materials and methods

2.1. Scenarios for fire accidents of waste piles

Scenarios for fire accidents of waste piles are described as follows. As a first step, piles had a primary heat generation by some reasons. In the case of waste piles, primary heat generation can be resulted from many kinds of causes such as reaction heat of metal with water, fermentation with microorganisms, autoxidation of organic materials, frictional heat caused by crushing, and/or remained heat in drying or crushing processes. Then, imbalance of heat release and generation rates brings heat accumulation for the piles. Once the heat accumulation or temperature rise of pile occurs, other exothermic reactions, mainly autoxidation of organic materials, would accelerate the temperature rise. Eventually, the reaction causes self-ignition. For evaluation of a fire accident caused by heat accumulation, it may be important to clear up the cause of primary heat generation and the mechanism of the heat accumulation and the ignition.

Although the thermal ignition theory is useful for estimating a heat accumulation, however, it is necessary to evaluate the heat accumulation by experiments with adiabatic storage test because of non-uniformity of wastes. Adiabatic calorimetry such as ARC was used in this work. We also used DSC and C80 to evaluate the primary heat generation and accumulation of heat, and HP-TG/DTA was used to determine the lowest ignition temperature.

2.2. Experimental materials

SD and RDF were used as samples. The SD was reported to have 60% of organic combustibles, 15% of moisture, and remains (Hosoda, Deguchi, Arakawa, Takeuchi, & Miura, 1991) and caused actual fire accidents many times in Hiroshima prefecture. The SD also contains Na, Mg, Al, Si, P, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Pb, Sr, Zr, Mo, Sn, Sb, and Ba as metal elements according to the X-ray analysis (Shimadzu Co., Ltd., Japan), and the amount of Fe and Al is 8 wt% and 1 wt%, respectively, which was analyzed with inductively coupled plasma atomic emission spectrometry (Seiko Co., Ltd., Japan).

The RDF from garbage, including kitchen waste, made at several RDF plants was used. Suzuki (2004) reported those elementary atomic compositions were C (50 wt%), H (7 wt%), O (30 wt%), N (1 wt%), S (0.5 wt%), and Cl (0.5 wt%). Table 1 shows the main compositions of RDF (Matsunaga, Yasuhara, Yamamoto, Shimizu, & Wakakura, 2005). Many of them were compressed into pellets (ϕ 10–20 mm \times 30–50 mm), with less than 10 wt% of water and about 2 wt% of calcium hydroxide for maintaining its hardness. These RDFs were used after cut into pieces of 5 mm or less, or crushed with cryogenic sample crusher (Japan Analytical Industry, Japan) and its diameter was less than 0.5 mm as a sample. For heat value measurement of RDF with water by using Multi Micro Calorimeter (Tokyo Riko Co., Ltd., Japan), the sample was cut to under 0.5 mm diameter and dried at 50 °C for 12 h under vacuum condition.

2.3. Experimental methods

DSC and C80 were used to obtain the primary heat generation of samples. The principle of measurement of C80 is similar to DSC, but C80 can manage much larger amount of sample mass than DSC measurement and the condition of mixing and/or stirring, or under

high pressure with various gases. The influence of water on the primary heat generation and the effect of the metallic powder, such as Fe and Al, were also evaluated by using these apparatuses.

HP-TG/DTA was used to evaluate the lowest ignition temperature of the samples. It can be used to measure with a small amount of sample (5–20 mg) in short period under high-pressured oxygen (1 MPa as standard). This method is commonly used to evaluate combustibility by HP-TG/DTA or HP-DSC (Wakakura & Sato, 1981). In this study, self-ignition temperature means the lowest ignition temperature measured by HP-TG/DTA.

As ARC has two different measurement modes; heat-wait-search step scanning mode (H-W-S mode) and isothermal scanning mode. ARC was usually used to evaluate the exothermic reaction such as thermal decomposition by the H-W-S mode, and heat accumulation of materials by the isothermal scanning mode. In both mode of ARC, after exotherm with heat generation rate reach above 0.02 K/min, the sample is kept in adiabatic conditions for the duration of the exothermic reaction. In this study, ARC was used with H-W-S mode to evaluate the heat accumulation start temperature that means self-heating start temperature in adiabatic condition.

And the wire basket heating test was also used to evaluate heat accumulations of samples by self-heating. In this work, a 10 cm cube basket (SUS, 0.053 mm mesh) was used and the sample amount was 1 L. And the temperature in three spots from the center of the basket at equal intervals and the oven temperature were measured.

And oxidized organic materials such as hydroperoxides give a lower start temperature of oxidation reaction than that of pure organic materials. Since RDF had a considerable heat profile during manufacturing, there is a possibility that polymer in RDF has been partially oxidized during its production. As an oxidized polymer, such as peroxide, plays as an initiator of autoxidation (Reich & Stivala, 1969), and CL analyzer was used to evaluate oxidation reactions. CL analyzer is one of the highest sensitive detectors of the ultraweak light emission during various chemical reactions including oxidation, thermodegradation, etc. (Zlatkevich, 1989).

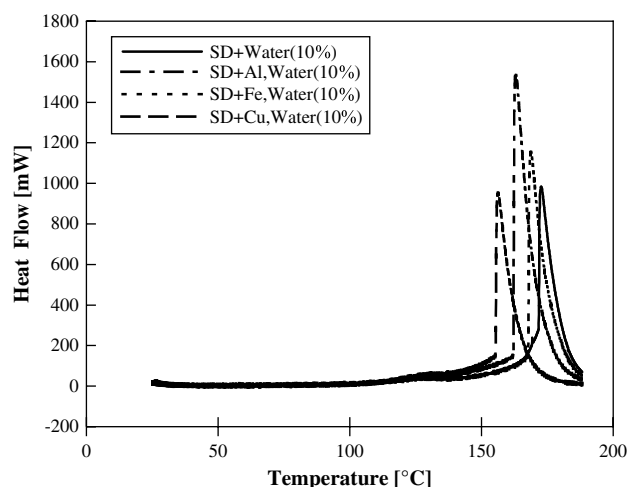


Fig. 1. Effects of additional water and metals for the primary heat generation of SD.

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