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Effect of reducing conditions on sludge melting process

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Abstract

The objective of this study was to compare the effects of CO/CO_2 reducing conditions with those of air oxidizing conditions on the pouring temperature of the sludge melting process and the heavy metal leachability of the resultant sludge slag. Synthetic sludge ash composed of SiO_2, CaO and Al_2O_3, as well as sewage sludge ash generated from a laboratory incinerator was employed. The experimental results indicated that the pouring temperatures are significantly reduced under the reducing conditions of CO/CO_2, or 24 and 77 °C lower than under air conditions for synthetic and sludge ash, respectively. The heavy metal leaching tests further indicate lower heavy metal concentrations present in the leachate under the reducing conditions, notably an order of magnitude lower in Zn. However, X-ray diffractogram indicates similar peaks for these two slags produced under different conditions.

Keywords: Sludge melting process; Pouring temperature; Heavy metal leachate; X-ray diffractogram

1. Introduction

The disposal of a large quantity of the sewage sludge in landfill in Taiwan has become a major issue because of public resistance and the unavailability of landfill sites. The best strategy is to reduce sludge quantity during the wastewater treatment process. If not feasible, sludge reduction and recovery should be a top priority in the subsequent sludge management system. Among many alternatives for sludge quantity reduction, sludge melting process has received considerable attention since 1990s (Sakai et al., 1990; Yashiki and Murakami, 1991). A typical coke-bed melting process is shown in Fig. 1. The sludge is fed on the top of the furnace and dropped on the coke bed. In this process, the temperature is maintained at 1350–1500 °C in order to melt the inorganic components and decompose the organic contents (Oku et al., 1990; Ohshima and Masuta, 1991). The melted material flows through the coke bed, is cooled in water or air, and ends up as the sludge slag, which can be used as construction materials, e.g., as aggregates for paving. After post-melting or sintering, the slag can also form the blocks and other crystal materials (Bijen, 1996; Endo et al., 1997; Okuno and Takahashi, 1997; Wiebusch and Seyfried, 1997).

Several concerns need to be addressed. The first is the fate of heavy metals under such high temperature conditions. A few studies indicate that more than 60% of Cd, Pb, Zn and Cu are present in the slag, and ver 60% of Ni, Cr and As are associated with fly ash (Takaoka et al., 1997). The heavy metals leaching from the fly ash and the melted slag are related to the leaching methods, the pH of the extracts, and the diameter of the slag (Ozaki et al., 1997). Nishino and Tahara (1998) further indicate that the amount of metal leaching from the slag is two to three orders of magnitude less than that from the original ash. To be able for practical applications of slag under different environmental conditions, the stability of metals associated with the slag must be quantified. The second concern is to optimize the temperature used in the melting process, as the operating temperature

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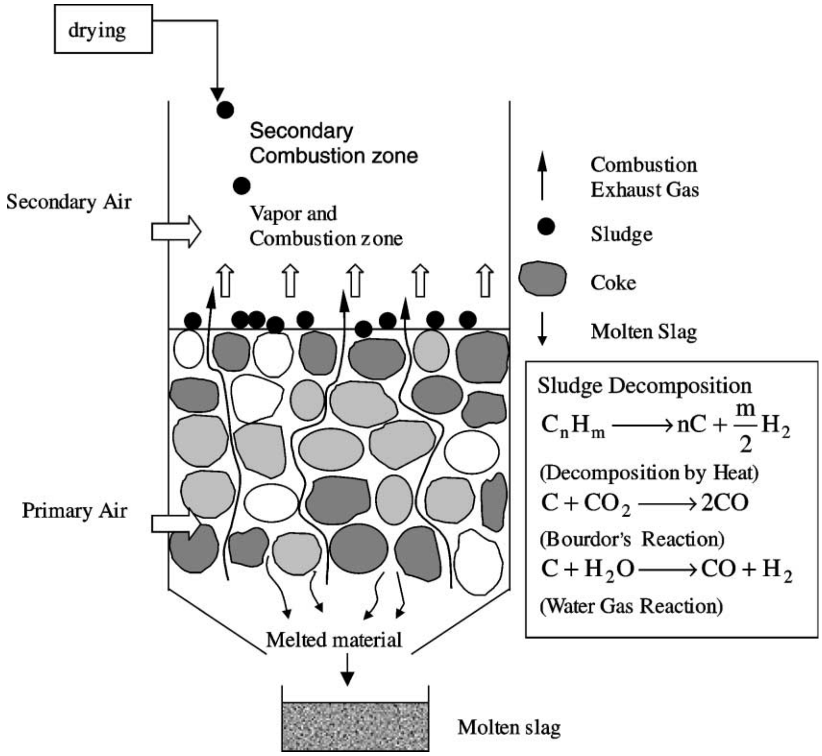

Fig. 1. Schematic diagram of coke-bed melting furnace.

clearly affects fuel consumption (Murakami et al., 1991a). To select a relatively low temperature in the melting process, it has been reported that the basicity index (weight ratio of CaO/SiO_2) could be used (Murakami et al., 1991b). The basicity associated with the relatively low temperature was reported to be 1.0 (Murakami et al., 1991b; Chen and Ouyang, 1993; Wang and Shao, 1993; Nishino and Tahara, 1998).

Typically, the pouring temperature, defined as the temperature at which the melted tested cone flows over the base and its height becomes one-third of the resulting bottom width (Murakami et al., 1991b), is determined in the laboratory under air or argon conditions. This value can serve as a referenced temperature to estimate the operating temperature in actual operation. In reality, the operating temperature also depends on the fluidity of the melted materials, and the water content of the feed sludge.

Several factors influence the pouring temperature, including for example, the distribution of CaO, SiO_2 and Al_2O_3. Unfortunately, the laboratory conditions for determining the pouring temperature differ greatly than those present in a coke environment. The coke bed is surrounded by a reducing state of CO and CO_2, with a typical weight ratio of $CO/CO_2 = 1.5$ (Kitamura, 1999). Thus, the preset operating temperature determined from the laboratory under air conditions may be insufficient or excessive in a real plant operation. Consequently, this study was undertaken to investigate the effect of CO/CO_2 reducing conditions on the pouring temperature of the sludge melting process. Moreover, the heavy metal leachability of the resultant sludge slag was also studied.

2. Materials and method

The experiment was divided into two parts to evaluate the effects of the reducing conditions (60 wt% CO + 40 wt% CO_2) on the sludge melting process. The first part used synthetic sludge ash and the second used sewage sludge ash.

2.1. Preparing the sludge samples

The SiO_2, CaO and Al_2O_3 samples were used to prescribe the synthetic sludge. The purity of the reagent in this test exceeded 97% (w/w), and, after grinding and sieving, the diameters of the samples were smaller than 0.127 mm. Thereafter, they were dispensed according to weight ratios, which were used as an operational parameter.

The synthetic sludge samples with 55 combinations of SiO_2, CaO and Al_2O_3 corresponding to the integer points of three coordinates on the pouring temperature-isotherm triangle were used for measuring the pouring temperature. Each combination was tested in triplicate in both air and CO/CO_2 systems. After the 55 integer points were tested in the triangular pyramid test, several decimal fraction points on the pouring temperature–isotherm triangle, such as 5:2.5:2.5, were selected near the low temperature points to re-run the same experiment. The results associated with every point considered in the experiment were analyzed, and compared between two systems.

The sewage sludge, from a sewage treatment plant, Taipei, Taiwan, was burned at 900 °C in a lab-scale incinerator. After grinding and sieving to 0.127 mm, the sludge ash was stored in an oven. The sludge ash was digested by the premixed HF, HNO_3, and $HClO_4$ acids, filtered, and its metal composition was determined by inductivity coupled plasma-atomic emission spectrometer (ICP-AES), with a sensitivity of ppm.

The premixed CO/CO_2 gas (CO/CO_2 volume ratio 2.4:1, weight ratio 60:40) used in this study was obtained from a chemical manufacturer.

2.2. TCLP test

The method for the toxicity characteristic leaching procedure (TCLP) follow that of Taiwan EPA's Standard Method NIEA R201.11 (ROC–EPA, 1997). The liquid-to-solid weight ratio was 20:1, with the extraction solution of acetic acid (pH = 2.9). The inductivity coupled plasma-mass spectrometer (ICP-MS) was used for metal analysis with a sensitivity in ppb range.

Table 1
Major chemical constituents of sludge ash from sewage treatment plant

Composition	Concentration (%)
SiO_2	38.5
Al_2O_3	7.8
MgO	0.6
P_2O_5	14.1
CaO	3.6
Fe_2O_3	7.8
Na_2O	0.4
K_2O	0.1

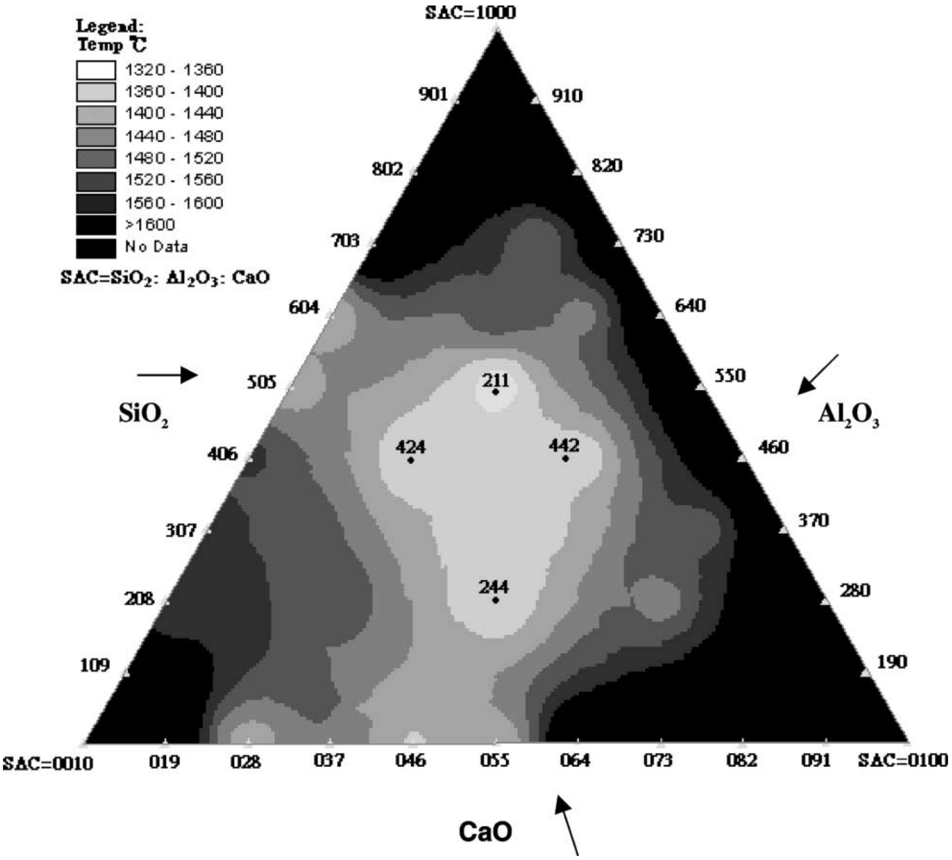

Fig. 2. Isotherms of pouring temperature under air conditions for synthetic sludge ash.

2.3. Triangular pyramid test

The triangular pyramid test in a tube furnace (carbolite) was used for determining the melting and pouring temperatures of samples. Samples were molded to the triangular pyramid pattern before they were placed into the furnace. A total of four sample tiles, including eight samples, could be employed during each test run. The highest temperature was set at 1600 °C, and the temperature increase was set at 5 °C/min, under conditions of either air or CO/CO_2. A high-resolution video system with an infrared camera recorded the shapes of the samples as they were heated to obtain the pouring temperatures. The increase in the temperature in the furnace was recorded. After meltdown, the molten samples were cooled in air in the furnace, and the tape was then replayed to determine the deformation temperature.

2.4. XRD test

The X-ray diffractogram (XRD) analysis was performed (MAC Sience MXP18) under the operating conditions of 30 kV and 30 mA. Samples were ground and sieved to a particle size smaller than 0.127 mm, and XRD data were obtained by using CuK_α radiation at a scanning rate of 4 degree/min. The peaks were identified using the joint committee on powder diffraction standards database.

3. Results and discussion

Table 1 indicates that the main chemical components of the sewage sludge ash are SiO_2 (38.5%), P_2O_5 (14.1%), Al_2O_3 (7.8%), Fe_2O_3 (7.8%) and CaO (3.6%). The high SiO_2 content of the samples may be due to the soil and sand entering the sewer system.

3.1. Effect of the reducing conditions on the pouring temperature

A preliminary study of synthetic sludge ash was first conducted to assess the feasibility of reducing the pouring temperature by shifting the experimental conditions from air to CO/CO_2. Fig. 2 shows isotherms plotted on a ternary phase diagram of melting synthetic ash under air conditions. The SAC acronym is an ab-

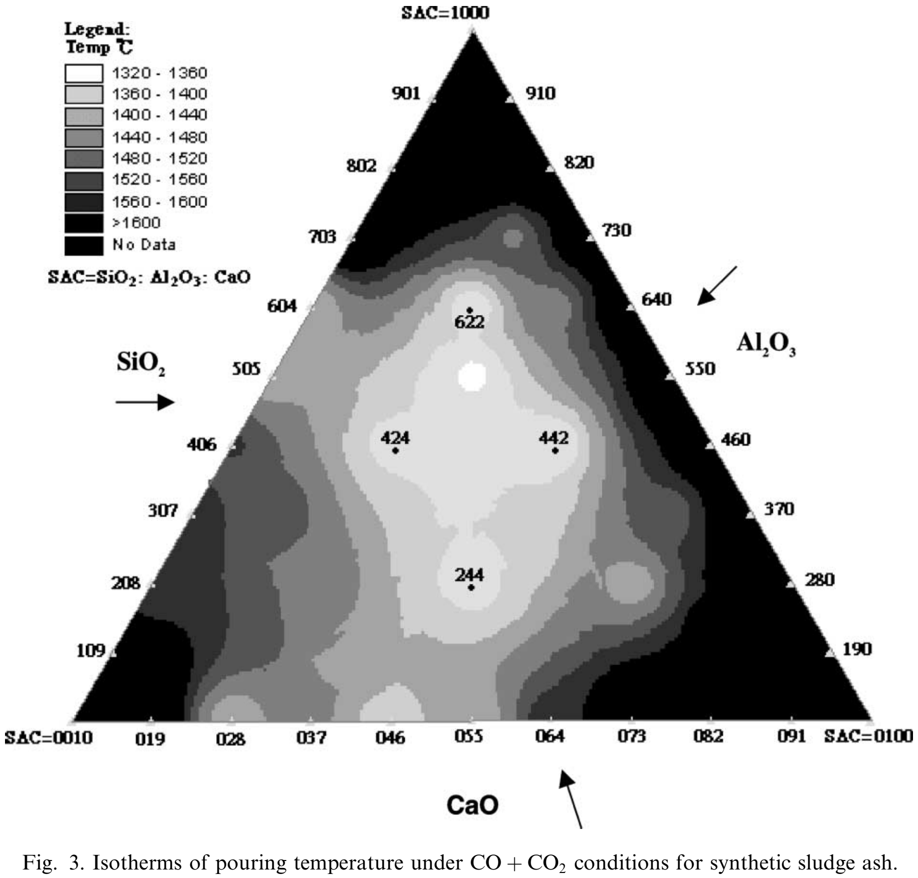

Fig. 3. Isotherms of pouring temperature under CO + CO_2 conditions for synthetic sludge ash.

breviation for SiO_2, Al_2O_3, and CaO, and the associated numerical values indicate the weight ratio of SiO_2, Al_2O_3 to CaO of the test samples. For example, SAC = 631 implies SiO_2:Al_2O_3:CaO = 6:3:1. As shown in Fig. 2, an evidently low pouring temperature zone was bounded by a kite-shape formed by connecting points of SAC = 424, 211, 442 and 244.

The low temperatures did not appear at previously reported value of $CaO/SiO_2 = 1$. This is partially due to the constituents present in the sludge (Al_2O_3 in our system), which in turn influence its eutectic temperature (Murakami et al., 1991b; Chiang, 2001). Nonetheless, the basicity with a flexible operational area is preferred over a constant value in a narrow operational range due to unhomogenous nature in sludge.

The isotherms in Fig. 3 show that CO/CO_2 conditions significantly alter the pouring temperature for the synthetic sludge ash. The kite-shaped area (SAC = 622, 424, 442 and 244) is larger than that in air melting system (Fig. 2). The pouring temperature differences between CO/CO_2 and air conditions under varying SAC ratios ranged from 1 °C (at SAC = 505) to 176 °C (at SAC = 622), with an average of 24 °C. The locations of relatively low pouring temperatures shown in Fig. 3 could also be indexed by $Al_2O_3/CaO = 0.5–2$ and $SiO_2 + CaO = 60–80\%$.

Table 2
Pouring temperature of sewage sludge molten slag

Melting conditions	Air	60% CO + 40% CO_2 (w/w)
Sample size	8	8
Pouring temperature (°C)		
Average temperature	1220	1143
Standard deviation	0.5	6.5
Melting temperature (°C)		
Average temperature	1210	1130
Standard deviation	7.1	6.1

Melting temperature: the temperature when the melted tested cone flows over the base and its height becomes half of the resulting bottom width.

The tendency of CO/CO_2 to exhibit lower pouring temperatures is also observed in the melting of sewage sludge ash (Table 2). The pouring temperature of 1143 °C under CO/CO_2 reducing conditions was much lower than that of 1220 °C in air system, or a difference of 77 °C. Table 2 also includes melting temperatures for comparison of the two systems; the same 80 °C difference.

3.2. Effect of the reducing conditions on TCLP and XRD results

The TCLP results (Table 3) show the compliance with Taiwan's regulatory standards for all samples including sludge ash. However, the melting conditions clearly affect metal leachability. As melting conditions switched from air to CO/CO_2, there exists one order of magnitude reduction for Cu (from 400 to 70 μg/l) and Zn (from 7000 to 800 μg/l). The exact reason(s) for the observed phenomenon is unknown; the presence of CO/CO_2 must play an important role in tightly binding some metals.

The dominant and stable phase in XRD patterns for either air or CO/CO_2 case for the sewage sludge slag sample is SiO_2, and to a lesser extent, Fe_2O_3 (Fig. 4). However, corundum (α-Al_2O_3) and some unidentified phases were identified under CO/CO_2 conditions. For practical purposes, the two XRD patterns are essentially the same.

Table 3
Heavy metal concentration in TCLP extracts of sewage sludge ash and sewage sludge molten slag

Heavy metals	Sewage sludge ash[a]		Sewage sludge slag (air condition)[b]		Sewage sludge slag ($CO + CO_2$ condition)[b]		Taiwan's regulatory thresholds (μg/l)
	(μg/l)	(mg/kg)	(μg/l)	(mg/kg)	(μg/l)	(mg/kg)	
As	ND	ND	30	0.6	2	0.04	2500
Cd	20	0.4	10	0.2	10	0.2	1000
T–Cr	100	2	ND	ND	ND	ND	2500
T–Hg	ND	ND	ND	ND	ND	ND	200
Pb	100	2	60	1.2	10	0.2	5000
Cu	3810	76	400	8	70	1	15 000
Zn	17 660	353	7010	140	810	16	25 000
Ni	NA	NA	670	13	430	9	–[c]
Mn	NA	NA	400	8	50	1	–[c]

ND: not detected; NA: not analyzed.

[a] Analyzed by ICP-AES.

[b] Analyzed by ICP-MS.

[c] No regulatory limitation in Taiwan.

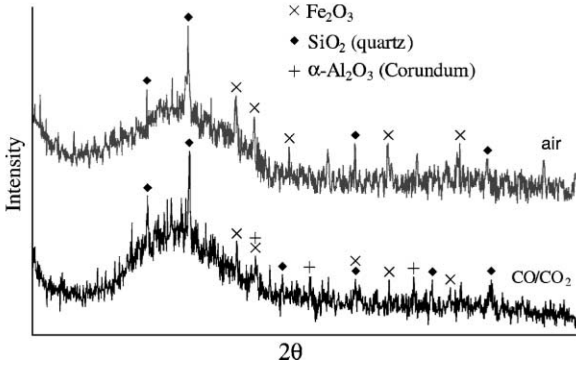

Fig. 4. X-ray diffractogram of sewage sludge slag from under air or CO/CO_2 conditions.

4. Conclusions

Reducing conditions generated by replacing air with 60% CO + 40% CO_2 effectively lowered the pouring temperature in the sludge melting process. The temperature differences of 24 and 77 °C could be obtained for synthetic sludge ash composed of SiO_2, CaO and Al_2O_3, and for sewage sludge ash, respectively. The leachability of heavy metals from the sludge slag is reduced for some metals as the melting conditions shifted from air to CO/CO_2.

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