Fuel Processing Technology 96 (2012) 88–97

Contents lists available at SciVerse ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Sintering characteristics of sewage sludge ashes at elevated temperatures

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ARTICLE INFO

Article history:
Received 23 August 2011
Received in revised form 20 December 2011
Accepted 21 December 2011
Available online 17 January 2012

Keywords:
Sewage sludge ash
Sintering
Mineral phase
X-ray analysis
SEM-EDX

ABSTRACT

In this work the sintering characteristics and mineral transformation behaviors of sewage sludge ash (SSA) at elevated temperatures were investigated by using ash fusion analyzer, X-ray fluorescence (XRF), X-ray diffraction (XRD) and scanning electron microscopy equipped with energy dispersive X-ray spectrometry (SEM/EDX). High initial fusion temperatures above 1100 °C were detected from the sewage sludge ashes (SSA 1 and SSA 2) with high Al contents. Corundum, quartz and calcium aluminum silicates were dominating crystalline phases identified from SSA 1 and SSA 2 sintered at elevated temperatures. For the SSA 3 with a high Fe content, low initial melting temperature of 994 °C was detected with observation of severe fusion behavior from the ash sintering tests. SEM analysis revealed that SSA 3 melted completely into a more homogeneous and continuous phase at high sintering temperatures. A significant amount of Fe bearing mineral phases and quartz (SiO_2) was identified from the sintered SSA 3. Diffraction intensities of hematite (Fe_2O_3), quartz (SiO_2) and alkali feldspar decreased with increasing sintering temperatures, suggesting interaction and re-assemblage of these mineral phases. In combining the XRD and SEM/EDX analyses, it is believed that formation of low melting temperature iron silicates is the main reason for sintering of SSA 3.

1. Introduction

Due to the rapid urbanization throughout the world, the amount of waste water is increasing dramatically with more processing requirements [1–3]. Sewage sludge, as a main by-product of waste water treatment process, is becoming a public issue due to the ever-increasing amount and risk to the environment [1]. Compared to conventional disposal ways, sewage sludge combustion is one of the promising methods with several advantages [2,3]. With a relative high heating value close to the brown coal, energy could be recovered from sewage sludge by means of combustion in different devices [2]. Through the combustion, the volume of sewage sludge can be effectively reduced to a small amount stabilized ash. Most of toxic organic species can be destroyed at high enough combustion temperatures with lower emissions. Heavy metals in sewage sludge are retained in incineration residues and possibly handled with minimum environmental impacts. [1–3].

Currently sewage sludge is combusted directly in different kinds of incinerators or co-combusted with other fuels in combustors [2,3]. However, compared to other solid fuels such as coal, the sewage sludge has higher and varied ash contents about 20 to 50 wt.% on a dry basis, which result in heavy loads on ash handling and flue gas cleaning system in a combustion device [2–4]. In particular, the chemical and mineral compositions in the sewage sludge ash have significant effects on their properties during combustion processes. Operational related problems have been often observed in combustion devices associated with sewage sludge ash sintering, agglomeration and slagging behaviors. These problems lead to declined energy production efficiencies, high maintenance costs and unscheduled shutdown of combustion systems [2–7]. Several studies have been carried out on ash behaviors during combustion of the sewage sludge. Formation of molten ash layers and droplets on sewage sludge char residue surfaces was reported by Cui et al [5], as two sewage sludge samples combusted in an electrical heated furnace in a pure oxygen atmosphere at 900 °C. With the increasing combustion time, sewage sludge burn residues were covered by fused ash and agglomerated together to form solid blocks [5]. Zhang et al studied combustion behaviors of two kinds of sewage sludge in a drop tube reactor with a fixed temperature of 1200 °C [6]. Molten ashes were observed from char particle surfaces as the fed sludge passing the tube furnace with 0.6 s residence time. It was suggested that interactions of major mineral compounds in sludge, including calcium oxides, phosphorus oxide and aluminosilicates, led to formation of large molten agglomerates [6]. Shao et al [7] reported agglomeration characteristics of the sewage sludge combustion in a bench-scale fluidized bed combustor. With higher combustion temperatures and using degraded sands as bed material, more severe agglomeration was observed with formation of large sintered pieces and aggregates in the combustor. SEM-EDX and XRD analysis on collected agglomerates revealed that formation of low melting points eutectics of Fe_2O_3 and SiO_2 in bed materials might be a main initiator for bed agglomeration. It was followed by possibly reactions of P, Mg and Ca from sewage sludge with Si from

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doi:10.1016/j.fuproc.2011.12.022

Table 1
Characterization of sewage sludge samples.

	Proximate analysis (wt.%, d)			Ultimate analysis (wt.%. daf)					
Sample	VM	FC	Ash	C	H	S	O[a]	N	HHV (MJ/Kg. daf)
SS1	48.61	4.69	46.70	46.25	6.36	1.89	35.6	9.9	17.5
SS2	49.68	4.20	46.12	49.01	6.89	1.8	35.2	7.1	19.4
SS3	52.01	5.79	42.20	47	6.4	1.19	37.5	7.91	18.4

VM, volatile matters; FC, fixed carbon; d, dry basis; daf, dry and ash free; HHV, higher heating value

[a] The O content was determined by difference.

sand particles to enhance further bed agglomeration [7]. Moreover, sintering characteristics of sewage sludge have been studied under varying sintering temperatures and time scales [8–11]. However, aims of these studies were to evaluate properties of sintered sewage sludge and/or ash residues as ceramic production feedstock in terms of compressive strength and bulk density. Available literature results are quite dispersive and limited to deeply understand sintering behaviors of different sewage sludge ashes. In addition, different methods have been applied to recover phosphorus from the waste water i.e. flocculation using precipitation chemicals such as iron sulfate, aluminum sulfate and calcium sulfate [2,12–14]. The ash content and chemical compositions of the sewage sludge are affected by utilization of different phosphorus precipitation agents. It results in different ash chemistries and mineral transformation properties during combustion of the sewage sludge consequently [12–14]. To author's knowledge, no work has been done to study effects of phosphorus precipitation agents on sewage sludge ash chemical and mineralogical composition transformation during sintering processes. A detailed knowledge of sewage sludge ash sintering characteristics, correlated with difference in their chemical and mineral compositions, need to be clarified.

In this study, ashes produced from three sewage sludge samples were used as representatives for the investigation. The characteristics and sintering behaviors of sewage sludge ashes were studied by XRF, ash fusion analyzer, XRD and SEM-EDX. Various indices based on ash chemical compositions were applied to predict sewage sludge ash fouling and slagging propensities. The results will be useful to achieve a better understanding of sewage sludge ash sintering mechanisms and provide useful references for utilization of sewage sludge as an energy source.

2. Materials and methods

2.1. Sample preparation and characterization

Sewage sludge samples (SS 1–SS 3) from three waste water plants were used in this work. The SS 1 and SS 2 were obtained from the plants where aluminum sulfate ($Al_2(SO_4)_3$) is applied for phosphorus participation during the waste water treatment. While the iron sulfate ($Fe_2(SO_4)_3$) is used in the plant where SS 3 was produced [13]. Prior to the experimental work, all three received wet sewage sludges were dried in an oven at 105 °C to get constant weight, which were then grounded to sizes less than 1 mm and stored in sealed containers for further characterization. ASTM standards (E 872) were performed to determine volatile matter of all sewage sludge samples. Elemental compositions of dried sewage sludge were measured by conducting an elementary analyzer (Vario MACRO CHNS). Heating value of each sludge sample was measured by a bomb calorimeter (IKA C5000). The ash content of each sludge sample was determined by ASTM standard D 1102. Two grams of oven dried sample was put into a porcelain crucible and heated in an electrical muffle furnace at 550 °C for 5 h under oxidizing atmosphere. Difference between the initial mass and the final mass was considered as ash content. Fusion behaviors of sewage sludge ashes (SSA) were examined with an ash fusion analyzer (Carbolite CAF Digital). Residues collected after ash content tests (550 °C) were shaped into cubic specimens and heated from 25 °C to 1600 °C with a heating rate 6 °C/min under an oxidizing atmosphere. The external shape changes of each specimen were recorded and characterized by following standard (ISO 540:1995). Four characteristic temperatures were identified and logged, including initial deformation temperature (IDT), softening temperature (ST), hemisphere temperature (HT), and flowing temperature (FT). To get reliable results, the ash fusion tests for each ash sample were performed three times, and average values are plotted together with deviations.

2.2. Ash sintering evaluation

To evaluate the sintering behaviors at elevated temperatures, each sewage sludge ash produced at 550 °C was loaded into crucibles and heated at three final temperatures (900 °C, 1000 °C and 1100 °C) in the same furnace, respectively. All samples were heated at desired final temperatures for 1 h to ensure sufficient time for chemical interaction and mineral phase transformation. After sintering treatment, all samples were cooled down to the room temperature for visual observation. Then, the sintered ash residues were carefully collected from the crucibles without destroying initial structures and stored for further analysis.

2.3. Chemical composition and microstructure analysis

The main chemical compositions of the sewage sludge ashes obtained at 550 °C were determined by X-ray fluorescence (XRF) spectrometry (Bruker S8). The mineral compositions of sewage sludge ashes produced from different sintering temperatures were analyzed with an X-ray diffractometer (Bruker D8 Focus) equipped with a SOL-XE detector. Operating conditions of the XRD were 40 KV and 40 mA Cu Ka ($\lambda = 1.54$ Å) radiation and step-scanned in the 2θ range 10°–80°. Crystalline phases contained in each sample were identified by instrument integrated data processing software TOPAS plus ICDD-PDF 2 database.

The morphology and microchemistry of sintered sewage sludge ashes were examined by a field emission scanning electron microscopy (FE-SEM, Carl Zeiss Supra) equipped with an energy dispersive X-ray spectrometer (EDX, Bruker). All ash residues produced from sintering tests were collected and embedded into epoxy resin. The samples mounted in the resin were cut, grinded and polished to get smooth cross-sections. The cross-sections were then coated with carbon and analyzed by SEM-EDX with spot analysis and element mapping methods.

Table 2
XRF analysis results of sewage sludge ash (wt.%).

Sample	Chemical compositions (oxides, wt.%)										Slagging and fouling indices					
	Al_2O_3	SiO_2	P_2O_5	Fe_2O_3	CaO	K_2O	Na_2O	MgO	TiO_2	SO_3	R_b	R_a/R_b	$R_a/R_{b(+p)}$	S_R	F_u	F_s
SSA1	31.74	26.71	16.71	6.80	13.08	0.69	0.47	1.08	0.45	2.27	22.13	0.38	0.66	56.03	0.44	1296
SSA2	29.43	23.54	18.33	9.54	11.20	1.41	1.02	0.97	1.15	3.41	24.23	0.45	0.79	51.91	1.09	1208
SSA3	13.33	26.32	16.35	30.21	6.33	1.58	1.13	1.85	0.79	2.11	39.09	0.97	1.42	41.98	2.61	1049