Thermochimica Acta 526 (2011) 29–34

Contents lists available at ScienceDirect

Thermochimica Acta

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

Effect of fluorine and chlorine on slag melting characteristics: Experimental study and simulation by neural networks

Jianjie Qian, Xuguang Jiang*, Fei Wang, Yong Chi, Jianhua Yan

State Key Laboratory of Clean Energy Utilization, Zhejiang University, Zheda Road 38#, Hangzhou 310027, Zhejiang Province, PR China

ARTICLE INFO

Article history:
Received 3 May 2011
Received in revised form 11 August 2011
Accepted 12 August 2011
Available online 19 August 2011

Keywords:
Melting characteristics
Hazardous waste
Chemical component
Fusion temperature
Neural network

ABSTRACT

Hazardous waste from chemical factories including fluorine and chlorine has rather low fusion temperatures. During incineration in a rotary kiln incinerator, hazardous waste including fluorine and chlorine melts and turns into slag, possibly adhering to the inner wall and leading to unstable operation of the incinerator. Prediction of the melting characteristics of hazardous waste including fluorine and chlorine hence plays an important role in preventing slagging. The effect of various chemical components on fusion temperatures (deformation temperature, DT; softening temperature, ST; hemisphere temperature, HT; and flow temperature, FT) has been investigated experimentally: Na_2O and NaF are the most remarkable chemical compounds among those investigated. Correlations between fusion temperatures and chemical components have been investigated; neural networks have been used to predict four characteristic melting temperatures and are verified by tested slag samples of hazardous waste including fluorine and chlorine. Relative errors of fusion temperatures (computed vs. measured) are mostly less than 1.2%.

1. Introduction

Hazardous waste from industrial production is becoming an ever-increasing concern as economic development progresses. The reported generation of industrial hazardous waste (IHW) in China was 14.3 million tons in 2009. Moreover, a wide variety of industrial hazardous waste is being created, most of which is harmful and very slow to decompose by natural process. Such waste causes tremendous concern for human life and potentially huge damage to the environment.

Incineration has been identified as the best disposal option for hazardous waste because it realizes a large reduction in volume as well as resources recovery [1,2]. Fly ash from a hazardous waste incinerator located in Medellin, Colombia was characterized [3]. Mass transfer of simulative hazardous waste particles has been tested in a rotary kiln [4]. The effect of the chemical components on the melting points of hospital waste slag has been analyzed already; it was observed that fusion temperature increased with the CaO content [5]. Combustion characteristics of particles of hazardous solid waste mixtures in fixed bed, and the effects of primary air rate, moisture, bed height and particle size on burning rate, ignition-front speed and temperatures in the bed were also investigated [6].

The characteristics of slag specimens from the incineration of hazardous waste including fluorine and chlorine are important parameters to optimize the incineration. In rotary kiln incineration, hazardous waste including fluorine and chlorine melts and turns into slag, possibly adhering to the inner wall. In other cases, the molten hazardous waste probably tumbles and rolls, bonding to other slag particles; finally large slag agglomerates are formed, blocking the exit of the rotary kiln. Continuous operation of the kiln will then have to be shut down. Therefore, the melting characteristics of slag from the incineration of hazardous waste including fluorine and chlorine are important for optimizing hazardous waste incineration and preventing slagging of rotary kiln incinerators.

In this paper, the melting characteristics of slag from the incineration of hazardous wastes including fluorine and chlorine have been researched by changing the contents of components, and correlations between fusion temperatures and components of slag from a rotary kiln incinerator have been verified by neural networks.

2. Experimental materials and methods

2.1. Characteristics of the slag

Slag samples were collected at a slag cooling facility under the exit of a rotary kiln from a hazardous waste treatment center in Quzhou, Zhejiang province. This is a general purpose, and the total feed is 15T/D. There were about 3T/D slag and 4T/D fly ash. Hazardous waste being treated discharged from fluoride chemicals

* Corresponding author. Tel.: +86 571 87952775; fax: +86 571 87952438.
E-mail addresses: jiangxg@zju.edu.cn, jiangxg@cmee.zju.edu.cn (X. Jiang).

0040-6031/$ – see front matter
doi:10.1016/j.tca.2011.08.015

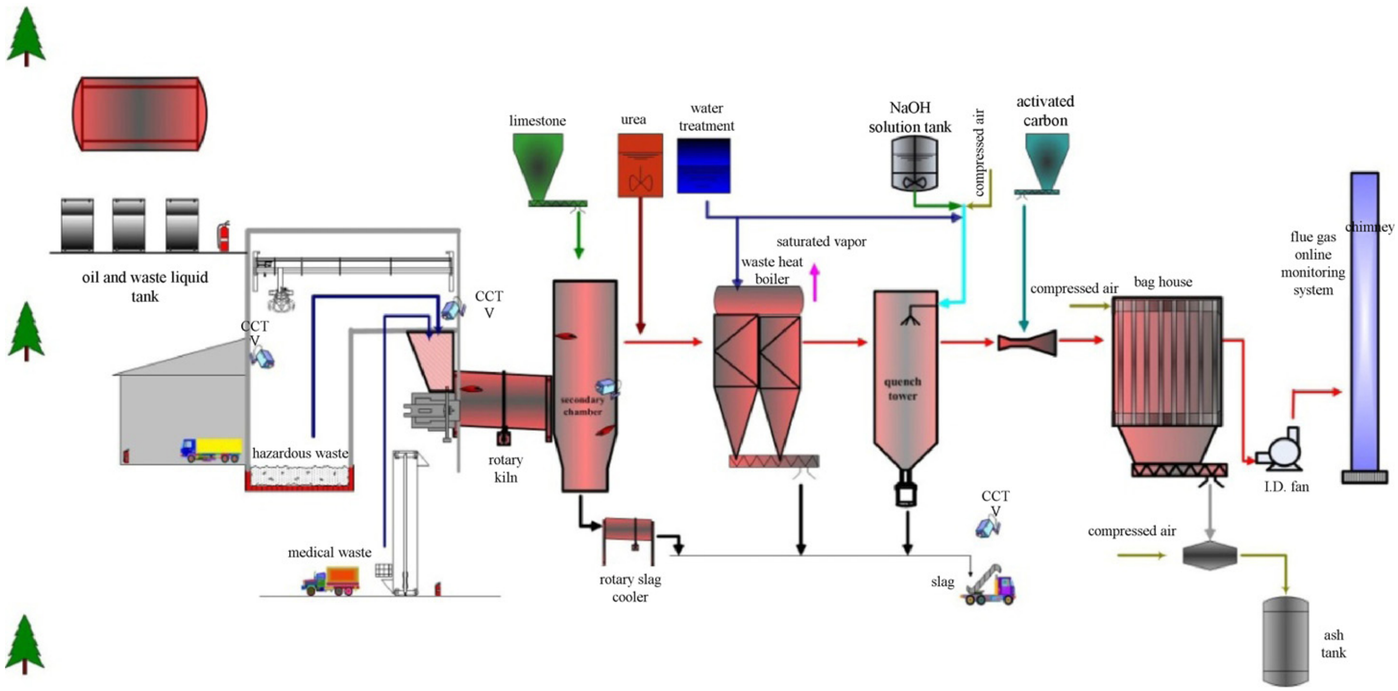

Fig. 1. The system flowchart of hazardous waste treatment center in Quzhou.

factories is residue from producing fluoborate. This kind of residue is inorganic and a kind of black brown solid. It is slagging of the wall. To make the slag samples are typical, these four kinds of samples are collected in the continuous and stable operation period. The system flowchart of the hazardous waste treatment center in Quzhou is shown in Fig. 1. The facilities include: rotary kiln, secondary chamber, waste heat boiler, cooling tower, bagfilter, I.D. fan and chimney. A reducing atmosphere is usually adopted in the rotary kiln in order to pyrolyze the residue. After the pyrolysis gas entered into the secondary combustion chamber dosed secondary air will make the pyrolysis gas incinerate. The operating temperature of the rotary kiln is about 600 °C, while the operating temperature of the secondary combustion chamber is from 850 °C to 1100 °C depending on the species of waste.

The sampled slag was melted at 900 °C and cooled at room temperature. The slag was crushed with a hammer and ground for analysis. X-ray fluorescence (XRF) was performed by ARL ADVANT' X IntelliPower TM4200 spectrometer.

The slag content is presented in Table 1 on a wt% basis. The chemical composition of slag cannot be considered an oxide like coal ash, due to the high content of fluorine and chlorine. In order to identify the chemical composition of slag more strictly, FactSage thermochemical software has been chosen to calculate reaction equilibrium and investigate the chemical composition of the slag.

The FactSage package runs on a PC operating under Microsoft Windows (R) and consists of a series of information, database, calculation and manipulation modules that enable one to access and manipulate pure substances and solution databases. The Equilib module is the Gibbs energy minimization workhorse of FactSage. It calculates the concentrations of chemical species when specified elements or compounds react or partially react to reach a state of chemical equilibrium [6]. The entry is shown in the Equilib reactants and database window where 15.77 g of Na is being equilibrated with variable amounts of Cl, Ca, F, K, O in 100 g of slag sample as shown in Table 1.

As shown in Fig. 2, the element of fluorine is turned into NaF completely according to the calculation that 5.36 g of fluorine could generate 11.85 g of NaF, and when the temperature is higher than 1000 °C, the solid of NaF turns into a gas state. Chlorine is turned into KCl, and then the remainder is transformed into NaCl. When the temperature is below 1000 °C, Na_2O_2 is formed; when the temperature is higher than 1000 °C, Na_2O is formed. When the temperature is lower than 200 °C, CaO_2 is produced; and when the temperature is higher than 200 °C, the production is CaO. According to chemical equilibrium, other elements are considered to be oxides. Results of Fig. 2 are in an ideal situation and used to simulate the slag to do experiment study. Therefore, the chemical components of incineration slag of hazardous waste including fluorine and chlorine could be considered as Table 2.

2.2. Experimental verification

The composition of incineration slag samples of hazardous waste including fluorine and chlorine, collected from a hazardous waste treatment center, is so complicated that it is difficult to obtain quantitative correlations between fusion temperatures and components. In order to study their effect on fusion temperatures, the ratio of components including oxides, NaCl, NaF, KCl was adjusted. According to the composition of incineration slag samples of hazardous waste including fluorine and chlorine in Table 2, oxides, NaCl, NaF, KCl (analytical reagent) were blended and the corresponding carbonates were substituted by the unstable oxides: Na_2O and CaO. The homogeneous mixture was crushed to powder smaller than 0.2 mm and marked as Sim-1. According to GB/T 219-1996 "Determination of Fusibility of Coal Ash" (China), four characteristic melting temperatures (deformation temperature,

Table 1
XRF analytic results of slag samples.

Sample	Content (wt)							
	Si	Na	Fe	Cl	Ca	F	Al	K
1#	15.77%	17.25%	6.75%	8.43%	4.63%	5.36%	2.37%	2.30%
2#	16.71%	18.94%	3.64%	6.34%	3.63%	4.84%	3.19%	4.16%
3#	23.22%	11.97%	8.09%	2.42%	2.95%	2.1%	2.69%	2.96%
4#	24.59%	10.85%	7.80%	2.10%	3.08%	2.27%	2.63%	2.76%