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Properties of ash generated during sewage sludge combustion: A multifaceted analysis

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ABSTRACT

This paper presents chemical properties of sewage sludge ashes required for determining their thermal characteristics. A novel approach, linking selected advanced analytical techniques with FactSage modelling, was developed and applied to obtain new information on deposit formation mechanisms that contribute to fouling and slagging. The mineral matter and fusion temperatures were investigated using a variety of analytical techniques including XRF, ICP-MS, XRD, SEM-EDX and AFT. The slagging and fouling indices were calculated and the sintering properties were predicted. The studied ashes were rich in P_2O_5, CaO, SiO_2 and Fe_2O_3, but their concentrations slightly differed. Phase analyses suggested the existence of calcium and phosphorus as main phases. Thermal behaviour of ashes was studied focusing on the mass loss, temperature peaks and thermic effects with the increasing of temperature up to 1200 °C under air atmosphere. The changes in concentration of ash compounds contributed to differences in ash fusion temperatures. FactSage thermochemical equilibrium calculations were used to predict the amount of liquid slag and solid phases, giving information about slagging properties of ashes. The general conclusion based on experimental studies is that sewage sludge ashes cause the slagging and fouling hazard while they reveal low corrosive effect.

1. Introduction

Environmental protection and new EU legislation drive the use of renewable fuels for energy production. Biomass and sewage sludge are known alternative energy sources. In addition, increases in the amount of sewage sludge have been affecting the environment, which has resulted in legislation changes in Poland. In the view of the recent legal regulation (7/16/2015) regarding the criteria and procedures for releasing wastes to landfilling, the thermal disposal of sewage sludge is important due to its gross calorific value, which is greater than 6 MJ/kg, and the problems that result from its use and application [1,2]. While biomass combustion or co-combustion processes are commonly used [3–9], sewage sludge combustion is rather new technology especially in large-scale devices [10,11]. Sewage sludge is the residual matter from the treatment of household and industrial wastewaters. In its dry form, sewage sludge could be considered as renewable fuel due to the high quantity of organics of sufficiently high calorific value, which can be thermally utilized. On the other hand, it contains microorganisms and harmful substances including heavy metals, poorly biodegradable organic compounds, bacteria, viruses, pharmaceuticals, hormones and dioxins [12]. There are several thermal technologies utilizing municipal sewage sludge to obtain useful energy. They include pyrolysis, gasification, combustion, and co-combustion processes [13–17] Currently, as many as 11 plants in Poland use sewage sludge as fuel. This technology is expected to be further developed while considering the benefits of co-combustion with other fuels [18]. The combustion of sewage sludge can cause operating problems due to high moisture content and a large amount of ash. Additionally, gaseous pollutants (CO, C_xH_y, NO_x, SO_x, PAHs, dioxins and furans) and particulate matter are generated [19,20].

The advantages of thermal processes are the large reduction in volume, the thermal destruction of toxic organics and the recovery

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of the energy from organic compounds present in the sludge. However, burning sewage sludge generates a large amount of ash containing mineral compounds (more than 30%) creating problems when other fuels are substituted by sewage sludge. The main elements in the sewage sludge ash are silicon, phosphorus, potassium, calcium, sulphur, chlorine and sodium [19]. Potassium content is important because it indicates a potential ash fusion and deposition by vaporization and condensation. In renewable fuels combustion K and Cl can be released in gas such as HCl, KCl and potassium exists as potassium silicate, aluminosilicate and sulphate. During the cooling process the gaseous potassium may condense on the coarse fly ash as KCl and K_2SO_4 [21]. Some of the gaseous potassium directly forms aerosols. The potassium, sulphur and chlorine enrichments in ash are very harmful because of corrosion risk. In the case of sewage sludge, the presence of heavy metals such as Pb, Cd, Cr, Cu, and Ni is a significant problem during the combustion process [22]. Alkali metals associated with sulphur and chlorine give serious operating problems such as slagging, fouling and corrosion of metal surface limiting heat transfer. The term of slagging is used to describe the formation and accumulation of slags on the furnace sections (refractory walls, water walls, and grates). The reactivity of slags and bed agglomerations depends on the chemical reaction between ash components in particularly silica, alkali, alkaline earth metals and other inorganic compounds present in the environment [23,24]. The term fouling is used to indicate the formation of ash deposits on heat transfer surfaces in the convective parts of the furnace.

Although sewage sludge combustion is applied in several locations with good efficiency, ash deposition is a new problem, which requires new solutions. There are many papers concerning the influence of chemical composition of biomass ash on deposition and corrosion processes e.g. Refs. [21,25,26]. The formation and transformation of sewage sludge ash are presented elsewhere [27,28], but details regarding mechanisms associated with deposit formation that contribute to slagging and fouling are still being studied. In order to better understanding of the mineral matter transformation at high temperatures, a FactSage Thermodynamics Model was used. The FactSage is based on minimization of the Gibbs energy of a system. The Gibbs energy minimization algorithms identify amount of various phases and the composition of the solution phases. Gibbs energy can be calculated from what is known of the chemical potential of the component by Ref. [29]:

$$G = \sum_i n_i \overline{G_i} \tag{1}$$

where: the n_i amount of the component i. Assuming some constraints such as p, T and overall composition, the Gibbs energy minimization algorithms find the amount of various phases and the composition of solution phases which give a global minimum in the total Gibbs energy of the system [30]. The Gibbs energy can be expressed as:

$$G(T) = \Delta H_{298} + \int_{298}^{T} C_p(T)dT - T\Delta\left(S_{298} + \int_{298}^{T} \frac{C_p(T)}{T}dT\right) \tag{2}$$

The values of ΔH_{298}, S_{298} and $C_p(T)$ are from thermodynamic databases.

Thermochemical calculations can indicate chemical composition in equilibrium, show amount of liquid slag and solid phases, and give information about slagging properties of ashes. The transformation and fusion of ash takes place at high temperatures, and kinetic limitations, mass transport, chemical potentials have all influence the calculated mineral phases. The sewage sludge ash is a very complex material in terms of physical and chemical properties. It consists of particles of different shape, a different chemical composition and phase. The intergranular boundaries and chemical composition of individual grains are significant impact on the sintering process. Moreover, physical and chemical properties of ash grains influence on the viscosity and line tension of intergranular boundaries (surface and volume diffusion of mobility ions), but viscosity and line tension of intergranular boundaries determine the sintering mechanism [31]. Therefore, thermodynamic analysis is interesting as a complement to standard and nonstandard ash tests that give detailed information about physical and chemical transformation of the ash.

The multifaceted description of sewage sludge ashes using advanced instrumental methods and supported by FactSage calculations with special emphasis on precise physico-chemical characteristics is exactly what this paper has to offer.

2. Materials and methods

2.1. Materials

Materials considered for this study consisted of four kinds of sewage sludge ashes. The samples were denoted as A_1, A_2, A_3, and A_4, respectively. The sewage sludge samples were taken from four existing municipal wastewater plants in Poland. Ash samples were obtained from existing energy units where the sewage sludge is combusted. Current knowledge of the ash formation mechanisms and interactions between the ingredients is insufficient to successfully avoid slagging and fouling of ashes on boiler surfaces. Various analytical methods determining physical and chemical characteristics of biomass and sewage sludge ashes are required in order to better understand the driving forces contributing to fouling/slagging.

2.2. Experimental procedures

The X-ray fluorescence (XRF, Riau ZSX Primus II) has been used to determine the main chemical composition of sewage sludge ashes (expressed as oxides in Table 1). There were two kinds of oxides then the chemical properties were taken into account. The basic oxides are Na_2O, K_2O, MgO, CaO and Fe_2O_3, and the acid oxides are SiO_2, Al_2O_3 and TiO_2.

TG–DSC technique (Thermogravimetry and Differential Scanning Calorimetry) was conducted using Netzsch STA 449 F3 Jupiter. The samples were heated in alumina crucibles from ambient temperature to 1200 °C at a constant rate of 10 °C/min and at a 40 ml/min flow of air. The mass of sample was 35 mg, pan capacity was c.a. 113 mm^3. The evolved gaseous products from decompositions were identified on-line using mass spectrometry (QMS Netzsch). The following ions, which are characteristic of the molecules of interest, were monitored: 18, 44, and 64 H_2O, CO_2 and SO_2, respectively.

The fusibility analysis was performed by a LECO AF700 Ash Fusion Determinator. Pre-prepared ash cones were mounted on a ceramic tray and placed into a high-temperature and rampable furnace. The tests were done under air atmosphere. The specially prepared pyramids are heated up to 1500 °C. The heating process of the ash cones was observed and monitored *via* video camera to determine deformation temperatures (a deformation temperature (IDT), a softening temperature (ST), a hemispherical temperature (HT) and a flow temperature (FT)). IDT is the temperature at which the first rounding of the apex of the cone occurs. ST is the temperature at which the cone has fused down to a spherical lump and the height becomes equal to the width of the base. At HT temperature the height becomes one-half of the width of the base. FT is the