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# Thermochemical principles of the production of lightweight aggregates from waste coal bottom ash

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## Abstract

Manufacturing lightweight aggregate (LWA) (i.e., porous ceramics) by means of a sintering technique requires a delicate balance among three conditions: (i) forming a sufficient amount of molten liquid phase during sintering, (ii) reaching an appropriate viscosity for solid-liquid suspension, and (iii) emitting a sufficient amount of gas that can be entrapped by the liquid phase to form pores. This study evaluates these three conditions in the production of LWAs made from two types of waste coal bottom ash (low-calcium and high-calcium), and relates them to the formation of LWA pore structure. A thermochemical analytical approach, including thermodynamic modeling and the Browning viscosity model, was used to quantify the extent of the liquid phase and calculate its viscosity. In conjunction with thermochemical analysis, an experimental approach including quantitative x-ray diffractometry, thermogravimetric analysis, and x-ray

computed tomography was also used to identify the candidate chemical compounds that contribute to gas emission during sintering and to evaluate the LWA pore structure. The results indicated that a mass fraction of at least 50 % for the liquid phase is required for a successful entrapment of emitted gaseous phases during sintering. Larger pores were observed in the microstructure of LWA samples made using high-calcium bottom ash in comparison to those made with low-calcium bottom ash. This observation was mainly attributed to the high-calcium samples forming liquid phases with lower viscosities and emitting higher amounts of gaseous phase during sintering than did the low-calcium samples. It was found that the gaseous phase was generated by hematite reduction and anhydrite decomposition, which led to the release of  $O_2$  and  $SO_2$ .

Keywords: Bottom ash, Gaseous phase, Lightweight aggregate, Liquid phase, Sintering, Viscosity, Coal combustion product

## Nomenclature for chemical compounds

Name	Chemical formula
Anatase	TiO <sub>2</sub>
Andradite	$Ca_3Fe_2Si_3O_{12}$
Anhydrite	CaSO <sub>4</sub>
Anorthite	CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>
Augite	(Ca,Na)(Mg,Fe,Al,Ti)(Si,Al) <sub>2</sub> O <sub>6</sub>
Brucite	Mg(OH) <sub>2</sub>
Calcite	CaCO <sub>3</sub>
Clinopyroxene	CaMgSi <sub>2</sub> O <sub>6</sub>
Combeite	Na <sub>2</sub> Ca <sub>2</sub> Si <sub>3</sub> O <sub>9</sub>
Cordierite	$Mg_2Al_4Si_5O_{18}$
Dolomite	CaMg(CO <sub>3</sub> ) <sub>2</sub>
Feldspar	NaAlSi <sub>3</sub> O <sub>8</sub>
Feldspar (Anorthite)	$CaAl_2Si_2O_8$
Gehlenite	Ca <sub>2</sub> Al <sub>2</sub> SiO <sub>7</sub>
Gypsum	CaSO <sub>4</sub> ·2H <sub>2</sub> O
Hematite	Fe <sub>2</sub> O <sub>3</sub>
Melilite	$Ca_2Mg(Si_2O_7)$
Merwinite	Ca <sub>3</sub> Mg(SiO <sub>4</sub> ) <sub>2</sub>
Mullite	$3Al_2O_3 \cdot 2SiO_2$
Nepheline	NaAlSiO <sub>4</sub>
Orthopyroxene	Mg <sub>2</sub> Si <sub>2</sub> O <sub>6</sub>

Portlandite	Ca(OH) <sub>2</sub>
Rankinite	Ca <sub>3</sub> Si <sub>2</sub> O <sub>7</sub>
Tridymite	SiO <sub>2</sub>
Wollastonite	CaSiO <sub>3</sub>
C: CaO, A: Al <sub>2</sub> O <sub>3</sub> , N: Na <sub>2</sub> O, S: SiO <sub>2</sub> , H: H <sub>2</sub> O	C-A-(N)-S-H
N: Na <sub>2</sub> O, A: Al <sub>2</sub> O <sub>3</sub> , S: SiO <sub>2</sub> , H: H <sub>2</sub> O	N-A-S-H
C: CaO, S: SiO <sub>2</sub> , H: H <sub>2</sub> O	C-S-H

## 1. Introduction

Bottom ash is a type of Coal Combustion Product (CCP) and is currently considered to be a waste material needing to be landfilled. In 2017, nearly 10 billion kg of bottom ash were produced from which only  $\approx$ 50 % was recycled [1]. Landfilling of unused bottom ash can impose a risk to the environment and human health [2,3]. Accordingly, new regulations made by the United States Environmental Protection Agency (EPA) [4] encourage new methodologies to convert CCPs into value-added products. Producing functional lightweight aggregate (LWA) for the construction industry from bottom ash can be a practical approach to help landfill diversion and recycling waste CCPs. Sintering is one of the techniques that can be employed in order to produce LWA from CCPs. However, successful production of LWA from CCPs requires an advanced understanding of the sintering mechanisms taking place during the production process.

Previous studies of LWA production from various starting waste materials [5–11] have suggested that a successful production of sintered LWA requires a sintering mechanism where three crucial conditions are reached concurrently during sintering [7,12]: (1) sufficient liquid/molten phase amount formation on the aggregate surface to maintain a viscous state for the LWA, (2) attaining an appropriate viscosity in the liquid-solid suspension to enable the entrapment emitted gas during sintering while preventing extreme LWA deformations under gravitational forces, and (3) appropriate amount of gaseous phase emission during sintering to form entrapped pores in the liquid phase that will result in successful bloating and LWA formation. Providing a balance among these three conditions can lead to successful design and production of functional LWA having desirable engineering properties for different industrial applications. Some of the applications are internal curing of concrete [5], lightweight concrete, lightweight fill for geotechnical applications, wastewater treatment [13], and green roofs. For applications such as internal curing of concrete properties are interconnected pores with appropriate porosity (> 20 % by volume) as well as appropriate water absorption/desorption properties (water absorption > 5% and minimum of 85% water desorption at 94% relative humidity [5,14]). In the case of using LWA in lightweight concrete and lightweight fill for geotechnical applications, the bulk density and

compressive strength are the important engineering properties, and the recommended values are 650 kg/m<sup>3</sup> - 1100 kg/m<sup>3</sup> and about 2 MPa, respectively [15,16]. For application in wastewater treatment, the pore structure and the ability to retain contaminants are the designing parameters [17]. *Figure 1* shows a schematic representation of a typical synthetic LWA, with development of a core and shell structure morphology after sintering [18].



Figure 1. Schematic representation of a synthetic LWA with core and shell morphology [7,18]

#### 1.1. Background on Conditions for Sintering

(1) Formation of liquid phase during sintering: During LWA production through sintering, formation of a liquid phase favors the integrity of the LWA and provides strength [19]. As a viscous medium, it captures emitted gas to form pores in the LWA (*Figure 1*). Lack of a sufficient amount of liquid phase not only prevents entrapment of the gaseous phase as pores, but also leads to poor LWA compressive strength due to inadequate particle bonding. To quantify the mass of liquid phase formed when waste coal ash is sintered, thermodynamic modeling can be used to predict the formation of the most stable phases (including the liquid phase) from the sintered materials with different chemical compositions [12,19,20]. The presence of more than 50 % of liquid phase (by total mass of feed materials) has been shown to be necessary for

production of high-quality LWA [20]. It has been also reported that an excessive amount of high viscosity liquid phase can result in pore sealing and reduction in sorption properties for the resulting LWA [10,21].

(2) Viscosity of liquid phase: Viscosity of the solid-liquid suspension during sintering is another crucial condition for LWA design and production. Low viscosity values cannot only lead to considerable deformation and collapse of the molten phase but also result in eruption of the emitted gaseous phase and generation of overly-large pores in LWA. The right viscosity can ensure stable entrapment of the gaseous phase leading to successful bloating behavior, forming a desirable LWA pore system. The dynamics of gas-filled pore growth, which determines the final pore size, in a viscous medium is highly dependent on the liquid phase viscosity [22]. It has been shown that the viscosity of the liquid phase is mainly dependent on its chemical composition [12,23,24] and can be predicted using empirical models such as those of Browning [24] and Urbain [25].

Few studies have quantified the viscosity of the solid-liquid phase in LWA production. Billen et al. [12] investigated the production of lightweight melt ceramics from bottom ash using NaOH as a fluxing agent to promote melting behavior so as to entrap emitted gaseous phases at sintering temperatures near 1160 °C. Their results showed that for production of lightweight melt ceramics, without any deformation under gravitational forces, the solid-liquid suspension should have a viscosity greater than 1000 Pa·s.

(3) Formation of gaseous phase: Liberation of an appropriate amount of gaseous phase is crucial for LWA production. The addition of hematite, pyrite, dolomite and calcite to non-bloating clays can lead to good bloating behavior for clay-based LWA [23]. However, calcite was not found to be a promising bloating agent for LWA production since its addition produces a low viscosity molten phase and results in overly-large pores and excessive deformation in the final LWA product [23]. Rincón et al. [26] reported that for successful production of a glass-based LWA, possessing high permeability and low density, there should be a delicate balance between viscous flow sintering and gas emission. They stated that gas emission can happen through oxidation and decomposition reactions at elevated temperatures where oxidation reactions involve release of  $CO_{x}$  (x=1,2) gas from carbon-containing compounds and decomposition originates from

carbonates or sulfates emitting CO<sub>2</sub> or SO<sub>x</sub> gases. Another type of decomposition can arise from reduction of metal oxides transforming from high valence states into low valence states, which leads to oxygen gas release [27,28]. Reduction of hematite (Fe<sub>2</sub>O<sub>3</sub>) and emission of oxygen during the sintering process has been proposed by researchers as a source of gas release for pore formation (Equation 1 and Equation 2) [26]. It has been found that the extent of this reduction is dependent on the unburnt carbon content available in the system [29]. Reduction of hematite highly depends on the partial pressure of oxygen. At 0.101 MPa (1 atm), this reduction happens at 1400 °C, which is significantly higher than the temperature at which a liquid phase forms on the surface of a typical LWA (i.e., 1100-1200 °C) [30]. By decreasing the oxygen partial pressure, however, reduction of hematite can shift to 1100 °C. This can be achieved by rapid sintering where the surface of LWA quickly turns into liquid phase and seals the entire LWA, and oxygen partial pressure decreases by carbon burning inside the LWA resulting in the reduction of hematite and the release of O<sub>2</sub> gas [31].

$$\begin{array}{ll} 6Fe_2O_3(s) \rightarrow 4Fe_3O_4(s) + O_2(g) & \mbox{Equation 1} \\ 2Fe_3O_4(s) \rightarrow 6FeO(s) + O_2(g) & \mbox{Equation 2} \end{array}$$

Wei and Lin [11] investigated the role of Fe compounds on LWA production from reservoir sediments containing silicate-alumina-based materials [32]. The material was dried and then ground to fine particles, and finally were shaped into pellets by applying 34.5 MPa (5000 psi) pressure. The sintering was carried out at 1050 °C and 1150 °C. They observed that the bloating mechanism occurred at the core of the LWA that was sintered at 1150 °C and was associated with the release of SO<sub>2</sub>, SO<sub>3</sub> and O<sub>2</sub> gases due to the decomposition of FeSO<sub>4</sub>. Wei et al. [33] investigated the effect of calcium compounds, including calcite and gypsum (CaSO<sub>4</sub>· 2H<sub>2</sub>O) additions, as bloating agents on LWA pore formation in coal fly ash mixed with waste glass. Their thermogravimetric analysis (TGA) results on pure calcite demonstrated a rapid mass loss from 600 °C to 780 °C and relatively no mass loss from 780 °C to 1200 °C. For gypsum, they observed a rapid decomposition starting at 100 °C and ending at 160 °C related to the release of water from the

gypsum structure. The mass loss from 160 °C to 1100 °C was negligible for gypsum. However, decomposition between 1100 °C and 1200 °C was observed and was associated with the decomposition of CaSO<sub>4</sub> to CaO and the release of SO<sub>2</sub> gas [34].

Previous works have described successful production of a novel LWA, spherical porous reactive lightweight aggregate (SPoRA), from high-calcium and low-calcium bottom ash [10,12], where the functionality of these LWA for internal curing of concrete was found to be promising [5]. This paper builds on these previous results to better understand the SPoRA sintering mechanisms by quantitatively evaluating the three crucial sintering conditions required for successful production of LWA: the correct amount of liquid phase formation, the correct viscosity of the liquid-solid suspension, and the correct amount of the emitted gas for pore formation. First, the liquid phase of the multi-component system of bottom ash and fluxing agent was quantified using thermodynamic modeling. Second, the viscosity of the liquid-solid phase was quantified using the output of thermodynamic modeling as inputs into the Browning and Krieger-Dougherty model equations [24,35,36]. Third, quantitative x-ray diffractometry (QXRD) and TGA were performed to assess the presence of the candidate chemical compounds that can lead to gas liberation during sintering and to understand the thermal behavior of geopolymerized (i.e., experienced/underwent the chemical rection between the dissolved species of aluminates and silicates in a highly alkaline environment to form a three-dimensional aluminosilicate network [37]) pellets during sintering. Finally, the interior physical features and the LWA pore structure were visualized using three-dimensional (3D) x-ray computed tomography (X-CT).

## 2. Materials and Research Methodology

#### 2.1. Materials

Two types of bottom ash, NV (low-calcium) and WP (high-calcium), were used in this study for LWA production [5,12]. The LWA manufacturing procedure started by drying the raw ash material, followed by sieving to the appropriate particle size distribution. Afterward, the prepared ash was mixed with various

NaOH solutions (molarities of 2.5 mol/L, 6.25 mol/L, and 10 mol/L) to achieve mass concentrations (mass of solid NaOH per mass of bottom ash) of 4 %, 10 %, and 16 %. NaOH solutions with a liquid to solid ratio of 0.4 were used for geopolymerization during the curing period as well as to serve as a fluxing agent to reduce the melting temperature of the mixture [5,12]. The mixture was then pelletized into spherical shape and cured at 40 °C and 30 % relative humidity (RH) for 24 h. Finally, the pellets were sintered at 1160 °C to produce SPoRA. The detailed SPoRA manufacturing process can be found elsewhere [5,12]. Samples were labeled as XX-YY%, where XX represents the bottom ash type (NV or WP), while YY% indicates the NaOH concentration.

#### 2.2. Research methodology

The research methodology was divided into two parts, analytical modeling and experimental investigation, to examine the required conditions for LWA production. The analytical part employed thermodynamic modeling and viscosity calculations to quantify liquid phase formation as a function of temperature during sintering and to calculate viscosity values for the resulting solid-liquid suspension. Experiments were used to study the chemical compounds that can lead to gas emission during the sintering process and quantify the amount of the emitted gaseous phase that leads to LWA pore formation. The pore-solid structure of LWA was investigated using X-CT with respect to the three conditions required for successful LWA production.

#### 2.2.1. Analytical modeling

The analytical modeling in this study was built on the previous work conducted by Billen et al [12] to understand the thermodynamic response and fluid behavior of solid-liquid suspension during sintering. Analytical modeling consisted of developing phase equilibria and quantification of liquid phase formation using the Factsage<sup>1</sup> software [38,39] as well as using the thermodynamic modeling outputs, including the chemical composition of the liquid phase, to calculate the viscosity of solid-liquid system.

### 2.2.1.1. Factsage simulation

The Factsage thermodynamic modeling software, along with the FToxide database [40], were used to predict multi-phase equilibria based on Gibbs' free energy minimization algorithm for the multi-component system during sintering [19,41]. The simulation was performed at 0.101 MPa (1 atm) under an ordinary air atmosphere, which was composed of 0.21 mole fraction oxygen and 0.79 mole fraction nitrogen, in accordance with the conditions of LWA sintering. The initial and final temperatures for the modeling were set to 800 °C and 1400 °C, respectively, with 50 °C intervals. The major chemical oxides of the ashes, which were used as the input in the Factsage software, were determined using x-ray fluorescence (XRF) [42] and are presented in Table 1 [5,12].. In addition, NaOH was used as the fluxing agent in the thermodynamic modeling.

Chemical Composition	Sample Name	
(% by mass)	NV	WP
SiO <sub>2</sub>	63.2	43.1
$Al_2O_3$	20.1	17.1
Fe <sub>2</sub> O <sub>3</sub>	6.66	7.29
CaO	3.51	22.5
$Na_2O$	1.43	1.19
MgO	0.97	4.10
Total	95.89	95.31

Table 1. Major chemical oxide compositions of NV and WP ashes used in this study

## 2.2.1.2. Viscosity calculations

<sup>&</sup>lt;sup>1</sup> Certain commercial equipment, software and/or materials are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the equipment and/or materials used are necessarily the best available for the purpose.

Empirical models have been developed to predict coal ash liquid phase (slag) viscosity based on a simplified slag chemical composition [25,43-45]. The empirical model developed by Browning et al. [24] was found to be more applicable for the prediction of the liquid phase (slag) viscosity [12] due to experimentally determined lower bias and higher accuracy compared with earlier developed models such as those of Watt and Fereday [44] and Urbain [25]. The Browning model assumes that the viscosity of the slag falls into a Newtonian region [46] and correlates viscosity with temperature (T) using a temperature shift  $(T_s)$  (Equation 3). T<sub>s</sub>, as presented in Equation 4, is a function of a composition parameter, i.e., A. A is defined as the weighted molar ratio of network formers (numerator of Equation 5) to network modifiers (denominator of Equation 5) elements as presented in Equation 5, where the quantity of each component is in mole fraction and their summation must add up to unity (Equation 6).

$$log_{10}\left(\frac{\eta_L}{T - T_s}\right) = \frac{14788}{T - T_s} - 10.931$$
Equation 3
$$T_s = 306.63 \ln(A) - 574.31$$
Equation 4

$$T_s = 306.63. \ln(A) - 574.31$$
 Equation -

$$A = \frac{3.19Si^{4+} + 0.855Al^{3+} + 1.6K^{+}}{0.93Ca^{2+} + 1.50Fe^{n+} + 1.21Mg^{2+} + 0.69Na^{+} + 1.35Mn^{n+} + 1.47Ti^{4+} + 1.91S^{2-}}$$
Equation 5  
Si^{4+} + Al^{3+} + Ca^{2+} + Fe^{n+} + Mg^{2+} + Na^{+} + K^{+} + Mn^{n+} + Ti^{4+} + S^{2-} = 1Equation 6

The composition of the liquid phase (slag) at different temperatures for each LWA was obtained using Factsage with varying fluxing agent concentrations and was used to estimate the viscosity of the liquid phase. It should be noted that during sintering at some temperatures, the LWA system is composed of liquid and solid phase concurrently; therefore, the suspension's (solid-liquid phase) viscosity becomes highly dependent on the volume fraction of solid phase. Thus, to estimate the viscosity of solid-liquid suspension, the Krieger and Dougherty model [47] was used (Equation 7).

$$\eta_s = \eta_L \left( 1 - \frac{\phi}{\phi_m} \right)^{-[\eta]\phi_m}$$
Equation 7

where  $\eta_s$  is the viscosity of the liquid-solid suspension,  $\eta_L$  is the liquid phase (slag) viscosity,  $\phi$  is the volume fraction of solids,  $\phi_m$  is the maximum particle packing fraction, and  $[\eta]$  is the intrinsic viscosity. This equation is applicable in the range of  $0 < \phi < \phi_m$ . In this study, it was assumed that particles are spheres leading to  $[\eta] = 2.5$ , and  $\phi_m$  was calculated according to Stovall et al. [48] model and was estimated to be 0.834. The densities of the solid and liquid phases are similar, so that this assumption is accurate to within a few percent. The Krieger and Dougherty model will reduce to the Einstein equation [35] [36] [49] at  $\phi < 0.02$ , which is associated with the dilute limit considered in Einstein's equation.

#### 2.2.2. Experimental investigation

Experiments consisted of four parts: (1) characterizing the properties of as-received raw materials, (2) characterizing the mineral phases of the geopolymerized pellets before sintering, (3) understanding the sintering process of the pellets at elevated temperature, and (4) characterizing the pore structure of the final SPoRA product.

Table 2 summarizes the techniques used to study each part.

Part	Test	Purpose
	XRF	To assess the chemical composition of ashes (discussed in Section 2.2.1.1 and conducted by the bottom ash provider)
(1): Raw Material Acquisition	QXRD	To quantify the mineral phases of ashes
	TGA	To determine the free carbon content of ashes
(2): Geopolymerization	QXRD	To assess formation of new mineral phases at different concentrations of NaOH in the geopolymerized pellets
(3): Sintering	TGA	To identify the candidate reactions and products that contribute to the formation of pores
(4): Final product	X-CT	To assess internal morphological features and the SPoRA pore structure

#### Table 2. Experimental program

## 2.2.2.1. Quantitative x-ray powder diffraction (QXRD)

X-ray diffraction analysis was performed using a Rigaku Smartlab instrument using steps of  $0.02^{\circ}$  in a  $10^{\circ}$  to  $70^{\circ} 2\theta$  range. A Cu<sub>Ka</sub> source operating at 40 kV and 40 mA was used during the test. Phase identifications and Rietveld refinements were performed using the open source Profex software [50].

To perform QXRD on the raw materials, the following procedure was adopted: (1) raw NV and WP ashes (with a particle size distribution described in [5]) were taken separately, (2) the powder was crushed using

a mortar and pestle, (3) the obtained powder was sieved through an ASTM #200 sieve (75  $\mu$ m mesh opening), (4) the portion of powder that was retained on the #200 sieve was re-crushed and sieved to make sure the entire powder passed through the #200 sieve, (5) 0.8 g ± 0.001g of the prepared powder was blended with 0.2 g ± 0.001g of Rutile (TiO<sub>2</sub>), used as a reference powder with purity greater than 99 % and mean particle size of 5  $\mu$ m, and (5) the final blended powder was used in the QXRD test. The same sample preparation procedure was used to prepare QXRD samples of geopolymerized pellets after curing in an environmental chamber at 40 °C and 30 % RH for 24 h.

#### 2.2.2.2. Thermogravimetric analysis (TGA)

TGA was carried out using a TA Instrument Q5000 IR model. To determine the unburned carbon content of the raw material, a 2-atmosphere TGA (2A-TGA) procedure using nitrogen and air gases adopted from [29] was performed according to *Figure 2*. This was mainly to separate the oxidization of carbon from other decomposition reactions occurring in the same range of temperatures. In this regard, temperature was increased to 100 °C and was kept there for 5 min under nitrogen atmosphere in order to evaporate the free water. Next, still under nitrogen gas, the temperature was increased to 750 °C with a ramp of 20 °C/min. Afterwards, under nitrogen gas, the temperature was decreased back to 100 °C with a ramp of 20 °C/min. In the next step, the gas was changed to air and temperature was kept at 100 °C for 5 min. Finally, under air, the temperature was increased to 1000 °C with a ramp of 20 °C/min. Raw materials were crushed using a mortar and pestle and were sieved through a #200 sieve. Crushing and sieving was repeated to ensure that the entire amount of the initial powder had a size smaller than 75  $\mu$ m. Sample masses of 30 mg to 40 mg were used in the TGA tests. Considering the melting behavior of LWA at sintering temperature near 1160 °C, a fine crucible refractory ceramic powder was used as a bed in the TGA pan to prevent any sintered material adhering to the crucible pan during melting.

For geopolymerized pellets, the same sample preparation procedure was adopted; however, TGA tests were performed under an air atmosphere only to simulate the actual sintering conditions in LWA production.

Samples were heated at a rate of 10 °C/min to 1160 °C (the sintering temperature) and then were held at this temperature for 4 min.



Figure 2. 2-atmosphere TGA (2A-TGA) applied for determination of unburnt carbon content of raw materials

## 2.2.2.3. X-ray computed tomography (X-CT)

X-CT was performed to non-destructively assess the LWA internal morphology. In this method, a series of projection images of the sample, which is mounted on a rotating stage, were collected. Using tomographic reconstruction, cross-sectional 2D slices were then obtained [51–53]. 3D sample visualization was obtained by vertically stacking the 2D slices. The X-CT was carried out using a Zeiss Versa XRM 500 system [5]. The x-ray tube was set for a voltage of 80 kV and a current of 87 mA. The exposure time per step for 360° rotation was  $\approx 0.6$  s. The images were taken with a voxel size of approximately 18 µm. For constructing 3D images, visualizing 2D slices, and videos, the Dragonfly software [54] was used.

#### 3. Results

This section discusses the results of thermodynamic predictions to quantify the liquid phase and its viscosity formed during sintering. The QXRD and the TGA/DTG results are also presented to assess the phase development before sintering and identify the potential compounds that could contribute to gas emission during sintering and consequently pore creation. Furthermore, the LWA pore structure was assessed using X-CT.

## 3.1. Thermodynamic predictions of LWA multi-component system during sintering

#### 3.1.1. Phase equilibria and quantification of liquid phase formation

*Figure 3* (left column) shows the predicted phase diagrams for NV ash with 0 %, 4 %, 10 %, and 16 % addition of NaOH as the fluxing agent. NaOH has three main effects on the sintering process according to thermodynamic modeling: (1) reducing the LWA melting temperature (ash + NaOH), (2) reducing the liquid phase viscosity (since Na<sup>+</sup> is a network modifier), and (3) initiating geopolymerization for the LWA (ash+NaOH) system. Thermodynamic modeling calculates equilibrium conditions only and does not consider any kinetics governing the sintering process, which may influence the quantity and the type of formed phases. For example, formation of a viscous liquid phase near the LWA surface may hinder the penetration of oxygen to the LWA inner core (discussed in Section 3.5), which can result in a reduction in atmospheric pressure in the outer area and alter the kinetics of phase formation phenomena.

A good quality LWA requires enough liquid phase (slag) to entrap emitted gas near the sintering temperature (1160 °C). The slag contents for NV-0%, NV-4%, NV-10%, and NV-16% at 1160 °C were estimated to be 2.6 %, 47.2 %, 59.5 %, and 97.8 %, respectively. *Figure 3* (right column) shows the predicted phase diagrams for WP ash with 0 %, 4 %, 10 %, and 16 % addition of NaOH. The slag content for WP-0%, WP-4%, WP-10%, and WP-16% at 1160 °C were estimated to be 10.3 %, 58.3 %, 65.3 %, and 85.5 %, respectively.

WP-0% had a lower initial melting temperature (i.e., 1100 °C) compared with NV-0% (i.e., 1150 °C). This can be justified by the fact that in a system without NaOH and major presence of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> compounds,

increasing the amount of CaO lowers the melting temperature for the CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> system due to the formation of compounds that have lower melting temperature than that of mullite (3Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub>) formed in a binary system of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> [55,56]. For NV ash, incorporation of a higher amount of NaOH led to the formation of higher Na-bearing Feldspar (NaAlSi<sub>3</sub>O<sub>8</sub>) content (as can be seen in the phase diagram), which has a melting temperature close to 1100 °C [55]. Therefore, the melting temperature of NV ash was reduced by increasing the NaOH concentration and higher liquid phase (slag) content was formed. The initial melting temperatures for NV-4%, NV-10%, and NV-16% were 1050 °C, 1050 °C and 900 °C, respectively.

Addition of NaOH to WP ash did not significantly change the melting temperature for the system (*Figure 3* (right column)). This can be explained by the formation of several Ca-bearing phases at elevated temperature in the WP geopolymerized pellets (NaOH added) that have high melting temperatures along with Nepheline (NaAlSiO<sub>4</sub>), which has a melting temperature between 1100 °C to 1256 °C [55]. Accordingly, the melting temperature of the WP-NaOH system remained higher compared to the NV + NaOH system. The melting temperatures for WP-4%, WP-10%, and WP-16% were predicted to be 1100 °C, 1100 °C, and 1000 °C, respectively. It should be noted that formation of Na-bearing phases such as Nepheline (at major quantities) in the WP-NaOH system helped to increase the liquid phase content.





Figure 3. Predicted phase diagrams for bottom ash with NaOH concentrations of 0 %, 4 %, 10 %, and 16 %: NV bottom ash (left column) and WP bottom ash (right column); C: CaO, A: Al<sub>2</sub>O<sub>3</sub>, N: Na<sub>2</sub>O, S: SiO<sub>2</sub>, M: MgO, F: Fe<sub>2</sub>O<sub>3</sub>

#### 3.1.2. Viscosity prediction for solid-liquid system

*Figure 4* shows the estimated viscosity values for solid-liquid systems as a function of temperature for NV and WP ashes with different concentrations of NaOH. Addition of NaOH as a fluxing agent decreased the viscosity values for both ashes at constant temperature. As presented in Equation 3 to Equation 6, slag viscosity is highly dependent on slag composition. Additionally, the fluxing agent influenced the slag viscosity values by (i) promoting formation of higher liquid phase content, and (ii) changing the composition of slag towards compositions with lower viscosity by increasing the Na<sup>+</sup> molar fraction.

NV ash (*Figure 4*a) possessed higher viscosity values compared with WP (*Figure 4*b). This can be explained using Equation 5 where the slag composition of NV had a higher Si<sup>4+</sup> molar fraction compared to WP, leading to higher viscosity values. Additionally, the mole fraction of  $Ca^{2+}$  was relatively negligible

for NV compared with WP so that  $Ca^{2+}$ , which also has a fluxing role [12,23,24], decreased the WP slag viscosity and consequently the solid-liquid suspension viscosity.



Figure 4. Viscosity calculations of solid-liquid system with different NaOH concentration for (a) NV ash and (b) WP ash (the green dashed lines show the furnace operating temperature, 1160 °C)

## 3.2. Gas formation during sintering

## 3.2.1. Determination of free (unburned) carbon and chemical compounds in raw

#### materials

Heating ash in an oxidizing atmosphere (here, air) leads to decomposition reactions overlapping with carbon oxidation, which makes the determination of the unburned carbon content complex [29,57]. Accordingly, a heating cycle is generally added in an inert atmosphere (here, nitrogen) before the oxidizing atmosphere to prevent carbon oxidation while promoting decomposition reactions [29,58]. In this study, a two atmosphere TGA (2A-TGA) procedure [57,58] was followed to measure the unburned carbon content.

*Figure 5* and *Figure 6* show the 2A-TGA curves for raw NV and WP ashes, respectively. The unburned carbon content mass fraction for the NV ash was 0.12 %, and for the WP ash 0.19 %.



Figure 5. 2A-TGA results of raw NV ash: (a) first step in nitrogen atmosphere, and (b) second step in air; derivative of mass is defined as the absolute value of change in the mass over the change in temperature



Figure 6. 2A-TGA results of raw WP ash: (a) first step in nitrogen atmosphere, and (b) second step in air; derivative of mass is defined as the absolute value of change in the mass over the change in temperature

Table 3 shows the QXRD results for the raw NV and WP ashes. A higher content of quartz was observed in the NV ash compared with the WP ash, which was consistent with XRF results [5,12]. A higher calcite

content was observed for WP obtained by QXRD (see Table 3), which was reflected in the higher CaO content obtained by XRF. In addition, hematite ( $Fe_2O_3$ ) and anhydrite ( $CaSO_4$ ) as two possible phases that can contribute to gas release at the sintering temperature were found to be higher for the WP ash compared with the NV ash.

QuartzSiO2KatoiteCa3Al2(SiO4)(3-x)(OIAnhydriteCaSO2MerwiniteCa3Mg(Si	H) <sub>4x</sub> (x=1.5-3) 4 O <sub>4</sub> ) <sub>2</sub> SiO <sub>2</sub>	$18.2 \pm 1.7$ 0.1 ± 0.1 0.4 ± 0.3 0.0 ± 0 10.6 ± 2.4	$8.1 \pm 0.3$ $0.3 \pm 0.2$ $1.9 \pm 0.2$ $1.2 \pm 1.3$
KatoiteCa <sub>3</sub> Al <sub>2</sub> (SiO <sub>4</sub> ) <sub>(3-x)</sub> (OlAnhydriteCaSOMerwiniteCa <sub>3</sub> Mg(Si	H) <sub>4x</sub> (x=1.5-3) 4 O <sub>4</sub> ) <sub>2</sub> SiO <sub>2</sub>	$0.1 \pm 0.1$ $0.4 \pm 0.3$ $0.0 \pm 0$ $10.6 \pm 2.4$	$0.3 \pm 0.2$ $1.9 \pm 0.2$ $1.2 \pm 1.3$
AnhydriteCaSOMerwiniteCa <sub>3</sub> Mg(Si	4 O4)2 SiO2	$0.4 \pm 0.3$ $0.0 \pm 0$ $10.6 \pm 2.4$	$1.9 \pm 0.2$ $1.2 \pm 1.3$
Merwinite Ca <sub>3</sub> Mg(Si	O4)2 SiO2	$0.0 \pm 0$ 10.6 ± 2.4	$1.2 \pm 1.3$
	SiO <sub>2</sub>	106 + 24	
Mullite 3Al <sub>2</sub> O <sub>3</sub> ·28		$10.0 \pm 2.4$	$0.9 \pm 0.2$
Hematite Fe <sub>2</sub> O <sub>3</sub>		$0.4 \pm 0.3$	$1.0 \pm 0.7$
Anorthite CaAl <sub>2</sub> Si <sub>2</sub>	08	$11.2 \pm 0.5$	$8.4 \pm 0.8$
Brucite Mg(OH	)2	$0.1 \pm 0.1$	$0.4 \pm 0.2$
Portlandite Ca(OH	)2	$0.0 \pm 0.1$	$0.2 \pm 0$
Augite (Ca,Na)(Mg,Fe,Al,	Ti)(Si,Al) <sub>2</sub> O <sub>6</sub>	$0.8 \pm 0.1$	$9.4 \pm 0.2$
Calcite CaCO	3	$0.9 \pm 0.2$	$4.6 \pm 0.7$
Gypsum CaSO4·2H	$H_2O$	$0.4 \pm 0.3$	$0.5 \pm 0.4$
Anatase TiO <sub>2</sub>		$1.2 \pm 0.1$	-

Table 3. Crystalline phase determination of raw ashes, in mass percent.

$0.6 \pm 0.2$
$9.8 \pm 0.6$
$520 \pm 12$
$5 32.9 \pm 1.2$

\*The number after ± shows one standard deviation of three replicates.

#### 3.3. Phase development through geopolymerization

Table 4 shows the crystalline phases of geopolymerized NV pellets after 24 h of curing at 40 °C and 30 % RH. The quartz content started to decrease considerably in 16 % NaOH addition. The anorthite content decreased and amorphous phase increased with increasing NaOH concentration. Considering the low CaO content (3.51%) of NV bottom ash, a geopolymerization reaction similar to that of class F fly ash [59] can be considered for NV bottom ash during curing so that the amorphous phase contains N-A-S-H gel [60]. N-A-S-H gel is formed through breaking Si-O-Si and Si-O-Al (i.e., from aluminosilicate sources) bonds into silica and alumina monomers by reacting with OH<sup>-</sup>; further interaction of monomers leads to the formation of dimers, trimers and/or polymers [55].

Table 5 shows the crystalline phases and their quantities for WP geopolymerized pellets. With increasing NaOH percentage, the content of the Ca-bearing phases (such as anorthite, calcite, and gehlenite) decreased while the amorphous phase content increased. WP had a high content of CaO (22.5 %) and accordingly, it can be considered as a class C fly ash for its geopolymerization reaction with NaOH. In this regard, the alkali cation (Na<sup>+</sup>) acts as a catalyzer via ionic exchange with Ca<sup>2+</sup> ions. The main product of this reaction is calcium alumina silicate hydrate (C-A-S-H) gel. With reaction progress, small amounts of alkalis can be taken up into the gel structure due to any charge imbalance [55]. It should be noted that increasing environmental pH (via higher NaOH concentration) favors the formation of C-A-S-H gel, which is probably reflected in the higher amorphous content [61].

Crystalline phases	Chemical formula	Raw NV	NV-4%	NV-10%	NV-16%
Quartz	SiO <sub>2</sub>	$18.2 \pm 1.7$	17.7	17.4	13.7
Anhydrite	CaSO <sub>4</sub>	$0.4 \pm 0.3$	0.3	0.1	0
Merwinite	Ca <sub>3</sub> Mg(SiO4) <sub>2</sub>	$0.0 \pm 0$	0.4	2	3.1
Mullite	3Al <sub>2</sub> O <sub>3</sub> ·2SiO <sub>2</sub>	$10.6 \pm 2.4$	12.2	8.5	8.0
Hematite	Fe <sub>2</sub> O <sub>3</sub>	$0.4 \pm 0.3$	0.2	0.7	0.4
Anorthite	CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	$11.2 \pm 0.5$	8.2	5	6.5
Brucite	Mg(OH) <sub>2</sub>	$0.1 \pm 0.1$	0.5	0.5	0.6
Portlandite	Ca(OH) <sub>2</sub>	$0.0 \pm 0.1$	0	0.1	0.0
Augite	(Ca,Na)(Mg,Fe,Al,Ti)(Si,Al) <sub>2</sub> O <sub>6</sub>	$0.8 \pm 0.1$	1.2	1.2	0.7
Calcite	CaCO <sub>3</sub>	$0.9 \pm 0.2$	0.4	0	0
Gypsum	CaSO <sub>4</sub> ·2H <sub>2</sub> O	$0.4 \pm 0.3$	0.4	0	0.43
Anatase	TiO <sub>2</sub>	$1.2 \pm 0.1$	1.2	2.0	1.7
Amorphous	-	$55.6 \pm 3$	57.2	62.5	64.8

Table 4. Crystalline phase of NV geopolymerized pellets, in mass percent

\*The number after ± shows one standard deviation of three replicates.

Crystalline phases	Chemical formula	Raw WP	WP-4%	WP-10%	WP-16%
Quartz	SiO <sub>2</sub>	$8.1 \pm 0.3$	8.8	6.1	5.8
Katoite	$Ca_{3}Al_{2}(SiO_{4})_{(3-x)}(OH)_{4x}$ (x=1.5-3)	$0.3 \pm 0.2$	0.1	0.3	0.3
Anhydrite	CaSO <sub>4</sub>	$1.9 \pm 0.2$	1.4	1.5	1.4
Merwinite	Ca <sub>3</sub> Mg(SiO <sub>4</sub> ) <sub>2</sub>	$1.2 \pm 1.3$	0.8	1.3	1.9
Mullite	3Al <sub>2</sub> O <sub>3</sub> ·2SiO <sub>2</sub>	$0.9 \pm 0.2$	0.9	0.9	0.4
Hematite	Fe <sub>2</sub> O <sub>3</sub>	$1.0 \pm 0.7$	0.5	0.4	0.2
Anorthite	CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	$8.4 \pm 0.8$	5.5	3.2	3.4
Brucite	Mg(OH) <sub>2</sub>	$0.4 \pm 0.2$	0.6	0.6	0.8
Portlandite	Ca(OH) <sub>2</sub>	$0.2 \pm 0$	0	0.1	0
Augite	(Ca,Na)(Mg,Fe,Al,Ti)(Si,Al) <sub>2</sub> O <sub>6</sub>	$9.4 \pm 0.2$	7.6	6.6	5.9

Table 5. Crystalline phase of WP geopolymerized pellets, in mass percent

Calcite	CaCO <sub>3</sub>	$4.6 \pm 0.7$	5.8	3.0	1.7	
Gypsum	CaSO <sub>4</sub> ·2H <sub>2</sub> O	$0.5 \pm 0.4$	0.5	0.8	0.4	
Dolomite	CaMg(CO <sub>3</sub> ) <sub>2</sub>	$0.6 \pm 0.2$	0	0	0.3	
Gehlenite	Ca <sub>2</sub> Al[AlSiO <sub>7</sub> ]	$9.8 \pm 0.6$	8.3	7.3	5.4	
Amorphous	-	$52.9 \pm 1.2$	59.4	67.7	72.1	

\*The number after ± shows one standard deviation of three replicates.

#### 3.4. Evaluation of sintering mechanism of geopolymerized pellets using TGA

TGA was performed on the geopolymerized pellets to simulate the sintering process and indirectly identify any possible reactions/decompositions that can lead to the formation of pores in the LWA. *Figure 7* (a1) to (a4) show the TGA and differential thermogravimetry curves (DTG) for NV ashes prepared with 0 %, 4 %, 10 %, and 16 % NaOH concentrations. During the heating ramp, several mass reductions were measured that were associated with DTG peaks. Peak H (40 °C to 100 °C) was attributed to the release of free water [62]. The increasing trend in peak H by increasing NaOH concentration was mainly associated with the deliquescence effect [63,64], by which the addition of NaOH increased the equilibrium RH in the ash. The second observed peak, i.e., G near 100 °C to 150 °C, was mainly attributed to the release of water from the gypsum structure [62]. The decomposition in the range of 400 °C to 550 °C (peak C) could be attributed to the decomposition of the amorphous phase in NV ash, most likely C-S-H [65]; the intensity of peak C decreased as NaOH concentration increased in the system preferably implying formations of other amorphous phases (i.e., peaks Am<sub>1</sub> and Am<sub>2</sub>) in the system [62]. Peak Am<sub>1</sub>, which developed in the higher NaOH samples, could be related to the release of water from amorphous N-A-S-H gel developed through geopolymerization [66], while peak Am<sub>2</sub> was most likely related to the release of water from the amorphous structure of C-A-(N)-S-H type gel [66,67]. The intensity of peak Am<sub>2</sub> increased as NaOH increased, which implied that an increasing pH environment favors the formation of C-A-(N)-S-H gel [55]. No significant decomposition (reaction) was observed after 900 °C for the NV samples. The gas release from 1100 °C to 1160 °C could be considered to contribute to pore formation in the LWA. For NV samples, the mass reductions from 1100 °C to 1160 °C for NV-0%, NV-4%, NV-10%, and NV-16% were found to be equal to 0.080 %, 0.218 %, 0.300 %, and 0.115 %, respectively.

Figure 7 (b1) to (b4) show the TGA curves for WP ashes prepared with 0 %, 4 %, 10 %, and 16 % NaOH concentrations. Similar to NV ash, the peak H in the WP TGA curves is related to the release of free water, where the height of the peak increased as the NaOH concentration increased mainly due to the deliquescence phenomenon. Peak G was attributed to the release of water from the gypsum structure. Peak C (~ 350 °C to 450 °C) was related to the release of water from amorphous C-S-H gel. The decreasing trend of peak C with increasing NaOH concentration implied the transformation of C-S-H towards formation of C-A-(N)-S-H gel (i.e., peak Am<sub>2</sub>) for the WP samples. Additional peaks of C', CH, and  $\overline{C}$  were observed that were most likely related to, respectively: (1) the presence of another form of C-S-H gel with different Si/Ca ratio than that of peak C leading to a different thermal decomposition range [62], (2) the decomposition of portlandite in geopolymerized pellets at ~ 450 °C [62], and (3) calcite (CaCO<sub>3</sub>) decomposition and emission of CO<sub>2</sub> gas at ~ 620 °C to 750 °C [62]. Peak C' disappeared as the NaOH concentration increased to form C-A-(N)-S-H gel (peak Am<sub>2</sub>). Peak  $\overline{C}$  also decreased as the NaOH concentration increased (the trend was also consistent with that of measured by QXRD, see Table 4), where calcite as a Ca-bearing phase was consumed to form C-A-(N)-S-H gel (peak Am<sub>2</sub>). Therefore, the intensity of the Am<sub>2</sub> peak increased as the NaOH concentration increased, which was compatible with the QXRD result (see Table 4) that there was an increase in amorphous phase content as the NaOH concentration increased. In contrast with the NV geopolymerized pellets, a decomposition reaction could be observed in the WP pellets near 1160 °C as demonstrated by peak  $\overline{H}$ +A. Peak  $\overline{H}$ +A is most likely associated with the release of gaseous phases from hematite and anhydrite [34,68]. The mass reductions recorded between 1100



°C and 1160 °C for WP-0%, WP-4%, WP-10%, and WP-16% were equal to 0.55 %, 0.48 %, 0.45 %, and 0.33 %, respectively.



Figure 7. TGA/DTG curves for NV and WP geopolymerized pellets with varying concentrations of
NaOH measured in air (H: H<sub>2</sub>O, G: Gypsum, C: C-S-H, C': (C-S-H)', Am<sub>1</sub>:N-A-S-H, C̄: CaCO3, Am<sub>2</sub>:
C-(N)-A-S-H, H̄: Hematite, A: Anhydrate; derivative of mass is defined as the absolute value of change in the mass over the change in temperature

It was hypothesized that due to the rapid sintering of LWA for 4 min, dihydroxylation (i.e., the release of water) of amorphous phases available in the geopolymerized NV and WP samples may shift towards higher temperatures and accordingly can contribute to the formation of pores near sintering temperatures (~1160 °C). To test this hypothesis, a heating ramp of 100 °C/min (equal to the safe maximum capacity of the TGA device) was used to mimic the rapid sintering of LWA in TGA for NV-10% and WP-10%. The results are plotted in *Figure 8* (a) and (b) with dashed and solid green lines for TGA and DTG curves, respectively. A slight temperature shift of peaks was observed by  $\approx \Delta 30$  °C [62]; however, no contribution from dehydroxylation (gaseous H<sub>2</sub>O release) of amorphous phases was observed near 1160 °C to contribute to pore formation during sintering.



Figure 8. TGA/DTG curves for NV and WP geopolymerized pellets with10% NaOH; the red lines are associated with a heating ramp of 20 °C/min while green lines indicate the TGA and DTG curves associated with a heating ramp of 100 °C/min

#### 3.5. Evaluation of pore structure using X-CT

To observe the effect of sintering on LWA pore formation, X-CT was carried out, before and after sintering, for the NV-10% and WP-10% samples. The X-CT results for the geopolymerized NV-10% and WP-10% samples (i.e., before sintering) are shown in *Figure 9* and *Figure 10*, respectively. Plane A\_A and B\_B were selected to represent the middle cross-section of LWA in two perpendicular directions. Light color defines regions with denser structure (i.e., solid phase) while darker color demonstrates regions with lesser density (i.e., pores). 2D slices of samples in both geopolymerized samples (*Figure 9* and *Figure 10*) only contained coarse (i.e., random shape) pores, resulting from the coarse granular structure of bottom ash during the sample preparation. *Figure 11* and *Figure 12* show the X-CT results of sintered samples for NV and WP LWA, respectively, made with 4 %, 10 %, and 16 % NaOH concentration. Comparing 2D slices before and after sintering for a sample made using 10 % NaOH, the porosity of LWA had increased by the end of the sintering process. The porosities of non-sintered NV-10% and WP-10%, which was measured using image analysis of XCT slices as the total volume of pores divided by the total volume of LWA and

reported as percentage (detailed procedure of porosity calculations can be found in [5]), were 36.4 % and 36.3 %, respectively. After sintering, NV-10% and WP-10% had porosities equal to 44% and 41.6%, respectively, as the formation of large pores could increase the porosity of LWA. Videos demonstrating the porous structure of all LWA made in this study were provided in Table S1 of the Supplemental Materials.

Generally, two zones can be identified on the 2D slices (except for NV-4% and WP-4%, most probably due to the lack of a liquid phase) of LWA, separated by white dashed lines (shown in *Figure 11* and *Figure 12*). The inner part is referred to as "core", while the outer part is referred to as "shell". For both LWA types shown in *Figure 11* and *Figure 12*, the rounded large pores were mainly formed in the shell region of the LWA. In contrast, the core appears to possess interconnected smaller pores that were not specifically created by gas release but rather by the sintering and grain growth mechanism [69]. A possible explanation for the different morphologies of LWA core and shell could be that the shell acted as an insulating layer, delaying heat transfer to the LWA core and also limiting the diffusion of oxygen to the core [18,68]. This phenomenon can lead to occurrence of a reducing atmosphere in the core of LWA while having a highly oxidizing atmosphere for the shell [70]. In addition, coalescence of the pores (i.e., pores jointing together) in the shell [69] led to the formation of stable pores with a larger volume.

Non-sintered	A_A	B_B



Figure 9. 3D reconstruction and 2D slices of NV-10% pellet after geopolymerization and before sintering;

Plane A\_A and B\_B were selected to represent the middle cross-section of LWA



Figure 10. 3D reconstruction and 2D slices of WP-10% pellet after geopolymerization and before sintering; Plane A\_A and B\_B were selected to represent the middle cross-section of LWA



Figure 11. 3D reconstruction and 2D slices of NV sintered LWA for 4 min; Plane A\_A and B\_B were

selected to represent the middle cross-section of LWA



Figure 12. 3D reconstruction and 2D slices of WP sintered LWA for 4 min; Plane A\_A and B\_B were

selected to represent the middle cross-section of LWA

Enlarged images of the A\_A 2D slices for NV-10% and WP-10%, LWA core and shell. are provided in *Figure 13*. The shell material around the large pores is denser than the core material in both LWA. It is speculated that the shell material not only provides the structural integrity for the LWA, but it may also help to strengthen the LWA [19].



Figure 13. A\_A 2D slices of (a) NV-10% and (b) WP-10%; enlarged sections of the core and shell are indicated by (C) and (S), respectively

## 4. Discussion

This section scrutinizes the production of LWA with respect to the three required conditions (i.e., sufficient liquid phase formation, appropriate viscosity for solid-liquid phase, and adequate gas release) and correlates each of them with observations made from the XCT images. In addition, a diagram to predict successful LWA production is discussed.

#### Formation of liquid phase during sintering:

Formation of a sufficient amount of liquid phase on the LWA surface to entrap the emitted gaseous phases is a critical condition that needs to be achieved during sintering for successful LWA pore formation. *Figure 14* shows the amount of the liquid phase at 1160 °C for the LWA investigated. An increase in the NaOH concentration resulted in a higher liquid phase content for both LWA made using NV and WP ashes. NaOH has a lower melting temperature compared with the multi-component ash system; therefore, it provides a medium for easier ion diffusion and grain growth resulting in a lower melting temperature of the ash and NaOH blend. For NV-0%, as shown in *Figure 14*, the liquid phase content was less than 3 % while addition of 4 % NaOH increased the liquid phase content for NV-4% to 47.2 %. Correlating this observation with 3D X-CT reconstruction and A\_A and B\_B 2D slices of NV-4% provided in *Figure 11*, no large rounded pore was observed for NV-4% LWA. This finding implies that although some gas release has occurred during sintering, the low liquid phase content could not entrap the emitted gaseous phases. On the other hand, when the liquid phase was raised to 50 % in NV-10% and more prominently in NV-16%, even a small amount of gas release could be entrapped by the liquid phase and larger pores formed (*Figure 11*, see A\_A and B\_B 2D slices of NV-16%).

Similar to the case of the NV ash, the addition of 4 % NaOH increased the liquid phase content for WP-4% LWA to 58.3 % while for WP-0% this value was only 10.3 %. As observed in the 2D slices of the WP-4% LWA in *Figure 12*, the amount of liquid phase was sufficient to successfully entrap the released gas during sintering near 1160 °C. Also similar to the NV LWA, an increase in NaOH concentration increased the quantity of the liquid phase at 1160 °C. Correlating the visualized 2D slices of WP LWA (see *Figure 12*) with the liquid phase content, it can be inferred that higher content of liquid phase triggered the higher amount of gaseous phase entrapment, and consequently larger pores were formed. However, it should be noted that an excess amount of liquid phase may create deformation in the sintered LWA due to unnecessary reduction in the liquid-solid viscosity (as will be discussed later) and the desired sphericity may not be achieved during the sintering process, as observed in sample WP-16% in *Figure 12*. It appears that a minimum amount of 50 % liquid content (shown by green dashed line in *Figure 14*) is necessary during sintering bottom ashes to provide sufficient particle binding along with bloating (look at 2D slices in *Figure 11* and *Figure 12*, in which the LWA with more that 50 % liquid phase demonstrated formation of round large pores in the shell).



Figure 14. The quantity of the liquid phase for NV and WP LWA at 1160 °C obtained using thermodynamic simulations (green dashed line shows the 50% limit)

Viscosity of liquid-solid phase during sintering:

Viscosity plays two simultaneous roles in successful LWA production. First, a high viscosity prevents excessive deformation of the LWA pellet during sintering so that the final product retains a round shape. Second, the viscosity of the liquid phase affects the LWA pore size distribution. Correlating the 3D reconstructions (*Figure 11*) and viscosity values for NV LWA (*Figure 4* (a)), it can be inferred that the viscosity of the NV LWA was high enough to limit the deformation of LWA so as to preserve a spherical shape. Although the WP LWA had lower viscosity values (*Figure 4*(b)) compared with the NV LWA, the same observation was made for WP-4% and WP-10%. The only WP LWA that had excessive deformation under gravitational force was WP-16%, which had a viscosity of 25.7 Pa·s at 1160 °C and a final elliptical shape. It appears a lower limit for liquid-solid viscosity is near that of WP-10%, which was 85 Pa·s, in order to retain the LWA spherical shape during sintering [12].

The second role of the viscosity in controlling the pore size distribution can be observed in the A\_A and B\_B 2D projections of the NV and WP LWA in *Figure 11* and *Figure 12*, respectively, where larger pores were formed in the WP LWA compared to the NV LWA. Since NV LWA had a higher viscosity compared with WP LWA, lower viscosity seemingly led to easier expansion of gas inside the liquid phase, resulting in the formation of larger pores. This observation can also be related to amount of gaseous release [22] close to the sintering temperature, which will be discussed in the following section. It is worth mentioning that another important factor that can affect the pore size in the LWA is the pressure difference inside the pore and liquid phase which is determined by the Laplace pressure. Based on the Laplace equation this pressure difference is dependent on the pore diameter and the surface tension of the interface between the gas inside the pore and the liquid phase [71]. It should be noted that the surface tension is also dependent on the viscosity of the liquid phase [72].

#### Formation of gaseous phase during sintering:

As was observed in *Figure 7*, the TGA/DTG results showed a more pronounced peak at 1160 °C for the WP LWA compared with the NV LWA. The mass reduction from 1100 °C to 1160 °C is believed to be associated with hematite and anhydrite compounds, the presence of which was confirmed by QXRD, to

release  $O_2$  and  $SO_2$  gases, respectively [34,70]. Both anhydrite and hematite were detected in raw ashes as well as in geopolymerized pellets (see

Table 2, Table 3, and Table 4). Moreover, the anhydrite content for the NV geopolymerized pellets was found to be smaller than in the WP pellets. This observation supports the fact that WP LWA have a higher potential for gas liberation at 1160 °C, which can be another possible explanation for the formation of bigger pores in WP LWA compared with NV LWA [22,73]. The reactions that can lead to gas liberation from the transition of hematite from Fe<sup>3+</sup> to Fe<sup>2+</sup> can happen through Equation 1 and Equation 2, while the reaction for anhydrite decomposition can be expressed as follows:

$$CaSO_4(s) \rightarrow CaO(s) + SO_2(g) + \frac{1}{2}O_2(g)$$
 Equation 8

As was observed in the DTG curves for WP geopolymerized pellets (*Figure 7* a1 to a4), the peak at 1160  $^{\circ}$ C seems incomplete i.e., the temperature was not high enough to enable complete decomposition. This may be attributed to the fact that a complete decomposition of CaSO<sub>4</sub> occurs at temperatures above 1200  $^{\circ}$ C [74,75]. A possible explanation for the reduction of hematite into wuestite (FeO) that could occur at a temperature range between 1100  $^{\circ}$ C and 1160  $^{\circ}$ C is the formation of liquid phase on the LWA surface that could hinder oxygen diffusion and create a reducing atmosphere in the LWA core, thus leading to hematite reduction [7,76].

In this study, the unburned carbon content for NV and WP ashes was small (0.12 % and 0.19 %, respectively), and complete oxidation of carbon in the form of CO<sub>2</sub> and CO release would happen at temperatures below 1000 °C [29] (see *Figure 5* and *Figure 6*), which had some overlap with the temperature at which the liquid phase started to form (see *Figure 3*). This indicates that there could have been some contribution from the unburnt carbon to reduce the hematite and result in the release of O<sub>2</sub> [68,76,77].

#### Required sintering conditions for successful production of spherical LWA:

*Figure 15* presents a holistic view of each LWA to provide the required conditions (liquid phase quantity, viscosity value, and emitted gas amount) during sintering for successful production of spherical LWA. It should be noted that NV-0% and WP-0% are not shown in the figure, since due to the lack of liquid phase

their viscosity was not calculable (see Section 2.2.1.2). It is proposed that a minimum value of 50 % liquid content (shown by red dashed line in *Figure 15*) and a minimum viscosity value of 100 Pa $\cdot$ s (shown by blue dashed line in Figure 15) are required for successful LWA production. For NV LWA, NV-0% and NV-4%, which had an inadequate amount of liquid phase (i.e., less than 50%), formation of rounded large pores was not observed in the X-CT images. The same observation was made for WP-0%, which also had an insufficient amount of liquid phase. On the other hand, for NV-10%, NV-16%, WP-4%, and WP-10%, a sufficient amount of liquid phase (50 % or more) accompanied with proper viscosity values (more than 100 Pa s), led to LWA production with the desired pore structure and particle sphericity. However, for WP-16%, the viscosity value was about 26 Pa s, which led to the deformation of the LWA under gravitational force and an undesired elliptical shape (see *Figure 12*). Based on Billen et al.'s melt ceramic model [12], an upper limit value of  $10^6$  Pa·s was proposed (shown by blue dashed line in *Figure 15*) to ensure a viscosity for the liquid phase to be able to entrap the gaseous phase and let the pellets expand during sintering. The value of 10<sup>6</sup> Pa·s is between the viscosity values of NV-4% and NV-10%, and implied that a NaOH concentration between 4% and 10% will probably result in the entrapment of pores in the LWA. Further research is needed to accurately determine this upper viscosity limit. Figure 15 could be used to design a successful LWA with respect to the three required conditions: sufficient amount of liquid phase, appropriate viscosity for solid-liquid suspension, and sufficient amount of gas release. If an LWA has the key three characteristics such that it falls in the working zone proposed in Figure 15, it can be expected to be a desirable LWA.



Figure 15. The shaded area shows the proposed representation of the conditions (i.e., liquid phase quantity, viscosity and gas release) required for successful LWA production

## 5. Conclusion

This paper investigated the three required conditions that need to be achieved during sintering for successful LWA production from waste coal bottom ash: (i) formation of a sufficient amount of the liquid phase, (ii) achievement of an appropriate viscosity for the combined liquid-solid phase, and (iii) emission of a sufficient amount of gaseous phase. Two types of coal bottom ash, low-calcium (NV) and high-calcium (WP), were studied to evaluate these three sintering conditions. The following main conclusions can be drawn from this study regarding the three necessary conditions for successful sintering/LWA production:

(i) The presence of at least 50 % (by mass) liquid phase enables successful gas entrapment and LWA pore formation. It was observed that for NV-4%, in which the liquid phase content was less than 50 %, no gas-filled rounded pores could be seen achieved in the LWA pore structure. However, all LWA

with more than 50 % liquid phase during sintering possessed round gas-filled pores in their structure (mainly in the outer shell part of the LWA structure).

- (ii) The viscosity of the liquid-solid suspension was found to influence LWA pore formation and control LWA deformation during sintering. A minimum viscosity of 100 Pa·s was found to be necessary to retain the spherical shape of the LWA pellets during sintering. Above this minimum value, the WP LWA, which had smaller viscosity values compared with the NV LWA, possessed larger gas-filled pores. Lower viscosity values not only allow easier movement of pores to coalesce, but also easier expansion of entrapped gases in the liquid phase medium. An upper limit of 10<sup>6</sup> Pa·s was proposed for the liquid-solid phase in order to still be able to entrap emitted gases.
- (iii) It was found that the emission of gaseous phases near the sintering temperature is necessary to create the desired LWA pore structure, given that the desired liquid phase content and viscosity values listed in (i) and (ii) are also achieved during sintering. All LWA demonstrated gas liberation near the sintering temperature where WP LWA showed a slightly higher amount of gaseous phase formation compared with NV LWA. The emitted gaseous phase was found to be most probably due to the reduction of hematite and the decomposition of anhydrite. Gas emission from other sources was at temperatures not near enough to the sintering temperature to be helpful in forming pores.

A diagram incorporating the three required conditions for successful production of LWA, i.e., formation of enough liquid phase, appropriate solid-liquid viscosity, and enough gas emission, was developed, and a working zone defined in the diagram. The working zone was constrained by a liquid phase of more than 50 %, and a viscosity upper limit of 10<sup>6</sup> Pa·s and a lower limit of 100 Pa·s. The diagram and the working zone predict whether the production of a LWA will be successful or not.

From a practical point of view and environmental perspective, a smaller NaOH concentration not only reduces the cost associated with LWA production, but also decreases the greenhouse gas emissions accrued during NaOH production. For successful LWA production from NV and WP ashes, a NaOH concentration

by mass between 4 % and 10 % was found to be an appropriate concentration range of this fluxing agent to achieve the desired three sintering conditions for successful LWA production at 1160 °C.

Future work is needed to investigate the bubble nucleation and growth mechanism in the LWA liquid phase and the kinetics that impose different atmospheres in the shell and in the core of the LWA. Future work may also involve evaluating the mechanical strength of the LWA made using bottom ash and its correlation with parameters such as chemical composition, crystalline structure, liquid phase quantity, and porosity. Preliminary results indicate that SPoRA has a comparable compressive strength with commercially available LWA; therefore, it is expected that SPoRA can be successfully used to produce lightweight concrete. If the LWA is used to produce lightweight concrete, the bonding performance of LWA with cement paste and characteristics of the Interfacial Transition Zone (ITZ) in the concrete need to be investigated to fully understand the LWA-cement paste physical and mechanical interaction.

One of the major concerns in recycling or beneficial use of bottom ash is related to leaching of heavy metals from this material. The production of LWA using a sintering method from different base materials (such as municipal solid waste incinerator ash, sewage sludge ash, fly ash, and bottom ash) that contain heavy metals, have been shown to be a potentially successful approach to decrease the leachability of heavy metals from these materials. This is because of the fact that sintering of materials at high temperature (i.e., greater than 1100 °C) enables liquid phase formation and then crystalline phase formation upon cooling. This can potentially lead to solidification of heavy metals by being bonded in the crystal structure [78–81]. Future work may also involve investigating the potential advantage of producing LWA from bottom ash using a sintering method to reduce the leachability of heavy metals from this material. Finally, the use of bottom ash to produce LWA can help to minimize the use of natural resources (e.g., clay, shale, and slate) to produce synthetic LWA for construction needs.

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