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Melt ceramics from coal ash: Constitutive product design using thermal and flow properties

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ABSTRACT

New US Environmental Protection Agency regulations for the disposal of coal combustion residues (CCR) incentivize bottom-up recycling efforts, to convert them into value-added applications. This study examines producing lightweight ceramic aggregates from CCR for concrete/geotechnical applications. More specifically, we argue that industrial residues such as coal bottom ash, despite their heterogeneity and diversity, are apt feedstock materials to constitutively design melt ceramics via high temperature recycling. A lot of knowledge on the feedstock (thermal and melt flow properties) is available, because of the historical interest in (molten) coal ash properties. It is shown how thermodynamics and empirically derived models and experimental observations on the viscosity, surface tension, heat capacity, enthalpy of fusion and thermal conductivity can be used to constitutively design melt ceramics. We created a custom model for the design of spherical porous reactive aggregates (SPoRA) from two different coal bottom ashes, using NaOH as an illustrative fluxing agent. To obtain the desired aggregate design, production should occur above the solidus temperature, yet viscous flow, caused by a low viscosity of the CCR melt, should be limited. The design method developed is able to discern the influence of various design parameters on the experimentally produced ceramic aggregates. A proper match between simulations and experimentally observed object shapes was obtained, allowing to define an operating window (temperature and residence time as function of fluxing agent addition) constitutively. This work shows how the available knowledge on coal ash assists the understanding and design of novel ceramic aggregate recycling processes.

1. Introduction

Almost half of the 107 million tonnes of coal combustion residues (CCRs) generated in the United States are not beneficially reused, but instead disposed of in surface ponds and landfills (Association, 2016). Recently, the United States Environmental Protection Agency (U.S. EPA) issued new rules on the disposal of such residues, requiring the closure of unlined surface impoundments within five years or retrofit with a composite liner consisting of a geomembrane and compacted clay layer, alongside leachate collection and groundwater control (Landers, 2015; EPA, 2015), which will significantly increase the disposal cost. The latter also increases the incentive for recycling efforts on off-spec fly ash and bottom ash.

Two main challenges that need to be considered in the recycling process of CCRs are: (1) the wide range of chemical varieties in CCRs, and (2) creation of a high value product that is easy to be commercialized. According to investigation of the composition of 1040 coal ash samples from the U.S. Geological Survey Coal Quality (COALQUAL) database, CCRs possess a wide variety in elemental concentrations, with SiO_2 between 13% and 80%, Al_2O_3 between 1.6% and 46%, CaO between 0.12% and 29% and Fe_2O_3 between 0.60% and 69%, on a mass basis and expressed as oxides (Karimi et al., 2014). Faced with this variety, creating a consistent product from a robust recycling process is challenging, and demands a thorough understanding of various influences that compositional changes may have on the sintering process. In creating recycling pathways for inorganic waste streams such as CCRs, a high market value should be sought by solving timely construction issues, such as cracking of concrete and the demand for lightweight

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materials, increasing the chances for commercialization. In this study, the production of spherical porous reactive aggregates (SPoRA) from CCRs was evaluated, for use as a construction material for concrete that combines an amorphous outer shell, to strengthen the concrete's interfacial transition zone (Kourti and Cheeseman, 2010), with a high internal porosity (low density), exploiting the residual carbon of coal bottom ash as a bloating agent. Several production methods and advantages of ceramic aggregates, such as their ability to immobilize heavy metals, were described earlier (Kourti and Cheeseman, 2010; Cheeseman et al., 2005; Verbinnen et al., 2014), yet a design guide to deal with other waste streams such as CCR is lacking.

The production of SPoRA from coal bottom ash (CBA) starts with a water based pelletization, followed by drying to prevent explosion by expanding steam, and high temperature sintering. Because the CBA has negligible hydraulic reactivity properties, pozzolanic binding of the pellets, which is required to handle the dried materials, is done by adding NaOH as an alkali activator. Synergistically, this NaOH reduces the required operating temperature during sintering, because of its fluxing effect, by interfering with silicate networks.

The recycling process proposed in this study for converting CBA to SPoRA, which are spherical lightweight aggregates, hinges on three criteria: (i) the pellets should have a fraction of molten phase, to ensure a glassy exterior, (ii) the pellets should retain a certain degree of sphericity after melting, and (iii) the generated gas should be captured effectively to generate pores within the aggregates. In this respect, the viscosity of the partially molten coal ash should be sufficiently high to limit macroscale deformation (collapse of the ball), and to minimize the coarsening and eruption of generated gas bubbles. Therefore, the production should occur at a temperature above the solidus temperature, ensuring the presence of molten phase, yet at temperature low enough to ensure a high viscosity.

There are several models to predict coal slag viscosities from their composition in a qualitative (Yuan et al., 2012), or quantitative way (Song et al., 2011; Browning et al., 2003; Urbain, 1987). These models were developed over the last decades owing to the interest from integrated gasification combined cycle (IGCC) operators in flow behavior of molten coal slags for tapping from shell entrained-flow gasifiers (Song et al., 2011). This earlier interest in molten coal ash has introduced new knowledge on understanding and predicting the flow/deformation behavior in melt ceramics processing of CCRs, allowing the creation of a process robust toward feedstock variations.

Because all of the viscosity models developed to date assume Newtonian rheological behavior of completely liquid slag, we amended the liquid viscosity calculated according to the model of Browning et al. (2003) with an account for solid phase by using the Einstein equation (Einstein, 1906). This requires knowledge of the formation of mineral phases in CBA as a function of the temperature, including their mass fraction and composition, which was thermochemically modeled using FactSage (Bale et al., 2002), as in earlier published reports (Yuan et al., 2012; van Dyk and Keyser, 2014; van Dyk et al., 2009). With the viscosity of the partially liquid ash known as a function of the temperature, a constitutive flow model allows to predict the extent of deformation of SPoRA from CBA, at various process conditions; temperature and residence time. Repeating this procedure for various amounts of fluxing agents (e.g. NaOH) added, we can tune the final geometry of the envisioned aggregates, by selecting the desired temperature dependent viscosity. Moreover, our modeling approach allows a priori exploration of feasible sintering processes as the CBA feedstock changes or use of different (green) fluxing agents (such as waste glass (Kourti and Cheeseman, 2010; Bourtsalas et al., 2015)), with no or limited experiments needed.

2. Materials and methods

2.1. Material characterization and preparation

Two distinct types of bottom ash were obtained, one with a relatively high calcium content identified as "WP", and a second containing a lower amount of calcium labeled as "NV" (Table 1). The elemental concentrations were measured using Bruker S8 Tiger Wavelength Dispersive X-ray Fluorescence equipment, according to ASTM D 4326. The elemental concentrations were converted to corresponding oxides, for reporting purposes and to facilitate thermodynamic modeling. Quantitative phase analysis of the samples, crushed into a powder of passing 45 μm size mesh and spiked with 10% corundum as internal standard, was done by X-ray diffraction (Bruker D2 PHASER with Cu radiation at 30 kV/10 mA). Scans were run over the range of 6°–80° with a step size of 0.0152° and a counting time of 1.5 s per step.

Table 1
Composition of the two bottom ash samples (NV and WP) used in this study, expressed as their oxides on a mass basis.

Chemical Composition [% m/m]	Sample Name	
	WP ash	NV ash
SiO_2	43.1	63.2
Al_2O_3	17.1	20.1
Fe_2O_3	7.29	6.66
SO_3	0.64	0.39
CaO	22.5	3.51
Na_2O	1.19	1.43
MgO	4.10	0.97
K_2O	0.41	1.13
P_2O_5	0.91	0.09
TiO_2	1.25	1.03
Total	98.52	98.53

Identical, spherical pellets of 16 mm diameter were produced from well-graded (particle size distribution according to Fuller's equation (Peronius and Sweeting, 1985) to achieve maximum density gradation with n = 0.5, with maximum particle size of 0.3 mm) bottom ash, using a purposely designed 3D printed ABS mold, consisting of a base and stamp with hemispherical voids. Before molding, the bottom ash was mixed with aqueous solutions (liquid to solid mass ratio (L/S) of 0.4 for WP ash and L/S of 0.5 for NV ash), with concentrations of NaOH of 1 M, 2.5 M, 5 M, 7.5 M and 10 M added to provoke alkali activation. The different L/S ratios used resulted in different NaOH additions on a mass basis; 1.6%, 4%, 8%, 12% and 16% for WP ash and 2%, 5%, 10%, 15% and 20% for NV ash. After drying at 40 °C and 30% RH chamber until constant weight, which was achieved after approximately 30 h, the dried pellets were placed on a bed of Ottawa sand in alumina trays (dimension 41 mm × 32 mm × 7 mm), and then were placed into a preheated Mellen NACCI tube furnace equipped with a 44 mm inner diameter alumina tube. A schematic representation of the sample in the tube furnace (diagonal cross section) is given in Fig. 1. The deformation of the spherical pellets upon partial melting was monitored following a quench at room temperature after two residence times; 4 min and 8 min.

2.2. Constitutive modeling of melt ceramics processing

Fig. 2 presents the modeling flow paths used in this study, starting from the coal ash composition. The new methodology presented for the prediction of final geometries, as a function of the temperature (T) and residence time (t) of the ceramic process, enables effective addition of fluxing agent (e.g. NaOH), and/or feedstock blending. For a known ash composition, the temperature dependent phase composition is determined through thermochemical calculations, using FactSage (Bale et al., 2002; Bale et al., 2016) software (FToxid database), for different amounts of NaOH added. Based on the calculated composition of the liquid phase, the viscosity is obtained using empirically derived models (Browning et al., 2003) corrected for the influence of the solids fraction by the Einstein equation (Einstein, 1906; Roscoe, 1952). The deformation of the partially molten coal ash is constitutively modeled