Fuel 106 (2013) 490–497

Contents lists available at SciVerse ScienceDirect

Fuel

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

Screening coal combustion fly ashes for application in geopolymers

Siska L.A. Valcke [a,*], Angelo J. Sarabèr [b], Penny Pipilikaki [a], Hartmut R. Fischer [a], Henk W. Nugteren [c]

[a] TNO, Van Mourik Broekmanweg 6, 2628 XE Delft, The Netherlands
[b] Vliegasunie BV, Belle van Zuylenlaan 3, 4105 JX Culemborg, The Netherlands
[c] Delft University of Technology, Department of Chemical Engineering, Product and Process Engineering Group, Julianalaan 136, 2628 BL Delft, The Netherlands

HIGHLIGHTS

- Feature sizing and chemical typing (FS&CT) is a new method for characterizing fly ash.
- FS&CT quantitatively measures *inter* particle variations in chemistry and size.
- FS&CT data can be used to assess fly ash reactivity in geopolymers.

ARTICLE INFO

Article history:
Received 22 April 2012
Received in revised form 17 December 2012
Accepted 18 December 2012
Available online 7 January 2013

Keywords:
Fly ash
Reactivity
Binder
Geopolymer
Feature sizing and chemical typing

ABSTRACT

Driven by cost and sustainability, secondary resource materials such as fly ash, blast furnace slag, and bottom ash are increasingly used for alternative types of concrete binders, such as geopolymers. Because secondary resources may be highly variable from the perspective of geopolymers, it is often a challenge to upscale these binder types to an industrial scale. This paper describes the testing of a screening method – feature sizing and chemical typing (FS&CT) using an electron microscope – in order to capture the heterogeneity of secondary resources in a quantitative manner. This automated technique is able to simultaneously measure inter particle variations in chemistry (energy dispersive X-ray spectra) and size (shape). Two key variables for application in geopolymers, Si:Al ratio and size, are measured using FS&CT for coal combustion fly ash and its fraction of potentially reactive aluminium-silicate particles. These measurements have been preliminary related to the reactivity of the fly ash in NaOH-solutions with high liquid/solid ratios as well as low liquid/solid ratios (geopolymers). As such the FS&CT method is found to be a useful alternative to commonly used bulk methods such as X-ray fluorescence (XRF) or manually operated electron microscopy that gives just an indication of local heterogeneity.

1. Introduction

Geopolymers are a type of inorganic binder generally consisting of an aluminium-silicate precursor and an alkali activating solution. Studies and experiments on alkali activated aluminium-silicate binders date back to the 1940–1950s [1,2] but have never been as popular as in the recent decade because of their potential for sustainable cement replacement in concrete [3–5]. Although the debate on their sustainability is still on-going, in the meantime, research, demonstrations and small scale plants have shown that geopolymers may also open pathways for new types of tailor made concrete having unique properties different to traditional cement concrete [6]. Driven by cost and sustainability, the aluminium-silicate precursors are very often secondary resource materials such as combustion products (fly ash, bottom ash), and blast furnace slag [1,7,8]. This creates a challenge for the upscaling of geopolymer concrete, because secondary resources are highly variable, in the first place related to their origin (an electric power plant, a blast furnace, a waste incinerator, etc.) but also weekly variations within the same production may occur (e.g., [9]).

If geopolymers are to be applied on a large scale, a screening method for quality control of highly variable secondary resource materials will be needed together with adequate mix adjustments in order to ensure continuous production. Also more scientific research using alternative screening methods is still needed to understand the main key variables influencing the final performance of the geopolymer binder and how to adjust mix design based on the input secondary resource materials. Currently, quality control for cement is done using bulk methods such as X-ray fluorescence (XRF) and X-ray diffraction (XRD), assuming that the clinker composition is continuous and uniform. Therefore, the

* Corresponding author. Tel.: +31 (0)88 866 32 73.
E-mail addresses: siska.valcke@tno.nl (S.L.A. Valcke), asaraber@vliegasunie.nl (A.J. Sarabèr), H.W.Nugteren@tudelft.nl (H.W. Nugteren).

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http://dx.doi.org/10.1016/j.fuel.2012.12.070

focus and aim of this paper is to evaluate an alternative screening method for secondary resource materials that quantitatively captures their heterogeneity, with the final aim of judging the potential reactivity of these materials in alkali activated binders. Here, fly ash is chosen as a secondary resource material.

Fly ash characteristics that have been stated in the literature to influence fly ash reactivity include [9–13]: amount of soluble silicon and aluminium (directly related to amorphous glass content), content of network modifying ions (calcium, iron, sodium, etc.), particle shape and size. Provis and van Deventer [14,15] have shown that the Si:Al ratio of the source material plays a major role in the geopolymerisation process, not only in the early dissolution rate, but also in gelation and precipitation rates. These scarce studies on fundamentally understanding the reaction processes of geopolymers currently focus on metakaolinite [14–16]. For metakaolinite, the Si:Al ratio is the main variable considered, while size is mostly neglected as a variable because the clay particles are so uniform and fine grained with a high specific surface that small variations in size will not affect the reaction kinetics and final geopolymer properties much [17]. Nevertheless, in the case of less uniform source materials with a broader variation in size, such as fly ash, size may become an important key variable, not only for the amount of available aluminium and silicon (variable specific surface) but also in the water demand and precipitation/polymerization rate as unreacted particles may act as nucleation sites and as such significantly enhance the formation of reaction products [18,19]. Considering the lack of quantitative methods that capture the heterogeneity of the above mentioned variables such as size and chemistry at once, this paper proposes an alternative screening method based on automated feature sizing and chemical typing (FS&CT) of a large number of individual particles using an SEM. It has mainly been applied in metallurgical and material sciences [20] and to the authors' awareness is not previously applied to fly ash or other secondary source materials for geopolymers. It should be noted that apart from chemistry and size, crystallinity is a key variable that influences the reactivity and geopolymer properties [12,13]. Unlike chemistry and size, the inter and intra particle variations in crystallinity are even more challenging to capture in heterogeneous fly ash, and it is not the aim of this paper to quantify the variation of this key variable for individual particles. Nevertheless, its significance will be taken into account in the discussion of the results.

For interpreting the significance of the results using the alternative screening method with respect to geopolymer reaction products and properties, a preliminary relation is sought between the fly ash characteristics and their reactivity (assessed using a dissolution method and solid state nuclear magnetic resonance (NMR)).

2. Materials

Ten fly ash samples were obtained from several Dutch coal fired power plants. Sampling was performed according to the standard sampling procedures for daily quality control of the by-products. The reactivity of these fly ash samples was pre-screened by assessing the setting time using a 10 M NaOH solution as activator. Based on this, three samples were selected that have similar workability for the same liquid to solid ratio (±0.25), but nevertheless show a very different hardening behaviour. The coding of the fly ash samples is F5, F6 and F7. Samples F5 and F6 are derived from power plants with a dry bottom boiler, firing hard coal and biomass (respectively 36 and 10% m/m). Sample F7 is derived from a power plant using a coal gasification process (so-called entrained flow gasifier). The bulk chemistry (XRF) of F5, F6 and F7 is given in Table 2.

3. Methods

3.1. Measurement of Si:Al ratio and size

3.1.1. Choice of method

To date, few quantitative techniques have been used to capture the Si:Al ratio of the potentially reactive fractions of heterogeneous materials appropriately. Si:Al ratios used in many papers on geopolymer processes are based on bulk silicon and aluminium measurements, including the aluminium and silicon of non-reactive (crystalline) phases [21]. Therefore, their bulk Si:Al ratio may not reflect the Si:Al ratio from the potentially reactive (glassy) fly ash fractions. A few papers have calculated the average Si:Al ratio for the potentially reactive (glassy) fractions only, by combining XRF and quantitative XRD [12,13,22]. However, it is known that the Si:Al ratio of the glassy phase varies between different particles and even within one particle, changing the reactivity of each particle [23–26]. The inter and intra particle variations can be studied on secondary electron (SE) and backscattered electron (BSE) images combined with energy dispersive spectrometry (EDS) using an electron microscope. However, this method is mostly performed on localized areas, resulting in poor statistics. EDS mapping combined with automated phase analysis as described and applied by Chancey et al. [26] is a good way of visualizing inter and intra particle variations, but we found that it is labour intensive to obtain statistically representative, quantitative datasets, especially when large particles are present that dominate the dataset. Lastly, it is noted that the full volume (weight) of fly ash particles is taken into account in the most commonly used bulk characterization methods (XRF, XRD, etc.). However, it is often only the outer rim of the larger fly ash particles that first reacts away [25,27,28] and only mainly the outer rim chemistry and structures should be characterized, while the chemistry of the inner core is irrelevant for the early reaction processes. Concerning measurements of size, there is a tendency for large particles to dominate the size distribution when using common particle size measurement tools such as laser diffraction because volume fractions are measured. However, it would be interesting to test a technique that is based on numbers of particles rather than volume or weight, such that the small particles - that may contribute significantly to the reactivity - are less dominated by the large particles.

To obtain statistically representative data and simultaneously capture inter particle variation in Si:Al ratio and size, feature sizing and chemical typing (FS&CT) in an SEM is used on powder samples. With this technique chemistry and particle geometry data are gathered for individual particles. The output of feature sizing and chemical typing (FS&CT) contains the characteristic parameters of each detected particle: size (maximum, minimum and mean

Table 1
Bulk chemical composition (volume percentage) as measured by XRF of F5, F6 and F7.

	F5 (%)	F6 (%)	F7 (%)
SiO_2	58.33	54.31	63.39
Al_2O_3	25.19	26.28	15.29
Fe_2O_3	6.03	6.04	6.52
CaO-tot	4.57	5.51	4.44
CaO-free	0.49	0.57	0.1
MgO	1.99	2.2	1.77
Na_2O	0.73	1.01	1.99
K_2O	2.01	1.75	3.77
TiO_2	1.3	1.31	0.8
P_2O_5	0.72	0.73	1.08
Na-eq	2.06	2.17	4.47
C (LOI)	3.37	2.43	1.03
Cl	<0.01	<0.01	0.069
SO_3	0.72	1.05	0.81