Fly ash as an assemblage of model Ca–Mg–Na-aluminosilicate glasses

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ABSTRACT

Model Ca–Mg–Na-aluminosilicate glasses based on compositions found in a calcareous fly ash were synthesised and their reactivity assessed in NaOH solution and in Portland cement paste. It was found that the reactivity followed the same trend in both systems and that the reaction of the glasses in pastes was very similar to that of the components of similar composition in the real fly ash. This finding indicates that the reactivity of glass in cement can be directly linked to the chemical composition of the glass. Further, when the reactivity of the glasses was normalized to their surface area, it was found that there exists a strong correlation with the NBO/T, the ratio of non-bridging oxygens and tetrahedral ions in the glass.

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1. Introduction

The key to understand the reactivity of fly ashes lies in improved materials characterization. The main difficulty here is that fly ash particles are extremely heterogeneous. Fly ash particles are a result of (1) the type and proportions of the inorganic components in the original coal particles and (2) the changes that these phases undergo during heating, including phase mixing, crystallization, selective vaporization and phase separation in the melt. With 50 to more than 90 wt.% [1,2] amorphous content and a huge number of possible glass compositions, fly ash is very difficult to characterize. Classical characterization techniques fail to distinguish between different fly ash glasses. Thus, little is known about what types of glasses constitute any fly ash and, further, how these glasses react in cement. Methods typically used to measure the degree of reaction of fly ash, such as selective dissolution, isothermal calorimetry, chemical shrinkage, backscattered electron image analysis based on grey level and morphology segmentation as well as mass-balance approaches only relate to the reaction of fly ash as a whole [3–6].

Recent findings [7–9] show that advanced electron microscopy techniques can identify the glasses present in a fly ash, quantify their amount and determine their chemical composition and particle sizes. The same technique can quantify the reaction of these individual glasses in cement paste directly [9]. SEM–EDS full element mapping and image analysis data demonstrate that the glasses present in fly ashes tend to belong to certain compositional populations and that these populations react at different rates.

To study the reactivity of the different glasses in detail, these were separately synthesised. Their chemical composition was chosen to match the chemical composition of glasses identified in a calcareous fly ash in the preceding paper [9]. Batch dissolution experiment provided an insight into the initial dissolution rates of these synthetic glasses in an alkaline environment. The new SEM–EDS technique [9] was used to track the consumption of the synthetic glasses in hydrating cement paste, which was then compared to the consumption of the real glasses in a fly ash. Slag glass of a chemical composition close to that of one of the investigated glasses was also included in the study. The SEM–EDS data was used to examine how the glass reaction in cement paste depends on the glass chemical composition and fineness.

2. Materials and methods

Four synthetic glasses (A, B, C, D), a slag (S) and a Portland cement (PC) were used in this study. For comparison, some of the results referring to the calcareous fly ashes FA1 and FA2 are taken from the previous study [9]. Chemical and phase composition of PC, fly ashes and slag are presented in Table 1. Their particle size distributions were measured by laser diffraction and are shown in Fig. 2.

2.1. Fly ash characterization and glass synthesis

The characterization and measurement of the degree of reaction of two calcareous fly ashes (FA1 and FA2) were carried out in a previous study [9]. Here we mainly focus on FA2 and its constituent glasses. It was composed of several main glass populations readily distinguishable as bright blobs in an Al–Si–Ca ternary frequency plot in Fig. 1. The ranges of chemical composition of these populations were in some cases very broad, in particular in the calcium-rich aluminosilicate region. Four

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Table 1
Bulk chemical analysis by XRF and phase composition by QXRD [wt.%].

	PC	FA1	FA2	S		PC	FA1	FA2	S
Al_2O_3	5.5	19.8	18.2	11.6	C_3S	66.3	–	–	–
SiO_2	20.7	42.3	33.6	36.7	C_2S	8.3	2.5	0.5	–
CaO	65.7	20.7	26.5	38.9	C_3A	8.7	2.0	4	–
Na_2O	0.2	0.3	1.9	0.2	C_4AF	7.7	1.0	1.5	–
K_2O	0.4	1.5	0.4	0.7	Quartz	0.5	1.3	3.5	–
MgO	1.5	2.2	6.4	7.8	Dolomite	1.1	–	–	–
Fe_2O_3	2.7	8.2	6.4	0.5	Calcite	1.8	–	–	–
SO_3	2.6	1.4	2.2	2.8	Periclase	–	–	2	–
TiO_2	0.3	0.7	1.3	0.9	Gypsum	2.6	–	–	–
P_2O_5	0.2	0.3	0.9	–	Anhydrite	3	1.8	2	–
					Free lime	–	1.7	0.6	–
Sum	99.8	97.2	97.7	100.0	Amorphous	–	89.7	85.9	100.0

dominant compositions identified as the centres of the blobs in the ternary plot were selected as marked (A) silicate, (B) Ca-silicate, (C) aluminosilicate and (D) Ca-rich aluminosilicate. Their full chemical composition was determined by EDS, simplified to a Ca–Mg–Na–Al–Si system and used as a target for the model glasses (Table 2). The minor components left out were the K, Fe, S, Ti, and P oxides: their mass totalled 6.7 wt.% for A, 8.8 wt.% for B, 4.8 wt.% for C and 11.2 wt.% for D.

The model glasses were synthesised from mixes of reagent-grade Al_2O_3, SiO_2, $CaCO_3$, Na_2CO_3 and MgO. The powders were mixed in an ethanol suspension for 4 h in a ceramic ball mill. The dried mixes were pelletized and melted at 1600 °C in Pt crucibles in a high-temperature chamber furnace (Borel MO 1700). An additional Pt crucible was used as a cover to minimize the volatilization of alkalis. The samples were heated at a slow rate of 5 °C/min up to 950 °C to allow for a complete decarbonation of the carbonates. Above 950 °C the heating rate was increased to 10 °C/min until 1600 °C. The samples were kept at the target temperature for 4 h to complete the melting and the homogenization. The glasses were then quenched in deionized water. Glass pieces were rinsed with isopropanol, dried and stored in a vacuum desiccator over silica gel until further use. The final chemical composition was measured by XRF (Table 2) and the presence of any crystalline phases was checked by X-ray powder diffraction (XRD) using a PANalytical PW3701 X'Pert diffractometer with Cu Kα radiation and a scanning range of 5° to 65° 2θ.

2.2. Sample preparation

The reaction of the model glasses and the slag was studied in two ways, in batch dissolution experiments, and separately in hydration as a blended cement paste. The dissolution experiment followed a protocol established by Snellings to study the dissolution rates of slags and synthetic glasses [10,11]. In this protocol large glass particles, around 100 μm, are selected, so the dissolution is not too fast and can be measured more accurately. The glasses were hand ground and dry-sieved to obtain the 50–125 μm fraction. Tiny particles adsorbed on surfaces were removed by cleaning of the glass in an ultrasonic bath with isopropanol in cycles of around 5 min. The isopropanol was replaced between the cycles and the washing continued until the supernatant was clear (usually after 3–5 cycles). The hydration study required glasses of fineness similar to the fly ash. The samples were therefore dry-ground in a disc mill and the particle size distributions were measured by laser diffraction in isopropanol dispersions using a Malvern MasterSizer S (Fig. 2).

2.3. Dissolution experiments

Initial dissolution rates were measured in batch dissolution experiment in a NaOH solution of pH 13.2, which corresponds to that of hydrated Portland cement pore solution. The NaOH solution was prepared with 5.6 g of analytical-grade NaOH per 1000 g of ultrapure water that was decarbonated by boiling. The concentration of the NaOH solution was 0.14 M. The experiment was carried out in 250 mL polypropylene bottles at 20 ± 1 °C. The bottles were cleaned with nitric acid and ultrapure water. To ensure far-from-equilibrium conditions for the measurement of the "initial rates" of dissolution and to avoid precipitation of hydrates, the solution to glass weight ratio was 1000. To avoid abrasion, solutions were not stirred. During the experiment, the solution was sampled at 1/4, 1/2, 1, 2, 4, 6, 8, 10, 20, 24, 30 and 48 h. Portions of 5 mL were taken, filtered (0.4 μm) and stored at 4 °C. After each sampling, 5 mL of the NaOH solution was added to keep the volume in the reactor constant. Doing so causes dilution, which was accounted for during data analysis. Silicon, aluminium and calcium aqueous concentrations were measured by ICP–OES with matrix-matched standards.
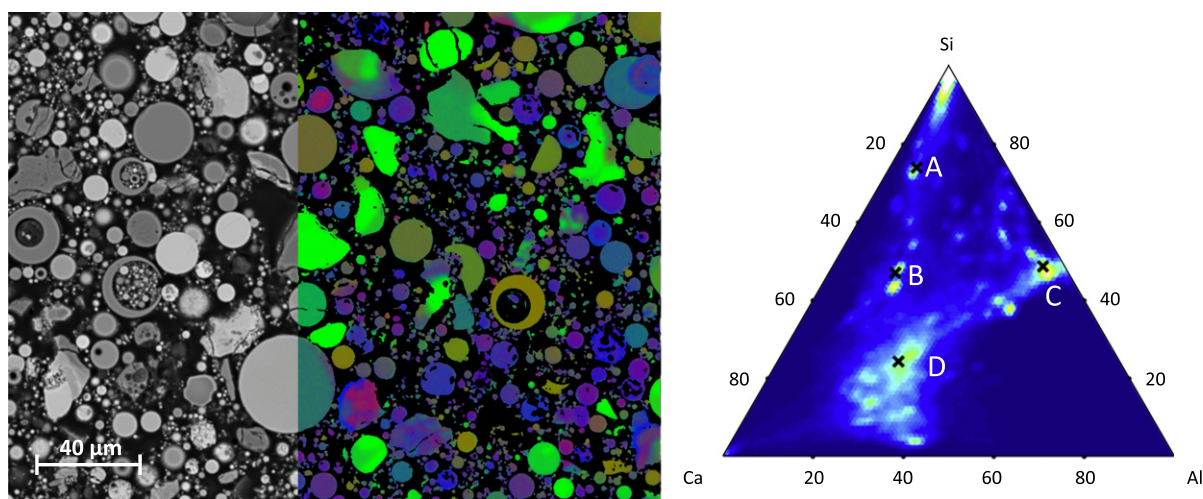

Fig. 1. Analysis of FA2: a BSE grey-level image shows the complex fly ash microstructure, an EDS overlay displays heterogeneity in distribution of elements, ternary frequency plot of the chemical composition from full chemical mapping shows blobs corresponding to the glass groups in the fly ash and the compositions selected for glass synthesis. Further details of the method can be found in [9].