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Examining the pozzolanicity of supplementary cementitious materials using isothermal calorimetry and thermogravimetric analysis

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ABSTRACT

It has recently been proposed that the pozzolanicity of supplementary cementitious materials can be determined by monitoring the heat released when supplementary cementitious materials are mixed with calcium hydroxide at high temperature and high pH. In this study, the heat release is measured using this procedure for a variety of different supplementary cementitious materials. In addition, thermogravimetric analysis is performed on the reacted material to determine the amount of calcium hydroxide consumed. The heat release and calcium hydroxide consumption can be used in conjunction to compare supplementary cementitious materials. Calcium hydroxide consumption can be used to determine the extent of reaction of supplementary cementitious materials in pastes where supplementary cementitious materials are used to replace a portion of cement.

1. Introduction

Large amounts of supplementary cementitious materials (SCMs) are currently being used in concrete as the SCMs can reduce costs, reduce carbon emissions, improve sustainability, and make the concrete more durable. Reserves of some SCMs are being reduced [1], necessitating the identification and use of newer SCMs, such as natural pozzolans [2,3], zeolites [4,5], calcined clays, etc. [6]. It is important to understand the pozzolanicity (considered here as the rate and degree of reaction of SCMs with calcium hydroxide in an alkaline medium) of these materials and resulting concrete properties to successfully utilize them in concrete.

SCMs modify cement hydration in complex ways. SCMs have a filler effect due to their physical presence (an increase in cement hydration extent due to nucleation on the SCM surface, dilution of cement leading to higher space availability for hydrate formation, dilution of cement resulting in a change in the pore solution, and changes in shearing conditions leading to a higher number of nucleation sites [7–9]). Aluminate ions released during the dissolution of SCMs may impede cement or SCM dissolution [10–13]. The reactivity of SCMs in concrete depends on the chemistry of the cement and the chemistry of the SCM, water-to-cementitious materials ratio (w/cm), and SCM replacement level [14,15]. The extent of reaction exhibited by some SCMs can be quite low (for example, the reaction extents of fly ash are reported to be approximately 20–30% at 91 days [15–22]).

Because of the aforementioned reasons, it is unlikely that a single pozzolanicity test is able to predict the performance of concrete with SCMs. While some properties like compressive strength depend on pore size and porosity [23,24], other aspects of performance involving the ingress of harmful species depend on the connectivity of pores [25]. Several methods have been proposed to study the pozzolanicity of SCMs, such as, the Chapelle test [26,27], the Frattini test [28–30], the saturated lime test [28,29], the strength activity index test [28,29], SCM dissolution tests [30], calorimetry based tests, as well as others [26,30]. Each of these tests has advantages and disadvantages. The capabilities of each of these tests to predict concrete properties have been discussed in detail elsewhere [1,27–30]. A pozzolanicity test performed under conditions similar to those in concretes with SCMs is likely to have the best chance to predict the properties of concretes made with SCMs. Isothermal calorimetry can be used to measure the heat release when SCMs are combined with calcium hydroxide at 40 °C and 0.5 M KOH [26,30]. This method can be used to determine SCM pozzolanicity and the authors state that the isothermal calorimetry method is “practical, repeatable and applicable to a wide range of

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SCMs, it furthermore delivers results rapidly and correlates well to the compressive strength development" [30]. Other researchers have suggested that, in addition to calorimetry, bound water contents in similar systems correlate well with compressive strength development [26]. It should be pointed out that heat release and bound water are primarily measures of reaction; strength also depends on other factors such as particle packing [31,32].

In this paper, a slightly modified version of the isothermal calorimetry method (the differences between the original method and this method are discussed in Section 2) is used to study the pozzolanicity of four fly ashes, four slags, two calcined clays, two silica fumes, a quartz, and a limestone. Isothermal calorimetry was used to measure the heat released upon the reaction of the SCMs with calcium hydroxide at 50 °C and in a 0.5 M KOH solution. Thermogravimetric analysis is performed on the resulting blends after 240 h in order to determine calcium hydroxide consumption of each system. By analyzing both calcium hydroxide consumption and the heat release insights about the hydraulic and pozzolanic nature of different SCMs are obtained. The calcium hydroxide consumption in this test can be used to determine SCM reaction extents in cement pastes containing SCM.

2. Materials and methods

Four fly ashes (FA1, FA2, FA3, FA4), four ground granulated blast furnace slags (S1, S2, S3, S4), two calcined clays (CC1, CC2), two silica fumes (SF1, densified and SF2, undensified), quartz (Q) and ground limestone (LS) were studied. Their chemical compositions and the loss on ignition (LOI) as obtained by XRF (using a device passing ASTM C114-15, Standard Test Methods for Chemical Analysis of Hydraulic Cement) are presented in Table 1. It was not possible to prepare samples for XRF for SF1 and Q using our laboratory set-up, therefore, for these materials, oxide contents provided by the manufacturer are presented. Mean particle size (d_{50}, μm) as obtained by laser diffraction is also provided in Table 1. It was not possible to measure particle size distribution of SF1 and SF2 using laser diffraction, therefore, these numbers are not presented. A more complete characterization of the raw materials would include (quantitative) X-ray diffraction and specific surface area as obtained by BET N_2 adsorption, as the specific surface area, glass composition, and mineralogy of the tested SCMs could strongly affect the response of an SCM in this test.

While the selected materials provide differences in oxide contents in each material class and between material classes, they do not necessarily represent the full range of oxide contents (or other properties) that occur with each material class and between material classes. Therefore, the conclusions obtained about heat release and calcium hydroxide consumption are applicable to the materials tested in this paper.

Reagent grade calcium hydroxide and potassium hydroxide were used to prepare the model systems. Blends were made by mixing a 3 to 1 mass ratio of calcium hydroxide and SCM with solutions of 0.5 M potassium hydroxide, maintaining a liquid-to-solid ratio of 0.9. The mixture design used here is somewhat different from the ones proposed earlier, which use additional sulfate [30] and carbonate [26]. Sulfate and carbonate are both known to result in changes in the hydrate phase assemblage when the SCMs are used in cement, and therefore, the response of the materials in this test [26,30]. However, oxide compositions of some of the tested materials were not known a priori, therefore additional sulfate and carbonate were not considered here.

For each test, 40 g of material was mixed was mixed in a plastic container using a spatula for 4 min. Normally, such mixing would be done using a mixer, but the amount of material was too small for using an automated mixer in our laboratory. It is known that the shearing conditions can affect hydration kinetics in alite and cement pastes [33], though the influence of mixing action on SCM-calcium hydroxide systems is unknown. Immediately after mixing, 7 g of material was transferred into a glass calorimeter ampoule, which was then placed in an isothermal calorimeter (TAM Air, TA Instruments) that had been preconditioned at 50 °C. Since the calorimeter is at higher temperature than the material and the ampoule, it takes approximately 45 min for the signal to stabilize, and this part of the signal is not recorded. For highly reactive SCMs like silica fumes, this could result in a slight underestimation of the total heat release. Performing internal mixing in the isothermal calorimeter in such cases could potentially help capture the response during the first 45 min.

The heat flow from the samples was recorded for 240 h, after which time the samples were removed from the calorimeter. Approximately 50 mg of material was taken from the sample and thermogravimetric analysis (Q50, TA Instruments) was performed on it to determine calcium hydroxide contents. The analysis was performed by heating from 23 to 500 °C, at a rate of 10 °C/minute in a nitrogen purged atmosphere. As the test was only run till 500 °C, bound water in these samples could not be measured. Bound water contents in such tests are known to correlate with compressive strength results [26], and are as such, quite important and will be considered in future work. Since the calcium hydroxide consumption is based on a comparison of the final and initial amounts of calcium hydroxide in the SCM-calcium hydroxide systems, hydration was not stopped, as this complicates analysis. Thermogravimetric analysis was done within 6 h of removing the samples from the isothermal calorimeter and maturity calculations indicated that

Table 1
Physical and chemical properties of all tested materials (% are mass %).

	Na_2O (%)	MgO (%)	Al_2O_3 (%)	SiO_2 (%)	SO_3 (%)	K_2O (%)	CaO (%)	Fe_2O_3 (%)	TiO_2 (%)	LOI (%)	d_{50} (μm)
FA1	2.46	1.00	23.71	55.70	0.25	0.81	10.50	3.75	0.71	0.94	27.2
FA2	1.01	2.84	21.30	41.62	1.59	1.49	17.13	8.14	1.28	3.01	19.5
FA3	6.69	4.09	18.36	35.48	2.73	0.81	20.38	5.27	1.11	4.53	12.4
FA4	0.69	2.59	20.51	56.76	0.46	1.35	9.74	6.21	1.17	0.37	14.6
S1	0.23	4.96	13.94	32.59	2.02	0.37	42.22	0.78	0.58	2.08	13.7
S2	0.31	10.68	10.46	34.56	1.11	0.44	39.13	0.70	0.48	1.79	10.2
S3	0.30	12.19	9.26	41.01	1.05	0.43	39.73	0.66	0.36	0.00	12.7
S4	0.25	10.89	8.23	37.71	1.07	0.43	39.08	0.74	0.33	0.75	11.8
CC1	0.05	0.15	43.10	51.92	0.11	0.23	0.14	1.52	2.01	0.58	12.5
CC2	0.22	0.38	27.78	61.82	0.11	3.27	0.33	3.35	0.39	2.23	24.0
SF1	0.29	2.43	0.88	91.47	0.25	0.76	1.06	1.80	0.01	0.67	–
SF2	0.00	0.00	0.00	93.47	0.00	0.00	0.00	0.00	0.00	3.82	–
Q	0.00	0.00	0.35	99.40	0.00	0.01	0.03	0.02	0.00	0.20	3.5
LS	0.00	0.77	0.24	0.66	0.13	0.06	55.44	0.10	0.02	42.49	13.7