Materials Characterization 136 (2018) 165–174

Contents lists available at ScienceDirect

Materials Characterization

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

Neutron scattering measurement of water content and chemical composition of alkali-glass powder reacted gel

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ARTICLE INFO

Keywords:
Alkali-glass powder reacted gel
Chemical composition
Prompt-gamma ray neutron activation analysis (PGAA)
Small-angle neutron scattering (SANS)
Small-angle X-ray scattering (SAXS)

ABSTRACT

Recent studies demonstrated that the added glass powder with high-alumina content could significantly reduce Alkali-Silica Reaction (ASR) damage in cement concrete. This paper aims to investigate the gel water content, chemical composition and expansion behavior of the alkali-glass powder reacted gel by using neutron scattering and other characterization techniques. Three types of samples were prepared with glass powder, sodium oxide and deuteroxide/hydrogen water with different molar ratios. The swelling potential of this alkali-glass powder reacted gel was much lower than that of the reported alkali-silica reacted gel. The gel water content and chemical compositions were characterized with small-angle neutron scattering (SANS) technique, supported by small-angle X-ray scattering (SAXS), prompt-gamma ray neutron activation analysis (PGAA) measurement. The SAXS test results showed the close scattering intensities, and thus similar internal microstructures among these samples. The elemental molar ratios of gels were obtained from the PGAA test results. Then the gel water molar ratio and mass density were determined by neutron scattering contrast calculation. The determined gel water content from neutron scattering analysis was validated with zero contrast analysis and TGA experimental measurement. Overall, this paper demonstrated the feasibility of using SANS technique to determine the water content of alkali-glass powder reacted gel.

1. Introduction

Due to its high pozzolanic reactivity, glass powder with high-alumina content has been applied as Supplementary Cementitious Materials (SCMs) in concrete production [1]. Replacing part of the Portland cement with fine glass powder can mitigate the recycling pressure for the accumulated waste glass [2] and reduce the generated greenhouse gas during cement production [3]. Particularly, the added glass powder can also reduce the early ASR damage [4–6] generated in the cementitious materials containing reactive glass aggregate [7,8], which is a serious sustainability issue for concrete infrastructure [9]. The mitigation mechanism of the added SCMs on ASR damage has been analyzed by different researchers [10–13]. One important aspect is that the added SCMs can participate in the pozzolanic reaction [14,15] and fix the alkali content in the generated CSH gel [10]. The CSH gel formed during the pozzolanic reaction has high calcium and low alkali content [16], which was found to be unexpansive and doesn't cause serious ASR damage [17–19]. Further studies demonstrated that the added glass powder can increase the aluminum concentration in concrete pore solution [4]. The aluminum content can decrease the dissolution rate of the amorphous silica in alkaline solution [11,12] and then reduce the amount of the generated deleterious ASR gel. Besides the discussion above, the added glass powder can also be activated by the high-alkaline concrete pore solution [20,21]. The added glass powder with sufficient alumina content can react with the alkaline pore solution, like fly ash [22,23], and form the alkali-glass powder reacted gel, which is similar to sodium aluminosilicate (N-A-S-H) gel [24,25]. Currently, the influence of the generated alkali-glass powder reacted gel on ASR damage is not clear and its chemical composition and water stability also has not been thoroughly studied [26]. This study aims to analyze the reacted gel with the small angle scattering (SAS) and prompt-gamma ray neutron activation analysis (PGAA) techniques to investigate its chemical composition and understand its influence on ASR damage.

The SAS technique can be separated into the small-angle neutron scattering (SANS) [27] and small-angle X-ray scattering (SAXS) [28] based on the flux source. When passing through the test specimen, the neutron/X-ray flux can be scattered by the nucleus/orbital electrons forming the material. The scattering can change the flux propagation direction and this effect will be described with the scattering vector (The direction difference between the incident and scattered beam

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https://doi.org/10.1016/j.matchar.2017.12.014
Received 16 August 2017; Received in revised form 24 November 2017; Accepted 11 December 2017

[29]). The measured result of the SAS test is the relationship between scattering intensity and scattering vector. The back calculation based on theoretical scattering model then needs to be further conducted for the detailed sample morphology information analysis [30], pore size distribution investigation [31], water state and content [32], phase identification [33], microstructure analysis [34] or chemical composition information [35]. Compared to the conventional microscale examination techniques (SEM, MIP or BET), the SAS technique has several advantages on cementitious materials characterization. Firstly, the SAS technique can examine the sample non-destructively, which is appropriate for the in-situ monitoring of the structural evolution during the hydration process [29], phase transformations at elevated temperature [36] or under high pressure [37]. Furthermore, the cementitious specimen can stay saturated during the SAS examination, which can avoid the oven-drying process and drying shrinkage [38]. Also the SAS technique can analyze the microstructure volumetrically instead of the surface examination during SEM/TEM test and a sample around 0.5 cm^3 will be examined during the SANS tests [39], which can be considered as a representative for the whole cementitious material. With its powerful penetration ability, the SAS technique can be applied to detect the blocked or closed pores during the pore size distribution analysis, which are probably inaccessible to the mercury or nitrogen molecules during the Brunauer–Emmett–Teller (BET) or mercury intrusion porosimetry examination (MIP) tests [39]. The SAS can also be further separated in to elastic scattering (passing without energy loss) [40] and inelastic scattering (passing with energy loss) [41,42]. This study will apply the elastic SAXS for internal microstructure examination (scattered by orbital electrons) and the elastic SANS (scattered by the nucleus) to investigate the chemical composition and gel water content of the alkali-glass powder reacted gels.

The SAS technique was firstly applied on the cementitious material characterization by Allen et al. [43]. Since then, the SAS technique has been widely used by different researchers to investigate the microstructure evolution or chemical composition of the cementitious materials [44–47]. Among them, Thomas et al. [48] used the SANS technique to investigate the CSH gel samples prepared with the mixture of deuteroxide and hydrogen water. The neutron scattering density of the CSH gel was further obtained based on zero contrast analysis. Allen et al. [35] built the relationship between the CSH gel chemical composition and mass density with the measured neutron scattering contrast. Both the CSH gel chemical composition and mass density were back calculated with the neutron scattering measurement results. Thomas et al. [21] further extended the study to analyze alkali-activated slag. The mass density and the gel water molar ratio were obtained based on the gel scattering contrast calculation. Compared to the wide application in CSH gel, the application of SAS technique on the ASR gel or the alkali activated materials is relatively limited as shown in the review reference [49]. Sun et al. [50] analyzed the microstructure and morphology of the alkali-glass powder gel with the USANS/SANS techniques and the back-calculated radius of the gel particles is in the range of 2–3 μm. The SEM examination was further conducted with the prepared gel and the consistence between the two results demonstrates the validity of the USANS/SANS technique. White et al. [51] applied the neutron total scattering technique to investigate the Nano-scale structure of metakaolin based geopolymer. It was found the geopolymer gel can be transformed to leucite at the temperature above 1000 °C. Maitland [52] employed both USAXS and SANS for the investigation of the geopolymer microstructure. The geopolymer can be considered as three separated phases (closed pore, open pore and the solid content) and the relationship between the three phases with the measured neutron scattering intensity were investigated. Steins [53] utilized the SANS and SAXS methods to study the influence of the aging factor on the metakaolin based geopolymer pore structure. The pore volume fraction was found to decrease with time. Phair et al. [54] analyzed the state of water in hydrating sodium disilicate with the quasi-elastic neutron scattering technique (QENS). Both the bonded and free water content can be observed with the QENS examination, which is in consistent with the observation from thermogravimetric (TGA) analysis. Currently, the application of SAS technique on the chemical composition analysis of ASR gel or alkali activated material has not been found to the best of the knowledge of the authors.

The neutron flux can also be further applied for the element type and concentration analysis. The scanned sample can generate the Gamma-ray when striking by the neutron flux and the wavelength of the emitted Gamma-ray is determined by the element type. The Prompt Gamma-ray Activation Analysis (PGAA) test was then developed based on the relationship between Gamma-ray wavelength and element type for the chemical composition analysis [55,56]. Compared to the traditional EDS test [57], the PGAA tests can analyze the sample in a saturated state. Furthermore, the measurement results of the PGAA are consistent with the values obtained from X-ray fluorescence (XRF) test [56]. Khelifi et al. [58] applied PGAA technique to measure the Ca/Si molar ratio in different concrete samples. The obtained values were verified with the chemical analysis results. Oliveira et al. [59] analyzed the raw materials for cement production with the PGAA methods. The concentration of silica, lime, alumina and iron oxide were obtained and the measured results were also verified with the chemically determined results. Naqvi et al. [60] applied the PGAA technique to analyze the chloride content in Portland cement samples and the minimum detectable concentration was investigated. The measured results were consistent with the Monte Carlo simulation results. Based on the discussion above, the PGAA method has demonstrated its capability for element identification and concentration measurement in the cementitious material.

This study aims to determine the gel water content and chemical composition within swelling process of the alkali-glass powder reacted gel by using neutron scattering and other characterization techniques. The sample prepared with glass powder, sodium oxide and deuteroxide/hydrogen water mixes were specifically designed for this study. The detailed mixture design and preparation process are mentioned in Section 2. Then the swelling test was conducted to examine the relative-low volume expansion of this glass powder reacted gel by comparing with reported alkali-silica reacted gel test results. The alkali-glass powder reacted gel samples with different D_2O/H_2O molar ratios were then examined by the SAXS (Small-angle X-ray scattering), PGAA and SANS tests in Section 3. The SAXS tests is firstly conducted to demonstrate that these samples have very similar X-ray scattering intensities and thus internal structures. This results verified that the sample neutron scattering intensity changed only depend on D_2O/H_2O molar ratios. In order to calculate the gel scattering intensity, the sample elemental molar ratios (alkali: silicon) and (aluminum: silicon) were determined by the PGAA test results. The neutron scattering intensities were later measured for water content characterization. In Section 4, the gel water molar ratio and the mass density were obtained with the relative gel scattering intensity ratios among three types of samples. In Section 5, the determined gel water content from neutron scattering analysis was validated with both zero contrast analysis and TGA experimental measurement. This study provides a complete and precise characterization method for determining water content and chemical formulation of alkali-glass powder reacted gels.

2. Sample Preparation and Swelling Potential Examination

2.1. Mixture Design and Sample Preparation

The alkali-glass powder gel samples were prepared with the glass powder (silica and alumina source), sodium oxide (alkali source) and deuteroxide/hydrogen water mixture. The detailed mix design is shown in Table 1, where Sample 1, Sample 2 and Sample 3 represent the samples prepared with 0%, 50% and 100% molar ratio of D_2O respectively. The glass powder and sodium hydroxide are obtained from Vitro Minerals (LA-600 Type) and Sigma-Aldrich respectively. The