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Effect of slag content and activator dosage on the resistance of fly ash geopolymer binders to sulfuric acid attack

Timothy A. Aiken*, Jacek Kwasny, Wei Sha, Marios N. Soutsos

School of Natural and Built Environment, Queen's University Belfast, Stranmillis Road, Belfast BT9 5AG, UK

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ABSTRACT

Geopolymer (GP) binders are an appealing alternative to Portland cement (PC) binders as they have the potential to reduce the CO_2 emissions associated with the cement and concrete industry. However, their durability in aggressive environments needs thorough examination if they are to become a viable alternative to traditional PC materials. This study investigated the effect of increasing slag content and activator dosage on the sulfuric acid resistance of fly ash GP binders. Their performance was also compared with that of neat PC mixes using various physical and microstructural techniques. The results show that increasing the slag content of fly ash GPs decreases porosity, but makes the reaction products more susceptible to sulfuric acid attack. It was also found that increasing the alkaline activator dosage of fly ash GPs has little impact on sulfuric acid resistance. Finally, GP binders displayed superior sulfuric acid resistance than their PC counterparts.

1. Introduction

The durability of concrete is an increasingly important property for concrete structures due to the growing demand for structures to have a long service life with minimal maintenance [1]. It is well known that traditional Portland cement (PC) concrete structures deteriorate when exposed to acidic environments [2]. Such conditions reduce the service life and increase the cost for maintenance or renewal, which is also harmful for the environment in terms of CO_2 emissions and natural resource conservation [3]. There are many ways in which concrete can come into contact with aggressive acidic media and there are numerous types of acid which are harmful to cementitious materials including mineral and organic acids. This study focuses on sulfuric acid which poses a considerable threat to the durability of concrete in multiple scenarios which are discussed below. Many industrial manufacturing processes such as fertiliser production and metal finishing use mineral acids such as sulfuric acid [4]. Acid precipitation is another common source of acid attack which occurs due to the incomplete combustion of fuels and industrial pollutants producing sulphur gases which form sulfuric acid when reacted with water [5, 6]. Additionally, sewer networks and wastewater systems worldwide suffer significant corrosion and deterioration due to sulfuric acid attack, resulting in large economic losses annually [7, 8]. Sulfuric acid, generated by sulphur/sulphide-oxidising bacteria has been identified as the corroding acid in sewer systems [9–11]. Unfortunately, the relative inaccessibility of sewer networks poses considerable challenges for maintenance and repair [12]. Sulfuric acid can also be present in groundwater or produced from the oxidation of sulphur bearing compounds in backfill, such as pyrite, causing degradation to concrete substructures [13]. The dissolution of hydrogen sulphide can also form sulfuric acid with a low pH on the concrete walls of geothermal wells [14]. Therefore, sulfuric acid is a major cause of degradation of concrete structures.

In order to reduce the CO_2 emissions related to the production of PC, the use of geopolymer (GP) materials has become an increasingly active area of research. GPs are alternative binding materials which are produced using materials such as ground granulated blast furnace slag (slag) and fly ash (also known as pulverised fuel ash). These materials are activated or hardened using solutions of alkali silicates and/or hydroxides [15]. Natural clays such as kaolinite in the form of metakaolin are also used to produce GP materials [16, 17] but are not the focus of the present study. Fly ash and slag are considered promising binder materials due to environmental benefits as they are by-products from other industries and can help reduce the demand for PC, and in turn, reduce CO_2 emissions. The production of 1 t of PC clinker emits ca. 0.9 t of CO_2. Approximately 8% of global CO_2 emissions are attributed to PC production [18]–[20]. However, geopolymer concrete produced with fly ash and slag has been shown to have between 50 and 90% less embodied CO_2 than PC concrete [21–23]. It is worth noting that the environmental benefit will vary depending on the source materials, transportation requirements and activator type [24]. Fly ash is a by-product from coal combustion in power stations. The demand for and use of fly ash as a construction material is increasing. However, there are still many countries where efficient utilisation of fly ash is a

* Corresponding author.
E-mail address: taiken02@qub.ac.uk (T.A. Aiken).

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major problem with as little as 7% being used effectively [25]. Slag is a by-product of steel manufacture and is produced when blast furnace slag is cooled rapidly in water resulting in glassy granules, these are then ground to form a fine powder [26]. It is important to determine the resistance of GP materials to acid attack in comparison with traditional PC materials before their use can become widespread. Potentially, GPs may be able to solve two of the main problems for traditional PC materials, namely, the large volume of CO_2 emissions and low resistance to aggressive acidic media.

The majority of studies in the literature on the acid resistance of GP materials report favourable performance. Rostami and Brendley [27] studied the sulfuric acid resistance of fly ash concrete and PC concrete with the addition of silica fume. After 90 days exposure to 20% sulfuric acid the fly ash concrete had a mass loss in the region of 4% compared with 25% for the PC based concrete. Similarly, Thokchom et al. [28] reported that fly ash GP mortars had much better performance in terms of mass loss when exposed to 10% sulfuric acid than their heavily corroded PC counterparts. An increase in mass loss was also reported when the alkali dosage (% of Na_2O) was increased. However, in a later publication it was stated that increasing the alkali dosage results in a higher residual compressive strength after sulfuric acid attack [29]. Bakharev [30] studied the resistance of fly ash GP pastes and PC pastes to 5% sulfuric acid. A superior performance was observed for the fly ash GP paste which was attributed to much lower calcium content. Lee and Lee [31] studied the resistance of fly ash and slag GP mortars to 10% sulfuric acid. They reported higher resistance of blends with lower slag content due to the nature of the binding gel produced. On the other hand, Lloyd et al. [32] reported that increasing the slag content increases the resistance of GP pastes exposed to sulfuric acid with pH controlled at 1.0. Allahverdi and Skvara [33, 34] studied the mechanism of sulfuric acid attack on fly ash and slag GP pastes containing 50% of each. They reported an ion exchange between the samples and attacking acid followed by shrinkage cracks and the formation of gypsum.

Many different variables have been studied including sample type, sample size, acid type and acid severity [35]. There are also many testing procedures and degradation indicators employed making it difficult to draw comparisons between studies [35]. Additionally, many studies only consider a single deterioration mechanism and few studies consider multiple indicators of deterioration which is necessary when studying different binder types. Acid attack is a complex phenomenon, particularly when studying different binder types. Therefore many indicators of acid attack were employed in this investigation including, physical, leaching and microstructural properties. Even when studying the acid attack of PC materials alone the use of multiple test methods is recommended to ensure a reliable estimation of acid resistance is achieved [36]. Furthermore, despite resistance to aggressive environments often being cited as a benefit of GP materials, there remain limitations in the understanding of the effects of acid attack to GP materials, particularly at microstructural level [37]. Therefore, the overall aim of this work was to study the sulfuric acid resistance of fly ash based GP mortars and pastes and to understand the mechanism of sulfuric acid attack. The main objectives were to:

- Investigate the influence of slag content on the sulfuric acid resistance of fly ash GP mixes,
- Determine the effect of increased activator dosage on the sulfuric acid resistance of neat, i.e. unblended, fly ash GP mixes,
- Compare the sulfuric acid resistance of GP mixes with conventional PC mixes.

2. Experimental programme

2.1. Methodology

In order to satisfy the objectives, the following variables were investigated:

- The effect of slag content on the acid resistance of fly ash GPs has been assessed by increasing the slag content in both mortar and paste mixes, i.e. 0%, 20%, 40% and 70% for mixes GP1, GP2, GP3 and GP4, respectively. All four mixes had Na_2O content of 7.5% and Na_2O/SiO_2 ratio of 1.25.
- The effect of increasing the alkaline activator dosage on the acid resistance of 100% fly ash GPs has been studied on mortar and paste mixes with different Na_2O content and Na_2O/SiO_2 ratio, i.e. 7.5% and 1.25 for mix GP1 and 11.5% and 0.95 for mix GP5.
- PC mortar and paste mixes with two different strength grades were used to allow comparison of GP and PC mortars with similar compressive strength. Mix PC1 had a comparable compressive strength to that of GP2 and GP5, while mix PC2 had a comparable compressive strength to that of GP3 and GP4.

All the mortar mixes investigated in this study were prepared with a paste content of 50%, so a fair comparison could be carried out between different binder types.

After 28 days of curing, mortar samples were immersed in 1, 3 and 5% sulfuric acid (w/w) solutions for a total duration of 56 days, while paste samples were immersed in 5% sulfuric acid solutions for 21 days. For both mortars and pastes the acid solutions were replenished every 7 days. Mortar mixes were used to study physical properties such as visual appearance, mass change, compressive strength, alkalinity loss and porosity. Paste mixes were used to study the leaching behaviour by pH and inductively coupled plasma mass spectrometry (ICP) analysis of the acid solutions. The paste mixes were also used to study microstructural properties by X-ray diffraction (XRD), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis. Paste mixes exposed to acid attack were compared with control paste mixes stored in water. For convenience, the overall outline of the testing programme is shown in Table 1, while a detailed description of each testing method is provided in Section 2.5 on testing procedures.

2.2. Materials

The fly ash used in this study was obtained from Power Minerals Ltd., Drax Power Station, North Yorkshire, UK and the slag was supplied by Civil and Marine Ltd-Hanson Company, member of the Heidelberg Cement Group, Essex, UK. The fly ash and slag conform to the standards of BS EN 450-1:2012 [38] and BS EN 15167-1:2006, respectively [39]. Portland cement CEM I 42.5N, produced by Quinn Cement in Northern Ireland, and conforming to the standards of BS EN197-1:2011 [40] was used as PC. The oxide compositions for fly ash, slag and PC obtained by X-ray florescence (XRF) are displayed in Table 2. The XRD patterns of fly ash, slag and PC are shown in Fig. 1. The main crystalline phases present in fly ash are quartz, mullite and hematite. The slag is almost completely amorphous with a broad peak or hump shown between 25 and 35° 2θ. The PC has many crystalline phases including alite, belite, aluminate, brownmillerite and gypsum.

The alkali activated fly ash and slag binders were activated by solutions of sodium silicate and sodium hydroxide. The sodium silicate solution was supplied by Fisher Scientific and consisted of 12.8% Na_2O, 25.5% SiO_2 and 61.7% water. The sodium hydroxide solution was prepared at 30% w/w by the dissolution of solid commercial grade (99% purity) sodium hydroxide and was allowed to cool to room temperature prior to sample preparation.

The aggregate used was siliceous lough sand abundant in quartz, sourced locally in Northern Ireland. Silica sand is not susceptible to acid attack allowing comparison to be carried out between the different pastes without dissolution of aggregate [41]. The sand had an oven-dry particle density of 2695 kg/m^3 and water absorption of 0.92 and 1% after 1 and 24 h, respectively. Both density and water absorption were determined according to BS 812-2:1995 [42]. The sand was oven dried at 105 ± 5 °C for at least 48 h to remove all moisture. It was then