Durability of fly ash based Geopolymer concrete against sulphuric acid attack

X. J. Song[a], M. Marosszeky[a], M. Brungs[b], R. Munn[a]
[a]School of Civil and Environmental Engineering, UNSW, Syndney, NSW, Australia, 2052
[b]School of Chemical Engineering and Industrial Chemistry, UNSW, Syndney, NSW, Australia, 2052
Tonysxj@unsw.edu.au

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ABSTRACT

In spite of a long-term recognition of the problem of sulphuric acid corrosion in concrete sewer pipes, this issue has not been satisfactorily resolved. Geopolymer binders have been reported as being acid resistant and thus are a promising and alternative binders for sewer pipe manufacture. This paper presents experimental data on the durability of fly ash based Geopolymer concretes exposed to 10% sulphuric acid solutions for up to 8 weeks. A class F fly ash based Geopolymer concrete was initially cured for 24 hours at either 23˚C or 70˚C. The compressive strength of 50-mm cubes at an age of 28 days ranged from 53MPa to 62MPa. After immersion in a 10% sulphuric acid having a fixed ratio of acid volume to specimen surface area of 8 ml/cm^2, samples were tested at 7, 28, and 56 days. The mass loss, compressive strength reduction, and the residual alkalinity were determined on the basis of modified ASTM C267 tests. The results confirmed that Geopolymer concrete is highly resistant to sulphuric acid in terms of a very low mass loss, less than 3%. Moreover, Geopolymer cubes were structurally intact and still had substantial load capacity even though the entire section had been neutralized by sulphuric acid.

KEYWORDS

Geopolymer; fly ash; acid resistance; durability, concrete pipe

1 INTRODUCTION

In spite of a long-term recognition of the problem of sulphuric acid corrosion in concrete sewer pipes, this issue has not been satisfactorily resolved. A research looked at ways of enhancing the acid resistance of Portland Cement (PC) based concretes, using the partial replacement of Portland cement by supplementary materials, the use of epoxy modified binders, and the use of limestone as a sacrificial aggregate [Song et al 2003]. The acid attack in terms of mass loss was reduced, however, even the improved concretes lost significant mass with immersion time. Sulphuric acid resistant binders are still required to enhance the long-term performance of concrete in sulphuric acid corrosion environments.

Sulphur concrete is sulphuric acid resistant. However, weighing the advantages and limitations of sulphur concrete based on the available published data, Malhotra [1988] emphasised that the indiscriminate use of sulphur as a binder for concrete cannot be recommended.

Geopolymer binders might be a promising alternative in the development of acid resistant concrete. Since Geopolymers are a novel binder that relies on alumina-silicate rather than calcium silicate hydrate bonds for structural integrity, they have been reported as being acid resistant. Davidovits et al [1990] found that metakaolin based Geopolymer has very low mass loss when samples were immersed in 5% sulphuric acid solutions for 4 weeks.

Class F fly ash is a cost effective feedstock for Geopolymer concrete. Fly ash based Geopolymer concrete can set at ambient (23˚C) and high temperatures (70˚C). Rostami and Brendley [2003] tested the acid resistance of alkali fly ash concrete (cured at 40-90˚C) in terms of mass loss. Beyond the measure of mass change, there is limited experimental data to provide insight into the sulphuric acid resistance of fly ash based Geopolymer concretes.

This paper reports experimental data on the response of Alkaline Activated Fly ash based Geopolymer (AAFG) concrete against 10% sulphuric acid solutions for up to 56 days, in terms of visual inspection, mass change, and residual compressive strength and alkalinity.

2 Fly ash based Geopolymer concretes and test procedures

2.1 Fly ash based Geopolymer concretes

Two class F fly ashes were activated by alkaline activators to form Geopolymer gel, which binds the silica sand and latite aggregate (< 10mm) to make Geopolymer concrete. The chemical composition of the fly ashes and alkaline activators is given in Table 1, whereas the mix design is listed in Table 2.

Oxide	Weight (%)				
	Fly ash 1	Fly ash 2	GP cement	Na_2SiO_3	NaOH
SiO_2	67.1	51.3	20.3	30.6	--
Al_2O_3	23.6	32.6	4.6	--	--
Fe_2O_3	3.70	11.5	4.5	--	--
CaO	0.80	2.50	65.1	--	--
Na_2O	0.60	0.20	0.04	9.50	30.1
K_2O	1.60	0.30	0.5	--	--
H_2O	--	--	--	59.9	69.9

Table 1: Chemical composition of starting materials

Two grades of AAFG concretes were prepared for this investigation. G54 represents a Geopolymer concrete synthesised at high temperature (12 hours at 70˚C) whereas G71 was achieved at ambient temperature (24 hours at 23˚C). The nominal compressive strength of 50-mm cubes at an age of 28 days is 62 MPa for G54 and 53 MPa for G71.

The control mix PC55 was made using type GP cement (Table 1) with a water/cement ratio of 0.35 and used silica sand and basalt aggregate (Table 2). The curing condition is as same as G54. Its 28 day compressive strength was 65.1 MPa, having a similar strength grade as Geopolymer G54.

Material	Fly ash 1	Fly ash 2	NaOH	Na_2SiO_3	Sand	Latite
% by mass	13.6	4.7	3.4	4.1	26.3	47.9
	Type GP 535Kg/m^3, water/cement = 0.35				24.0	44.4

Table 2: Mix design of concretes

2.2 Acid resistance testing

At an age of 28 days, 15 AAFG concrete cubes from each mix were immersed in 10% sulphuric acid solution based on a modified ASTM C267 test. Three cubes were weighed for mass change, nine were crushed for residual compressive strength after being immersed in acid for 7, 28 and 56 days, and the remaining three were used for long-term visual observation. Three cubes from PC55 were used to measure mass change. In addition, at the end of the acid exposure period, the cubes that were used to assess mass loss were split to examine their residual alkalinity.

A 10% (by mass) sulphuric acid solution was directly diluted from 98% concentrated sulphuric acid with tap water. The 10% sulphuric acid does not represent the actual service condition encountered in sewer pipes, but such a concentration of acid has been used by the Los Angles County for 15 years to test the sulphuric acid resistance of products [Redner 1998]. The use of a 10% sulphuric acid environment provides accelerated experimental data within 8 weeks. The ratio of the sulphuric acid volume to specimen exposure area was fixed at 8 ml/cm^2. The acid concentration was monitored via titration and refreshed weekly.

3 Experiment results and discussion

3.1 Visual inspection

As can be seen in Fig. 1, the binder in the normal PC55 concrete shows significant degradation the aggregate becoming exposed after only 4 weeks in 10% sulphuric acid. By contrast, Geopolymer concrete cubes, G71 and G54, remained structurally intact in the same acidic environments after 56 days, though some very fine localised cracks were observed.

Figure 1. Appearance of concrete specimens expored in 10% sulphuric acid (Left: PC55 for 28 days, right: AAFG for 56 days)

3.2 Mass change

The mass change (negative means mass loss) with immersion time is shown in Fig. 2. The mass change was calculated according to ASTM C267. AAFG concretes, both G54 and G71, have very low mass loss, less than 3%. The PC55 concrete, on the contrary, experienced significant deterioration, losing up to 41%, of its mass within 4 weeks.

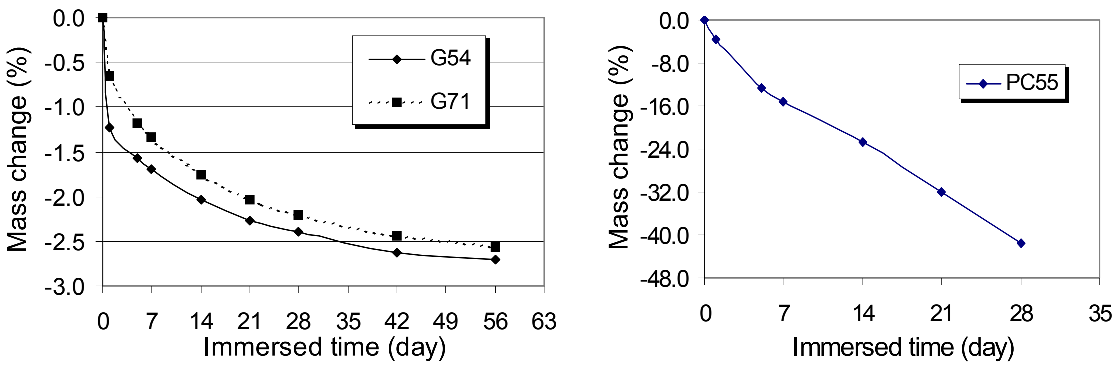

Figure 2. Mass change in 10% sulphuric acid

3.3 Compressive strength change

Since the AAFG cubes were structurally intact after acid immersion, they were crushed to identify the influence of acid attack on strength change. Nine cubes in three groups were crushed after being immersed in acid for 7, 28 and 56 days. Fig. 3 shows the reduction of compressive strength of AAFG concretes as a function of immersion time. It should be stressed that the strength values at 56 days in Fig. 3 were calculated by the ultimate failure load and the measured section area. The influence of slight cracking has not been considered as it is difficult to quantify.

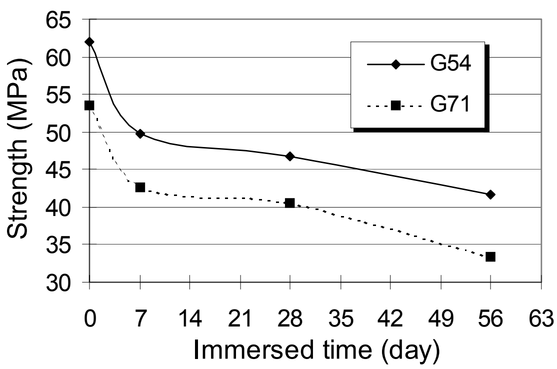

Figure 3. Compressive strength change of AAFG concretes in 10% sulphuric acid

3.4 Residual alkalinity

The residual alkalinity of concrete cubes after sulphuric acid attack was roughly determined by spraying 1% phenolphthalein on the freshly fractured surface [Rendell and Jauberthie 1999]. As shown in Fig. 4, AAFG concretes showed colourless while PC55 was still magenta indicating that the concrete in the centre of the specimen still has a pH above 9.

The pH values of AAFG concrete G54 and G71 were further investigated by powder method [Pavlik 1994]. Two powder samples were collected and identified by their location as the edge and the centre, the zones being separated by the brown line on the cross section (Fig. 4). The pH values of hardened Geopolymer concretes before and after acid attack are presented in Table 3. After acid attack for 56 day, the entire AAFG concrete cubes became acidic with pH value as low as 3.

Figure 4. Residual alkalinity indicated by the phenolphthalein (From left to right: PC55, G71, G54)

Sample	Before acid	After acid -- edge	After acid -- centre
G54	11.2	3.1	6.1
G71	11.0	2.9	8.0

Table 3: pH values of AAFG concretes before and after acid attack

3.5 Discussion the occurrence of fine cracks

The occurrence of very fine cracks on Geopolymer cubes in Fig. 1 was further investigated. It should be stressed that the fine cracks were not evenly distributed on the surface, they appeared only in local areas. As the exposure time progressed (e.g. 112 days), some white reaction products were found within cracks on one of three cubes used for long term exposure. The white products were observed under a Scanning Electron Microscopy (SEM -- Hitachi S4500) coupled with an Oxford Energy Dispersive Spectrometer (EDS). The crystals were observed to have a hexagonal section (Fig 5), which is similar to the SEM image taken by Rendell and Jauberthie [1999]. The EDS data clearly show the dominant elements of calcium and sulphur and hence the white products are gypsum.

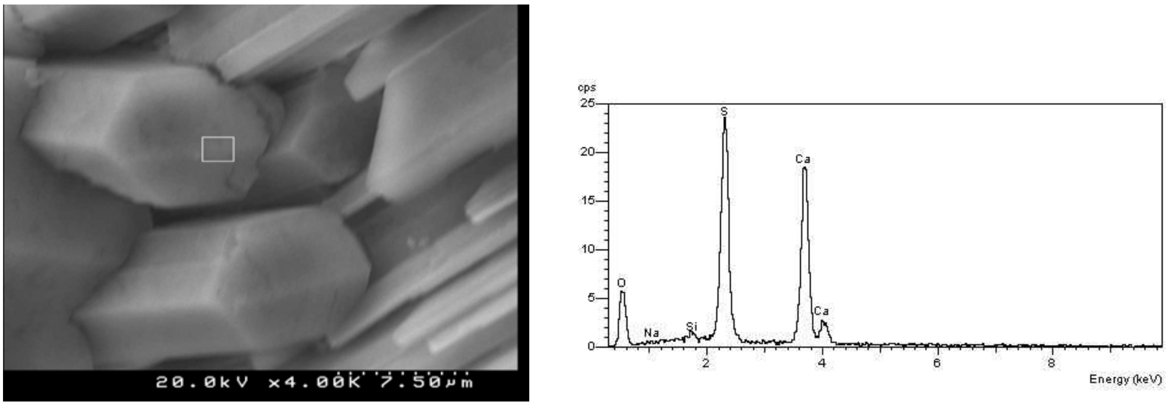

Figure 5: SEM of gypsum crystal and EDS data

The expansion of gypsum has been long known in sulphuric acid attack on PC concrete [Rendell and Jauberthie 1999], however the question remained where does the calcium come from? The class F fly ashes contain very low lime (Table 1). The solubility of sand and latite was determined by dissolving 50-g dry sample in 100-g 30% nitric acid solution for five hours. It is clear in Table 4 that the latite aggregates have a slightly higher solubility that the sand.

Though the solubility of latite aggregates is low, when they were examined carefully, a few pieces were found with a very slight white deposit. Several pieces of such aggregate were picked out to cast Geopolymer concrete Cr-3 whereas Geopolymer mortar Cr-2, without any latite aggregate, was made as the control. After exposure in 10% sulphuric acid for 70 days, the comparative results were significant (Fig. 6). Geopolymer mortar Cr-2 had no cracks whereas the Geopolymer concrete with latite aggregate once again exhibited visual cracking (Fig. 6, right). Clearly then, the cause of cracking, as shown in both Fig. 1 and Fig. 6, is attributed to the contamination the basalt aggregate, where the white stains reacted with sulphuric acid and formed gypsum. The volume expansion of gypsum caused the localised cracks. This test confirmed that the Geopolymer mortar did not swell at all under 10% sulphuric acid solution. Therefore, the selection of aggregate is critical in developing sulphuric acid resistant Geopolymer concretes.

Name	Fine sand	Coarse sand	Latite
By mass (%)	0.9	0.6	2.6

Table 4. Solubility of sand and Latite

Figure 6: Comparison of Geopolymer mortar (left) with concrete (right)

3.6 Discussion the sulphuric acid resistance of Geopolymer concretes

The appearance of the exposed samples (Fig. 1) clearly indicated that AAFG concrete is durable (regardless of the fine cracks) in 10% sulphuric acid up to 56 days. In the case of PC concrete, the hydration compounds were neutralised by sulphuric acid and gradually the binder disintegrated, thus exposing the aggregates.

The mass change agrees with the visual appearance in Fig. 1. The very low mass loss of Geopolymer concretes in this paper is consistent with the findings of Davidovits [1990] and Rostami and Brendley [2003]. Moreover, the trend of mass loss becomes essentially constant at longer exposure time. This indicates that the Geopolymer concretes presented in this paper are sulphuric acid resistant as they stabilized without further mass change.

The residual compressive strength has not been previously used to evaluate the acid resistance of PC concrete because of the rough surface and the exposed aggregate after acid immersion. In this investigation, however, Geopolymer concrete remains structurally intact. The compressive strength was used in this research to evaluate the impact of acid attack on mechanical performance. Although the strength reduction (Fig. 3) was significant within the first week of immersion, this trend then became stable with residual strength up to 33 ~ 42 MPa after 56 days acid exposure. The strength loss was measured in the range of 32 ~ 37%. The residual load capacity indicates that some bonds still exist even the entire section was neutralized by acid. On the other hand, however, the acidity presents a challenge for the use of steel reinforcement under acidic conditions.

In addition, it is very interesting to compare the acid resistance between G54 and G71. There is a significant difference in the 28 days strength development. As expected, G54 has higher compressive strength than G71 due to the effect of higher temperature curing. However, both of them have a very similar trend in resisting sulphuric acid attack, in terms of mass change (Fig. 2), compressive strength reduction (Fig. 3), and the residual alkalinity (Fig. 4). Therefore AAFG concretes are acid resistant regardless of curing conditions. It also seems that Geopolymer concretes have the potential to be used in the production of precast sewer pipes (high temperature curing) as well as in the repair of corroded pipes (ambient curing).

4 Conclusions

Based on above experimental data and discussion, the following conclusions can be drawn:

AAFG binders were found to exhibit much lower mass change than PC concretes. Moreover, Geopolymer cubes were structurally intact and still had substantial load capacity even though the entire section had been neutralized by sulphuric acid. However, steel reinforcement cannot be used in such low pH environments. Hence either alternate reinforcement needs to be used or the permeability of Geopolymer materials has to be substantially improved.

AAFG binders have high sulphuric acid resistance regardless of the curing conditions, at ambient condition (23˚C) or high temperature (70˚C). They have very similar degradation trends.

The requirement for materials selection, especially the presence of calcium, is critical in developing sulphuric acid resistant Geopolymer concrete. The high purity siliceous aggregates is strongly recommended.

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