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Cement and Concrete Research 35 (2005) 1486 – 1494

Cement and Concrete Research

Using limestone aggregates and different cements for enhancing resistance of concrete to sulphuric acid attack

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Received 30 May 2003; accepted 14 March 2005

Abstract

A research program was undertaken to improve concrete's resistance against sulphuric acid attack. Six concretes were investigated, four using calcareous limestone aggregates and two using silicious aggregates. Cements used in these concretes included a portland cement, a binary cement containing ground granulated blast furnace slag, and two ternary cements containing slag and silica fume or fly ash and silica fume. All the concretes had the same water/cement ratio of 0.4, with compressive strengths in the range of 45 MPa and 58 MPa at the age of 28 days. In the experiment, concrete cylinders were immersed in 1% sulphuric acid solution and they were periodically examined for appearance, measured for mass change and tested in compression up to 168 days. The concrete using limestone aggregates and the ternary cement containing silica fume and fly ash performed the best.

Keywords: Sulphuric acid attack; Concrete; Fly ash; Silica fume; Slag; Limestone aggregates; Silicious aggregates

1. Introduction

Concrete is the most widely used construction material for sewer structures. However, the environment in some sewer structures can become very acidic due to formation of sulphuric acid converted from hydrogen sulphide by bacterial action. Significant deterioration of concrete in such harsh environments has been reported worldwide, for example, in Australia [1], Japan [2], Arabian Gulf countries [3], Germany [4], South Africa [5], and the USA [6]. Deterioration of a sewer system may result in serious problems such as the loss of ability to transport sewerage, contamination of ground and groundwater, excessive ground settlements, and cave-ins [7].

Very high costs are involved with repair of deteriorated sewer structures. In the USA, sulphuric acid attack is responsible for billions of dollars of damage to concrete wastewater collection and treatment systems [8]. In the state of South Australia alone an estimated budget for maintaining the existing wastewater infrastructure is A$48 million per annum [9].

Although it has been reported that some new materials can be more acid resistant such as concretes using melted sulphur as the binder or high proportions of polymer modified binders, these materials are too expensive for most practical applications. Therefore, the research into improvement of acid resistance of normal concretes is still attractive.

Over the past 20 years, the use of supplementary cementitious materials (SCM) in concrete has become very common due to their technological, economical, and environmental benefits. The use of SCM such as silica fume and fly ash in concretes has been found to improve the resistance of concrete to sulphuric acid attack because of the reduced presence of calcium hydroxide, which is most vulnerable to acid attack [10]. Using silica fume in binary cement system as a partial replacement of ordinary portland cement was found to be effective in reduction of

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doi:10.1016/j.cemconres.2005.03.006

Table 1
Chemical composition of cements and SCMs

Oxide	Type GP cement	Slag blended cement	Silica fume	Fly ash
CaO	65.1	50.4	0.4	0.8
SiO_2	20.3	28.2	>90	67.1
Al_2O_3	4.6	9.5	0.9	23.6
Fe_2O_3	4.5	2.3	1.5	3.7
SO_3	2.6	2.9	–	–
MgO	1.1	3.9	1.0	0.6
K_2O	0.5	0.4	0.9	1.6
Na_2O	0.04	0.09	0.4	0.6

acid attack [10–12]. Some other research works [11,13,14] showed remarkable improvement in the acid resistance of concrete using fly ash. It was also reported [15] that the use of a ternary cement consisting of 10% silica fume and up to 60% fly ash had a better performance than other SCM concretes, despite weight loss of the concrete samples of up to 25% after 56 days immersion in 1% sulphuric acid solution.

Calcareous aggregates such as limestone were studied in laboratory and applied in engineering practice as sacrificial aggregates in concrete subjected to sulphuric acid attack. It was found that the life of sewer pipes using limestone aggregates was longer than that using siliceous aggregates by 3–5 times in South Africa [5] and 1.9 times in Australia [1]. A laboratory test [16] with 0.2% sulphuric acid showed that the acid consumption by a limestone aggregate concrete was 4 to 8 times greater than that by a siliceous aggregate concrete. By neutralising the acidic environment, sacrificial limestone aggregates could be used to prolong the service life of concrete structures [17].

Sulphuric acid of 1% concentration was considered to be representative of aggressive sewer environments [18] and 1% sulphuric acid solution has been used in many laboratory tests to investigate the acid resistance of concretes for sewer structures [19]. In such a relatively strong acid solution, the concrete deterioration was often found to be very severe for most concretes either using SCM in the cement or using sacrificial limestone aggregate. Theoretically, the use of both sacrificial aggregate and blended SCM cement in concrete should further improve the acid resistance of concrete; however, such studies were not found in the literature.

In this research program, limestone aggregates were used together with a binary or ternary cement to investigate the acid resistance of these concretes. Six concretes were investigated including two reference concretes using siliceous aggregates and four concretes using limestone aggregates. Concrete cylinder samples were immersed in 1% sulphuric acid solution over 168 days and the samples were regularly investigated by visual inspection of surface deterioration, measuring mass change and testing load-bearing capacity in compression. Concrete samples after 168 days immersion in acid were also examined with scanning electronic microscope (SEM) for features of paste–aggregate interfacial zones and analysed with energy dispersive X-ray (EDX) micro-analyser for evidence of reaction products of acid attack.

2. Experimental details

2.1. Materials

The materials used in this investigation were locally sourced and they satisfied the requirements of respective Australian Standards. Table 1 presents the results of typical chemical compositions of the two cements, a shrinkage limited portland cement (Type GP) and a blended cement (Type GB) with approximately 60% of ground granulated blast furnace slag, a silica fume and a low-calcium, fine fly ash used in this research program.

The coarse aggregates used in this investigation were 20/10 mm siliceous crushed river gravels and 25 mm graded limestone aggregates. The fine aggregates used were a coarse silica river sand, a fine silica dune sand, and 4 mm graded limestone sand. The typical chemical composition of the limestone aggregates is shown in Table 2.

Table 3 presents acid soluble fractions of the cementitious materials and aggregates determined according to the relevant Australian standards. The acid soluble fraction of the silica sands is only 3% and that of the siliceous crushed river gravels is only 0.1%. However, the limestone aggregates used in this investigation is 99.5% acid soluble.

A water reducer and a superplasticiser, both of normal setting type, were used in the concrete mixes to achieve a target slump of 90±10 mm.

2.2. Concrete proportions and specimen preparation

Six concrete mixes were designed with different cements and aggregates for investigation of their resistance in 1% sulphuric acid solution. The mixture proportions of these concretes are shown in Table 4. Four of the six concretes use coarse and fine limestone aggregates (C2, C3, C4 and C6) and the other two reference concretes (C1 and C5) use siliceous gravel coarse aggregates and silica sands.

Each of the six concretes was mixed with a pan-mixer. Ten cylinder specimens (100 mm in diameter and 200 mm in length) were cast from each concrete. Two cylinder specimens of each concrete were cured in saturated lime-water and tested for standard 28-day compressive strength according to AS-1012 [20]. The other eight cylinder specimens of each concrete for acid attack testing were

Table 2
Chemical composition of limestone aggregates

Oxide	CaO	MgO	Al_2O_3	SiO_2	K_2O	Fe_2O_3	LOI
(%)	54.2	0.61	0.37	0.88	0.08	0.31	43.4

Table 3
Acid soluble fractions of materials

Material type	Acid soluble fraction (%)
Portland cement (Type GP)	99.8
60% Slag blended cement	99.5
Fly ash	10
Silica fume	5
Crushed river gravel aggregates	0.1
Silica sands	3
Limestone aggregates	99.5

cured in limewater for 7 days followed by air curing at 23 °C until 28 days. The 7 days curing regime was adopted to simulate the curing regime in most concrete construction sites.

2.3. Sulphuric acid solution for immersion test

The ASTM C267 [21] test method was modified for testing concrete in this investigation. A sulphuric acid of 1% concentration was chosen for this accelerated laboratory investigation to simulate the aggressive environment of some sewer structures. The ratio of the acid volume (in millilitre) to the surface area of specimens (in cm^2) was fixed at 8. All the concrete cylinders were continuously immersed in weekly refreshed 1% sulphuric acid during the test period.

2.4. Measuring initial mass and monitoring mass change of samples

The mass change of a sample in percentage to the initial mass is a widely used indicator for assessment of the deterioration of concrete subjected to acid attack. In this investigation at the concrete age of 28 days, eight cylinders from each concrete were immersed in tap water for 3 days and the initial mass of each sample was determined under the saturated surface dry (SSD) condition. At age 31 days, these cylinders were immersed in 1% sulphuric acid solution. The measurements of mass changes of the cylinders at the SSD condition were taken weekly within the first four weeks and monthly afterwards until 168 days. At each time of mass measurement, the cylinder samples were rinsed with tap water, brushed gently with a wire brush to remove loose particles and then weighted for their SSD masses.

2.5. Visual inspection of concrete samples

During the immersion period in 1% sulphuric acid solution, the cylinder samples were periodically retrieved from the acid solution for visual inspection of the surface appearance. Photographs were also taken of cylinder samples after immersion in the acid over different time periods to record changes in surface appearance.

2.6. Crushing load testing

Mass change is a simple traditional measurement in acid attack tests. However, the mass change result could depend on the sample size and cement type and, could also be significantly influenced by the way of treating the reaction products and decomposed cement paste on samples in a test. Therefore, the load-bearing capacity of cylinder samples was considered by the authors of this paper to be a more reliable performance measure of the resistance of concrete to acid attack.

When trying to measure the compressive strength of a cylinder sample, however, a difficulty could arise in measuring the diameter of the cylinder after acid attack because the diameter could become irregular or with exposed aggregates. To avoid this difficulty, the load-bearing capacity of a cylinder sample may be judged by the maximum load recorded in a compressive test. The maximum load in testing a cylinder sample before or after acid attack is defined in this paper as “crushing load” and this method of measuring the load-bearing capacity of concrete samples is named “crushing load test”. It was found in our measurements that the variation from the average diameter of the standard cylinder moulds was less than ± 0.1 mm, which contribute very little error to the comparison of crushing loads between cylinders.

In this investigation, two cylinders from each concrete were tested at 28 days for the standard compressive strength after limewater curing. Their average crushing load was calculated as the benchmark for comparison with the crushing load of the other cylinders after immersion in 1%

Table 4
Proportions of cements and concretes

Concrete no.	Cement proportion					Concrete proportion		
	W/C	GP (%)	SG (%)	SF (%)	FA (%)	Cement (kg/m^3)	Fine agg. (kg/m^3)	Coarse agg. (kg/m^3)
C1—S+GP	0.4	100	0	0	0	425	708	1110
C2—L+GP	0.4	100	0	0	0	425	670	1150
C3—L+GP+SG	0.4	40	60	0	0	425	645	1150
C4—L+GP+SG+SF	0.4	37.2	55.8	7	0	425	635	1150
C5—S+GP+SG+SF	0.4	37.2	55.8	7	0	425	715	1050
C6—L+GP+FA+SF	0.4	60	0	7	33	425	715	1050

W/C—Water to cement ratio; GP—Portland cement; SG—Slag; SF—Silica fume; FA—Fly ash; S—Siliceous aggregates; L—Limestone aggregates; agg.—Aggregate.

sulphuric acid. During this investigation, two cylinder samples from each concrete were tested in compression to determine their average crushing load after 28, 56 and 168 days immersion in 1% sulphuric acid.

3. Test results and discussions

3.1. The pH value of sulphuric acid solution

The pH value of the 1% sulphuric acid solution was monitored with a digital pH meter. It was kept in the range of 1.27 to 1.35 by weekly adjusting the pH value using 98% sulphuric acid. The solution was thoroughly stirred twice a week in order to reduce differential concentrations of the acid within the solution tank.

All cylinder specimens representative of the six concretes for a particular test were immersed in the same solution tank and therefore were assessed under the same corrosive environment. It should be pointed out, however, that this test environment might exaggerate the acid attack for limestone concretes, as the protective layer formed around limestone concrete samples, i.e. a lower local acid concentration caused by consumption of acid by limestone aggregate, was largely interrupted by stirring the solution twice a week. Thus the protection provided by the neutralisation of acid by limestone aggregates near the sample surface was partly discounted in this investigation.

3.2. Visual inspection of cylinders

Typical surface appearances of the cylinder samples of six concretes after 168 days immersion in 1% sulphuric acid are shown in Fig. 1.

It is clearly shown in Fig. 1 that the reference concrete C1, containing portland cement and siliceous aggregates, has suffered the most severe damage with exposure of coarse aggregates and significant loss of cement mortar. For the limestone concretes C2, C3 and C4, the acid attack occurred to both cement mortar and limestone aggregates. The expansion of cement mortar was observed on the end surfaces, where the cement mortar was raised slightly above limestone coarse aggregates. Concrete C5 was made with siliceous aggregates and a ternary cement containing both slag and silica fume. While the cylinder surface of concrete C5 appeared to have changed only slightly, the surface mortar layer had become so soft that a small external force (scratching by finger nails) damaged the surface layer. Cracks were also visible at edges of the cylinder of concrete C5. Concrete C6, which used limestone aggregates and the ternary cement containing silica fume and fly ash, had the best surface appearance among the six concretes. The body of the C6 concrete cylinder remained generally intact, except for some gypsum formed on the cylinder surface and a slight expansion of cement mortar noticed on the end surfaces.

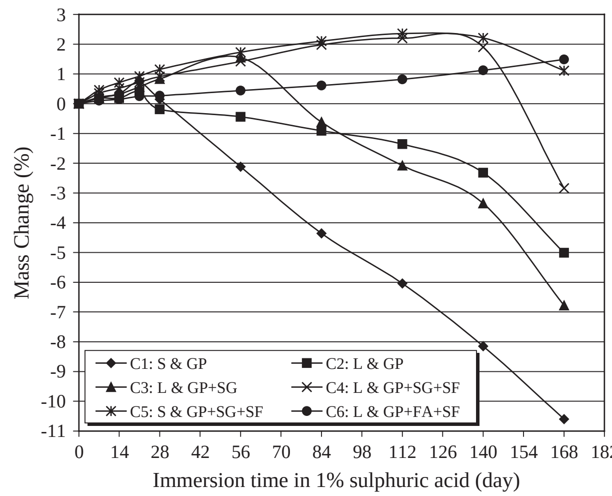

Fig. 2. Mass changes of cylinder samples after immersion in 1% sulphuric acid.

3.3. Mass changes of cylinders over immersion time

The mass change of the cylinders of each concrete with the immersion time in 1% sulphuric acid solution is plotted in Fig. 2. As shown in this figure, all the cylinders had mass gain over the first 21 days immersion in the acid solution. Cylinders of the reference concrete C1 then started losing mass with immersion time. Cylinders of concretes C2 and C3 began to lose mass after 56 days immersion, whilst the cylinders of concretes C4 and C5 did not show mass

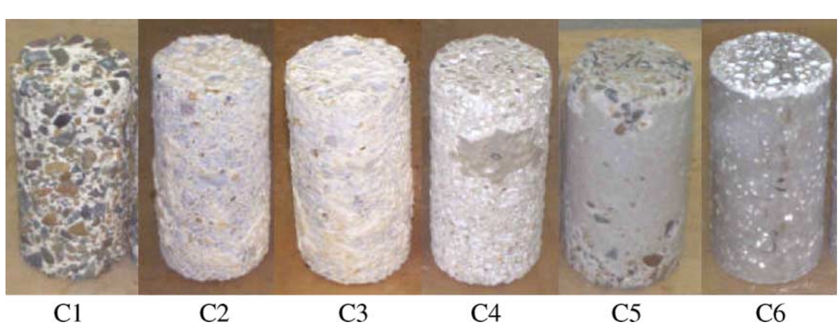

Fig. 1. Concrete cylinders after 168 days immersion in 1% sulphuric acid.

reduction until 140 days. Only the cylinders of concrete C6 had a slight mass gain continuously over the total immersion period in 1% sulphuric acid solution. After 168 days immersion, the cylinders of concretes C5 and C6 had 1.1% and 1.5% mass gain respectively, while the concretes C2, C3 and C4 lost mass by 2.8% to 6.8% respectively. In contrast, the reference concrete C1 had the greatest mass loss of 10.6%.

The mass gain during the early immersion period in 1% sulphuric acid solution could be attributed to a number of factors, which include continued hydration of cement, formation of gypsum and increase in absorbed water in samples. It was interesting to note that relatively higher mass gains occurred with the concretes C3, C4 and C5 which all had a high proportion of slag in the cement. Further investigations are needed in this regard. It was also observed in visual inspections that the specimen surface of concretes C1 and C2 became significantly rough after only 21 days immersion in acid, which appeared to indicate that surface layers of these two portland cement concretes were more vulnerable to acid attack.

In general, the mass change results appeared to indicate that the dissolution caused by hydrogen ions lagged behind the action caused by sulphate ions at the early days of immersion in acid. The former action would mainly cause dissolution and mass loss, however, the latter could initially lead to mass gain and finally result in mass loss due to excessive expansion and cracking. The combined actions of dissolution and expansion gradually caused the surface layer of cement mortar to fail, which brought about significant mass reduction of the cylinders.

3.4. Crushing load changes of cylinders over immersion time

Table 5 presents the results of the standard compressive strength and crushing load at 28 days for each concrete as well as the crushing loads of concrete cylinders after 28, 56 and 168 days immersion in 1% sulphuric acid.

The standard 28-day crushing load of each concrete is used as the benchmark for comparison of the crushing load of the cylinders after immersion in the acid solution for 28, 56 and 168 days. Fig. 3 shows the relative change of crushing load against the immersion time up to 168 days for all six concretes. The relative change of crushing load of a concrete was the percentage gain or loss in the crushing load in relation to the standard crushing load at 28 days.

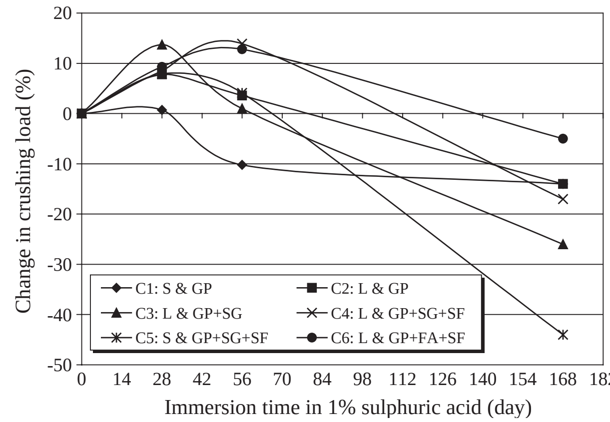

Fig. 3. Relative changes in crushing loads after immersion in 1% sulphuric acid.

After immersion in 1% sulphuric acid for 28 days, the cylinders of each concrete recorded an increase in the crushing load, in the range between 0.7% (C1) and 13.7% (C3). After immersion to 56 days, most of the concrete mixes started to record decreased crushing loads except for C4 and C6, which still recorded a gain in the crushing load. However, all concretes showed decrease in the crushing loads but at very different rates after further immersion to 56 or 168 days. At the end of 168 days immersion in 1% sulphuric acid solution, the limestone concrete C6 had the best acid resistance of six mixes with only 5% loss in the crushing load, while the other three limestone concretes (C2, C3 and C4) experienced more significant losses of 14% to 26% in crushing load, compared with standard cured samples. The concrete C5 recorded the most significant loss of 44% in crushing load which was much greater than the 14% loss of the reference concrete C1.

The increase in crushing load during the initial period of immersion in acid solution was likely due to continued hydration of cement and an early formation of gypsum and ettringite, which would fill the pores of concrete. However, further formation of gypsum and ettringite resulted in expansion, which together with dissolution of cement paste in acid solution led to softening of the cement matrix and a

Table 5
Crushing loads of six concretes before and after acid immersion

	Concrete mix	C1	C2	C3	C4	C5	C6
Standard 28 days	Crushing load (kN)	423.7	454.8	414.1	405.8	358.4	410.3
	Strength (MPa)	53.8	57.9	52.6	51.5	45.4	52.6
After 28 days Acid	Crushing load (kN)	426.8	490.3	470.7	440.2	386.7	448.4
Immersion	Ratio to standard 28 days	1.01	1.08	1.14	1.09	1.08	1.09
After 56 days Acid	Crushing load (kN)	380.5	471.0	418.0	462.0	373.0	463.0
Immersion	Ratio to standard 28 days	0.90	1.04	1.01	1.14	1.04	1.13
After 168 days Acid	Crushing load (kN)	365.0	390.0	308.0	336.0	201.0	389.0
Immersion	Ratio to standard 28 days	0.86	0.86	0.74	0.83	0.56	0.95

Fig. 4. A crushed cylinder of C5 after 168 days immersion in 1% sulphuric acid.

subsequent decrease in the crushing load of cylinder samples. The softening of cement matrix due to excessive expansion and dissolution was also observed during visual inspection of the concrete samples.

It was noticed that the change of crushing load with immersion time for the reference concrete C1 had an unusual characteristic. Its crushing load had suddenly decreased between 28 and 56 days while being relatively stable for the first 28 days and also between 56 and 168 days. The change in crushing load of the control concrete C1 using portland cement and siliceous aggregates might be explained as follows. Over the first 28 days immersion in acid solution, the deterioration due to acid was not very significant and crushing load of C1 cylinders showed little change. However, the damage of the surface layer of the C1 cylinders became more significant after further immersion to 56 days. The sudden drop in crushing load of concrete C1 after 56 days immersion represented a significant loss of surface mortar layer of the cylinder specimens. Since the coarse siliceous aggregates were generally not affected by the acid solution, further acid attack was directed towards the cement mortar between the coarse aggregates. To significantly affect the crushing load of cylinders, such attack needs to dislodge the outer layer of coarse aggregates resulting in another sudden decrease of the crushing load. It appears that, for concrete C1, another significant drop in crushing load could be expected some time after 168 days immersion.

However, the other control concrete C5, which used slag blended cement and siliceous aggregates behaved differently. The crushing load increased during the first 28 days immersion period followed by a slow drop between 28 and 56 days, then a very significant drop in crushing load between 56 and 168 days immersion. Fig. 1 shows that the surface mortar layer of concrete C5 remained mostly intact after 168 days immersion despite significant softening of this surface layer. The difference in the surface layer between the concretes C5 and C1 is clearly shown by comparison of their appearances in Fig. 1 and their mass changes in Fig. 2. Such a difference was likely attributed to the cement type, concrete C1 using portland cement and C5 using a ternary blended cement containing slag and silica fume (see Table 4). It appeared that the ternary cement paste of C5 had better adhesion to aggregates than portland cement paste and therefore had much lower weight loss. However, the softened surface mortar layer of C5 cylinders had greatly lost its strength as indicated by the drop in the crushing load.

Fig. 4 shows a cylinder of concrete C5 tested after 168 days immersion in acid solution. It was noted that a layer of concrete separated from the cylinders during the test which included both the surface mortar and the outer layer of coarse siliceous aggregates. This indicated that the acid had penetrated deeply into concrete C5 and resulted in the destruction of the cement matrix binding the outer layer of coarse aggregates. This also helped to explain the distinct drop in crushing load of C5 cylinders after 168 days immersion in acid solution.

Fig. 5 presents the ratios of crushing loads for six pairs of concretes using different types of cements or aggregates. The influences of cement and aggregate types are discussed in the following sections.

3.4.1. Influence of limestone aggregates

After immersion in acid solution for 28, 56 and 168 days, crushing load ratios C2/C1 and C4/C5 at each age were greater than those after standard 28 days curing. In other words, the residual crushing loads of limestone concrete (C2 and C4) were higher than those concretes using siliceous aggregates (C1 and C5). Particularly, the ratio C4/C5 increased continuously with the immersion time and reached 1.67 after 168 days immersion in the acid solution. The ratio C2/C1 increased up to 56 days immersion but declined after 168 days immersion. As discussed, the crushing load of concretes using siliceous aggregates appeared to reduce in steps corresponding to significant destruction of the surface

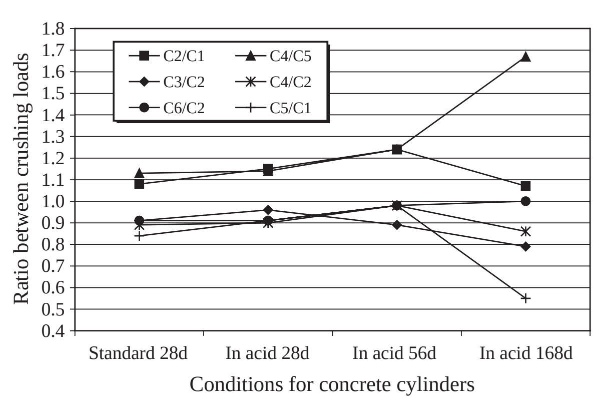

Fig. 5. Ratios between crushing loads of concretes using different cements or aggregates.

mortar layer and the cement matrix binding the outer layer of coarse aggregates, while the crushing load of concrete using limestone aggregates reduced with immersion time at a lower rate and without significant drops.

The corrosion kinetics and neutralization capacity were two factors claimed to determine the rate of acid attack on concrete [22]. In concrete using silicious aggregates, only cement hydration products react with acid and the effect of neutralization during acid attack would be very limited. Table 3 presents acid soluble fractions of cementitious material and aggregates used in this investigation. For the concretes (C1 and C5) using siliceous aggregates, the acid soluble fraction of the silica sands is only 3% and that of the siliceous crushed gravel aggregates is only 0.1%. However, the limestone aggregates used in the concretes (C2, C3, C4 and C6) of this investigation is 99.5% acid soluble. The limestone is composed mainly of calcium carbonate, which will react with acid and the concrete would then have much greater capacity to neutralize acid in local areas surrounding the concrete. The neutralization effect of sacrificial calcareous aggregates could significantly reduce the local acid concentration and the rate of acid attack on concrete.

In this investigation, sulphuric acid for immersion of concrete specimens was refreshed weekly. The acid concentration near the specimen surface would be close to or only slightly lower than that of the bulk acid solution. However, in a real concrete structure in contact with acidic soil or atmosphere, reduction in acid concentration at concrete surface could be significant due to local neutralisation reactions between the acid and cement paste and calcareous aggregates. It would be expected that, in most practical situations, the use of limestone aggregates in concrete could achieve more significant beneficial effects on reduction of acid concentration near concrete surface and subsequent reduction of deterioration rate than the observations shown in this laboratory investigation.

3.4.2. Influence of different types of cement

In Fig. 5, the ratios of the crushing load for limestone concretes C3, C4 and C5 using binary or ternary cements are compared to their reference concrete C2 using portland cement. The ratio of C3/C2 initially increased over the first 28 days immersion then continuously declined with further immersion time. This indicated that the 60% slag cement for concrete C3 was not as durable as the portland cement for C2 in the acidic environment. The use of ternary cement with both slag and silica fume improved the crushing load capacity of concrete C4 up to 56 days immersion, but the ratio of C4/C2 reduced after 56 days immersion in the acid solution. On the other hand, concrete C6 using the ternary cement with a combination of silica fume and fly ash performed better than the reference concrete C2. The ratio of C6/C2 increased with the overall immersion period up to 168 days. The crushing load of concrete C6 after 168 days immersion in 1% sulphuric acid was only 5% lower than that after 28 days standard curing.

When comparison is made between the two concretes, C1 and C5, which used siliceous aggregates, the ratio of C5/C1 increased over the first 56 days immersion followed by a significant drop between 56 and 168 days. The ternary cement with slag and silica fume used in concrete C5 was the same as that for concrete C4. The test results of both siliceous and limestone aggregate concretes indicated that concretes made with both binary slag cement and ternary cement with slag and silica fume were less durable than portland cement concrete in the acid environment.

3.4.3. Comparison between crushing load and mass change results

Fig. 6 presents the ratios of the sample mass for the same six pairs of concretes shown in Fig. 5 using different types of cements or aggregates. The major differences between the two figures in relation to the influences of cement and aggregate types are discussed as follows.

As shown in Figs. 5 and 6, both the ratios of crushing loads and the ratios of masses of the six pairs of concretes did not have very significant changes after up to 56 days immersion in 1% sulphuric acid. However, after immersion for 168 days in acid, the relative performance of the six pairs of concretes indicted by the two parameters became very different and in fact was opposite in several cases. For example, the crushing load ratio C4/C5 increased significantly after immersion for 168 days, which indicated an obvious benefit of using limestone aggregates (in C4) than using silicious aggregates (in C5) for the same cement type. However, the recorded mass ratio C4/C5 had dropped significantly after immersion for 168 days, showing a higher mass loss of concrete C4 compared to that of C5. As shown in Fig. 3, concrete C5 had the lowest crushing load within the six concretes after 168 days immersion, despite an approximate 1% mass gain of C5 over the same period as shown in Fig. 2.

For another pair of concretes C5 and C1 using the same silicious aggregates but different cements, the crushing load ratio C5/C1 dropped dramatically after immersion for 168 days, indicating a much lower strength loss of C1 using Type GP portland cement. However, mass ratio C5/C1

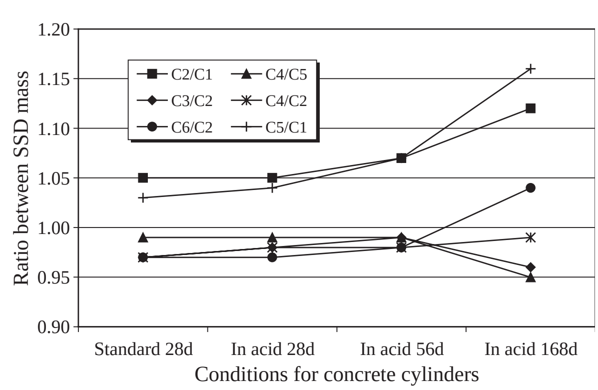

Fig. 6. Ratios between masses of concrete pairs using different cements or aggregates.

Fig. 7. Cracks in the paste and at the paste–aggregate interface in concrete C1.

increased significantly after immersion for 168 days, showing a higher mass loss of concrete C1.

The lack of correlation between the results of mass change and crushing load is clearly shown in the above comparisons between concrete pairs C4/C5 and C5/C1 and can be further shown by comparisons between other concrete pairs in Figs. 5 and 6. It was found in this investigation that the mass loss of concrete samples depended greatly on the cement type and the mass loss result could be misleading with regard to the strength loss of concrete after acid attack. On the other hand, the crushing load test directly measured the load-bearing capacity of concrete samples after acid attack. It is concluded that the crushing load test is a more reliable performance test method than the mass change measurement for assessment of concrete deterioration in acid environments.

3.5. SEM examination and EDX analysis of concrete samples

Concrete samples were taken from freshly broken cylinders of concrete C1 using siliceous aggregates and

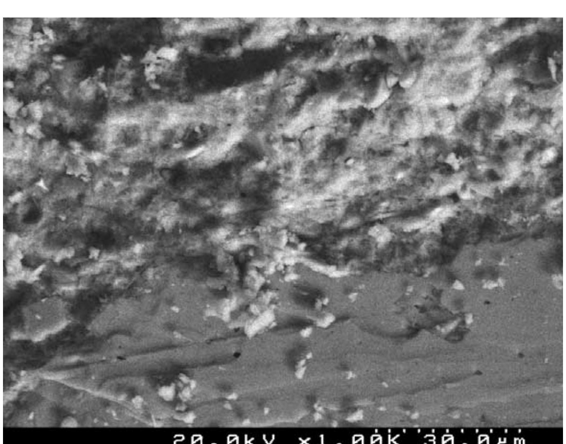

Fig. 8. No obvious cracking at the paste–aggregate interface in concrete C2.

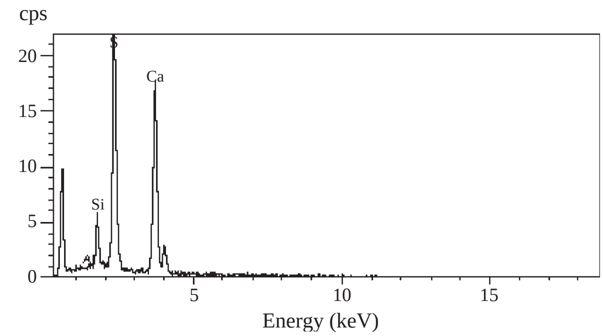

Fig. 9. EDX spectrum of an area of acid attacked mortar/paste in concrete C2.

concrete C2 using limestone aggregates after the cylinders were immersed in 1% sulphuric acid for 168 days. These concrete samples were further prepared and examined under scanning electronic microscope (SEM) for features of the paste–aggregate interfacial zones and analysed with energy dispersive X-ray (EDX) micro-analyser for evidence of the reaction products of acid attack.

Fig. 7 shows an image of a C1 concrete sample containing a piece of siliceous gravel aggregate. While the siliceous aggregate was intact after concrete is immersed in 1% sulphuric acid for 168 days, cracks were observed at the paste–aggregate interface and in the surrounding mortar.

Fig. 8 is an image of a C2 concrete sample containing a piece of limestone aggregate, however, no cracks were found in the paste–aggregate interfacial zone around the limestone aggregate. An EDX spectrum of an acid attacked mortar/paste area in the limestone concrete is presented in Fig. 9. A significant amount of sulphur, obviously due to sulphuric acid attack, was identified from the EDX spectrum. Fig. 10 shows a SEM image of the reaction products of sulphuric acid attack of cement paste and these reaction products are in the typical form of gypsum and ettringite. The SEM examination results showed that, in contrast to that in the concrete using siliceous aggregates, the paste–aggregate interfacial zone in the limestone aggregate concrete remained continuous without obvious

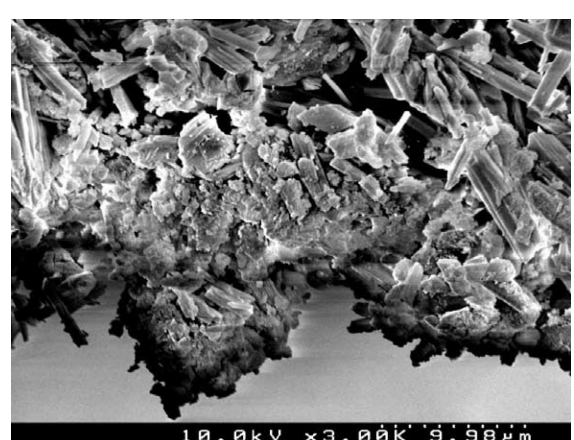

Fig. 10. Reaction products in concrete due to sulphuric acid attack.

cracking under acid attack. This appeared to occur because the limestone aggregates were also attacked by sulphuric acid and therefore no obvious discontinuity would form at the paste–aggregate interfacial zone.

The observation of continuous interfacial zones in the limestone concrete provided an explanation to the test results (Section 3.4.1) of higher residual crushing loads of the limestone concretes (C2 and C4) when compared to the concretes (C1 and C5) using siliceous aggregates. Cracking at paste–aggregate interfaces in the concretes using siliceous aggregates could also be related to the distinct drop in their crushing loads and the loss of concrete surface layer containing the outer layer of coarse aggregates (Fig. 4).

4. Conclusions

Based on the test results by immersing concrete samples in 1% sulphuric acid solution, the following observations and conclusions are summarized:

1. After immersion in 1% sulphuric acid for 28, 56 and 168 days, the residual crushing loads of the limestone concrete C2 and C4 were higher than their reference concrete C1 and C5 using siliceous aggregates. The results indicates that limestone aggregates may be used as a sacrificial medium to reduce the acid concentration near concrete surface and decrease the rate of deterioration of concrete subjected to acid attack.
2. SEM examinations showed, while cracking at the paste–aggregate interface was found in the concrete using siliceous aggregates, the paste–aggregate interfacial zone in the limestone concrete remained continuous without cracking under acid attack. The better condition of interfacial zones in the limestone concrete could be an important factor for its better performance in this investigation under sulphuric acid attack.
3. The concrete (C6) made with limestone aggregates and the ternary cement containing 7% silica fume and 33% fly ash was found to have excellent acid resistance in 1% sulphuric acid solution and the best of the six concretes tested in this investigation.
4. Concretes made with either the slag cement (C3) or the ternary cement containing slag and silica fume (C4 and C5) were found to be less durable than their comparable portland cement concrete (C1 and C2) in the acid environment. Further research work is needed in this area to find the mechanisms of deterioration of blended cement containing slag in acid solutions.
5. The crushing load test used in this investigation directly measures the load bearing capacity of cylinder samples after acid attack and it is considered to be a more reliable performance test method than the mass change measurement for assessment of concrete deterioration in acid environments.

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