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Resistance of self-consolidating concrete to sulfuric acid attack with consecutive pH reduction

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Abstract

Self-consolidating concrete (SCC) is increasingly being used in numerous concrete applications some of which are vulnerable to sulfuric acid attack. The mixture design of SCC is different than that of normal concrete, and thus its long-term durability characteristics are still uncertain. This study aims at investigating the resistance of a variable range of SCC mixture designs to sulfuric acid attack. The main test variables include the cementitious materials type (single, binary, ternary and quaternary binders), the sand-to-total aggregates mass ratio, and the inclusion of fibre reinforcement (single and hybrid). The investigation comprised two consecutive 6-week phases of immersion of test specimens in sulfuric acid solutions with a maximum pH threshold of 2.5 and 1.0, respectively. In total 24 SCC mixtures were tested. The study reveals that the rate of attack, as expressed by mass loss versus time, is controlled by different factors at each exposure phase. The advantages of blended binders and hybrid (steel+polypropylene) fibres in improving the resistance of SCC to sulfuric acid attack are highlighted. Microanalysis conducted upon test termination elucidates the damage mechanisms, and it is shown that there is no direct correlation between the rate of attack expressed by mass loss and the compressive strength loss after exposure to sulfuric acid.

Keywords: Self-consolidating concrete; Sulfuric acid; pH; Blended cement; Fibre reinforcement

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1. Introduction

1.1. Background

Degradation of concrete members exposed to aggressive sulfuric acid environments is a key durability issue that affects the life cycle performance and maintenance costs of vital civil infrastructure. Sulfuric acid in groundwater, chemical waste [1], or generated from the oxidation of sulfur bearing compounds (e.g. pyrite) in backfill can attack substructure concrete members [2]. Moreover, concrete structures in industrial zones are susceptible to deterioration due to acid rain of which sulfuric acid is a chief component [1]. Considerable damage can occur to sewage systems by biogenic sulfuric acid corrosion. Parker [3] attributed this to a chemical–microbial interaction in sewage systems [4].

The effect of sulfuric acid on concrete is more detrimental than that of sulfate attack; in addition to attack by sulfate ions, there is a dissolution effect caused by hydrogen ions [5]. Corrosion of concrete due to sulfuric acid can generally be characterized by the following reactions [6]:

$$\mathrm{Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4.2H_2O} \tag{1}$$

$$\mathrm{CaSiO_2.2H_2O + H_2SO_4 \rightarrow CaSO_4 + Si(OH)_4 + H_2O} \tag{2}$$

$$\begin{aligned}&\mathrm{3CaO.Al_2O_3.12H_2O + 3(CaSO_4.2H_2O)}\\&\quad\mathrm{+ 14H_2O \rightarrow 3CaO.Al_2O_3.3CaSO_4.32H_2O.}\end{aligned} \tag{3}$$

The primary reaction product manifested on the concrete surface is gypsum that is associated with volume expansion (factor of 2.2 compared to the volume of reactants), which can induce tensile stresses in concrete, resulting in cracking and spalling [7]. If not washed out, the accumulation of gypsum on the surface of concrete may slow down the corrosion rate due to surface sealing [8]. Further reaction of gypsum with calcium aluminate phases in the cementitious matrix can form ettringite,

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which has more volume increase (up to a factor of 7) than that of gypsum, thus leading to more micro- and macro-cracking. In addition, sulfuric acid decomposes the cementitious matrix by decalcifying calcium silicate hydrate (C–S–H), thus contributing to strength loss [6].

To evaluate the resistance of concrete to sulfuric acid, three testing approaches have been adopted in the literature: chemical, micro-biological and in-situ tests. In chemical tests, mortar or concrete specimens are immersed in 1 to 5% sulfuric acid solutions for a specified time period with or without pH control. Micro-biological tests are peculiar to simulating biogenic sulfuric acid corrosion of concrete by accelerating growth of bacteria, which produce sulfuric acid, on concrete samples placed in environmentally controlled chambers. Exposure of concrete to specific sulfuric acid environments can also be investigated using in-situ tests [6].

Although there is a general agreement between the trends of results exhibited by chemical and micro-biological tests in comparing the resistance of different concretes to sulfuric acid attack, some discrepancies can occur [7,9]. While in chemical immersion tests the concentration of the sulfuric acid solution used can be similar for all concrete mixtures considered, the interaction between bacteria and cementitious constituents in micro-biological tests governs the concentration of sulfuric acid produced on the surface of each concrete sample [10]. Most investigations have used visual inspection and/or mass loss as acceptable indicators for evaluating the resistance of concrete to sulfuric acid attack. Yet, brushing or no-brushing before regular weighting of specimens exposed to sulfuric acid was an influential procedure on results obtained and related conclusions [6]. It was recommended that a consistent brushing method be used for all specimens within the same study to obtain a reliable comparison between the behavior of different concrete mixtures subjected to sulfuric acid attack [1].

1.2. Previous research

To extend the service life of concrete structures exposed to sulfuric acid attack, two approaches have been adopted: improving the chemical resistance of concrete using different mixture proportioning and incorporating innovative materials, and preventing the growth of the bacteria producing sulfuric acid using biocides [11]. Several researchers have studied the effect of cement type, cement content, water-to-cementitious materials ratio (w/cm) [1,10,12], supplementary cementitious materials (SCMs) [13,14], and polymeric materials [7,9] on improving the resistance of mortar or concrete to sulfuric acid attack.

In a series of chemical tests with different sulfuric acid concentrations of 1–3%, Fattuhi and Hughes [12] showed that sulfate resistant portland cement (SRPC) did not offer marked improvement compared to that of ordinary portland cement (OPC) in reducing the mass loss of mortar or concrete specimens. Also, they indicated that for high (greater than 1%) sulfuric acid concentrations, minimizing the cementitious materials content in concrete can effectively reduce the rate of acid attack expressed by mass loss. Because acid specifically attacks cementitious constituents, concretes with a low w/cm and a high cementitious volume fraction are more vulnerable to greater mass loss. The effect of reducing the w/cm on improving the resistance of concrete to sulfuric acid attack was only significant at lower acid concentrations (1%) [1].

Calcium aluminate cements are generally more resistant to chemical and biogenic sulfuric acid attack than portland cements [e.g. [10]]. Unlike portland cements, the hydrates of calcium aluminate cements consist of hydrous alumina gel and calcium aluminate hydrates. At pH levels above 4.0, the inert hydrous alumina gel acts as a diffusion barrier. At pH levels below 4.0, the hydrous alumina gel dissolves, but with the positive effect of increasing the neutralization capacity/acid consumption, thus reducing the rate of acid attack [15].

Data in the literature on the effect of SCMs on the resistance of concrete to sulfuric acid attack is contradictory. For instance, Durning and Hicks [16] and Mehta [17] reported that the incorporation of silica fume increased the resistance of concrete to 1% sulfuric acid attack due to reduced calcium hydroxide content and lower permeability. Conversely, Monteny et al. [18] reported a negative effect of silica fume incorporation in concrete specimens exposed to 0.5% sulfuric acid. They stated that a refined pore structure with higher capillary suction would cause deeper penetration of acidic solutions into concrete and increase the exposed surface area in contact with acid [18]. These studies [16–18] applied wire brushing to specimens. At higher concentrations of sulfuric acid solutions, Durning and Hicks [16] and Roy et al. [14] (no wire brushing) showed that silica fume did not improve the resistance of concrete and mortar to 5% sulfuric acid solutions. On the contrary, in a 5% sulfuric acid solution, Yamoto et al. [19] showed that time intervals to reach 25% mass loss were almost doubled for 30% silica fume concrete specimens relative to control specimens without silica fume. No information was given on the method of loose materials removal in Yamoto et al. [19].

Monteny et al. [18] reported that the highest resistance to a 0.5% sulfuric acid solution was achieved by a binary binder mixture comprising more than 60% ground granulated blast furnace slag. Conversely, Chang et al. [20] recently reported that binary binder concrete mixtures prepared with 60% slag and ternary binder mixtures with 56% slag and 7% silica fume had inferior performance compared to that of a 100% OPC mixture when immersed in a 1% sulfuric acid solution with a pH of 1.27. Chang et al. [20] and Tamimi [21] reported that ternary binder concrete mixtures comprising ordinary portland cement, fly ash and silica fume had high resistance to 1% sulfuric acid solutions even with wire brushing. Data on the resistance of ternary and quaternary binder concrete mixtures at high concentrations of sulfuric acid solutions are extremely limited.

1.3. Self-consolidating concrete (SCC)

Several new concrete technologies have emerged to combat durability problems of concrete and to improve its performance in aggressive environments [11]. For instance, self-consolidating concrete (SCC) readily flows and consolidates under its own weight with little or no vibration. It was developed in the late

Table 1
Chemical and physical properties of cement and supplementary materials

	OPC	SRPC	Silica fume	Fly ash	Slag	Limestone powder
SiO_2 (%)	19.8	22.3	94.0	48.9	35.0	0.3
CaO (%)	63.2	63.8	0.4	3.8	36.1	–
Al_2O_3 (%)	5.0	3.5	0.1	23.3	11.2	–
Fe_2O_3 (%)	2.4	4.0	0.1	14.9	0.5	–
MgO (%)	3.3	2.8	0.4	0.7	11.4	–
K_2O (%)	1.2	0.4	0.9	1.7	0.5	–
SO_3 (%)	3.0	2.1	1.3	0.2	3.3	–
Na_2O (%)	0.1	0.1	0.1	0.6	0.5	–
TiO_2 (%)	0.3	–	0.3	–	0.6	–
$CaCO_3$ (%)	–	–	–	–	–	99.0
Loss on ignition (%)	2.5	0.9	4.7	0.3	–	–
Specific surface area (m^2/kg)	410	377	19,530	280	468	3200
Specific gravity	3.17	3.15	2.12	2.08	2.90	2.70
C_3S	61	54	–	–	–	–
C_2S	11	23	–	–	–	–
C_3A	9	1	–	–	–	–
C_4AF	7	14	–	–	–	–

1980s primarily to minimize the need for skilled labor, reduce vibration noise, construction injuries and construction time, and to enhance finish surfaces. The fresh properties and rheological characteristics of SCC are different than that of normal concrete, but both SCC and normal concrete may exhibit comparable mechanical properties if designed for similar strength grades. Yet, due to the difference in mixture design and placement, and consolidation techniques, the durability of SCC may be different than that of normal concrete and thus needs thorough investigation [22].

Several concrete elements have been reported to be susceptible to the chemical attack of sulfuric acid, including foundations (groundwater containing sulfuric acid due to oxidization of pyrite in backfill), industrial floors of chemical plants, basement walls of buildings near chemical plants, superstructures (due to acid rain). Sewage pipe systems suffer a special type of biogenic corrosion. Although there has been a growing use of SCC in numerous concrete applications, an extensive review of literature indicates that there is dearth of information on the resistance of SCC to sulfuric acid attack. Also, the role of SCMs, which are commonly incorporated in SCC, in such aggressive exposures is ambiguous. It was reported that after 18 weeks of immersion in a 1% sulfuric acid solution, an SCC mixture containing 47% carboniferous limestone powder as a cementitious replacement had a mass loss of 9% compared to 21% for a normal concrete mixture, despite that it had a lower 28-day compressive strength than that of the normal concrete mixture [23].

SCC usually has a higher volume fraction of paste incorporating combinations of SCMs, and often lower w/cm than that of normal concrete. This can make it vulnerable to deterioration by high concentration sulfuric acid solutions. Previous research did neither investigate a variable range of SCC mixtures incorporating combinations of SCMs nor use high concentrations of sulfuric acid, yet this is necessary to evaluate the suitability of this material under aggressive sulfuric acid exposures. This study aims at investigating the resistance to aggressive sulfuric acid solutions of a variable range of SCC mixtures incorporating binary (two component), ternary (three component) and quaternary (four component) binders, with and without fibre reinforcement. The effects of the coarse aggregate volume fraction, which is an important parameter for the rheology of SCC, and air-entrainment are also explored. An effort is made to capture the main mechanism of degradation and explore the possible relationship between mass loss and degradation of mechanical properties.

2. Experimental program

2.1. Materials

Twenty four SCC mixtures with a w/cm of 0.38 (180 kg/m^3) were prepared. The mixtures were divided into three groups: group A (non-air-entrained SCC with sand-to-total aggregates mass ratio [S/A] of 50%), group B (air-entrained SCC mixtures with S/A of 40 and 60%), and group C (air-entrained SCC with fibre reinforcement and sand-to-total solid [coarse aggregate plus fibres] mass ratio of 50%). The binders used included CSA Type 10 (ASTM Type I) ordinary portland cement (OPC), CSA Type 50 (ASTM Type V) sulfate resistant portland cement (SRPC), silica fume (SF), fly ash (FA), slag (S), and limestone filler (LF). The chemical and physical properties for the various binders are listed in Table 1. These materials were used to prepare single, binary, ternary and quaternary binders.

The total cementitious materials (binder) content was kept constant at 470 kg/m^3 to provide a high volume fraction of fine materials (paste volume of 325–350 l/m^3), conforming to common SCC mixture design guidelines [e.g. [24]]. The fine aggregate was natural siliceous sand with a fineness modulus of 2.80, a saturated surface dry specific gravity of 2.65 and water absorption of 1.5%. Crushed stone with a maximum nominal size of 19 mm, a saturated surface dry specific gravity of 2.68 and water absorption of 0.8% was also used. To improve flowability of the SCC mixtures, a polycarboxylate-based high-range water reducing admixture (HRWRA) with a specific gravity of 1.07 and a solid content of 43% was incorporated in all mixtures. A viscosity modifying admixture (VMA) based on a solution of modified polysaccharide with a specific gravity of 1.0 was also employed to enhance stability of the SCC mixtures. For all mixtures, the dosages of HRWRA and VMA were

Table 2a
Proportions of binders per cubic meter of concrete

Binder description	Binder code	Cement (kg)	Silica fume (kg)	Slag (kg)	Fly ash (kg)	Limestone (kg)
100% SRPC	SRPC	470	–	–	–	–
100% OPC, OCI	OCI	470	–	–	–	–
100% OPC	B1	470	–	–	–	–
92% OPC, 8% SF	B2	430	40	–	–	–
50% OPC, 5% SF, 45% S	B3	235	25	210	–	–
50% OPC, 15% LF, 20% S, 15% FA	B4	235	–	95	70	70
50% OPC, 5% SF, 25% S, 20% FA	B5	235	25	120	90	–

Table 2b
Proportions of groups A, B and C mixtures per cubic meter of concrete

Binder code	Mix. ID	Steel fibres (kg)	Poly-propylene fibres (kg)	Fine aggregate (kg)	Coarse aggregate (kg)	Air-entraining agent (ml/100 kg of binder)	f'_c loss (%)
Group A							
SRPC	SRPC	–	–	870	870	–	18.4
OCI	OCI	–	–	860	865	–	6.1
B1	B1-N-50	–	–	870	870	–	3.3
B2	B2-N-50	–	–	860	860	–	5.8
B3	B3-N-50	–	–	855	855	–	−15.9[a]
B4	B4-N-50	–	–	845	845	–	3.8
B5	B5-N-50	–	–	840	840	–	16.7
Group B							
B1	B1-A-40	–	–	655	1015	45	21.2
	B1-A-60	–	–	1015	655	35	23.8
B2	B2-A-40	–	–	640	990	70	22.5
	B2-A-60	–	–	990	640	50	14.3
B3	B3-A-40	–	–	640	985	70	−4.9
	B3-A-60	–	–	985	640	60	3.1
B4	B4-A-40	–	–	625	970	110	6.2
	B4-A-60	–	–	970	625	95	22.0
B5	B5-A-40	–	–	625	965	120	8.5
	B5-A-60	–	–	965	625	100	16.1
Group C							
B1	B1-A-S	40	–	830	805	35	26.9
	B1-A-P	–	1	825	820	40	9.5
	B1-A-H	30	1	830	805	40	12.2
B2	B2-A-H	30	1	825	795	60	34.0
B3	B3-A-H	30	1	820	790	65	15.3
B4	B4-A-H	30	1	805	780	100	4.4
B5	B5-A-H	30	1	800	775	105	8.9

[a] Negative value of compressive strength loss indicates strength increase.

adjusted to maintain a slump flow of 650±30 mm and L-box (3∅10 mm bars with 50 mm gaps) ratio (H_2/H_1) not less than 0.70. A multi component synthetic air-entraining admixture (AEA), based on tall oil, with a specific gravity of 1.01 was used in group B and C mixtures to obtain a fresh air content of 5±1% while achieving the targeted slump flow and L-box values. An organic corrosion inhibitor (OCI) consisting of amines and esters in an emulsion with a density of 0.98 kg/l was used at a dosage of 5 l/m^3 in one SCC mixture.

In group C mixtures, micro-reinforcement of polypropylene fibrillated fibres, with a specific gravity of 0.91 and graded length, complying with ASTM C 1116, Type III 4.1.3, were added at a single dosage of 0.1% by volume. In addition, macro-reinforcement of crimped steel fibres complying with ASTM A 820 with a specific gravity of 7.85, length of 38 mm, aspect ratio of 34, and tensile strength of 966–1242 MPa were used at dosages of 0.4 and 0.5% by volume. Based on trial mixtures, these shapes, lengths, and moderate volumes of micro- and macro-reinforcement have proven adequate for achieving the characteristic flowability and passing ability of SCC with minimal clustering of fibres.

2.2. Procedures

Constituent materials were mixed in a mechanical mixer in accordance with the ASTM C 192 standard procedure. Tables 2a–b show the proportions of the tested SCC mixtures. For each mixture, replicates of 75 mm×150 mm concrete cylinders were prepared without vibration/compaction. All specimens were demolded after 24 h and moist cured at 20 °C and 95% RH for 56 days. It was shown that the moist curing period of concrete does not significantly affect its resistance to attack by sulfuric acid having a high concentration (above 1%), even if concrete were exposed to a short curing period such as 3 days [25].

Several concrete structural elements are susceptible to chemical attack by sulfuric acid, including foundations (groundwater containing sulfuric acid due to oxidization of pyrite in backfill), industrial floors of chemical plants, basement walls of buildings near chemical plants, superstructures (due to acid rain), etc. Comparatively, sewage pipe systems suffer a special type of biogenic acid corrosion. In the former applications, chemical acid immersion tests can simulate the attack by sulfuric acid since bacteria are not involved. However, in the case of sewage systems, a combination of both chemical and microbiological tests maybe more adequate. In the present study, chemical immersion tests were adopted to assess the resistance of SCC used in different applications such as foundations, walls, floors, pipes, etc., to the chemical attack of sulfuric acid. Chemical immersion tests best suited this purpose since there is dearth of information on the resistance of SCC to sulfuric acid attack. This testing approach can give a more general idea on a broad range of applications than that of specific biogenic tests.

Specimens were fully immersed for two consecutive 6-week phases in an aggressive sulfuric acid solution with an initial concentration of 5%. Before immersion, the specimens were left to dry under 20 °C and 50% RH for 30 min to record their initial mass. Each group of mixtures had its own acid bath. This is to provide similar acidic environments for the single, binary, ternary and quaternary binder mixtures in each group. In phase I, the initial pH (0.9) of the solution increased quickly, but was controlled at a maximum threshold value of 2.5 by titration with concentrated sulfuric acid, and was kept constant thereafter during this phase. At the start of phase II, the solution was renewed with a fresh one with the same initial concentration (5%), but the maximum pH threshold was set to 1.0 until termination of the test. Regular stirring of the solution was conducted during titration to allow for a homogenous distribution of the acid. There is currently no standardized procedure to test the resistance of concrete to sulfuric acid attack. However, the ASTM C 267 test method [26] provides general guidelines to test the chemical resistance of mortars and polymer concretes. The pH variation regime adopted herein simulates the transition from severe to very severe chemical exposure conditions that can occur under severe field conditions.

Specimens were extracted from the solution weekly, rinsed three times with tap water to remove loose reaction products, blotted with a paper towel and left to dry under 20 °C and 50% RH for 30 min before weighing and visual inspection [26]. For each specimen, the cumulative mass loss at each week (ML_t) was calculated by:

$$\mathrm{ML}_t = \left(\frac{M_t - M_\mathrm{i}}{M_\mathrm{i}}\right) \times 100 \tag{4}$$

where

M_t	Mass at time t (kg)
M_i	Initial mass before exposure to sulfuric acid (kg).

After 12 weeks of exposure, specimens were tested for residual compressive strength, which was calculated using the original cross-sectional area [26], to determine the strength loss with reference to the initial strength before exposure (similar to the mass loss expressed by Eq. (4)). To determine the calcium hydroxide content in SCC specimens at 56 days, differential scanning calorimetry (DSC) at a heating rate of 10 °C/min was conducted on powder samples passing #200 sieve (75 μm) from companion specimens unexposed to sulfuric acid attack. X-ray diffraction (XRD) was conducted on powder specimens drawn from deteriorated concrete surfaces to identify the main phases of the reaction products. To investigate the degradation mechanism on the surface of specimens, microanalysis was conducted on specimens from selected mixtures. Thin sections were prepared for transmitted light optical microscopy, while fracture surfaces from specimens tested under compression were examined using scanning electron microscopy (SEM). Energy dispersive X-ray analysis was used in conjunction with the microanalysis studies.

3. Results and discussion

3.1. Mass loss

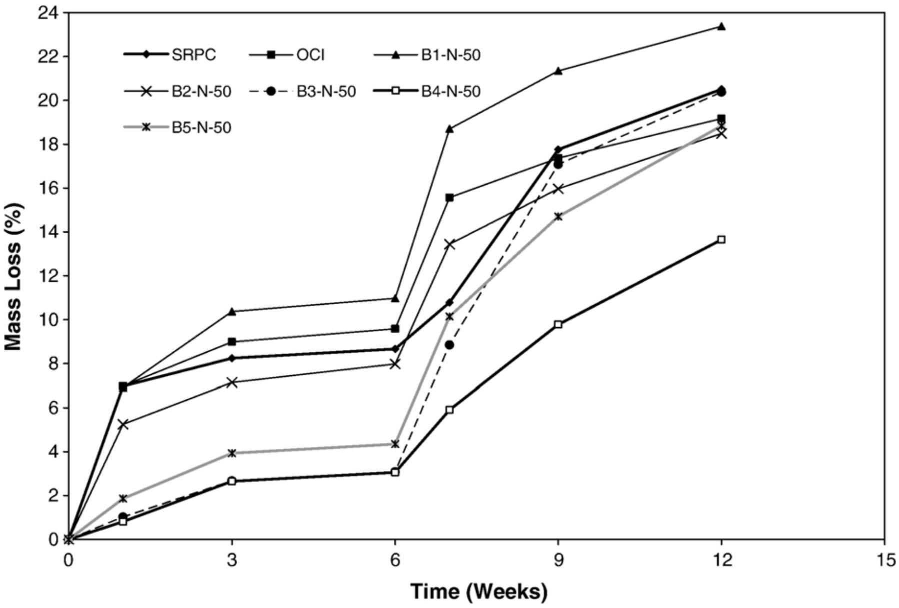
3.1.1. Group A

The mass loss results for group A mixtures are shown in Fig. 1. At the end of phase I, the mass loss ranged from 3.05 to 10.98%, while it ranged from 13.65 to 23.37% at the end of phase II. This marked increase in mass loss complies with the reduction of the maximum pH threshold from phase I (2.5) to phase II (1.0). This reflects the high severity of the phase II solution resulting in a higher rate of attack compared to that of the phase I solution.

It can be observed in Fig. 1 that the type of binder had a pronounced effect on mass loss results. Analysis of variance (ANOVA), at a significance level $\alpha = 0.05$, shows that the variation in the type of binder used had an F value of 73.2, which is larger than the corresponding critical F value of 2.4. In statistical analysis of random variables, exceeding the critical value for an F-distribution density function reflects that the tested variable affects the mean of results [27]. After 6 and 12 weeks of exposure, the control SCC specimens (B1-N-50), prepared with 100% OPC, had the highest mass loss of 10.98% and 23.37%, respectively, whereas specimens from mixture SRPC prepared with 100% sulfate resistant portland cement had slightly lower corresponding mass loss of 8.67% and 20.51%, respectively. The difference in mass loss between mixtures B1-N-50 and SRPC was almost constant (average of 2.5%) in the two phases. Since SRPC and OPC pastes typically encompass large volume fractions of calcium hydroxide (CH) and C–S–H, both are vulnerable to sulfuric acid attack. Before exposure to sulfuric acid, DSC results shown in Fig. 2 indicate that pastes from B1-N-50 and SRPC mixtures had large calcium hydroxide endothermic peaks (at a temperature of about 450 °C) corresponding to enthalpies of 63.6 and 52.65 J/g, respectively. After exposure to sulfuric acid solutions, XRD results in Fig. 3 show that both mixtures had virtually similar dominant phases of gypsum on the surface in contact with the acid. The ettringite phase was absent in the exposed surface owing to the low pH at this region. Comparatively, in deeper regions of specimens, where the pH was above 11, acicular ettringite clusters associated with micro-cracks (e.g. Fig. 4) were only observed in specimens from mixtures prepared with 100% OPC. The absence of ettringite in specimens from SRPC was likely due to its lower C_3A content.

The incorporation of OCI at a dosage of 5 $\mathrm{l/m^3}$ of concrete led to some improvement in the resistance to sulfuric acid attack compared to that of the control mixture (Fig. 1), especially at the end of phase II (18% reduction in mass loss). Since the control mixtures and mixtures incorporating OCI were prepared with 100% OPC, both had comparable calcium hydroxide contents as shown by the DCS results in Fig. 2. The XRD diffractograms in Fig. 3 confirm similar dominant gypsum phases for the OCI and the control mixtures after exposure to sulfuric acid. This reduction in mass loss can be mainly attributed to the action of OCI.

Previous work by the first author [28] and other studies [29] showed that OCI effectively reduced diffusion of chloride ions



Notes
SRPC: 100% sulfate resistant portland cement.
OCI: 100% OPC with 5 l/m^3 OCI.
B1: 100% OPC; B2: 92% OPC + 8% SF, B3: 50% OPC + 5% SF + 45% S; B4: 50% OPC + 15% LF + 20% S + 15% FA; B5: 50% OPC + 5% SF + 25% S + 20% FA.
N: non air-entrained.
50: S/A is 50%.

Fig. 1. Rate of mass loss over time for group A mixtures.

into concrete since OCI works as a hydrophobic pore liner, from calcium salts of fatty acids, which reduces the ingress of ions and water into the concrete pore structure, thus reducing acid penetrability in the cementitious matrix. The observed reduction in mass loss due to OCI addition is comparable to that reported in previous work [30], which used similar OCI dosage in normal concrete exposed to sulfuric acid solutions (initial concentration of 7 and 3%, respectively) with a pH of 0.3 and 0.6. On the other hand, Daczko et al. [11] reported that incorporating 5 l/m^3 of OCI in concrete exposed to a sulfuric acid solution with a pH of 1.0 led to a significantly lower mass loss than that of the control mixture. This variation in the level of improvement offered by OCI may be attributed to the difference in the initial concentration of sulfuric acid, which was not reported in Daczko et al. [11]. The pH value indicates the acid strength or dissolution degree; strong acids have low pH values, while

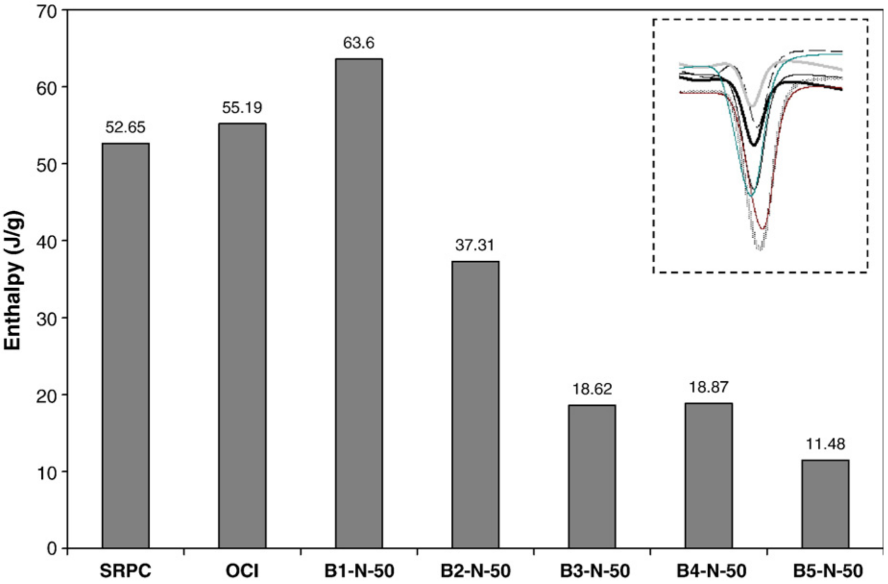


Fig. 2. DSC results for calcium hydroxide heat flow peaks of group A mixtures at 56 days.

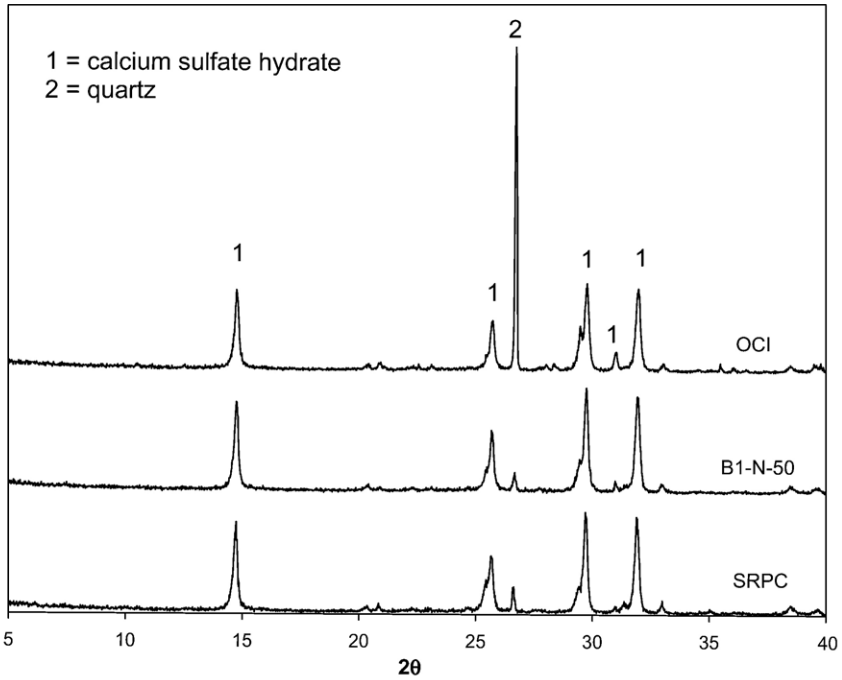


Fig. 3. XRD for specimens prepared with 100% portland cements after 12 weeks of exposure to sulfuric acid.

weak acids have high pH values. Yet, the pH value does not reflect the actual concentration of an acidic solution. Thus, to better describe the severity of an acidic medium to which concrete is exposed, it is important to specify both the concentration and pH range during exposure.

At the end of phase I, all concrete mixtures with binary, ternary and quaternary binders had markedly lower rate of attack and mass loss than that of the control mixture. For the binary mixture B2-N-50, the mass loss was about 27% lower than that of the control mixture. The reduction in mass loss was more significant for the ternary (72%) and quaternary (average of 66%) mixtures. From a mixture proportioning perspective, this can be ascribed to a dilution effect of cement due to a high replacement level (50%) in ternary and quaternary mixtures compared to only 8% in the binary mixture. SCMs react with CH and water to produce C–S–H (pozzolanic reaction). Increasing the replacement level of OPC by SCMs is inversely proportional to the amount of calcium hydroxide generated. This is depicted by the DSC results in Fig. 2, where enthalpies of calcium hydroxide for the ternary and quaternary binder mixtures were significantly less than that of the binary and control mixtures. Thereby, the ternary and quaternary binder mixtures had limited calcium hydroxide contents available for the acid–base reaction compared to that of the binary and control mixtures, thus resulting in a lower rate of attack. The abundance of calcium hydroxide in the paste seems to be the controlling factor for the reaction between the sulfuric acid solution and concrete at a pH of 2.5.

ANOVA indicates that the interaction between the binder type and consecutive pH reduction had some effect on mass loss results since it had an *F* value of 16.8, which is larger than the corresponding critical *F* value of 2.4. In phase II, mixtures with

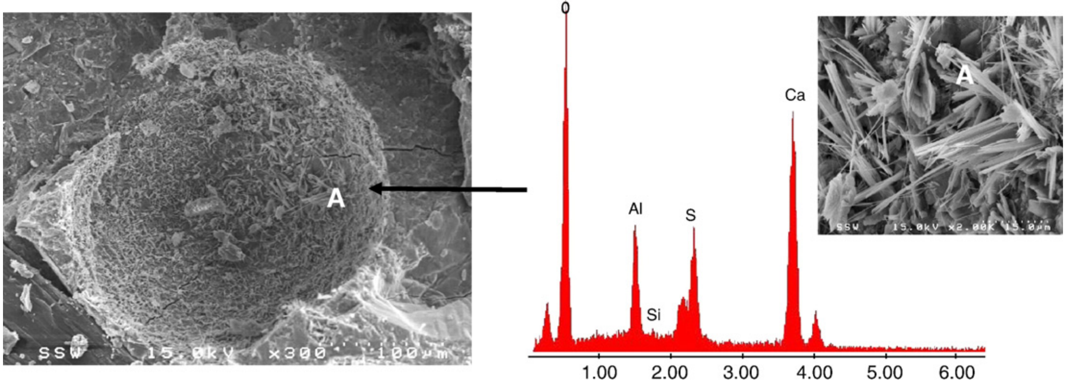


Fig. 4. Clustering of ettringite and associated micro-cracking.

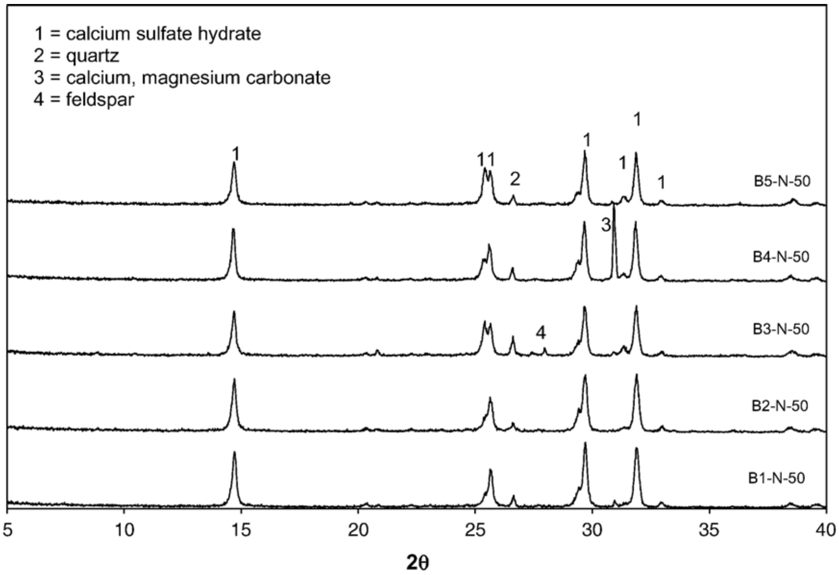


Fig. 5. XRD for specimens made from single, binary, ternary and quaternary binders after 12 weeks of exposure to sulfuric acid.

all binder types showed increased mass loss due to the pH reduction, but at different rates. XRD results in Fig. 5 revealed no fundamental differences between the behavior of specimens from composite cements and OPC exposed to sulfuric acid solutions. All XRD diffractograms were dominated by strong peaks of gypsum without any ettringite peaks. It is worth nothing that amorphous phases, which may exist in deteriorated blended pastes, could not be detected by XRD.

The dominant effect of the calcium hydroxide content on mass loss results shown in phase I diminished in phase II, particularly for blended binders. The ternary mixture B3-N-50, prepared with 50% OPC, 45% slag and 5% silica fume had a higher rate of mass loss compared to that of other blended mixtures, but maintained a mass loss lower (15% reduction) than that of the control mixture. At the end of phase II, the quaternary mixtures B4-N-50 and B5-N-50 had lower mass loss than that of the ternary mixture (B3-N-50). At the end of phase II, the binary mixture B2-N-50 had a comparable performance (21% mass loss reduction with reference to the control mixture) to that of the quaternary mixture B5-N-50 incorporating silica fume (20% mass loss reduction with reference to the control mixture). The quaternary mixture B4-N-50 prepared with 50% OPC, 15% limestone filler, 20% slag and 15% fly ash had the highest mass loss reduction of 42% at the end of phase II. This may be

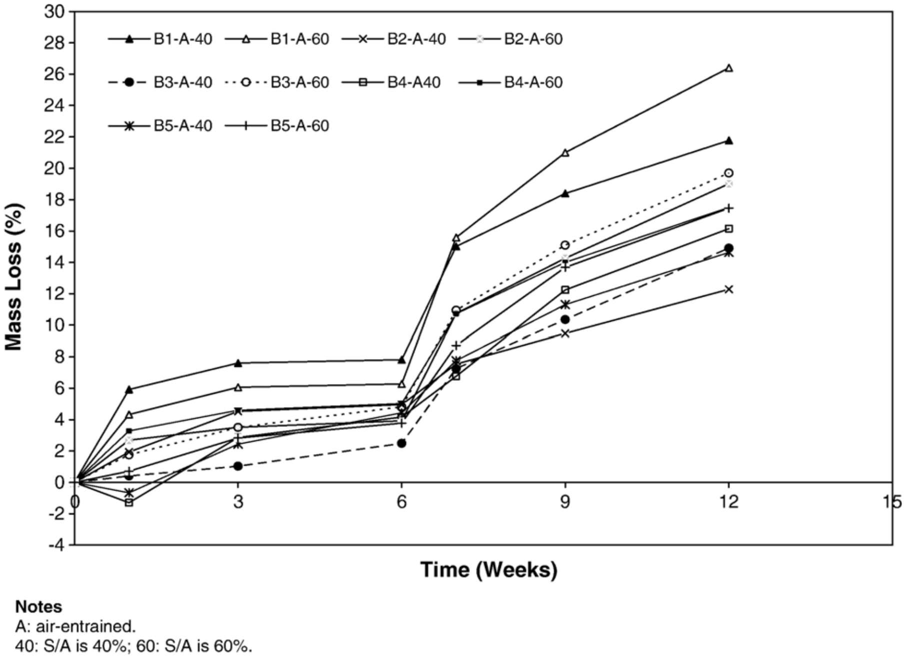


Fig. 6. Rate of mass loss over time for group B mixtures.

ascribed to the incorporation of limestone in this blended binder. In an acidic environment, limestone filler in the cementitious matrix has a chemical role of neutralizing/consuming the acid [15]. From Fig. 5, the existence of strong peaks of calcium/magnesium carbonates on the surface of specimens from mixture B4-N-50 suggests that limestone possibly created a local buffer at the concrete surface, i.e. lower acid concentration and higher pH near the surface, which led to a slower degradation rate. However, due to the regular stirring of the acidic solution, this buffer layer was partially disturbed, which might have limited its beneficial effect. The behavior of blended binders is discussed in detail in the subsequent section.

3.1.2. Group B

The mass loss results for group B mixtures are shown in Fig. 6. At the end of phases I and II, mass loss ranged from 2.48 to 7.82% and from 12.28 to 26.41%, respectively. Some mixtures exhibited mass gain during the first week of immersion due to solution absorption, which is customary at early ages of chemical immersion tests. Similar to group A, the reduction in pH from phase I to II led to a notable increase in the rate of mass loss as shown by the large slope at the start of phase II in Fig. 6. By comparing Figs. 1 and 6, irrespective of the different S/A, the rate of attack on non-air-entrained SCC (group A mixtures) is generally similar to that of air-entrained SCC (group B mixtures) with slight improvement for some air-entrained mixtures at phases I and II. Hence, in agreement with previous research [5], air-entrainment may offer limited, if any, improvement to SCC exposed to severe or very severe sulfuric acid attack.

Similar to group A, the type of binder had a pronounced effect on mass loss results for group B mixtures. After 6 and 12 weeks of exposure, mixtures prepared with 100% OPC (B1-A-40 and B1-A-60) had higher mass loss than that of the corresponding mixtures prepared with binary, ternary and quaternary binders at similar S/A. In phase I, this is ascribed to the limited calcium hydroxide content in blended binder mixtures compared to that of the control mixtures, as discussed earlier. At S/A of 40%, the reduction in mass loss for the binary, ternary and quaternary mixtures with reference to the control mixture (B1-A-40) was similar to that of group A in the sense that ternary (68% reduction) and to a lesser degree quaternary (45% reduction) mixtures performed better than the binary mixture (37% reduction). However, at S/A of 60%, the binary mixture B2-A-60 had better or comparable mass loss reduction to that of ternary and quaternary mixtures. At the end of phase II, for S/A of 40%, the binary mixture B2-A-40 had a better performance (44% mass loss reduction with reference to the control mixture) than that of the ternary (32% reduction) and the quaternary (average of 29% reduction) mixtures. Nevertheless, at S/A of 60%, quaternary mixtures (average of 34% mass loss

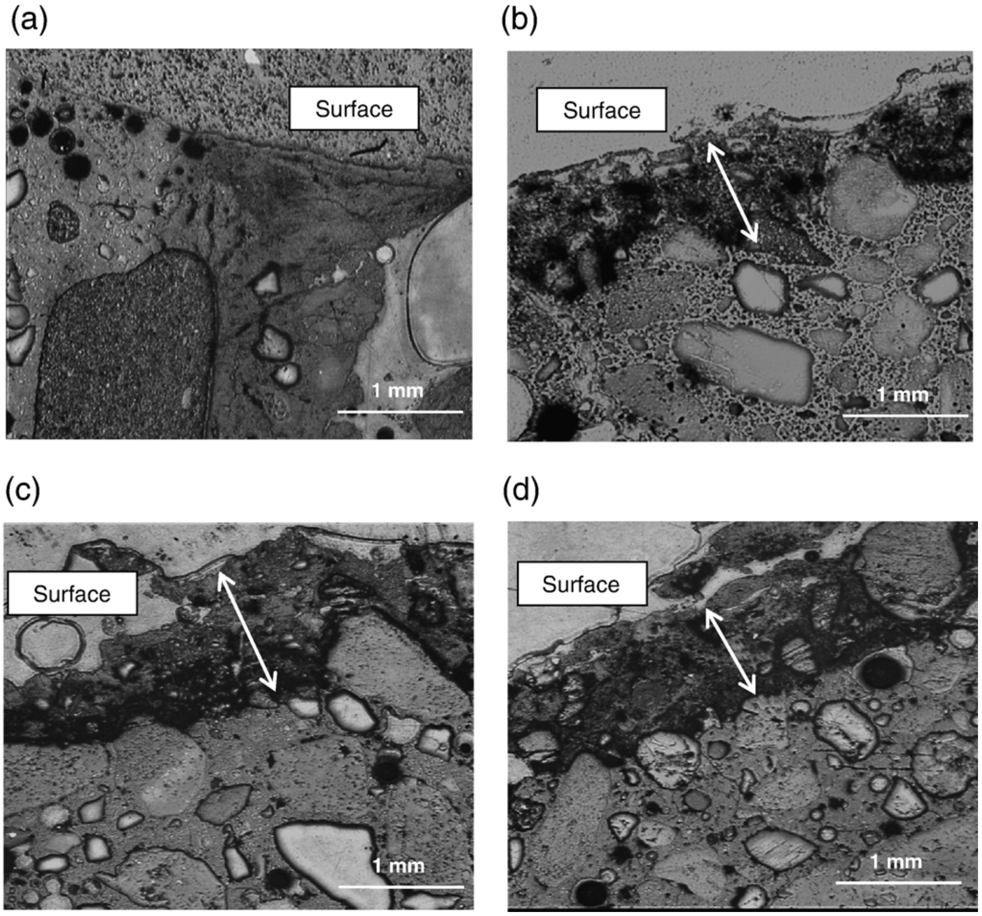


Fig. 7. Typical thin sections of SCC specimens from mixtures: (a) B1-A-40, (b) B2-A-40, (c) B3-A-40, (d) B5-A-40 after 12 weeks of exposure to sulfuric acid.

reduction) performed better than the binary (28% reduction) and ternary (25% reduction) mixtures. Thereby, complying with phase I observations, it is suggested that the effect of the binder type on reducing mass loss is sensitive to the S/A at each pH level.

Similar to group A in phase II, there was a significant increase in the rate of mass loss for specimens from all mixtures in group B, as shown in Fig. 6. This suggests an important contribution of C–S–H decomposition to mass loss results in this phase, though with different effects for OPC and blended binder mixtures. Detwiler et al. [31] reported that C–S–H produced by pozzolanic reactions of SCMs has a different structure and calcium-to-silicate ratio (C/S of about 1.0) than that of conventional C–S–H (C/S of about 3.0) produced by OPC hydration. Also, C–S–H produced by SCMs has a higher binding capacity for alkalis and alumina [31]. Decomposition (release of Ca^{2+}) of C–S–H starts below a pH of 9.0, implying a contribution to mass loss results in both phases I and II, though

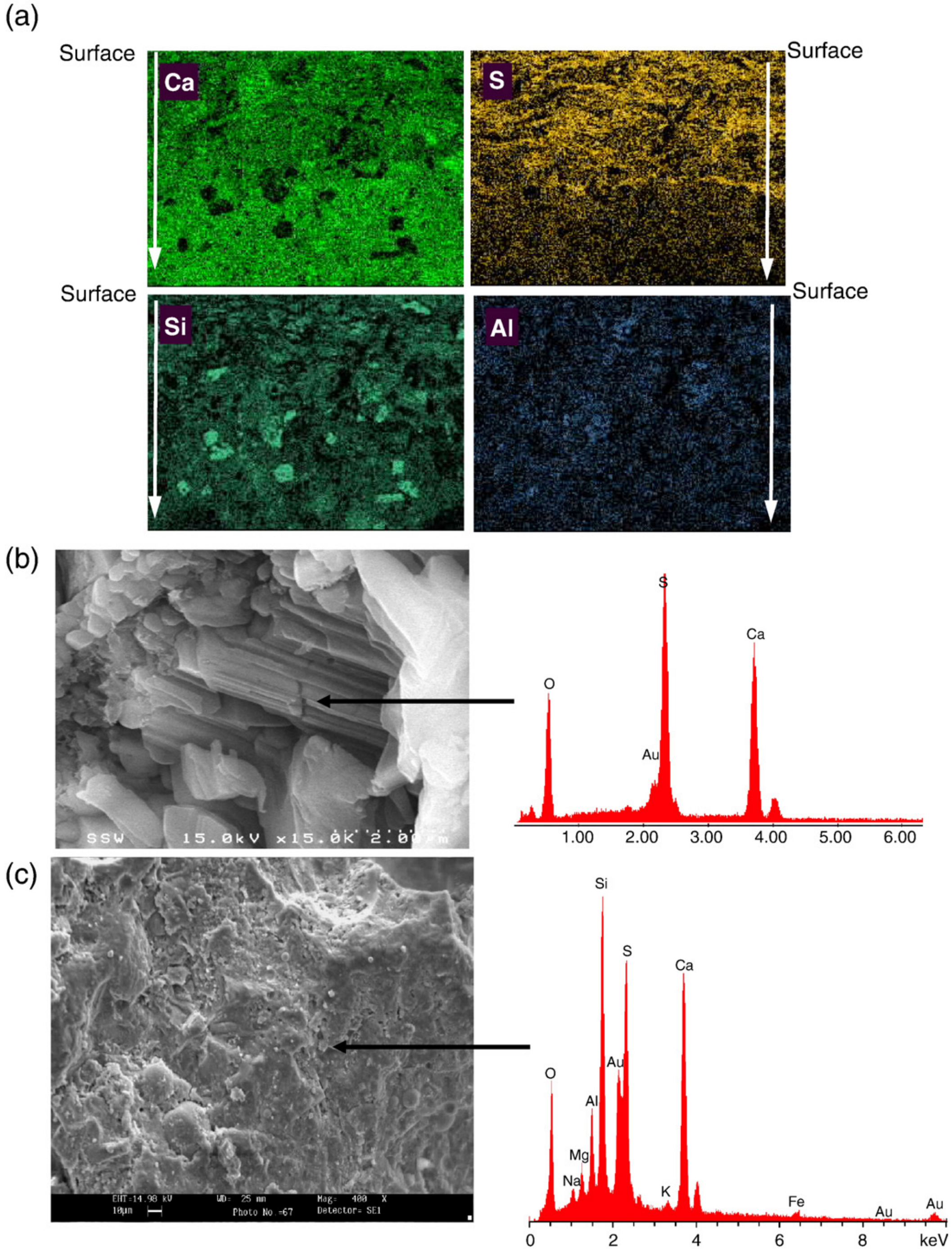


Fig. 8. Example of microanalysis for a specimen from a quaternary binder mixture (B5-A-40) showing: (a) elemental distribution in thin sections, (b) gypsum crystals on exposed surface, (c) precipitation of gypsum in hydrous silica.

with different levels since at the higher pH threshold, the calcium hydroxide content showed a major role. It was also stated [32] that while decalcification of C–S–H with a high C/S is preferential and produces a structure vulnerable to further acidic attack, dissolution of C–S–H with a low C/S occurs at a slower rate and produces dense silico-aluminous gel.

Fig. 7 shows thin sections of specimens prepared with single, binary, ternary and quaternary binders (B1-A-40, B2-A-40, B3-A-40, and B5-A-40) under transmitted light microscopy (25X) after 12 weeks of exposure to severe sulfuric acid attack. For the binary, ternary and quaternary binder specimens, Fig. 7b–d exhibit a deteriorated zone (defined by the arrows) below the exposed surface, underlain by sound concrete. On the contrary, this zone is absent in the thin section of the control specimen, which implies direct exposure of the cementitious matrix to sulfuric acid solutions. Spatial elemental distribution by EDX (e.g. Fig. 8a) for sections from specimens made with blended binders revealed low intensity of calcium (Ca) and high intensity of sulfur (S) in the deteriorated zone. Silicon (Si) and aluminium (Al) occurred in considerable amounts in this zone. Microanalysis by SEM and EDX for fracture surfaces from specimens prepared with blended binders indicated that the deteriorated zone identified under transmitted light microscopy is comprised of gypsum (e.g. Fig. 8b) encapsulated by a rich media of hydrous silica with aluminium and magnesium (e.g. Fig. 8c). This amorphous media surrounding gypsum crystals was not detected by XRD. Apparently, the existence of this zone in specimens from blended binders relatively sealed the intact concrete from the surrounding sulfuric acid solution, thus limiting damage relative to the control specimens prepared with 100% OPC, which did not possess a similar zone. Hence, this zone acted as a protective layer, which likely slowed down the rate of acid diffusion into sound concrete, and in turn reduced the degradation rate (mass loss). It is worth noting that this zone was still preserved even with the regular removal of loose materials by rinsing with water at the time of weighing specimens.

In phase I, during the first 3 weeks of immersion, the role of S/A was not definite since sulfuric acid attack acted mainly on the outer shell of specimens. This layer is mostly a mortar phase with a limited coarse aggregate content. Subsequently, the rate of attack slowed down with no much difference between mass loss values at 3 and 6 weeks. Fig. 9 shows an example of this slow degradation process with no marked difference between mixtures with S/A of 40 and 60%. In phase II, when the pH dropped to 1.0, the rate of attack increased, and S/A affected the mass loss results significantly. For all binder types, mass loss results decreased with S/A reduction likely because of a higher volume fraction of coarse aggregates on the surface, which better resist acid than cement paste. At the end of phase II, mixtures with S/A of 40% had 8 to 35% lower mass loss than that of corresponding mixtures with S/A of 60%. After deterioration of the outer shell, a higher surface area of inert coarse aggregates was exposed to sulfuric acid solution that had to travel through longer paths around coarse aggregates to react with cementitious materials. Hence, incorporating a higher

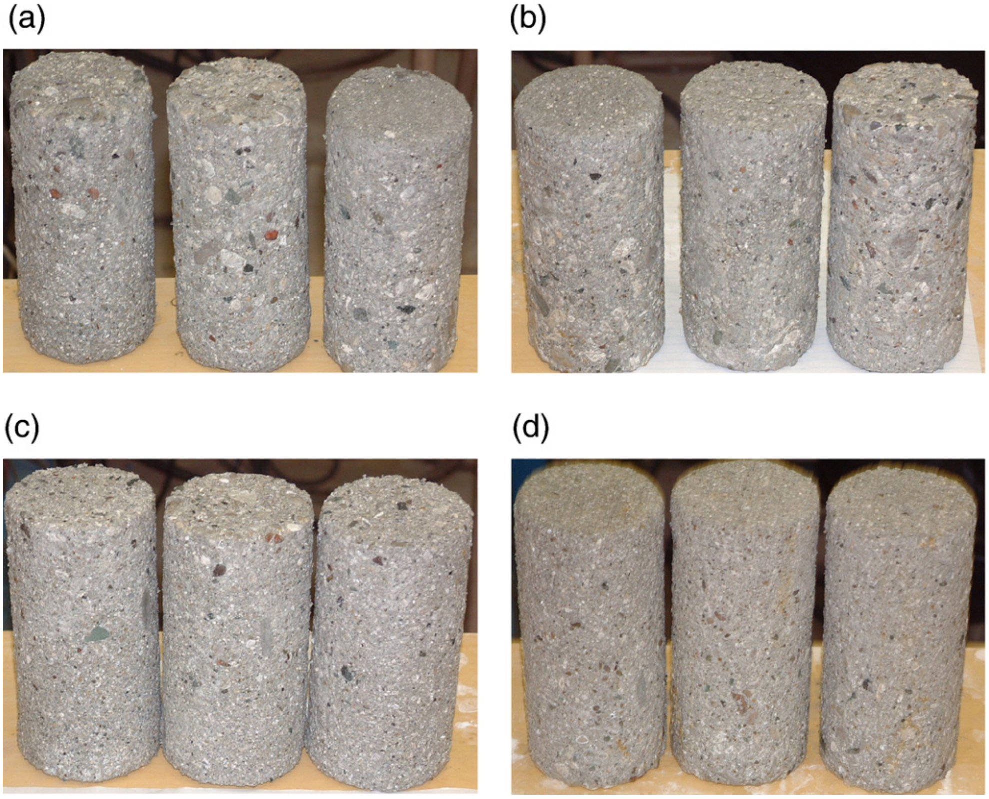
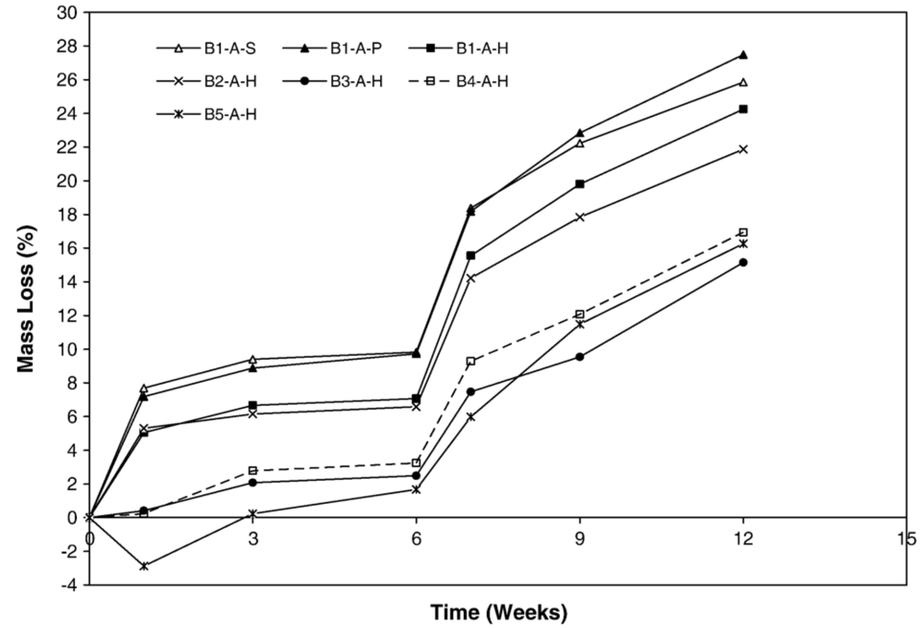


Fig. 9. Degradation of SCC specimens by sulfuric acid: (a) B5-A-40 after 3 weeks of immersion, (b) B5-A-40 after 6 weeks of immersion, (c) B5-A-60 after 3 weeks of immersion, (d) B5-A-60 after 6 weeks of immersion.



Notes
S: steel fibres; P: polypropylene fibres; H: hybrid fibres.
Sand-to-total solid mass ratio is 50% for group C mixtures.

Fig. 10. Rate of mass loss over time for group C mixtures.

volume fraction (up to 380 l/m^3) of coarse aggregates in SCC is effective at improving its resistance to sulfuric acid, even at a high cementitious content (470 kg/m^3).

3.1.3. Group C

The mass loss results for group C mixtures are shown in Fig. 10. For phases I and II, the results ranged from 1.67 to 9.83% and from 15.15 to 27.48%, respectively. From Fig. 10, by comparing the behavior of mixtures B1-A-S, B1-A-P and B1-A-H prepared with 100% OPC with steel, polymer and hybrid (steel+polymer) fibres, respectively, it can be observed that the incorporation of hybrid fibres generally led to better performance than using each fibre type individually. The rational behind incorporating hybrid fibres is the combination of the advantageous effects of polymer micro-fibres and steel macro-fibres. According to Johnston [33], while polymer micro-fibres contribute to pre-crack behavior by impeding the nucleation and coalescence of micro-cracks, steel macro-fibres can bridge macro-cracks, thus contributing to the control of crack propagation [33].

Similar to groups A and B, variation in the binder type had a pronounced effect on mass loss results of air-entrained SCC specimens with hybrid fibre reinforcement. The control SCC mixture (B1-A-H) prepared with 100% OPC had the highest mass loss compared to that of the binary, ternary and quaternary binder mixtures with hybrid fibre reinforcement. As discussed earlier, this can be mainly ascribed to the limited calcium hydroxide content and the formation of a protective zone in specimens from blended binders relative to the control specimens.

The role of hybrid fibre reinforcement in controlling cracks and increasing the tensile capacity of the cementitious matrix can lead to improved matrix integration in acidic environments by limiting swelling and disruptive pressures from voluminous reaction products. The initiation and propagation of micro-cracks in the cementitious matrix due to gypsum and ettringite formation resulting from the sulfuric acid attack were evident by microanalysis (e.g. Fig. 4). Visual inspection ensured the positive effect of hybrid fibre reinforcement. For example, Fig. 11 shows less degradation and swelling after 12 weeks of exposure for specimens B5-A-H from group C relative to specimens B5-N-50 from group A (similar sand-to-total solid mass ratio and binder types). However, the positive effect of the hybrid fibre reinforcement was not fully reflected by the mass loss results. Considering that the hybrid fibre reinforcement in group C mixtures incorporated steel fibres with a high specific gravity (7.85) compared to that of other constituents, detachment of small volumes containing steel fibres may yield a relatively higher mass loss. It was observed that some steel fibres were dislodged from the surface of specimens due to corrosion/dissolution during the very severe acidic exposure of phase II solution. Thus, in acidic environments, the criterion of mass loss may relatively overestimate the degradation rate of concrete mixtures incorporating steel fibres.

3.2. Relationship between mass loss and compressive strength loss

After 12 weeks of exposure, specimens were tested for compressive strength to determine the percentage of strength loss with reference to the initial strength before exposure to sulfuric acid attack. The percentages of compressive strength loss for all mixtures are listed in Table 2b. The relationship between mass loss and compressive strength loss is shown in Fig. 12 as a percentage of their initial values before exposure. It

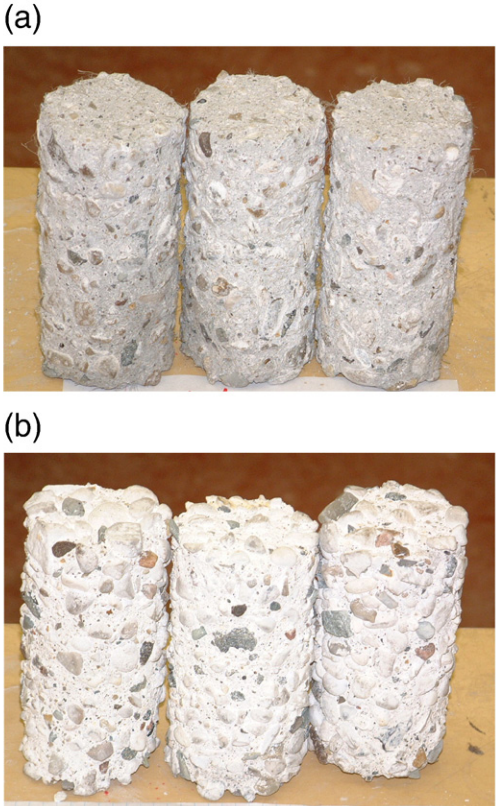


Fig. 11. Degradation of SCC specimens after 12 weeks of exposure to sulfuric acid attack showing less degradation and swelling of (a) B5-A-H compared to (b) B5-N-50.

can be observed that data points are scattered reflecting disassociation of the two data sets without any definitive trend. Two data points exhibited strength gain rather than strength loss after sulfuric acid exposure. Discrepancy between mass loss and strength loss after exposure to acidic media was also reported in other studies [20,34], but without explanation. In contrast, it has been suggested that there was a correlation between mass loss and compressive strength loss after exposure to sulfuric acid solutions [30]. Most of the available literature on the resistance of concrete to sulfuric acid attack has not discussed the correlation between mass loss and strength loss; consequently, this relationship remains questionable.

The inconsistency of the relationship between mass loss and compressive strength loss can be explained in terms of the observed degradation mechanisms in the present study. Microanalysis showed that there was a deteriorated zone in the outer rim of the thin sections of specimens from mixtures made with blended binders, while it was absent in the surface of single binder specimens made from 100% OPC. Inner parts of concrete beyond the surface zone (about 10 mm from the surface) for all mixtures appeared to be still sound, as confirmed by the elemental spatial distribution (e.g. 8a) of thin sections showing increasing intensity of calcium and silicon towards the concrete core. This is in agreement with observations of Yamanaka et al. [4] on in-service sewer pipes in Japan, which suffered biogenic sulfuric acid corrosion. They reported a successive alkalinity decrease from the inner concrete core to its surface exposed to sulfuric acid. While the outer surface had a pH of 2.15, the inner core had a pH of 12, implying that the concrete core was still sound [4].

In the present study, mass loss over time reflected the successive decomposition of concrete specimens starting from the exposed surface and moving inwards. The fundamental factors controlling mass loss from the exposed surface were the content of calcium hydroxide and the existence of a deteriorated (protective) zone. The latter had a significant role in slowing down the kinetics of the acidic reaction by reducing the acid diffusion into the sound concrete matrix. Other factors that influenced mass loss results were S/A and the inclusion of steel fibres.

The compressive strength of a concrete specimen is mainly dependent on the characteristics of the concrete matrix (binder content and type, w/cm, aggregate content, etc.), consolidation

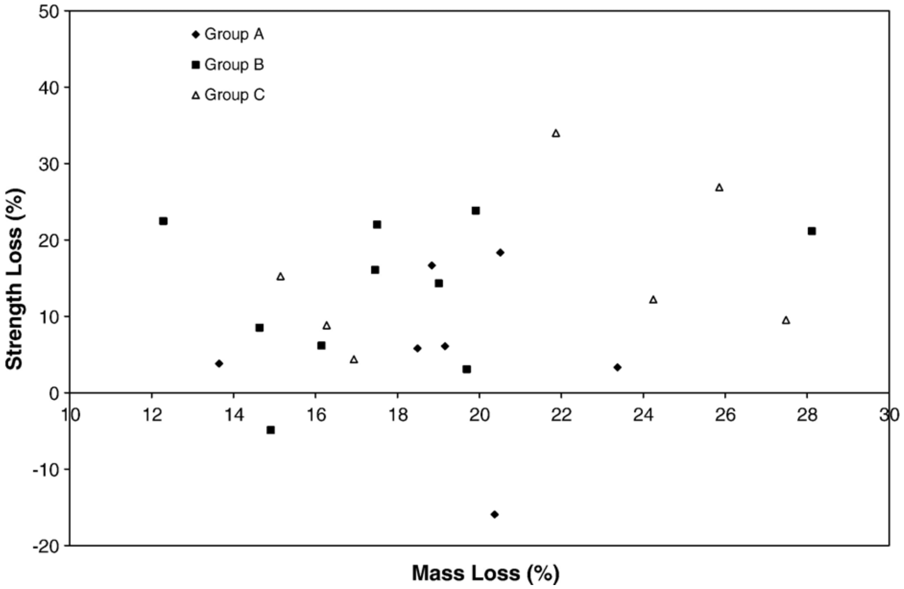


Fig. 12. Mass loss versus compressive strength loss after 12 weeks of exposure to sulfuric acid.

method (conventional concrete versus SCC), curing regime, geometry, and aspect ratio. After exposure to sulfuric acid solutions, SCC specimens had a softened surface zone underlain by a sound part, which represents the bulk cross-section of specimens. The observed compressive strength reduction after exposure depended on the ratio of deteriorated-to-sound cross-section. The existence of a deteriorated (protective) zone, especially in specimens made with blended binders, can decrease mass loss of specimens due to limiting acidic diffusion into the cementitious matrix. Conversely, the occurrence of this zone can increase strength loss results since it has weak mechanical properties. On the other hand, a concrete specimen prepared from a single binder may exhibit a high mass loss after sulfuric acid exposure due to a high S/A (low coarse aggregate volume fraction); nevertheless, it can still maintain a high compressive strength (small strength loss) due to a limited/absent deteriorated zone at the surface.

In addition, in chemical immersion tests, there are two processes with conflicting effects simultaneously occurring in the cementitious matrix: decomposition of the surface and continual hydration/densification of the core (bulk cross-section). While the first causes moss loss, the second can cause strength increase, particularly for binders comprising high dosages of SCMs (e.g. slag and Class F fly ash) that exhibit long-term strength gain. This might explain the strength gain of two mixtures (B3-N-50 and B3-A-40) incorporating a dosage of 45% slag after 12 weeks of exposure to sulfuric acid solutions.

After exposure to sulfuric acid solutions, the change in aspect ratio and variability of geometry (diameter) across the height of specimens (e.g. Fig. 11) led to planes of stress concentration, load eccentricity and non-uniform stress distribution during compression testing. This had a pronounced effect on the reliability of the determined crushing load. Also, by considering the effective cross-sectional area of the sound core instead of the initial cross-sectional area, the calculated compressive strength after exposure can be higher than its initial value. Thus, it is somewhat difficult to compare compressive strength values of specimens after exposure to their initial values obtained from intact samples. The preceding discussion reveals that the loss in compressive strength may be inappropriate for quantifying the rate of attack on concrete exposed to sulfuric acid. Also, any relationship between mass loss and compressive strength loss should be taken cautiously since the two manifestations are governed by different factors and are not directly related.

4. Conclusions

Considering the growing use of SCC in numerous concrete applications that are vulnerable to attack by sulfuric acid, this research studied the performance of a wide scope of SCC mixtures (total of 24 mixtures) subjected to a chemical attack by sulfuric acid solutions with consecutive pH reduction. The following conclusions can be drawn:

- The resistance of SCC to sulfuric acid attack was moderately improved by OCI addition, while SRPC and air-entrainment offered little improvement in severe and very severe sulfuric acid solutions.
- In phase I exposure with a pH threshold of 2.5, an improved performance in the resistance of SCC to sulfuric acid was achieved using binary, ternary, and quaternary binders. The primary effect of ternary and quaternary binders was ascribed to the dilution effect of OPC due to the high volume replacement by SCMs (50%), which reduced the calcium hydroxide content available for reaction with acid.
- In phase II exposure with a pH threshold of 1.0, the role of the calcium hydroxide content diminished and the prominent contribution of C–S–H decalcification to mass loss appeared to be the governing factor. Decalcification of C–S–H with high C/S (100% OPC mixtures) produced a surface vulnerable to direct acid attack, whereas decomposition of C–S–H with a relatively lower C/S produced a protective zone, which limited acid diffusion into the cementitious matrix, and thus reduced mass loss of specimens from blended binder mixtures.
- Specimens from mixtures with quaternary binder blends showed the best performance in terms of a slower rate of degradation compared to that of the ternary and binary binder mixtures depending on the S/A at each pH level.
- In phase II exposure, increasing the volume fraction of coarse aggregates was effective at reducing the mass loss of SCC mixtures exposed to sulfuric acid attack due to minimizing the cementitious surface available for reaction with acid. Thus, it is recommended that for SCC applications that are vulnerable to severe sulfuric acid attack, mixture designs should not abide by conventional methods that recommend reduced volumes of coarse aggregates in SCC mixtures.
- The inclusion of hybrid micro- and macro-fibres can be effective in retaining the cementitious matrix integrity and controlling disruptive pressures resulting from voluminous reaction products.
- Compressive strength loss did not have a direct relation with mass loss of SCC specimens under sulfuric acid attack. This was ascribed to multiple factors with some conflicting effects on the two parameters. Generally, it may be inappropriate to express the rate of concrete deterioration due to sulfuric acid attack in terms of compressive strength loss.

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