RESISTANCE OF CONCRETE INCORPORATING PORTLAND LIMESTONE CEMENT TO SULFURIC ACID

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ABSTRACT

Concrete has long been the most popular choice for constructing key infrastructural elements such as sewer pipes, water treatment facilities, industrial floors and foundations. However, many field cases from all around the world have shown that concrete elements in these environments are severely damaged due to biogenic and/or chemical sulfuric acid attack. Since high alkalinity is required for the stability of the cementitious matrix, concrete is highly prone to acid attacks, which decalcify and disintegrate the hydrated cement paste to various levels based on exposure conditions and type of concrete. Numerous studies have been conducted to enhance the durability of concrete and understand the influence of key mixture design parameters on its resistance to sulfuric acid attack. Yet, there is dearth of information on the behaviour of a new type of cement in North America, which contains a high level (5 to15%) of interground limestone powder (portland limestone cement: PLC), under acidic attack. Hence, the aim of this study is to investigate the effect PLC with or without supplementary cementitious materials (SCMs) on the durability of concrete exposed to acidic attack. The study comprised 13 weeks (90 days) immersion of test specimens in 5% sulfuric acid solutions with pH in the range of 0.1 to 2.5. Physical and microstructural results reveal that PLC may improve the resistance of concrete to sulfuric acid attack, whereas the SCMs had a mixed effect on the results.

Keywords: Portland limestone cement, sulfuric acid, pH, SCMs, durability.

1. INTRODUCTION

Acid attack on concrete is known since 1895 (Olmstead and Hamlin 1900) and the extent of this durability issue is quite global and widespread. The increase in reported attacks by acidic media on concrete structures has drawn much attention to this topic in recent times likely due to the growing sources of acidic media resulting from population growth, and in turn increased urban activities and industrialisation (Duchesne and Berton 2013). Concrete is particularly prone to acidic attack since it is highly alkaline, and thus it engages in reactions whenever exposed to acids or salts triggering reactions similar to acids (e.g. ammonium-based salts). Significant quantities of free acids, in the form of leakages and random spillages, may occur in industrial environments. However, sulfuric acid (H_2SO_4) attack in sewer pipes is the most widely reported attack on concrete by inorganic acids (House and Weiss 2014; O'Connell et al. 2010; Islander et al. 1991; Parker 1951), which is also referred to as microbially induced corrosion (MIC) of concrete since sulfuric acid is generated by bacterial activities. MIC in wastewater collection and treatment systems is well-documented in North America, Europe, the Middle East, South Africa and Australia (House and Weiss 2014). A report in 1991 estimated that the repair or replacement of only 25 miles of corroded concrete sewer pipe, due to sulfuric acid attack, in Los Angeles County would cost $130 million (U.S. EPA 1991). In addition, sulfuric acid attack on concrete can also originate from backfilling with pyratic aggregates (Hobbs and Taylor 2000; Tagnit-hamou et al. 2005) or use of pyratic aggregates in concrete (Tagnit-hamou et al. 2005). Hence, development of preventive measures to mitigate acidic attack on concrete is of utmost importance for key infrastructural facilities in urban, industrial and agricultural zones.

It has been reported that for concrete made with acid resistant aggregates (e.g. quartz), only the cement paste matrix is vulnerable to acid attack (Beddoe and Dorner 2005). On the other hand, if concrete is made with carbonaceous aggregates such as limestone and dolomite, an additional neutralization reaction (between acids and aggregates) is expected. The degree of neutralisation offered by limestone aggregates depends on their porosity. For aggregates with lower porosity, the reaction with the acid takes place only at the aggregate surface adjacent to the pore solution, whereas for aggregates with higher porosity, acid ions also get into the pores, which amplifies the neutralization process due to the higher exposed surface area (Beddoe and Dorner 2005). Indeed, the acid neutralization effect offered by limestone is limited by the fixed volume of limestone aggregate in concrete. Hughes and Guest (1978) compared the resistance of concrete mixtures incorporating ordinary portland cement (OPC or GU) and siliceous or limestone aggregates to sulfuric acid solutions with concentrations of 0.016% and 0.020% by mass. The authors reported that the surface of concrete with siliceous aggregates was more uneven than that with limestone aggregates. According to another study (De Belie et al. 2004), the smoother surface texture is because that limestone aggregates degrade progressively in layers; the surface of the aggregates and surrounding matrix are exposed to the same acidic media, which implies that the paste and the aggregates have a similar rate of deterioration. Chang et al. (2005) investigated the resistance of different concrete mixtures incorporating siliceous and limestone aggregates made with binary and ternary binders containing blends of fly ash, silica fume and blast-furnace slag to 1% sulfuric acid solution with a pH of 1.27 to 1.35. The results showed that mixtures prepared with limestone aggregates had higher residual compressive (crushing) load compared to that of the corresponding ones with siliceous aggregates. Irrespective of the type of aggregates, concrete made with both binary (GU and slag) and ternary (GU, slag and silica fume) binders were less resistant to the acidic exposures than the concrete made from single binders (GU) in terms of the residual crushing load. Nevertheless, specimens made from ternary cement (containing silica fume and fly ash) had the best performance in terms of visual assessment and mass loss results (Chang et al. 2005).

It was reported that using up to 15% limestone filler (ground in a laboratory mill to a specific surface of 370 m^2/kg) as replacement of GU can improve the resistance of concrete to sulfuric acid (Ghrici et al. 2007). Bassuoni et al. (2007) showed that limestone fillers (specific surface of 3200 and 12000 m^2/kg) and aggregates (coarse and fine) perform well in sulfuric acid media with moderate aggression (3% sulfuric acid solution with a pH of 2), but higher fineness (specific surface of 12000 m^2/kg) of limestone fillers comparatively accelerated the rate of mass loss of concrete in a highly aggressive (5% concentration with a pH of 1) sulfuric acid solution. Recently, a new type of cement has been introduced to the North American market which contains a high level (up to 15%) of interground limestone powder (portland limestone cement: PLC). This product is manufactured by intergrinding clinker with limestone and natural gypsum on an industrial scale rather than blending limestone powder as filler. A detailed study (Marzouki et al. 2013) found that by intergrinding more limestone with clinker (0-35% replacement) the specific surface of the resultant cement gradually increases (from 260 m^2/kg to 480 m^2/kg). This study showed the possibility of improving strength gain by finer grinding of clinker with limestone and argued that PLC up to 25% limestone replacement can perform similar to ordinary portland clinker over time. While there are a number of studies on the hydration and strength characterization of concrete made from PLC (e.g. Marzouki et al. 2013; Ramezanianpour et al. 2009; Tsivilis et al. 1999) and its response to durability issues such as sulfate attack (e.g. Ramezanianpour and Hooton 2013), alkali aggregate reactions and chloride ions penetration (Ghiasvand et al. 2015; Thomas et al. 2010), there has been dearth of information on the beneficial effect, if any, of PLC on the performance of concrete subjected to acidic media. Therefore, the objective of the current study was to investigate the response, in terms of physico-mechanical properties and microstructural features, of concrete made with PLC without or with supplementary cementitious materials (SCMs) to a high concentration sulfuric acid solution.

2. EXPERIMENTAL PROGRAMME

2.1 Materials and Mixtures

The cements used in this study were general use cement (GU) and portland limestone cement (PLC) that includes approximately 12% interground limestone by mass of clinker, which meets CSA A3001; six mixtures were prepared in this study, some of which contained Type F fly ash and silica fume as SCMs meeting CSA A3001 (2013). To achieve a constant workability level (slump of 75 to 125 mm) for all mixtures, a high-range water reducing admixture, based on polycarboxylic acid and complying with ASTM C494 Type F (2015), was used at dosages in the range of 200 to 400 ml/100 kg of binder. Well-graded natural gravel (9.5 mm) was used as coarse aggregate; its

specific gravity and absorption were 2.65 and 2%, respectively. The fine aggregate was well graded river sand with a specific gravity, absorption, and fineness modulus of 2.53, 1.5% and 2.9, respectively.

The water-to-binder ratio (w/b) and total binder content for the six mixtures were kept constant at 0.4 and 390 kg/m^3, respectively. Single binder (control) mixtures were prepared from 100% GU or PLC, while blended binder mixtures incorporated GU or PLC with either 30% fly ash (Type F) or 5% silica fume (SF) as a replacement of the total binder content. The proportions of the concrete mixtures are given in Table 1. Concrete was mixed in a mechanical mixer to prepare triplicates of prismatic specimens (50×50×285 mm) and cylindrical specimens (75×150mm), which were cured at standard conditions (22±2˚C and 98% RH) for 28 days according ASTM C192 (2015).

2.2 Acid Exposure

After curing, the initial physico-mechanical properties (mass and compressive and splitting tensile strengths) of the concrete specimens were determined. Afterwards, 18 concrete prisms and 18 concrete cylinders (three replicates per each mixture) were fully immersed (approximate ratio between the volume of acidic solution and total volume of concrete specimens immersed in the solution = 2) in a high concentration (5% by volume) sulfuric acid solution to facilitate accelerated and aggressive exposure conditions similar to Bassuoni and Nehdi (2007) and Roy and Arjunan (2001). Concrete elements such as foundations (groundwater containing sulfuric acid due to oxidization of pyrite in backfill), industrial floors of chemical plants, basement walls of buildings near chemical plants and superstructures (due to acid rain) are susceptible to chemical attack by sulfuric acid. While all these exposures can be simulated by chemical immersion tests, sewage pipe systems suffer a special type of biogenic sulfuric acid corrosion and may require a combination of both chemical and microbiological tests. The present study adopted chemical immersion tests to assess, in general, the acid resistance of concrete made of PLC compared to GU counterparts, in order to cover a wider spectrum of applications involving acidic media. GU and PLC specimens were fully immersed for two consecutive 45-day (i.e. 90 days) time intervals in aggressive sulfuric acid solutions with an initial concentration of 5%. After the first time interval (45 days), the solutions were renewed with fresh ones. Each group (GU and PLC) of mixtures had its own acid bath to provide similar acidic environments for the GU and PLC mixtures and isolate the neutralization effect (if any) to the PLC mixtures. In both time intervals, the initial pH (0.1) of the solution increased rapidly and reached an average value of 2.5 without any pH control. It is worth mentioning that there is currently no standardized procedure to test the resistance of concrete to sulfuric acid attack; the test regime adopted herein simulates very aggressive chemical exposure conditions that may occur under severe field conditions.

Table 1: Proportions of mixtures per cubic meter of concrete

Mixture ID.	Cement (kg/m^3)	Water (kg/m^3)	Fly Ash (kg/m^3)	Silica Fume (kg/m^3)	Coarse Aggregate (kg/m^3)	Fine Aggregate (kg/m^3)	28 day Compressive Strength (MPa)
GU group							
GU	390	156	-	-	1228	614	55
GUF	273	156	117	-	1200	600	46
GUSF	370	156	-	20	1212	606	65
PLC group							
PLC	390	156	-	-	1228	614	60
PLCF	273	156	117	-	1200	600	47
PLCSF	370	156	-	20	1212	606	62

2.3 Tests

The compressive and splitting tensile strengths of concrete cylinders and prims at 28 days were determined according to ASTM C39 (2015) and C496 (2011), respectively. Specimens were extracted from the solution weekly, rinsed three times within the solution to remove loose reaction products, blotted with a paper towel and left to dry at 20°C and 50% RH for 30 min before visual assessment and recording their masses. For each specimen, the cumulative mass loss at the end of each week (ML_t) was calculated by:

$$[1] \qquad ML_t = \frac{(M_t - M_i)}{M_i} \times 100$$

where, M_t is the mass of specimen at time t (kg), and M_i is the initial mass of specimen before exposure to sulfuric acid (kg).

After 90 days of exposure to 5% sulfuric acid solutions, all cylindrical specimens were tested for residual splitting tensile load relative to that of companion specimens stored in the curing chamber (22±2°C and 98% RH) for the same period of time, according to Equation 2:

$$[2] \qquad L = \frac{L_a - L_c}{L_c} \times 100$$

where, L is the average change in splitting tensile load of specimens from a specific mixture, L_a is the average splitting tensile load of the specimens immersed in the acidic solution for 90 days, and L_c is the average splitting tensile load of the corresponding specimens stored in standard curing conditions for 90 days.

To investigate the degradation mechanisms within the surface of specimens, microanalysis was conducted on fracture surfaces from selected mixtures, which were examined using scanning electron microscopy (SEM). These samples were carbon coated and examined under the secondary mode of SEM; in addition, energy-dispersive X-ray analysis (EDX) was also used to characterize the crystals identified during the SEM investigation. To complement the observations from SEM, thermal analysis using differential scanning calorimetery (DSC) were conducted on powder samples extracted from the surface (0 to 20 mm) of selected specimens exposed to the sulfuric acid attack. This powder was prepared from carefully extracted fracture pieces (not including large coarse aggregate) of specimens, which were pulverized to fine powder passing through sieve #200 (75 μm).

3 RESULT AND DISCUSSION

3.1 Visual Assessment

Immediately after immersion in the solution, the acid started to react with all the concrete specimens from the GU and PLC groups as indicated by numerous air bubbles rising up to the surface of the solution. Since the first day of exposure, white powdery material (identified as gypsum by DSC) deposited progressively on the surface of all specimens, with no notable differences among specimens from the single or blended binders in the GU and PLC groups throughout the entire exposure. Continual leaching of gypsum led to an off-white residue in the bottom of containers with a consistency similar to cement paste. At the end of the first week of immersion, all the specimens had exposed aggregates, and with the progression of acidic reactions, they became significantly exposed with incidental disintegration of coarse aggregate. After 45 days of exposure, when the solution was renewed, debonding of aggregate from the paste was notable. At the end of exposure (90 days), all specimens generally had uneven surfaces (due to using siliceous aggregate) surrounded by soft paste, which implicates the decomposition of the cementitious matrix at and near the reaction zone with the acidic solution. Figure 1 depicts the visual progression of damage at different ages of exposure. At the end of the exposure, the manifestations of damage were comparable for specimens made from the single and blended binders in the GU and PLC groups. Thus, other physico-mechanical parameters and microstructural features are needed to evaluate the relative performance of the mixtures.

Figure 1: Feaures of damage of concrete specimens immersed in the 5% sulfuric acid solutions after 1 (left),7 (middle) and 13 (right) weeks.

3.2 Mass Loss

The trends of mass loss for specimens from all mixtures exposed to the 5% sulfuric acid solutions are shown in Figure 2, and the total mass loss of the mixtures with its standard error bars is shown in Figure 3. After 90 days of exposure, the mass loss of the GU and PLC mixtures ranged from 18 to 23% and 20 to 23%, respectively. Since the first week of exposure, notable mass loss of about 4 to 5% was observed for all the mixtures, and the rate of mass loss continued to increase up to the fourth week of exposure. Subsequently, the rate of mass loss was minimal or unchanged between the fifth and seventh week of exposure, due to absorption of solution and the increase of the pH in the solution up to 2.5; however, the rate of mass loss increased sharply from the seventh week up to the end of exposure due to renewing the sulfuric acid solutions. At the end of exposure, concrete mixtures made from GU and GU with silica fume (GUSF) had relatively higher total mass loss (about 17% and 4%, respectively) than that of the corresponding specimens made from PLC. This trend might be due to the acid neutralization effect offered by the limestone component (12% by mass of clinker) in PLC. However, specimens made from the GU and fly ash binder (GUF) yielded less mass loss (reduction of 12%) than that of the PLCF specimens. Within the GU group, the standard error bars (Figure 3) indicate that the use of 30% fly ash had a significant effect on the average mass loss results, as it led to 24% reduction in mass loss compared to the control specimens (GU). Comparatively, the combination of 5% silica fume with 95% GU had no significant effect on the mass loss results. For the PLC mixtures, incorporation of fly ash with PLC (PLCF) had no significant effect on the mass loss results (overlapping range of error bars with the PLC specimens), while incorporation of silica fume notably increased the amount of mass loss by 13% compared to the control (PLC) and fly ash (PLCF) specimens. The higher mass loss of concrete prepared with silica fume in comparison to mixtures (PLC containing 6-20% limestone) without silica fume under a sulfuric acid exposure has also been reported in other studies (e.g. Girardi et al. 2010). Indeed, the mass loss results suggest that the type of binder affect the behavior of concrete in the acidic solution; thus, the reaction and sound zones in the mixtures, were further studied by thermal and microscopy analyses (Section 3.4).
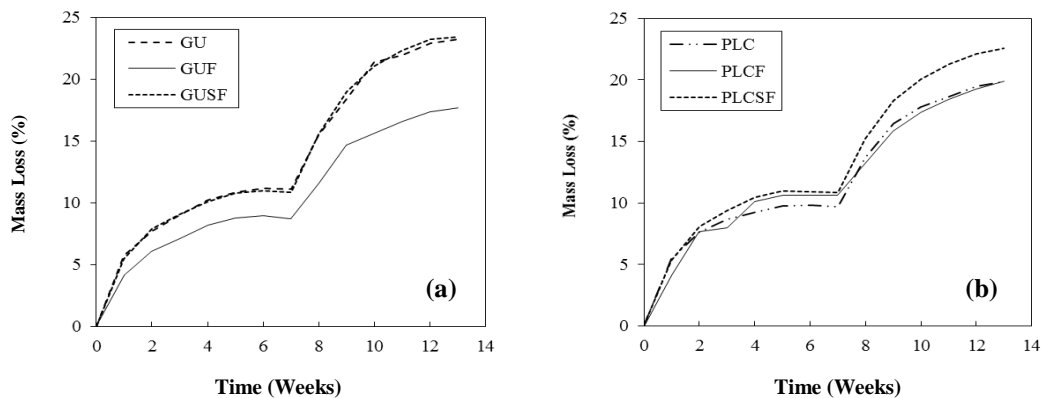

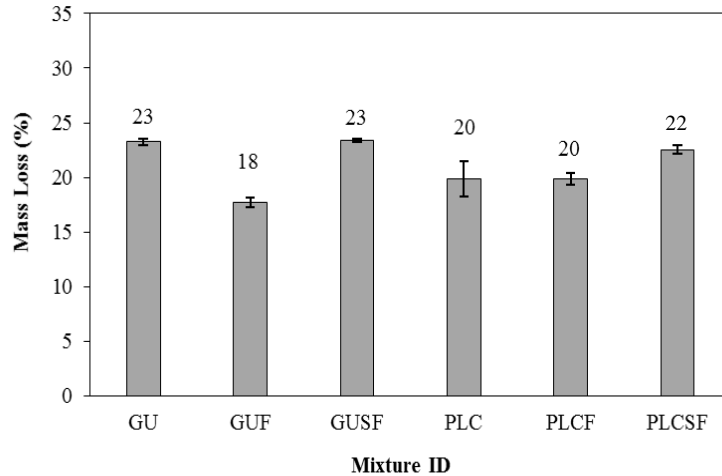Figure 2: Average mass loss with time for mixtures with: (a) GU, and (b) PLC.

Figure 3: Average mass loss after 90 days of exposure.

3.3 Change of Splitting Tensile Load

The common approach in previous studies on the resistance of concrete to sulfuric acid attack is to determine mass loss and residual compressive strength of specimens to evaluate the relative performance of various concrete mixtures. Since the development pattern of flexural and tensile strengths is similar to that of compressive strength (Hooton et al. 2007) and concrete in practice frequently fails under tensile stresses, the current study focused on determining the change in splitting tensile load following the recommendations of Miletić et al. (1998) and Bassuoni and Nehdi (2012). The change in splitting tensile load (crushing load at failure) of all mixtures is depicted in Figure 4. At the end of exposure, GU specimens had a slight increase in the splitting tensile load (about 6%), while the splitting tensile load for the PLC specimens was almost unchanged. The highest loss in splitting tensile load was observed for the specimens made from the GU and fly ash binder (GUF), even though these specimens yielded the lowest mass loss (18%) among all the mixtures. Similarly, the PLC specimens comprising fly ash (PLCF) had the highest loss (10%) in the splitting tensile load in the PLC group. Specimens containing silica fume had a mixed trend in terms of the change of the splitting tensile load, as GUSF specimens had minor loss (1%), while the PLCSF specimens had a loss of 8% despite that specimens from both mixtures showed a comparable mass loss of about 23%.
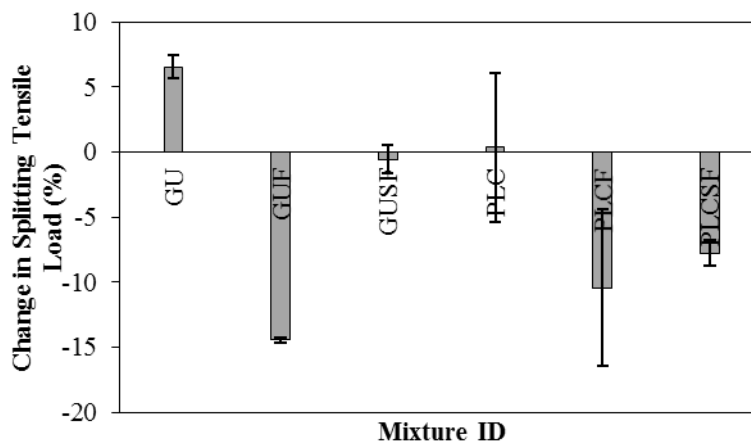

Figure 4: Change of the splitting tensile load of all mixtures after 90 days of immersion in the 5% sulfuric acid solutions.

Figure 5 illustrates the relationship between the mass loss and change in splitting tensile load of specimens. It can be observed that there is a scatter of data among the six mixtures, with counterintuitive trends in the sense that mixtures with lower mass loss (e.g. GUF and PLCF) had higher loss in the splitting tensile load and vice versa. While some researchers (e.g. Chang et al. 2005) argue that the use of crushing load provides a more reliable indicator than the mass change for assessing the deterioration of concrete in acidic environments, others (e.g. Miletić et al. 1998, Bassuoni and Nehdi 2007) showed that these two parameters are not correlated. Previous studies (Bassuoni et al. 2007; Siad et al. 2010) also did not find any specific relationship between these parmaters and reported strength (compressive) gain, relative to the intial strength before exposure, of many mixtures after immersion in acidic solutions. The observed results for the change in splitting tensile load (loss or gain) have been affected by multiple factors such as the geometry of tested specimens and type of binder. For example, in contrast to testing unexposed specimens stored in the curing room, concrete specimens exposed to the acidic solution had a relatively variable geometry (uneven surface, Figure 1) along their height leading to planes of stress concentration, load eccentricity and non-uniform stress distribution, which might have contributed to reducing the crushing load of some specimens (GUF, PCF, PLCSF). The behaviour of GUF and PLCF specimens can be also attributed to the higher later-age strength gain of the concrete specimens comprising 30% fly ash stored in the curing chamber (i.e. higher loss in the percentage of crushing load, Equation 2), which is typical of Class F fly ash (Mehta and Monteiro, 2014). In addition, the crushing load is influenced by the volume of the sound concrete core of specimens or the effective volume. It was stated that the inner core of concrete may undergo significant densification in an acidic medium due to continual hydration of the paste, reduction in calcium-to-silicate ratio and polymerisation of C–S–H (Macías et al. 1999). This argument may be substantiated by the specimens (GU, GUSF, PLC) that showed comparable or even slightly higher splitting tensile load than that of the corresponding specimens stored in the curing room for the same time interval. Hence, it can be deduced the mass loss and change in strength of concrete exposed to acidic media are two independent parameters; the former reflects the deterioration/decomposition that takes place in the exposed surface, while the latter is affected by a number of parameters including the texture of testing surface and alteration of the bulk volume of the sound core of specimens.
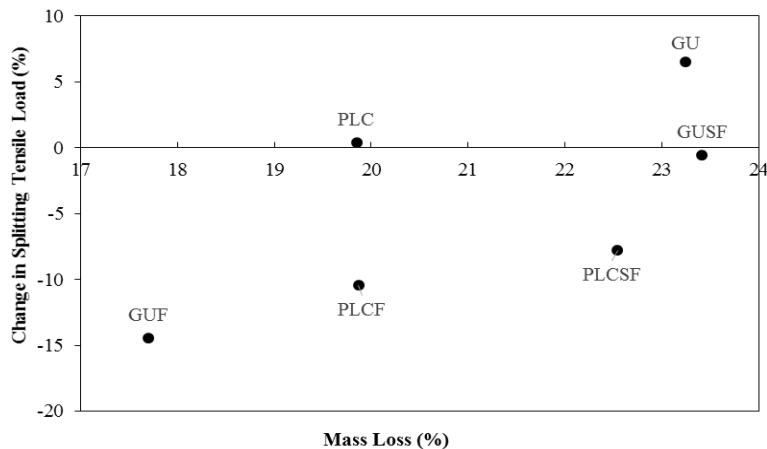

Figure 5: Mass loss versus change in splitting tensile load after 90 days of exposure to the 5% sulfuric acid solutions.

4. THERMAL AND MICROSTRUCTURAL ANALYSES

Table 2 provides a summary for the DSC analysis of the main phases (ettringite, gypsum, portlandite) in the cementitious matrix of all mixtures with their corresponding enthalpies, and Figure 6 shows exemplar micrographs from the SEM analysis. After 90 days of exposure, micrographs taken from fracture surfaces of the exposed specimens (0 to 10 mm from the surface) indicated that the surface of concrete underwent significant deterioration due to the sulfuric acid attack (Figure 6a). As confirmed by EDX, the reaction zones (0 to 2 mm from the exposed surface) comprising gypsum crystals (e.g. Figure 6b) with incidental features of ettringite in areas towards the sound paste [more than 6 mm from the exposed surface] (e.g. Figure. 6c), where the pH of the matrix was still sufficiently high to maintain the stability of ettringite. It is worth noting that the reaction zone within all specimens were notably thin (0 to 2 mm in thickness), as the deteriorated surface readily deposited in the containers, and thus the powder

samples prepared for the DSC tests contained a considerable part of the sound matrix. The amounts of portlandite, as expressed by enthalpy, in specimens from GU, GUSF, PLC, and PLCSF mixtures stored in the curing chamber were comparable to that in the corresponding specimens immersed in the acid solutions (Table 2). This suggests that the sound part of the exposed specimens had a continual hydration activity, which generally links to the trends of the change in the splitting tensile load for these specimens. Specimens incorporating 5% silica fume had less portlandite than that in the control specimens (Table 2), which might make the C-S-H more vulnerable to decomposition in acidic media. This trend was primarily visible for the PLCSF compared to PLC specimens.

Table 2: Enthalpies (J/g) of the main phases in the cementitious matrix

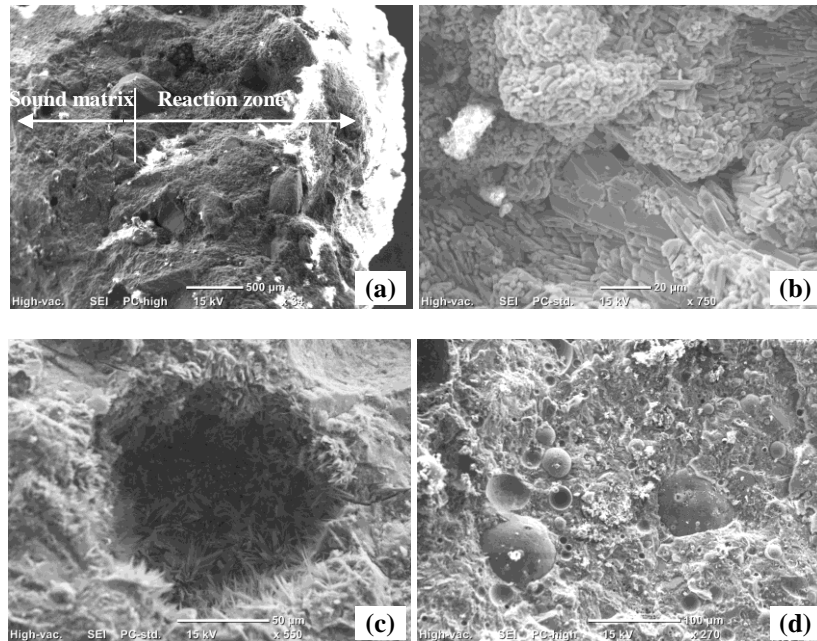| Mixture ID. | After 90 days in the sulfuric acid solutions | | | After 90 days in the curing chamber |
	Ettringite (90-100°C)	Gypsum (120-135 °C)	Portlandite (420-440 °C)	Portlandite (420-440 °C)
GU group				
GU	13.9	5.2	58.1	56.8
GUF	8.2	3.8	31.3	16.3
GUSF	5.3	14.7	38.6	40.1
PLC group				
PLC	5.6	3.7	52.8	50.9
PLCF	7.7	5.2	30.7	18.5
PLCSF	2.9	4.6	37.8	38.5

Figure 6: Exemplar micrographs for: (a) deteriorated surface and sound part (GUSF), (b) gypsum crystals in the reaction zone (PLC), (c) ettringite rosettes growing in an air void away from the surface (GU), and (d) unreacted fly ash particles within the reaction zone (PLCF).

For the fly ash mixtures GUF and PLCF, however, the amounts of portlandite in the specimens stored in the curing chamber were 40 to 50% that in the corresponding specimens immersed in the acid solution. In the curing chamber, there was efficient later-age pozzolanic activity of Class F fly ash as indicated by the consumption of portlandite, which augments the earlier discussion in Section 3.3 about the marked loss of strength for mixtures containing fly ash. However, when these mixtures were immersed in the sulfuric acid solutions, it seems that the pozzloanic reactivity of fly ash was considerably discounted or hindered, as indicated by the increase in the portlandite content due to the hydration reactions of the GU component in the binder (Table 2), and the occurrence of numerous unreacted fly ash particles in and away from the reaction zone (e.g. Figure 6d), especially that these specimens were cured for 28 days only. It appears that the existence of abundantly unreacted fly ash particles, encapsulated by gypsum crystals within the reaction zone might help discounting the rate of sulfuric acid attack on the cementitious matrix. According to Table 2 and Figure 6d, it can be deduced that fly ash particles acted as inert filler in acidic media (Kim et al. 2003), in a similar manner to siliceous aggregate, thus the paste volume vulnerable to acid reactions was reduced. Perhaps, if the fly ash specimens were adequately cured (56 days or more) before exposure, this filler effect might have diminished. In the PLCF specimens, the effect of fly ash was not magnified by the neutralization capacity of the limestone component, as the substitution of PLC by 30% fly ash diluted the amount of limestone to about 8% roughly, and the total paste volume of PLCF was more (6%) than that of PLC. Hence, the net effect led to a comparable behaviour for specimens made from PLC and PLCF.

5. CONCLUSIONS

Considering the high concentration of sulfuric acid solutions, period of exposure, testing methods, and the material types as well as proportions used in this study, the following conclusions can be drawn:

- Visual assessment did not show distinctive features of damage among specimens made from the single and blended binders in the GU and PLC groups.
- The mass loss and change in strength of concrete exposed to acidic media are two independent parameters; the former reflects the decomposition that takes place in the exposed surface, while the latter is affected by other parameters including the testing surface and alteration of the bulk volume of the sound part.
- Specimens from the PLC mixture had less total mass loss than that of the corresponding specimens from the GU mixture, due to the acid neutralization effect offered by the limestone component (12% by mass of clinker) in PLC.
- While 5% silica fume tended to increase the vlunerability of paste to decomposition in acidc media, specimens containg 30% fly ash had better resistance to the sulfuric acid attack, as reflected by the mass loss results. GUF and PLCF specimens, which were cured for 28 dys, comprised variable sizes of unreacted fly ash particles which acted as inert filler in the reaction zone, in a similar manner to siliceous aggregate, thus reducing the volume of paste vulnerable to acidic attack.
- In the PLCF specimens, the effect of fly ash was not amplified by the neutralization capacity of the limestone component, since the substitution of PLC by 30% fly ash diluted the amount of limestone powder in the binder; hence, the net effect led to a comparable behaviour to specimens made from the PLC mixture.

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REFERENCES

Bassuoni, M. T., and Nehdi, M. L. 2007. Resistance of self-consolidating concrete to sulfuric acid attack with consecutive pH reduction. *Cement and Concrete Research*, 37: 1070–1084.

Bassuoni, M. T., Nehdi, M. L., and Amin, M. 2007. Self-compacting concrete: using limestone to resist sulfuric acid. *ICE - Construction Materials,* 160: 113–123.

Bassuoni, M. T., and Nehdi, M. L. 2012. Resistance of self-consolidating concrete to ammonium sulphate attack. *Materials and Structures*, 45: 977–994.

Chang, Z. T., Song, X. J., Munn, R., and Marosszeky, M. 2005. Using limestone aggregates and different cements for enhancing resistance of concrete to sulphuric acid attack. *Cement and Concrete Research*, 35: 1486 – 1494.

De Belie, N., Monteny, J., Beeldens, A., Vincke, E., Van Gemert, D., and Verstraete, W. 2004. Experimental research and prediction of the effect of chemical and biogenic sulfuric acid on different types of commercially produced concrete sewer pipes. *Cement and Concrete Research*, 34: 2223–2236.

Ghiasvand, E., Ramezanianpour, A. A., and Ramezanianpour, A. M. 2015. Influence of grinding method and particle size distribution on the properties of Portland-limestone cements. *Materials and Structures*, 48: 1273–1283.

Girardi, F., Vaona, W., and Di Maggio, R. 2010. Resistance of different types of concretes to cyclic sulfuric acid and sodium sulfate attack. *Cement and Concrete Composites*, 32: 592–602.

Hobbs, D. W., and Taylor, M. G. 2000. Nature of the thaumasite sulfate attack mechanism in field concrete. *Cement and Concrete Research*, 30: 529–533.

Hooton, R., Nokken, M., and Thomas, M. 2007. Portland-Limestone Cement: State-of-the-Art Report and Gap Analysis for CSA A3000. *Cement Association of Canada*, University of Toronto.

House, M. W., and Weiss, W. J. 2014. Review of Microbially Induced Corrosion and Comments on Needs Related to Testing Procedures. *4th International Conference on the Durability of Concrete Structures*, Purdue University, West Lafayette, IN, USA.

Islander, R. L., Devinny, J. S., Mansfeld, F., Postyn, A., and Shih, H. 1991. Microbial Ecology of Crown Corrosion in Sewers. *Journal of Environmental Engineering*, American Society of Civil Engineers, 117: 751–770.

Kim, A. G., Kazonich, G., and Dahlberg, M. 2003. Relative solubility of cations in class F fly ash. *Environmental Science and Technology*, 37: 4507–4511.

Macías, A., Goñi, S., and Madrid, J. 1999. Limitations of Köch-Steinegger test to evaluate the durability of cement pastes in acid medium. *Cement and Concrete Research*, 29: 2005–2009.

Marzouki, A., Lecomte, A., Beddey, A., Diliberto, C., and Ben Ouezdou, M. 2013. The effects of grinding on the properties of Portland-limestone cement. *Construction and Building Materials*, 48: 1145–1155.

Mehta, P.K. and Monteiro, P.J.M. 2014. *Concrete*, McGraw Hill Education, USA.

Miletić, S., Ilić, M., Ranogajec, J., Marinovič-Neducin, R., and Djurić, M. 1998. Portland Ash Cement Degradation in Ammonium-Sulfate Solution. *Cement and Concrete Research*, 28: 713–725.

O'Connell, M., McNally, C., and Richardson, M. G. 2010. Biochemical attack on concrete in wastewater applications: A state of the art review. *Cement and Concrete Composites*, 32: 479–485.

Parker, C. D. 1951. Mechanics of Corrosion of Concrete Sewers by Hydrogen Sulfide. *Sewage and Industrial Wastes*, 23: 1477-1485.

Ramezanianpour, A. A., Ghiasvand, E., Nickseresht, I., Mahdikhani, M., and Moodi, F. 2009. Influence of various amounts of limestone powder on performance of Portland limestone cement concretes. *Cement and Concrete Composites*, 31: 715–720.

Ramezanianpour, A. M., and Hooton, R. D. 2013. Sulfate resistance of Portland-limestone cements in combination

with supplementary cementitious materials. *Materials and Structures*,46: 1061-1073.

Roy, D., and Arjunan, P. 2001. Effect of silica fume, metakaolin, and low-calcium fly ash on chemical resistance of concrete. *Cement and Concrete Research*, 3: 1809–1813.

Siad, H., Mesbah, H., Khelafi, H., Kamali-Bernard, S., and Mouli, M. 2010. Effect of mineral admixture on resistance to sulphuric and hydrochloric acid attacks in self-compacting concrete. *Canadian Journal of Civil Engineering*, 37: 441–449.

Tagnit-hamou, A., Saric-coric, M., and Rivard, P. 2005. Internal deterioration of concrete by the oxidation of pyrrhotitic aggregates. *Cement and Concrete Research*, 35: 99–107.

Thomas, M. D. A., Hooton, D., Cail, K., Smith, B. A., De Wal, J., and Kazanis, K. G. 2010. Field Trials of Concretes Produced with Portland Limestone Cement. *Concrete international*, 35: 35–41.

Tsivilis, S., Chaniotakisb, E., Badogiannis, E., Pahoulasa, G., and Ilias, A. 1999. A study on the parameters affecting the properties of Portland limestone cements. *Cement and Concrete Composites*, 21: 107–116.