RESPONSE OF CONCRETE TO INCREMENTAL LEVELS OF SULFURIC ACID ATTACK

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Abstract: Concrete elements in sanitary sewer pipes, wastewater treatment plants, pumping lift stations, junction chambers, etc. are exposed to acidic environments. However, many field cases 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 acidic attack, which can decalcify and disintegrate the hydrated cement paste to various levels based on exposure conditions and type of concrete. Hence, the aim of this study is to investigate the resistance of concrete incorporating different types of cement (general use or portland limestone cement (PLC) and supplementary cementitious materials (SCMs) to progressive levels of sulfuric acid attack. The study comprised full immersion of test specimens in sulfuric acid solutions for two consecutive time intervals (twelve weeks 12 weeks each) at a pH of 4.5 followed by a pH of 1.0. Physical and microstructural results revealed that surface deterioration of concrete under sulfuric acid attack was dependent on the level of solution aggression. While PLC may slightly improve the resistance of concrete to sulfuric acid attack, SCMs may affect the performance of concrete adversely.

Keywords: Sulfuric acid, Portland limestone cement, SCMs, pH, Surface deterioration.

1   INTRODUCTION

Sulfuric acid is one of the most aggressive and destructive chemicals, which can cause severe degradation and damage to concrete structures. Concrete deterioration due to this acidic solution has been documented worldwide, for example, 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]. High alkalinity of concrete make it engages in reactions when 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], due to the so-called microbially induced corrosion (MIC) of concrete, which significantly reduces the lifespan of concrete infrastructure. 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. Beddoe and Dorner (2005) reported that using acid resistant aggregates in concrete such as (e.g. quartz) limits the damage to paste matrix. Compared to quartz, the neutralization capacity of concrete made with carbonaceous aggregates, such as limestone or dolomite, will increase with the volume fraction of calcite in the aggregate. However, at lower porosity, the reaction between acids and limestone aggregates

occurs at aggregate surface, which will not amplify the neutralization process due to the lower exposed surface area [Beddoe and Dorner 2005; 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 general use cement (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 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 in 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 by 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 cement 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 sulfuric acid solution with incremental levels of aggression.

2   EXPERIMENTAL PROGRAM

2.1   Materials and Mixtures

The cements used in this study were GU and PLC, 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, specimens were fully immersed (solution-to-specimens' volume ratio of 2) in sulfuric acid solution to provoke mild and severe exposures. Concrete elements such as foundations (groundwater containing sulfuric acid due to oxidization of pyrite in backfill or as an aggregate), 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. 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. Two consecutive time intervals (12 weeks each, phase I and phase II) involving sulfuric acid solutions with concentrations of 0.00015% and 1.12% and pH thresholds of 4.50 and 1, respectively were implemented in this study (Figure1). Each group (GU and PLC) of specimens 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. Upon immersion of specimens, the initial pH of the solution was kept constant within each phase. At the end of phase I, the solutions was replaced with a fresh one with higher level of agression (phase II). There is currently no standardized procedure to test the resistance of concrete to sulfuric acid attack. However, the ASTM C267 (2012) test method provides general guidelines to test the chemical resistance of mortars and polymer concretes. The concentrations and pH range adopted herein simulate incremental exposure (mild to severe) conditions, which may occur in the field.

Table 1: Proportions of mixtures per cubic meter of concrete

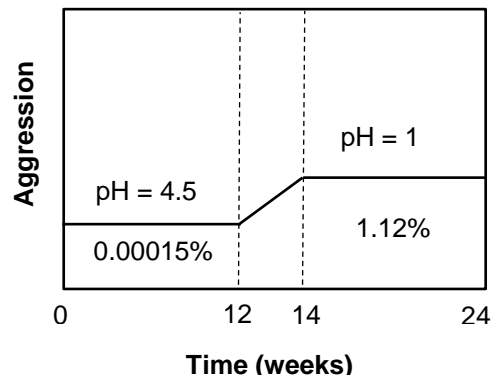| Mixture ID.	Cement (kg/m³)	Water (kg/m³)	Fly Ash (kg/m³)	Silica Fume (kg/m³)	Coarse Aggregate (kg/m³)	Fine Aggregate (kg/m³)	28 day Compressive Strength (MPa)
GU group							
GU	390	156	-	-	1228	614	55
GUF	273	156	117	-	1200	600	46
GUSF	370	156	-	20	1212	606	65
PLC group							
PLC	390	156	-	-	1228	614	60
PLCF	273	156	117	-	1200	600	47
PLCSF	370	156	-	20	1212	606	62

Figure 1: Incremental aggression of the sulfuric acid exposure.

2.3   Tests

Before exposure, the initial masses at 28 days were recorded for the concrete prisms to calculate the cumulative mass change versus time of exposure. 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] $ML_t = \dfrac{(M_t - M_i)}{M_i} \times 100$

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 Phase I, cylindrical specimens were tested for residual splitting tensile load according to ASTM C496 (2011) 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] $L = \dfrac{L_a - L_c}{L_c} \times 100$

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 at specific time, and L_c is the average splitting tensile load of the corresponding specimens stored in standard curing conditions at the same period of time. This mechanical test was not possible at the end of Phase II due to irregularities of the surface of specimens due to significant mass losses.

Microanalysis was conducted on fracture surfaces from selected specimens, which were examined using scanning electron microscopy (SEM). These samples were carbon coated and studied under the secondary mode of SEM; in addition, energy-dispersive X-ray analysis (EDX) was used to characterize the crystals identified during the SEM investigation. To complement the observations from SEM, thermal analysis using differential scanning calorimetry (DSC) were conducted on powder samples extracted from the surface (0 to 10 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   RESULTS AND DISCUSSION

3.1   Visual assessment

After 12 weeks of exposure (Phase I), all the GU and PLC specimens subjected to continuous immersion in the low concentration (0.00015% and pH threshold of 4.5) remained intact without distinctive features of damage (Figure 2a). However, after immersion in the higher concentration solution (phase II; 1.12% concentration and pH threshold of 1.0), 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. At the end of Phase II exposure, a significant amount of off-white residue deposited in the bottom of containers which implicates the continuous leaching of the corroded layer of concrete to the acidic solution. Figure 2b depicts the visual features of damage of deteriorated specimen after Phase II.
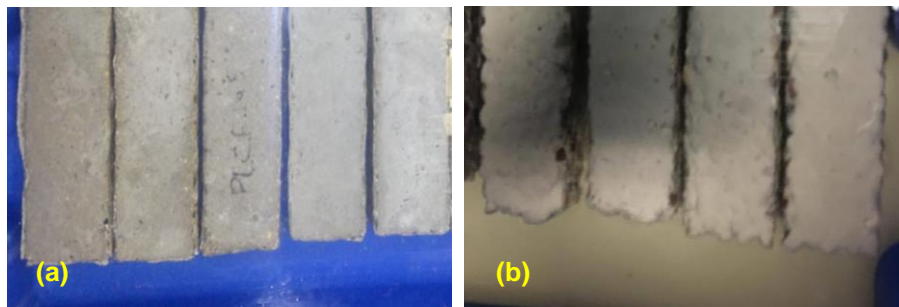

Fig. 2: Features of damage of concrete specimens immersed in the sulfuric acid solutions after: (a) Phase I, and (b) Phase II.

3.2   Mass Change

The trends of mass change for specimens from all mixtures exposed to the consecutive 0.00015% and 1.12% sulfuric acid concentrations are shown in Figure 3(a)-(b). During Phase I, the specimens showed a steady mass gain (maximum of 0.6%) with time, without notable differences among specimens from the single and binary binders in the GU and PLC groups. This might be mainly attributed to solution absorption, which is expected at early stages of chemical immersion tests at low acidic concentrations. During Phase II, the rate of mass change of specimens was approximately 0.65% (loss) per week and continued to increase steadily up to the end of this exposure. The total mass loss of the GU and PLC groups ranged from 6 to 8% and 5 to 6%, respectively, without notable differences among specimens from the single and blended binders. This was statistically supported by the analysis of variance (ANOVA) at a significance level $\alpha = 0.05$. According to ANOVA, exceeding the critical value (F_{cr}) of an F-distribution density function reflects that the tested variable significantly affects the mean of the results [Montgomery, 2014]. For example, the results of mass loss showed that the variation in the type of binder in the GU group (GUF and GUSF) relative to the reference binder had F values of 0.08 and 2.85, respectively, which were less than the F_{cr} of 7.70. These trends were also valid for the PLC counterparts.
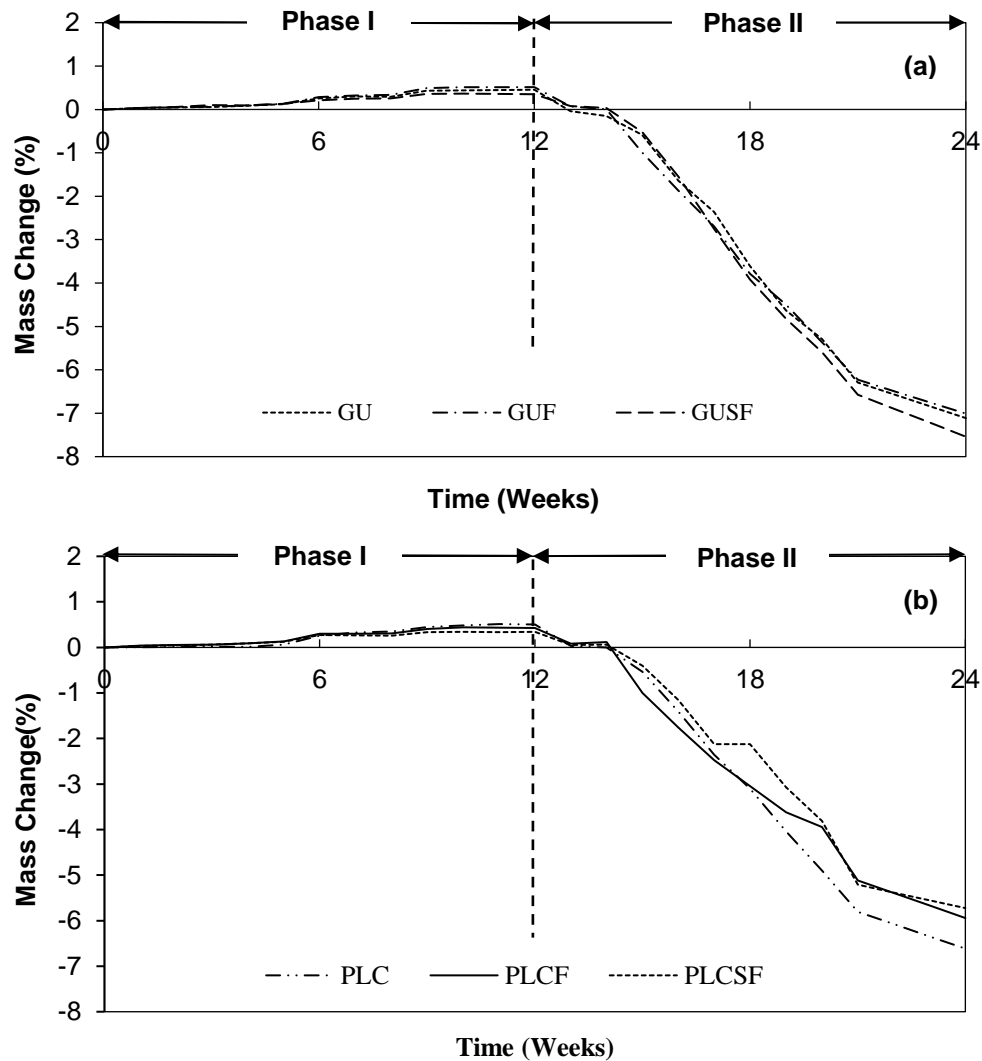
Figure 3: Average mass change with time for mixtures from the: (a) GU, and (b) PLC groups.

3.3   Change of Splitting Tensile Load

Since compressive loads may tend to close cracks originating from deposition of reaction products in the confined pore space and concrete in practice frequently fails under tensile stresses, the current study determined the change in splitting tensile load of exposed specimens relative to counterparts kept in a curing chamber for the same period of time. The change in splitting tensile load (crushing load at failure) of all specimens with its standard error bars after Phase I is shown in Figure 4. At the end of this exposure, the general trend for almost all specimens was a slight increase (less than 2.5%) in the splitting tensile load, which may be ascribed to some deposition of reaction products (gypsum) in the pore structure of the reaction zone at the surface of specimens, resulting in densification and corresponding minor increases in splitting tensile load. At the end of Phase II, all specimens generally had uneven surfaces (due to using siliceous aggregates) surrounded by soft paste, suggesting the decomposition of the cementitious matrix at and near the reaction zone, thus the splitting tensile test was not performed after this phase.
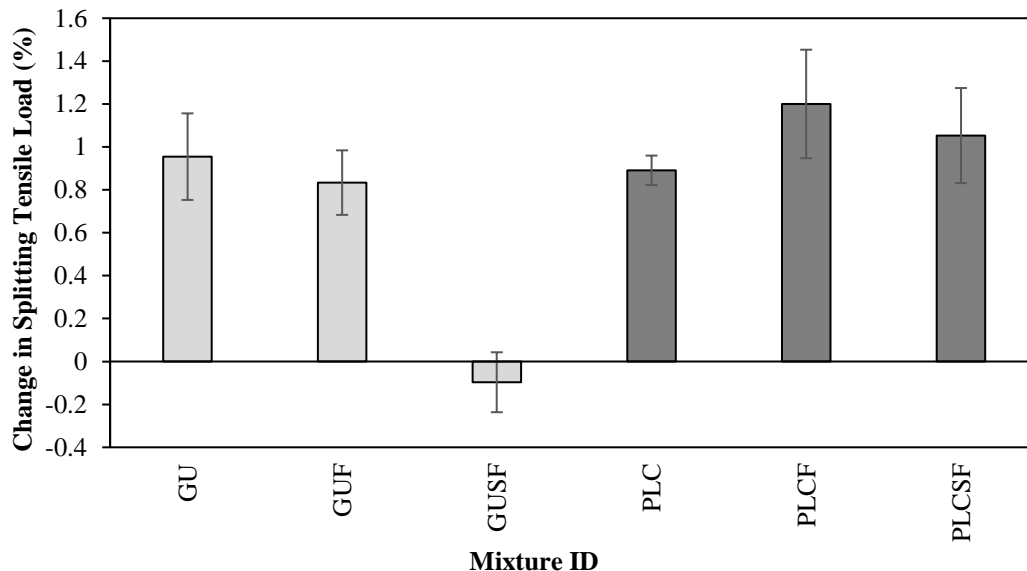

Figure 4: Change of the splitting tensile load of all specimens after 12 weeks of immersion in the low concentration sulfuric acid solution (Phase I).

3.4   Thermal and Microstructural Analyses

A semi-quantitative analysis based on the enthalpy concept (integration of heat flow peaks over temperature) can determine the relative phase formation, as the enthalpy of each phase is directly related to its amount [Brawn 1998]. 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 after phase I and phase II and Figures 5 and 6 show exemplar micrographs from the SEM and EDX analyses. After Phase I, micrographs taken from fracture surfaces (0 to 10 mm from the surface) of the exposed specimens indicated that the surface of concrete was intact, except that gypsum crystals were infilling some voids near the exposed surface (e.g. Figure 5). These trends were further corroborated by the DSC tests, as shown in Table 2. Gypsum was identified in all the samples as the key reaction product between the sulfuric acid solution and hydrated cement paste. However, it seems that the amount of gypsum formed in Phase I was insufficient to induce pressure to the confined pore space; thus, the samples did not suffer from surface deterioration (Figure 2a) and showed marginal increase in splitting tensile load. The drop in portlandite contents (after Phase I) in blended binder specimens incorporating fly ash and silica fume (in both the GU and PLC groups) was likely due to both effects of the

reduced cement content, the progression of pozzolanic reaction and the neutralization reaction with acid in the reaction zone in specimens.

Comparatively, after phase II, all the specimens underwent significant deterioration due to sulfuric acid attack (e.g. Fig. 6). As confirmed by EDX, the reaction zone comprised mainly of gypsum crystals in a coarse and decalcified matrix. These trends were further corroborated by the DSC analysis (Table 2). In both GU and PLC groups, the portlandite content in the blended specimens after Phase I (90 days) significantly decreased. As mentioned earlier, the depletion of the amount of portlandite in the matrix was due to dilution of the cement component and increased pozzolanic activity, resulting in production of additional/secondary C-S-H gel. However, this led to more volume of cementitious gel vulnerable to decomposition in severely aggressive acidic media as these specimens exhibited the highest amount of gypsum after Phase II. Finally, the slight improvement in the PLC specimens (less mass loss) might be due to the acid neutralization effect offered by the higher limestone (12%) component in PLC.

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

Mixture ID.	After Phase I (12 weeks)			After Phase II (24 weeks)			After 12 weeks in the curing chamber
	Ettringite	Gypsum	Portlandite	Ettringite	Gypsum	Portlandite	Portlandite
GU group							
GU	3.3	94.9	45.9	2	146	14.4	56.8
GUF	2.9	77.7	6.5	3.9	271.2	1.3	16.3
GUSF	3.3	76.5	12.6	1.0	242.8	8.6	40.1
PLC group							
PLC	4.3	54.2	45.2	2.9	193.6	16.6	50.9
PLCF	5.7	77.8	8.9	0.6	241.1	1.1	18.5
PLCSF	4.9	52.1	14.7	0.4	233	7.4	38.5

*Ettringite, Gypsum and Portlandite decomposed at 90-100°C, 120-135°C, and 420-450°C, respectively.
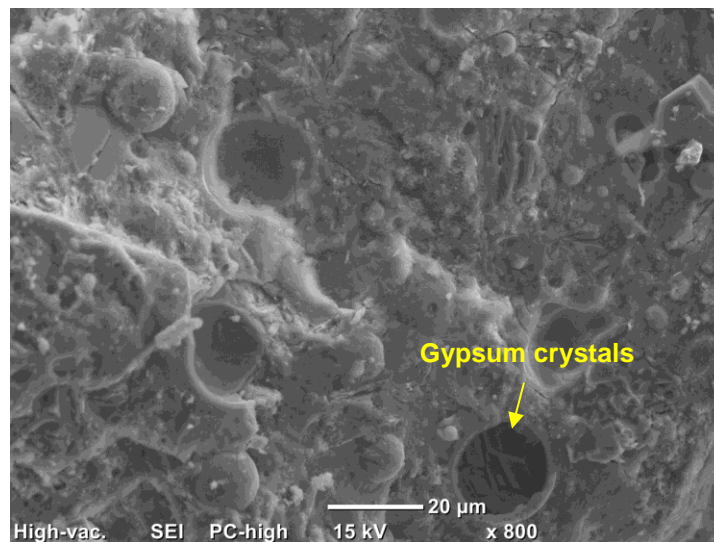

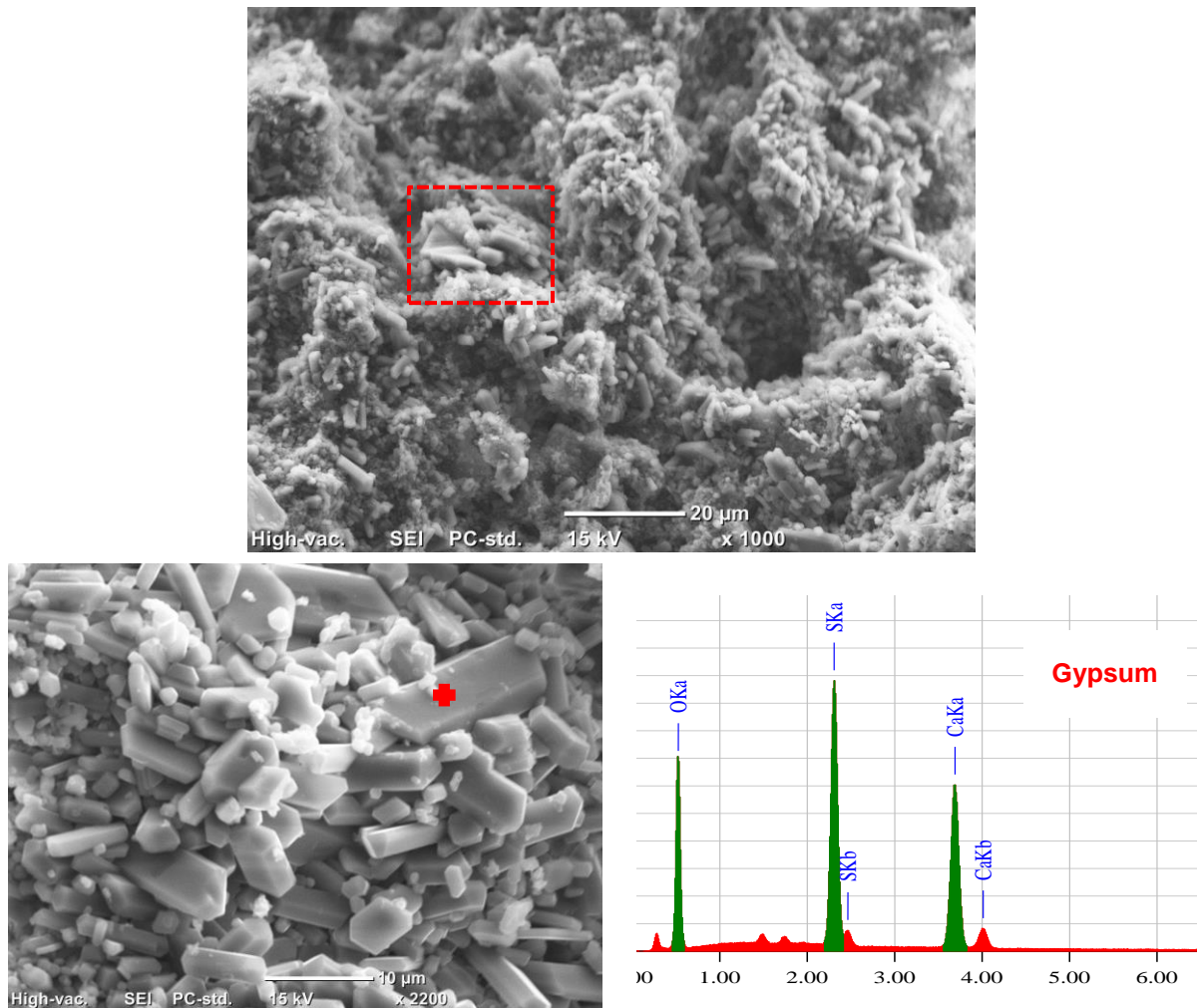Figure 5: Exemplar micrograph from SEM for an PLCF specimen after Phase I.

Figure 6: Exemplar micrographs of SEM and EDX analyses for an PLCSF specimen showing gypsum crystals in the reaction zone with corresponding EDX.

4   CONCLUSIONS

Based on the test results carried out by immersing concrete specimens in sulfuric acid solutions with incremental level of aggression (mild to severe), the following conclusions are drawn:

- Visual assessment of the mild exposure (Phase I) did not show distinctive features of damage among all specimens, while continuous leaching of the surface occurred during Phase II since the first cycle of exposure.

- All PLC specimens had marginally lower mass losses compared to the GU specimens. This slight improvement might be ascribed the acid neutralization effect offered by the higher limestone (12%) component in PLC.

- After Phase II, the mass loss results did not show distinctive trends between the single and blended binders in both the GU and PLC groups.

- In Phase I, gypsum formation was insignificant in specimens and it led to some strengthening of the cementitious matrix. Comparatively, the amount of gypsum formation increased with the level of aggression (Phase II), especially in matrices made from blended binders with higher volume of cement gel. This might implicate that concrete made from blended binders may suffer from significant deterioration under sever sulfuric acid conditions.

Acknowledgement

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