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Performance of blended concrete with supplementary cementitious materials under sulfuric acid - a systematic review

Comportamento de concreto misto com materiais cimentícios suplementares sob ácido sulfúrico - uma revisão sistemática

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ABSTRACT

Supplying sewerage systems in cities and factories has a high cost, both for design, execution, and maintenance. Reinforced concrete exposed to the aggressive acids produced by wastewater microorganisms receives costly coatings to avoid corrosion and impairment of structural functions. Thus, this systematic review had two main goals: (1) to identify the supplementary cementitious materials (SCM) that improve concrete resistance to chemical sulfuric acid attack (H_2SO_4) and (2) describe the performed tests to access concrete resistance to H_2SO_4 in laboratory conditions. After analyzing the scientific references collected on indexed bases, the study showed that the test methods used to appraise samples resistance do not follow a standard protocol, hindering quantitative analysis between distinct studies results. In general, concrete resistance to H_2SO_4 is evaluated by immersing concrete samples in high concentrated acid solutions and assessing its compressive strength and mass change on a 28 or 30 days base sequence. Using SCMs improve resistance to sulfuric acid, and binders made with silica fume had the best results. This review may encourage the creation of test protocols to assess the resistance of concrete to H_2SO_4 that allow further statistical analysis of the research results.

Keywords: SCM. Concrete durability. Concrete corrosion. Sulfuric acid attack.

RESUMO

Prover esgotamento sanitário em cidades e fábricas possui custos elevados tanto de projeto, quanto de execução e de manutenção. O concreto armado exposto aos ácidos agressivos produzidos pelos microrganismos dos efluentes acabam recebendo revestimentos custosos para evitar a corrosão e o comprometimento de suas funções estruturais. Assim, esta revisão sistemática teve dois objetivos principais: (1) identificar os materiais cimentícios suplementares (MCSs) que melhoram a resistência do concreto à corrosão por ácido sulfúrico de origem química (H_2SO_4) e (2) descrever as pesquisas laboratoriais realizadas para avaliar a resistência do concreto ao H_2SO_4. Após analisar as referências coletadas, o estudo mostrou que os métodos utilizados para avaliar a resistência dos corpos de prova de concreto não seguem um protocolo padrão, o que dificulta a análise quantitativa dos resultados de diferentes estudos. Em geral, a resistência do concreto ao H_2SO_4 é avaliada pela imersão dos corpos de prova em soluções com alta concentração de ácido e medição da resistência à compressão e da mudança de massa em períodos sequenciais de 28 ou 30 dias. O uso de MCSs aumenta a resistência ao ácido sulfúrico, sendo que os ligantes compostos por sílica ativa apresentam os resultados mais promissores. Espera-se que esta revisão encoraje a criação de protocolos de ensaio para avaliar a resistência do concreto ao H_2SO_4 que permitam uma análise estatística mais aprofundada dos resultados de diferentes pesquisas.

Palavras-chave: MCS. Durabilidade do concreto. Corrosão do concreto. Ataque de ácido sulfúrico.

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1. INTRODUCTION

Since the XIX century [1], researchers have worried about the microbiologically induced corrosion (MIC) of concrete in sewer structures due to the high cost of those installations—investments of thousands of millions of US dollars are demanded to develop sanitary facilities with a service life of at least 100 years [2]. However, since the concrete deterioration in the sewer environment can significantly reduce the service life of sewer networks, the 100 years requirement goes down to 10 years or fewer in extreme cases [3]. To cope with this, several researchers have evaluated how concrete in sewer structures behaves to understand how MIC takes place.

In general, the corrosion process has four steps [2–6]. The first occurs on the submerged biofilm of sewage facilities when anaerobic sulfate-reducing bacteria (SRB) act on the organic matter settled there, releasing aqueous hydrogen sulfide (H_2S), which escapes from the sewage in gaseous form. The next three steps occur right on the concrete surface and end up producing sulfuric acid (H_2SO_4), as schematized in Figure 1.

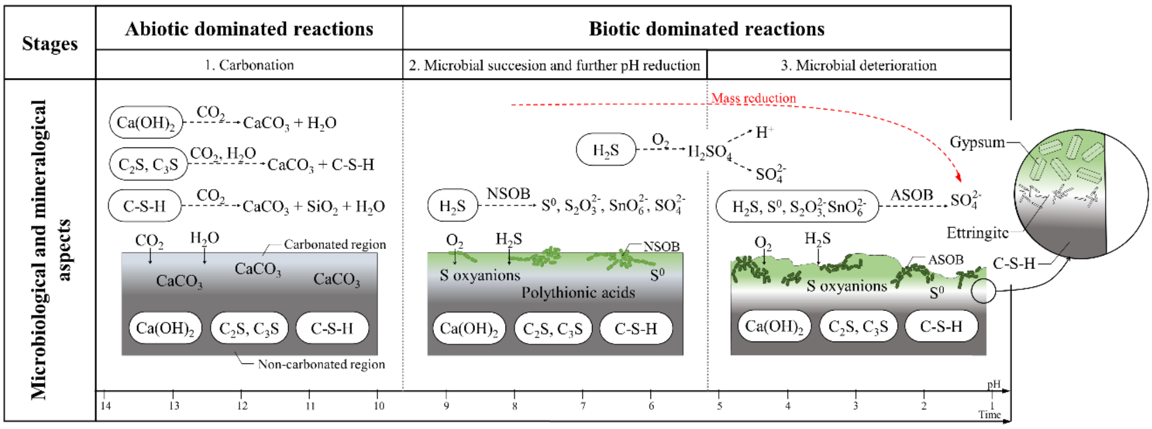

Figure 1: The three stages of microbiologically induced corrosion of concrete, compiled from the studies of WU *et al*. [2], ROBERTS *et al*. [6], ISLANDER *et al*. [7], and WEI *et al*. [8]. Carbonation equations adapted from SULAPHA *et al*. [9] and ZHANG, GHOULEH, and SHAO [10]. Note: the gray gradient in concrete indicates how sound is the material. NSOB: neutrophilic sulfur-oxidizing bacteria; ASOB: acidophilic sulfur-oxidizing bacteria.

The biogenic sulfuric acid reacts with concrete calcium compounds, such as calcium hydroxide ($Ca(OH)_2$), and generate a soft and porous gypsum layer that cracks [11] and detaches from concrete [5] due to volume increasing and wastewater turbulence. This process reduces concrete durability and increases the contact area for further corrosion [4], accelerating the degradation. Although biogenic sulphuric acid is the main cause of MIC in concrete, other corrosive elements can reduce concrete durability. Carbonation process, for example, can reduce concrete alkalinity and depassivate steel rebar [12]. Since biogenic sulfuric acid does not direct corrode steel rebar, chloride ions and oxygen penetrate through the porous layer formed during the MIC and react with the steel interface [13]. To avoid these pathologies and improve concrete service life, wastewater facilities currently employ corrosion-proof linings; however, they often have a high cost [14].

A more economical alternative to the expensive coatings involves developing a concrete self-resistant to the corrosion in sewers. Supplementary cementitious materials (SCM) have some promising results in laboratory conditions, mainly because, when added to concrete, they can reduce water demand, increase long-term strength, and improve durability in aggressive environments [15]. Understanding how SCM can contribute to concrete resistance under biogenic sulfuric acid corrosion and how researchers pursue this resistance are correlated goals.

However, to evaluate concrete resistance to corrosion in sewer conditions, we need a ratified, generally accepted testing method—which still does not exists [16–18], even though various methods have been developed and tested to evaluate concrete resistance to MIC (e.g., see [19]).

Therefore, we undertake a systematic literature review with two mains objectives: (1) to identify the SCM that better improve concrete resistance to sulfuric acid corrosion; and (2) to describe the chemical tests developed in the laboratory conditions to simulate corrosion in wastewater facilities.

2. MATERIALS AND METHODS

This review followed the PICO question: (P) in concrete made with different types of SCM, (I) the chemical corrosion of these specimens by sulfuric acid-(C) compared to the corrosion of concrete made with Ordinary Portland Cement-(O) leads to a lesser reduction of mechanical properties? Figure 1 illustrates the systematic review protocol undertaken in this research and the subsections below report the review process.

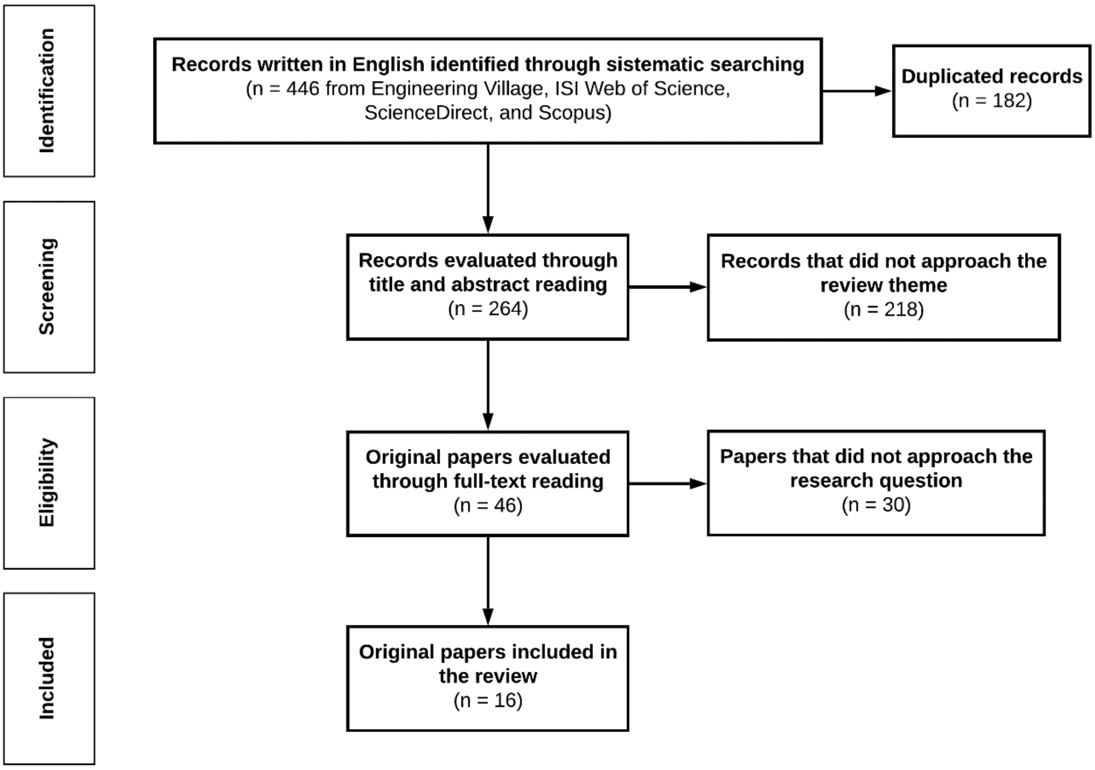

Figure 2: Systematic review flowchart.

2.1 Data sources

The Engineering Village, ISI Web of Science, ScienceDirect, and Scopus databases were searched from their inception to December 2020. The search string were: concrete and ("sulfuric acid" or "sulphuric acid") and (corrosion or deterioration) and (durability or resistance). The searches yielded 446 records. Excluding duplicates, we evaluated 264 papers.

2.2 Study selection

The review protocol limited the search to journal papers published in English (Table 1 lists other exclusion criteria adopted in this review). Reviewed the titles and paper abstracts, 46 out of 264 appeared to match the selection criteria. After a full review, 16 papers were selected [16, 20–34], representing 15 studies (the data published by [26, 27] regards the same research).

Table 1: Number of excluded papers per criteria.

CRITERIA	EXCLUDED
Do not have control samples made of Ordinary Portland cement	10
Do not report the behavior of concrete made with SCM	6
Do not evaluate concrete corrosion by chemical H_2SO_4	4
Added fibers or coated the concrete samples	3
Literature review	1
Inaccessible	6

The exclusion criteria aimed to identify studies carried out under similar parameters to collect data for a metanalysis. However, the methods undertaken showed no common ground for generalization, which prevented a statistical approach.

2.3 Critical appraisal process

Two investigators independently reviewed each study and scored its quality based on Table 2. The table also summarizes the rationale for the critical appraisal criteria. The papers received overall ratings of strong (6), moderate (4-5), or weak quality (0-3).

Table 2: Criteria for quality assessment.

CRITERIA		RATIONALE
I	The study indicated concrete samples dimension and mix proportions	Reproducibility.
II	The study used different mix proportions for the same supplementary cementitious material or evaluated	Comparisons between different replacement/addition rates of the same material to identify the most efficient.
III	The study indicated samples curing conditions before corrosion (e.g., average temperature, relative humidity, curing time)	Reproducibility.
IV	The study declared acid solution exchange/adjustment	Reproducibility and concern regarding the acid attack trustworthiness.
V	The study described the treatment given to concrete after removal from the corrosive medium	Reproducibility.
VI	The study evaluated concrete both compressive strength and mass change	Possibility to conduct statistical analysis that correlates both variables.

As well as the exclusion criteria, the quality assessment aimed to identify which parameters researchers considered when evaluating concrete resistance to chemical sulfuric acid. The proposed criteria focused on the studies' reproducibility since many biases can come from vague statements.

3. RESULTS AND DISCUSSION

3.1 Studies quality

Chemical tests developed to simulate corrosion in wastewater facilities show a mixed concern regarding its reproducibility: 10 studies were of "strong" or "moderate" quality against five "weak" quality papers (Table 3). Almost all studies met criteria I, II, and VI—which was expected (the first and the second criteria were related to concrete samples manufacturing; the sixth criterion was an exclusion one). By accomplishing criterion II, the raised literature collaborates with further researches since they provide the best replacement (for SCM).

Table 3: Studies critical appraisal.

CRITERIA / REF.	I	II	III	IV	V	VI	OVERALL QUALITY ASSESSMENT
[20]	●			●			Weak
[33]	●	●	●	●	●	●	Strong
[22]	●	●	●	●	●	●	Strong
[26, 27]	●	●	●	●	●	●	Strog
[34]	●	●	●	●	●	●	Strong

REF. \ CRITERIA	I	II	III	IV	V	VI	OVERALL QUALITY ASSESSMENT
[25]	●	●				●	Weak
[30]	●	●			●	●	Moderate
[23]	●	●	●	●	●	●	Strong
[16]	●	●	●	●	●	●	Strong
[24]				●	●		Weak
[31]	●	●	●			●	Moderate
[32]	●	●				●	Weak
[21]	●					●	Weak
[29]	●	●	●	●	●	●	Strong
[28]	●	●		●		●	Moderate

However, the other criteria did not achieve promising results. Some studies lack data regarding the sample treatment before assessing its properties and the applied curing conditions (even though concrete curing conditions directly affect its strength-mainly when SCM partially replaces cement [35]). Self-consolidating concrete curing, for example, is not evidenced among the studies. To improve tests reproducility, studies should report the average temperature, relative humidity, and the curing period adopted for the experiment, despite the concrete type. Some studies also lacked information about the corrosive medium adjustment. As discussed in section 3.2.2, the reaction between concrete and sulfuric acid increases the soaking solution pH, and, In a real scenario, the sewer microorganisms continuously produce sulfuric acid, keeping the corrosive attack constant. If a study does not adjust the solution pH, the corrosion tends to decay and promote dubious results [36].

3.2 Corrosion tests design

Researchers attempted to evaluate concrete resistance to degrade under sulfuric acid attack (focus of this research) fall under three major groups: in situ tests, microbiological tests, and pure chemical tests. An enlighten discussion regarding some of the available test methods are given in [19].

In situ tests in sewerage rely on concrete corrosion trustworthiness: samples are submerged (as in [37]) or suspended over the wastewater (as in [38, 39]). Considering that concrete corrosion in sewers takes time to start damaging the structures, concrete samples under in situ conditions must be evaluated under sensitive methods (such as microstructural analysis) to show resistance results in a reasonable time [40, 41]. Since these methods demand a long time to obtain profitable, generalizable results and are usually difficult to implement, in situ tests are not practical for routine testing [19].

In microbiological tests (e.g., [42–44]), concrete samples lie in a bacterial environment with a gaseous (mainly composed of H_2S and its ions) and a liquid phase (which is inhabited by corrosive microorganisms, such as bacteria and fungus). Controlling parameters such as temperature, humidity, and H_2S concentration leads to an enhanced simulation of all stages of microbiologically concrete corrosion [19, 44]. Since devices that mimic in situ conditions are expensive and sophisticated to usual performance-based specifications [3], some researchers are trying to develop cheaper methods and equipment to evaluate concrete resistance under MIC.

A relatively simple method is the pure chemical tests, which simulate the corrosion stage after environment acidification due to sulfur-oxidizing microorganisms [19, 45]. They mainly consist of immersing concrete samples in a sulfuric acid solution (or in a solution made with other mineral acids, e.g. hydrochloric acid [36], or diluted sulfate salt) and measuring parameters such as mass loss, compressive strength change, and microscopic alterations [19]. Compared to microbiological tests, the chemical tests figure as a more practical and less expensive method for evaluating concrete resistance to corrosion. However, to assess the results obtained from acid immersion tests, some factors should be considered, as discussed below for the selected papers of this review and synthesized in Table 4.

3.2.1 Tests general design

Half the studies [16, 25–27, 30–34] accelerated the corrosion process by removing loose particles through brushing, rinsing with water, or both before evaluating concrete resistance to sulfuric acid attack (see Table 5, 2nd column). Some researchers also kept the concrete drying before evaluation [16, 21, 25–27, 30–32]. Those mechanisms simulate the fluctuations of wastewater level and the removal of material due to wastewater flow: two main steps of the sewers cyclic process [40] related to higher corrosion rates [42]. However, some authors [46] criticized the advantages of pursuing such mechanisms; they reported similar values for concrete physical and mechanical parameters with and without brushing under the same acid solution.

Table 4: Corrosion tests general design.

REF.	TEST GENERAL DESIGN	SAMPLES DIMENSIONS	CURING BEFORE IMMERSION	ACID CONCENTRATION	ACID ADJUSTMENT
[20]	**Continuous immersion**.	**Cylinders** (45x90) mm	**28 days**. Cured in water.	1% H_2SO_4*	Weekly
[33]	**Continuous immersion**. Samples were rinsed to remove loose particles, blotted with a paper towel, and left to dry for 30 min under room temperature before evaluation.	**Cylinders** (75x150) mm	**56 days**. Cured at 20 °C and 95% RH.	5% H_2SO_4 (first week = pH 2.5; consecutive weeks = pH 1.0)*	Weekly
[22]	**Continuous immersion**.	**Cubes** (150x150x150) mm	**90 days**. Cured in water tank (27±2 °C) for 7 days followed by water curing in lab environment (27±5 °C, 50±10% RH) until 90 days.	1% H_2SO_4*	Monthly
[26] [27]	**Continuous immersion**. Samples were rinsed with tap water to remove loose particles and left to dry for 30 min under room temperature before evaluation.	**Cubes** (100x100x100) mm	**28 days**. Cured at 20 °C and 95% RH.	5% H_2SO_4	Weekly
[47]	**Continuous immersion**.	**Cubes** (100x100x100) mm	Samples were placed into the aggressive curing environment immediately after removal from molds.	5% H_2SO_4	-
[34]	**Continuous immersion**. Samples were brushed under running water every 7 days and then returned to the solution (brushing was ceased when the run-off color reverted to clear water).	**Cubes** (100x100x100) mm	**28 days**. Cured at 20 °C in a water tank.	1% H_2SO_4, pH 1.5*	28 days
[25]	**Continuous immersion**.	**Cubes** (50x50x50) mm	**10 days.**	H_2SO_4 in three different concentrations: 5%, 10%, and 15%	-
[30]	**Continuous immersion**. Half the samples were brushed to remove loose	**Cubes** (100x100x100) mm	-	1% H_2SO_4, pH 1.0	-

REF.	TEST GENERAL DESIGN	SAMPLES DIMENSIONS	CURING BEFORE IMMERSION	ACID CONCENTRATION	ACID ADJUSTMENT
	particles and left to meet Saturated Surface Dried (SSD) conditions before mass loss evaluation.				
[23]	**Continuous immersion**. Samples were brushed carefully to remove the loose particles from the surface. They were then left for drying under room temperature for 1 h before evaluation.	**Cubes** (100x100x100) mm	**3 days**. Cured in water (20±1 °C) and then sealed in polythene sheets and kept in a storage laboratory until the day of testing (20±1 °C, 65±1% RH).	3% H_2SO_4, pH 3.0*	Weekly or when the pH level went up
[16]	**Continuous immersion**. Samples were rinsed with tap water, brushed carefully to remove loose particles and left to meet Saturated Surface Dried (SSD) conditions before evaluation.	**Prisms** (50x50x285) mm **Cylinders** (75x150) mm	**28 days**. Cured at 22±2 °C and 98% RH.	5% H_2SO_4 (initial pH = 2.0)	45 days
[24]	**Continuous immersion**. Samples were rinsed with tap water to remove loose particles and left to dry for 30 min under room temperature before evaluation.	**Cubes** (150x150x150) mm	**28 days.**	2% H2SO4, pH 6.0*	-
[31]	**Continuous immersion**.	**Cubes** (100x100x100) mm	**28 days**. Cured in water.	5% H_2SO_4	-
[32]	**Continuous immersion**.	**Cubes** (100x100x100) mm	Samples were cured in water until testing (25 °C).	1% H_2SO_4, pH 1.0	-
[21]	**Continuous immersion**.	**Cubes** (150x150x150) mm	-	5% H2SO4	-
[29]	**Continuous immersion**. Samples were air-dried for 2 h under room temperature before evaluation.	**Cylinders** (55x100) mm	**28 days**. Cured in a standard moisture room (25±2 °C, 100% RH).	H_2SO_4 in three different pH: 1.5, 3.0, 4.5, and 6.5	Weekly
[28]	**Continuous immersion**. Samples were cleaned to remove loose particles before evaluation.	**Cubes** (100x100x100) mm	**28 days**. Cured in water.	10% H_2SO_4	Monthly

Note: **-** indicates that the paper did not reported data regarding this topic.
* indicates that the paper stated that concentration/pH was kept constant. RH = relative humidity.

In sulfuric acid solutions, sulfate ions of the acid medium react with cement calcium compounds to generate gypsum (Figure 1), which precipitate onto the concrete and slow the corrosive attack, reducing both hydrogen ion consumption and mass loss [36, 48]. Since studies show that the time demanded for the sulfuric acid medium become saturated with gypsum after immersing the concrete samples is lesser than 24 hours [36, 48], adjusting the acid medium concentration daily appear as an option. However, the assessed papers do not follow this principle since the lower adjustment period reported is a week (as seen in [20, 23, 26, 27, 29, 33]). Also, the constant renewal of acid solutions may delivers large amounts of toxic material for disposal [36], which must be avoided.

Therefore, an option to mimic sulfuric acid corrosion mechanisms in laboratory conditions is using an acid solution-thus dispensing mechanical apparatus to brush or rinse the concrete samples and avoiding the solution constant renewing. ALEXANDER and FOURIE [36] proposed using hydrochloric acid solutions instead of sulfuric acid solutions; since both acids completely dissociate in solution, generating equal amounts of hydrogen ions, those acid mediums possess the same ability to degradate concrete. Regarding corrosion byproducts, when cement calcium dissolves into hydrochloric acid solution, it forms calcium chloride ($CaCl_2$)-which does not precipitate due to its greater solubility (~74.5 g/100 mL at 20 ºC) [49] compared with solubility of calcium sulphate (~0.2 g/100 mL at 25 ºC) [50].

3.2.2 Acid solution concentration

When concrete reacts with sulfuric acid, hydroxide ions diffuse to the soaking solution through the corrosion layer from the inner concrete [51], which increases the medium pH. In a sewer environment, the recurrent metabolic process of microorganisms keeps the pH of the concrete surface low and constant to a certain threshold, which varies according to the colonyzing microbes, but is generally between 2.0 and 1.0 [7]. When testing different sulfuric acid concentrations, FOURIE [48] identified that high concentrated acid solutions (pH lower than 1.0) hinders the detection of any improvement in concrete resistance to corrosion that could be acceptable for weaker sulfuric acid environments, thus generating biased results. Besides the labor demanded to maintain the corrosion process in immersion tests constant, the author state that a sulfuric acid solution with a pH ranging between 2.0 and 1.0 better represents the corrosive sewer environment than solutions with lesser pH (in agreement with the bacterial environment proposed by [7]).

However, only five papers [29, 30, 32–34] kept the acid solution's pH close to the treshold stated by FOURIE (FOURIE, 2007), and none of them renewed the solution at a daily-base (importance discussed in section 3.2.1). Only two studies [25, 29] evaluated concrete resistance in different acidification levels—and they led to some contrasting results.

SAPUTRA, SHOHIBI, and KUBOUCHI [25] reported equivalent reductions for concrete samples made with the same replacement rate of fly ash under 5%, 10%, and 15% sulfuric acid solution. Their results are analogous to GU, VISINTIN, and BENNETT's [46] research, which identified equivalent reductions in compressive strength at approximately 100 days in 3% solution (pH 0.52) and 400 days in 1% solution (pH 1.0) when evaluating conventional and alkali-activated concrete. However, this pattern conflict with the results of WU, HU, and LIU [29], who reported different behaviors of the same concrete mix when subjected to acid solutions with different pH. Therefore, the optimal replacement of cement by SCM for a given sulfuric acid solution-or for a given test procedure—could not always be the most effective for another acid concentration. Future studies should submit concrete mixtures with different SCM replacement rates to acid solutions with different pH to verify this gap.

3.2.3 Assessments undertaken

The assessments undertaken rely mostly on concrete physical and mechanical properties (Figure 3); microstructural analyses were reported only in six papers. Using compressive strength and mass change to evaluate concrete resistance indicates a concern regarding its structural stability. Since many researchers could not define a direct relationship between mass and compressive strength change [21, 26, 29, 30, 45], further analyses-such as determining binder mineral and chemical composition, its alkalinity, and its resistance to aggressive ion penetration-should focus on understanding the micro process related to concrete corrosion under sulfuric acid [52].

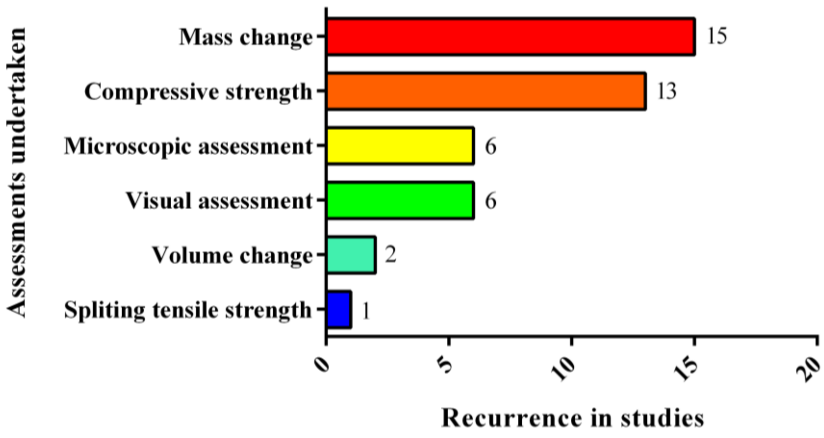

Figure 3: Recurrence of the assessments undertaken after H_2SO_4 attack.

Regarding results presentation, we identified some barriers to posterior analyses of the data reported in the papers. The absence of a standardized protocol for assessing concrete resistance to sulfuric acid attack led the studies to propose, each one, their specific dates to perform compressive strength and mass change measurements (Figure 4). Assessing concrete properties on a 28 days base sequence (28, 56, 84 etc.) prevailed among the studies, followed by a 30 days base sequence (30, 60, 90 etc.).

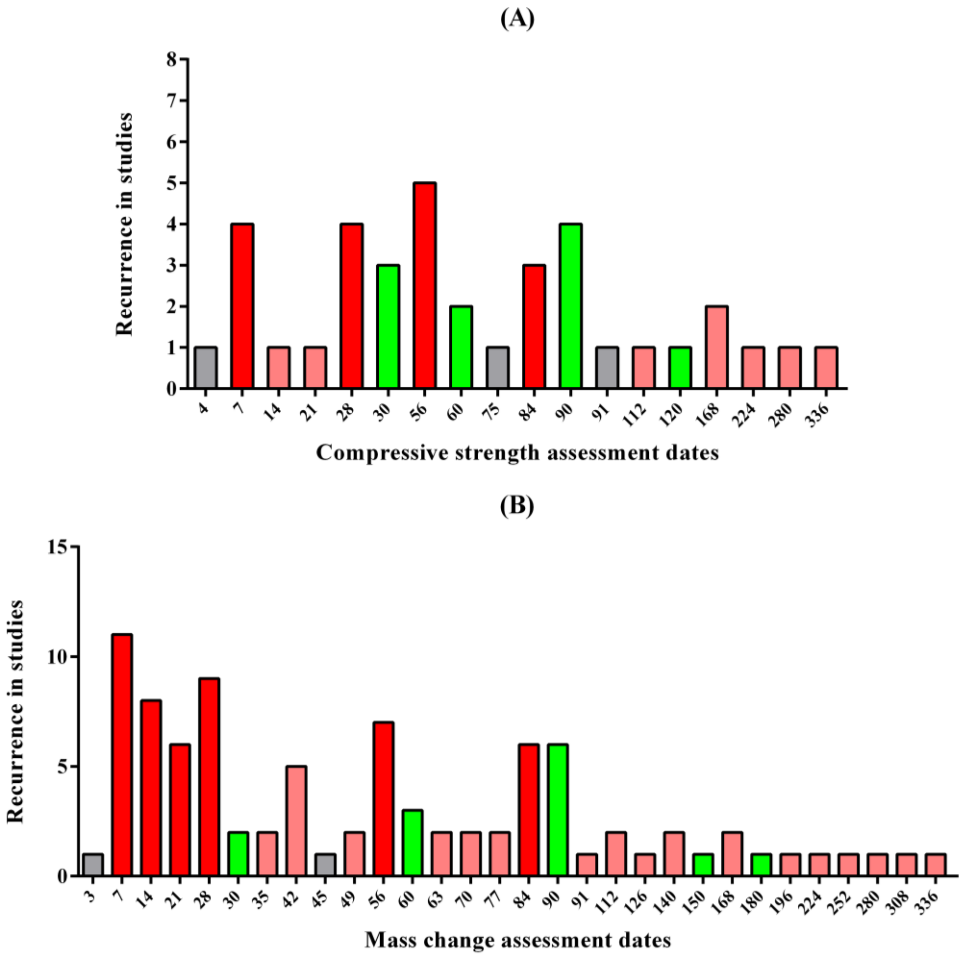

Figure 4: Dates recurrence for assessing concrete compressive strength (A) and mass change (B) after sulfuric acid attack. Red bars indicate dates multiples of seven (dark red – dates more used for assessment; soft red – less used dates). Green bars indicate dates multiples of 30. Grey bars indicate the remaining dates.

Eight papers [16, 20, 22, 25, 27, 32–34] that evaluated compressive strength do not present tests' exact results, preventing potential meta-analysis that could generalize the results and bring forth new findings. As to mass change, six papers [20, 23, 24, 27, 28, 31] do not indicated how they calculated their gain/loss percentages, affecting tests' reproducibility.

3.3 Materials performance

The rationale for replacing cement with other materials is the constant search for more sustainable and yet resistant materials, which can be achieved by using SCM—they can improve characteristics such as consistency, workability, permeability, and long-term strength and can be cheaper than cement [53]. Reactive SCM can also change concrete chemical composition through their inherent self-cementing or pozzolanic properties. By replacing cement with alternative materials that neutralize or do not react with the aggressive agent, we can produce a more corrosion-resistant material.

3.3.1 Use of secondary binders

Secondary binders were evaluated in 12 of the 15 studies, as seen in Table 6. The most assessed SCM were fly ash (four studies), silica fume (two studies), and limmestone filler (two studies).

Limestone filler is a partially reactive SCM that improves cementitious materials early strength due to its particle size distribution and its heterogeneous nucleation [54]. Adding high rates of limestone filler to cement (>15% [55]) may worsen concrete durability [56, 57], which can be related to its higher calcium content. In sulfuric acid solutions with pH of 1, using this SCM reported higher corrosion of cementitious samples due to their higher dissolution rate induced by its higher fineness (particle size lower than 3.2 µm) [58]. However, using a low proportion (~10%) of limestone filler causes no significant changes in concrete sulfate resistance [57] and blending it with a pozzolanic material at levels of about 30% induce higher compressive strength under sulfuric acid solution than conventional concrete [59] due to the combination of cementing and pozzolanic properties [60]. Although a study [26, 27] already shows a better performance of other SCM, further analysis should evaluate the chemical and physical properties of limestone filler under sulfuric acid environment to explain its behavior.

Fly ash (class F), metakaolin, natural pozzolan, pulverized burnt clay waste, and silica fume, in their turn, are pozzolanic SCM. During the pozzolanic activity, the amorphous alumino-silicate spheres react with cement calcium hydroxide and form additional cementing products (calcium silicate hydrate - CSH; calcium aluminate hydrate - CAH) [31, 61, 62], which are less susceptible to corrosion and reduce concrete microstructural porosity. SCM fineness also helps to achieve a Better packing and filling of pores. The amorphous alumino-silicate spheres enter the voids between unreacted particles and aggregates in the hydrated matrix (micro-filling effect) [23, 63–65], thus densifying the concrete and reducing the ingress of moisture and aggressive chemicals. Since those properties are common in every pozzolanic SCM, we must compare the characteristics of those materials individually.

Regarding chemical composition, fly ash, metakaolin, natural pozzolan, and pulverized burnt clay waste have the most variables (as seen in [31, 62, 66] due to their raw material composition and combustion-cooling conditions [15, 62]. However, fly ash tends to have a higher calcium content than metakaolin and natural pozzolan (class F fly ash can have from 0.5 to 19.3% of calcium oxide, while metakaolin can have from 0 to 3.4% [62] and natural pozzolan can have from 0.6 to 9.0% [26, 27, 67, 68]. Since calcium compounds react with sulfuric acid and generate weaker and porous byproducts, concrete made with high calcium SCM can have a weaker performance in sewer environments-as seen by [29] when comparing the performance of samples made with metakaolin, silica fume, and fly ash. The higher calcium content in fly ash chemical composition combined with its greater particle size and surface area when compared to other SCM [69] lead to a lower pozzolanic activity (as seen in [70]), which slows the formation of more stable cementing products. This lower reactivity indicates that the chemical composition variability shall be accounted for when testing SCM for larger-scale uses.

Silica fume, in its turn, has more than 85% of silica in its chemical composition [15, 62, 71] and a higher pozzolanic activity than fly ashes [70] and natural pozzolans [72]. Combined with nanosilica (which has a surface are in in the order of 10 to 1.000 m^2/g [69]), studies shows that silica fume can reduce the ingress of moisture and aggressive chemicals into cementitious materials [71] and the mass loss under sulfuric acid attack [29]. Therefore, blending cement with silica fume can be an alternative for reducing concrete corrosion in sewer environments.

Table 5: Secondary binders evaluated in the studies.

REF.	SECONDARY BINDER EVALUATED	QUANTITATIVE RESULTS PRESENTATION	STUDIES CONCLUSIONS
[20]	LF	Graph	**Self-consolidating concrete (SCC) containing 47% LF lost 40% less mass than the standard concrete**. The authors argued that the lower cement content in SCC reduced calcium hydroxide production in concrete, which led to a lesser mass loss.
[29]	FA, MK, SF	Graph and table	**Shotcrete made with MK or SF had the best results for compressive strength**, which the authors associated with the permeable voids reduction in the samples. For all concrete mixes, mass loss under pH 1.5 acid ranged between 2.95% and 3.7%; the concrete with 5% of silica fume demonstrated the lesser mass change. The authors identified the optimum replacement for all acid solutions considering compressive strength and mass loss; however, the values differ for each acid concentration. They also identified a lower correlation between mass change and compressive strength.
[31]	PBCW	Graph and table	**Concrete made with 20% PBCW lost less compressive strength and less mass than the standard concrete** (a resistance loss of 23.8% against 46.9% and a mass change of -5.0% against +4.15% in a 5% H_2SO_4 solution before 90 days). The authors argued that replacing cement with PBCW leads to the formation of secondary CSH and CAH, thereby reducing calcium hydroxide (which is susceptible to corrosion) and reducing interconnectivity among concrete pores.
[32]	FWFS	Graph	**Concrete made with 40% FWFS lost less mass than the standard concrete**. After 180 days, that mixture showed the lowest mass loss compared with concrete made with distinct FWFS replacements in the same water-cement ratio (w/c). The paper reported that the best w/c was 0.45, followed by 0.35.
[34]	GGBS	Graph and table	**Concrete made with 70% GGBS lost less mass and less compressive strength than the standard concrete**. The paper presented mass change through g/m² and compressive strength through percentage decay following the corrosion process. However, the authors argued that none of the samples adequately addressed distinct durability for being used in wastewater infrastructure.
[22]	SF	Graph	**Concrete made with 5% SF lost nearly 5% less compressive strength and 10% less mass than the standard concrete before 48 days in a 1% H_2SO_4 solution, considering the same w/c (0.25)**. The study showed that mixtures with w/c 0.25 had a lesser compressive strength loss and a higher mass loss than samples made with a higher w/c ratio. The authors argued that the lower w/c ratio leads to a more intense initial deterioration of the concrete surface; however, the inner matrix was unaffected by the acid attack.
[25]	FA	Graph	**Concrete containing 75% FA lost less compressive strength and mass than the standard concrete in all immersion media** (e.g., a resistance loss of 17% against 41% and a mass change of -1.3% against -5.2% in a 15% H_2SO_4 solution before four days). They

REF.	SECONDARY BINDER EVALUATED	QUANTITATIVE RESULTS PRESENTATION	STUDIES CONCLUSIONS
			argued that using FA improves the resistance to sulfuric acid corrosion because it reduces the amount of calcium hydroxide, which minimizes the formation of gypsum and ettringite—both expansive byproducts that reduce the durability and compressive strength of concrete.
[26] [27]	FA, PZ, LF	Graph	SCC made with 32.7% FA (strength class = 50 MPa) lost less compressive strength than the standard SCC (loss of 44.5% against 54.8% after 84 days). SCC made with 50% PZ (strength class = 70 MPa) lost less compressive strength than the standard SCC (loss of 31.9% against 35.1% after 84 days). **For all strength classes, SCC made with FA or with PZ lost less mass than the standard SCC (while the SCC made with LF had a higher mass loss)**. The authors identified that change in compressive strength does not properly indicates concrete surface deterioration after exposure to H_2SO_4. They also stated that increasing cement content increases the risk of corrosion, despite improved compressive strength.
[28]	FA	Graph and table	**Concrete containing FA, in all percentages, lost less compressive strength and less mass than the standard concrete**. The paper reported that concrete made with a w/c ratio of 0.55 showed the highest acid resistance when compared with concrete made with lower w/c and the same FA addition. When comparing only the cement replacement percentage, samples containing 40% fly ash obtained the best durability values. The authors did not discuss the rationale of their results.

Note: CAH: calcium aluminate hydrates; CH: calcium hydroxide (portlandite); CSH: calcium silicate hydrates; FA: fly ash; FWFS: fine waste foundry sand; GGBS: ground granulated blast-furnace slag; LF: limestone filler; MK: metakaolin; PBCW: pulverized burnt clay waste; PLS: plasticizer; PZ: natural pozzolan; RL: natural rubber latex; SF: silica fume.

3.3.2 Use of tertiary and quaternary binders

Using tertiary and quaternary binders in concrete still needs further researches. The raised literature does not explain how combining different SCM can improve concrete resistance, which leads to a non-standardization of the cement replacement rate by SCM, except for BARBHUIYA and KUMALA [23], which varied fly ash in a 10% scale until 50% (Table 6).

Table 6: Tertiary and quaternary binders evaluated in the studies.

REF.	BINDERS WITH SCM USED
[16]	95% OPC + 5% SF* 90,5% OPC + 9,5% NS* **70% OPC + 30% FA** 65% OPC + 30% FA + 5% SF* 62% OPC + 28.5% FA + 9,5% NS* 57% OPC + 28.5% FA + 5% SF + 9,5% NS*
[21]	67% OPC + 15% FA + 8% SF + 10% LS
[22]	95% OPC + 5% SF **80% OPC + 15% FA + 5% SF**

REF.	BINDERS WITH SCM USED
[23]	80% OPC + 10% FA + 10% UFFA
	70% OPC + 20% FA + 10% UFFA
	60% OPC + 30% FA + 10% UFFA
	50% OPC + 40% FA + 10% UFFA
	40% OPC + 50% FA + 10% UFFA
[24]	70% OPC + 22.5% FA + 7.5% RHA
[30]	99.7% OPC + 0.3% NS
	99% OPC + 1% NS
	98% OPC + 2% NS
	93% OPC + 7%
	93% OPC + 6.7% SF + 0.3% NS
	93% OPC + 5% SF + 2% NS
	92% OPC + 7% SF + 1% NS
	90% OPC + 9% SF + 1% NS
[33]	92% OPC + 8% SF
	50% OPC + 5% SF + 45% SLG
	50% OPC + 20% FA + 5% SF + 25% SLG
	50% OPC + 15% FA + 20% SLG + 15% LF

Notes: Bold letters indicate the best resistant concrete binder in the study. * indicates approximated values. FA: fly ash; LF: limestone filler; MK: metakaolin; OPC: ordinary Portland cement; SF: silica fume; SLG: slag.

BASSUONI and NEHDI [33], and KUMAR and PRASAD [21] achieved better resistance results when partially replacing cement with silica fume, fly ash, and other SCM. GOYAL *et al*. [22] also reported better results for using silica fume and fly ash in concrete despite using only silica fume, but they did not discuss why adding fly ash improved concrete performance. However, AMIN and BASSUONI [16] had a greater mass loss when replacing cement with 28.5% fly ash, 0.5% silica fume, and 1% nano-silica; concrete made only with 30% fly ash as SCM had a lower mass loss. The authors argued that the high content of gypsum in the tertiary binder increased the volume of cementitious gel vulnerable to decomposition in the sulfuric acid solution.

Studies also lack data regarding how they chose to combine the SCM in concrete and at that specific rate. Only KUMAR and PRASAD [21] reported an optimizing method based on the compressive strength of concrete specimens. Initially, they made concrete samples with distinct levels of fly ash as cement replacement. After testing the samples for compressive strength, they picked the fly ash rate that returned the greater strength as its optimum rate. Hereafter, they fixed the fly ash rate and varied silica until identifying the best silica fume rate following the higher compressive strength. Finally, they used the optimized fly ash and silica fume to determine the optimum lime sludge content for the concrete samples.

Since the method proposed by [23] for optimizing cement replacement by SCM does not consider the sulfuric acid attack, future studies should analyze experimental data from corrosion tests to predict the evaluated SCM optimum replacement rate. Further studies should also explain how the concrete reaction products' microstructural arrangement can produce sulfuric acid-resistant concrete.

4. CONCLUSIONS

Researches evaluate, under various test methods, several concrete mixtures resistance to sulfuric acid attack-the last stage of microbiologically induced concrete corrosion. To synthesize this body of knowledge and encourage new studies, we carried out a systematic review to answer which supplementary cementitious materials better improve concrete resistance to sulfuric acid corrosion and how researchers assess concrete resistance to sulfuric acid through chemical immersion tests. We find that:

- Chemical immersion tests to assess concrete resistance to sulfuric acid do not follow a standard protocol. In general, tests tend to evaluate concrete resistance to sulfuric acid by immersing concrete samples in high concentrated acid solutions (> 5%, pH ~1.0), removing loose particles poorlyadhered after immersion, and assessing concrete compressive strength and mass change on a 28 or 30 days base sequence. Even though there is no standard for evaluating corrosion in sewers, researchers must define parameters to perform their tests and facilitate assessing the results of different studies through meta-analysis. Since corrosion in sewerage implies chemical and physical degradation of concrete, an easier way to mimic concrete corrosion could be immersing concrete samples in acid solutions that generate soluble byproducts when reacting with cementitious compounds.

- Using pozzolanic SCM improves concrete resistance to sulfuric acid because they densify the hydrated matrix through the micro-filling effect and the formation of additional compounds less susceptible to corrosion. Blending cement with silica fume had the best results against sulfuric acid corrosion when compared to other SCM. Silica fume's better performance can be associated with its higher silica content and intense pozzolanic reaction; those properties reduce the amount of material susceptible to acid corrosion and strengthen concrete.
- Little is known about how combining distinct SCM can contribute to concrete resistance to sulfuric acid corrosion. Further studies should evaluate how each binder contributes to concrete durability in an acid environment through chemical and physical properties. To identify the best replacement rates for each material in concrete, researchers should model experimental data from corrosion tests to predict the optimum replacement rate of a given SCM.

5. REFERENCES

[1] OLMSTEAD, W.H., HAMLIN, H., "Converting Portions of the Los Angeles Outfall Sewer into a Septic Tank", *Engineering News and American Railway Journal*, v. XLIV, n. 19, pp. 317–318, 1900.

[2] WU, M., WANG, T., WU, K., *et al.*, "Microbiologically induced corrosion of concrete in sewer structures: A review of the mechanisms and phenomena", *Construction and Building Materials*, v. 239, p. 117813, 2020. DOI: 10.1016/j.conbuildmat.2019.117813.

[3] O'CONNELL, M., MCNALLY, C., RICHARDSON, M.G., "Biochemical attack on concrete in wastewater applications: A state of the art review", DOI: 10.1016/j.cemconcomp.2010.05.001. *Cement and Concrete Composites*, v. 32, n. 7, pp. 479-485, 2010.

[4] PARANDE, A.K., RAMSAMY, P.L., ETHIRAJAN, S., *et al.*"Deterioration of reinforced concrete in sewer environments", DOI: 10.1680/muen.2006.159.1.11. *Proceedings of the Institution of Civil Engineers*, v. 159, n. 1, pp. 11-20, 2006.

[5] O'DEA, V., "Understanding biogenic sulfide corrosion", *Materials Performance*, v. 46, n. 11, pp. 36–39, 2007.

[6] ROBERTS, D.J., NICA, D., ZUO, G., *et al.*, "Quantifying microbially induced deterioration of concrete: Initial studies", DOI: 10.1016/S0964-8305(02)00049-5. *International Biodeterioration & Biodegradation*, v. 49, n. 4, pp. 227–234, 2002.

[7] ISLANDER, R.L., DEVINNY, J.S., MANSFELD, F., *et al.*"Microbial ecology of crown corrosion in sewers", *Journal of Environmental Engineering*, v. 117, n. 6, pp. 751–770, 1991.

[8] WEI, S., JIANG, Z., LIU, H., *et al.* "Microbiologically induced deterioration of concrete - A review", DOI: 10.1590/S1517-83822014005000006. *Brazilian Journal of Microbiology*, v. 44, n. 4, pp. 1001–1007, 2013.

[9] SULAPHA, P., WONG, S.F., WEE, T.H., *et al.* "Carbonation test of concrete containing mineral admixtures", *Journal of Materials in Civil Engineering*, v. 15, pp. 134–143, 2003.

[10] ZHANG, D., GHOULEH, Z., SHAO, Y., "Review on carbonation curing of cement-based materials", DOI: 10.1016/j.jcou.2017.07.003. *Journal of CO2 Utilization*, v. 21, n. July, pp. 119–131, 2017.

[11] MIRON, L.E.R.D., MAGAÑA, M.E.L., "Influence of Sulfur Ions on Concrete Resistance to Microbiologically Induced Concrete Corrosion", In: MIRON, L.E.R.D., KOLEVA, D.A. (eds.), *Concrete Durability: Cementitious Materials and Reinforced Concrete Properties, Behavior and Corrosion Resistance*, New York: Springer International Publishing, 2017, pp. 11–22.

[12] SANTOS, B.S., AMORIM JUNIOR, N.S. de, RIBEIRO, D. V., "Degradação das matrizes cimentícias", In: RIBEIRO, D. V. (ed.), *Princípios da ciência dos materiais cimentícios: produção, reações, aplicações e avanços tecnológicos*, 1st ed., Curitiba: Appris, 2021, pp. 441–520.

[13] SONG, Y., WIGHTMAN, E., TIAN, Y., *et al.*"Corrosion of reinforcing steel in concrete sewers", DOI: 10.1016/j.scitotenv.2018.08.362. *Science of the Total Environment*, v. 649, pp. 739–748, 2019.

[14] BRANDT, E.M.F., SANTOS, J.M.B., SOUZA, C.L. de, *et al.* Contribuição para o aprimoramento de projeto, construção e operação de reatores UASB aplicados ao tratamento de esgoto sanitário - Parte 4: Controle de corrosão e emissões gasosas", DOI: 10.4322/dae.2018.041. *Revista DAE*, v. 66, n. 214, pp. 56–72, 2018.

[15] THOMAS, M., *Supplementary cementing materials in concrete*, DOI: 10.1201/b14493. London: CRC Press, 2013.

[16] AMIN, M., BASSUONI, M.T., "Response of concrete with blended binders and nanoparticles to sulfuric acid

attack", DOI: 10.1680/jmacr.17.00081. *Magazine of Concrete Research.*, v. 70, n. 12, pp. 617–632, 2017.
[17] AMIN, M., BASSUONI, M.T., "Resistance of concrete incorporating portland limestone cement to sulfuric acid", In: *2016 Annual Conference of the Canadian Society for Civil Engineering*, 2016, pp. 1–11.
[18] SAND, W., "Microbial Corrosion and its Inhibition", In: REHM, H.-J., G. REED (eds.), *Biotechnology: Special Processes*, 2ª., Wiley-VCH Verlag GmbH & Co. KGaA, 2001, pp. 265–316.
[19] WANG, T., WU, K., KAN, L., *et al.* "Current understanding on microbiologically induced corrosion of concrete in sewer structures : a review of the evaluation methods and mitigation measures", DOI: 10.1016/j.conbuildmat.2020.118539. *Construction and Building Materials*, v. 247, p. 118539, 2020.
[20] AL-TAMIMI, A.K., SONEBI, M., "Assessment of self-compacting concrete immersed in acidic solutions", DOI: 10.1061/(ASCE)0899-1561(2003)15:4(354). *Journal of Materials in Civil Engineering*, v. 15, n. 4, pp. 354–357, 2003.
[21] KUMAR, V.V.P., PRASAD, D.R., "Influence of supplementary cementitious materials on strength and durability characteristics of concrete", DOI: 10.12989/acc.2019.7.2.075. *Advances in Concrete Construction*, v. 7, n. 2, pp. 75–85, 2019.
[22] GOYAL, S., KUMAR, M., SIDHU, D.S., *et al.* "Resistance of mineral admixture concrete to acid attack", DOI: 10.3151/jact.7.273. *Journal of Advanced Concrete Technology*, v. 7, n. 2, pp. 273–283, 2009.
[23] BARBHUIYA, S., KUMALA, D., "Behaviour of a Sustainable Concrete in Acidic Environment", DOI: 10.3390/su9091556. *Sustainability*, v. 1556, n. 9, p. 13, 2017.
[24] NARDE, A.R., GAJBHIYE, A.R., "Durability studies on concrete with fly ash, rice husk ash and quarry sand", *International Journal of Civil Engineering*, v. 9, n. 2, pp. 587–595, 2018.
[25] SAPUTRA, A.H., SHOHIBI, M., KUBOUCHI, M., "Effect of Fly Ash Fortification in the Manufacture Process of Making Concrete towards Characteristics of Concrete in Sulfuric Acid Solution", DOI: 10.7454/mst.v19i3.3045. *Makara Journal of Technology*, v. 19, n. 3, pp. 133–140, 2015.
[26] SIAD, H., MESBAH, H.A., KHELAFI, H., *et al.* "Effect of mineral admixture on resistance to sulphuric and hydrochloric acid attacks in selfcompacting concrete", DOI: 10.1139/L09-157. *Canadian Journal of Civil Engineering*, v. 37, n. 3, pp. 441–449, 2010.
[27] SIAD, H., MESBAH, H.A., BERNARD, S.K., *et al.* "Influence Of Natural Pozzolan On The Behavior Of Self-Compacting Concrete Under Sulphuric And Hydrochloric Acid Attacks, Comparative Study", *Arabian Journal for Science and Engineering*, v. 35, n. 1, pp. 183–195, 2010.
[28] VAN NGUYEN, C., LAMBERT, P., TRAN, Q.H., "Effect of Vietnamese Fly Ash on Selected Physical Properties, Durability and Probability of Corrosion of Steel in Concrete", DOI: 10.3390/ma12040593. *Materials (Basel)*, v. 12, n. 4, 2019.
[29] WU, L., HU, C., LIU, W.V., "Effects of pozzolans on acid resistance of shotcrete for sewer tunnel rehabilitation", DOI: 10.1080/21650373.2018.1519645. *Journal of Sustainable Cement-Based Materials*, v. 8, n. 1, pp. 55–77, 2019.
[30] HENDI, A., RAHMANI, H., MOSTOFINEJAD, D., *et al.* "Simultaneous effects of microsilica and nanosilica on self-consolidating concrete in a sulfuric acid medium", DOI: 10.1016/j.conbuildmat.2017.06.165. *Construction and Building Materials*, v. 152, pp. 192–205, 2017.
[31] AJAYI, E.O., BABAFEMI, A.J., "Effects of Pulverized Burnt Clay Waste Fineness on the Compressive Strength and Durability Properties of Concrete", DOI: 10.4186/ej.2018.22.2.83. *Engineering Journal*, v. 22, n. 2, pp. 83–99, 2018.
[32] MAKUL, N., SOKRAI, P., "Influences of fine waste foundry sand from the automobile engine-part casting process and water-cementitious ratio on the properties of concrete: A new approach to use of a partial cement replacement material", DOI: 10.1016/j.jobe.2018.09.004. *Journal of Building Engineering*, v. 20, n. March, pp. 544–558, 2018.
[33] BASSUONI, M.T., NEHDI, M.L., "Resistance of self-consolidating concrete to sulfuric acid attack with consecutive pH reduction", DOI: 10.1016/j.cemconres.2007.04.014. *Cem. Concr. Res.*, v. 37, pp. 1070–1084, 2007.
[34] O'CONNELL, M., MCNALLY, C., RICHARDSON, M.G., "Performance of concrete incorporating GGBS in aggressive wastewater environments", DOI: 10.1016/j.conbuildmat.2011.07.036.*Construction and Building Materials*, v. 27, n. 1, pp. 368–374, 2012.
[35] MEHTA, P.K., MONTEIRO, P.J.M., *Concrete: Microstructre, Properties, and Materials*, 3rd ed. New York: The McGraw-Hill Companies, Inc., 2006.
[36] ALEXANDER, M.G., FOURIE, C., "Performance of sewer pipe concrete mixtures with portland and calcium aluminate cements subject to mineral and biogenic acid attack", DOI: 10.1617/s11527-010-9629-1. *Materials and Structures/Materiaux et Constructions*, v. 44, n. 1, pp. 313–330, 2011.
[37] PARANDE, A.K., BABU, B.R., PANDI, K., *et al.* "Environmental effects on concrete using Ordinary and Pozzolana Portland cement", DOI: 10.1016/j.conbuildmat.2010.06.027. *Construction and Building Materials*, v. 25, n. 1, pp. 288–297, 2011.
[38] WELLS, T., MELCHERS, R.E., "Modelling concrete deterioration in sewers using theory and field observations", DOI: 10.1016/j.cemconres.2015.07.003. *Cement and Concrete Research*, v. 77, pp. 82–96, 2015.
[39] KILISWA, M.W., SCRIVENER, K.L., ALEXANDER, M.G., "The corrosion rate and microstructure of Portland cement and calcium aluminate cement-based concrete mixtures in outfall sewers: A comparative study", DOI:

10.1016/j.cemconres.2019.105818. *Cement and Concrete Research*, v. 124, n. December 2018, pp. 1–13, 2019.
[40] DE BELIE, N., MONTENY, J., TAERWE, L., “Apparatus for accelerated degradation testing of concrete specimens”, DOI: 10.1617/13765.
Materials and Structures/Materiaux et Constructions, v. 35, n. 251, pp. 427–433, 2002.
[41] TITTELBOOM, K. Van, DE BELIE, N., HOOTON, R.D., “Test Methods for Resistance of Concrete to Sulfate Attack – A Critical Review”, in *Performance of Cement-Based Materials in Aggressive Aqueous Environments. RILEM State-of-the-Art Reports 10,* ALEXANDER, M.G., A. BERTRON, N. DE BELIE, eds. RILEM, 2013, pp. 251–287.
[42] MORI, T., NONAKA, T., TAZAKI, K., *et al.* “Interactions of nutrients, moisture and pH on microbial corrosion of concrete sewer pipes”, DOI: 10.1016/0043-1354(92)90107-F. *Water Res.*, v. 26, n. 1, pp. 29–37, 1992.
[43] YANG, Y., JI, T., LIN, X., *et al.* “Biogenic sulfuric acid corrosion resistance of new artificial reef concrete”, DOI: 10.1016/j.conbuildmat.2017.10.007. *Construction and Building Materials,* v. 158, pp. 33–41, 2018.
[44] XIE, Y., LIN, X., JI, T., *et al.* “Comparison of corrosion resistance mechanism between ordinary Portland concrete and alkali-activated concrete subjected to biogenic sulfuric acid attack”, *Construction and Building Materials*, v. 228, 2019.
[45] HOUSE, M., CHENG, L., BANKS, K., *et al.* “Concrete Resistance to Sulfuric Acid Immersion: The Influence of Testing Details and Mixture Design on Performance as It Relates to Microbially Induced Corrosion”, DOI: 10.1520/acem20170134. *Advances in Civil Engineering Materials*, v. 8, n. 1, pp. 544–557, 2019.
[46] GU, L., VISINTIN, P., BENNETT, T., “Evaluation of accelerated degradation test methods for cementitious composites subject to sulfuric acid attack; application to conventional and alkali-activated concretes”, DOI: 10.1016/j.cemconcomp.2017.12.015. *Cement and Concrete Composites*, v. 87, pp. 187–204, 2018.
[47] MUHAMMAD, B., ISMAIL, M., “Performance of natural rubber latex modified concrete in acidic and sulfated environments”, DOI: 10.1016/j.conbuildmat.2011.12.099. *Construction and Building Materials*, v. 31, pp. 129–134, 2012.
[48] FOURIE, C.W., “Acid resistance of sewer pipe concrete”, PhD. dissertation, University of Cape Town, South Africa, 2007.
[49] ROPP, R.C., “Group 17 (H, F, Cl, Br, I) Alkaline Earth Compounds”, In: *Encyclopedia of the Alkaline Earth Compounds*, Amsterdam: Elsevier LTD, 2013, pp. 869–909.
[50] LEBEDEV, A.L., KOSORUKOV, V.L., “Gypsum Solubility in Water at 25°C”, DOI: 10.1134%2FS0016702917010062. *Geochemistry International*, v. 55, n. 2, pp. 171–177, 2017.
[51] MIN, H., SONG, Z., “Investigation on the Sulfuric Acid Corrosion Mechanism for”, *Advances in Materials Science and Engineering*, v. 2018, pp. 1–10, 2018.
[52] BRANDT, A.M., JÓŹWIAK-NIEDŹWIEDZKA, D., “Diagnosis of Concrete Quality by Structural Analysis”, DOI: 10.1520/acem20120004.*Advances in Civil Engineering Materials*, v. 1, n. 1, pp. 1–22, 2012.
[53] DUCHESNE, J., “Alternative supplementary cementitious materials for sustainable concrete structures: a review on characterization and properties”, DOI: 10.1007/s12649-020-01068-4. *Waste and Biomass Valorization*, n. 0123456789, 2020.
[54] AQEL, M., PANESAR, D., “Physical and chemical effects of limestone filler on the hydration of steam cured cement paste and mortar”, DOI: 10.21041/ra.v10i2.481. *Revista ALCONPAT*, v. 10, n. 2, pp. 191–205, 2020.
[55] IRASSAR, E.F., “Sulfate attack on cementitious materials containing limestone filler - A review”, DOI: 10.1016/j.cemconres.2008.11.007. *Cement and Concrete Research*, v. 39, n. 3, pp. 241–254, 2009.
[56] MAKHLOUFI, Z., BEDERINA, M., BOUHICHA, M., KADRI, E.H., “Effect of mineral admixtures on resistance to sulfuric acid solution of mortars with quaternary binders”, DOI: 10.1016/j.phpro.2014.07.048. *Physics Procedia*, v. 55, pp. 329–335, 2014.
[57] IRASSAR, E.F., “Sulfate attack on cementitious materials containing limestone filler - A review”, DOI: 10.1016/j.cemconres.2008.11.007. *Cement and Concrete Research*, v. 39, n. 3, pp. 241–254, 2009.
[58] BASSUONI, M.T., NEHDI, M., AMIN, M., “Self-compacting concrete : using limestone to resist sulfuric acid”, DOI: 10.1680/coma.2007.160.3.113.*Proceedings of Institution of Civil Engineers*, v. 160, n. CM3, pp. 113–123, 2007.
[59] MAKHLOUFI, Z., BEDERINA, M., BOUHICHA, M., *et al.* “Effect of mineral admixtures on resistance to sulfuric acid solution of mortars with quaternary binders”, DOI: 10.1016/j.phpro.2014.07.048. *Physics Procedia*, v. 55, pp. 329–335, 2014.
[60] MENÉNDEZ, G., BONAVETTI, V., IRASSAR, E.F., “Strength development of ternary blended cement with limestone filler and blast-furnace slag”, DOI: 10.1016/S0958-9465(01)00056-7. *Cement and Concrete Composites*, v. 25, n. 1, pp. 61–67, 2003.
[61] KHAN, M.I., “Nanosilica/silica fume”, in *Waste and Supplementary Cementitious Materials in Concrete: Characterisation, Properties and Applications,* Amsterdam: Elsevier LTD, 2018, pp. 461–491.
[62] PANESAR, D.K., *Supplementary cementing materials*, In: MINDESS, S. (ed.), Developments in the Formulation and Reinforcement of Concrete, 2nd ed. Amsterdam: Elsevier LTD, 2019. pp. 55-85.
[63] JUSTICE, J.M., KURTIS, K.E., “Influence of Metakaolin Surface Area on Properties of Cement-Based Materials”,

DOI: 10.1061/(asce)0899-1561(2007)19:9(762). *Journal of Materials in Civil Engineering*, v. 19, n. 9, pp. 762–771, 2007.

[64] ZHANG, B., TAN, H., SHEN, W., *et al.* "Nano-silica and silica fume modified cement mortar used as Surface Protection Material to enhance the impermeability", DOI: 10.1016/j.cemconcomp.2018.05.012. *Cement and Concrete Composites*, v. 92, n. January, pp. 7–17, 2018.

[65] SAHA, A.K., "Effect of class F fly ash on the durability properties of concrete", DOI: 10.1016/j.serj.2017.09.001. *Sustainable Environment Research*, v. 28, n. 1, pp. 25–31, 2018.

[66] LOTHENBACH, B., SCRIVENER, K., HOOTON, R.D., "Supplementary cementitious materials",

[67] HABERT, G., CHOUPAY, N., MONTEL, J.M. *Cement and Concrete Research*. v. 41, n. 12, pp. 1244–1256, 2011. DOI: 10.1016/j.cemconres.2010.12.001., GUILLAUME, D., ESCADEILLAS, G., "Effects of the secondary minerals of the natural pozzolans on their pozzolanic activity", DOI: 10.1016/j.cemconres.2008.02.005. *Cement and Concrete Research*, v. 38, n. 7, pp. 963–975, 2008.

[68] RODRÍGUEZ-CAMACHO, R.E., URIBE-AFIF, R., "Importance of using the natural pozzolans on concrete durability", DOI: 10.1016/S0008-8846(01)00714-1. *Cement and Concrete Research.*, v. 32, n. 12, pp. 1851–1858, 2002.

[69] SOBOLEV, K., GUTIÉRREZ, M.F., "How nanotechnology can change the concrete world", DOI: 10.1002/9780470588260.ch16. *American Ceramic Society Bulletin*, v. 84, n. 11, pp. 113–116, 2014.

[70] WENG, J.K., LANGEN, B.W., WARD, M.A., "Pozzolanic reaction in Portland cement, silica fume, and fly ash mixtures", DOI: 10.1139/l97-025. *Canadian Journal of Civil Engineering*, v. 24, n. 5, pp. 754–760, 1997.

[71] ZHANG, B., TAN, H., SHEN, W., *et al.* "Nano-silica and silica fume modified cement mortar used as Surface Protection Material to enhance the impermeability", DOI: 10.1016/j.cemconcomp.2018.05.012. *Cement and Concrete Composites.*, v. 92, n. January, pp. 7–17, 2018.

[72] POON, C.S., LAM, L., KOU, S.C., *et al.* "A study on the hydration rate of natural zeolite blended cement pastes", DOI: 10.1016/S0950-0618(99)00048-3. *Construction and Building Materials*, v. 13, n. 8, pp. 427–432, 1999.

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