

Review

Zero-Cement Concrete Resistance to External Sulfate Attack: A Critical Review and Future Needs

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Abstract: The durability of zero-cement concrete or alkali-activated materials (AAMs) is a subject of controversy, especially when exposed to sulfate attacks. This can be due to the different elemental and microstructural compositions of the broad alkali-activated systems that exhibit different degradation mechanisms in sulfate-rich environments. Various parameters, such as properties of raw source materials (nature, fineness, and mineralogy), activators (type and concentration), mixture design, curing regime, types of sulfate salt and sulfate ion concentrations, and weathering conditions, are considered to have a significant impact on zero-cement concrete sulfate attack resistance. Furthermore, the adequacy of the standard sulfate immersion tests raises more concerns about the reported behavior. This paper presents a critical review of the current aging protocol associated with ordinary cement resistance and zero-cement concrete or AAMs to external sulfate attack.

Keywords: alkali-activated materials; zero-cement concrete; sulfate attack; sulfate type; concentration; condition



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1. Introduction

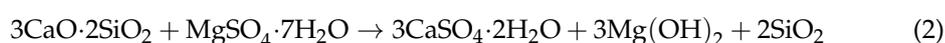
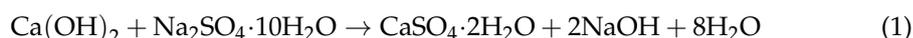
The external sulfate attack, resulting from the invasion of sulfuric ions in soils, underground, marine, or industrial wastewaters, is a significant deterioration process of concrete in-service. Although sulfates usually damage the cement-paste matrix, their adversity depends on the types of cement (binder) used, nature and concentrations of sulfate solutions, concrete quality, and surrounding conditions. In general, cement paste pores are filled with a highly basic solution (i.e., pH > 12.5). Hence, any medium with a lower pH value will represent an aggressive environment for the cement matrix [1]. Concrete exposed to sulfate attack suffers from expansion, cracking, strength loss, and eventually disintegration [2].

In recent years, there has been an increasing emphasis on the durability of concrete under sulfate attack environments and increasing concern about their premature failure and costly rehabilitation techniques [3]. The suitability of cement-based concrete standards and measures available in the literature to simulate the long-term resistance to external sulfate attack is still controversial. On the other hand, all durability specifications and related standards were established, assuming ordinary Portland cement (OPC) as the sole binder. The inadequacy of the current standards in considering the replacement of OPC by alkali-activated materials (AAMs) has limited its expansion in the market. Few attempts to study the resistance of AAMs to sulfate attack were recorded [4]. On the other hand, there is still a dearth of information on AAMs' resistance to these environments.

Therefore, this review's primary purpose is to present a critical analysis of the adequacy of classical/advanced sulfate tests in the field of alkali-activated materials to understand the underlying mechanisms governing the deterioration of those mixtures. It also raises questions about the possibility of developing a new modeling approach that considers the interaction between AAMs and sulfates.

2. Chemistry and Physics behind External Sulfate Attack

Dissolved sulfates from external sources (i.e., soil and groundwater) can migrate and react with the hydrated paste matrix leading to the formation of gypsum, ettringite, and sometimes thaumasite. These products may cause expansion, cracking, softening, and disintegration of concrete. During the reactions between sodium sulfate (Na_2SO_4) or magnesium sulfate (MgSO_4) salts with other primary mineral phases (cement clinker, carbonates, and calcium silicate hydrate (C–S–H)), different reaction products are developed [5,6]. Ammonium sulfate, sulfuric acid, and magnesium sulfate are other forms of sulfate solutions that can decompose the cementitious matrix by inducing decalcification of C–S–H, which contributes to strength loss [7]. Reactions between different sulfate solutions and paste matrix products are shown in the following equations.



where (H_2O) is water, (NaOH) is sodium hydroxide, and $\text{Mg}(\text{OH})_2$ is magnesium hydroxide (brucite), respectively. In addition to gypsum formation, expansion is usually associated with ettringite formation in the inner regions of the cementitious matrix with high pH, which can contribute to specimen swelling and softening of pastes (strength reduction). Furthermore, magnesium silicate hydrate (M–S–H) may be formed after the reaction between $\text{Mg}(\text{OH})_2$ and aqueous silica.

According to [6,8], the consumption of calcium hydroxide (C–H) in Na_2SO_4 solutions do not result in loss of alkalinity due to NaOH production. However, Na_2SO_4 may cause the decalcification of C–S–H after the depletion of C–H in the cementitious matrix. On the other hand, the low solubility (0.01 g/l) of brucite, as well as the low pH (<10.5) of the pore solution due to the C–H consumption, increases the reaction rate in the MgSO_4 solution. As a result, C–S–H releases C–H to restore its pH balance, but C–H responds in a continuous cycle of reactions and reacts with MgSO_4 , transforming it into gypsum and brucite.

3. AAM Deterioration

The multidimensionality concerns associated with AAMs' resistance to sulfate attack (externally or internally) have led to a scientific focus to understand the decay mechanisms and consequences on AAMs structures. Various parameters such as raw source materials (nature, fineness, and mineralogy), activators (type and concentration), mixture design, curing regime, sulfate ion, and concentration, in addition to weathering conditions, are believed to affect the resistance to sulfate attack. According to their main elemental reaction products, alkali-activated materials can be classified into two categories: high-calcium and low-calcium AAM systems. For example, alkali-activated slag (AAS) belongs to the high-calcium $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ (C–A–S–H in cement notation) gel class in addition to the formation of secondary phases. In contrast, alkali-activated low-calcium fly ash (class F) (AAFA) or metakaolin (AAMK) generates gels classified as $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ (N–A–S–H in cement notation). It is important to note that the activator's selection dramatically affects the chemistry of high- and low-calcium systems [9,10]. For example, in the AAS system, the crystalline phase of the hydrotalcite gel type is produced with either NaOH or water glass [11], while calcium carbonate is formed in Na_2CO_3 activated systems [12].

The most dominant theme of sulfate attack that leads to expansion and cracking in high-calcium AAMs is the ettringite and gypsum precipitation [13–16]. A source of aluminum (Al) and calcium is needed after penetration of sulfates to react and form calcium sulfoaluminate ($\text{C}_6\text{AS}_3\text{H}_{32}$) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) [17]. However, alkali-activated systems are incredibly resistant to sulfate attack, given the presence of hydrotalcite gels, absence of portlandite, and tightly bound aluminum in the C–(A)–S–H, N–A–S–H, and N–(C)–A–S–H [18]. El-Sayed et al. [19] reported better durability and higher resistance to ettringite formation in AAS mixtures activated with $\text{NaOH} + \text{Na}_2\text{SiO}_3$ than with NaOH , in a 5% MgSO_4 solution for 180 days. Similar conclusions were drawn by Puertas et al. [20],

who detected traces of ettringite in NaOH-activated FA/slag mortars compared with NaOH + Na₂SiO₃ mixed solution in Na₂SO₄ solutions. This was attributed to the increase in the Na content due to Na₂SiO₃ addition leading to a more stable and high-strength microstructure. Ismail et al. [21] and Saavedra et al. [22] reported that magnesium sulfates were more aggressive due to gypsum formation and C–S–H decomposition. Since Al was assumed to participate in N–A–S–H gels' structure, ettringite was not detected.

On the other hand, low-calcium AAM systems typically demonstrate adequate sulfate resistance due to the development of a more robust structure [23]. An extensive study by Bakharev [24] reported the resistance of AAFA concretes to 5% Na₂SO₄, 5% MgSO₄, and 5% Na₂SO₄ + 5% MgSO₄ for 5 months using either NaOH + KOH, NaOH, or Na₂SiO₃ activators. It was concluded that the AAM compressive strengths using NaOH + KOH and Na₂SiO₃ activators decreased by 65% and 18% in Na₂SO₄ solution, respectively, but increased by 4% using NaOH. Conversely, in the MgSO₄ solution, an increase in the strength was observed during the utilization of NaOH and NaOH + KOH activators by 12% and 35%, respectively, while a reduction by 24% using Na₂SiO₃ activator. This was attributed to the migration of alkalis into solution during the exposure to Na₂SO₄. In MgSO₄ solutions, both mixtures prepared using Na₂SiO₃ and a mixture of NaOH + KOH showed the migration of alkalis into sulfate solutions and diffusion of Mg²⁺ and Ca²⁺ to the subsurface areas of specimens. It was noted that exposure to 5% Na₂SO₄ + 5% MgSO₄ resulted in the least strength changes compared to cement-based specimens. Thokchom et al. [25] reported the performance of AAFA mortars exposed to 10% MgSO₄ solution for 24 weeks. The variation in Na₂O % was found to have a significant influence on the pH value, causing the migration of more alkalis from specimens into the MgSO₄ solution. Mortars produced with higher Na₂O % behaved better than those with lower alkali content.

These controversial findings are attributed to the various assessment criteria and evaluation methods associated with the microstructural changes during sulfate attacks. Unifying assessment criteria and evaluation methods will help identify the deterioration process and understand its related damaging products.

4. Current Standards and Specifications for Sulfate Resistance

Building materials must meet the minimum standards outlined in building codes to pre-qualify concrete mixtures in different exposures along with standard test methods [26]. Therefore, specifications should be evolved on an ad hoc basis to develop and add new testing techniques or set new specification limits for various commercially available binders. However, standards are widely criticized for not being responsive to new research findings and lagging behind recent material technology and construction practices. A summary of the primary current and former standards and specifications for concretes prone to sulfate attack is presented in the following subdivisions.

4.1. North America

ASTM C 452 standard, which was developed in 1946 and initially published in 1960, was the first standardized test in North America for assessing the sulfate resistance of conventional concrete material. Throughout this standard, concrete resistance to sulfate attack is evaluated by measuring the expansion of mortar bars produced from ordinary cement and extra gypsum blend, making a total SO₃ content of 7% by mass of cement. Before mortar bars are made, gypsum should be added to Portland cement; hence, the transport properties do not control the attack rate. This technique would accelerate the experiment by reducing the time for sulfate ingress to mixtures. Cast mortar bars are then stored in water at 23 °C, and expansion is measured for up to 14 days. The sulfate-resisting Portland cement (Type V) expansion must not exceed 0.04% after 14 days (Table 1). It should be noted that this standard is unsuitable for testing blended cement or blends of Portland cement with pozzolans or slags (ASTM C 1012). The main aim of using blended cement in concrete is to reduce the diffusion of external aggressive constituents such as sulfate solutions. Hence, sulfate reactions start immediately due to an admixed gypsum that does not reflect the role

of blended cement in slowing the diffusion of external sulfate solutions. These blended systems' nature depends on consumed calcium hydroxide to provide resistance and reduce permeability, thus requiring hydration before sulfate exposure.

Table 1. Different standards, specifications, and building codes for concrete prone to sulfate attack.

Standard	Class of Exposure	Category	Concentration of Sulfates as SO_4^{2-}		Max. w/cm	Min. Strength (MPa)	Cementitious Material
			Dissolved in Water (ppm)	Water-Soluble in Soil (% by Mass)			
ACI318 (2014)	S0	Negligible	<150	<0.10	N/A	17	N/A
	S1	Moderate	≥ 150 and <1500	≥ 0.10 and <0.20	0.50	28	Type II or equivalent [§]
	S2	Severe	≥ 1500 and $\leq 10,000$	≥ 0.20 and ≤ 2.00	0.45	31	Type V or equivalent [§]
	S3	V. Severe	$>10,000$	>2.00	0.40	31	Type V plus pozzolan/slag cement
CSA A23.1(2014)	S-1	V. Severe	$>10,000$	>2.00	0.40	35 ^b	HS or HSb
	S-2	Severe	1500–10,000	0.60–2.00	0.45	32 ^b	HS
	S-3	Moderate	150–1500	0.20–0.60	0.50	30 ^b	MS, MSb
NBR 12,655 (2015)	I	Low	0–150	<0.10	0.60	20	SR
	II	Moderate	150–1500	≥ 0.10 and <0.20	0.50	35	SR
	III and IV	Severe and V. Severe	>1500	≥ 0.20	0.45	40	SR
EN 206-1:2013	XA1	Mild	≥ 200 and ≤ 600	≥ 0.20 and ≤ 0.30	0.55	30	High SRPC CEM III/B
	XA2	Moderate	>600 and ≤ 3000	≥ 0.30 and ≤ 1.20	0.5	30	High SRPC CEM III/B
	XA3	V. Severe	>3000 and ≤ 6000	>1.20 and ≤ 2.40	0.45	35	High SRPC CEM III/B
IS 456 (2000)	I	Mild	<300	<0.2	0.55	20	OPC or OPC/slag or OPC/pozzolan cement
	II	Moderate	300–1200	0.2–0.5	0.50	25	OPC or OPC/slag or OPC/pozzolan cement or SRPC
	III	Severe	1200–2500	0.5–1.0	0.45	30	OPC/slag or OPC/pozzolan or SRPC
	IV	V. Severe	2500–5000	1.0–2.0	0.45	35	SRPC
	V	Extreme	>5000	>2.0	0.40	40	SRPC
AS 3972	A2	Mild	<1000	<0.50	0.55	25	GP, GB
	B1	Moderate	1000–3000	0.50–1.0	0.55	32	GP, GB
	B2	Moderate	3000–10,000	1.0–2.0	0.50	40	SR
	C1 and C2	Severe and V. Severe	$>10,000$	>2.0	0.45	≥ 50	SR

N/A: Not applicable (no special requirement); MSb: Moderately sulfate-resistant blended hydraulic cement (CSA A3001-03); ^b: Compressive strength at 56 days; MS: Moderately sulfate-resistant blended hydraulic cement (CSA A3001-03); HSb: Highly sulfate-resistant blended hydraulic cement (CSA A3001-03); GP: General-purpose cement; SR: Sulfate-resisting cement; GB: General-purpose blended cement; [§]: same performance criteria.

Another standard is the ASTM C 1038, published in 1985. It is similar to ASTM C 452, except that no additional gypsum is added. However, the test only applies to a Portland cement binder. This test method determines how a mortar bar is expanded when stored in water containing sodium sulfate. The expansion limit is set to 0.02% after 14 days of immersion. Since this standard attempted to set minimum concrete requirements exposed to an externally aggressive environment, the 14-day expansion limit was decreased to half compared to ASTM C 452. Hypothetically, this could be due to slow concrete deterioration after exposure to external sulfate substances and, as a result, a potential decrease in the expansion (owing to volume change). However, the sulfate attack mechanism in ASTM C 1038 does not represent the field's conditions realistically. Therefore, a new approach was needed for field-like testing conditions using ordinary or blended cement; thus, ASTM C1012 was published.

ASTM C 1012 was established by the ASTM C01.29 sulfate resistance subcommittee, based on an understanding of the ASTM C452 boundaries, and published in 1984. The committee started the formulation of a new performance test that would apply to Portland cement in addition to Portland cement blends. In this test, the addition of sulfate to the mortar is prevented during the mixing process. However, after the mortar has reached a specific strength, specimens are immersed in a high concentration of sodium sulfate solution (5.0% Na_2SO_4 at 23 °C). Then, the change in length (expansion) is measured.

Given the high variation over many years, the subcommittee established a minimum strength requirement of 20 MPa before immersion, regardless of the cement material used, in addition to solution molarity of 0.352 Na₂SO₄.

To meet the ASTM C1012 test procedure, ACI 201.2R Guide to Durable Concrete has established four classes of sulfate exposure and their corresponding prescriptive measures. These limits are still used in North American specifications such as ACI 318 and CSA A23.1 for blended cement (ASTM C 595, C 1157, C 989, and C 1240 and CSA A3001).

The expansion limits rely on the severity of desired exposure conditions. The test criterion requires a maximum expansion limit of 0.10% for 6 months of exposure to moderate sulfate (S1) environment while maximum limits of 0.05% and 0.10% for severe sulfate exposure environment (S2) at 6 and 12 months, respectively.

For exposure to an extremely severe sulfate environment, the standard permits up to 0.10% expansion after 18 months of exposure. ASTM C 1012 has rapidly become the only critical performance test for cementitious systems and concretes exposed to sulfate-rich environments [27]. Since it has been considered to represent the field exposure conditions more closely than the ASTM C452, specifically when sulfates penetrate the mortar before hydration product formation. However, the only disadvantage can be that the test is too slow, as it takes an average of 6 months before important test outcomes are achieved.

On the other hand, the Canadian specification (CSA A 3004-C8) was adapted from ASTM C1012 to evaluate blended cement mortar bars' expansion due to external sulfate attack through two procedures. Procedure A is the same as in ASTM C1012, where mortar bars are exposed to 5% Na₂SO₄ solution at 23 °C, to determine the resistance to the ettringite form of sulfate attack. Procedure B is the same as Procedure A, but the storage conditions are different. Mortar bars are stored at 5 °C in the same sulfate solution to trace the potential of sulfate thaumasite attack, as outlined in the 13th edition of CSA A3004-C8. However, Procedure B was withdrawn in the fifth update of the 2013 version as its findings in compliance with CSA protocol A3004-C8 have not contributed to the concrete resistance of sulfate. Furthermore, Procedure A expansion limits are appropriate for showing good concrete resistance to sulfate attack (CSA-Group, 2018).

CSA A3004-C8 also outlines the abridged prescriptive requirements for concretes under different exposure classes besides the limiting values such as the maximum water-to-cement ratio, minimum compressive strength, and testing age. It should be noted that, instead of the regular 28-day strength, the Canadian standard specified 56-day compressive strength for certain exposure groups due to the potential use of blends of Portland cement (Table 1). Other international standard codes are quite similar in their testing procedures and conditions; however, their evaluation techniques and failure criteria may differ [28–30].

4.2. Australia

The Australian Standard AS 2350 was developed and derived from ASTM C1012 to determine the potential of different cement types in a sulfate-rich environment. Test results demonstrate that the ASTM mortar bars (25 × 25 × (285) or 160 mm) displayed minimal expansion relative to the German bars (10 × 40 × 160 mm) using different cement types. It also showed that after 16 weeks of immersion in a 5% Na₂SO₄ solution, it is possible to distinguish between the various cement types. Hence, it adopted and updated ASTM C452 and C1012 test methods to establish a more reliable and rapid test protocol. Based on these results, using the adjusted mortar bar (15 × 40 × 160 mm) that was cured for 7 days is the most convenient and practical measure for sulfate attack specified in AS 2350. According to AS 3972 "General purpose and blended cements", the maximum expansion criterion for sulfate-resistant cement (Type SR) should be below 900 με at 16 weeks (0.09%). However, this criterion is not appropriate for different types of SR cement, whether Portland or blended cement.

4.3. Europe

The European standard EN 206-1 (BSI, 2013) identifies several sulfate exposure classes and specifies some concrete characteristics to be used accordingly (Table 1). However, in the European specifications, there is no equivalent standard to ASTM C1012 for determining the sulfate resistance of Portland or blended cement (EN 197-1, 2000). Therefore, an amendment to EN 197-1 (2000) was adopted in 2006 by proposing seven cement types, CEM I cement with ($C_3A \leq 5\%$), slag cement (CEM III B/C), and pozzolan cement (CEM IV A/B) with low ($C_3A \leq 9\%$) for concretes functioning in sulfate environments [26]. It should be noted that exposure classifications in EN 206-1 are considered for use in the South African National Standard SANS 10100-2 in a revised format to fit South Africa's conditions.

In Germany, the evaluation of sulfate attack follows the old German method, DIN 1164:1958, derived from the Wittekindt method. The method involves the exposure of 10 mm × 40 mm × 160 mm cement mortar prisms, with defined masses of cement, fine and coarse sand plus w/c ratio, to a high concentration of Na₂ SO₄ solution renewed monthly. The concentrated solution used in the original Wittekindt method was 0.15 mole Na₂ SO₄ or 14,400 mg/L SO₄²⁻ [31]. The SO₄²⁻ concentration is 2.4 times higher than the upper limits of the XA3 exposure class to chemical attack, which is by far the most aggressive class compared to those set by current European standards (EN 206-1:2013). It is worth noting that these limitations are proposed for aqueous solutions only and not for soils without freeze–thaw scenarios. On the other hand, the renewal of solutions to preserve the concentration of SO₄²⁻ to allow the attack to continue is another crucial issue mentioned in the Wittekindt method. This can be because, in reality, the origin of SO₄²⁻ is continuously renewed, depending on the fresh supply of sulfate ions at either a lower or higher rate.

4.4. India

The Indian IS 456 (2000) code, first published in 1953 and entitled “Practice Code for Plain and Reinforced Concrete for General Construction,” is considered a convenient benchmark for durability-related parameters. In terms of sulfate attack, excessive amounts of water-soluble sulfate (SO₃) in most cement and some aggregates may cause concrete to expand and deteriorate. Hence, the overall SO₃ quantity in concrete mixtures, as specified in IS 456, shall not exceed 4% by mass of cement. However, concrete mixtures containing IS 6909 compliant super-sulfated cement shall not apply the 4% limit. According to the sulfate concentration severity, three exposure conditions were qualitatively defined for external sulfate attack: mild, moderate, and severe. However, the fourth revision of IS 456 standard was adopted and developed to include detailed durability factors. Two environmental exposure conditions, i.e., very severe and extreme exposure conditions, have been added, as shown in Table 1. The guideline also includes recommendations for concrete mixtures prone to sulfate attacks, such as the type of cement used, the minimum cement content, and the maximum water/cement ratio.

4.5. Brazil

Two Brazilian committees developed NBR 13583 CB/CE-18 to determine the dimensional variation of cement mortar bars exposed to sodium sulfate solution. The test method includes preparing mortar bars (25 × 25 × 285 mm) for length change measurements. This is followed by a curing procedure, 48 h (first stage) in a humid chamber, then 12 days (second stage) in a lime-saturated water solution before the exposure to sodium sulfate solution. After 14, 28, and 42 days, the mortar bars' resulting expansion should be determined. NBR 13583 is believed to be a comparative analysis standard since it does not specify the maximum expansion limit to which the composition may or may not be considered resistant to sulfate attack. On the other hand, the Technical Brazilian Standard Association, ABNT NBR 12655 (2015), suggested four aggressive exposure environments (Table 1) in addition to the minimum in-service concrete requirements to be met before sulfate exposure.

4.6. China

The Chinese GB 749 standard, adapted in 1954 from the H114-54 Soviet Union standard, measures concrete resistance to sulfate attacks from the relative flexural strength of mortar prisms. Strength tests are performed on mortar bars (10 mm square-section \times 30 mm) that are immersed in a Na_2SO_4 solution or any field-like environment, in addition to mortar bars immersed in plain water for comparison. It should be noted that GB 749 is considered a simple evaluation criterion technique. One explanation can be that this approach does not reveal the concentration of sulfate solution. In other words, the effect of sulfate concentration, i.e., high and low SO_4^{2-} on the mechanism of attack is not taken into consideration [32].

Later, the GB 2420 test method was developed based on the GB 749 limitations, but a change in the prism length dimension of $10 \times 10 \times 60$ mm was made before the full immersion in a 3% Na_2SO_4 solution. The pH level of sulfate solutions should be maintained at 7.0 for exposure periods of 28 days and up to 6 months by titrating at 1 N H_2SO_4 . Since GB 2420 is intended to be an accelerated test to investigate different cement types, the experiment should be performed concurrently with the GB 749 test to provide more reliable results. Mortar bars with a relative flexural strength of ≤ 0.80 at the age of 6 months are classified as low sulfate resistance. GB 2420 may eventually reflect the cement's ability to withstand gypsum crystallization, but this method does not reveal the potential to resist sulfate completely.

5. Type and Concentration of Sulfate

The exposure to Na_2SO_4 appears to be favorable for AAM structural evolution and system densification, which corresponds to Na_2SO_4 's defined function as an activator [33]. Under existing test protocols, exposure of AAMs to Na_2SO_4 solutions generally does not promote material expansion or cracking, as the former deterioration mechanisms are linked to the formation of secondary ettringite and gypsum products. On the other hand, leaching of Ca^{2+} , Na^+ , and Mg^{2+} from active minerals was reported to instigate the disintegration of microstructural frameworks [34–36]. In contrast, MgSO_4 attack can lead to decalcification of C–A–S–H gels, in addition to gypsum and MgOH_2 formation [34,36].

Since ASTM standards have been proposed as methods for investigating the sulfate resistance of cement-based materials, their reliabilities were questioned and criticized for a long time. ASTM C1012, for example, is widely believed to overlook important field performance parameters for concrete structures exposed to sulfate attacks [5,6,26,27]. A closer look at the standard reveals that the sulfate attack mechanisms are pertinent to the composition of sulfate solution but more to the SO_4^{2-} ion. Thus, ASTM C 1012 does not cover solutions other than Na_2SO_4 ; in addition, it marginalizes other sulfate solutions such as MgSO_4 that are available for simulating environmental exposure conditions in the field. However, the attack mechanism and the manifestation of damage vary depending on the cation that accompanies sulfate ions such as Ca^{2+} , Na^+ , Mg^{2+} , and Fe^{3+} . For example, Na_2SO_4 solution attacks tricalcium aluminate (C_3A) and calcium hydroxide (C–H) and forms ettringite and gypsum reaction products resulting in severe cracking due to expansive expansion stresses generated. On the other hand, all cement reaction products, even C–S–H, are attacked when the attacking solution is MgSO_4 . To the best of found knowledge, the maximum expansion of Portland cement mortar was reported after the exposure to MgSO_4 [37]. In such circumstances, a dense brucite layer forming on the surface makes the surface degradation imperceptible until the late period of attack, while a decrease in strength starts very early.

Sulfate-resisting Portland cement (SRPC) is a blended cement designed to promote the quality of concrete that is vulnerable to sulfate attacks. However, the SRPC did little to combat the attack against MgSO_4 . For instance, replacing cement with 70% of blast-furnace slag mortar did not last long in the MgSO_4 solution, and similarly, the partial replacement with silica fume (SF) was detrimental [38,39]. Concretes containing supplementary cementitious materials (SCMs) such as SF are beneficial in their resistance to Na_2SO_4 only but are particularly susceptible to MgSO_4 attacks [40,41]. As a case in point, Giergiczny [42] reported a significant decrease in strength and a substantial amount of gypsum in mortars with 10% SF after a year of exposure to 0.123 mole/L MgSO_4 solution. This significantly confirms that the C–S–H decalcification and brucite growth $\text{Mg}(\text{OH})_2$ are critical degradation processes during the MgSO_4 attack. The use of Na_2SO_4 and MgSO_4 sulfate solutions is widespread, as these salts can produce a high SO_4^{2-} environment due to their high solubilities. Prior research has suggested using solutions containing both sulfate types in equimolar quantities or in proportions that simulate the field condition [43–45]. When MgSO_4 is used in a procedure similar to ASTM C1012, it should be noted that vigorous stirring of the solutions is often necessary to prevent the growth of brucite, which slows down the rate of damage [27]. On the other hand, ammonium sulfate has been used occasionally in some studies. However, this salt has been shown to damage concrete more than Na_2SO_4 [46]. In particular, cement containing SF performed worse than cement with low C_3A in ammonium sulfate solutions [47]. As different sulfate solutions cause divergent types of damage, a proper parameter must be used to define the damage. For instance, expansion indicates a stronger Na_2SO_4 attack, while strength loss is a more suitable predictor of the MgSO_4 attack on cement-based materials. Therefore, using one single parameter such as expansion may not be sufficient to define damage [48,49]. The ASTM C 1012 standard does not cover those measures.

There is a consensus that the test method ASTM C 1012 accelerates the attacking mechanism for submerged samples in a high concentration of sulfate solution. The most frequently used solution concentration is 5% Na_2SO_4 (0.35 mole/L) and 5% MgSO_4 (0.41 mole/L). It should be noted that the maximum concentration of sulfate dissolved in water is $\geq 1\%$ among all standards, while water-soluble in the soil is $\geq 2\%$. To conduct an accelerated test, the use of “natural” concentration values of sulfate ions in the solution appears not acceptable. Therefore, higher sulfate concentrations in solutions would enable the attack to develop faster [50]. Only a few research works in literature illustrate the use of a very high concentration sulfate solution, i.e., 10% Na_2SO_4 . The two main arguments put forward are that the deterioration mechanism may be quite different from the chemical attack to be simulated due to the high sulfate concentration that may be close to or above the solubility level. For example, Yu et al. [51] measured the sulfate profile of immersed mortar samples in Na_2SO_4 solutions. The authors observed that the sulfate penetration depth is independent of the sulfate concentration and sample size. However, highly concentrated sulfate solutions will promote gypsum formation [52,53]. However, 10% of MgSO_4 solutions are used for accelerated experiments [54] without any signs of salt crystallization.

Since, in most cases, AAMs do not contain portlandite but mostly C–S–H, and because of aluminum’s vital presence in C–A–S–H and hydrotalcite gels, this form of binding material could be highly resistant to sulfate attack [4,55,56]. Therefore, to predict its performance in rich sulfate environments, the synergistic effect of different sulfate concentrations and types should be considered to simulate field conditions. Table 2 summarizes the resistance of AAMs to external sulfate attacks, reviewed in previous studies.

Table 2. Summary of AAM resistance to external sulfate attacks reviewed in studies.

Precursors	Activators	Sulfates	Aging Protocol			Reference
			Corrosion Period	Corrosion Products	Deteriorating Environment	
Slag	NaOH + Na ₂ SiO ₃	5% Na ₂ SO ₄ 5% MgSO ₄	12-month	Gypsum	5% MgSO ₄	[28]
FA	NaOH NaOH + KOH	5% Na ₂ SO ₄ 5% MgSO ₄ 5% (Na ₂ SO ₄ + MgSO ₄)	5-month	Precipitates	5% Na ₂ SO ₄ 5% MgSO ₄	[24]
FA	NaOH + Na ₂ SiO ₃	10% MgSO ₄	24-week	Anhydrite, Ettringite	10% MgSO ₄	[25]
Slag	NaOH + Na ₂ SiO ₃	5% Na ₂ SO ₄	3-month	Gypsum, Ettringite	5% Na ₂ SO ₄	[4]
Slag + POFA	NaOH + Na ₂ SiO ₃	5% Na ₂ SO ₄ 5% MgSO ₄	6-month	Anhydrite, Brucite, Serpentine	5% Na ₂ SO ₄	[34]
Slag	NaOH + Na ₂ SiO ₃	10% Na ₂ SO ₄ 10% MgSO ₄	12-month	Gypsum, M-S-H	10% MgSO ₄	[30]
Slag + NVP	NaOH + Na ₂ SiO ₃	5% Na ₂ SO ₄ 5% MgSO ₄	730-day	Gypsum, Brucite	5% MgSO ₄	[36]

POFA: Palm Oil Fuel Ash. Gypsum: CaSO₄ 2H₂O. Brucite: Mg(OH)₂. Serpentine: Mg₃Si₂O₅(OH)₄ 12H₂O. Anhydrite: CaSO₄. NVP: Natural Volcanic Pozzolan.

Alkali-activated concretes, particularly high-calcium precursors, are affected by the type of cation Na or Mg in sulfate solutions. Komljenović et al. [4] investigated the resistance of alkali-activated slag (AAS) mortars to immersion in a 5% Na₂SO₄ solution. It was reported that after 90 days of immersion, AAS mortars showed no mass loss and an 11% increase in strength. This could be due to the continuous formation of AAS reaction products due to the sulfate medium's high alkalinity. These results are in agreement with Bakharev et al. [28], where AAS mixtures exposed to 5% Na₂SO₄ showed more resistance than to 5% MgSO₄ solutions after 365 days (Table 2), which was also observed by Beltrame et al. [49].

The author attributed the strength loss of AAS in MgSO₄ solution to the absence of portlandite Ca(OH)₂ that allows the formation of a protective brucite Mg(OH)₂ layer. This promoted the direct attack of Mg ions on the C–S–H structure besides the formation of M–S–H and gypsum expansive products.

Yusuf [34] and Salami et al. [35] investigated the resistance of AAS–ultrafine palm oil fuel ash (POFA) mortars to 5% Na₂SO₄ and 5% MgSO₄ solutions. In Yusuf [34], slag inclusion up to 20% in mortars contributed to better sulfate resistance. The Na₂SiO₃/NaOH ratio variation resulted in a negligible strength retention difference. The residual strengths for the slag-free mortars were 16.5% (in Na₂SO₄) and 76.8% (in MgSO₄) after 6 months, respectively. The investigation attributed the severe deterioration of mortars exposed to 5% Na₂SO₄ solution to the leaching of active minerals (Ca²⁺, Mg²⁺, Na⁺), instigating the disintegration of the microstructural framework. However, better strength retention was observed in MgSO₄ solution owing to the formation of surficial white deposits and crystallized anhydrite (CaSO₄). Similar results were obtained by Salami et al. [35] in terms of the resistance to sulfate attack. The exposure to 5% Na₂SO₄ and 5% MgSO₄ solutions for 9 months confirmed that the deterioration of mortars depends on the type of cations carried by sulfate solutions. Mithun and Narasimhan [30] studied the resistance of AAS concrete using copper slag (CS) as an alternative to natural river sand with up to 100% by volume. It was concluded that the replacement of CS by natural sand had reinforced the produced alkali-activated mixtures. After 12 months of exposure to 10% Na₂SO₄ solutions, no strength deterioration was observed in AAS with CS. Contrary to that, in 10% MgSO₄

solutions, mixtures suffered from a higher degradation rate due to the constant attack of Mg ions on the C-S-H structure, forming M-S-H and gypsum.

6. Specimens' Composition, Shape, and Size

The primary assessment for the sulfate attack test is the length change of the mortar prisms, although the size of prisms differs. ASTM C 1012 and most other standards specified the composition of mortar prisms, i.e., a sand-to-cement ratio of 2.75:1 and w/c of 0.485. Higher w/cm ratios of ≥ 0.50 and the higher sand-to-cement ratio of 3 or 4 were also used in other experiments. However, the higher w/cm used in specimens contributes to greater total porosity and permeability, promoting the ingress of sulfate and quick deterioration. The cement-rich samples showed better workability, higher expansion, and higher capillary pore content per unit volume of mortar at a constant w/cm ratio. However, paste or mortar prisms will affect the process of deterioration by eliminating the physical effect of the inferential-transition zone (ITZ) between the hydrated cement paste and aggregates [6,7,27]. The presence of the ITZ may impact the resistance of concrete mixtures to sulfate attack as it is richer in C-H and characterized by its higher porosity.

Various studies have demonstrated the significant effect of samples' composition, geometry, and scale on the concrete resistance to sulfate attack. According to the assessment's main objective, besides the acceleration needed for the test, samples' geometry and composition might vary. Various research methods have been commonly used, such as lean mortar bar tests with different cross-sectional sizes. Indeed, there are inconsistencies associated with the samples' structure in the wide-ranging test protocols and international standards (Table 3). For example, the cross section of specimens in various codes ranges from 25 × 25 mm in ASTM methods to 10 × 10 mm in GB methods, 15 × 40 mm in AS methods, and 10 × 40 mm in DIN 1164 (German–Wittekindt flat prism technique). These inconsistencies have affected the proper simulation of field-like conditions. Tables 1 and 3 summarize the main test methods, along with their requirements.

Table 3. Different performance requirements for concrete susceptible to sulfate attack.

Standard	Class of Exposure	Performance Requirements—Maximum Expansion (%)						Sample Size
		At 14 Days	At 112 Days	At 3 Months	At 6 Months	At 12 Months	At 18 Months	
ACI 318 (2014)	S-0							25 × 25 × 285
	S-1				0.10			
	S-2				0.05	0.10		
	S-3						0.10	
ASTM C452	*	0.04						25 × 25 × (285) or 160
ASTM C1038-95	*	0.04						25 × 25 × 285
ASTM C1012	*				0.05	0.1		25 × 25 × 285
AS 2350-14	*		0.09					15 × 40 × 160
CSA A3004-C8	S-1				0.05	0.10	0.10 §	25 × 25 × 285
	S-2				0.05	0.10	0.10 §	
	S-3				0.10	0.10	0.10 §	
DIN 1164:1985				$\leq 0.50^a$				10 × 40 × 160
GB 2420 and 749					$\leq 0.08^{**}$			10 × 10 × 60
IS 12330-1988	*	≤ 0.045						25 × 25 × 250
NBR 13583								25 × 25 × 285

* For high-sulfate-resistance (HSRPC) cement type. ** Relative flexural strength. ^a Expansion difference ($\Delta\epsilon$). § Maximum expansion when tested using CSA A3004-C8 Procedure B at 5 °C, %.

Unlike square-section prisms (i.e., 10 × 10 mm or 25 × 25 mm), flat-section mortars of 10 × 40 mm or 15 × 40 mm have shown earlier and higher expansion values than their counterparts. Recent research appears to validate the view that when the size of mortar prisms increased, expansion began to be delayed [51,57,58]. Yu et al. [51], for example,

pointed out the occurrence of expansive forces when sulfates penetrate the mixtures, which are hindered by the core. Therefore, the use of flat prisms will help overcome the constraining effect of the core. In which sulfate components can penetrate the inside of the specimen in less time and produce more consistent outcomes. However, the reported expansion values would be much lower with thicker specimens. In addition, the attack will disintegrate the surface of the specimen due to opposed expansion between layers. Concerning the behavior of AAMs in the sulfate environment, Beltrame et al. [49] suggested that the use of 10×60 mm prismatic paste samples increased the expansion rate.

7. pH of the Solution

The average pH of 1.8 million soil samples collected from different locations in North America was ≤ 6.0 [59], while the average pH of seawater was around 8.0 [3]. Some sulfate attack experimental systems allow pH monitoring to better simulate conditions in the field, i.e., groundwater or seawater, besides accelerating the test procedure [60]. For example, by constant sulfuric acid titration (H_2SO_4), Mehta [61] suggested a preliminary immersion test with a low Na_2SO_4 solution pH value of 6.2. Brown [62] followed the same method and found that monitoring the pH significantly accelerated the rate of sulfate attack by increasing the consumption of sulfate ions simultaneously as the leaching of hydration products. This accelerated the onset of mortar expansion due to the formation of ettringite products. Cao et al. [63], on the other hand, demonstrated that lowering the pH of sulfate solutions (pH ≈ 3) had a significant impact on the resistance of FA (class F) + silica fume and slag blended systems due to C-S-H decalcification.

Fernandez-Altale [64] and Chabreliel [65] noted that maintaining a constant pH of sulfate solutions had delayed the expansion and prevented leaching. The pH of the initial Na_2SO_4 bathing solution in the ASTM C 1012 ranges between (6.0 and 8.0). Meanwhile, after immersion of specimens, the pH value increases gradually to ≥ 12.0 due to the leaching of alkalis from concrete to the surrounding solution. It should be noted that the pH of the sulfate solution is not controlled in the commonly used standard. Therefore, the used ASTM standard is not a fully valid indication of the field condition, and if used to predict field performance, discrepancies may arise.

Varying performance is reported for AAMs, ranging from superior to weak when exposed to aggressive sulfate environments. This can be due to the wide-ranging mixture formulation starting from the precursor and activator selection to the dosage used and the curing condition ending with the test protocol used. In general, the use of an appropriate high-alkaline activator in AAMs would increase the system's pH and protect it from sulfate attacks. In addition, the use of a carbonate anion, for example, accompanying the activator, may decrease the risk for decalcification, thereby increasing the solubilization of silica and alumina [66]. Questioning the binder's composition and the microstructure of AAC will indeed detect its deterioration mechanism in terms of the total matrix porosity and alkali leaching to the sulfate solution [67]. Therefore, monitoring the pH of the sulfate solution and conducting leaching tests will help track the amount of leachable elements and increase these materials' credibility.

8. Single Damage-Factor Tests

Different test methods are used to study the external sulfate attack mechanisms and effects, such as ASTM C1012 "Standard Test Method for Length Change of Hydraulic-Cement Mortars Exposed to a Sulfate Solution." This international ASTM C1012 test procedure has frequently been used but criticized due to its limitation (orientation–expansion effect). Taylor [68] pointed to the fact that laboratory studies focus on expansion and specimen cracking, but experiences in the field indicate a higher loss of adhesion and strength as a predominant sign of deterioration. Moreover, most existing standardized durability testing methods have mainly been developed to test Portland cement systems' long-term durability performance. On the other hand, the use of a single damaging technique, as seen in ASTM C1012, will affect the general understanding of attack mechanisms. This

is very important as the transport mechanism in partially exposed concrete structures does not appear to cause the same distress as in entirely exposed concrete components. Diffusion (as an exposure method addressed in ASTM C1012) is the primary transport mechanism that causes a higher deterioration rate under saturated conditions. Diffusion is also known to be slower than other mechanisms, as an aqueous ionic transport mechanism, and is not apparent until a thermal or concentration gradient is generated. Therefore, the “sulfate-related deterioration rate defies the expectations of the relevant models,” as stated by Santhanam et al. [48].

In partially exposed sulfate structures, the lower portion may be saturated with seawater or groundwater, while the upper portion remains at ambient temperature and humidity conditions. The deterioration usually happens when the sulfates are drawn into the concrete, permeated upwards, and then evaporated upon reaching the surface (wicking action). As a result, various types of degradation, i.e., leaching, microcracking, paste and permeability characteristics alteration, efflorescence, and surface scaling, may present. The degradation can be accelerated by transferring larger amounts of sulfates throughout the matrix. For example, several studies have shown that concrete partially immersed in a sodium sulfate solution can experience significant surface scaling above the solution level [69–74].

To date, this physical form of sulfate attack is not evident when testing a fully saturated specimen, the standard method of exposure. In addition, there is no standard test available for the partially immersed concrete in sulfate solutions. The absence of standardized testing and evaluation criteria for AAMs represents one of the main barriers facing its spread as no reliable long-term durability data are available. Similar to OPC, the intake of sulfate is much slower if it depends on pure diffusion only, but the use of consecutive damaging mechanisms, such as loading/unloading, wetting/drying, and freeze/thaw cycles, allows for the uptake of more aggressive substances that accelerate the rate of deterioration. Thus, integrated testing methods are essential to predict AAMs' different damage mechanisms better while being exposed to sulfate attacks.

9. Multiple Damage-Factor Tests

Field concrete undergoes wetting and drying cycles due to fluctuations in water levels caused by flooding, rainwater runoff, tides, and the cyclic migration of sulfate-containing groundwater through capillarity into the above-ground portion of structures. Such activities induce sulfate salts' crystallization under the concrete surface layer leading to cracking, scaling, and delamination. Current testing approaches cannot predict or capture these complicated deterioration mechanisms (i.e., continuous immersion exposure). In addition, standard immersion tests have frequently presented different performances relative to the observed ones in real-field cases [75]. This might be due to the techniques applied and indoor test procedures in current standard tests such as ASTM C1012 that overlook the critical field conditions. Therefore, a mandatory shift to performance-based specifications for concretes demands elaborating a performance-based evaluation policy that better depicts field conditions.

The question of whether wetting–drying cycles and the underlying mechanisms of this form of damage are physical or chemical is still controversial among researchers. For example, Kalousek et al. [76] investigated the length change of concrete cylinders exposed to Na_2SO_4 solutions by 2.1% in a 20-year long-term research program. Specimens were subjected to wetting–drying cycles to accelerate the test. The specimens were immersed in sulfate solutions for 16 h at room temperature in each cycle, then air-dried for 8 h at 54 °C. After one year in wetting–drying exposures, it was found that eight years of continuous immersion exposure caused comparable damage to concrete specimens under wetting–drying. On the other hand, De Almeida [77] proposed immersing samples in 16% Na_2SO_4 solutions for 2 h (wetting) followed by drying at 105 °C for 10 to 15 h. It was concluded that specimens failed under physical rather than chemical action. Nehdi and Hayek [78] carried out a study in which mortar cylinders were partially immersed in 10% sodium and 10% magnesium sulfate

solutions and exposed to 32–95% constant or cyclic relative humidity (RH) for up to 151 h. Their extensive study found a thick efflorescence layer on the surface of partially immersed specimens in 10% Na₂SO₄ solution only, particularly with cyclic RH. The study of Sahmaran et al. [79] reported the resistance of mortar samples to a 5% sulfate solution accompanied by wetting–drying cycles. Each cycle consisted of the exposure at room temperature for 6 days, followed by drying for 1 day at 100 °C. The wetting–drying exposure was observed to be more aggressive than continuous immersion exposure and contributed to the complete disintegration of the samples within 17 weeks due to repeated hydration and evaporation of sulfate salts. Similarly, Haynes et al. [74] conducted an experiment on partially immersed concrete cylinders in (5% Na₂SO₄) and exposed to various temperatures and RH. It was concluded that samples disintegrated after the exposure to cycles between 20 °C with 82% RH and 40 °C with 31% RH in two-week intervals.

On the other hand, Loser and Leemann [80] introduced a new accelerated sulfate resistance test to Swiss norms. Four cycles of drying and immersion were applied to concrete mixtures throughout different protocols in an oven at 50 or 40 °C. To increase expansion during further immersion, the change from drying for 2 days and immersion for 5 days (Protocol 1) to 5 days drying and 2 days immersion (Protocol 2) was applied. The Na₂SO₄ concentration has to be doubled (Protocol 3), and the MgSO₄ is used instead of Na₂SO₄ in Protocol 4, using a mixed solution of Na₂SO₄ + MgSO₄ (Protocol 5). In Protocols 6 and 7, drying was extended to 12 days at 50 °C and 40 °C, respectively. It was concluded that the use of Protocol 2 should lead to higher ingress of sulfate in addition to the prolongation of the drying step up to 12 days. However, the use of Protocols 3, 4, and 5 did not increase specimen expansion.

More research is still needed on sulfate attack assessments, including wetting–drying cycles. Several researchers [81–83] reported that wetting and drying cycles had no significant adverse impact on AAMs' performance. Some micro-cracks have been introduced due to changes in temperature and/or humidity conditions [81,84]. However, several questions remain unanswered at present, such as the real mechanisms of deterioration after these cycles (e.g., the dry/wet cycles, acceleration of mass transport or leaching of calcium and alkalis) and the degree and time of drying that can simulate the real field conditions. Variations in these parameters remain a challenging task for researchers and standardization agencies. Furthermore, similar to partial immersion exposure tests, there is no standard test available for concrete exposed to drying and wetting cycles. The performance of alkali-activated concrete in various exposure environments simulating field-like conditions needs to be addressed. This procedure will provide an adequate understanding of the mechanisms of deterioration of AAMs in the evaporation zones, resembling partially buried concrete elements, to develop reliable data on their durability.

10. Modeling the Sulfate Attack in Concrete

Several studies have focused on developing various models that can reliably predict the performance of concrete when subjected to sulfate attack. For instance, Atkinson and Hearne [85] proposed an empirical-based model to predict the sulfate-induced degradation of concrete fully immersed in sulfate solutions as shown:

$$X_S \text{ (cm)} = 0.55C_3A ([Mg] + [SO_4]) t(y) \quad (3)$$

where C₃A stands for the tricalcium aluminate content of the cement, [Mg] and [SO₄] are the molar concentrations in magnesium and sulfates, respectively, and *t*(*y*) is the immersion period in years.

Kurtis et al. [86] developed empirical models to predict the behavior of concrete partially submerged in sodium sulfate solutions. The two following expressions were developed to predict the expansion of concrete mixtures made of cement with different C₃A:

(a) Concrete mixtures made of cement with low C₃A content (i.e., <8%)

$$\text{Exp} = 0.0246 + [0.0180(t)(w/c)] + [0.00016(t)(C_3A)] \quad (4)$$

- (b) Concrete mixtures made of cement with high C_3A content ($>10\%$)

$$\ln(\text{Exp}) = -3.753 + [0.930(t)] + [0.0998 \ln((t)(C_3A))] \quad (5)$$

Atkinson and Hearn [87] proposed a mechanistic-based model to predict the service life of concrete exposed to sulfate attack. The proposed model is based on assumptions that sulfate ions penetrate the concrete by diffusion and expansively react with aluminates in the concrete leading to cracking and delamination of concrete surfaces. Cefis and Comi [88] proposed a weakly coupled approach to simulate the mechanical response of concrete exposed to sulfate attack. Tixier and Mobasher [89] developed a chemomechanical mathematical model to simulate the response of concrete exposed to external sulfate solutions. Several other approaches were also developed and proposed to predict the behavior of cementitious materials or concrete exposed to sulfate attack [90–93]. However, to date, in the literature, there is no modeling approach available for predicting the behavior of zero-cement concrete or AAMs when exposed to an environment prone to sulfate. Therefore, future studies need to focus on developing models capable of predicting the behavior of green structures made with zero-cement concrete or AAMs when exposed to sulfate attacks.

11. Conclusions, Remarks, Recommendations

Sulfate attack is a well-known problem leading to concrete structures' deterioration. However, much of the current debate revolves around the lack of consensus on the variables governing the attack mechanisms in international standards and specifications. As illustrated in the previous sections, these include the concentration of solutions, test conditions, sample size, testing periods, insensitivity of the measurement tools to the progression of sulfate attack, and unpredictable relationship to field degradation mechanisms [94]. This also led to an inconclusive debate on whether the current standards and specifications can cope with the variation in the new commercially available binders. In general, blended cement types were found inefficient as their performance depends on the physical and chemical characteristics of source materials, the type of Portland cement used in the blend, and the dosage. On the other hand, the severity of the sulfate attack can be limited to some extent by a combination of compositional control and permeability control. According to Mehta [43], for the development of sulfate-resistant concrete, monitoring the permeability (w/cm) is considerably more important than controlling the chemistry of cementitious binders. The findings of the Hearn and Young [95] investigation support the claim that achieving good resistance to sulfate attacks with different cations is linked to the use of low w/cm (<0.40). It has to be noted that the role of w/cm was addressed in all of the specifications and building codes listed in Table 1, where all specifications endorse the use of a low w/cm value (<0.45) for severe attack conditions.

Research worldwide focuses on using other robust, sustainable, and greener binders, promoting higher durability capacity for structures vulnerable to aggressive environments. Among those binders, the AAM system is a promising alternative for OPC. However, due to their different reaction properties and microstructures relative to OPC, the attack mechanisms and evaluation techniques should differ. Existing standards and test methods were questioned for their authenticity and reliability relevant to alkali-activated concrete resistance to sulfate attack.

This paper presents a critical review of the compatibility of current OPC-related aging protocols with AAM resistance to external sulfate attacks. The following conclusions can be drawn based on the results and discussion:

- Understanding the resistance of zero-cement concrete developed by using a high volume of waste materials that have been alkaline-activated using a wide range of activators requires a high level of effort to be spent on the relevant standards for the recognition of decay and deterioration mechanisms of these binders. Further

validation is needed in both laboratory and field studies to determine the concrete mixtures' overall permeability to control AAMs' transport properties.

- Sulfate attack tests for assessing the zero-cement concrete or AAMs' sulfate resistance are based on test methods for conventional OPC concrete mixtures, despite their different reactions' mechanisms and microstructures. Therefore, selecting the correct test conditions and techniques will allow the accurate assessment of zero-cement concrete performance under different aggressive conditions.
- Particular attention should be paid to cation accompanying salt and its concentration in sulfate-rich environments while analyzing AAM structures' resistance. This will alter AAMs' deterioration mechanism, leading to the decay of these binders when exposed to aggressive environments.
- Monitoring mechanisms for mass loss, strength loss, leaching of active minerals, and matrix cracking due to chemical attacks are recommended to help determine the degradation mechanisms of AAMs exposed to external sulfate attacks.
- Developing holistic assessment techniques to detect sulfate attacks' synergistic effects and single to multiple damage mechanisms under accelerated real-field conditions to determine potential durability is needed.
- In the literature, there is a lack of studies that focus on modeling the behavior of zero-cement concrete or AAMs under sulfate attack. Therefore, to improve the durability of future green concrete structures, more effort needs to be devoted to developing reliable models capable of predicting the behavior of zero-cement concrete or AAMs when exposed to sulfate attacks.

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