NUMERICAL ASSESSMENT OF EXTERNAL SULFATE ATTACK IN
CONCRETE STRUCTURES. A REVIEW.

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ABSTRACT

The slow progress of the external sulfate attack and the large size and criticality of typical structures affected by this phenomenon establish numerical modeling as a key tool to assess the future evolution of concrete structures exposed to sulfate-rich environments. The present review examines a selection of the most relevant numerical models developed during the last two decades to identify and explain the principles and simulation approaches commonly adopted. Assumptions associated with each approach are described to fully disclose the limitations and capabilities of each model. Guidance on model selection is provided based on the outcomes required. Finally, major areas holding significant potential to improve the reliability of the predictions are identified and discussed.

Keywords: Sulfate Attack (C), Concrete (E), Durability (C), Modeling (E)

1. INTRODUCTION

External sulfate attack (ESA) is a degradation process that compromises the durability of concrete elements exposed to sulfate environments. There is certain controversy on which mechanisms are associated with the term ESA. In this paper, ESA refers to the degradation caused by the chemical reactions triggered by sulfate ingress that results in the mass formation of expansive products and the dissolution of calcium-bearing phases. These chemical processes might lead to cracking, progressive reduction of strength and stiffness, overall expansion and mechanical failure inside or outside the
region directly affected by the sulfate penetration [1–3]. Even though surface scaling of concrete due to crystallization of water-soluble sulfate salts is an important degradation process where sulfates are involved, here are not included in the term ESA.

Foundations, nuclear or industrial waste containments and tunnel linings have been affected by ESA. The large size and criticality of these structure elements limit the efficiency of common remedial actions, often placing the monitoring of the structural behavior as the only possible procedure. This scenario prompted the industry to seek ways to optimize the assessment of ESA in existing properties and established the development of reliable prediction models as a key challenge for structural durability.

Several simplified empirical and mechanistic relations were developed during the 1980s and 1990s. Empirical relations refer to analytical models based on direct observations, measurements or extensive experimental data records while mechanistic relations are those procedures based on a simplified understanding of the attack mechanisms. Most of them were derived from accelerated laboratory tests performed with small-scale specimens within a framework of a limited understanding of the mechanisms associated with the attack and poor computational capabilities. In general, early models were developed to predict the penetration of the sulfate degradation depth [4–6] and later evolved towards the estimation of the evolution of expansions [7–10].

The main drawback associated with empirical models is their limited applicability, as these are only valid for elements subjected to the same conditions used in the tests (usually small specimens in highly aggressive environments). On the other hand, most simplified mechanistic models present over-simplified approaches that neglect important aspects of the attack, such as the size of the structure or the interactions between damaged and undamaged regions of the element. Consequently, empirical and simplified mechanistic relations struggle to provide reliable predictions of the long-term performance.

Since the early 2000s, the efforts on numerical modeling have shifted towards a more comprehensive simulation of the different processes involved during the attack. Ionic transport, chemical reactions and micro and macro-structural damage are computed through advanced iterative calculations. The use of complex algorithms improve the capacity of the models to reproduce the specific field conditions found in practice, which allows more realistic predictions.

However, discrepancies on the general perception of ESA, computational procedures and particular mechanisms of the attack (expansion mechanisms or the role of gypsum,
amongst others) led to the development of a large pool of advanced numerical models based on a wide variety of approaches. The complexity inherent to the set of principles adopted by each model and the common practice of neglecting a full disclosure of the associated assumptions and limitations often confuse practitioners and prevent them from being used.

The present paper aims to shed light on ESA modeling in order to inform practitioners of assessment tools and ultimately provide assistance for the selection of the most appropriate modeling alternative for each application. The understanding of the simplifications and hypotheses assumed by the models is not possible without a profound knowledge on the real phenomena. For that, the first section of this paper is devoted to describe all the processes involved during the attack and introduce the main uncertainties that have been later reflected in the models developed.

A selection of the most relevant numerical models developed over the last 20 years to evaluate ESA are reviewed. The scope of this review is to emphasize the capabilities and limitations of the different models based on the simulation approach adopted to reproduce the different processes involved during the attack. Guidance on ESA model selection is provided based on the capabilities of the models in terms of the outputs provided. Finally, major areas that currently compromise the accuracy of the assessments are identified and discussed. It should be emphasized that this review is strictly limited to those numerical models that incorporate iterative calculation schemes. A survey of empirical or simplified mechanistic relations is beyond the scope of this paper and can be found elsewhere [1].

2. FUNDAMENTALS OF THE EXTERNAL SULFATE ATTACK

Most research on complex degradation processes is usually focused on specific aspects of the attack, as it is often unbearable to perform a meaningful study of the overall phenomenon. This necessary approach might unintentionally lead to over simplified perceptions of ESA, which is often directly or indirectly categorized as a pure chemical or physical phenomenon.

This section aims to disclose the full extent of ESA in order to set the foundation to understand and discuss the simplifications or hypotheses assumed by the numerical models reviewed in the following sections. Even though ESA might compromise the durability of a wide variety of cement-based structures [1,2], Figure 1 illustrates a group of end bearing piles before and after the attack to depict a schematic representation of the different mechanisms involved, specifying the scale at which these are developed.
The attack can be divided in four main processes: transport, chemical reactions, expansive forces and the mechanical response.

2.1. Transport process

The development of ESA requires the penetration of sulfate ions from an external source into the cement paste fraction of the concrete. For that, the open porosity of the concrete structure has to be in direct contact with a sulfate-rich media. The connection between the external aqueous media and the pore solution alter the equilibrium conditions in the liquid system, leading to a net mass flow. The characteristics of the mass flow can be described based on the saturation level of the pore structure.

In saturated conditions and under no pressure gradients, sulfate penetration and other ionic fluxes are mainly driven by electrochemical potential gradients (chemical and electrical potential) [11]. The chemical potential difference, usually referred to as diffusion, transfers charged solutes from areas of high concentration to areas of lower concentration. Electrical potential gradients are generated in the pore solution due to the different speeds of the charged solutes. Faster ions create an electric field that slows these ions down and accelerates the slower ones to preserve the electroneutrality throughout the liquid system [11].
Besides the electrochemical potential gradients, there are other transport mechanisms that might also affect the movement of ionic species in saturated conditions. In non-isothermal systems, temperature gradients promote ionic flux by a phenomenon usually referred to as Soret effect or thermal diffusion [12]. Finally, the flux of ionic species might be altered by chemical activity effects related to ion/ion and ion/solvent interactions when the ionic strength of the pore solution is high [13].

In unsaturated conditions, ionic transport also occurs indirectly by liquid movement from the external media into the pore network. The sulfate-rich aqueous solution is absorbed into the interior of the material by capillary forces arising from the contact of the pores of the material with the liquid phase [11,14]. Notice that under full saturation conditions this phenomenon should not be considered as the velocity of the liquid is null. However, in partially saturated concrete subjected to drying-wetting cycles at the surface, the sulfate ingress caused by moisture flux should not be disregarded.

2.2. Chemical reactions

The reactive system of cementitious materials is composed of the aqueous pore solution, vapor phase inside the pores and the unhydrated and hydrated solid phases of the cement paste (aggregates are usually considered inert). According to the second law of thermodynamics, in isolated conditions the different components tend to be in equilibrium to minimize the internal energy of the system. However, the mass fluxes caused by the interaction between the external aqueous media and the reactive system during ESA modify the position of the equilibrium state and promote a series of chemical reactions to restore minimum energy in the system.

The chemical reactions triggered during ESA vary depending on the sulfate salt present in the external media. The influence of the sulfate salt on the chemical reactions and subsequent damage generated can be explained in terms of solubility and interaction between the cation of the salt and the other reactive compounds of the system. The main salts associated with ESA are sodium sulfate (Na$_2$SO$_4$), calcium sulfate (CaSO$_4$) and magnesium sulfate (MgSO$_4$) [15]. Table 1 shows the solubility of the salts in water at 20 ºC and the maximum sulfate concentration potentially reached in solutions saturated with each salt. The solubility of CaSO$_4$ is about 100 times smaller than the solubility of Na$_2$SO$_4$ or MgSO$_4$. The high stability of this salt reduces the maximum sulfate concentration in solution to about 1.5 g/l, which greatly limits the deleterious effects caused by this form of attack. On the other hand, the damage generated by Na$_2$SO$_4$ and MgSO$_4$ solutions might be more significant due to the potential high sulfate concentrations and crystallization pressures developed during the attack.
Table 1. Solubility in water at 20°C and sulfate concentration in saturated conditions

<table>
<thead>
<tr>
<th>Sulfate salt</th>
<th>Solubility (g/l)</th>
<th>$[SO_4^{2-}]_{aq}$ (g/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$SO$_4$</td>
<td>195.0</td>
<td>131.9</td>
</tr>
<tr>
<td>CaSO$_4$·2H$_2$O</td>
<td>2.6</td>
<td>1.5</td>
</tr>
<tr>
<td>MgSO$_4$</td>
<td>337.0</td>
<td>268.9</td>
</tr>
</tbody>
</table>

ESA caused by magnesium sulfate is strongly influenced by the presence of magnesium ions in solution from the sulfate salt. The formation of magnesium hydroxide lowers the pH of the pore solution, which promotes the transformation of the C-S-H gel into a M-S-H phase without binding properties. This transformation causes softening and disintegration of the matrix and the formation of gypsum and brucite. A review of the chemical reactions related to magnesium sulfate environments can be found in [17].

ESA caused by sodium sulfate follows a completely different damage mechanism, characterized by ettringite and gypsum formation in such a quantity that the material sustains physical and chemical damage. Physical damage is usually related to the generation of expansive forces at the pore-level, which are explained in detail in section 2.3. Chemical damage refers to the degradation of mechanical properties in the cementitious matrix of the hardened concrete caused by the chemical reactions triggered by sulfate penetration.

The most commonly reported reactions are listed in Table 2 [9,18,19]. Eqs. (1) - (3) describe the reactions between sodium sulfate ions with portlandite (CH), tricalcium aluninate (C$_3$A) and monosulfate (C$_4$A$_{3}$H$_{12}$) to form gypsum (C$_{3}$S$_{2}$H$_{12}$), ettringite (C$_6$A$_{3}$S$_{1}$H$_{12}$) and sodium hydroxide (NaOH). Gypsum is only formed in certain sulfate concentrations and pH conditions of the solution. High sulfate concentrations lead to the precipitation of gypsum, while lower sulfate concentrations lead to no or very little gypsum precipitation [20,21]. The gypsum precipitated in Eq. (1) may react with the hydrated aluninate phases, namely tricalcium aluminate, tetracalcium aluminate hydrate (C$_4$AH$_{13}$), monosulfate and hydrogarnet (C$_3$AH$_6$) to produce ettringite, as summarized in Eqs. (4) - (7).

Even though some researchers suggest that sodium ions in solution could modify the solubility of the silicate phases and alter the morphology of the C-S-H gel [22,23], it is generally accepted that the presence of sodium from the sulfate salt does not
significantly alter the development of the attack. As described in Eqs. (1) - (7), gypsum and ettringite formation requires calcium which is mainly obtained by the dissolution of calcium hydroxide. However, at late stages of the attack or under shortage of portlandite, calcium might be obtained from C-S-H gel. The C-S-H phase is responsible for strength and stiffness in the cementitious matrix and its dissolution might cause a mechanical strength loss and micro-crack formation.

Table 2. Main chemical reactions related to ESA caused by Na$_2$SO$_4$ salts and corresponding expansion factors.

<table>
<thead>
<tr>
<th>Primary reactive</th>
<th>Chemical reaction</th>
<th>Eq.</th>
<th>Expansion factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>$CH$</td>
<td>$CH + Na_2SO_4 + 2H \rightarrow C\bar{S}H_2 + 2NaOH$</td>
<td>(1)</td>
<td>1.27</td>
</tr>
<tr>
<td>$C_3A$</td>
<td>$C_3A + 3Na_2SO_4 + 3CH + 32H \rightarrow 6NaOH + C_6A\bar{S}<em>3H</em>{32}$</td>
<td>(2)</td>
<td>2.76</td>
</tr>
<tr>
<td>$C_4A\bar{S}H_{12}$</td>
<td>$3C_4A\bar{S}H_{12} + 3Na_2SO_4 \rightarrow 6NaOH + 2Al(OH)_3 + 21H + 2C_6A\bar{S}<em>3H</em>{32}$</td>
<td>(3)</td>
<td>0.52</td>
</tr>
<tr>
<td>$C_3A$</td>
<td>$C_3A + 3C\bar{S}H_2 + 26H \rightarrow C_6A\bar{S}<em>3H</em>{32}$</td>
<td>(4)</td>
<td>1.25</td>
</tr>
<tr>
<td>$C_4AH_{13}$</td>
<td>$C_4AH_{13} + 3C\bar{S}H_2 + 14H \rightarrow C_6A\bar{S}<em>3H</em>{32} + CH$</td>
<td>(5)</td>
<td>0.48</td>
</tr>
<tr>
<td>$C_4A\bar{S}H_{12}$</td>
<td>$C_4A\bar{S}H_{12} + 2C\bar{S}H_2 + 16H \rightarrow C_6A\bar{S}<em>3H</em>{32}$</td>
<td>(6)</td>
<td>0.54</td>
</tr>
<tr>
<td>$C_3AH_6$</td>
<td>$C_3AH_6 + 3C\bar{S}H_2 + 2OH \rightarrow C_6A\bar{S}<em>3H</em>{32}$</td>
<td>(7)</td>
<td>0.89</td>
</tr>
</tbody>
</table>

2.3. Expansive forces

It is well established that certain chemical reactions between the pore solution and the cement paste generate expansive forces at the pore-level. These are primarily responsible for the “visible” consequences of the ESA, such as expansion, cracking and spalling of the hardened material [1]. However, there is still no agreement on the expansion mechanism underlying the degradation typically observed. Several mechanisms have been suggested in the literature to explain how some precipitation/dissolution processes are converted into actual expansions. A comprehensive review of the suggested theories can be found in [1,24]. Here, the two theories that stand as the most discussed are described in detail.

2.3.1. Volume increase approach

The volume increase approach assumes that the expansions observed are the result of the additional volume generated by the expansive products precipitated during the attack [9,18]. Expansive products are defined as those phases that take up more space.
than the volume used by the reactants consumed for its formation. Usually, the numerical expression described in Eq. (8) is adopted to quantify an expansion factor ($\nu$) [9].

$$\nu = \frac{\sum \text{solid product volumes} - \sum \text{solid reactant volumes}}{\sum \text{solid reactant volumes}}$$  \hspace{1cm} (8)

As indicated by Eq. (8), only the volume occupied by solid reactants and products are considered. This assumes that the aqueous species consumed during the reaction (e.g. water molecules) are instantly replaced by new molecules entering the system from an external source. Table 2 includes the expansion factors ($\nu$) of the main chemical reactions involved during the ESA. The molar volumes of all phases considered in the calculations are shown in Table 3. The molar volumes of Na$_2$SO$_4$, NaOH and Al(OH)$_3$ are not considered as it is assumed that these species are dissolved in the aqueous phase.

Linear expansion associated with each expansive chemical reaction listed in Table 2 can be estimated by multiplying the corresponding expansion factor ($\nu$), the molar volume ($V_m$) and the molar concentration of solid reactants consumed (CA$^r$) [18]. Total linear expansions ($\varepsilon_1$) triggered during ESA are defined as the sum of expansions associated to each chemical reaction considered (Eq. (9)). In Eq. (9), the term $n$ corresponds to the number of chemical reactions considered.

$$\varepsilon_1 = \sum_{i=1}^{n} \left[ (1 + \nu_{i} V_{m_i} CA^r_i) \right]^{1/3} - 1 \right]$$  \hspace{1cm} (9)

At present, there is no experimental evidence suggesting that expansions can be entirely explained by the additional volume generated from ettringite or gypsum formation.

Even though Kunther et al. stated that there seems to be a link between the coexistence...
of ettringite and gypsum and the tendency for expansion [24], a direct connection between the amount of expansive phases formed and expansion generated has not been documented.

### 2.3.2. Crystallization pressure theory

The crystallization pressure theory states that expansions are caused by the crystallization pressure exerted on the pore walls due to the formation of ettringite [28,29]. In this case, the driving force promoting the degradation during the ESA are the high activities of the reactants. The pressure ($p$) exerted by an ettringite crystal of molar volume ($V_{Et}$) may be expressed by Eq. (10) [30]. The term $R$ corresponds to the gas constant, $T$ is the absolute temperature and $K_{Et}$ is the equilibrium constant of ettringite. The ionic activity product of ettringite ($Q_{Et}$) might be calculated as indicated in Eq. (11).

$$p = \frac{RT}{V_{Et}} \ln \left( \frac{Q_{Et}}{K_{Et}} \right)$$

$$Q_{Et} = (C_{Ca^{2+}}C_{Al(OH)^{3+}})^6(C_{OH^-}C_{Al(OH)^{4+}})^2(C_{SO_4^{2-}}C_{OH^-})^3(C_{H_2O}C_{SO_4^{2-}})^{26}$$

There are two necessary conditions for expansion to occur [28,30]. First, the ettringite crystal must be growing from a supersaturated solution ($Q_{Et} > K_{Et}$). Otherwise, the pressure obtained by Eq. (10) equals 0 or negative. Second, the crystal must grow in confined conditions and exert the expansive forces to the pore walls in order to convert the chemical energy into mechanical work. This condition explains why not all ettringite formed is expansive, as the crystals need to be confined in order to exert pressure.

The pressure at the crystal/liquid interface ($p$) can be also expressed in terms of the interfacial free energy ($\gamma_{CL}$) for a particular crystal curvature ($\kappa_{CL}$). Eq. (12) states that at equilibrium, the energetic condition of the atoms on the surface of a crystal due to its morphology is balanced with the concentration of ions in the adjacent solution. Several researchers have used this relation to assess the influence of crystal size and shape on the potential crystallization pressure developed during ettringite growth in confined conditions [29–32].

$$p = \kappa_{CL} \gamma_{CL} = \frac{RT}{V_{crystal}} \ln \left( \frac{Q_{Et}}{K_{Et}} \right)$$
Eq. (12) indicates that small crystals with high curvatures are in equilibrium with a higher concentration than larger macroscopic crystals. Consequently, small crystals potentially generate higher crystallization pressures as long as sulfate supply is not restricted. On the other hand, large crystals are unable to exert significant pressures and therefore, are unlikely to be the origin of damage [31,32]. Accordingly, the expansive force developed during sulfate attack is mainly determined by the locations of ettringite growth in the microstructure rather than the total volume of ettringite formed [29,33].

The crystallization pressure theory has been thoroughly discussed from a theoretical standpoint in several publications (e.g. [28,29,34]). However, experimental evidences that support this theory for the specific case of the ESA are still scarce. Notice that to estimate crystallization pressures by Eq. (10), one needs to measure the composition of the pore solution at different locations within the pore network of the specimen, which is currently not possible [34]. Several authors have attempted to quantify crystallization pressures generated during ESA by alternative experimental approaches [32,34]. Despite the promising results, no author has been able to validate those pressures by reproducing the macroscopic expansions measured experimentally.

2.4. Mechanical response

Sections 2.2 – 2.3 described a series of processes occurring at the pore-level during ESA that leads to chemical degradation and the generation of expansive forces in the hardened matrix of the material. However, the description of these phenomena does not quantify the actual mechanical consequences associated, as chemical reactions per se are not necessarily harmful [35]. To account for that, the dissolution of calcium-bearing phases and the expansive forces generated should be translated into some sort of physical and chemical damage and macroscopic expansions.

If ESA was an internal attack that affected uniformly all the element or structure, the local mechanical response of the material would be representative of the macroscopic behavior of the element. This scenario is depicted in Figure 2a, where $\varepsilon_{\text{macro}}$ and $\varepsilon_{\text{local}}$ correspond to macroscopic and local expansions, respectively.
However, the degradation caused by ESA progresses gradually from the external surface towards the inner layers of the material, as sulfate ions penetrate and react with compounds from the hydrated cement paste. Consequently, a multi-layered pattern is formed with an external damaged layer and an internal sound core (Figure 2b). In this case, the expansive forces generated at the pore level within the attacked region cannot be fully released by deformations since the sound core of the element acts as a restriction to maintain compatibility. Because of that, the macroscopic expansions developed are usually considerably lower than the local expansions generated. In fact, due to the large sound/attacked region ratios commonly observed in field conditions, significant macro expansions are rarely reported. Moreover, the mechanical interaction between sound and damage regions generates an auto-balanced tension state, leading to microcracking in the attacked region due to compressive stresses and possible mechanical failures outside the zone directly affected by the sulfate penetration.

3. COMPUTER-BASED MODELS FOR ESA ASSESSMENT

This section reviews a selection of the most relevant numerical models developed during the last 20 years that incorporate complex iterative calculation schemes to assess the deleterious effects of ESA. This review does not aim to describe in detail each one of the assessment methods. Instead, the capabilities and limitations of the different
options are examined based on how the different processes involved during the attack are simulated. Table 4 lists all models evaluated in this review and classifies them based on the processes considered: transport (T), chemical reactions (C), expansive forces (E) and mechanical response (M). Pure transport or chemical models are not included in this review.

Table 4 highlights that not all advanced ESA models simulate aspects related to the main processes involved during the attack (T,C,E,M). Early models focused efforts on the modeling of the reactive-transport phenomenon (identified as T-C in Table 4). Evaluations based on this approach indirectly perceives ESA solely as a chemical attack and assumes that the deleterious effects can be assessed by the study of the transport process and the chemical reactions triggered, without converting the chemical reactions into actual damage or strength loss.

Table 4. ESA processes simulated by the assessment tools.

<table>
<thead>
<tr>
<th>Authors</th>
<th>Year</th>
<th>Ref.</th>
<th>Transport (T)</th>
<th>Chemical reactions (C)</th>
<th>Expansive forces (E)</th>
<th>Mechanical response (M)</th>
<th>Category</th>
</tr>
</thead>
<tbody>
<tr>
<td>P.N. Gospondinov et al.</td>
<td>1999</td>
<td>[36]</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td>T-C</td>
</tr>
<tr>
<td>F. Schmidt-Döhl &amp; F.S. Rostasy</td>
<td>1999</td>
<td>[37,38]</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td>T-C-E-M</td>
</tr>
<tr>
<td>R. Tixier &amp; B. Mobasher</td>
<td>2003</td>
<td>[18,40]</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td>T-C-E-M</td>
</tr>
<tr>
<td>Y. Maltais et al.</td>
<td>2004</td>
<td>[21]</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td>T-C</td>
</tr>
<tr>
<td>E. Rigo et al.</td>
<td>2005</td>
<td>[41]</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td>T-C-E-M</td>
</tr>
<tr>
<td>M.A. Shazali et al.</td>
<td>2006</td>
<td>[42]</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td>T-C-M</td>
</tr>
<tr>
<td>E. Samson &amp; J. Marchand</td>
<td>2007</td>
<td>[43]</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td>T-C</td>
</tr>
<tr>
<td>B. Bary</td>
<td>2008</td>
<td>[44]</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td>T-C-E-M</td>
</tr>
<tr>
<td>M. Basista &amp; W. Weglewski</td>
<td>2009</td>
<td>[45]</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td>T-C-E-M</td>
</tr>
<tr>
<td>B. Lothenbach et al.</td>
<td>2010</td>
<td>[20]</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td>T-C</td>
</tr>
<tr>
<td>S. Sarkar et al.</td>
<td>2010</td>
<td>[19]</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td>T-C-E-M</td>
</tr>
<tr>
<td>A. Idiart et al.</td>
<td>2011</td>
<td>[46]</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td>T-C-E-M</td>
</tr>
<tr>
<td>X.-B. Zuo et al.</td>
<td>2012</td>
<td>[47]</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td>T-C-E-M</td>
</tr>
<tr>
<td>B. Bary et al.</td>
<td>2014</td>
<td>[48]</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td>T-C-E-M</td>
</tr>
<tr>
<td>T. Ikumi et al.</td>
<td>2014</td>
<td>[49]</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td>T-C-E-M</td>
</tr>
<tr>
<td>Y. Yu et al.</td>
<td>2015</td>
<td>[50]</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td>T-C-E-M</td>
</tr>
<tr>
<td>N. Cefis &amp; C. Comi</td>
<td>2017</td>
<td>[51]</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td>T-C-E-M</td>
</tr>
<tr>
<td>J. Zhang et al.</td>
<td>2017</td>
<td>[52]</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td>T-C-E-M</td>
</tr>
</tbody>
</table>

T-C-E models incorporate the simulation of the expansive forces generated at the pore-level. By that, it is acknowledged both the chemical and physical nature of ESA. However, similarly to T-C models, the chemical reactions or the expansive forces monitored are not converted into actual damage and strains. During the last decade, a significant number of models have introduced mechanical aspects to quantify the damage generated and/or the macro-scale response of the attacked element. Models that only account for the chemical damage are identified as T-C-M in Table 4. Models that
quantify the degradation caused by both the chemical reactions and the expansive forces generated at the pore-level are identified as T-C-E-M.

The following sections present an in-depth analysis of the modelization approaches adopted by these models to simulate the transport process, chemical reactions, expansive forces and the mechanical response associated to the ESA.

3.1. Modeling of the transport process

As introduced in section 2.1, ionic transport between the liquid phase in the external media and the pore solution might be caused by two main processes: electrochemical potential gradients and advection. The unidirectional flux of each ionic species present in solution ($F_i$) can be expressed as in Eq. (13), where the first term refers to the electrochemical effects and the second term quantifies the ionic transport due to aqueous solution motion.

$$F_i = - \frac{D_i^0}{RT} c_i \frac{\partial}{\partial x} (\mu_i) + c_i \nu$$

In Eq. (13), $c_i$, $D_i^0$ and $\mu_i$ refers to the concentration, the diffusion coefficient and the electrochemical potential of the ionic species $i$, respectively. $R$ is the ideal gas constant, $T$ is the thermodynamic temperature and $\nu$ is the velocity of the liquid phase. The electrochemical potential $\mu_i$ is defined as indicated in Eq. (14).

$$\mu_i = \mu_i^0 + RT \ln(\gamma_i c_i) + z_i F \psi$$

The terms $\mu_i^0$, $\gamma_i$ and $z_i$ correspond to the electrochemical potential in the standard state, the chemical activity coefficient and the valence number of the ionic species $i$, respectively. $F$ is the Faraday constant and $\psi$ is the electrical potential. Substituting Eq. (14) into Eq. (13) yields the general ionic transport equation (Eq. 15) [43].

$$F_i = - D_i^0 \frac{\partial c_i}{\partial x} - \frac{D_i^0 z_i F}{RT} c_i \frac{\partial \psi}{\partial x} - D_i^0 c_i \frac{\partial \ln \gamma_i}{\partial x} - \frac{D_i^0 c_i \ln(\gamma_i c_i)}{T} \frac{\partial T}{\partial x} + c_i \nu$$
The mass conservation equation must be introduced into Eq. (15) to obtain the time-dependent response of the system. The unidirectional mass equation for an ionic species diffusing through an infinitesimal layer of liquid phase with thickness $\partial x$ can be expressed as indicated in Eq. (16). The combination of Eq. (15) and Eq. (16) gives the complete mass transport equation (Eq. (17) [43]). Reactions taking place solely in the liquid phase (homogenous reactions) are usually neglected in ESA models and are not considered in this formulation.

\[
\frac{\partial c_i}{\partial t} = \frac{\partial}{\partial x} \left( D_i \frac{\partial c_i}{\partial x} + \frac{D_i z_i F}{RT} \frac{\partial \psi}{\partial x} + D_i c_i \frac{\partial \ln y_i}{\partial x} + \frac{D_i c_i \ln (y_i c_i)}{T} \frac{\partial T}{\partial x} - c_i v \right)
\]

Notice that Eq. (17) refers to the transport of ions in the liquid phase. However, solving the equations at the pore scale requires the consideration of the exact geometry of the pore network, which is currently impossible. Instead, Eq. (17) is usually solved at the structure level. For that, the different components within a volumetric unit of concrete are considered. Concrete is composed by a solid matrix and a pore network, which can be fully or partially saturated with aqueous phase. In the case of being partially saturated, vapor should be also accounted as a component of concrete. Samson and Marchand applied an averaging technique to cementitious materials and proposed Eq. (18) as the averaged form of Eq. (17) [43].

\[
\frac{\partial (wC_i)}{\partial t} = \frac{\partial}{\partial x} \left( D_i w \frac{\partial C_i}{\partial x} + \frac{D_i z_i F}{RT} wC_i \frac{\partial \psi}{\partial x} + D_i wC_i \frac{\partial \ln y_i}{\partial x} + \frac{D_i C_i \ln (y_i c_i)}{T} w \frac{\partial T}{\partial x} - C_i v \right) - R
\]

The uppercase parameters $C_i$ and $V$ correspond to the average of the corresponding quantity in Eq. (17). $D_i$ is the diffusion coefficient at the macroscopic level, which differs from $D_i^0$ by the consideration of the geometrical complexity of the pore network. The averaging process introduces the additional term $w$ to account for the volumetric water content. In saturated conditions this term can be assumed to be equal to the connected porosity of the material. However, the consideration of this term in non-saturated conditions requires the modeling of moisture levels or the liquid water content. Details on the different approaches used to model moisture transport can be found in [15]. The term $R$ is introduced to account for the increase or decrease of local availability of ionic species due to chemical reactions (usually dissolution/precipitation processes). The different approaches to model the chemical reactions ($R$) are explained in section 3.2.
Eq. (18) provides a comprehensive mathematical framework to simulate the ionic transport associated to ESA based on the interaction of five transport mechanisms: diffusion (i), electrical potential (ii), chemical activity (iii), temperature and (iv) advection (v). However, ESA models rarely consider all mechanisms listed. Table 5 examines the main characteristics of the transport modules included in the numerical models evaluated, grouped by the categories defined in Table 4. While the diffusion mechanism is simulated in all models reviewed, advection, electrical coupling and chemical activity are only considered in about 50, 25 and 20% of the models, respectively.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Mechanisms</th>
<th>Saturation level</th>
<th>Ionic species</th>
<th>Diffusion coeff.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Diffusion</td>
<td>Electrical</td>
<td>Chemical</td>
</tr>
<tr>
<td>[36]</td>
<td></td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
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<td>[39]</td>
<td></td>
<td>X</td>
<td>X</td>
<td>X</td>
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<tr>
<td>[21]</td>
<td></td>
<td>X</td>
<td>X</td>
<td>X</td>
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<td>[43]</td>
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<td>X</td>
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<td>X</td>
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<tr>
<td>[20]</td>
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<td>X</td>
<td></td>
<td>X</td>
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<tr>
<td>[37,38]</td>
<td></td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>[18,40]</td>
<td></td>
<td>X</td>
<td>X</td>
<td>X</td>
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<td>X</td>
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<tr>
<td>[44]</td>
<td></td>
<td>X</td>
<td></td>
<td>X</td>
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<tr>
<td>[45]</td>
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<td>[19]</td>
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<td>[49]</td>
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<td>[50]</td>
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<td>[51]</td>
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<td>X</td>
<td>X</td>
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</tr>
<tr>
<td>[52]</td>
<td></td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>

Advection is associated to ionic transport caused by changes on moisture conditions in the pores. Therefore, models that include an advection term are able to account for non-saturated conditions. The only exception is the model presented by Mironova et al. [39], which considers advection in fully saturated conditions. In this case, the advection is attributed to the movement of ions caused by liquid push out of the capillary as a result of capillary filling with solid chemical products.
The fewer number of models considering the effects of electrical coupling and chemical activity is mainly explained by the complexity associated to the simulation of these phenomena, which require a full description of the ionic species in the solution. This is reflected on Table 5, where all models that simulate electrical coupling or chemical activity include multi-ionic transport modules. Reported results suggest that this increase of computational complexity might be justified in the case of the electrical coupling, as simulations made without electrical coupling showed significant discrepancies with the measurements [43,50]. However, currently there are no clear evidences that justify the consideration of the chemical activity gradients in ESA transport models. Yu et al. [50] obtained very similar results with and without coupling the chemical activity term, which might suggest that the contributions of chemical activities are not critical.

The main distinctive feature between reactive-transport models (T-C) and those including mechanical considerations (T-C-M and T-C-E-M) is found on the formulation adopted to consider the diffusion coefficient(s). All T-C models listed in Table 5 alter the diffusion coefficient during the simulation based only on changes of porosity due to precipitation or dissolution of solid phases. Pore filling caused by precipitation processes are reflected by a reduction of diffusivity whereas increase of porosity caused by dissolution processes is considered through an increase of diffusivity. A review on the different approaches used to quantify the variations of diffusivity caused by porosity changes can be found in [53].

On the other hand, most T-C-M and T-C-E-M models incorporate the effects associated to damage generation on the diffusion coefficient of the ionic species. Strength loss, cracking and spalling are usually reflected as an increase of diffusivity since it is considered that these might introduce easier penetration paths towards the inner layers of the material. These models quantify the diffusivity increase by simple relations based on the bulk damage [19,38,40–42,45,49,52] or the crack width [46] generated. Additionally, the model presented by Yu et al. [50] simulates the mechanism of ionic diffusion in cracked cementitious materials by a combination of a traditional approach (modification of diffusivity based on continuum damage mechanics) and the introduction of an additional term in Eq. (18) to describe the capillary suction effect brought by newly formed unsaturated cracks.

3.2. Modeling of chemical reactions

Table 6 summarizes the approaches used by recent advanced numerical models to simulate the chemical reactions associated to the ESA, which can be based on chemical kinetic laws (K), chemical equilibrium algorithms (E) or a combination of both.
Table 6. Characteristics of the chemical modules included in advanced ESA models.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Species monitored</th>
<th>Chemical kinetics (K)</th>
<th>Chemical equilibrium (E)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ions in solution</td>
<td>Solid phases</td>
<td>1st order</td>
</tr>
<tr>
<td>[36]</td>
<td>Sulfate</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>[39]</td>
<td>Sulfate</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>T-C</td>
<td>[21] Full composition</td>
<td>Full composition</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[43] Full composition</td>
<td>Full composition</td>
<td></td>
</tr>
<tr>
<td>T-C-E</td>
<td>[47] Sulfate</td>
<td>Aluminates</td>
<td>X</td>
</tr>
<tr>
<td>T-C-M</td>
<td>[42] Sulfate</td>
<td>Gypsum</td>
<td>X</td>
</tr>
<tr>
<td>[37,38]</td>
<td>Full composition</td>
<td>Full composition</td>
<td>X</td>
</tr>
<tr>
<td>[18,40]</td>
<td>Sulfate</td>
<td>Aluminates</td>
<td>X</td>
</tr>
<tr>
<td>[41]</td>
<td>Full composition</td>
<td>Full composition</td>
<td>X</td>
</tr>
<tr>
<td>[44]</td>
<td>Sulfate, Calcium</td>
<td>Ettringite, Gypsum</td>
<td>X</td>
</tr>
<tr>
<td>[45]</td>
<td>Sulfate</td>
<td>Ettringite</td>
<td>X</td>
</tr>
<tr>
<td>[19]</td>
<td>Full composition</td>
<td>Full composition</td>
<td>X</td>
</tr>
<tr>
<td>[46]</td>
<td>Sulfate</td>
<td>Aluminates</td>
<td>X</td>
</tr>
<tr>
<td>[48]</td>
<td>Full composition</td>
<td>Full composition</td>
<td>X</td>
</tr>
<tr>
<td>[49]</td>
<td>Sulfate</td>
<td>Aluminates</td>
<td>X</td>
</tr>
<tr>
<td>[50]</td>
<td>Full composition</td>
<td>Full composition</td>
<td></td>
</tr>
<tr>
<td>[51]</td>
<td>Sulfate</td>
<td>Aluminates</td>
<td>X</td>
</tr>
<tr>
<td>[52]</td>
<td>Sulfate</td>
<td>Aluminates</td>
<td>X</td>
</tr>
</tbody>
</table>

3.2.1. Kinetic laws

Models based on chemical kinetic laws (K) use partial differential equations with empirical reaction rate constants to estimate the precipitation of products and the consumption of reactants. Even though Table 2 describes up to seven chemical reactions typically involved during ESA, none of the models reviewed adopt this number of kinetic laws. Instead, the chemical processes are usually simplified into one or two chemical reactions to account for gypsum (\(\text{CaSO}_4 \cdot 2\text{H}_2\text{O}\)) formation from portlandite (\(\text{CH}\)) and sulfate ions (\(\text{SO}_4^{2-}\)) (Eq. (19)) and/or ettringite (\(\text{C}_6\text{Al}_2\text{Si}_3\text{O}_{10}\(\text{H}_2\text{O}\)) \(\times\text{H}_2\text{O}\)) formation from the interaction of sulfates with the aluminate phases (\(\text{AI}\)) (Eq. (20)).

\[
\text{CH} + [\text{SO}_4^{2-}] \rightarrow [\text{CaSO}_4 \cdot 2\text{H}_2\text{O}] \tag{19}
\]

\[
a[\text{AI}] + b[\text{SO}_4^{2-}] \rightarrow c[\text{C}_6\text{Al}_2\text{Si}_3\text{O}_{10}\(\text{H}_2\text{O}\)) \tag{20}
\]
The aluminate phases considered vary in each model, usually being monosulfate, tetracalcium aluminate hydrate, tricalcium aluminate or an equivalent grouping of the previously mentioned phases. The terms $a$, $b$ and $c$ included in Eq. (20) correspond to the specific stoichiometric coefficients of the aluminate phase, sulfates and ettringite, respectively. As defined by the chemical reaction described in Eq. (1), all stoichiometric coefficients in Eq. (19) are set to one.

According to Table 6, the majority of models based on rate laws only consider sulfate and aluminate consumption [40,46,47,49,51,52] or sulfate consumption and ettringite formation [45]. Both approaches are equivalent as the processes simulated correspond to the same chemical reaction (Eq. (20)). On the other hand, only two models simulate gypsum formation through kinetic laws [42,44]. In the early models from Gospodinov et al. [36] and Mironova et al. [39], it is not clear which chemical phenomenon is being modelled since only sulfate consumption is accounted. Solid phase formation is indirectly quantified by the term “chemically reacted ions”, without specifying to which phase it refers.

The law of mass action states that the rate of a chemical reaction at a constant temperature is directly proportional to the product of the concentrations or activities of the substances that influence the rate. The sum of the exponents at which each concentration term is raised defines the order of the kinetic law. Therefore, models based on first-order reactions describe a rate proportional to the concentration of a single reactant whereas in second-order kinetic laws the rate is proportional to the concentration of two reactants. Table 6 indicates that the majority of ESA models based on kinetic laws adopt either first or second-order equations, being the latter the most common approach.

The rate law for the chemical reaction described in Eq. (19) is usually described in terms of either the consumption of sulfate (Eq. (21)) or a combination of sulfate and portlandite (Eq. (22)).

\[ \text{rate} = \frac{\partial SO_{4}^{2-}}{\partial t} = -k_1[SO_{4}^{2-}] \]  
\[ \text{rate} = \frac{\partial SO_{4}^{2-}}{\partial t} = -k_2[SO_{4}^{2-}][CH] \]  

The terms $k_1$ and $k_2$ correspond to rate constants for first and second-order reactions, respectively. Different terminologies for the rate constants are used to emphasize that despite both parameters belong to the same chemical reaction, its values may not be
equal. This is reflected on the units traditionally used, \( \text{time}^{-1} \) and \( \text{concentration}^{-1} \cdot \text{time}^{-1} \) for \( k_1 \) and \( k_2 \), respectively. Multiplying the units of \( k \) by the concentration factors (expressed as square brackets) give the rate in units of \( \text{concentration} \cdot \text{time}^{-1} \). A negative sign is placed before the rate as the concentration of a reactant decreases during the reaction.

The kinetic laws used for the simulation of the chemical reaction that controls ettringite precipitation (Eq. (20)) are usually defined in terms of either the sulfate concentration (Eq. (23)) or the sulfate and aluminate concentration (Eq. (24)).

\[
\begin{align*}
\text{rate} & = \frac{\partial SO_4^{2-}}{\partial t} = -k_1 b[SO_4^{2-}] \quad (23) \\
\text{rate} & = \frac{\partial SO_4^{2-}}{\partial t} = -k_2 b[SO_4^{2-}][Al] \quad (24)
\end{align*}
\]

In this case, the rate law for each reactant and product is modified by the stoichiometric coefficients \( a, b \) and \( c \) according to the expression described in Eq. (25). Final formulations of first and second-order kinetic laws for aluminate consumption and ettringite formation are included in Eqs. (26) - (29).

\[
\begin{align*}
\frac{1}{-a} \frac{\partial Al}{\partial t} & = \frac{1}{-b} \frac{\partial SO_4^{2-}}{\partial t} = \frac{1}{c} \frac{\partial c_0AS_3H_{32}}{\partial t} \quad (25) \\
\frac{\partial Al}{\partial t} & = -k_1 \frac{a}{b} [SO_4^{2-}] \quad (26) \quad \frac{\partial Al}{\partial t} = -k_2 \frac{a}{b} [SO_4^{2-}][Al] \quad (28) \\
\frac{\partial c_0AS_3H_{32}}{\partial t} & = \frac{c}{b} k_1 [SO_4^{2-}] \quad (27) \quad \frac{\partial c_0AS_3H_{32}}{\partial t} = \frac{c}{b} k_2 [SO_4^{2-}][Al] \quad (29)
\end{align*}
\]

The use of first-order kinetic laws to quantify the formation rate of ettringite and gypsum assumes that neither portlandite (calcium) nor aluminate concentrations are reaction-limiting factors. Such a hypothesis may not remain true over the whole duration of the attack, as complete depletion of some of the reactants could occur in some locations. Bary et al. [44] partially tackled this limitation by introducing restrictions on the maximum amount of ettringite formed based on the initial alumina content.

Shazali et al. [42] adopted a multi-ordered chemical reaction rate equation inspired by the work from Saetta et. al [54]. This approach is based on normalized influence
functions to represent the effects of temperature, pore water content, sulfate concentration and portlandite availability. Even though the consideration of temperature and humidity in the rate law seems positive, the approach adopted to quantify its effects is not validated and might be too simplified to justify the additional semi-empirical parameters introduced.

3.2.2. Chemical equilibrium

The alternative to the approaches based on purely empirical chemical kinetic laws (K) is the calculation of the current chemical equilibrium state by means of a chemical equilibrium code (E). Equilibrium approaches use thermodynamic data of all solid, aqueous and gas species present in the system to predict the concentrations of the constituents on a chemical equilibrium state. This is achieved by finding the concentrations of the chemical species that simultaneously minimizes the Gibbs free energy of the system and satisfies a system of equilibrium constants. The consideration of all constituents complicates the calculations and increases the number of input parameters but provides a full description of the species present in the system throughout the attack.

As shown in Table 6, the consideration of the full composition of the aqueous solution and solid phases is a common feature of all chemical modules that include equilibrium calculations. Thermodynamic modeling of ESA is usually described in terms of equilibrium between the liquid (pore solution) and the solid hydrated phases of the cement paste. In fact, all ESA models reviewed solely account for heterogeneous reactions based on dissolution/precipitation processes of solid hydration products.

Even though the specific phases considered vary slightly in each model, the majority include the following mineral phases: Portlandite, C-S-H gel, ettringite, monosulfate, hydrogarnet, gypsum and sodium sulfate (mirabilite). The aqueous pore solution is usually simulated by the following ionic species: K⁺, Na⁺, Ca²⁺, SO₄²⁻, OH⁻ and Al(OH)₄⁻. The dissolution process of the clinker phases is commonly not considered in such calculations since the pore solutions tend to be highly undersaturated with respect to these phases due to its slow dissolution rate [15].

Two conceptually equivalent methods are generally used to calculate chemical equilibrium in ESA models. The most common method consists on solving the system of mass balance and mass action equations known as Law of mass action (LMA). LMA system of equations models the equilibrium condition of the reactions for a given set of species. Dissolution/precipitation reactions are usually simulated by the equilibrium
relationship described in Eq. (30) [55]. If the activity product of the ions in solution involved in the reaction is above the solubility product, precipitation occurs to decrease the ionic activity of the reactants. Otherwise, dissolution occurs. Notice that the concentrations of pure solids and liquids are not considered.

\[ K_m = \prod_{i=1}^{N_i} (c_i y_i)^{\nu_{mi}} \quad \text{For } m=1,...,M \]  

The term \( K_m \) corresponds to the solubility constant of the solid phase \( m \). \( c_i \) is the concentration of species \( i \) in solution and \( \nu_{mi} \) is the stoichiometric coefficient of the \( i \)th ion in the \( n \)th hydration product. If \( M \) number of species are considered to be in equilibrium with the solution, then \( M \) simultaneous equations should be solved to determine the concentration of each species at equilibrium. The term \( y_i \) corresponds to the chemical activity coefficient. The activity coefficient is computed in all ESA models reviewed by means of the modified Davies model [13], which is valid for solutions with high ionic strength. The only exception is presented by Schmidt-Döhl and Rostasy [37,38] and Rigo et al. [41], who simulated the activity coefficients of solved ions by the Pitzer theory and the Gibbs-Duhem equation [56,57]. Additionally, mass and charge balance restraints are imposed to assure that no mass is lost or created during precipitation/dissolution processes and that the sum of positive charges equal the sum of negative charges in the system.

Alternatively, chemical equilibrium can be calculated by directly minimizing the Gibbs free energy of the system (GEM). The GEM approach is based on mass and charge balance of the whole system and the equilibrium composition is calculated automatically from the stochiometrically possible phases [15]. The only information required is the stoichiometric coefficients of the concerned chemical species and their thermodynamic data [37,38]. Despite the advantages reported of GEM over LMA [58], only the ESA models from Schmidt-Döhl and Rostasy [37,38] and Rigo et al. [41] adopt this approach (Table 6). This situation might be explained by the complexity of integrating equilibrium solvers based on GEM into the reactive transport calculators.

The coupling of chemical and transport modules has been traditionally approached in two sequential steps. The first step is solely concerned with the resolution of the transport equations presented in section 3.1. The new ionic concentrations are then corrected in a second step to ensure chemical equilibrium between the ions in the pore solution and the different hydrated compounds of the cement paste. Solid phases are dissolved or precipitated accordingly. This loop is repeated for each time step considered in the simulation. The description of the chemical reactions as algebraic
mass action equations (LMA method) fits well in this scheme and allows the treatment
of the reactive transport phenomenon as a mixed problem involving the solution of
algebraic and partial differential equations.

The treatment of the reactive transport phenomenon as two separate sequential
algorithms (transport and chemistry) is possible due to the local equilibrium assumption
(LEA) adopted by all ESA models that include chemical equilibrium calculations. LEA
assumes that the rate of the reaction is large with respect to the ionic and fluid transport
processes. This assumption seems reasonable based on the presence of dissolution or
precipitations fronts for the main species involved in the ESA within a region close to
the external surface of the specimen. This indicates that chemical reactions are the
governing process on the reactive transport phenomenon, at least prior to the generation
of significant damage [59]. Samson and Marchand [43] corroborated the validity of this
assumption for ionic transport problems in cementitious materials based on the
dimensionless Damköhler number.

3.2.3. Combination of kinetic laws and chemical equilibrium

Finally, some ESA models adopt a third approach consisting on a combination of
chemical equilibrium calculations and kinetic laws [37,38,41,48]. These models are
mainly based on the same principles described for pure equilibrium models. However,
the chemical equilibrium equations of certain phases are replaced by kinetic laws to
account for phase formation in non-equilibrium conditions.

Bary et al [48] replaces the dissolution/precipitation equation of ettringite by the kinetic
law described in Eq. (31). The term \(k\) corresponds to the kinetic coefficient expressed as
concentration-time\(^{-1}\). \(Q_{\text{CaAS}_2H_32}\) and \(K_{\text{CaAS}_2H_32}\) are the ion activity and equilibrium
solubility product of ettringite, respectively. By adopting this approach, ettringite does
not necessarily reach equilibrium at the end of each time step of the simulation, which
is a required condition to reproduce crystallization pressures associated to ettringite
growth in supersaturated solutions.

\[
\frac{\partial C_{\text{CaAS}_2H_32}}{\partial t} = k \left( \frac{Q_{\text{CaAS}_2H_32}}{K_{\text{CaAS}_2H_32}} - 1 \right)
\]  

(31)

3.3. Modeling of the expansive forces
Table 7 examines the main approaches adopted by T-C-E and T-C-E-M models to simulate the expansive forces generated at the pore-level during the ESA.

### 3.3.1. Volume increase theory

Table 7 highlights that expansive forces are usually quantified by the volume increase associated to ettringite formation. The consideration of the volume change caused by other hydration products is not widely implemented, as it requires an advanced chemical module able to compute all hydrated phases in the cement paste. As indicated in Table 6, this is not a common feature amongst T-C-E and T-C-E-M models.

Models based on the volume increase theory usually consider that not all aluminate reacted generates expansions, as the pore network is able to accommodate a certain amount of expansive products without exerting any pressure to the pore walls. A pressure on the surrounding walls may be only exerted if the crystals become too large and/or too numerous to fit into the available space. Consequently, the general equation described in section 2.3.1 to estimate local linear expansions (Eq. (9)) is usually modified to capture this phenomenon. Eq. (32) [18] quantifies the capacity to accommodate expansive products by the fraction \( f \) of the concrete initial connected porosity \( \varphi_0 \) that has to be filled prior expansion starts.

\[
\varepsilon_1 = \text{Max.}\left\{\left[(1 + nV_mCA^r - f\varphi_0)^{1/3} - 1\right], 0\right\} \tag{32}
\]

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Vol. increase</th>
<th>Cryst. pressure</th>
<th>Mode</th>
<th>Expansive phases</th>
<th>Pore network capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[36]</td>
<td></td>
<td></td>
<td></td>
<td>Ettringite</td>
<td></td>
</tr>
<tr>
<td>[39]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T-C-E</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[47]</td>
<td></td>
<td></td>
<td></td>
<td>Ettringite</td>
<td>1 Pore ( f\varphi_0 )</td>
</tr>
<tr>
<td>T-C-M</td>
<td>[42]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[37,38]</td>
<td>X</td>
<td>X</td>
<td></td>
<td>Ettringite</td>
<td>1 Pore ( f\varphi_0 )</td>
</tr>
<tr>
<td>[18,40]</td>
<td>X</td>
<td>X</td>
<td></td>
<td>Ettringite</td>
<td>1 Pore ( f\varphi_0 )</td>
</tr>
<tr>
<td>[41]</td>
<td>X</td>
<td>X</td>
<td></td>
<td>Ettringite</td>
<td>1 Pore ( f\varphi_0 )</td>
</tr>
<tr>
<td>[44]</td>
<td>X</td>
<td>X</td>
<td></td>
<td>Ettringite</td>
<td>1 Pore ( f\varphi_0 )</td>
</tr>
<tr>
<td>[45]</td>
<td>X</td>
<td>X</td>
<td></td>
<td>Ettringite</td>
<td>1 Pore ( f\varphi_0 )</td>
</tr>
<tr>
<td>[19]</td>
<td>X</td>
<td>X</td>
<td></td>
<td>All solids</td>
<td>1 Pore ( f\varphi_0 )</td>
</tr>
<tr>
<td>[46]</td>
<td>X</td>
<td>X</td>
<td></td>
<td>Ettringite</td>
<td>1 Pore ( f\varphi_0 )</td>
</tr>
</tbody>
</table>

Table 7. Main features of the modeling approaches to simulate ESA expansive forces.
The considerations of the overall initial porosity and a unique buffer coefficient assume that all complexity of the concrete porosimetry can be reduced to a single pore where all expansive products precipitate. This is equivalent to say that the precipitation and expansion occur simultaneously in all pores regardless of their size, as the amount of expansive products precipitated in each pore is proportional to its volume. Through this approach, the models are not able to account for expansive pressures generated during early stages of the attack as the expansions computed are null until the amount of ettringite precipitated fills the entire buffered volume ($f \varphi_0$). A schematic representation of the simplifications assumed by Eq. (32) is shown in Figure 3.

T. Ikumi et al. [49] adopted an alternative methodology to compute expansions to tackle this limitation. The model presented is based on a more realistic representation of the concrete porosimetry by discretizing the real pore size distribution of the material into a finite number of pores, each one representing a volume fraction of the total porosity ($\varphi_i$). Then, a parameter referred to as ettringite formation rate is used to quantify and distribute the ettringite formed within the pores considered. The contribution to the total local expansion of each pore size is estimated based on its volume ratio filled by ettringite and its individual capacity to accommodate expansive phases ($f_1 \varphi_i$). This methodology acknowledges that not all ettringite precipitated during the attack contributes with the same weight into the expansive forces generated. Instead, ettringite precipitated in small pores is likely to generate higher and earlier pressures than ettringite growing in larger pores due to a faster filling rate and a smaller capacity to accommodate expansive products.
Cefis and Comi [51] present the only model that completely neglects the buffer capacity of the pore network during the estimation of expansive forces. These authors consider ettringite to be formed through a topochemical reaction occurring between the hydrated products of cement and the sulfate. In topochemical reactions, the product is formed directly in the surface of the reactants, therefore all volume variation due to ettringite formation is translated into expansive forces. The validity of this approach has been questioned by several authors, who claimed that the crystal structure of C₃A or monosulfate is completely different to that of ettringite, so direct transformation is not a plausible theory [34].

3.3.1. Crystallization pressure theory

The number of models quantifying the expansive forces generated through the crystallization pressure theory is minimal (Table 7). The prevalence of the volume increase in modeling might be explained by the combination of two factors. First, the crystallization pressure theory requires the full definition of the activities of ionic species in contact with the ettringite crystals, which is only possible through chemical equilibrium calculations. Second, the algorithm should be able to compute ettringite growth in supersaturated solutions. Notice that the latest requirement is usually not compatible with the first one, as most ESA models able to provide a full description of the ionic species and solid phases are solely based on chemical equilibrium calculations, which guarantees that the solution is never supersaturated with respect to any solid phase in the microstructure.

Bary et al. presents the only model that adopted solely the crystallization pressure theory to simulate the expansive forces generated during the ESA [44]. The authors are able to compute crystallization pressures as the chemical module adopted is based on chemical kinetics, not on equilibrium assumptions. Consequently, Bary et al. do not apply the general equation described in Eqs. (10)-(11), as this model does not provide a full description of the ionic solution and solid phases. Instead, the authors use the simplified version described in Eq. (33), which is only defined by current and equilibrium sulfate and calcium concentrations. It is unclear how calcium and sulfate concentrations at chemical equilibrium ($C_{Ca^{2+}}^0$, $C_{SO_4^{2-}}^0$) are estimated through this kinetic approach.

$$p = \frac{RT}{V_{Et}} \ln \left( \frac{[C_{Ca^{2+}}]^2 [C_{SO_4^{2-}}]^2}{[C_{Ca^{2+}}^0]^2 [C_{SO_4^{2-}}^0]^2} \right)$$

(33)
The model is applied with a relatively good accuracy to predict cracking initiation. However, it leads to macroscopic expansions of about two orders of magnitude lower than typical experimental data [48]. According to the authors, the crystallization pressures developed do not permit generation of sufficient macroscopic strains with the elastic approach adopted. Crystallization pressures of the order of several thousands of MPa would be necessary to get calculated free expansions comparable to measured ones.

Bary et al. presented another ESA model in 2014 that incorporated an alternative approach to explain the macroscopic expansions [48]. This model introduced a macroscopic bulk strain to reproduce the increase of volume caused by secondary ettringite formation through an equivalent equation of Eq. (32). By adding this consideration, the expansions are a result of both the additional volume generated by ettringite formation and the crystallization pressure exerted on the pore walls by the supersaturated solution. In this case, the expansions predicted were similar to the ones obtained in the test. Bary et al. pointed out that the contribution of the crystallization pressure was negligibly small compared to the bulk strain produced by secondary ettringite formation [48]. This may suggest that the model was basically able to reproduce measured expansions due to the application of the volume increase theory.

### 3.4. Modeling of the mechanical response

T-C-M and T-C-E-M models incorporate mechanical modules to convert the degradation processes generated at the pore-scale into actual damage and/or macroscopic expansions. Table 8 shows the characteristics of the main approaches adopted by the selection of models reviewed to simulate the local and non-local mechanical response.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Local mechanical response</th>
<th>Non-local mechanical response</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Stress-induced cracking</td>
<td>Chemical-induced strength loss</td>
</tr>
<tr>
<td></td>
<td>Isotropic damage variable</td>
<td>Isotropic damage variable</td>
</tr>
<tr>
<td></td>
<td>Discrete interface elements</td>
<td>Discrete interface elements</td>
</tr>
<tr>
<td>T-C</td>
<td>[36]</td>
<td>[47]</td>
</tr>
<tr>
<td></td>
<td>[39]</td>
<td></td>
</tr>
<tr>
<td>[21]</td>
<td>[43]</td>
<td></td>
</tr>
<tr>
<td>[20]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 8. Characteristics of the mechanical modules considered in advanced ESA models.
3.4.1. Local mechanical response

The local mechanical response accounts for the damage generated within the region directly affected by sulfate penetration. In this region, models recognize the generation of damage associated to the expansive forces (referred to as stress-induced cracking in Table 8) and the decalcification of hydrated phases (referred to as chemical-induced strength loss in Table 8). T-C-M models can only compute chemical damage while T-C-E-M models are potentially able to account for both, chemical and stress-induced damage.

Stress-induced cracking

Stress-induced microcracking has been traditionally reproduced by a damage variable based on continuum damage mechanics. The early approach presented by Tixier and Mobasher [18] has been widely implemented and served as a basis for most of the models developed (e.g. [19,50,52]). In this case, the constitutive response of the material is simulated by a simple uniaxial stress-strain law that related the local strains with the damage developed. The damage is quantified by an isotropic scalar variable usually ranging from 0 to 1 based on a crack density parameter. Three regions are usually defined [18]:

- Linear-elastic response: The material is considered undamaged,
- Prepeak region: Microcrack initiation leading to a linear decrease of the mechanical properties and/or increase of diffusivity,
Postpeak region: Microcracks coalesce into a single main crack and the deformation is represented as the opening of a single dominant crack with a gradual decrease in the load-carrying capacity of the matrix.

Approaches based on continuum damage mechanics have important limitations when it comes to predict crack patterns or the spalling effects. For example, Sarkar et al. [19] adopt a failure criterion based on an arbitrary number of elements of the discretization reaching the maximum damage state, without any mechanical justification. However, this approach might be sufficient to identify crack appearance and estimate an approximate crack pattern [44].

The model presented by Idiart et al. [46] represents an important contribution in this field. The main feature of this model is the nonlinear fracture mechanics-based crack propagation procedure, which considers the effect of cracking explicitly in the degradation process. For that, zero-thickness interface elements are introduced in all the aggregate–matrix contacts and also in predetermined locations within the matrix. Notice that this model is able to capture accurately the main crack patterns inside and outside the region directly affected by sulfate penetration.

Chemically-induced strength loss

Even though all models included in Table 8 incorporate chemical modules to account for the chemical reactions triggered by sulfate penetration, there are only two models that quantify the chemical damage associated [42,51]. Shazali and coworkers [42] assume that the strength loss experienced by concrete is entirely caused by the decalcification of hydrated phases due to gypsum formation. Chemical damage is quantified by a local relative strength loss \( p nL \) function that represents an empirical relation between the degree of reaction \( G_n \) and the loss of strength (Eq. (34)). The terms \( a \) and \( m \) correspond to fitting parameters defined on the basis of experimental data.

\[
p nL = (1 - a^{-m}) \left[ 1 - \frac{1}{1 + (a G_n)^m} \right] \quad (34)
\]

The model presented by Cefis and Comi is the only model that accounts for both chemical damage and expansive forces [51]. In this case, it is considered that the decalcification of concrete causes the formation of diffuse microcracks. Similarly to [42,60], this phenomenon is quantified by an isotropic damage variable \( d \) expressed as
a function of the reaction extent ($\xi$) (Eq. (35)). Where $r_1$, $r_2$ and $r_3$ are material dependent parameters. Unfortunately, from the results presented it is not possible to distinguish the relative weight of chemical damage into the overall degradation obtained.

\[
d = \frac{1 - \exp(-r_1 \xi)}{1 + \exp(-r_1 \xi + r_2)} r_3
\]  

(35)

3.4.2. Non-local mechanical response

It seems common sense that a large pile of 2 m diameter should be more durable against the ESA than a micro-pile of 30 cm diameter under the same exposure conditions. Unlike internal degradation processes, the region directly affected by sulfate penetration is usually restricted to a few centimeters close to the external surface. The sound region, which in most real structures constitutes a larger area, contributes to reduce the damage caused by the attack due to equilibrium and compatibility with the damaged area. Several recent works highlight the importance of the size of the element on ESA resistance [10,59].

Table 8 shows that the majority of models quantifying damage include a full tenso-deformational analysis on the whole section of the attacked element to account for these phenomena. By that, these models are able to quantify macroscopic expansions over time and estimate the stress distribution generated inside and outside the attacked region. Damage estimations in models without tenso-deformational analyses might not correspond well with reality, especially in structures with large sound/damaged region ratios.

Stress distribution monitoring on the whole section of the element opens up the possibility to account for damage generation outside the regions directly affected by sulfate penetration. However, Table 8 indicates that this is not commonly implemented in ESA models. In fact, the only model able to account for the energy dissipated in the fracture processes outside the penetrated region is the one presented by Idiart et al. [46]. The approach adopted by the authors is explained in section 3.4.1.

3.5. ESA Model selection
The review presented in sections 3.1-3.4 highlights a large pool of models available based on different approaches and principles with varying degrees of complexity. This wide variety of options often confuse practitioners in the selection of the appropriate model to use for each application. Numerical models are commonly used to provide key data to support decision-making on different aspects related to ESA durability. For each project, the information desired varies depending on its particular needs. For example, in some structures the durability requirements might be defined in terms of limitations on the penetration of external agents, while in other applications the main concerns might be related to the dimensional stability or crack formation.

As not all models reviewed are able to provide the same information, the selection of a suitable model involves pairing of the required data with the outputs of the numerical model. For that, it is essential to understand the capabilities of each model reviewed in terms of the outcomes provided. Table 9 relates typical required data during ESA assessments with the qualified models able to provide such information. The required data listed covers different aspects associated to the transport process, the chemical reactions and the mechanical response of the attacked element. Notice that Table 9 is purely defined by the potential capabilities of the models and the actual accuracy of the predictions is not considered here.

### Table 9. Qualified models for the most common desired outputs in ESA assessments.

<table>
<thead>
<tr>
<th>Desired outputs</th>
<th>T-C</th>
<th>T-C-E</th>
<th>T-C-M</th>
<th>T-C-E-M</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Transport</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfate concen.</td>
<td>[36]</td>
<td>[39]</td>
<td>[21]</td>
<td>[43]</td>
</tr>
<tr>
<td>Calcium concen.</td>
<td>[21]</td>
<td>[43]</td>
<td>[20]</td>
<td></td>
</tr>
<tr>
<td>Full ionic concen.</td>
<td>[21]</td>
<td>[43]</td>
<td>[20]</td>
<td></td>
</tr>
<tr>
<td><strong>Chemical</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ettringite concen.</td>
<td>[21]</td>
<td>[43]</td>
<td>[20]</td>
<td></td>
</tr>
<tr>
<td>Gypsum concen.</td>
<td>[21]</td>
<td>[43]</td>
<td>[20]</td>
<td></td>
</tr>
<tr>
<td>Aluminate concen.</td>
<td>[21]</td>
<td>[43]</td>
<td>[20]</td>
<td></td>
</tr>
<tr>
<td>Full phase comp.</td>
<td>[21]</td>
<td>[43]</td>
<td>[20]</td>
<td></td>
</tr>
<tr>
<td><strong>Mechanical</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chem. strength loss</td>
<td></td>
<td>[42]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Local cracking</td>
<td></td>
<td></td>
<td>[10]</td>
<td>[44]</td>
</tr>
<tr>
<td>Non-local cracking</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Expansions</td>
<td></td>
<td></td>
<td>[46]</td>
<td>[44]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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<td>[48]</td>
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<td></td>
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<td>[52]</td>
</tr>
</tbody>
</table>

As expected, the eligible options diminish with the increase of complexity of the outcomes desired. All models reviewed are able to provide a basic outcome such as the sulfate concentration during the attack. However, the number of options is reduced by a factor of 3 when the required data are the expansions evolution. If the chemical strength loss caused by decalcification or non-local cracking are to be quantified, the number of qualified models is dramatically reduced.
4. RESEARCH PRIORITIES

This section aims to identify the major areas that currently compromise the accuracy of the assessments provided by ESA models based on the review presented in section 3. The literature review features ESA models with advanced transport and chemical modules (e.g. [20,21,43,48,50]) able to provide full ionic and phase composition during the attack and account for several transport mechanisms. The high degrees of sophistication may be attributed to the traditional perception of the ESA as a pure chemical attack, which led to focus efforts on the simulation of the reactive-transport process.

Additionally, the modeling of transport and chemical processes shares the same basis as a wide variety of phenomena comprehensively studied during the last decades, such as the transport of contaminants in soils or the thermodynamic modeling of geochemical systems. Contributions made in other areas have been adopted by ESA models, resulting in reactive-transport modules with advanced features. Consequently, the authors do not identify major hurdles related to the simulation of the reactive-transport process that compromise its accuracy.

Reliable estimations of the mechanical response during the ESA require an accurate quantification of the damage mechanisms generated at the micro-scale (chemical damage and expansive forces) and the translation of its effects to the macro-scale. The current state of the art on structural analysis features several advanced methods able to perform this translation precisely, considering the interactions between sound and damage regions of the attacked element (e.g. FEM with fracture-based constitutive laws [46]). Therefore, the validity of the results provided by the mechanical model is greatly defined by the accuracy of the expansive forces and the chemical damage predicted at the pore-level.

Table 9 highlights the shortage of ESA models attempting to quantify the deterioration of the materials mechanical properties caused by leaching and dissolution of calcium bearing phases. The few attempts reported address the simulation of this phenomenon through over simplified approaches with fitting parameters defined on the basis of experimental data not easily acquirable. Additional research is required to provide accurate estimations of the chemical damage and enable a widespread incorporation of this phenomenon in advanced ESA models.
As discussed in the review, the majority of numerical models acknowledge the expansive forces generated at the pore-scale as the main degradation mechanism associated with ESA. The lack of consensus on the mechanism by which the presence (or formation) of ettringite causes overall expansion and cracking have been translated into the modeling field. Even though the volume increase theory does not currently stand as the most plausible theory due to its simplicity, most numerical models have adopted this approach to simulate the expansive forces generated.

Estimations provided through this approach are strongly influenced by the capacity of the pore network of the material to accommodate expansive phases. However, there is not any reliable quantification of this parameter. Consequently, models adopt different values arbitrarily, often treating this variable as a fitting parameter. The early works of Atkinson and Hearne [4], and Clifton and Pommersheim [9] assumed that only 5% of the volume of ettringite formed was translated into actual expansions. Clifton and Pommersheim [9] additionally considered that expansion occurs only when the reaction products fill the entire volume of capillary porosity ($f=100\%$). More recently, Tixier and Mobasher fixed this parameter in a range between 5% - 40% of the initial porosity [18,61]. Basista and Weglewski [45] and Yu et al. [50] arbitrarily assumed it to be 50 and 36%, respectively. Discrepancies of such ranges question the accuracy of the assessments. The role of porosity during the attack should be further studied in order to provide procedures or guidelines to estimate the capacity of a specific material to accommodate expansive phases.

The simulation of expansive forces through the crystallization pressure theory is still at an early stage and the few attempts reported are still far from being able to reproduce the real behavior of specimens exposed to ESA. The models that adopted this approach are unable to reproduce the main feature of this theory, which is that only ettringite growing in small pores is likely to build up enough pressure to cause damage. To capture this phenomenon it is necessary to consider a more realistic representation of the pore network and be able to account for ettringite growth in different locations within the pore structure based on local saturation conditions. This is not compatible with current ESA reactive-transport models. Further research is needed to assess the viability of this modeling approach and justify the increase of computational complexity involved over the simpler volume increase theory.

5. CONCLUSIONS

This review of the most representative ESA models developed during the last 20 years identified the most common modeling approaches adopted and the capabilities and limitations associated with each one of them. It is important to highlight that in this
paper, the term ESA exclusively refers to the degradation triggered by chemical
reactions between sulfate ions and the cement paste. The simulation of damage
attributed to physical sulfate attack such as crystallization of water-soluble sulfate salts
is not addressed. The following specific conclusions may be derived from the present
study:

- A significant number of advanced ESA models do not simulate all of the main
  processes involved in the ESA (transport process, chemical reactions, generation
  of expansive forces and the mechanical response), which may limit the scope of
  the predictions.

- The literature review features models with advanced transport and chemical
  modules able to provide full ionic and phase composition during the attack and
  account for several transport mechanisms.

- Practically all models that quantify damage associated with ESA assume that the
  only source of degradation are the expansive forces generated at the pore
  network by ettringite formation. Chemical damage associated to the dissolution
  of calcium-bearing phases is rarely quantified.

- Improvement on the accuracy of the expansive forces estimated at the pore-level
  and the chemical damage generated in the material are identified as current
  major research priorities in ESA modeling.

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